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Development of Tools for the Study of Heavy-Element Containing Periodic Systems in the CRYSTAL Code and their Application

Doctoral Thesis

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Abstract

This thesis investigates the development of first-principles methods for the study of heavy-element containing periodic systems, as well as their application, in particular to crystalline lanthanide oxides. The Generalized Kohn-Sham Density Functional Theory (GKS-DFT, i.e. in which density functional approximations are built directly from KS orbitals, using so-called hybrid functionals) was shown to provide a particularly effective means to correct for self-interaction errors that plague more conventional local or semi-local formulations in a scalar-relativistic (SR) context. As such, the SR GKS-DFT scheme allowed for a detailed characterization of the electronic structure of the lanthanide sesquioxide series, and enabled (for the first time) to rationalize all known electronic and structural pressure-induced phase transitions in the prototypical strongly-correlated and mixed-valence material EuO.

But the hybrid functional approach proved even more useful when developing instead fully relativistic theories and algorithms, which include not only SR effect, but also spin-dependent relativistic effects, such as spin-orbit coupling (SOC). Coincidentally, this thesis reports the first implementation for a self-consistent treatment of SOC in periodic systems with a fraction of exact non-local Fock exchange in a two-component spinor basis (2c-SCF). The numerous advantages of using such a formulation, as opposed to the more approximate treatments of previously existing implementations, are discussed. These advantages originate from the ability of the Fock exchange operator to locally rotate the magnetization of the system with respect to a starting guess configuration (local magnetic torque). In addition, the non-local Fock exchange operator permits to include in the two-electron potential the contribution of the spinors that are mapped to certain spin-blocks of the single-particle density matrix. This allows for a proper treatment of the orbital relaxation of current densities, and their coupling with the other density variables. As a result, it is shown that the lack of Fock exchange (or even its more approximate treatment in a one-component basis, as with previous implementations) from more conventional formulations of the KS-DFT means that the calculation would not allow to access the full range of time-reversal symmetry broken states. This is because, it is shown that in the absence of Fock exchange, the band structure is constrained by a sum rule, linking the one-electron energy levels at opposite points in the first Brillouin zone ($\mathbf{k}_j$ and $-\mathbf{k}_j$).

What a Drollery.

Dr. Jefferson Maul de Andrade

Thank You / Grazie / Merci

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There are many others to thank, but unfortunately this page is already full, which reminds the author that he must regretfully now instead move on to discuss some science.

This thesis is dedicated to two great men who have made all of this work possible, and who have unfortunately passed away during the course of this thesis. They are Victor Ronald Saunders and Claudio Marcelo Zicovich-Wilson.

Table of Contents

1 Introduction

The coherent behaviour of Rare-Earth Elements (REE, i.e. lanthanides) in planetary processes renders them an invaluable geochemical tracer [55]. It is therefore no surprise that the breadth of their applications in geosciences covers the entirety of our planet, from surficial and acquatic applications [231, 287], hydrothermal processes [28], through to deep mantle and core geochemistry [125, 286, 294, 326]. Apart from their usefulness as geochemical tools, the REEs have significant technological applications in the manufacturing industry, including automotive catalysis, metallurgy, the manufacturing of ceramics and magnets, cell phones and many others [55, 231, 329]. Their great usefulness in this diverse array of applications stems principally from the possibility of manipulating the rich charge and spin degrees of freedom that are made available by the presence of d- and f- type bands in REE containing materials. This, however also means that the REEs are particularly difficult to study from a theoretical point of view. On the one hand, the localization in energy and space of the d- and f- type bands means that they occur in so-called strongly-correlated materials, which require particularly sophisticated electronic structure theories, even for a correct qualitative treatment [43, 104, 145]. On the other hand, the fact that the REEs are so heavy means that such theories must also properly take into account the treatment of relativistic effects (to be defined below) [101, 258, 262].

Indeed relativistic effects are nowadays known to have a profound effect on the electronic structure of materials. Famous examples of the importance of relativistic effects on the physical and chemical properties of materials include the yellow colour and nobility of gold, as well as the liquidity of mercury [258]. However, relativistic effects are not only important for studying elements that are so low in the periodic table, because they can also be crucial for a correct description of certain properties of materials containing the most abundant element (by mass) on Earth, namely iron [148, 166, 236].

The electronic structure of such materials can be studied by solving Schrödinger's equation, which is based upon the assumption that everything that there is to be known about a material system can be entirely described by a quantity called the wavefunction. This equation was derived in his seminal paper in 1926 [274]. This theory, however indeed does not include relativistic effects, meaning that it does not account for the fact that the speed of light is finite. For certain applications, in particular the calculation of properties most sensitive to valence electrons on light atoms of the periodic table, this is not problematic. The difficulty arises, rather when dealing with high-speed particles, whose velocity is not negligeable when compared to that of the speed of light. This is the case for electrons close to the core region of atoms, or for valence electrons in atoms of the heavier portion of the periodic table, like the REEs. In this case a more appropriate theory is one which marries both major developments in 20th century physics. This marriage of Schrödinger's quantum theory with Einstein's relativistic one, was provided just two years (!) after the publication of Schrödinger's paper, by a young British physicist named Paul Adrien Maurice Dirac [81].

The union of the quantum and relativistic theories by Dirac is indeed one of the great triumphs of theoretical physics, and has opened the possibility for the modern modelling of materials. This was immediatly recognized by Dirac who famously stated in 1929 (the present author has bolded some of the text in the following quote) [82]:

"*...The underlying physical laws for the mathematical theory of a* ***large part of physics and the whole of chemistry*** *are thus* ***completely known*** *and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble. It therefore becomes desirable that* ***approximate practical methods of applying quantum mechanics should be developed****, which can lead to an explanation of the main features of complex atomic systems without too much computation....*"

Ninety one years later, the objective of this thesis essentially follows very closely these suggestions of Prof. Dirac. The goal is on the one hand to develop appropriate electronic structure theories and algorithms for the treatment of heavy elements (i.e. transition metals, lanthanides, actinitides,...) in periodic systems. On the other hand, it is also necessary to test the developed theories (new and old) on challenging strongly-correlated systems, as a means to assess their usefulness.

There are two principal classes of relativistic effects which emerge from Dirac's equation. The first class is represented by scalar operators and is therefore called scalar-relativistic effects (SR). These are mainly manifested as relativistic corrections to the electron mass and generally result in the contraction of *s*- and *p*-type bands, as well as the expansion of *d*- and *f*- type bands [101, 258, 262, 267]. The second class of effects is described by a vector operator and is referred to as spin-orbit coupling (SOC) effects. The SOC effect is related to the coupling of the spin of a reference electron with the magnetic field created by charged particles in motion relative to this reference electron [267]. In contrast to the SR effects, the SOC one not only shifts the electronic energy levels of the system, but also changes the overall symmetry of the wavefunction. This means, on the one hand that it can be crucial to include SOC in the calculation even for a correct qualitative description of the material system, but on the other hand, that its inclusion in a modern computer program involves major restructuring. One of the focuses of this thesis is such a generalization of a program for SR calculations on periodic systems to also include SOC.

The platform on which the algorithms are developed and tested in this thesis is the Crystal program [94]. This is a publicly distributed program for quantum mechanical calculations on periodic systems in zero dimensions (molecules), one dimension (polymers), two dimensions (surfaces) and three dimensions (crystalline solids). The calculations performed using such approaches are indeed termed *ab initio*, or from first principles. The Crystal code has been developed in an international collaboration effort over the last five decades, with the first public version being distributed in 1988 and the most recent one in 2017.

This thesis is based on seven scientific papers [75, 76, 77, 78, 79, 80, 104]. Papers III is a yet-to-be published manuscript, while the rest have already been published in scientific journals. In the first part of this thesis (related to papers I, II and III), the usefulness of the existing SR approach in the Crystal code is assessed through calculations on strongly-correlated REE oxides. This includes the lanthanide sesquioxides Ln_2O_3 (with Ln=La, Ce, Pr, Nd), in paper II, and high pressure polymorphs of the europium monoxide EuO, in paper III [80]. Before these calculations could be performed however, the code needed to be improved in one respect, as follows.

In order to perform successfull *ab initio* calculations, the wavefunction must be expanded in a set of basis functions. In particular, this is achieved in the Crystal program using the so-called Linear-Combination of Atomic Orbitals (LCAO) method. In the LCAO approach, the material's wavefunction is represented using a linear combination of functions, each of which closely resembles an analytical solution of the Schrödinger or Dirac equations for an isolated atom, and are hence called atomic orbitals. These atomic orbitals are in turn represented using a linear combination of Gaussian functions, multiplied by a spherical harmonic with a given angular momentum l. The Crystal program was initially designed to perform calculations with functions of angular momentum up to $l = 2$ (d-type atomic orbitals). The program was generalized to f-type functions ($l = 3$) around 2003 with Crystal03 [270]. In paper I, efficient algorithms are developed for the generalization of the Crystal program to g-type atomic orbitals ($l = 4$), for a more complete expansion of the material's wavefunction. This work ends up to be particularly important for REE-containing materials which are characterized by occupied f-bands and hence, the g-functions provide a first set of basis functions to describe their polarization.

In paper II, the usefulness of the approach was successfully demonstrated on the Ln_2O_3 sesquioxides. In particular, the need for using so-called hybrid functionals of the density-functional theory (DFT) — a particular strategy for solving Schrödinger's or Dirac's equation — containing a fraction of exact non-local Fock exchange, was demonstrated. This paved the way for paper III, in which the same approach was applied to the more challenging problem of rationalizing the mechanism for high pressure electronic phase transitions in EuO.

In the second part of the thesis (related to papers IV, V, VI and VII), the Crystal program is generalized to include SOC effects through a so-called two-component self-consistent field (2c-SCF) procedure. Paper IV discusses the bulk of the work involved in generalizing the program to self-consistently treat SOC using the Hartree-Fock (HF) approximation for calculations on molecules. The relative merits of the implementation is discussed by comparison against similar existing ones. Strategies are discussed to overcome challenges associated with the rugged energy landscape of the typical systems studied using this approach. In paper V the approach is extended to also treat electron correlation through the non-collinear DFT. In paper VI formal arguments are developped to highlight the importance of the non-local Fock exchange term for the self-consistent treatment of SOC. In paper VII the approach is generalized to treat periodic systems in 1D, 2D and 3D.

The chapters of the thesis are organized as follows. Chapter 1 was this introduction that you have just read (congratulations, by the way, on getting this far! ☺). In chapter 2, Dirac's equation is briefly derived and associated approximations are discussed to bring it to a more practically solvable two-component form. In chapter 3, it is discussed how the wavefunction can be approximated by a particularly convenient form, the Slater determinant. This permits to expand it in a basis of one-electron functions, which brings us to introducing paper I. In chapter 4 we discuss the periodic HF approximation and the DFT approach and introduce paper II. In chapter 5 we discuss the calculation of certain one-electron properties that can be obtained from such calculations (for example,the electron density and its derivatives) and introduce paper III. In chapter 6, we discuss the generalized HF approximation, that is to say the HF approximation in the context of a 2c-SCF to treat SOC, and introduce paper IV. Chapter 6 also discusses the non-collinear DFT approach and introduces paper V. Afterwards we discuss the treatment of another one-electron property, this time obtained only from a 2c-SCF, the orbital-current density and introduce paper VI. Finally, we discuss aspects related to generalizing the 2c-SCF approach to periodic systems and introduce paper VII. In chapter 7 we draw conclusions and suggestions for future work. In each case, mathematical details are kept to a minimum. For a more thorough description of the developped theories and algorithms appendices are provided and properly cited throughout the text. These appendices are intended as “stand-alone” texts, which can be accessed by the reader *au besoin* if more depth is needed in a given subject. Each of them hence follows an independent notation which is most appropriate for the associated topic. All chapters are written in a.u. Hartree atomic units, apart from chapter 2, which is written in SI units.

2 Relativistic Quantum Mechanics and Dirac's Equation

2.1 Time-Dependent Equation for the Free Electron

Our goal here is to derive Dirac's equation — which provides us with a proper relativistic generalization of quantum mechanics — for a free electron. We start with the corresponding classical expression for the energy E of the system, which just consists of the following kinetic energy expression [101, 262]:

$$E = \frac{\mathbf{p}^2}{2m} \ . \tag{2.1}$$

where $\mathbf{p}$ is the canonical momentum of the electron and m is its mass. Using the correspondence principle, in which classical variables are promoted to operators [101]:

$$E \rightarrow i\hbar\frac{\partial}{\partial t} \quad \mathbf{p} \rightarrow -i\hbar\boldsymbol{\nabla} \ , \tag{2.2}$$

we arrive at the corresponding time-dependent Schrödinger equation:

$$\frac{-\hbar^2}{2m}\boldsymbol{\nabla}^2\Psi(\mathbf{r},t) = i\hbar\frac{\partial}{\partial t}\Psi(\mathbf{r},t) \ , \tag{2.3}$$

where $\Psi(\mathbf{r},t)$ is the complex-valued wavefunction and its square modulus:

$$|\Psi(\mathbf{r},t)|^2 = \Psi^*(\mathbf{r},t)\Psi(\mathbf{r},t) \qquad \int|\Psi(\mathbf{r},t)|^2 d\mathbf{r} = 1 \ , \tag{2.4}$$

is positive-definite and conserved. The modulus of the wavefunction is interpreted as a probability density (i.e. the probability of finding the electron at position $\mathbf{r}$ in space, at time t). The operator $\boldsymbol{\nabla}$ denotes the Cartesian vector of derivatives and $\hbar$ is the reduced Planck's constant. Clearly Eq. (2.3) is not a proper relativistic theory ($\Psi(\mathbf{r},t)$ is not Lorentz invariant), because the space-time variables are not treated on the same footing, as Eq. (2.3) is second order in space, but first order in time.

A logical attempt to instead derive an equation in which the space and time derivatives are of the same order might be to start from the energy-momentum relation of special relativity:

$$E^2 = \mathbf{p}^2c^2 + m^2c^4 \ , \tag{2.5}$$

where c denotes the speed of light. Applying again the correspondence principle of Eq. (2.2), we arrive at the Klein-Gordon equation [101, 262]:

$$\left(-\hbar^2c^2\boldsymbol{\nabla}^2 + m^2c^4\right)\phi(\mathbf{r},t) = -\hbar^2\frac{\partial^2}{\partial t^2}\phi(\mathbf{r},t) \ . \tag{2.6}$$

In Eq. (2.6) we now have the desired symmetry between the order of derivatives in space and time, because both are of order two. The quantity $\phi(\mathbf{r},t)$ is then a relativistic scalar, but unfortunately it is not a wavefunction. The problem lies in the fact that it is impossible to define a probability density which is both conserved and positive definite from Eq. (2.6). Dirac's idea was then to try and instead start from the square root of Eq. (2.5):

$$E = c\sqrt{\mathbf{p}^2 + m^2c^2} \ , \tag{2.7}$$

and then develop an equation which is instead first order in time and space. The taking of a square root in Eq. (2.7) implies an arbitrariness in the choice (positive or negative) of the sign of E. For the time being we choose a positive sign out front of the square root in Eq. (2.7). Later we will also discuss the meaning of the choice of this sign. It is then convenient to suppose that the argument in the square-root in Eq. (2.7) can be developed in a perfect square [101, 262]:

$$\mathbf{p}^2 + m^2c^2 \equiv (\boldsymbol{\alpha} \cdot \mathbf{p} + \boldsymbol{\beta} mc)^2 \ , \tag{2.8}$$

where the quantities $\boldsymbol{\alpha}_x$, $\boldsymbol{\alpha}_y$, $\boldsymbol{\alpha}_z$ and $\boldsymbol{\beta}$ are yet to be determined. For Eq. (2.8) to be valid, the quantities $\boldsymbol{\alpha}_x$, $\boldsymbol{\alpha}_y$, $\boldsymbol{\alpha}_z$ and $\boldsymbol{\beta}$ are subject to certain constraints, namely [101, 262]:

$$\begin{aligned} \boldsymbol{\beta}^2 &= \mathbb{I} && \text{(2.9a)} \\ \boldsymbol{\alpha}_i\boldsymbol{\beta} + \boldsymbol{\beta}\boldsymbol{\alpha}_j &= \mathbf{0} && \text{(2.9b)} \\ \boldsymbol{\alpha}_i\boldsymbol{\alpha}_j + \boldsymbol{\alpha}_j\boldsymbol{\alpha}_i &= 2\mathbb{I} \otimes \delta_{ij} \ , && \text{(2.9c)} \end{aligned}$$

where in Eq. (2.9), i and j are Cartesian indices, the $\mathbf{0}$ and $\mathbb{I}$ are the zero and identity elements, respectively, of the algebraic structure of the $\boldsymbol{\alpha}_i$ and $\boldsymbol{\beta}$ (to be specified), $\otimes$ is the element-wise product and δ_{ij} is the Kronecker delta. Eq. (2.9) implies that the $\boldsymbol{\alpha}_i$ and $\boldsymbol{\beta}$ must anticommute, they can therefore not be scalar real or complex numbers. It is logical to hence choose them as matrices. In fact, Eq. (2.9) is satisfied by the following set of matrices:

$$\boldsymbol{\alpha}_i = \begin{pmatrix} \mathbf{0}_2 & \boldsymbol{\sigma}_i \\ \boldsymbol{\sigma}_i & \mathbf{0}_2 \end{pmatrix} \tag{2.10a}$$

and:

$$\boldsymbol{\beta} = \begin{pmatrix} \mathbb{I}_2 & \mathbf{0}_2 \\ \mathbf{0}_2 & -\mathbb{I}_2 \end{pmatrix} \ , \tag{2.10b}$$

where in Eq. (2.10) the $\boldsymbol{\alpha}_i$ and $\boldsymbol{\beta}$ are represented in terms of other 2×2 matrices. The $\mathbb{I}_2$ is the 2×2 identity matrix, $\mathbf{0}_2$ is a 2×2 matrix of zeros, and the $\boldsymbol{\sigma}_i$ (again here $i = x, y, z$ is a Cartesian index) are the 2×2 Pauli matrices:

$$\boldsymbol{\sigma}_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad \boldsymbol{\sigma}_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \quad \boldsymbol{\sigma}_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \ . \tag{2.11}$$

We now have explicit expressions for the matrices that enter Eq. (2.8). Finally, substituting Eq. (2.8) in Eq. (2.7), and using the correspondance principle from Eq. (2.2), we arrive at the Dirac equation for the free-electron [101, 262]:

$$\mathbf{h}_D\boldsymbol{\Psi}(\mathbf{r},t) = \left(-i\hbar c\boldsymbol{\alpha}\cdot\boldsymbol{\nabla} + \boldsymbol{\beta} mc^2\right)\boldsymbol{\Psi}(\mathbf{r},t) = i\hbar\frac{\partial}{\partial t}\boldsymbol{\Psi}(\mathbf{r},t) \ . \tag{2.12}$$

2.2 Time-Independent Equation for the Free Electron

Exactly as is done for the non-relativistic theory of Schrödinger, we now explore the possibility of writing a time-independent version of the Dirac equation for the free electron, in the case where it can be represented as a stationary state. That is to say, we assume that the wavefunction can be written as a product of a time-dependent part $\varphi(t)$ and a time-independent part $\boldsymbol{\psi}(\mathbf{r})$ [101]:

$$\boldsymbol{\Psi}(\mathbf{r},t) \equiv \varphi(t)\,\boldsymbol{\psi}(\mathbf{r}) \ . \tag{2.13}$$

Substitution of Eq. (2.13) in Eq. (2.12) yields [101]:

$$\left[\mathbf{h}_D\boldsymbol{\psi}(\mathbf{r})\right]/\boldsymbol{\psi}(\mathbf{r}) = \left[i\hbar\frac{\partial}{\partial t}\varphi(t)\right]/\varphi(t) \ , \tag{2.14}$$

where in Eq. (2.14), the divisions must be interpreted as being performed element-wise. The left hand side of Eq. (2.14) depends only on $\mathbf{r}$ and the right hand side depends only on t. For this to happen, both sides must be equal to a constant, which we call the energy E. This yields the time-independent Dirac equation:

$$\mathbf{h}_D\boldsymbol{\psi}(\mathbf{r}) = E\boldsymbol{\psi}(\mathbf{r}) \ . \tag{2.15}$$

The time-dependent Dirac wavefunction $\boldsymbol{\Psi}(\mathbf{r},t)$ is expressed in terms of all possible time-independent solutions of Eq. (2.15) $\boldsymbol{\psi}_n(\mathbf{r})$ as follows:

$$\boldsymbol{\Psi}(\mathbf{r},t) = \sum_n c_n e^{-iE_n t/\hbar}\boldsymbol{\psi}_n(\mathbf{r}) \ , \tag{2.16}$$

where n labels the different possible solutions of Eq. (2.15) and the c_n are the coefficients of the linear expansion.

2.3 Many Body Representations of the Hamiltonian

The sections 2.1 and 2.2 provided the appropriate relativistic theory for treating an isolated electron. This in itself has little interest for modelling of materials and molecules, in which the system consists of many atoms. The isolated electron problem can be mapped to an isolated electron in an external field (caused by the presence of the other particles) using the so-called minimal electromagnetic coupling substitution, as follows [267]:

$$\mathbf{p} \to \mathbf{p} + e\boldsymbol{\mathcal{A}} \quad E \to E + e\phi \ , \tag{2.17}$$

in which $\mathscr{A}$ is the external vector potential and ϕ is the external scalar potential. For most calculations, the Born Oppenheimer approximation is usually adopted, in which we assume that the motion of the electrons is decoupled from that of the much heavier nuclei. In such a case, the many-body Hamiltonian is obtained by substituting Eq. (2.17) and Eq. (2.12) in Eq. (2.15), with the ϕ being the scalar potential of the electrons and clamped nuclei. $\mathscr{A}$ is the vector potential of the many electron problem in the reference frame of the clamped nuclei. The Hamiltonian is then written as the sum of a purely electronic term, a term that couples the electrons with the nuclei V_{eN} and a nuclear-nuclear interaction term V_{NN}. The Hamiltonian then takes the general form [101, 267]:

$$\begin{aligned} \mathbf{H}_D &= \sum_i \mathbf{h}_D(i) + \mathbb{I}_4 \otimes V_{NN} + \sum_{i>j} \mathbf{g}(i,j) \\ &= \sum_i \left(-i\hbar c \boldsymbol{\alpha}_{(i)} \cdot \boldsymbol{\nabla}_i + \boldsymbol{\beta}'_{(i)} mc^2\right) + \mathbb{I}_4 \otimes \left[V_{eN}(i) + V_{NN}\right] + \sum_{i>j} \mathbf{g}(i,j) \ , \end{aligned} \tag{2.18}$$

where the indices i and j label the coordinates of individual electrons (not to be confused with the $i = \sqrt{-1}$) and $\mathbf{g}(i, j)$ is the two-electron part of the potential (to be defined). In Eq. (2.18) the global energy scale of the problem has been shifted for convenience by introducing the matrix $\boldsymbol{\beta}' = \boldsymbol{\beta} - \mathbb{I}_4$. The notation $\boldsymbol{\alpha}_{(i)}$ (and $\boldsymbol{\beta}'_{(i)}$) is intended to mean the matrix $\boldsymbol{\alpha}$ (and $\boldsymbol{\beta}'$) which acts only on those functions that depend on the electron coordinate i. This is not to be confused with the matrix $\boldsymbol{\alpha}_i$, which is the i Cartesian component of $\boldsymbol{\alpha}$. The term $V_{eN}(i)$ is the classical electron nucleus interaction potential:

$$V_{eN}(i) = -\sum_A \frac{Z_A e^2}{r_{Ai}} \ , \tag{2.19}$$

in which the sum is performed over all nuclei A in the system, with nuclear charge Z_A. The e is the elementary charge and r_{Ai} is the distance between electron i and the nucleus A. In Eq. (2.18), V_{NN} is the classical nuclear-nuclear potential:

$$V_{NN}(i) = \sum_{B>A} \frac{Z_A Z_B}{R_{AB}} \ , \tag{2.20}$$

where R_{AB} is the distance between nucleus A and nucleus B.

In the end Eq. (2.18) is essentially very similar to Eq. (2.15), but with the sums over the coordinates of all electrons in the system, and with the added contributions from $V_{eN}(i)$, V_{NN} and $\mathbf{g}(i, j)$. The only term that remains to be defined to write the Hamiltonian is the two-electron interaction term $\mathbf{g}(i, j)$.

It turns out that, in contrast to the non-relativistic theory, it is actually not possible to write down an exact analytical expression for $\mathbf{g}(i, j)$. This is because, in a relativistic theory, the electrons interact with each other through the transmission and absorption of photons, which now travel at a finite speed [101]. The study of such interactions is called quantum electrodynamics, QED, through which it is possible to develop practical approximations for the two-electron interaction term, but not exact ones. This means that practical calculations on many-body systems are never exactly Lorentz invariant.

The simplest approximation for $\mathbf{g}(i, j)$ can be obtained by considering only contributions from the scalar potential of the many-electron problem in the reference frame of the clamped nuclei, and ignoring contributions instead from the vector potential [267]. In this case, the $\mathbf{g}(i,j)$ reduces to the Coulomb interaction:

$$\mathbf{g}(i,j) \approx \mathbf{g}^{Coulomb}(i,j) \equiv \mathbb{I}_4 \otimes g^{Coulomb}(i,j) = \mathbb{I}_4 \otimes \frac{e^2}{r_{ij}} \,, \tag{2.21}$$

in which r_{ij} is the distance between electrons i and j. Such an approximation can be adopted for reasons of practicality, because in this case the two-electron operator takes the same analytical form as in the non-relativistic case. For a calculation in which the two-electron operator is approximated as in Eq. (2.21), the Hamiltonian is called Dirac-Coulomb. A more accurate approximation, which goes beyond the Dirac-Coulomb one, involves also considering contributions from the vector potential of the electronic problem, in which case the so-called Breit interaction term is obtained [40]. The approximation for $\mathbf{g}(i,j)$ then reads as follows [101, 267]:

$$\mathbf{g}(i,j) \approx \mathbf{g}^{Coulomb}(i,j) + \mathbf{g}^{Breit}(i,j) \tag{2.22a}$$

where the Breit interaction $\mathbf{g}^{Breit}(i,j)$ is written as a sum of the Gaunt and gauge terms, as follows:

$$\begin{aligned} \mathbf{g}^{Breit}(i,j) &= \mathbf{g}^{Gaunt}(i,j) + \mathbf{g}^{gauge}(i,j) \\ &= -e^2 \left[\frac{\boldsymbol{\alpha}_{(i)} \cdot \boldsymbol{\alpha}_{(j)}}{r_{ij}} + \frac{\left(\boldsymbol{\alpha}_{(i)} \cdot \boldsymbol{\nabla}_i\right)\left(\boldsymbol{\alpha}_{(j)} \cdot \boldsymbol{\nabla}_j\right) r_{ij}}{2} \right] . \end{aligned} \tag{2.22b}$$

In the case where the two-electron operator is represented from Eq. (2.22), the approximate Hamiltonian is referred to as the Dirac-Coulomb-Breit (DCB) one [101, 267]. The expression for $\mathbf{g}(i,j)$ is then correct to order $O\left(c^{-2}\right)$ [101]. The Gaunt and gauge terms therefore represent collectively the first correction to the electron-electron interaction potential which takes into account retardation effects (effects originating from the fact that two electrons interact with each other through photons, which travel at a finite speed) [101, 267]. All terms included beyond the DCB approximation are called QED contributions and are sometimes included in atomic calculations, for the construction of pseudopotentials [87, 101, 151, 152, 153, 173, 277]. Here, we call such a Hamiltonian going beyond the DCB the DCB+QED Hamiltonian. Finally it is noted that because of the origins of the Breit interaction in terms of the vector potential of the electronic problem, it is logical that the Breit term is intimately related to magnetic effects, such as the SOC effect. The inclusion of the Breit interation in a calculation is therefore important for a proper treatment of SOC and closely related effects [101, 267].

2.4 The Dirac Wavefunction

From Eq. (2.10) we have seen that the quantities $\boldsymbol{\alpha}$ and $\boldsymbol{\beta}$, and hence the Dirac Hamiltonian $\mathbf{H}_D$ from Eq. (2.18), are 4×4 matrices. This means that the Dirac wavefunction must be a 4×1 quantity (called a four-component spinor). The different components of this 4×1 vector read as follows, for the time-independent problem:

$$\boldsymbol{\psi}\left(\mathbf{r}\right)=\begin{pmatrix}\psi^{L,\alpha}\left(\mathbf{r}\right)\\ \psi^{L,\beta}\left(\mathbf{r}\right)\\ \psi^{S,\alpha}\left(\mathbf{r}\right)\\ \psi^{S,\beta}\left(\mathbf{r}\right)\end{pmatrix}. \tag{2.23}$$

The fact that the wavefunction in Dirac's relativistic theory is composed of four components is reminiscent of Einstein's classical theory of relativity, in which space-time is also described by a four component quantity (i.e. a four-vector comprising of time and the three spatial dimensions). The interpretation of two of the four components is clear enough by comparison to the usual non-relativistic procedure. Those components denoted by the α (β) superscript being related principally to spin $+\frac{1}{2}$ $(-\frac{1}{2})$ components of the wavefunction. On the other hand, the L and S superscripts denote the so-called large and small components. Insight into the meaning of these latter superscripts can be obtained by returning to Eq. (2.7) and now considering the possibility of both positive and negative signs in front of the square root:

$$E=\pm\sqrt{\mathbf{p}^2c^2+m^2c^4}\ . \tag{2.24}$$

The presence of both positive and negative signs means that E belongs to the following range [267]:

$$E\in\left(-\infty,-mc^2\right]\bigcup\left[mc^2,\infty\right)\ , \tag{2.25}$$

which shows that the total energy lies in either of two continuums that are seperated by an interval of width $2mc^2$ [101, 267]. The L component of the wavefunction principally describes the states in the positive band, while the S component principally describes those in the negative band. So if a positive sign is chosen in Eq. (2.24), and the resulting Dirac equation is solved, then the wavefunction will be dominated by the L, rather than S component, hence the names large and small.

The negative energy solutions can be shown to be related mathematically to the positive energy ones through the so-called charge conjugation operator [101]. The action of this operator on the Dirac wavefunction involves both time-reversal and a change of sign of the charge of the particles. So if the Dirac equation for the electronic problem is solved for the positive energy solution, then the negative energy solution can be interpreted as the solution for the positronic problem. Hence, the small component of the wavefunction has a small effect for describing electrons, but a large effect for describing positrons. Since in calculations on molecules and materials, we are almost always interested in describing electrons rather than positrons, it is useful to consider getting rid of the small component (exactly because as the name suggests, we already know that it is small!) of the wavefunction, as a means to simplify the calculation. Methods which follow this prescription are termed two-component approaches and are the subject of the following section.

2.5 Two-Component Forms

Variants of the Dirac equation are here discussed, in which the small component of the wavefunction is eliminated through some sort of decoupling transformation. We consider the DC Hamiltonian for the polyatomic case. To simplify the notation, we rewrite Eq. (2.15), making use of Eq. (2.18) in a particularly compact form, as follows:

$$\left(c\boldsymbol{\alpha}\cdot\mathbf{p}+\boldsymbol{\beta}'mc^2+\mathbb{I}_4\otimes V\right)\boldsymbol{\psi}=E\boldsymbol{\psi}\;, \tag{2.26}$$

in which the explicit dependence on the electron and nuclear coordinates has been surppressed, and the potential V includes the nuclear-nuclear V_{NN} electron-nuclear V_{eN} and electron-electron Coulomb $\mathbf{g}^{Coulomb}$ terms. It is then convenient to introduce the notation $\boldsymbol{\psi}^L=\left[\psi^{L,\alpha},\psi^{L,\beta}\right]^T$ and $\boldsymbol{\psi}^S=\left[\psi^{S,\alpha},\psi^{S,\beta}\right]^T$ into Eq. (2.23), and substitute it in Eq. (2.26) taking into account the form of the $\boldsymbol{\alpha}_x$, $\boldsymbol{\alpha}_y$, $\boldsymbol{\alpha}_z$ and $\boldsymbol{\beta}'$ matrices from Eq. (2.10), to find the following two coupled equations for the large and small components of the wavefunction [101]:

$$\begin{aligned}(V-E)\,\boldsymbol{\psi}^L+c\,(\boldsymbol{\sigma}\cdot\mathbf{p})\,\boldsymbol{\psi}^S &= \mathbf{0}_2 && \text{(2.27a)}\\ c\,(\boldsymbol{\sigma}\cdot\mathbf{p})\,\boldsymbol{\psi}^L+\left(V-E-2mc^2\right)\boldsymbol{\psi}^S &= \mathbf{0}_2\;, && \text{(2.27b)}\end{aligned}$$

in which the notation $\boldsymbol{\sigma}=\left[\boldsymbol{\sigma}_x,\boldsymbol{\sigma}_y,\boldsymbol{\sigma}_z\right]^T$ has been introduced to denote the vector of Pauli matrices. The small component $\boldsymbol{\psi}^S$ can be isolated from Eq. (2.27b), to yield [101, 267]:

$$c\boldsymbol{\psi}^S=\frac{1}{2m}\left[1-\frac{V-E}{2mc^2}\right]^{-1}(\boldsymbol{\sigma}\cdot\mathbf{p})\,\boldsymbol{\psi}^L\;. \tag{2.28}$$

We note in passing that taking the non-relativistic limit of Eq. (2.28), i.e. by taking the limit $c\to\infty$:

$$\lim_{c\to\infty}c\boldsymbol{\psi}^S=\frac{1}{2m}(\boldsymbol{\sigma}\cdot\mathbf{p})\,\boldsymbol{\psi}^L\;, \tag{2.29}$$

yields an important constraint for practical calculations with the Dirac equation. Eq. (2.29) is indeed intimately related to the so-called kinetic balance approach, in which a proper non-relativistic limit of the large and small components of the wavefunction is ensured by constraining the basis functions χ^S_μ and χ^L_μ on which they are expanded to obey Eq. (2.29). For example, in the case of so-called restricted kinetic balance, we have [101, 299]:

$$\chi^S_\mu=\frac{1}{2m}(\boldsymbol{\sigma}\cdot\mathbf{p})\chi^L_\mu\;. \tag{2.30}$$

Indeed, modern relativistic basis sets are nowadays designed to be constrained in some way by Eq. (2.29) [113, 302, 322]. Early calculations, in which the basis functions were not consistent with Eq. (2.29) were indeed subject to convergence problems [221, 265].

Otherwise, Eq. (2.28) also provides a means to approximately decouple the small component from the large component. This can be achieved by approximating the factor in the square bracket in Eq. (2.28) in a geometric series, as follows [101]:

$$\left[1 - \frac{V - E}{2mc^2}\right]^{-1} = 1 + \frac{V - E}{2mc^2} + \left[\frac{V - E}{2mc^2}\right]^2 + \dots \; . \tag{2.31}$$

Keeping only the first two terms in Eq. (2.31) and substituting the result in Eq. (2.28), then Eq. (2.27a) and renormalizing the large component (because, of course, it is the four-component wavefunction that is normalized, not the large component by itself), the first two-component approximation to the Dirac equation, namely the Pauli equation, is obtained:

$$\mathbf{H}_{Pauli}\tilde{\boldsymbol{\psi}}^L = E\tilde{\boldsymbol{\psi}}^L \; , \tag{2.32}$$

where the tilde on top of the $\tilde{\boldsymbol{\psi}}^L$ indicates that the large component of the wavefunction has been renormalized and in which the Pauli Hamiltonian $\mathbf{H}_{Pauli}$ reads as follows [101, 267]:

$$\mathbf{H}_{Pauli} = \mathbb{I}_2 \otimes \left[\frac{\mathbf{p}^2}{2m} + V - \frac{1}{8m^3c^2}\mathbf{p}^4 + \frac{1}{8m^2c^2}\boldsymbol{\nabla}^2 V\right] + \frac{1}{4m^2c^2}\boldsymbol{\sigma} \cdot (\nabla V) \times \mathbf{p} \; . \tag{2.33}$$

It is then easy to see that taking the non-relativistic limit of Eq. (2.33), that is to say by taking the limit $c \to \infty$, the Schrödinger Hamiltonian is obtained, because the three terms in Eq. (2.33) with c in the denominator (the third, fourth and fifth terms) would vanish. So all relativistic effects included in Eq. (2.33) originate from these third, fourth and fifth terms. The third term is obviously an SR effect (because it is described by a scalar operator) and is called the mass-velocity term. To understand the origin of this name, it is insightful to expand the relativistic energy expression from Eq. (2.7) in a Taylor series to find [101]:

$$mc^2\sqrt{1 + \left(\frac{\mathbf{p}^2}{mc}\right)^2} = mc^2 + \frac{\mathbf{p}^2}{2m} - \frac{\mathbf{p}^4}{8m^3c^2} + \dots \; . \tag{2.34}$$

The third term in Eq. (2.34) is identical to the third term in the Pauli Hamiltonian from Eq. (2.33). So the third term in Eq. (2.33) is the first relativistic correction of the energy which takes into account the variation of the mass with the velocity. The fourth term in Eq. (2.33) describes another SR effect and is the so-called Darwin term. It is related to an effect with no classical analogue, that is sometimes called the *Zitterbewegung* (german for “trembling motion”), because this was the word that was used when first discussed by Schrödinger in 1930 [275].

The *Zitterbewegung* is a circular motion of the electron that is caused by the spontaneous creation of electron-positron pairs and their subsequent annhilation [167, 314]. Indeed, it is easy to see that from Eq. (2.16), the time-dependent Dirac wavefunction is in general expressed as a superposition of all possible solutions to the time-independent equation, which includes both the electronic and positronic states. So as the electronic wavefunction evolves in time, it will inevitably lead to the creation and interaction of electron-positron pairs, which explains the existence of the *Zitterbewegung*.

Finally, the fifth term in Eq. (2.33) can be interpreted as the definition of the SOC interaction. We note that insertion of the electron nucleus interaction potential V_{eN} from Eq. (2.19) into the fifth term in Eq. (2.33) yields a familiar form of the SOC operator [267]:

$$\mathbf{h}_{SO}(i) = \frac{e^2}{4m^2c^2} \sum_A \frac{Z_A}{r_{Ai}^3} \mathbf{L}_{Ai} \cdot \boldsymbol{\sigma} \ , \tag{2.35}$$

where $\mathbf{L}_{Ai} = \mathbf{r}_{Ai} \times \mathbf{p}_i$ is the angular momentum operator.

It is also noted that a similar Hamiltonian to the one in Eq. (2.33) exists, which approximates the DCB one instead of the DC one, and is sometimes called the Breit-Pauli Hamiltonian [41, 124]. While the Pauli and Breit-Pauli Hamiltonians can be useful to provide a clear physical picture of relativistic quantum mechanics, unfortunately they cannot be used as such for self-consistent calculations. The origin of the problem stems mainly from the mass-velocity term, which has no lower bound and can therefore cause variational collapse of the wavefunction in a practical calculation [318]. Another way of explaining this problem is that, close to the nucleus, the spatial derivative of the wavefunction might be large, so that the expectation value of $|\mathbf{p}| > mc$, and the series expansion in Eq. (2.34) would not converge [101]. For practical calculations, the need to calculate derivatives of the potential in Eq. (2.33) for the SOC and Darwin terms is also inconvenient, because it would lead to either very complicated mathematical expressions, or at the very least, some problems of numerical stability. The Pauli and Breit-Pauli Hamiltonians have however been successfully used for the second-variational or perturbative treatment of relativistic effects [36, 37, 73, 74, 206, 257, 295, 296, 349, 350].

The need for variationally stable Hamiltonians has led to the development of alternative (so-called "regular") two-component theories which can instead be used for self-consistent calculations. Various methods exist, some of which can produce exact representations of the positive energy spectrum of the DC Hamiltonian and others are approximations. Amongst these methods, we can cite the ZORA, FORA and IORA (zeroth- first- and infinite-order regular approximations) ones [56, 102, 204, 297, 317]. It is however very cumbersome to develop analytical algorithms for performing calculations with the ZORA Hamiltonian and related methods. This means that these methods work perfectly well with computer programs that perform the calculation using a numerical procedure [307]. They can however hardly be applied to programs for performing analytical calculations, which means in particular that the ZORA and related methods are best suited for calculations using the DFT, rather than wavefunction methods [267]. The difficulty can be easily seen by looking at the expression for the ZORA Hamiltonian [101, 267]:

$$\mathbf{H}_{ZORA} = \mathbb{I}_2 \otimes V + (\boldsymbol{\sigma} \cdot \mathbf{p}) \frac{c^2}{2mc^2 - V} (\boldsymbol{\sigma} \cdot \mathbf{p}) \ . \tag{2.36}$$

Here, the presence of the potential V in the denominator of the second term in Eq. (2.36) largely complicates the development of analytical algorithms [267].

The Douglas-Kroll-Hess (DKH) family of methods represent, on the other hand, regular two-component approximations for which efficient analytical algorithms have been developed [13, 25, 27, 44, 91, 235, 243, 261, 319, 333]. In the most accurate variant of the DKH methods, the small component can be decoupled exactly from the large component, to fully reproduce the positive energy spectrum of the DC Hamiltonian

[26, 185]. The principal idea behind these methods is to develop a decoupling transformation which, unlike the Pauli Hamiltonian, does not truncate the series expansion in Eq. (2.34), because, as explained earlier, it is exactly this truncation which leads to most problems of the Pauli approach. This decoupling transformation is named after the authors who first developed the procedure and is called the Foldy-Wouthuysen transformation [123]. We take this opportunity to note that it is indeed extremely fortunate that the most famous approach to perform such a "folding" of the small-component onto the Hamiltonian is named after an author called Foldy!

A particularly efficient means of carrying out the Foldy-Wouthuysen transformation is represented by the so-called eXact two-component (X2C) method [99, 172, 203, 208, 209, 210, 244, 279, 280, 288]. As the name suggests this approach can also reproduce exactly the positive energy spectrum of the DC Hamiltonian. It is based on the idea that the Foldy-Wouthuysen transformation matrix can be constructed for DFT or HF calculations, from the eigenstates of the one-electron part of the DC Hamiltonian (i.e. excluding the two-electron term $\mathbf{g}^{Coulomb}$) [99]. The approach therefore consists of a two-step procedure, in which the four-component eigenstates of the one-electron DC Hamiltonian are initially found. Then, the Foldy-Wouthuysen matrix is subsequently built and used to fully solve the many-body problem (now including the two-electron term $\mathbf{g}^{Coulomb}$) in a two-component form [267]. The superior combination of efficiency and accuracy of the X2C approach means that it has become popular in recent years and is now implemented in several computer programs for calculations on molecular systems [1, 2, 3, 307].

Lastly, it is stressed that because all of these two-component approaches (whether of the Pauli, ZORA, DKH or X2C type) involve a decoupling transformation of the large and small components to allow the calculation of the energy, a similar transformation would also need to be applied for the calculation of properties. So for example, a property like the electron density would not be accurately calculated simply by taking the square modulus of the resulting wavefunction $\tilde{\boldsymbol{\psi}}^{L}$. Failure to include the necessary property transformation would result in so-called picture-change errors, which can result in errors larger than the relativistic effects themselves [18, 100, 186, 262, 267].

2.6 The Pseudopotential Approximation

Very often relativistic effects are studied in those systems containing heavy atoms, in which the relativistic effects are most important. In this case, the presence of a very large number of electrons makes for long sums in Eq. (2.18) and correspondingly expensive calculations. What is more, the possibly large number of electrons in the core region have little participation in determining many physical and chemical properties, which are often dominated by valence electrons. Useful means to deal with these issues are the so-called pseudopotential or (relativistic)-effective-core potential, (R)ECP, approximations. The (R)ECPs are effective potentials representing frozen configurations of core electrons, that are obtained by fitting to atomic calculations [52, 84, 86, 256, 276]. Methods which are on the other hand not subject to the frozen-core approximation are referred to as all-electron (AE) approaches. The fitting of the (R)ECP can be performed to non-relativistic atomic calculations, in the ECP case, or atomic calculations with generally any approximation to the Dirac equation, in the RECP case. Once the fitting has been performed, and the parameters of the relativistic effective potential $\mathbf{U}^{REP}$ are extracted, then it is used to solve a simplified version of Eq. (2.18), in which the sums over electron coordinates now only run over those of the N_v valence electrons:

$$\tilde{\mathbf{H}}_D = \sum_{i}^{N_v} \tilde{\mathbf{h}}_D(i) + \mathbb{I} \otimes \tilde{V}_{NN} + \sum_{i>j}^{N_v} \tilde{\mathbf{g}}(i,j) \,, \tag{2.37}$$

where the tilde over the $\tilde{\mathbf{H}}_D$, $\tilde{\mathbf{h}}_D$ and $\tilde{\mathbf{g}}$ indicate that the many-body and one-electron Dirac Hamiltonians, as well as the two-electron operator now have an approximated form, from the RECP approximation. In Eq. (2.37), the size of the identity operator $\mathbb{I}$ and of the bold quantities may be 1×1, 2×2 or 4×4, because this actually depends on how the polyatomic, valence-electron problem is solved. Typically, if the RECP is fitted from atomic calculations performed with an approximation to the Dirac equation that only includes SR effects (i.e. mass-velocity- and *Zitterbewegung*-related effects), then the polyatomic, valence-electron problem is solved using a one-component wavefunction, and the $\mathbb{I}$, as well as the bold quantites in Eq. (2.37) have a size of 1×1. In this case the fitting can be achieved using the SR Dirac Hamiltonian, or the Wood-Boring or Cowan-Griffin Hamiltonians [68, 86, 334]. Otherwise, if not only SR, but also SOC effects are included in the RECP, then the DC, DCB or even a DCB+QED Hamiltonians can be used for the atomic calculations upon which the fitting is performed. Generally, in this SOC-including case, the valence-electron problem is solved in a two-component form, and hence the $\mathbb{I}$, as well as the bold quantities in Eq. (2.37) have a size of 2×2 [86].

Eq. (2.37) can indeed be written in a more explicit form, as follows:

$$\tilde{\mathbf{H}}_D = \sum_{i}^{N_v} \left[\mathbb{I} \otimes \left(\frac{\mathbf{p}^2}{2m} + \tilde{V}_{eN}(i) + \tilde{V}_{NN} + \sum_{i>j}^{N_v} g^{Coulomb}(i,j) \right) + \sum_{A} \mathbf{U}^{REP}\left(i, \mathbf{A}\right) \right] , \tag{2.38}$$

where $\mathbf{A}$ is the position in space of nucleus A and the tilde over the $\tilde{V}_{eN}$ and $\tilde{V}_{NN}$ indicates that they have been modified from Eqs. (2.19) and (2.20), respectively, and are now expressed in terms of effective nuclear charges Z_A^{eff} and Z_B^{eff}, to account for the modification of the core by the RECP, as follows:

$$\tilde{V}_{eN}(i) = -\sum_{A} \frac{Z_A^{eff} e^2}{r_{Ai}} \,, \tag{2.39a}$$

and for the nuclear-nuclear term:

$$\tilde{V}_{NN}(i) = \sum_{B>A} \frac{Z_A^{eff} Z_B^{eff}}{R_{AB}} \,. \tag{2.39b}$$

The effective nuclear charges of center A is calculated as the difference $Z_A^{eff} = Z_A - n_A$ between the true charge of this center, Z_A, and the number of core electrons included in the RECP for center A, n_A.

In the passage from Eq. (2.37) to Eq. (2.38), it is assumed that all explicitly relativistic operators (e.g. mass-velocity-, Darwin-, Breit-, SOC-type operators) are included in the $\mathbf{U}^{REP}$. This assumption means that all core-core SR and SO electron-electron interactions are implicitly included in the RECP and the generally less important valence-valence SR and SO interaction are neglected. All relativistic effects that are left to be treated variationally are the core-valence SR and SO interactions. In the following we discuss the form of the potential $\mathbf{U}^{REP}$ for the SOC-including case. RECPs including only SR effects can then be obtained from these expressions as a limiting case. The brief discussion only highlights the main aspects and a more ample discussion can be found in paper IV.

The procedure for including both SR and SO effects in the RECP was pioneered by Ermler, Pitzer and co-workers [108]. The $\mathbf{U}^{REP}$ can be expanded exactly in terms of purely radial functions $U_{lj}^{REP}(r_{Ai})$ and angular functions $\mathbf{P}_{lj}\left(\Omega_{Ai}\right)$, depending on the solid angle Ω_{Ai}, for each angular-momentum l and total-angular momentum j components, as follows [108, 256]:

$$\mathbf{U}^{REP}\left(i,\mathbf{A}\right) = \sum_{l=0}^{\infty}\sum_{j=j_\beta}^{j_\alpha} U_{lj}^{REP}(r_{Ai})\mathbf{P}_{lj}\left(\Omega_{Ai}\right) \ , \tag{2.40}$$

where the abbreviated notation $j_\alpha = |l+1/2|$ and $j_\beta = |l-1/2|$ has been introduced in Eq. (2.40). The angular functions $\mathbf{P}_{lj}\left(\Omega_{Ai}\right)$ are written in terms of the eigenfunctions of the Dirac or Pauli Hamiltonians, as follows [59]:[1]

$$\mathbf{P}_{lj}\left(\Omega_{Ai}\right) = \sum_{m_j=-j}^{j} |\mathbf{l},\mathbf{j},\mathbf{m_j}\rangle\langle\mathbf{l},\mathbf{j},\mathbf{m_j}| \ , \tag{2.41}$$

in which the $|\mathbf{l},\mathbf{j},\mathbf{m_j}\rangle$ are angular projectors onto the eigenfunctions of the Dirac or Pauli Hamiltonians for the one-electron atom. The action of $\langle\mathbf{l},\mathbf{j},\mathbf{m_j}|$ on a generic one-electron spin-dependent function $|\boldsymbol{\phi}^\sigma\rangle$, with $\sigma = \alpha$ or β, evaluated in the position basis, reads as follows:

$$\langle\mathbf{l},\mathbf{j},\mathbf{m_j}|\boldsymbol{\phi}^\sigma\rangle = \vec{\boldsymbol{\sigma}} C^*_{l,m_l,j,m_j,\sigma} \int d\Omega_{Ai} X_{l_\sigma}^{m_\sigma}\left(\Omega_{Ai}\right)\boldsymbol{\phi}^\sigma(\mathbf{r}_i) \ , \tag{2.42}$$

in which the $C_{l,m_l,j,m_j,\sigma}$ are Clebsch-Gordon coefficients, $X_{l_\sigma}^{m_\sigma}$ are real spherical harmonics (the exact values of l_σ and m_σ are provided in Ref. [59]) and $\vec{\boldsymbol{\sigma}} = \vec{\boldsymbol{\alpha}}$ or $\vec{\boldsymbol{\beta}}$ are the simultaneous eigenfunctions of the spin operators $\mathbf{S}_z$ and $\mathbf{S}^2$, and read as follows:

$$\vec{\boldsymbol{\alpha}} = \begin{pmatrix}1\\0\end{pmatrix} \quad \text{and} \quad \vec{\boldsymbol{\beta}} = \begin{pmatrix}0\\1\end{pmatrix} \tag{2.43}$$

On the other hand, the radial functions $U_{lj}^{REP}(r_{Ai})$ appearing in Eq. (2.40) are typically represented as linear combinations of Gaussian functions multiplied by powers of the electron-core distance r_{Ai} [86]:

$$U_{lj}^{REP}(r_{Ai}) = \sum_k c_{klj}^A r_{Ai}^{n_{klj}} e^{-\alpha_{klj}^A r_{Ai}^2} \ , \tag{2.44}$$

where the powers n_{klj} typically take on a value of 0, -1 or -2 [86]. The fitting procedure of the RECP then

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[1] The use of the bra-ket notation in this section is chosen for consistency with the pseudopotential and ECP literature, but is formally an abuse of the notation as originally intended [83]. See Appendix A for a proper definition.

consists of finding the optimal values of the coefficients c^{A}_{klj} in the linear combination in Eq. (2.44), as well as the exponents a^{A}_{klj} for different values of the angular momentum and total angular momentum, in order to best reproduce the configuration of electrons from the reference atomic calculations. The fact that the U^{REP}_{lj} are represented in terms of Gaussian functions is purely for reasons of numerical convenience, as will become more clear latter on. Two principal approaches are used for this fitting. The energy-consistent method aims to find the best c^{A}_{klj} and a^{A}_{klj} that reproduce the energy spectrum of the reference atomic calculations for the ground and a set of excited states. The shape-consistent method, on the other hand aims to reproduce the shape of the orbitals from the reference calculations, as well as the energy spectrum, for a given fixed state [86].

The presence of a spin dependence in Eq. (2.42) means that it is difficult to work with the potential expressed as in Eq. (2.40). It is hence beneficial to re-express the potential $\mathbf{U}^{REP}$ in terms of a spin-independent part U^{AREP} and a spin-dependent part $\mathbf{U}_{SOREP}$, making use of Eq. (2.45), as shown below [108]:

$$\mathbf{U}^{REP}(i,\mathbf{A}) = U^{AREP}(i,\mathbf{A}) + \mathbf{U}_{SOREP}(i,\mathbf{A}) \ , \tag{2.45}$$

where the potential $\mathbf{U}^{REP}$ has been written as a sum of a purely SR term U^{AREP} (averaged relativistic effective potential) and an SO term $\mathbf{U}_{SOREP}$.

The U^{AREP} is in turn expanded in a set of purely radial function $U^{AREP}_{l}(r_{Ai})$ and angular functions $P_l(\Omega_{Ai})$, for each angular-momentum component l, as follows:

$$U^{AREP}(i,\mathbf{A}) \approx U^{AREP}_{L}(r_{Ai}) + \sum_{l=0}^{L}\left[U^{AREP}_{l}(r_{Ai}) - U^{AREP}_{L}(r_{Ai})\right] P_l(\Omega_{Ai}) \ , \tag{2.46}$$

where the expansion is approximated up to angular momentum L and the angular functions P_l are projectors onto each angular momentum component l, as follows:

$$P_l(\Omega_{Ai}) = \sum_{m=-l}^{l} |l,m\rangle\langle l,m| \ , \tag{2.47}$$

in which the $|l,m\rangle$ are projectors onto real spherical harmonics $\mathcal{X}^{m}_{l}$ [86, 226, 256]. These are now independent of spin, in contrast to the $|\mathbf{l},\mathbf{j},\mathbf{m_j}\rangle$ of Eq. (2.41). For example, the action of $\langle l,m|$ on a generic one-electron function $|\boldsymbol{\phi}\rangle$, which may or may not depend on spin, evaluated in the position basis, reads:

$$\langle l,m|\boldsymbol{\phi}\rangle = \int d\Omega_{Ai}\mathcal{X}^{m}_{l}(\Omega_{Ai})\,\boldsymbol{\phi}(\mathbf{r}_i) \ . \tag{2.48}$$

The radial function $U^{AREP}_{l}(r_{Ai})$ can be expressed in terms of the $U^{REP}_{lj}(r_{Ai})$ of Eqs. (2.40) and (2.44), as follows [256]:

$$U^{AREP}_{l}(r_{Ai}) = \frac{1}{2l+1}\left[lU^{REP}_{lj_\beta}(r_{Ai}) + (l+1)\,U^{REP}_{lj_\alpha}(r_{Ai})\right] \ . \tag{2.49}$$

Otherwise, the spin-dependent part of the operator $\mathbf{U}_{SOREP}$ in Eq. (2.45) is written also in terms of the angular function P_l of Eq. (2.47), as well as radial function $U_l^{SOREP}(r_{Ai})$, as follows [108, 256]:

$$\mathbf{U}_{SOREP}(i,\mathbf{A}) \approx \frac{1}{2}\sum_{l=1}^{L-1} U_l^{SOREP}(r_{Ai})\, P_l(\Omega_{Ai})\, \mathbf{L}_{Ai}\cdot\boldsymbol{\sigma} P_l(\Omega_{Ai}) \ , \tag{2.50}$$

where the expansion has been again approximated by truncation, now up to a maximum angular momentum of $L-1$. The alert reader can notice the similarity between Eqs. (2.50) and (2.35), both of which indeed represent the SOC operator in terms of a product of the angular momentum operator $\mathbf{L}_{Ai}$ with the vector of Pauli matrices $\boldsymbol{\sigma}$.

Finally, the radial functions $U_l^{SOREP}(r_{Ai})$ in Eq. (2.50) can be expressed in terms of the $U_{lj}^{REP}(r_{Ai})$ extracted from the fitting procedure and appearing in Eqs. (2.40) and (2.44), as follows [108, 256]:

$$U_l^{SOREP}(r_{Ai}) = \frac{2}{2l+1}\left[U_{lj_\alpha}^{REP}(r_{Ai}) - U_{lj_\beta}^{REP}(r_{Ai})\right] \ . \tag{2.51}$$

We note that different authors use different definitions for the U_l^{SOREP}, which may be different from Eq. (2.51) up to an l-dependent pre-factor, and this must be carefully taken into account when making the input for a calculation. The fact that the RECP can be seperated in a purely SR term and a spin-dependent term in Eq. (2.45), means that purely SR RECPs can be easily constructed by simply setting $\mathbf{U}_{SOREP}(i,\mathbf{A}) = \mathbf{0}$. As a consequence, the RECP approximation permits to include SR effects in a calculation for no additional cost, when compared to the non-relativistic ECP method, because these two approaches only differ in the chosen Hamiltonian for the reference atomic calculation. The fact that the RECP method makes treating SR effects essentially free, is not a minor point, and has indeed rendered it the most popular method to include SR effects in calculations on molecules and materials. In fact, almost all molecular programs can nowadays perform one-component calculations with purely SR RECPs [1, 3, 14, 127, 237, 282, 315, 331]. The situation is completely different for performing calculations with RECPs that include spin-dependent relativistic effects through the $\mathbf{U}_{SOREP}(i,\mathbf{A})$. In this case, the presence of a SOC operator changes the symmetry of the electronic wavefunction. This means that the programs usually structured for performing one-component calculations, using real algebra must then be generalized to perform two-component calculations with complex algebra and relativistic space-spin symmetry. Nevertheless, in recent years, efforts have gone towards treating SOC through spin-dependent RECPs in some computer programs for molecular calculations [15, 240, 346].

Although the RECP method is subject to the frozen-core approximation, there are indeed many advantages to using it for treating both SR and SOC effects, when compared to AE approaches (e.g. the DC, DCB, ZORA, DKH, X2C approaches). On the one hand, unlike the AE two-component approaches, the RECP method allow us to perform calculations in a two-component spinor basis, without having to correct for picture-change errors. Additionally, the expression for the Hamiltonian in Eq. (2.38) is relatively simple, so that efficient analytical algorithms are available [226, 256]. In comparison, of course the AE approches are generally more expensive, because in the AE case the core electrons need to be fully treated variationally. But even with this additional cost, in practice, it is not clear exactly in which cases the AE approaches are more accurate than the RECP one. Indeed, almost all relativistic AE calculations are performed at best at the DC level. The DC Hamiltonian is, as discussed in section 2.3, by no means exact, because it is missing the two-electron contribution that originates from the electronic vector potential and gives rise to the Breit and further QED interactions. In contrast, using the RECP method, the two-electron potential can be pushed beyond the DC approximation at the single-atom stage, for little additional computational cost. Indeed, calculations have previously been reported, in which the RECP built from a DCB atomic reference resulted in a calculation on the polyatomic molecule that appeared to be more accurate than the much more expensive AE four-component DC one [85, 330]. So in practical calculations, an RECP build from a DCB or DCB+QED atomic reference calculation might, at least in some cases, be more accurate than an AE DC calculation. On the other hand, of course, an RECP can never be more accurate than the Hamiltonian from which it is modeled.

There are, however, specific calculations for which the AE approach is clearly necessary. These are the calculations of those properties which are directly related to the core electron configuration. This include X-ray, nuclear magnetic resonance, or Mössbauer spectroscopic calculations, for example, which would not be accurately performed by the RECP approach that is subject to the frozen-core approximation. Any AE approach can also be expected to almost always be more accurate than the RECP one for calculations on very light atoms, in which relativistic effects are small.

Because of the arguments elaborated above, almost all calculations reported in this thesis have been performed with the RECP approximation. Fortunately, we did not need to make any of the RECPs, because an extensive library of high quality RECPs, generated by the energy-consistent method, is made available to us by Michael Dolg and the Stuttgart-Köln group [6]. Another useful library, this time of RECP generated by the shape-consistent method, is made available to us by Phillip A. Christiansen and the Columbus group [4].

3 Expansion of the Wavefunction in a Finite Basis

3.1 Slater Determinant Representation and the Slater-Condon Rules

From chapter 2, we now have appropriate (approximate) expressions for many-body relativistic Hamiltonians, which we can use to develop approximate methods to solve the Dirac equation for molecules and materials. We are however still missing an appropriate representation of the wavefunction. In principle, the many-body Dirac wavefunction would depend on the coordinates of all the particles in the system. We have seen that we can seperate the nuclear problem from the electronic one using the Born-Oppenheimer approximation, such that we can solve seperately for the electronic part of the wavefunction, and drop the dependence on the coordinates of the nuclei. But still, for a system with N electrons, the Dirac wavefunction expressed in the position basis $\boldsymbol{\psi}(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N)$ depends on the coordinates of all of the electrons. This means that the simple calculation of an expectation value in the position basis would involve a $3N$-dimensional integral, surely making any calculation impossible if it involves more than a few electrons. The workaround to this problem was formulated by John C. Slater and Eugene U. Condon in 1929 and 1930, respectively [65, 293]. They formulated what are known as the Slater-Condon rules, which allow to reduce the calculation of the expectation values to integrals of at most 6 dimensions, instead of $3N$ dimensions. The trick is to represent the many-electron wavefunction $|\boldsymbol{\psi}\rangle$ as a sum of products of one-electron functions, as follows:

$$|\boldsymbol{\psi}\rangle = \sum_I c_I |\boldsymbol{\Phi}_I\rangle \tag{3.1}$$

where the $|\boldsymbol{\Phi}_I\rangle$ are products of one-electron functions $|\boldsymbol{\phi}_i\rangle$, in which i labels one of the N singly-occupied one-electron functions, for example:

$$|\boldsymbol{\Phi}_1\rangle = |\boldsymbol{\phi}_1\rangle \tilde{\otimes} |\boldsymbol{\phi}_2\rangle \tilde{\otimes} \ldots \tilde{\otimes} |\boldsymbol{\phi}_N\rangle \,, \tag{3.2}$$

where $\tilde{\otimes}$ is a generic product, whose exact form is to be specified. The index I in Eq. (3.1) determines the ordering of the subscripts i in Eq. (3.2). The $|\boldsymbol{\psi}\rangle$, $|\boldsymbol{\Phi}_I\rangle$ and $|\boldsymbol{\phi}_i\rangle$ can be of dimension 1×1, 2×1 or 4×1, depending on whether a one-component, two-component or four-component approximation for the Dirac equation is solved. In this thesis, we are mostly interested in approximations involving only one of the $|\boldsymbol{\Phi}_I\rangle$, so substituting Eq. (3.2) in Eq. (3.1), we write:

$$|\boldsymbol{\psi}\rangle \approx |\boldsymbol{\Phi}_1\rangle = |\boldsymbol{\phi}_1\rangle \tilde{\otimes} |\boldsymbol{\phi}_2\rangle \tilde{\otimes} \ldots \tilde{\otimes} |\boldsymbol{\phi}_N\rangle \,. \tag{3.3}$$

We will see later that this is an appropriate form for the wavefunction in the HF approximation, or for the Kohn-Sham (KS) DFT, which are the approaches used for nearly all calculations reported in this thesis. Wavefunctions involving more than one term in Eq. (3.1), are appropriate forms for correlated wavefunction methods, like the configuration-interaction method (CI), which are outside the scope of this discussion, although relativistic CI calculations are reported in paper VI.

What is missing now to better exactly define the form of the wavefunction from Eq. (3.3) is to define exactly how to perform the product $\tilde{\otimes}$. One constraint on the form of this product is given to us by the Pauli exclusion principle, which states that two or more identical fermions cannot occupy exactly the same quantum state. More specifically, Wolgang Pauli showed in 1925 that the wavefuncton is actually antisymmetric with respect to the exchange of two particles, that is to say[241]:

$$\langle r_1, r_2, \ldots, r_N | \psi \rangle = \psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) = -\psi(\mathbf{r}_2, \mathbf{r}_1, \ldots, \mathbf{r}_N) \ . \tag{3.4}$$

The repulsion of particles with similar quantum numbers that arises because of the need to obey the Pauli exclusion principle is called Pauli repulsion. Eq. (3.4) implies that the product expression in Eq. (3.3), must be written as an antisymmetric product in the position basis, as follows:

$$\begin{aligned} \psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) &\approx \mathcal{A}(\langle r_1|\phi_1\rangle \times \langle r_2|\phi_2\rangle \times \cdots \times \langle r_N|\phi_N\rangle) \\ &= \mathcal{A}(\phi_1(\mathbf{r}_1) \times \phi_2(\mathbf{r}_2) \times \cdots \times \phi_N(\mathbf{r}_N)) \ , \end{aligned} \tag{3.5}$$

where $\mathcal{A}$ is an antisymmetrizer which ensures that the wavefunction ψ in Eq. (3.5) changes sign upon exchange of any of the $\mathbf{r}_i$. One way of respecting the antisymmety criterion as written in Eq. (3.5) is to write the ψ as a determinant containing all of the $|\phi_i\rangle$. Such a wavefunction is called a Slater determinant and reads as follows [158]:

$$\psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) \approx \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(\mathbf{r}_1) & \phi_2(\mathbf{r}_1) & \ldots & \phi_N(\mathbf{r}_1) \\ \phi_1(\mathbf{r}_2) & \phi_2(\mathbf{r}_2) & \ldots & \phi_N(\mathbf{r}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_1(\mathbf{r}_N) & \phi_2(\mathbf{r}_N) & \ldots & \phi_N(\mathbf{r}_N) \end{vmatrix} \ , \tag{3.6}$$

in which the pre-factor containing $\sqrt{N!}$ out front of the determinant in Eq. (3.6) is included as a normalization constant. With Eq. (3.6), we now have a means to represent the wavefunction in a convenient form. But in order to develop practical algorithms, we still need to know how to efficiently evaluate expectation values, using the Slater determinant representation. In order to do this, we need a compact notation to write different kinds of Slater determinants. The notation we adopt here is as follows. A Slater determinant wich differs from $|\psi\rangle$ by one $|\psi_m^p\rangle$ or two $|\psi_{mn}^{pq}\rangle$ orbitals is denoted as:

$$\begin{aligned} &\psi(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N) \\ \approx\ &\mathcal{A}(\ \langle r_1|\phi_1\rangle \times \langle r_2|\phi_2\rangle \times\ \ldots\ \times \langle r_N|\phi_N\rangle\ ) \end{aligned} \tag{3.7a}$$

$$\begin{aligned} &\psi_m^p(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N) \\ \approx\ &\mathcal{A}\Big(\ \langle r_1|\phi_1\rangle \times \langle r_2|\phi_2\rangle \times\ \ldots\ \times \langle r_m|\phi_p\rangle \times\ \ldots\ \times \langle r_n|\phi_n\rangle \times\ \ldots\ \times \langle r_N|\phi_N\rangle\ \Big) \end{aligned} \tag{3.7b}$$

$$\begin{aligned} &\psi_{mn}^{pq}(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N) \\ \approx\ &\mathcal{A}\Big(\ \langle r_1|\phi_1\rangle \times \langle r_2|\phi_2\rangle \times\ \ldots\ \times \langle r_m|\phi_p\rangle \times\ \ldots\ \times \langle r_n|\phi_q\rangle \times\ \ldots\ \times \langle r_N|\phi_N\rangle\ \Big) \ . \end{aligned} \tag{3.7c}$$

So the notation $\boldsymbol{\psi}_m^p$ means "take orbital m in Eq. (3.6) and replace it by orbital p". In Eq. (3.7) and throughout this section, the superscripts and subscripts m, n, o label occupied (occ) orbitals, p, q, r label virtual (virt, or unoccupied) orbitals and i, j, k label generic (both occupied or virtual) orbitals. When it is convenient, the abbreviated notation $|\boldsymbol{\phi}_i\rangle = |i\rangle$ will be used.

We have seen from Eq. (2.18) and Eq. (2.38) that the approximate forms of the Dirac Hamiltonian will be constructed from operators that depend on the coordinates of at most two-electrons. Slater and Condon have shown that the consequence of this for Slater determinants is that expectation values can be calculated using integrals over the coordinates of one or two electrons [65, 293]. To write down explicitly expressions for the Slater-Condon rules, it is useful to introduce the two-electron integral, involving the generic two-electron operator $O^{[2]}$, and one-electron operators $\mathbf{O}^{[1]}$, as follows:

$$(mp|O^{[2]}|nq) \equiv \int d\mathbf{r}_i \, \boldsymbol{\phi}_m^\dagger(\mathbf{r}_i)\mathbf{O}^{[1]}(\mathbf{r}_i)\boldsymbol{\phi}_p(\mathbf{r}_i) \int d\mathbf{r}_j \; O^{[2]}(\mathbf{r}_i, \mathbf{r}_j) \, \boldsymbol{\phi}_n^\dagger(\mathbf{r}_j)\mathbf{O}^{[1]}(\mathbf{r}_j)\boldsymbol{\phi}_q(\mathbf{r}_j) \, , \tag{3.8}$$

and the one-electron integrals:

$$(m|O^{[1]}|p) \equiv \int d\mathbf{r}_i\boldsymbol{\phi}_m^\dagger(\mathbf{r}_i)\mathbf{O}^{[1]}(\mathbf{r}_i)\boldsymbol{\phi}_p(\mathbf{r}_i) \, . \tag{3.9}$$

For a one-electron operator in a two-component spinor basis, it is also convenient to introduce the following notation:

$$\mathbf{O}^{[1]}(\mathbf{r}_i) = \begin{pmatrix} O^{\alpha\alpha}(\mathbf{r}_i) & O^{\alpha\beta}(\mathbf{r}_i) \\ O^{\beta\alpha}(\mathbf{r}_i) & O^{\beta\beta}(\mathbf{r}_i) \end{pmatrix} \tag{3.10}$$

Furthermore, we assume that any operator $\mathbf{O}$ can be written as a sum of operators which depend individually on the coordinates of one electron $\mathbf{O}^{[1]}$ or two electrons $O^{[2]}$:

$$\mathbf{O}\left(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N\right) = \sum_i \mathbf{O}^{[1]}(\mathbf{r}_i) + \frac{1}{2}\sum_i\sum_{j\neq i}\mathbf{O}^{[1]}(\mathbf{r}_i)O^{[2]}(\mathbf{r}_i, \mathbf{r}_j)\mathbf{O}^{[1]}(\mathbf{r}_j) \, . \tag{3.11}$$

Before proceeding further, we now provide two examples of the application of Eq. (3.8) to the operators introduced in chapter 2.

The first example is the Gaunt operator of Eq. (2.22). Inserting the form of this operator in Eq. (3.8):

$$\begin{aligned} (mp|g^{Gaunt}|nq) &= -\int d\mathbf{r}_i \, \boldsymbol{\phi}_m^\dagger(\mathbf{r}_i)\alpha\boldsymbol{\phi}_p(\mathbf{r}_i) \cdot \int d\mathbf{r}_j \, \frac{1}{r_{ij}} \, \boldsymbol{\phi}_n^\dagger(\mathbf{r}_j)\alpha\boldsymbol{\phi}_q(\mathbf{r}_j) \\ &= -\sum_{c=x,y,z} \int d\mathbf{r}_i \, \boldsymbol{\phi}_m^\dagger(\mathbf{r}_i)\alpha_c\boldsymbol{\phi}_p(\mathbf{r}_i) \int d\mathbf{r}_j \, \frac{1}{r_{ij}} \, \boldsymbol{\phi}_n^\dagger(\mathbf{r}_j)\alpha_c\boldsymbol{\phi}_q(\mathbf{r}_j) \, . \end{aligned} \tag{3.12}$$

The second example is the Coulomb two-electron operator in Eq. (2.38). Inserting this one now in Eq. (3.8):

$$\begin{aligned}(mp|g^{Coulomb}|nq) &= \int d\mathbf{r}_i\ \boldsymbol{\phi}_m^\dagger(\mathbf{r}_i)\mathbb{I}\boldsymbol{\phi}_p(\mathbf{r}_i)\otimes\int d\mathbf{r}_j\ \frac{1}{r_{ij}}\ \boldsymbol{\phi}_n^\dagger(\mathbf{r}_j)\boldsymbol{\phi}_q(\mathbf{r}_j)\\ &= \int d\mathbf{r}_i\ \boldsymbol{\phi}_m^\dagger(\mathbf{r}_i)\boldsymbol{\phi}_p(\mathbf{r}_i)\int d\mathbf{r}_j\ \frac{1}{r_{ij}}\ \boldsymbol{\phi}_n^\dagger(\mathbf{r}_j)\boldsymbol{\phi}_q(\mathbf{r}_j)\ . \end{aligned} \tag{3.13}$$

The Slater-Condon rules for evaluating expectation values (or matrix-elements) of such an operator **O** are as follows [65, 293].

If a matrix-element is calculated between two-determinants that are identical:

$$\langle\psi|\mathbf{O}|\psi\rangle \approx \sum_m^{\in occ}(m|O^{[1]}|m) + \frac{1}{2}\sum_m^{\in occ}\sum_n^{\in occ}\left[(mm|O^{[2]}|nn) - (mn|O^{[2]}|nm)\right]\ , \tag{3.14a}$$

where in the above we use an approximated equal sign, instead of an equal sign, because the $|\psi\rangle$ has been approximated by a single Slater determinant.

If the determinants differ by one orbital:

$$\langle\psi|\mathbf{O}|\psi_m^p\rangle \approx (m|O^{[1]}|p) + \sum_n^{\in occ}\left[(mp|O^{[2]}|nn) - (mn|O^{[2]}|np)\right]\ . \tag{3.14b}$$

If the determinants differ by two orbitals:

$$\langle\psi|\mathbf{O}|\psi_{mn}^{pq}\rangle \approx (mp|O^{[2]}|nq) - (mq|O^{[2]}|np)\ . \tag{3.14c}$$

Finally, if the determinants differ by more than two orbitals:

$$\langle\psi|\mathbf{O}|\psi_{mno...}^{pqr...}\rangle \approx 0\ . \tag{3.14d}$$

3.2 Expansion of One-Electron Functions in a Finite Basis

We have seen from section 3.1 how expectation values of many-electron operators can be evaluated in terms of relatively simple one- or two-electron integrals, involving one-electron functions. The first step towards building an algorithm to actually calculate the required integrals is now to expand the one-electron functions in a basis. For periodic systems, or materials, the relevant one-electron functions are called crystalline-orbitals (COs), while for molecular systems, they are called molecular orbitals (MOs). We postpone aspects related to the treatment of the lattice to section 4.3, so for now we assume that we are working with MOs. We also henceforth assume that the Dirac equation is solved in a one-component form, or a two-component form, so that the MOs have a size of 1 × 1 or 2 × 1.

The MOs are written as a direct product of space and spin functions, as follows:

$$|i\rangle = |i^\alpha\rangle\otimes|\alpha\rangle + |i^\beta\rangle\otimes|\beta\rangle \tag{3.15}$$

The projection of the MO $|i\rangle$ onto the basis of positions of electron j, $\langle r_j|$ hence reads as follows:

$$\begin{aligned}\langle r_j|i\rangle &= \langle r_j|i^{\alpha}\rangle \otimes |\alpha\rangle + \langle r_j|i^{\beta}\rangle \otimes |\beta\rangle \\ &= \sum_{\mu} c^{\alpha}_{\mu i}\chi_{\mu}\left(\mathbf{r}_j\right) \otimes |\alpha\rangle + c^{\beta}_{\mu i}\chi_{\mu}\left(\mathbf{r}_j\right) \otimes |\beta\rangle \,, \end{aligned} \tag{3.16}$$

where the χ_{μ} are atomic orbitals (AOs) and the coefficients of the linear expansion $c^{\alpha}_{\mu i}$ and $c^{\beta}_{\mu i}$ are, in general, unknown complex numbers, to be determined by the calculation procedure. The remaining products with spin functions are evaluated as follows, for generic indices σ and $\sigma' = \alpha$ or β:

$$\langle \sigma'| \left(|i^{\sigma}\rangle \otimes |\sigma\rangle\right) = |i^{\sigma}\rangle\langle\sigma'|\sigma\rangle = |i^{\sigma}\rangle\delta_{\sigma\sigma'} \,, \tag{3.17}$$

where $\delta_{\sigma\sigma'}$ is the Kronecker delta function.

We now need to choose a particular analytical form for the AOs $\chi_{\mu}\left(\mathbf{r}_j\right)$. A good starting point for this purpose is to look at the analytical solution of the Schrödinger or Dirac equation for the Hydrogen atom. These solutions are composed of a product of a Slater-type function $e^{-\gamma r_j}$ with a complex-solid-spherical harmonic (CSSH) $Y^m_{l,n}\left(\mathbf{r}_j\right)$. Such an AO is called a Slater-type orbital (STO), and reads as follows:

$$\begin{aligned} W\left(\gamma, \mathbf{r}_j, n, l, m\right) &= r_j^{2n+l} P_l^{|m|}\left(\cos\theta_j\right) e^{im\varphi_j} e^{-\gamma r_j} \\ &= Y^m_{l,n}\left(\mathbf{r}_j\right) e^{-\gamma r_j} \,, \end{aligned} \tag{3.18}$$

in which θ_j and φ_j are the azimuthal and polar angles of electron j in a spherical coordinate system. The $P_l^{|m|}$ in Eq. (3.18) is a Legendre function. We could very well use the STOs W to represent our AOs χ_{μ}, but the problem is that it is relatively complicated to evaluate integrals containing STOs. We therefore look to alternate solutions. One particularly attractive choice is the use of Gaussian functions, as first suggested by Samuel Francis Boys in 1950 [39]. It is indeed much easier to evaluate integrals with Gaussian functions rather than STOs. For example, the definite integral of a Gaussian function from 0 to x is just the error function:

$$\operatorname{erf} x = \frac{2}{\sqrt{\pi}} \int_0^x e^{-|\mathbf{r}_j|^2} dr_j \,, \tag{3.19}$$

Moreover, the product of two Gaussians, centered respectively at the points $\mathbf{A}_{\mu}$ and $\mathbf{A}_{\nu}$ is itself a Gaussian function:

$$\begin{aligned} e^{-\gamma|\mathbf{r}_j-\mathbf{A}_{\mu}|^2} e^{-\tilde{\gamma}|\mathbf{r}_j-\mathbf{A}_{\nu}|^2} &= \exp\left[-\xi|\mathbf{r}_j - \mathbf{P}|^2 + |\mathbf{P}|^2 - \frac{\gamma|\mathbf{A}_{\mu}|^2 + \tilde{\gamma}|\mathbf{A}_{\nu}|^2}{\xi}\right] \\ &= \exp\left[-\frac{\gamma\tilde{\gamma}}{\xi}|\mathbf{R}|^2\right] e^{-\xi|\mathbf{r}_j-\mathbf{P}|^2} \,, \end{aligned} \tag{3.20}$$

in which $\xi = \gamma + \tilde{\gamma}$, $\mathbf{P} = \frac{\gamma\mathbf{A}_{\mu}+\tilde{\gamma}\mathbf{A}_{\nu}}{\xi}$ and $\mathbf{R} = \mathbf{A}_{\mu} - \mathbf{A}_{\nu}$. Eq. (3.20), can of course be extended to any arbitrary number of Gaussians. So for example, the product of four Gaussians is just another Gaussian. The usefulness of this relation for evaluating one- and two-electron integrals cannot be understated. For example, Eq. (3.20) could greatly simplify the integrals in Eq. (3.8) that involve four functions, which can be centered at one, two, three or four different points in space. This motivates using Gaussian-type orbitals (GTOs) instead of STOs for performing the calculation.

As a matter of fact, a Slater-type function can be represented exactly in terms of a Gaussian function, using the following integral transform [142, 187, 335]:

$$r_j^{n-1} e^{-\gamma r_j} = \frac{1}{2^n \sqrt{\pi}} \int_0^\infty s^{-(n+1)/2} H_n \left[\frac{\gamma}{2\sqrt{s}} \right] \exp\left[-\frac{\gamma^2}{4s} \right] e^{-s|\mathbf{r_j}|^2} ds \ , \tag{3.21}$$

where H_n is a Hermite polynomial. We can approximate the integral in Eq. (3.21) using numerical quadrature, and write:

$$e^{-\gamma r_j} \approx \sum_k c_k e^{-\gamma_k |\mathbf{r_j}|^2} \ , \tag{3.22}$$

where the c_k and γ_k are, in principal, numerical quadrature coefficients. Substituting Eq. (3.22), in Eq. (3.18), we have:

$$\begin{aligned} W\left(\gamma, \mathbf{r}_j, n, l, m\right) &= Y_{l,n}^m\left(\mathbf{r}_j\right) e^{-\gamma r_j} \approx Y_{l,n}^m\left(\mathbf{r}_j\right) \sum_k c_k e^{-\gamma_k |\mathbf{r_j}|^2} \\ &\equiv \sum_k c_k S\left(\gamma_k, \mathbf{r}_j, n, l, m\right) \ , \end{aligned} \tag{3.23}$$

in which the functions S are CSSH GTOs:

$$S\left(\gamma, \mathbf{r}_j - \mathbf{A}, n, l, m\right) = Y_{l,n}^m\left(\mathbf{r}_j - \mathbf{A}\right) e^{-\gamma|\mathbf{r_j} - \mathbf{A}|^2} \tag{3.24}$$

Eq. (3.23) justifies using CSSH GTOs to express the AOs χ_μ. The CSSH GTOs are indeed very similar to the basis functions in which the AOs are expanded in the Crystal program. The actual basis functions are the real-solid-spherical harmonic (RSSH) GTOs, which are related to the CSSH GTOs, as follows:

$$R(\gamma, \mathbf{r}_j - \mathbf{A}, n, l, 0) = S(\gamma, \mathbf{r}_j - \mathbf{A}, n, l, 0) \tag{3.25a}$$

$$R(\gamma, \mathbf{r}_j - \mathbf{A}, n, l, |m|) = \mathrm{Re}\left[S(\gamma, \mathbf{r}_j - \mathbf{A}, n, l, |m|)\right] \tag{3.25b}$$

$$R(\gamma, \mathbf{r}_j - \mathbf{A}, n, l, -|m|) = \mathrm{Im}\left[S(\gamma, \mathbf{r}_j - \mathbf{A}, n, l, |m|)\right] \tag{3.25c}$$

The use of RSSH GTOs instead of CSSH GTOs is only for numerical convenience, because it means that the program can be built using real algebra instead of complex algebra. The RSSH GTOs are build from homogeneous Cartesian polynomials, and read:

$$R(\gamma, \mathbf{r}_j - \mathbf{A}, n, l, m) = X_{l,n}^m(\mathbf{r}_j - \mathbf{A}) e^{-\gamma|\mathbf{r}_j - \mathbf{A}|^2} \ , \tag{3.26}$$

where the RSSH $X_{l,n}^m(\mathbf{r}_j - \mathbf{A})$, can be simply expressed in terms of the Cartesian components r_{xj}, r_{yj} and r_{zj}, as well as A_x, A_y and A_z of the vectors $\mathbf{r}_j$ and $\mathbf{A}$, as follows [163, 254]:

$$X^m_{l,n}(\mathbf{r}_j - \mathbf{A}) = \sum_{tuv}^{(t+u+v=l+2n)} D^m_l(t,u,v)(r_{xj} - A_x)^t (r_{yj} - A_y)^u (r_{zj} - A_z)^v \ , \tag{3.27}$$

in which the $D^m_l(t,u,v)$ are coefficients that can be obtained from recurrence relations [254]. The sum in Eq. (3.27) runs over all possible triplets t, u, v of positive integers $t \geq 0$, $u \geq 0$ and $v \geq 0$ which satisfy the relation $t + u + v = 2n + l$. The individual AOs χ_μ are then written as a linear combination of RSSH GTOs, as follows:

$$\chi_\mu\left(\mathbf{r}_j - \mathbf{A}_\mu\right) = N_\lambda N^m_l \sum_k N_l\left(\gamma^\lambda_k\right) d^\lambda_k R(\gamma^\lambda_k, \mathbf{r}_j - \mathbf{A}_\mu, n, l, m) \ , \tag{3.28}$$

where the N_λ, N^m_l and $N_l\left(\gamma^\lambda_k\right)$ are normalization coefficients, whose exact expressions can be found in paper I. The coefficients d^λ_k and exponents γ^λ_k are, in general, unknown. In practice, they are usually determined by minimizing the total energy of a reference system, but can also be re-optimized for each calculation [71]. The AOs are indeed grouped into shells λ. All AOs with the same azimuthal l and principal n quantum numbers are grouped into the same shell λ and share the same coefficients d^λ_k and exponents γ^λ_k. This means, for example that for a shell with $l = 1$ and $n = 1$ (i.e. $1p$ shell), that the $1p_x$, $1p_y$ and $1p_z$ AOs share the same d^λ_k and γ^λ_k, which reduces both time and memory requirements for a calculation. In Crystal, like in many other programs, basis functions with $n > 0$ are not actually used to expand the AOs, because different values of the d^λ_k and γ^λ_k are simply used instead to distinguish, for example the $1p$ functions from the $2p$ functions. The RSSH $X^m_{l,n}$ with $n > 0$ are however used as auxiliary functions, for the evaluation of integrals.

3.3 Evaluation of One- and Two-Electron Integrals

Now that we have chosen the proper analytical form for the one-electron functions, we can discuss explicit algorithms for the calculation of one-electron and two-electron integrals. We spare the reader of most mathematical details of the approach, which are discussed at a greater depth in paper I, and in Appendix B. Most methods for calculation of integrals are for the case in which the one-electron functions are not expanded in RSSH GTOs R, but rather Cartesian GTOs C, which read:

$$C(\gamma, \mathbf{r}_j - \mathbf{A}, t, u, v) = \left(r_{jx} - A_x\right)^t \left(r_{jy} - A_y\right)^u \left(r_{jz} - A_z\right)^v e^{-\gamma|\mathbf{r}_j - \mathbf{A}|^2} \ . \tag{3.29}$$

The CGTOs in Eq. (3.29) are related to RSSH GTOs of Eq. (3.26) through the coefficients $D^m_l(t,u,v)$ in Eq. (3.27), that is to say:

$$R(\gamma, \mathbf{r}_j - \mathbf{A}, n, l, m) = \sum_{tuv}^{(t+u+v=l+2n)} D^m_l(t,u,v) C(\gamma, \mathbf{r}_j - \mathbf{A}, t, u, v) \ . \tag{3.30}$$

The most widespread approach for evaluating one- and two-electron integrals in a basis of CGTOs is the one described in the seminal paper of McMurchie and Davidson [225]. There are however other notable approaches, such as the Rys quadrature method of Dupuis, Rys and King [96, 98], which is implemented in the historically significant Hondo program of Michel Dupuis and co-workers [97]. Another notable approach for evaluating one- and two-electron integrals is that of Obara and Saika (OS) [238]. The OS method was refined by Head-Gordon and Pople, who found that it is particularly well suited for evaluating integrals involving high angular momentum d- or f-type functions [156]. The Head-Gordon and Pople variation of the OS procedure is implemented in the Psi4 program [311].

All of the aforementionned approaches involve evaluating the required integrals in an auxiliary basis and then connecting the auxiliary basis to the relevant CGTOs using recurrence relations. Then, if the AOs are expanded in RSSH GTOs instead of CGTOs, the integrals are subsequently transformed through Eq. (3.30). Saunders suggested an alternate approach, in which the RSSH GTOs are directly expanded in the auxiliary basis, which, if carefully programmed, can diminish the cost of the calculation, because it avoids having to perform the expansion in Eq. (3.30) [268]. Other than this key distinction, the approach of Saunders is essentially a variant of the McMurchie and Davidson procedure, in which the auxiliary functions for calculating the integrals are the so-called Hermite Gaussian-type functions (HGTF) [225, 268]. The HGTF Λ are expressed as follows:

$$\Lambda(\gamma, \mathbf{r}_j - \mathbf{A}, t, u, v) = \left(\frac{\partial}{\partial A_x}\right)^t \left(\frac{\partial}{\partial A_y}\right)^u \left(\frac{\partial}{\partial A_z}\right)^v e^{-\gamma|\mathbf{r}_j - \mathbf{A}|^2} \ . \tag{3.31}$$

The advantage of evaluating integrals in the auxiliary HGTF basis is clear from Eq. (3.31), because, in contrast to CSSH GTOs, RSSH GTOs or CGTOs, the expression out front of the Gaussian function in Eq. (3.31) does not depend on $\mathbf{r}_j$, so that it can be simply taken out of the integral. The HGTF obtain their name thanks to their close connection to Hermite polynomials [254]:

$$\Lambda(\gamma, \mathbf{r}_j - \mathbf{A}, t, u, v) = H_t\left[\gamma^{1/2}\left(r_{jx} - A_x\right)\right] H_u\left[\gamma^{1/2}\left(r_{jy} - A_y\right)\right] H_v\left[\gamma^{1/2}\left(r_{jz} - A_z\right)\right] \gamma^{(t+u+v)/2} e^{-\gamma|\mathbf{r}_j - \mathbf{A}|^2} \ . \tag{3.32}$$

A pair of RSSH GTOs are expanded in a linear combination of HGTFs, as follows [268]:

$$R(\gamma, \mathbf{r}_j - \mathbf{A}_\mu, n, l, m) R(\tilde{\gamma}, \mathbf{r}_j - \mathbf{A}_\nu, \tilde{n}, \tilde{l}, \tilde{m}) = \sum_{tuv} E\left[n, l, m, \tilde{n}, \tilde{l}, \tilde{m}, t, u, v\right] \Lambda(\xi, \mathbf{r}_j - \mathbf{P}, t, u, v) \ , \tag{3.33}$$

in which the explicit dependence of E on the centers $\mathbf{A}_\mu$ and $\mathbf{A}_\nu$, as well as the exponent γ and $\tilde{\gamma}$ has been dropped. In paper I and Appendix B, the equations are provided in the basis of CSSH GTOs instead of RSSH GTOs for consistency with previous authors [88, 89, 268]. The relevant equations can however be transformed to an RSSH GTO basis using Eq. (3.25). Practically, Eq. (3.25) implies that the recurrence relations in paper I and Appendix B can be transformed to the basis of RSSH GTOs by changing the sign of the imaginary terms and of the quantum numbers m or $\tilde{m}$ (depending on which one is being increased), contained in these imaginary terms. For example, in Eq. (A.9) of Appendix B, the fourth term would become:

$$\underbrace{iE[l, l, \tilde{l}, \tilde{m}, t, u-1, v]}_{\text{in a CSSH GTO basis}} \rightarrow \underbrace{-E[l, -l, \tilde{l}, \tilde{m}, t, u-1, v]}_{\text{in a RSSH GTO basis}} \tag{3.34}$$

In Eq. (3.33), the coefficients E vanish if any of the following logical conditions are true:

$$E\left[n, l, m, \tilde{n}, \tilde{l}, \tilde{m}, t, u, v\right] = 0 \text{ if any } \begin{cases} t + u + v > 2n + 2\tilde{n} + l + \tilde{l} \\ t < 0 \\ u < 0 \\ v < 0 \\ n = -0 \\ \tilde{n} = -0 \\ l = -0 \\ \tilde{l} = -0 \\ m = -0 \\ \tilde{m} = -0 \end{cases} , \tag{3.35}$$

where, for instance, $m = -0$ means that m approaches zero from the negative direction. For example, the term in Eq. (3.34) is zero for $l = 0$, because in this case, the index $m = -l = -0$. The application of the logical conditions in Eq. (3.35) to Eq. (3.33) generates the following total number $N^E\left(l, \tilde{l}\right)$ of possibly non-zero coefficients E for a given value of n and $\tilde{n}$ [268]:

$$N^E\left(l, \tilde{l}\right) = \frac{\left(l + \tilde{l} + 1\right)\left(l + \tilde{l} + 2\right)\left(l + \tilde{l} + 3\right)}{3!} . \tag{3.36}$$

Taking into account the multiplicity of the quantum numbers m and $\tilde{m}$, there are $N^E_{\text{coeff}}\left(l, \tilde{l}\right) = (2l + 1)\left(2\tilde{l} + 1\right) N^E\left(l, \tilde{l}\right)$ total coefficients for a given shell couple [75].

The coefficients E are then fully calculated using the formulas provided in Eq. (A.7)-(A.10) of Appendix B. The procedure for determining the coefficients E might appear somewhat complicated, but the point is that once they are calculated, then one- and two-electron integrals can be obtained very easily. For example, the simplest integral is the overlap integral $S_{\mu\nu}$, which through the expansion in Eq. (3.28) reads as follows:

$$\begin{aligned} S_{\mu\nu} &= \int d\mathbf{r}_j\, \chi_\mu\left(\mathbf{r}_j - \mathbf{A}_\mu\right) \chi_\nu\left(\mathbf{r}_j - \mathbf{A}_\nu\right) \\ &= N_\lambda N_{\tilde{\lambda}} N_l^m N_{\tilde{l}}^{\tilde{m}} \sum_{k\tilde{k}} N_l\left(\gamma_k^\lambda\right) N_{\tilde{l}}\left(\tilde{\gamma}_{\tilde{k}}^{\tilde{\lambda}}\right) d_k^\lambda d_{\tilde{k}}^{\tilde{\lambda}} \int d\mathbf{r}_j\, R(\gamma_k^\lambda, \mathbf{r}_j - \mathbf{A}_\mu, n, l, m) R(\tilde{\gamma}_{\tilde{k}}^{\tilde{\lambda}}, \mathbf{r}_j - \mathbf{A}_\nu, \tilde{n}, \tilde{l}, \tilde{m}) \end{aligned} \tag{3.37}$$

Then, substituting Eq. (3.33) for the remaining integral in Eq. (3.37) [254]:

$$\begin{aligned}
&\int d\mathbf{r}_j\, R(\gamma_k^\lambda, \mathbf{r}_j - \mathbf{A}_\mu, n, l, m) R(\tilde{\gamma}_{\tilde{k}}^{\tilde{\lambda}}, \mathbf{r}_j - \mathbf{A}_\nu, \tilde{n}, \tilde{l}, \tilde{m}) \\
= &\sum_{tuv} E\left[n, l, m, \tilde{n}, \tilde{l}, \tilde{m}, t, u, v\right] \int d\mathbf{r}_j\, \Lambda(\xi, \mathbf{r}_j - \mathbf{P}, t, u, v) \\
= &\; E\left[n, l, m, \tilde{n}, \tilde{l}, \tilde{m}, 0, 0, 0\right] \left(\frac{\pi}{\xi}\right)^{3/2} . \qquad (3.38)
\end{aligned}$$

The E coefficients can be used to calculate the integrals required to determine the total energy of the system for a given configuration of nuclei. On the other hand, if it is desired to determine the optimal geometrical arrangement of nuclei in the system, then derivatives of the total energy with respect to nuclear displacements (forces) must be evaluated. The analytical calculation of forces then requires derivatives of the one- and two-electron integrals with respect to a displacement B_b, where $B = A_\mu$ or A_ν and $b = x, y$ or z is a Cartesian component. The derivatives of the integrals can be calculated by expanding the derivative of a product of two RSSH GTOs, as follows [75]:

$$\frac{\partial}{\partial B_b}\left[R(\gamma, \mathbf{r}_j - \mathbf{A}_\mu, n, l, m) R(\tilde{\gamma}, \mathbf{r}_j - \mathbf{A}_\nu, \tilde{n}, \tilde{l}, \tilde{m})\right] = \sum_{tuv} G_b^B\left[n, l, m, \tilde{n}, \tilde{l}, \tilde{m}, t, u, v\right] \Lambda(\xi, \mathbf{r}_j - \mathbf{P}, t, u, v) . \quad (3.39)$$

The calculation of the coefficients G_b^B can be achieved using recurrence relations which are derived for $b = x$ in Ref. [89] and for $b = y, z$ in Appendix B and reported in Appendix B of paper I. We also take the opportunity in Appendix B to derive the formulas that would be needed to calculate the analytical second derivatives of the integrals. These formulas are useful for the prospect of being able to calculate the analytical Hessian of the system and hence analytical vibrational frequencies, for example. The second-derivatives of the integrals are calculated through coefficients F_{bc}^{BC}, where similarly $C = A_\mu$ or A_ν and $c = x, y$ or z in an expansion that reads as follows:

$$\frac{\partial}{\partial B_b}\frac{\partial}{\partial C_c}\left[R(\gamma, \mathbf{r}_j - \mathbf{A}_\mu, n, l, m) R(\tilde{\gamma}, \mathbf{r}_j - \mathbf{A}_\nu, \tilde{n}, \tilde{l}, \tilde{m})\right] = \sum_{tuv} F_{bc}^{BC}\left[n, l, m, \tilde{n}, \tilde{l}, \tilde{m}, t, u, v\right] \Lambda(\xi, \mathbf{r}_j - \mathbf{P}, t, u, v) . \quad (3.40)$$

The formulas for the F_{bc}^{BC} have, however not yet been fully tested or implemented in the Crystal program.

3.4 Significance of Contribution from Paper I

This chapter is concluded by highlighting the significance of the work published in paper I [75]. Paper I was authored by (in this order) the present author of this thesis, as well as Profs. Alessandro Erba and Roberto Dovesi of the Università di Torino, Italy. The author's contribution to paper I was performing most of the research and writing of the paper, because the other two authors adopted a supervisory role. This paper presents the extension of the approaches in the Crystal program to g-type ($l = 4$) functions. The inclusion of the g-type functions in the calculation procedure is particularly important for heavy-element (for example REEs) containing periodic systems [75]. As such, the work done in paper I opened the possibility of performing the calculations reported in papers II and III. The main aspects of the program which have been generalized include the calculation of the total energy, analytical forces and the response properties of periodic systems to external electric fields, up to fourth order. Some one-electron properties have also been generalized, like the calculation of the density of states (DOSs) and band structures. The calculations have been generalized for use with several approximate Hamiltonians, including the HF approximation and the DFT, in the local-density, generalized gradient, meta-generalized gradient and hybrid approximations.

The bulk of the work that was involved in generalizing all of these calculation procedures was the extension of Saunders' algorithm to g-type functions [268]. Indeed, in its initial release in 1988, the Crystal code was only generalized to d-type ($l = 2$) functions. In 2003, just two years before Saunders' retirement, calculations were made possible with f-type ($l = 3$) functions, with the Crystal03 program [270, 305]. The great Victor R. Saunders pushed the algorithm as far as he could with the tools that were available to him at the time. Thirteen years later, in 2016, at the beginning of the author's PhD, the availability of sufficiently efficient methods of symbolic computation meant that the algorithm could then be pushed further to g-type functions, as will be elaborated on below [64, 184].

Table 3.1: Number N^E_{coeff} of coefficients E needed to evaluate one- and two-electron integrals involving a shell couple of increasingly high quantum numbers.

l-$\tilde{l}$ or $\tilde{l}$-l	s-s	p-p	d-d	f-f	g-g
N^E_{coeff}	1	90	875	4116	13365

The difficulty in working the Saunders' algorithm can be appreciated by considering the need to apply the logical conditions of Eq. (3.35) to each of the many terms in Eqs. (A.7)-(A.10) of Appendix B. In practice, this procedure generates a catastrophic number of logical statements ("*if*" statements), making the direct application of the recurrence relations to calculate the E (and G^B_b) coefficients *on-the-fly* an exceedingly slow task. The workaround is to instead pre-calculate the symbolic expressions for the E (and G^B_b) coefficients (by going through the recurrence relations, for example, "*by hand*") and programming directly the obtained expressions. This is indeed what was done in the Crystal program for $l = 0, 1, 2, 3$ ($s-, p-, d-, f-$type functions). The problem is that then, the Crystal program only contained long lists of explicit symbolic expressions of the E (and G^B_b) coefficients for successively higher quantum numbers and different values of the indices t, u and v in Eq. (3.33). No code existed that made actual use of the recurrence relations. What is more, while the recurrence relations for the E and G^B_x coefficients were already documented in the literature [89, 254, 268], the recurrence relations for the G^B_y and G^B_z had not been previously published. They are now documented in Appendix B of paper I and a detailed derivation is provided in Appendix B of this thesis. Another significant contribution of paper I to the documentation of Saunders' method is in Appendix A of paper I, which provides an algorithm for applying the recurrence relations to calculate the E (and G^B_b)

coefficients up to arbitrarily high quantum numbers. Indeed, even if the formulas for the recurrence relations are known, it is not trivial to work out exactly in which order they must be used. The order in which the recurrence relations should be used is now documented in the literature from paper I.

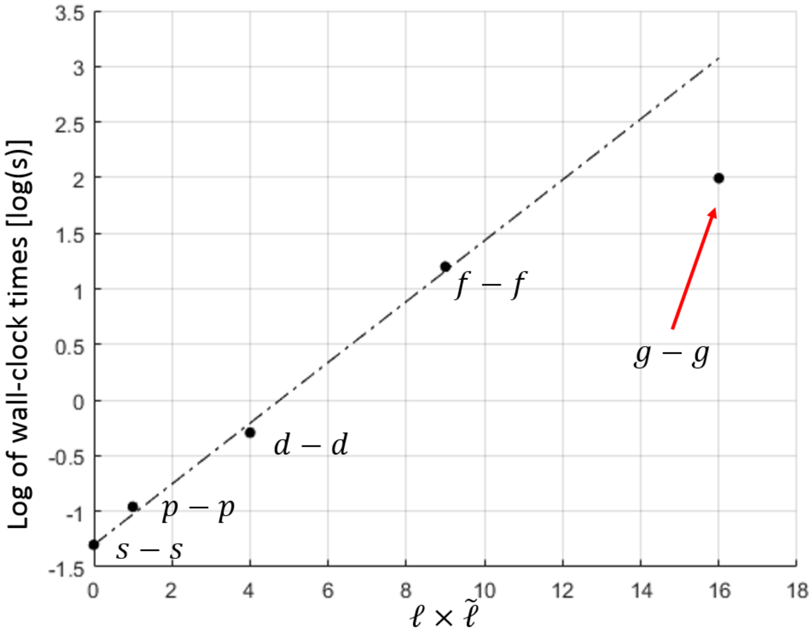

Figure 3.1: The figure shows the log of the wall-clock time needed for 100 thousand calls to the routines needed to evaluate the E coefficients for shell couples of increasingly high quantum numbers. The dashed line reports the best fit for the existing routines for comparison with the new g-type function routine.

The algorithm of Appendix A of paper I, making direct use of the recurrence relations, was programmed using the computer algebra system (CAS) for performing symbolic computation provided in MATLAB. Symbolic computation — at variance with standard numerical computation — means using a computer to manipulate the symbols of mathematical expressions as a mathematician or scientist would by hand. A programming language which enables symbolic computation is called a CAS [64]. For example, a programmer can input the mathematical expression $x = a + b$ into a CAS and prompt the system to evaluate x^2, at which point the output would read $a^2 + b^2 + 2ab$. The CAS performs this computation using knowledge of integer algebra, the existence of the strings of characters x, a and b, as well as instructions (stored in memory) which specify the action of basic algebraic operators (e.g. addition, subtraction, multiplication, integration, exponentiation, etc...) on strings of characters like x, a and b [64]. A CAS is not so useful for computing a mathematical expression like in our trivial example $x^2 = a^2 + b^2 + 2ab$, but can be very useful, for example for determining the symbolic expressions of indefinite integrals or derivatives of high order. In paper I, the need to use a CAS to determine the symbolic expressions of the E coefficients through repeated application of the recurrence relations is evidenced in Table 3.1, which reports the number N^E_{coeff} of coefficients, calculated making use of Eq. (3.36), for shell couples of increasingly high quantum numbers. For example, in order to expand an RSSH GTO shell couple of type s-s, through Eq. (3.33), only one coefficient (namely $E[0,0,0,0,0,0,0,0,0]$) is needed. On the other hand, in order to expand an RSSH GTO shell couple of type p-p (including the pairs of AOs of the type p_x-p_x, p_x-p_y, p_x-p_z, p_y-p_x, p_y-p_y, p_y-p_z, p_z-p_x, p_z-p_y, p_z-p_z) with Eq. (3.33), a total of 90 coefficients are needed. The reader can appreciate the nightmare involved in having to work through the recurrence relations by hand to generate the hundreds or thousands of coefficients that are then needed to expand an RSSH GTO shell couple of type d-d, f-f or g-g! Fortunately, this nightmare can be avoided by using a CAS to perform the symbolic computation instead of working out the expressions by hand.

Once the expressions for the E and G^B_b coefficients were calculated symbolically with the CAS provided in MATLAB, explicit FORTRAN routines were generated. Table 2 of paper I reports a comparison on the relative amount of time needed to calculate the E coefficients using these explicit routines, against a more implicit routine which makes direct use of the algorithm reported in Appendix A of paper I, in which the expressions for the E coefficients are calculated *on-the-fly* by making direct use of the recurrence relations. The table shows that the explicit routines result in the one- and two-electron integrals being calculated faster by about a factor of 100, if they include shell couples involving g-functions. The table also shows that the total amount of lines of code for the explicit routines to calculate the E coefficients involving g-functions is 60,732. What is not reported in paper I, is the amount of lines of code for the explicit routines for the more complicated G^B_b coefficients. This was not reported at the time, simply because the symbolic calculations needed to generate the explicit routines for the G^B_b were not completed until many months after paper I had already been published. In the end, the explicit routines for the G^B_b coefficients were an incredible 927 thousand lines of code!

Finally, we document the relative efficiency of these new explicit routines against the previously existing ones in the CRYSTAL code. Figure 3.1 reports the log of the wall-clock time needed to calculate the E coefficients for shell couple pairs of increasingly high quantum numbers. (s-s, p-p, d-d, f-f, g-g). Except for the g-g routine, the other ones use the approach which was already existing in the CRYSTAL code. The dashed line on the figure shows the best fit for the existing routines, which plots above the timing of the g-g, indicating a favourable comparison.

4 The Self-Consistent Field Approach

4.1 The Generalized Hartree-Fock Equations

From chapters 2 and 3 we now know how to represent both the Hamiltonian and wavefunction, so that we are now ready to discuss how we are going to solve the Dirac equation. The first method discussed is the HF or mean-field approximation, which treats the many-electron problem as the set of coupled problems of each individual electron in the external potential created by all of the other electrons. This means that in the HF method, the electron-electron repulsion is somehow averaged, and the potential describing this repulsion must be calculated iteratively. The iterative procedure from which the one-electron energies, wavefunctions and potentials are determined is called the self-consistent field (SCF) procedure. The HF method is often used as a starting point for more accurate methods which include more explicit electron-electron repulsion terms (electron correlation). As we will see, mathematically the HF approximation consists of representing the wavefunction as a single Slater determinant, see Eq. (3.6), then finding the one-electron orbitals composing the determinant that yield the lowest energy, under the constraint that they remain orthonormal.

Here, we are interested in deriving the relevant expressions using the relativistic Hamiltonian for the pseudopotential approximation given in Eq. (2.38), because this was the Hamiltonian used in almost all of the calculations reported in this thesis. Correspondingly, the one-electron orbitals comprising the associated Slater determinant are actually valence orbitals. We start the derivation of the HF approximation, by first stating that we are searching for the ground-state solution, and hence the energy (which is the expectation value of the Hamiltonian) must be a minimum:

$$E = \min_{\psi \to N} \langle \psi | \mathbf{H}_D | \psi \rangle \; . \tag{4.1}$$

Eq. (4.1) is nothing other than the statement of the variational principle. As was discussed earlier — see discussion associated with Eqs. (2.30) and (2.33) — certain forms of the Hamiltonian $\mathbf{H}_D$ are incompatible for use with variational calculations. In the following, we assume that the Hamiltonian has been appropriatly regularized such that a variational calculation can be performed.

Provided that the wavefunction ψ is approximated as a single Slater determinant, we can calculate the energy E from the first of the Slater-Condon rules provided by Eq. (3.14). So the expression for the total energy of the system reads as follows:

$$E = \sum_{m}^{\in occ} (m|h_D|m) + \frac{1}{2} \sum_{m}^{\in occ} \sum_{n}^{\in occ} \left[(mm|nn) - (mn|nm) \right] \; , \tag{4.2}$$

where the following compact notation has been introduced:

$$(mm|nn) \equiv (mm|g^{Coulomb}|nn) \quad \text{and} \quad (mn|nm) \equiv (mn|g^{Coulomb}|nm) \; , \tag{4.3}$$

and the two-electron integral in Eq. (4.3) must of course be interpreted by substituting the two-electron operator of Eq. (2.38) into Eq. (3.8), as demonstrated in Eq. (3.13).

Here we use Eq. (4.2) to calculate the energy of the ground state wavefunction $\boldsymbol{\psi}$, but we note that the same type of expression (as per the first Slater-Condon rule) could also be used to calculate the energy of any excited state wavefunction, provided that it can be represented as a single Slater determinant.

For the one-electron orbitals $|i\rangle$ to represent a basis upon which the many-electron state $|\boldsymbol{\psi}\rangle$ is expanded, they must be orthonormal. So the minimization procedure of the energy must ensure that the occupied states $|m\rangle$ remain orthonormal to all other states $|j\rangle$:

$$\langle m|j\rangle = \delta_{mj} \qquad \forall m \in occ,\ \forall j \in occ \cup virt\ . \tag{4.4}$$

The method used to minimize a function under a set of equality constraints is called the method of Lagrange multipliers. The associated Lagrangian $\mathcal{L}$ can be formed by combining Eq. (4.1) with Eq. (4.4), including the orthogonality constraints for all of the one-electron orbitals, as follows:

$$\mathcal{L}(\{\boldsymbol{\phi}_o\}) = \sum_{m}^{\in occ}(m|h_D|m) + \frac{1}{2}\sum_{m}^{\in occ}\sum_{n}^{\in occ}[(mm|nn) - (mn|nm)] - \frac{1}{2}\sum_{m}^{\in occ}\sum_{j}\epsilon_{mj}\left(\langle m|j\rangle - \delta_{mj}\right)\ , \tag{4.5}$$

where ϵ_{mj} are the Lagrange multipliers, and $\{\boldsymbol{\phi}_o\}$ represents the set of occupied orbitals $\{\boldsymbol{\phi}_o\} = \ldots, \boldsymbol{\phi}_m, \ldots, \boldsymbol{\phi}_n, \ldots$. Since the Lagrange multipliers are arbitrary, we can choose them to be a diagonal matrix and write:

$$\mathcal{L}(\{\boldsymbol{\phi}_o\}) = \sum_{m}^{\in occ}(m|h_D|m) + \frac{1}{2}\sum_{m}^{\in occ}\sum_{n}^{\in occ}[(mm|nn) - (mn|nm)] - \sum_{m}^{\in occ}\epsilon_{m}\left(\langle m|m\rangle - 1\right)\ , \tag{4.6}$$

The solution of the problem can then be obtained by finding the stationary point of the Lagrangian. According to the calculus of variations, this can be done by first determining the functional derivative of $\mathcal{L}$. The first variation of the Lagrangian reads as follows in the position basis:

$$\begin{aligned} d\mathcal{L}(\{\boldsymbol{\phi}_o\}) &= \mathcal{L}(\ldots, \boldsymbol{\phi}_m + \delta\boldsymbol{\phi}_m, \ldots, \boldsymbol{\phi}_n + \delta\boldsymbol{\phi}_n, \ldots) - \mathcal{L}(\ldots, \boldsymbol{\phi}_m, \ldots, \boldsymbol{\phi}_n, \ldots) \\ &= \sum_{m}^{\in occ}\int d\mathbf{r}_i \frac{\delta\mathcal{L}(\{\boldsymbol{\phi}_o\})}{\delta\boldsymbol{\phi}_m^{\dagger}}\delta\boldsymbol{\phi}_m^{\dagger} + \frac{\delta\mathcal{L}(\{\boldsymbol{\phi}_o\})}{\delta\boldsymbol{\phi}_m}\delta\boldsymbol{\phi}_m\ . \end{aligned} \tag{4.7}$$

The functional derivatives $\frac{\delta\mathcal{L}(\{\boldsymbol{\phi}_o\})}{\delta\boldsymbol{\phi}_m^{\dagger}}$ and $\frac{\delta\mathcal{L}(\{\boldsymbol{\phi}_o\})}{\delta\boldsymbol{\phi}_m}$ can then be determined by taking the first variation of Eq. (4.6) in the position basis and comparing the result with Eq. (4.7). Taking the first variation of Eq. (4.6) by substituting it in Eq. (4.7), and using the established notation for one- and two-electron integrals from Eqs. (3.9) and (3.8), we have:

$$\begin{aligned} d\mathcal{L}(\{\boldsymbol{\phi}_o\}) &= \sum_{m}^{\in occ}\int d\mathbf{r}_i\delta\boldsymbol{\phi}_m^{\dagger}(\mathbf{r}_i) \\ &\times \underbrace{\left[\mathbf{h}_D(\mathbf{r}_i)\boldsymbol{\phi}_m(\mathbf{r}_i) + \sum_{n}^{\in occ}\left\{\boldsymbol{\phi}_m(\mathbf{r}_i)\int d\mathbf{r}_j\,\frac{1}{r_{ij}}\,\boldsymbol{\phi}_n^{\dagger}(\mathbf{r}_j)\boldsymbol{\phi}_n(\mathbf{r}_j) - \boldsymbol{\phi}_n(\mathbf{r}_i)\int d\mathbf{r}_j\,\frac{1}{r_{ij}}\,\boldsymbol{\phi}_n^{\dagger}(\mathbf{r}_j)\boldsymbol{\phi}_m(\mathbf{r}_j)\right\} - \epsilon_m\boldsymbol{\phi}_m(\mathbf{r}_i)\right]}_{\frac{\delta\mathcal{L}(\{\boldsymbol{\phi}_o\})}{\delta\boldsymbol{\phi}_m^{\dagger}}} + h.c.\ , \end{aligned} \tag{4.8}$$

where the *h.c.* indicates the Hermitian-conjugate. The term in the large square bracket has been identified as $\frac{\delta\mathcal{L}(\{\boldsymbol{\phi}_o\})}{\delta\boldsymbol{\phi}_m^\dagger}$ by comparison of Eq. (4.7) with Eq. (4.8).

Eq. (4.8) can be written more succinctly using the bra-ket notation, as follows:

$$d\mathcal{L}(\{\boldsymbol{\phi}_o\}) \;=\; \sum_m^{\in occ}(\delta m|h_D|m) + \sum_m^{\in occ}\sum_n^{\in occ}[(\delta mm|nn) - (\delta mn|nm)] - \sum_m \epsilon_m\langle\delta m|m\rangle + h.c. \quad . \tag{4.9}$$

Eq. (4.9) can then be written as:

$$d\mathcal{L}(\{\boldsymbol{\phi}_o\}) = \sum_m^{\in occ}\langle\delta m|\underbrace{\left[(\bullet|h_D|m) + \sum_n^{\in occ}[(\bullet m|nn) - (\bullet n|nm)] - \epsilon_m\langle\bullet|m\rangle\right]}_{\frac{\delta\mathcal{L}(\{\boldsymbol{\phi}_o\})}{\delta\boldsymbol{\phi}_m^\dagger}} + h.c. \,. \tag{4.10}$$

So the symbol $\bullet$ is just place-holder, waiting patiently for her friends $|m\rangle$ or $\langle m|$ to walk by and fall nicely into the one- or two-electron integral. Setting $\frac{\delta\mathcal{L}(\{\boldsymbol{\phi}_o\})}{\delta\boldsymbol{\phi}_m^\dagger}$ to zero, we find immediately the Hartree-Fock equations:

$$\mathbf{F}(m)|m\rangle = \epsilon_m|m\rangle \;, \tag{4.11}$$

where the one-electron Fock operator $\mathbf{F}(m)$ has been defined as follows:

$$\mathbf{F}(m) = \mathbf{h}_D(m) + \mathbf{C}(m) - \mathbf{K}(m) \;, \tag{4.12a}$$

in which the $\mathbf{C}(m)$ and $\mathbf{K}(m)$ are the so-called one-electron Coulomb and Fock exchange operators. The Coulomb operator reads:

$$\mathbf{C}(m) = \sum_n^{\in occ}(\bullet\,\bullet\,|nn) \tag{4.12b}$$

and the exchange operator reads:

$$\mathbf{K}(m) = \sum_n^{\in occ}(\bullet n|n\bullet) \tag{4.12c}$$

The action of these operators on the orbital $|m\rangle$ is as follows:

$$\begin{aligned}
\mathbf{C}(m)|m\rangle &= \sum_{n}^{\in occ}(\bullet\bullet|nn)|m\rangle = \sum_{n}^{\in occ}(\bullet m|nn) \\
\langle m|\mathbf{C}(m)|m\rangle &= \sum_{n}^{\in occ}\langle m|(\bullet m|nn) = \sum_{n}^{\in occ}(mm|nn) \\
\mathbf{K}(m)|m\rangle &= \sum_{n}^{\in occ}(\bullet n|n\bullet)|m\rangle = \sum_{n}^{\in occ}(\bullet n|nm) \\
\langle m|\mathbf{K}(m)|m\rangle &= \sum_{n}^{\in occ}\langle m|(\bullet n|nm) = \sum_{n}^{\in occ}(mn|nm)\ . \qquad (4.12d)
\end{aligned}$$

Substituting Eq. (4.12) in Eq. (4.2), it is possible to write the HF energy in terms of the Fock operator, as follows:

$$E = \frac{1}{2}\sum_{m}^{\in occ}\left[(m|h_D|m) + (m|F|m)\right]\ . \qquad (4.13)$$

4.2 The Kohn-Sham Density Functional Theory

The DFT can be viewed as a parallel and equivalent theory to that of Schrödinger or Dirac, in which (in the non-relativistic case) the properties of the system are determined entirely from the fermion density n, instead of the wavefunction. At its core, this theory is based on the two Hohenberg-Kohn (HK) theorems, formulated in 1964 by Pierre Hohenberg and Walter Kohn, initially for the non-relativistic case [165]. Nowadays, relativistic variants of the HK theorems have also been formulated [105, 106, 259, 260]. In the initial HK formulation of the DFT, the exact (non-relativistic) energy of the many-body system is represented as follows [165]:

$$E = \int d\mathbf{r}_j\ \left\{F_{HK}[n] + n\left(\mathbf{r}_j\right)V^{ext}\left(\mathbf{r}_j\right)\right\}\ , \qquad (4.14)$$

where F_{HK} is the unknown exact (apart from relativistic effects) HK functional, and V^{ext} is a potential from external fields. We note that the HK functional has been written in Eq. (4.14) as $F_{HK}[n]$ and not $F_{HK}\left[n\left(\mathbf{r}_j\right)\right]$, because the exact HK functional might be, in general, non-local and hence does not just depend on the density evaluated at one point in space. The external potential V^{ext} might be, for example, in the Born-Oppenheimer approximation, the external potential from the clamped nuclei, including V_{eN} and V_{NN} from Eqs. (2.19) and (2.20) [101]. The first HK theorem states that there is a one-to-one connection between the external potential V^{ext} (and therefore the energy) and the fermion density. The second HK theorem states that if n is built from a state that is a solution to the Schrödinger equation, then the energy obtained from n is a lower bound for that state. So the first theorem essentially states that the energy can be determined solely from the density n, and the second theorem states that the procedure to determine the energy, for example for the ground state, is a minimization procedure. We note that for our purposes n is the electron density, but more generally the theory can be applied to any fermionic system [159, 165].

In practice, what makes the DFT so useful is the possibility to treat electron correlation in some way, while still using a single-particle equation (called the Kohn-Sham equation), very similar in form to Eq. (4.11), thanks to the formulation of Kohn and Sham (KS-DFT) [192]. In the KS-DFT, we choose a reference system composed of individual non-interacting fermions, which yields the same density at every point in space as the interacting system. The non-interacting reference system is defined in the sense that each fermion upon which it is composed is described by a wavefunction, built from KS orbitals which obey the following one-electron equation [31]:

$$-\frac{1}{2}\boldsymbol{\nabla}_i^2|\boldsymbol{\phi}_i\rangle + V_{KS}|\boldsymbol{\phi}_i\rangle = \epsilon_i|\boldsymbol{\phi}_i\rangle \,, \tag{4.15}$$

where the potential V_{KS} is formally defined by the requirement that the non-interacting system yields the same density as the interacting system of interest. Because the non-interacting system is composed of fermions, it must be subject to the Pauli exclusion principle, see Eq. (3.4). The wavefunction of the non-interacting reference is hence a single Slater determinant, that is composed of one-electron KS orbitals. The density of both the reference and interacting systems, is then simply determined from the KS orbitals, as follows:

$$n\left(\mathbf{r}_j\right) = \sum_m^{occ} \boldsymbol{\phi}_m^\dagger(\mathbf{r}_j)\boldsymbol{\phi}_m(\mathbf{r}_j) \,. \tag{4.16}$$

Then, according to the KS prescription, the exact HK functional is partitioned as follows:

$$\int d\mathbf{r}_j\, F_{HK}[n] = \frac{1}{2}\int d\mathbf{r}_j\, n\left(\mathbf{r}_j\right)\int d\mathbf{r}_i\, \frac{n\left(\mathbf{r}_i\right)}{r_{ij}} + T + E_{xc} \,, \tag{4.17}$$

where T is the kinetic energy of the reference non-interacting system, and E_{xc} is the so-called exchange-correlation (xc) energy. Therefore, the non-interacting system is connected to the actual system of interest through the xc energy E_{xc}. In principle, E_{xc} contains all effects beyond the single Slater determinant approximation, the difference between the kinetic energy of the interacting and non-interacting systems, and all electron-electron interactions, apart from the first term on the r.h.s. of Eq. (4.17). The xc energy E_{xc} can be written in terms of independent exchange E_x and correlation E_c contributions, as follows:

$$E_{xc} = E_x + E_c \,. \tag{4.18}$$

It is important to appreciate that the seperation in Eq. (4.18) is purely for mathematical convenience, in the sense that exchange and correlation only have a physical meaning when described together [31]. For example, the Fock exchange operator of Eq. (4.12c) reproduces exactly the exchange energy (i.e. the energy associated to Pauli repulsion) of a single Slater determinant, but would not reproduce the exchange energy of a system whose Hamiltonian contains more explicit correlation terms.

In this way, E_{xc} is such that F_{HK}, as defined in Eq. (4.14) gives the exact non-relativistic energy of the system. In practice, E_{xc} is expressed as an integral over space of the approximated xc functional F_{xc}, as follows:

$$E_{xc} \approx \int d\mathbf{r}_j\, F_{xc}\left[\mathbf{Q}\left(\mathbf{r}_j\right)\right] = \int d\mathbf{r}_j\, F_x\left[\mathbf{Q}\left(\mathbf{r}_j\right)\right] + \int d\mathbf{r}_j\, F_c\left[\mathbf{Q}\left(\mathbf{r}_j\right)\right] \,, \tag{4.19}$$

in which $\mathbf{Q}\left(\mathbf{r}_j\right)$ is a set of variables that are formed from the electron density $n\left(\mathbf{r}_j\right)$ and its derivatives evaluated at $\mathbf{r}_j$, and the xc functions F_{xc} has been written in terms of exchange F_x and correlation F_c contributions. In the case where F_{xc} is approximated as a function of $n\left(\mathbf{r}_j\right)$ only, then it is called a local-density approximation (LDA). If F_{xc} depends also on the first derivatives of the density evaluated at $\mathbf{r}_j$, then it is called a generalized-gradient approximation (GGA). Otherwise, if F_{xc} depends additionally on the second-derivatives of the density, then it is a meta-generalized-gradient (mGGA) approximation. In general, approximations to F_{xc} can also be built by directly using the KS orbitals, rather than just the density (and its derivatives), in which case the term *generalized* KS-DFT is sometimes used [129, 248, 278]. In particular, if the KS orbitals are used to reproduce the non-local Fock exchange potential of Eq. (4.12c), then so-called *hybrid* approximations are formed, as originally suggested by Axel Becke in 1993 [30]. The arguments of Becke are indeed so remarkably simple and elegant that the author feels that it is compulsory to outline them here, mostly out of respect for this great Canadian. Formally the non-interacting reference is connected to the interacting system through a parameter λ, according to the so-called adiabatic-connection theorem, as follows [154]:

$$E_{xc} = \int_0^1 d\lambda \, \varepsilon_{xc}(\lambda) \ , \tag{4.20}$$

where $\varepsilon_{xc}(\lambda)$ is the xc energy at intermediate coupling strength [30]. So λ is a parameter that varies continuously between 0 (for the non-interacting system) to 1 (for the actual interacting system of interest). Then, we admit that the xc energy E_{xc} is split into a larger exchange E_x and smaller correlation E_c contribution, according to Eq. (4.18). Because we expect E_c to be smaller, we can simply approximate it using an LDA, GGA or mGGA formula, according to Eq. (4.19), and concentrate on treating E_x through the adiabatic connection theorem, hence we have:

$$E_x = \int_0^1 d\lambda \, \varepsilon_x(\lambda) \ , \tag{4.21}$$

then, for the non-interacting KS reference, because its wavefunction is a Slater determinant, $\varepsilon_x(0)$ is just the energy contribution from the non-local Fock exchange operator from Eq. (4.12d):

$$\varepsilon_x(0) = \sum_m^{\in occ} \langle m|\mathbf{K}(m)|m\rangle \ . \tag{4.22}$$

On the other hand, we can approximate $\varepsilon_x(1)$ for the interacting system using an LDA, GGA or mGGA formula according to Eq. (4.19):

$$\varepsilon_x(1) \approx \int d\mathbf{r}_j \, F_x\left[\mathbf{Q}\left(\mathbf{r}_j\right)\right] \ . \tag{4.23}$$

Substituting Eqs. (4.22) and (4.23) into Eq. (4.21) and approximating the integral over λ using a two point quadrature, we find:

$$E_x \approx (1-a)\int d\mathbf{r}_j \, F_x\left[\mathbf{Q}\left(\mathbf{r}_j\right)\right] + a\sum_m^{\in occ} \langle m|\mathbf{K}(m)|m\rangle \ , \tag{4.24}$$

where a is the dimensionless fraction of non-local Fock exchange. In 1996, Perdew, Burke and Ernzerhof

(PBE) provided formal arguments to show that the fraction of non-local Fock exchange should be around one quarter ($a \approx 0.25$) [247]. Most approximate hybrid functionals indeed include an a close to this value [9, 32, 35, 150, 160, 170, 247, 300]. In particular, the PBE0 functional of Adamo and Barone, based on the GGA approximation to F_{xc} of PBE [246], uses exactly the value $a = 0.25$ [9].

Let us now compare the energy expression in the KS-DFT to the HF one in Eq. (4.13). Substituting Eq. (4.16) in the first term on the r.h.s. of Eq. (4.17), and comparing the result with Eq. (4.12d), we find:

$$\int d\mathbf{r}_j \, n\left(\mathbf{r}_j\right) \int d\mathbf{r}_i \, \frac{n\left(\mathbf{r}_i\right)}{r_{ij}} = \sum_m^{\in occ} \langle m|\mathbf{C}(m)|m\rangle \; . \tag{4.25}$$

So the first term on the r.h.s. of Eq. (4.17) is just the electron-electron Coulomb energy. Therefore, Eq. (4.17) is identical to the HF energy expression of Eq. (4.13) in the non-relativistic limit, apart from E_{xc} replacing the energy contribution from the Fock exchange operator $\mathbf{K}(m)$. As a result, the one-electron KS equations resemble very closely Eq. (4.11), with the important distinction that the Fock exchange operator is replaced by the xc potential $\mathbf{V}_{xc}$, which reads:

$$\mathbf{V}_{xc}\left[n\right] = \mathbb{I} \otimes \frac{\delta E_{xc}}{\delta n\left(\mathbf{r}_j\right)} \; . \tag{4.26}$$

More specific details on the formalism of KS-DFT is reported in Appendix F and papers V, VI and VII. In particular strategies are discussed on how to generalize the KS-DFT to describe a system of relativistic, rather than non-relativistic fermions. We note simply here that, in principal, relativistic variants of the KS-DFT are based on the so-called four-current $\mathcal{J} = \left[\mathcal{J}_0, \mathcal{J}_x, \mathcal{J}_y, \mathcal{J}_z\right]$, in the four component approach, whose components are defined as follows [105, 106, 259, 260]:

$$\mathcal{J}_i\left(\mathbf{r}_j\right) = c \sum_m^{occ} \boldsymbol{\phi}_m^\dagger(\mathbf{r}_j)\alpha_i\boldsymbol{\phi}_m(\mathbf{r}_j) \quad \forall i \in 0, x, y, z \; , \tag{4.27}$$

where in Eq. (4.27) the index $i = 0, x, y, z$ labels the components of $\mathcal{J}$ and by convention $\boldsymbol{\alpha}_0 = \mathbb{I}_4$, so that $\mathcal{J}_0$ coincides with the density from Eq. (4.16). In the two-component approach, the formalism is called the spin-current density-functional theory (SCDFT) and is based on the density n, as defined in Eq. (4.16), the magnetization $\mathbf{m} = \left[m_x, m_y, m_z\right]$, the orbital-current density $\mathbf{j} = \left[j_x, j_y, j_z\right]$, and the three spin-current densities $\mathbf{J}_x = \left[J_{xx}, J_{xy}, J_{xz}\right]$, $\mathbf{J}_y = \left[J_{yx}, J_{yy}, J_{yz}\right]$ and $\mathbf{J}_z = \left[J_{zx}, J_{zy}, J_{zz}\right]$[33, 105, 255, 283, 310, 320, 321]. The Cartesian components of the magnetization are calculated in terms of the Pauli matrices $\boldsymbol{\sigma}_i$ and the KS orbitals, as follows:

$$m_i\left(\mathbf{r}_j\right) = \sum_m^{occ} \boldsymbol{\phi}_m^\dagger(\mathbf{r}_j)\boldsymbol{\sigma}_i\boldsymbol{\phi}_m(\mathbf{r}_j) \quad \forall i \in x, y, z \; . \tag{4.28}$$

On the other hand, the orbital-current density $\mathbf{j}$ reads:

$$\mathbf{j}\left(\mathbf{r}_j\right) = \frac{1}{2i} \sum_m^{occ} \boldsymbol{\phi}_m^\dagger(\mathbf{r}_j)\left[\boldsymbol{\nabla}_j\boldsymbol{\phi}_m(\mathbf{r}_j)\right] - \left[\boldsymbol{\nabla}_j\boldsymbol{\phi}_m^\dagger(\mathbf{r}_j)\right]\boldsymbol{\phi}_m(\mathbf{r}_j) \; . \tag{4.29}$$

The three spin-current densities $\mathbf{J}_x$, $\mathbf{J}_y$ and $\mathbf{J}_z$, are defined as follows [33, 255, 310, 321]:

$$\mathbf{J}_i\left(\mathbf{r}_j\right) = \frac{1}{2i}\sum_m^{occ} \boldsymbol{\phi}_m^\dagger(\mathbf{r}_j)\boldsymbol{\sigma}_i\left[\boldsymbol{\nabla}_j\boldsymbol{\phi}_m(\mathbf{r}_j)\right] - \left[\boldsymbol{\nabla}_j\boldsymbol{\phi}_m^\dagger(\mathbf{r}_j)\right]\boldsymbol{\sigma}_i\boldsymbol{\phi}_m(\mathbf{r}_j) \quad \forall i \in x, y, z \; . \tag{4.30}$$

Finally, we cite the notable approach of von Barth and Hedin which is used for including m_z in the calculation procedure of non-relativistic KS-DFT, allowing for a treatment of spin polarization, for example with the local spin density approximation (LSDA), or GGA, mGGA and hybrid variants. It is noteworthy however, that this approach formally violates the first of the HK theorems [323].

4.3 Treatment of Infinite Periodic Systems

4.3.1 Direct and Reciprocal Lattices

So far we have discussed the general theory on methods for solving the Dirac equation, but we have not yet specified how to deal with infinite periodic systems. In principle, the procedure would imply solving Eq. (4.11), or the equivalent one-electron KS equation, for a system containing an infinite number of electrons. This appears at first glance to be completely impossible. Thankfully, as we will see, the problem can be reduced to a computationally manageable form by transforming the one-electron equations to reciprocal space, via so-called Bloch functions, and by taking advantage of translational symmetry.

A periodic system is associated with a direct lattice, which is defined in one-, two- or three- dimensions (1D, 2D, 3D) by the 3 × 1 basis vectors (called the direct primitive lattice vectors) $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$ that define the direct primitive cell. All three basis vectors are needed to define a 3D periodic system, and the 2D (or 1D) case can be obtained as a special case by setting, for example, $\mathbf{a}_3 = [0, 0, 0]^T$ (and $\mathbf{a}_2 = [0, 0, 0]^T$). The direct primitive cell is the smallest pattern that can be repeated in direct space along the basis vectors to reproduce the full periodic system. We can define a general lattice vector (or just lattice vector, for short) $\mathbf{g}$ as a linear combination of the three basis vectors, as follows:

$$\mathbf{g} = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3 \qquad \forall n_1, n_2, n_3 \in \mathbb{Z} \; , \tag{4.31}$$

where n_1, n_2 and n_3 are integers. A general coordinate of electron j in direct space can be represented in fractional coordinates, as follows:

$$\mathbf{r}_j = x_1\mathbf{a}_1 + x_2\mathbf{a}_2 + x_3\mathbf{a}_3 \qquad \forall x_1, x_2, x_3 \in \mathbb{R} \; , \tag{4.32}$$

where x_1, x_2 and x_3 are real numbers. Two points $\mathbf{r}_j$ and $\mathbf{r}'_j$ are called translationally equivalent if they can be connected by a lattice vector $\mathbf{r}'_j = \mathbf{r}_j + \mathbf{g}$. A function $f(\mathbf{r}_j)$ evaluated at two translationally equivalent points is called periodic if it satisfies the equality $f(\mathbf{r}_j + \mathbf{g}) = f(\mathbf{r}_j)$. This notion can also be extended to operators, such that a periodic operator is an operator defined in a Hilbert space of periodic functions. For every direct lattice, we define the reciprocal lattice by the basis vectors (called the primitive reciprocal lattice vectors) $\mathbf{b}_1$,

$\mathbf{b}_2$, $\mathbf{b}_3$ which satisfy the following orthogonality relations:

$$\mathbf{a}_i \cdot \mathbf{b}_j = 2\pi\delta_{ij} \qquad \forall i, j \in 1, 2, 3 \ . \tag{4.33}$$

Similarly, to what was done for the direct lattice in Eq. (4.31), a general reciprocal lattice vector is defined as follows:

$$\mathbf{K} = n_1\mathbf{b}_1 + n_2\mathbf{b}_2 + n_3\mathbf{b}_3 \qquad \forall n_1, n_2, n_3 \in \mathbb{Z} \ , \tag{4.34}$$

and a general coordinate of electron j in reciprocal space reads:

$$\mathbf{k}_j = x_1\mathbf{b}_1 + x_2\mathbf{b}_2 + x_3\mathbf{b}_3 \qquad \forall x_1, x_2, x_3 \in \mathbb{R} \ . \tag{4.35}$$

Substituting Eqs. (4.34) and (4.31) in Eq. (4.33), we find the following orthogonality relation between reciprocal and direct lattice vectors:

$$\mathbf{g} \cdot \mathbf{K} = 2\pi z \ , \tag{4.36}$$

where z is an integer. From Euler's formula, we can therefore deduce the following important identity:

$$e^{i\mathbf{g}\cdot\mathbf{K}} = 1 \ . \tag{4.37}$$

The volumes of the direct Ω_d and reciprocal Ω_r primitive cells read:

$$\Omega_d = (\mathbf{a}_1 \times \mathbf{a}_2) \cdot \mathbf{a}_3 \ , \tag{4.38a}$$

$$\Omega_r = (\mathbf{b}_1 \times \mathbf{b}_2) \cdot \mathbf{b}_3 \ . \tag{4.38b}$$

Substituting Eq. (4.38) in Eq. (4.33), we find that the volumes of the direct and reciprocal primitive cells are inversely proportional:

$$\Omega_r = \frac{(2\pi)^3}{\Omega_d} \ . \tag{4.39}$$

The reciprocal primitive cell centered at the origin is often called the first Brillouin zone (FBZ).

4.3.2 Crystalline Orbitals and Bloch Functions

We define the Bloch functions $\varphi_\mu\left(\mathbf{r}_j, \mathbf{k}_i\right)$ as the Fourier transform of the AOs $\chi_\mu\left(\mathbf{r}_j - \mathbf{A}_\mu - \mathbf{g}\right)$, defined in Eq. (3.28), as follows:

$$\varphi_\mu\left(\mathbf{r}_j, \mathbf{k}_i\right) = \frac{1}{\sqrt{\Omega_r}} \sum_{\mathbf{g}=-\infty}^{\infty} \chi_\mu\left(\mathbf{r}_j - \mathbf{A}_\mu - \mathbf{g}\right) e^{i\mathbf{g}\cdot\mathbf{k}_i} \ . \tag{4.40}$$

In the following we simplify the notation for sums on lattice vectors. We drop the boundaries ∞ and $-\infty$, and it is understood that any sum on lattice vectors runs over the infinite set. Bloch functions satisfy a number of important properties that make them an appropriate basis in which the one-electron HF or KS equations can be expanded. Firstly, Bloch functions satisfy Bloch's theorem, which can be stated as follows:

$$\varphi_\mu\left(\mathbf{r}_j + \mathbf{h}, \mathbf{k}_i\right) = e^{i\mathbf{k}_i\cdot\mathbf{h}}\varphi_\mu\left(\mathbf{r}_j, \mathbf{k}_i\right) \ , \tag{4.41}$$

where $\mathbf{h}$ is a lattice vector, as defined in Eq. (4.31). We can show indeed that the Bloch function in Eq. (4.40) verifies Eq. (4.41), by working out the effect of a translation by the lattice vector $\mathbf{h}$:

$$\varphi_\mu\left(\mathbf{r}_j + \mathbf{h}, \mathbf{k}_i\right) = \frac{1}{\sqrt{\Omega_r}}\sum_{\mathbf{g}}\chi_\mu\left(\mathbf{r}_j - \mathbf{A}_\mu - \mathbf{g} - \mathbf{h}\right)e^{i\mathbf{g}\cdot\mathbf{k}_i} \ . \tag{4.42}$$

Then, since the sum over $\mathbf{g}$ is infinite, we can arbitrarily make the substitution $\mathbf{g} \to \mathbf{g} + \mathbf{h}$ and find:

$$\varphi_\mu\left(\mathbf{r}_j + \mathbf{h}, \mathbf{k}_i\right) = e^{i\mathbf{h}\cdot\mathbf{k}_i}\frac{1}{\sqrt{\Omega_r}}\sum_{\mathbf{g}}\chi_\mu\left(\mathbf{r}_j - \mathbf{A}_\mu - \mathbf{g}\right)e^{i\mathbf{g}\cdot\mathbf{k}_i} = e^{i\mathbf{h}\cdot\mathbf{k}_i}\varphi_\mu\left(\mathbf{r}_j, \mathbf{k}_i\right) \ . \tag{4.43}$$

Eq. (4.43) completes the proof of Bloch's theorem. So the Bloch functions can be evaluated in adjoining cells of the direct lattice by multiplying them by the appropriate phase factor. But Bloch's theorem also shows us that Bloch functions are eigenfunctions of the direct-space translation operator $\mathcal{T}$. This is because, from Eq. (4.41):

$$\mathcal{T}\varphi_\mu\left(\mathbf{r}_j, \mathbf{k}_i\right) = \varphi_\mu\left(\mathbf{r}_j + \mathbf{h}, \mathbf{k}_i\right) = e^{i\mathbf{k}_i\cdot\mathbf{h}}\varphi_\mu\left(\mathbf{r}_j, \mathbf{k}_i\right) \ . \tag{4.44}$$

This also means that Bloch functions are eigenfunctions of any operator that commutes with $\mathcal{T}$. For example, we know that the Hamiltonian of a crystalline system must itself have the same symmetry as the crystal, and therefore be a periodic operator. Any periodic operator commutes with the translation operator $\mathcal{T}$. So eigenfunctions of the Hamiltonian of a periodic system must be Bloch functions. Furthermore, for a new point in reciprocal space denoted as $\mathbf{k}_i' = \mathbf{k}_i + \mathbf{K}$, substituting Eq. (4.37) and Eq. (4.40) in Eq. (4.41), we find:

$$\begin{aligned}
\varphi_\mu\left(\mathbf{r}_j + \mathbf{h}, \mathbf{k}_i'\right) &= e^{i\mathbf{k}_i'\cdot\mathbf{h}}\varphi_\mu\left(\mathbf{r}_j, \mathbf{k}_i'\right) = e^{i(\mathbf{k}_i+\mathbf{K})\cdot\mathbf{g}}\varphi_\mu\left(\mathbf{r}_j, \mathbf{k}_i'\right) \\
&= e^{i\mathbf{k}_i\cdot\mathbf{h}}\varphi_\mu\left(\mathbf{r}_j, \mathbf{k}_i'\right) = e^{i\mathbf{k}_i\cdot\mathbf{h}}\frac{1}{\sqrt{\Omega_r}}\sum_{\mathbf{g}}\chi_\mu\left(\mathbf{r}_j - \mathbf{A}_\mu - \mathbf{g}\right)e^{i\mathbf{g}\cdot(\mathbf{k}_i+\mathbf{K})} \\
&= e^{i\mathbf{k}_i\cdot\mathbf{h}}\varphi_\mu\left(\mathbf{r}_j, \mathbf{k}_i\right) \ .
\end{aligned} \tag{4.45}$$

Then, comparing Eq. (4.45) with Eq. (4.41) we conclude that Bloch functions are periodic in reciprocal space:

$$\varphi_\mu\left(\mathbf{r}_j, \mathbf{k}_i\right) = \varphi_\mu\left(\mathbf{r}_j, \mathbf{k}_i + \mathbf{K}\right) \ . \tag{4.46}$$

This gives us the important conclusion, that by expressing equations in the Bloch function basis, *the periodic system is entirely described by considering only one of the infinite reciprocal primitive cells*. This means that we only need to solve the one-electron HF equation, that is to say Eq. (4.11), or the equivalent one-electron KS equation, at those points contained in one of the reciprocal primitive cells. By convention, we choose the cell centered at the origin, that is to say the FBZ. The FBZ is typically sampled on a regular grid of points called the Monkhorst-Pack net [232].

It is therefore logical to expand the one-electron states of the periodic system (the COs), as in Eq. (3.16), but using Bloch functions rather than AOs, as follows:

$$\begin{aligned} \langle r_j, k_i | i \rangle &= \langle r_j, k_i | i^{\alpha} \rangle \otimes |\alpha\rangle + \langle r_j, k_i | i^{\beta} \rangle \otimes |\beta\rangle \\ &= \sum_{\mu} c^{\alpha}_{\mu i \{\mathbf{k}_i\}} \varphi_{\mu} \left(\mathbf{r}_j, \mathbf{k}_i \right) \otimes |\alpha\rangle + c^{\beta}_{\mu i \{\mathbf{k}_i\}} \varphi_{\mu} \left(\mathbf{r}_j, \mathbf{k}_i \right) \otimes |\beta\rangle \ . \end{aligned} \tag{4.47}$$

4.3.3 One-Electron Equation in the Bloch Function Basis

We now show how the one-electron HF (or KS) equation can be expressed in the Bloch function basis, which provides a means for modeling of materials. Applying the bra- $\langle m|$ to both sides of Eq. (4.11), we find:

$$\langle m | \mathbf{F}(m) | m \rangle = \epsilon_m \langle m | m \rangle \ . \tag{4.48}$$

Now defining the following resolution of the identity:

$$\mathbb{I} = \int d\mathbf{r}_j \ |r_j, k_m\rangle\langle r_j, k_m | r_j, k_m \rangle\langle r_j, k_m| = \int d\mathbf{r}_j \ |r_j, k_m\rangle\langle r_j, k_m| \ , \tag{4.49}$$

and substituting Eq. (4.49) in Eq. (4.48), we find:

$$\begin{aligned} \int d\mathbf{r}_j \ \langle m | r_j, k_m \rangle \langle r_j, k_m | \mathbf{F}\left(m\right) | r_j, k_m \rangle \langle r_j, k_m | m \rangle &= \int d\mathbf{r}_j \ \langle m | r_j, k_m \rangle \mathcal{F}(m) \langle r_j, k_m | m \rangle \\ &= \epsilon_m \int d\mathbf{r}_j \ \langle m | r_j, k_m \rangle \langle r_j, k_m | m \rangle \ , \end{aligned} \tag{4.50}$$

where $\mathcal{F}(m) = \langle r_j, k_m | \mathbf{F}\left(m\right) | r_j, k_m \rangle$ is the representation of the Fock operator in the basis of Bloch functions. Then expanding the COs in Eq. (4.50) according to Eq. (4.47), we obtain the following matrix equation:

$$\begin{bmatrix} \mathbf{c}^{\alpha}_{\{\mathbf{k}_m\}} \\ \mathbf{c}^{\beta}_{\{\mathbf{k}_m\}} \end{bmatrix}^{\dagger} \begin{bmatrix} \mathbf{F}^{\alpha\alpha}_{\{\mathbf{k}_m\}} & \mathbf{F}^{\alpha\beta}_{\{\mathbf{k}_m\}} \\ \mathbf{F}^{\beta\alpha}_{\{\mathbf{k}_m\}} & \mathbf{F}^{\beta\beta}_{\{\mathbf{k}_m\}} \end{bmatrix} \begin{bmatrix} \mathbf{c}^{\alpha}_{\{\mathbf{k}_m\}} \\ \mathbf{c}^{\beta}_{\{\mathbf{k}_m\}} \end{bmatrix} = \begin{bmatrix} \mathbf{c}^{\alpha}_{\{\mathbf{k}_m\}} \\ \mathbf{c}^{\beta}_{\{\mathbf{k}_m\}} \end{bmatrix}^{\dagger} \begin{bmatrix} \mathbf{S}^{\alpha\alpha}_{\{\mathbf{k}_m\}} & \mathbf{0} \\ \mathbf{0} & \mathbf{S}^{\beta\beta}_{\{\mathbf{k}_m\}} \end{bmatrix} \begin{bmatrix} \mathbf{c}^{\alpha}_{\{\mathbf{k}_m\}} \\ \mathbf{c}^{\beta}_{\{\mathbf{k}_m\}} \end{bmatrix} \boldsymbol{\epsilon}_{\{\mathbf{k}_m\}} \ , \tag{4.51}$$

where we use the convention that the matrices with double spin indices have a size of $n_{\mu} \times n_{\mu}$, if there are n_{μ} Bloch functions for electron m. The matrices $\mathbf{c}^{\alpha}_{\{\mathbf{k}_m\}}$ and $\mathbf{c}^{\beta}_{\{\mathbf{k}_m\}}$, containing the coefficients $c^{\alpha}_{\mu m \{\mathbf{k}_m\}}$ and $c^{\beta}_{\mu m \{\mathbf{k}_m\}}$, have a size of $n_{\mu} \times 2n_{\mu}$, and the diagonal matrix $\boldsymbol{\epsilon}_{\{\mathbf{k}_m\}}$, containing the Lagrange multipliers or one-electron energies, has a size of $2n_\mu \times 2n_\mu$. The matrix elements $F^{\sigma\sigma'}_{\mu\nu\{\mathbf{k}_m\}}$ and $S^{\sigma\sigma'}_{\mu\nu\{\mathbf{k}_m\}}$ read as follows:

$$F^{\sigma\sigma'}_{\mu\nu\{\mathbf{k}_m\}} = \Omega_r \int d\mathbf{r}_j \, \varphi^*_\mu\left(\mathbf{r}_j, \mathbf{k}_m\right) \mathcal{F}^{\sigma\sigma'}(m) \varphi_\nu\left(\mathbf{r}_j, \mathbf{k}_m\right) \tag{4.52a}$$

$$S^{\sigma\sigma'}_{\mu\nu\{\mathbf{k}_m\}} = \delta_{\sigma\sigma'} \Omega_r \int d\mathbf{r}_j \, \varphi^*_\mu\left(\mathbf{r}_j, \mathbf{k}_m\right) \varphi_\nu\left(\mathbf{r}_j, \mathbf{k}_m\right) \ , \tag{4.52b}$$

where for the Fock operator, the notation from Eq. (3.10) was explicitly used. Then mutiplying both sides of Eq. (4.51) by the inverse of the Hermitian-conjugate of the CO coefficient matrix, we find the HF equations in the Bloch function basis:

$$\begin{bmatrix} \mathbf{F}^{\alpha\alpha}_{\{\mathbf{k}_m\}} & \mathbf{F}^{\alpha\beta}_{\{\mathbf{k}_m\}} \\ \mathbf{F}^{\beta\alpha}_{\{\mathbf{k}_m\}} & \mathbf{F}^{\beta\beta}_{\{\mathbf{k}_m\}} \end{bmatrix} \begin{bmatrix} \mathbf{c}^{\alpha}_{\{\mathbf{k}_m\}} \\ \mathbf{c}^{\beta}_{\{\mathbf{k}_m\}} \end{bmatrix} = \begin{bmatrix} \mathbf{S}^{\alpha\alpha}_{\{\mathbf{k}_m\}} & \mathbf{0} \\ \mathbf{0} & \mathbf{S}^{\beta\beta}_{\{\mathbf{k}_m\}} \end{bmatrix} \begin{bmatrix} \mathbf{c}^{\alpha}_{\{\mathbf{k}_m\}} \\ \mathbf{c}^{\beta}_{\{\mathbf{k}_m\}} \end{bmatrix} \boldsymbol{\epsilon}_{\{\mathbf{k}_m\}} \ , \tag{4.53}$$

From Eq. (2.38) it is clear enough that if the relativistic Hamiltonian being approximated by the HF prescription does not contain the spin-dependent operator $\mathbf{U}_{SOREP}$, then the associated Fock operator will be diagonal in spin space. That is to say, if $\mathbf{U}_{SOREP} = \mathbf{0}$, then $\mathcal{F}^{\sigma\sigma'}(m) = \delta_{\sigma\sigma'}\mathcal{F}^{\sigma\sigma'}(m)$. So, in the absence of $\mathbf{U}_{SOREP}$, we can simplify Eq. (4.53) and obtained a set of two decoupled equations, one for each spin component, as follows:

$$\mathbf{F}^{\alpha\alpha}_{\{\mathbf{k}_m\}} \mathbf{c}^{\alpha\alpha}_{\{\mathbf{k}_m\}} = \mathbf{S}^{\alpha\alpha}_{\{\mathbf{k}_m\}} \mathbf{c}^{\alpha\alpha}_{\{\mathbf{k}_m\}} \boldsymbol{\epsilon}^{\alpha\alpha}_{\{\mathbf{k}_m\}} \tag{4.54a}$$

$$\mathbf{F}^{\beta\beta}_{\{\mathbf{k}_m\}} \mathbf{c}^{\beta\beta}_{\{\mathbf{k}_m\}} = \mathbf{S}^{\beta\beta}_{\{\mathbf{k}_m\}} \mathbf{c}^{\beta\beta}_{\{\mathbf{k}_m\}} \boldsymbol{\epsilon}^{\beta\beta}_{\{\mathbf{k}_m\}} \ , \tag{4.54b}$$

in which double spin indices now appear, for example, on the matrices $\mathbf{c}^{\alpha\alpha}_{\{\mathbf{k}_m\}}$ and $\boldsymbol{\epsilon}^{\alpha\alpha}_{\{\mathbf{k}_m\}}$ in Eq. (4.54) to specify that they have a size of $n_\mu \times n_\mu$. Eq. (4.53) is a representation of the generalized HF equations in the basis of Bloch functions, while Eq. (4.54) is a similar representation of the unrestricted HF equations. Another notable variant is the restricted HF equations, in which the α and β components of the wavefunction are restricted to the same form, so that only one of Eq. (4.54a) or Eq. (4.54b) would need to be solved. The term generalized HF hence refers to the HF procedure, in which the one-electron functions are not pure α or β states, but are instead mixed spin states. This is not to be confused with the previously discussed generalized KS procedure, in which the term "generalized" is instead used to refer to the fact that the xc functional is built from KS orbitals, rather than the electron density. An unfortunate consequence is that, then a different terminology needs to be used to distinguish the representation of the KS equations according to the scheme in Eq. (4.53) or the one in Eq. (4.54). In order to resolve this ambiguity, here we call the scheme in Eq. (4.53) the two-component HF (or KS) approach, and the scheme in Eq. (4.54) is called the one-component HF (or KS) approach. Strategies for the solution of Eqs. (4.53) and (4.54) (and their equivalent KS variants) are discussed further in chapter 6, as well as Appendices C-G and papers IV-VII.

4.4 Significance of Contribution from Paper II

We conclude this chapter by discussing the significance of the work achieved in paper II [104]. This paper was authored by (in this order) Prof. Khaled El-Khelany of the University of Minia, Egypt; Mr. Corentin Ravoux, at the time a Master's student at the Centrale Supélec, France; the present author of this thesis; Prof. Pietro Cortona of the Centrale Supélec, France; Profs. Yuanming Pan and John Tse of the University of Saskatchewan, Canada; Prof. Alessandro Erba of the Università di Torino, Italy. The author's contribution to this paper was to perform some of the calculations and provide an advisory role to the two first authors, who did the rest of the calculations. Paper II was mostly written by Prof. Alessandro Erba, who — along with the other authors — provided a supervisory role. This paper discusses an application of the generalized KS variant of the one-component scheme outlined in Eq. (4.54) to the lanthanide sesquioxides Ln_2O_3, where Ln=La, Ce, Pr, Nd. The strong localization in space and energy of the partially occupied f-band in these materials means that they have widespread technological applications [10, 132]. In particular, the ease at which Cerium can be oxidized from Ce_2O_3 (containing Ce^{3+} with an unpaired electron f^1 in the f-band) to CeO_2 (containing Ce^{4+} with an empty f-band) means that it has important applications in catalysis [43, 95, 309]. Correspondingly, it has been extensively studied in the last two decades, using a wide variety of computational techniques [43, 66, 111, 136, 145, 155, 211, 290, 291, 292, 337]. Indeed, the ground electronic state of Ce_2O_3 is well understood in the literature as a broken-symmetry antiferromagnetic state with two unpaired electrons in the $4f$-band that are well localized on each Ce center [145, 249]. On the other hand, before the publication of paper II, a good understanding of the ground electronic state of the other members of the series was still missing. This may have been because, one of the main challenges in studying these materials is that the presence of the partially occupied f-band can lead (and indeed does in the case of the lanthanide sesquioxides) to a diverse array of metastable electronic configurations. In this case, it must be appreciated that there is absolutely no guarantee that the Roothaan-Hall procedure [149, 264], that is to say, the procedure by which Eq. (4.54) can be practically solved self-consistently will converge to the lowest energy state. Indeed, even though mathematically, convergence theorems can be rigorously established for certain ways of solving the SCF equations, these theorems are i) only true for the restricted HF procedure with integer occupations (not the KS procedure with fractional occupations that is usually used for solid state calculations, with exception of the method described in Ref. [49], which, however, can only be conjectured to converge numerically to a solution of the KS equations) ii) while it can be proven that some approaches converge, no approach can be proven to converge to the ground state [48, 50, 51, 57, 182, 199, 200, 269]. As a matter of fact, some confusion as to the nature of the ground state of Ce_2O_3 (in terms of exactly which f orbitals could be denoted as being partially occupied) existed before the publication of paper II, and previous studies had reported convergence to metastable solutions [111, 112, 155, 179, 196, 211]. In our case, the fact that our calculations were performed with local orbitals (in contrast to most previous studies), meant that a symmetry analysis of the COs could be easily performed, and the calculation could be constrained to each of the many possible symmetry allowed electronic configurations for the occupation of the f-band, such that the most stable configuration could be safely found and characterized. This permitted, in particular, to resolve an apparent disagreement in the literature on the occupation of the f-band in Ce_2O_3 as being simply the result of different conventions for the orientation of the crystallographic axes w.r.t. the Cartesian ones.

In paper II, the use of analytical algorithms based on local orbitals, as opposed to more numerical methods based on plane wave basis sets of most previous studies, also meant that we could take advantage of considerable numerical accuracy and safely predict a more stable antiferromagnetic (as opposed to ferromagnetic) ground state for all three of the Ce_2O_3, Pr_2O_3 and Nd_2O_3 sesquioxides, even though the energy differences were sometimes below the meV scale. The agreement of our calculations based on global-hybrid functionals on Ce_2O_3 with previous studies based on range-seperated hybrids, or DFT+U approaches, increased our confidence on the results obtained instead for the other end-members of the series, for which instead no comparison was available.

Finally, paper II reported the first application of an algorithm for calculations with so-called self-consistent hybrid functionals to strongly correlated materials. The self-consistent hybrid approach is an efficient means to deal with the infamous self-interaction error (SIE) of modern density-functional approaches. The SIE is the manifestation of the fact that by choosing approximate functionals to represent E_{xc} in Eq. (4.17), it is not guaranteed that the electron-electron interaction energy will vanish for a single particle interacting with itself. On the other hand, in the HF procedure, from Eq. (4.12d), it is easy to see that for a single orbital (for the case $n = m$), the exchange term $-\langle m|\mathbf{K}(m)|m\rangle$ cancels exactly with the Coulomb term $\langle m|\mathbf{C}(m)|m\rangle$. In other words, the HF procedure is free from any kind of SIE. It is therefore logical that by including a fraction a of Fock exchange, through hybrid functionals, as in Eq. (4.24), that problems associated to SIE in the KS-DFT will be diminished. Then, the question remains as to which value for a is best for a specific system of interest.

If a is a system-specific quantity, then it is logical to think that it should be somehow related to the static electronic screening of the system. As a matter of fact, in the last decade theoretical arguments have been developed — based principally on many-body perturbation theory — to suggest that a can be practically approximated as the inverse of the system's static dielectric constant ε_∞ [12, 67, 103, 193, 222, 234, 285, 338]. The obvious problem then appears that the fraction of Fock exchange a depends on ε_∞, but the calculation of the static dielectric constant ε_∞ itself depends on the approximated functional, and hence on a. So Ref. [289] proposed that a should be determined through a self-consistent procedure, using the single-point algorithm, in which the optimal system-dependent fraction a of non-local Fock exchange is determined iteratively through the dielectric constant (i.e. choose initial a, then iterate $a \to \varepsilon_\infty \to a \to \varepsilon_\infty \to \dots$ until convergence). This algorithm has now been used in a number of applications [20, 116, 128, 130, 137, 138, 139, 140, 164, 178, 227, 233, 239, 263, 312, 313]. The method propsed in Ref. [289] is not the only means to self-consistently correct for SIE in the KS-DFT, because Matteo Cococcioni and friends have developed a popular approach, over the last 15 years, for a self-consistent determination of the effective on-site interaction U in the Hubbard model [62, 63, 122, 169, 201, 202, 217].

Our application of the self-consistent hybrid functional method to the lanthanide sesquioxides was achieved using the algorithm of Erba [107]. At each iteration, the system's static dielectric constant ε_∞ is calculated from the wavefunction's response to the external electric field, using a coupled-perturbed KS procedure, otherwise known as density functional perturbation theory [117, 118, 119, 120, 171, 188, 189]. This approach allowed us to obtain — in a non-empirical way— an accurate description of the band gap of the series, which nicely reproduced the experimental trend, regardless of the chosen approximation for the xc functional. This result has significant implications for the future prediction of material properties from the KS-DFT.

5 One-Electron Properties

5.1 One-Electron Properties and the Density Matrix

Let us collect the coefficients of Eq. (4.47) of all of the occupied COs into a quantity called the reciprocal space single-particle density matrix:

$$P^{\sigma\sigma'}_{\mu\nu\{\mathbf{k}_j\}} \equiv \frac{1}{\Omega_r} \sum_m^{occ} \frac{1}{N_{m\{\mathbf{k}_m\}}} \left[c^{\sigma}_{\mu m\{\mathbf{k}_m\}} \right]^* c^{\sigma'}_{\nu m\{\mathbf{k}_m\}} \theta \left[\epsilon_F - \epsilon_{\{\mathbf{k}_m\}} \right] , \tag{5.1}$$

where θ is the Heaviside step function, and ϵ_F is the Fermi energy. The $N_{m\{\mathbf{k}_m\}} = 1$ if m is over or under the Fermi energy ϵ_F at the point $\mathbf{k}_m$. Otherwise, if m is exactly at the Fermi energy at the point $\mathbf{k}_m$, then $N_{m\{\mathbf{k}_m\}}$ is the number of states that are degenerate with m at the point $\mathbf{k}_m$.

It is clear from Eq. (5.1) that $P^{\sigma\sigma'}_{\mu\nu\{\mathbf{k}_j\}}$ is a Hermitian quantity:

$$P^{\sigma\sigma'}_{\mu\nu\{\mathbf{k}_j\}} = \left[P^{\sigma'\sigma}_{\nu\mu\{\mathbf{k}_j\}} \right]^* \tag{5.2}$$

The density matrix can be Fourier transformed to direct space, as follows:

$$P^{\sigma\sigma'}_{\mu\nu\{\mathbf{g}\}} = \int_{\Omega_r} d\mathbf{k}_j \, e^{i\mathbf{g}\cdot\mathbf{k}_j} P^{\sigma\sigma'}_{\mu\nu\{\mathbf{k}_j\}} \quad \Leftrightarrow \quad P^{\sigma\sigma'}_{\mu\nu\{\mathbf{g}\}} = P^{\sigma'\sigma}_{\nu\mu\{-\mathbf{g}\}} . \tag{5.3}$$

The density matrix is a useful concept, amongst other reasons, because, once Eq. (4.53) has been solved, it allows to express one-electron properties of the system in the AO basis. For example, consider the electron density, calculated from the occupied COs, as follows:

$$n = \sum_m^{occ} \langle m | \hat{n} | m \rangle . \tag{5.4}$$

where $\hat{n}$ is the density operator, which reduces to unity in the AO basis. Defining the following resolution of the identity:

$$\mathbb{I} = \int_{\Omega_r} d\mathbf{k}_j \, |r_j, k_m\rangle\langle r_j, k_m | r_j, k_m \rangle\langle r_j, k_m| = \int_{\Omega_r} d\mathbf{k}_j \, |r_j, k_m\rangle\langle r_j, k_m| , \tag{5.5}$$

Then, substituting Eqs. (5.5), (5.1), (4.47) and (4.40) in Eq. (5.4), we find:

$$n\left(\mathbf{r}_j\right) = \sum_{\mu\nu} \sum_{\mathbf{g}} \mathrm{Re} \left[P^{\alpha\alpha\oplus\beta\beta}_{\mu\nu\{\mathbf{g}\}} \right] \chi_\mu \left(\mathbf{r}_j - \mathbf{A}_\mu \right) \chi_\nu \left(\mathbf{r}_j - \mathbf{A}_\nu - \mathbf{g} \right) , \tag{5.6}$$

where the following notation has been used for the spin-blocks of the density matrix:

$$P^{\alpha\alpha\oplus\beta\beta}_{\mu\nu\{\mathbf{g}\}} \equiv P^{\alpha\alpha}_{\mu\nu\{\mathbf{g}\}} + P^{\beta\beta}_{\mu\nu\{\mathbf{g}\}} \tag{5.7a}$$

To write succinctly the expressions also for other properties, it will be useful to extend the notation in Eq.

(5.7a) also to other spin-blocks of the matrix:

$$P^{\alpha\alpha\ominus\beta\beta}_{\mu\nu\{\mathbf{g}\}} \equiv P^{\alpha\alpha}_{\mu\nu\{\mathbf{g}\}} - P^{\beta\beta}_{\mu\nu\{\mathbf{g}\}} \tag{5.7b}$$

$$P^{\beta\alpha\oplus\alpha\beta}_{\mu\nu\{\mathbf{g}\}} \equiv P^{\beta\alpha}_{\mu\nu\{\mathbf{g}\}} + P^{\alpha\beta}_{\mu\nu\{\mathbf{g}\}} \tag{5.7c}$$

$$P^{\beta\alpha\ominus\alpha\beta}_{\mu\nu\{\mathbf{g}\}} \equiv P^{\beta\alpha}_{\mu\nu\{\mathbf{g}\}} - P^{\alpha\beta}_{\mu\nu\{\mathbf{g}\}} \tag{5.7d}$$

The Cartesian components m_i of the magnetization vector $\mathbf{m}$, see Eq. (4.28), are written in terms of the occupied COs and the Pauli matrices $\boldsymbol{\sigma}_i$ as follows:

$$m_i = \sum_m^{occ} \langle m|\boldsymbol{\sigma}_i|m\rangle \qquad \forall i \in x, y, z \ . \tag{5.8}$$

Proceeding as for Eq. (5.6) and using the explicit expressions for the Pauli matrices from Eq. (2.11), we find:

$$m_x\left(\mathbf{r}_j\right) = \sum_{\mu\nu}\sum_{\mathbf{g}} \ \mathrm{Re}\left[P^{\beta\alpha\oplus\alpha\beta}_{\mu\nu\{\mathbf{g}\}}\right] \ \chi_\mu\left(\mathbf{r}_j - \mathbf{A}_\mu\right)\chi_\nu\left(\mathbf{r}_j - \mathbf{A}_\nu - \mathbf{g}\right) \ , \tag{5.9a}$$

$$m_y\left(\mathbf{r}_j\right) = -\sum_{\mu\nu}\sum_{\mathbf{g}} \ \mathrm{Im}\left[P^{\beta\alpha\ominus\alpha\beta}_{\mu\nu\{\mathbf{g}\}}\right] \ \chi_\mu\left(\mathbf{r}_j - \mathbf{A}_\mu\right)\chi_\nu\left(\mathbf{r}_j - \mathbf{A}_\nu - \mathbf{g}\right) \ , \tag{5.9b}$$

$$m_z\left(\mathbf{r}_j\right) = \sum_{\mu\nu}\sum_{\mathbf{g}} \ \mathrm{Re}\left[P^{\alpha\alpha\ominus\beta\beta}_{\mu\nu\{\mathbf{g}\}}\right] \ \chi_\mu\left(\mathbf{r}_j - \mathbf{A}_\mu\right)\chi_\nu\left(\mathbf{r}_j - \mathbf{A}_\nu - \mathbf{g}\right) \ . \tag{5.9c}$$

A more explicit derivation of Eqs. (5.6) and (5.9) is provided in Appendix F for the non-periodic limit. The orbital-current density, see Eq. (4.29), reads as follows in the CO basis:

$$\mathbf{j} = \frac{1}{2i}\sum_m^{occ} \langle m|\boldsymbol{\nabla}|m\rangle - \langle m|\boldsymbol{\nabla}^\dagger|m\rangle \ . \tag{5.10}$$

Proceeding again as in Eq. (5.6), the expression in the AO basis reads:

$$\begin{aligned}\mathbf{j}\left(\mathbf{r}_j\right) \ &= \ \frac{1}{2}\sum_{\mu\nu}\sum_{\mathbf{g}} \mathrm{Im}\left[P^{\alpha\alpha\oplus\beta\beta}_{\mu\nu\{\mathbf{g}\}}\right]\{\chi_\mu\left(\mathbf{r}_j - \mathbf{A}_\mu\right)\left[\boldsymbol{\nabla}_j\chi_\nu\left(\mathbf{r}_j - \mathbf{A}_\nu - \mathbf{g}\right)\right] \\ &- \ \left[\boldsymbol{\nabla}_j\chi_\mu\left(\mathbf{r}_j - \mathbf{A}_\mu\right)\right]\chi_\nu\left(\mathbf{r}_j - \mathbf{A}_\nu - \mathbf{g}\right)\} \ .\end{aligned} \tag{5.11}$$

A derivation of Eq. (5.11) is provided in Appendix B of paper VII, also for the non-periodic case. Now for the spin-current densities $\mathbf{J}_i$, see Eq. (4.30), the expression in the CO basis is as follows:

$$\mathbf{J}_i = \frac{1}{2i}\sum_m^{occ} \langle m|\boldsymbol{\nabla}\boldsymbol{\sigma}_i|m\rangle - \langle m|\boldsymbol{\nabla}^\dagger\boldsymbol{\sigma}_i|m\rangle \qquad \forall i \in x, y, z \ . \tag{5.12}$$

In Appendix C of paper VII, we show how the $\mathbf{J}_x$, $\mathbf{J}_y$ and $\mathbf{J}_z$ can also be calculated from the density matrix as follows:

$$\begin{aligned}
\mathbf{J}_x\left(\mathbf{r}_j\right) &= \frac{1}{2}\sum_{\mu\nu}\sum_{\mathbf{g}} \mathrm{Im}\left[P^{\beta\alpha\oplus\alpha\beta}_{\mu\nu\{\mathbf{g}\}}\right]\{\chi_\mu\left(\mathbf{r}_j-\mathbf{A}_\mu\right)\left[\boldsymbol{\nabla}_j\chi_\nu\left(\mathbf{r}_j-\mathbf{A}_\nu-\mathbf{g}\right)\right] \\
&- \left[\boldsymbol{\nabla}_j\chi_\mu\left(\mathbf{r}_j-\mathbf{A}_\mu\right)\right]\chi_\nu\left(\mathbf{r}_j-\mathbf{A}_\nu-\mathbf{g}\right)\}\,, \qquad (5.13a)
\end{aligned}$$

$$\begin{aligned}
\mathbf{J}_y\left(\mathbf{r}_j\right) &= \frac{1}{2}\sum_{\mu\nu}\sum_{\mathbf{g}} \mathrm{Re}\left[P^{\beta\alpha\ominus\alpha\beta}_{\mu\nu\{\mathbf{g}\}}\right]\{\chi_\mu\left(\mathbf{r}_j-\mathbf{A}_\mu\right)\left[\boldsymbol{\nabla}_j\chi_\nu\left(\mathbf{r}_j-\mathbf{A}_\nu-\mathbf{g}\right)\right] \\
&- \left[\boldsymbol{\nabla}_j\chi_\mu\left(\mathbf{r}_j-\mathbf{A}_\mu\right)\right]\chi_\nu\left(\mathbf{r}_j-\mathbf{A}_\nu-\mathbf{g}\right)\}\,, \qquad (5.13b)
\end{aligned}$$

$$\begin{aligned}
\mathbf{J}_z\left(\mathbf{r}_j\right) &= \frac{1}{2}\sum_{\mu\nu}\sum_{\mathbf{g}} \mathrm{Im}\left[P^{\alpha\alpha\ominus\beta\beta}_{\mu\nu\{\mathbf{g}\}}\right]\{\chi_\mu\left(\mathbf{r}_j-\mathbf{A}_\mu\right)\left[\boldsymbol{\nabla}_j\chi_\nu\left(\mathbf{r}_j-\mathbf{A}_\nu-\mathbf{g}\right)\right] \\
&- \left[\boldsymbol{\nabla}_j\chi_\mu\left(\mathbf{r}_j-\mathbf{A}_\mu\right)\right]\chi_\nu\left(\mathbf{r}_j-\mathbf{A}_\nu-\mathbf{g}\right)\}\,. \qquad (5.13c)
\end{aligned}$$

5.2 Direct Space Representation of One-Electron Properties on a Discrete Grid

To gain physical insight on the results of a calculation, it can be useful to analyze the n, $\mathbf{m}$, $\mathbf{j}$ and $\mathbf{J}_c$ in, for example, a 2D or 3D contour map representation. Even if these depictions do not provide physical insight, they can be useful to make sexy plots to impress girls! The SCF procedure gives us the density matrix $P^{\sigma\sigma'}_{\mu\nu\{\mathbf{g}\}}$, which can be written to disk after completion of the calculation. Then, using knowledge of the chosen form for the χ_μ, see Eq. (3.28), we have all the necessary ingredients needed to calculate the n, $\mathbf{m}$, $\mathbf{j}$ and $\mathbf{J}_c$ on a discrete grid of points in $\mathbf{r}_j$ space and develop algorithms to make pretty plots! The calculation of the density variables is also a necessary ingredient for the calculation of certain spectroscopic properties, like the Mossbauer isomer shift, the Fermi contact hyperfine interaction and X-ray structure factors, to name a few.

In Crystal, a code existed (written, of course, by the great V.R. Saunders) to calculate the $n\left(\mathbf{r}_j\right)$ and $m_z\left(\mathbf{r}_j\right)$, as well as their spatial derivatives up to fourth order on a grid of points, provided that they could be expanded in AOs with up to angular-momentum $l = 2$ functions (d-type functions). The calculation of the derivatives of the density is a key ingredient for topological analysis of the density, using Richard Bader's famous Quantum Theory of Atoms-in-Molecules [16, 17]. Such an analysis can be performed using the Topond program of Carlo Gatti and Silvia Casassa, which is interfaced with Saunders' code for the calculation of the density variables and their derivatives [34, 135]. The topological analysis of the electron density of periodic systems with Topond has generated renewed interest in the last five years, leading to the publication of many applications in a diverse array of fields [11, 21, 22, 23, 24, 38, 42, 47, 53, 58, 69, 70, 109, 110, 114, 115, 126, 131, 133, 143, 144, 146, 161, 176, 181, 195, 197, 205, 214, 215, 216, 218, 219, 220, 228, 229, 230, 242, 253, 266, 273, 281, 303, 304, 324, 325, 332, 336, 341, 342, 343, 344, 348]. The fact that Saunders' code is only general to $l = 2$ functions however means that it is impossible to perform this analysis for heavy elements containing occupied f-type functions in the valence basis set. It is also interesting to generalize Saunders' code to calculate also the m_x and m_y components of the magnetization as well as the orbital-current density $\mathbf{j}$, and spin-current densities $\mathbf{J}_x$, $\mathbf{J}_y$ and $\mathbf{J}_z$ such that the density or topological analysis could also be performed in tandem with a relativistic two-component SCF.

This section discusses work that was done to generalize Saunders' code for the calculation of the electron and spin density on a grid of points to work also with f-type and g-type functions, as well as the density variables m_x, m_y, $\mathbf{j}$, $\mathbf{J}_x$, $\mathbf{J}_y$ and $\mathbf{J}_z$. Amongst other things, this work allowed for the plotting of one-electron properties, which permitted to perform the analysis in papers III-VII. This work is also notably the first step to provide a code to perform topological analysis of the density in heavy element containing periodic systems.

Eqs. (5.6), (5.9) and (5.11) all involve the key ingredient of a product of AOs $\chi_\mu\chi_\nu$, or a product of an AO with the gradient of another AO $\chi_\mu\boldsymbol{\nabla}_j\chi_\nu$ in Eq. (5.11), which need to be evaluated at different points in space on a grid in $\mathbf{r}_j$. The calculation of the first order derivatives of, for example the electron density (denoted as $\boldsymbol{\nabla}_j^{(1)}n\left(\mathbf{r}_j\right)$) also involves similar quantities. From Eq. (5.6), we have:

$$\begin{aligned}\boldsymbol{\nabla}_j^{(1)}n\left(\mathbf{r}_j\right) &= \sum_{\mu\nu}\sum_{\mathbf{g}}\mathrm{Re}\left[P^{\alpha\alpha\oplus\beta\beta}_{\mu\nu\{\mathbf{g}\}}\right]\left\{\left[\boldsymbol{\nabla}_j^{(1)}\chi_\mu\left(\mathbf{r}_j-\mathbf{A}_\mu\right)\right]\chi_\nu\left(\mathbf{r}_j-\mathbf{A}_\nu-\mathbf{g}\right)\right.\\ &+ \left.\chi_\mu\left(\mathbf{r}_j-\mathbf{A}_\mu\right)\left[\boldsymbol{\nabla}_j^{(1)}\chi_\nu\left(\mathbf{r}_j-\mathbf{A}_\nu-\mathbf{g}\right)\right]\right\}. \qquad (5.14)\end{aligned}$$

The expression for the second derivative of the density reads:

$$\begin{aligned}\boldsymbol{\nabla}_j^{(2)}n\left(\mathbf{r}_j\right) &= \sum_{\mu\nu}\sum_{\mathbf{g}}\mathrm{Re}\left[P^{\alpha\alpha\oplus\beta\beta}_{\mu\nu\{\mathbf{g}\}}\right]\left\{2\left[\boldsymbol{\nabla}_j^{(1)}\chi_\mu\left(\mathbf{r}_j-\mathbf{A}_\mu\right)\right]\left[\boldsymbol{\nabla}_j^{(1)}\chi_\nu\left(\mathbf{r}_j-\mathbf{A}_\nu-\mathbf{g}\right)\right]\right.\\ &+ \left.\left[\boldsymbol{\nabla}_j^{(2)}\chi_\mu\left(\mathbf{r}_j-\mathbf{A}_\mu\right)\right]\chi_\nu\left(\mathbf{r}_j-\mathbf{A}_\nu-\mathbf{g}\right)+\chi_\mu\left(\mathbf{r}_j-\mathbf{A}_\mu\right)\left[\boldsymbol{\nabla}_j^{(2)}\chi_\nu\left(\mathbf{r}_j-\mathbf{A}_\nu-\mathbf{g}\right)\right]\right\}. \qquad (5.15)\end{aligned}$$

and so on, up to fourth order. Similar expressions can also be developed for the magnetization components, using however the appropriate spin-blocks of the density matrix from Eq. (5.9). The reader can notice the similarity between Eqs. (5.14) and (5.11), the only differences being that the real part of the density matrix is used in Eq. (5.14) instead of the imaginary part, and an addition occurs between the two products of AOs, instead of a subtraction. The calculation of the spin-current densities can also be done in a very similar way from Eq. (5.13). So the calculation of all density variables essentially comes down to the evaluation of a product of AOs (or their derivatives) on a grid of points, and then combining them with the relevant block of the density matrix. In the implementation of Saunders, the product of AOs was expanded in the basis of HGTF, using Eq. (3.33). The product of AOs was first evaluated for an s-s shell couple, then the recurrence relations for the $E\left[n,l,m,\tilde{n},\tilde{l},\tilde{m},t,u,v\right]$ coefficients were used to increase the quantum numbers, and generate the relevent expressions for shell couples of higher angular momentum, up to d-d, and for the product of the derivatives of the AOs, up to fourth order. This generates a very efficient, but extremely complex algorithm, which cannot be easily generalized to higher angular momentum. Here, a completely new code was generated based on a different, simpler strategy, making again use of the CAS in MATLAB for symbolic computation, as will be explained below.

The AOs are easily expressed in terms of RSSH GTOs from Eq. (3.28). So the evaluation of the AOs (and their derivatives), involves essentially a product of a Gaussian function with (the derivative of) an RSSH $X_{l,0}^{m}$. The expressions for the RSSH were generated symbolically up to $l = 4$ g-type functions using the following two recurrence relations [254]:

$$X_{l+1,0}^{\pm(l+1)}(\mathbf{r}_j - \mathbf{A}) = (2l+1)\left[(r_{jx} - A_x)X_{l,0}^{\pm l}(\mathbf{r}_j - \mathbf{A}) \mp (r_{jy} - A_y)X_{l,0}^{\mp l}(\mathbf{r}_j - \mathbf{A})\right] , \tag{5.16a}$$

and:

$$\begin{aligned} X_{l+1,0}^{m}(\mathbf{r}_j - \mathbf{A}) &= \frac{1}{l - |m| + 1}\Big[(2l+1)(r_{jz} - A_z)X_{l,0}^{m}(\mathbf{r}_j - \mathbf{A}) \\ &- (l + |m|)\left(\mathbf{r}_j - \mathbf{A}\right)^2 X_{l-1,0}^{m}(\mathbf{r}_j - \mathbf{A})\Big] , \end{aligned} \tag{5.16b}$$

The starting point for the recurrence is $X_{0,0}^{0} = 1$ and the convention $X_{0,0}^{-0} = 0$ is understood. The algorithm starts by calculating the $X_{l+1,0}^{(l+1)}$ and $X_{l+1,0}^{-(l+1)}$ at each iteration for $l = 1, 2, 3, 4$ using Eq. (5.16a). The RSSH $X_{l,0}^{m}$, with $m \neq l$ are then generated for successively higher l and the magnetic quantum number in the range $m \in [-l+1, l-1]$. These steps are summarized in the following, where quantum numbers in bold are being increased:

$$1) X_{\mathbf{l},0}^{\mathbf{l}}(\mathbf{r}_j - \mathbf{A}) \quad 2) X_{\mathbf{l},0}^{-\mathbf{l}}(\mathbf{r}_j - \mathbf{A})$$

$$3) X_{0,0}^{\mathbf{m}}(\mathbf{r}_j - \mathbf{A}) \quad 4) X_{\mathbf{l},0}^{m}(\mathbf{r}_j - \mathbf{A})$$

Once the expressions for the RSSH are determined, their derivatives are calculated symbolically (up to fourth order), and they are combined with Gaussian functions in explicit routines that contain the symbolic expression of the (derivatives of the) AO shell couple.

An example of a pretty plot that can be depicted using this algorithm is given in Figure 5.1. This plot gives a contour map of the magnetization field **m** obtained after a fully relativistic two-component SCF calculation on an infinite chain of Ge_2H. The plot can be used to analyze the different solutions that are obtained as a function of the orientation for the guess magnetization.

Another example of a pretty plot that can be depicted with the new program, this time from a SR one-component calculation, is provided in Figure 5.2. This plot depicts the effect of interatomic interactions on the electron density n contribution of some inner orbitals (representing the $4s^2 4p^6 4d^{10}$ Eu and $1s^2$ O electrons) in the cubic crystal of EuO. The plot is generated by taking the difference of the electron density calculated in the EuO crystal under a hydrostatic pressure of 24.3 to 48.5 GPa and a reference of non-interacting atomic densities. In this case, the plot can be used to show the effect of explicitly treating these orbitals in the valence basis set. If these orbitals did not participate in the interatomic interactions, then the isosurfaces would plot at zero, and the shapes of the surfaces would not change by increasing pressure. Because the isosurface shapes change considerably in the different panels, we can see that the inner orbitals

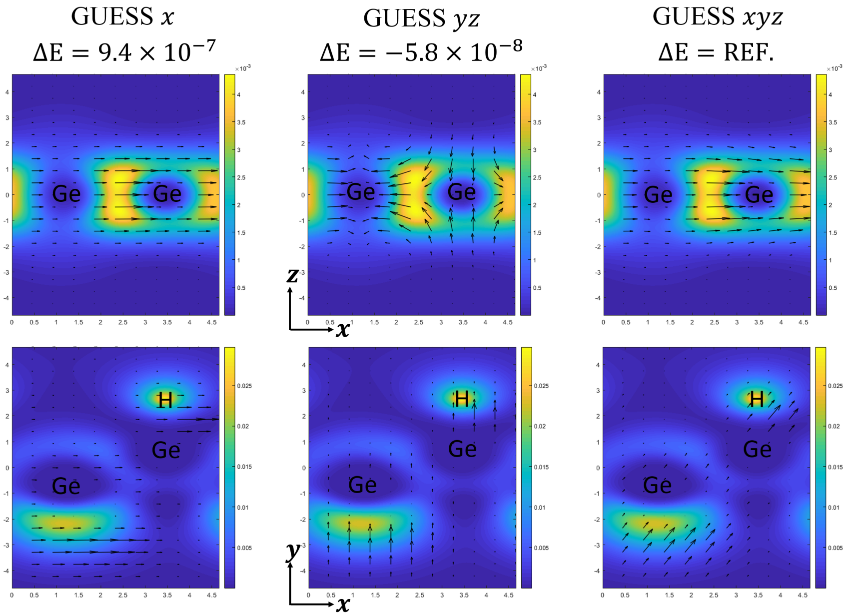

Figure 5.1: Contour map of the magnetization field **m** for a two-component SCF non-collinear LDA calculation on an infinite chain of Ge_2H. The periodic direction is along the x axis and the figures are plotted along two orientations, and for three different guess magnetizations. The energy differences of the different spin textures is denoted on top of the figures by the ΔE, which are taken w.r.t. the rightmost panels, that are obtained with a guess magnetization along the xyz diagonal. The colours represent the magnitude of the magnetization vector, while the orientation and length of the arrows represent the local orientation of **m** and its magnitude as projected on the plane of the plot.

participate actively in the relaxation of the electronic structure of EuO under pressure. Figure 5.2 was generated using the CRYSPLOT plotting program [29].

5.3 Significance of Contribution from Paper III

We conclude this chapter by commenting on the significance of the work done in paper III [80]. Paper III was authored by (in this order) the present author of this thesis; Prof. Alessandro Erba of the Università di Torino, Italy; Prof. Yuanming Pan of the University of Saskatchewan, Canada; Prof. Bartolomeo Civalleri of the Università di Torino, Italy; Prof. John Tse of the University of Saskatchewan, Canada. The author's contribution to this paper was to perform most of the research and writing of the paper, because the other authors adopted a supervisory role. This one, like paper II, was an application of the generalized one-component SR KS scheme described in Eq. (4.54). This time, we applied the procedure to study some pressure-induced phase transitions in the prototypical mixed-valence and strongly-correlated material EuO. Paper III is a yet-to-be-published manuscript.

The ambient pressure cubic phase of EuO has indeed generated great interest in the field of spintronics, because of the presence of the perfectly ferromagnetically coupled f-band with 7 unpaired electrons [8, 180,

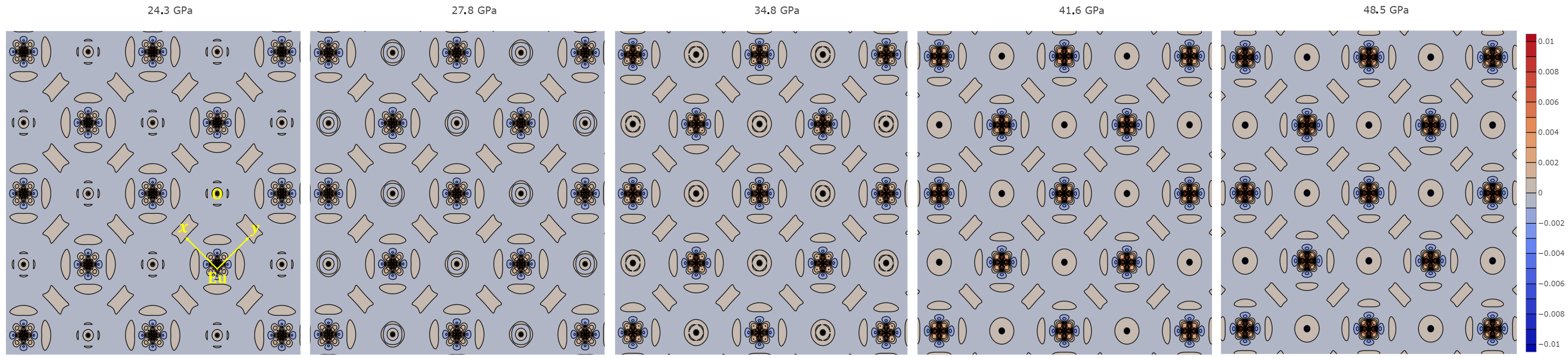

Figure 5.2: Effect of interatomic interactions on the electron density of some inner orbitals of a cubic crystal of EuO. The electron density is plotted as the difference between the *n* obtained in the EuO crystal and a lattice consisting of a superposition non-interacting atomic densities. They are plotted for when the EuO crystal is subject to five different hydrostatic pressures ranging from 24.3 to 48.5 GPa.

272, 298, 328]. It is however also particularly difficult to study from a theoretical point of view, because the presence of the well localized f-states in tandem with the more itinerant s, p and d ones means — again, as in paper II — that it is particularly sensitive to the infamous SIE of conventional density functional approximations. Previous studies have been performed on the pressure induced phase transitions in EuO with methods based on a plane wave basis set and a wide variety of approaches to correct for the SIE [250, 251, 327, 328, 345]. None of these have been able to reproduce all of the phase transitions that have been reported experimentally.

Three phase transitions are known to occur in EuO in the pressure range from 0 to 60 GPa. The first two are isostructural, and only involve a change in the electronic state, as well as the volume, but not the crystal structure. These are reffered to as isostructural volume collapses (IVCs). On the other hand, the third and highest pressure phase transition also involves a change in the structure. The two IVCs have been known to exist experimentally, since at least fourty years ago [8, 177, 351]. An IVC occuring at about 12 or 13 GPa is now well understood as being due to a metal-to-insulator transition, and the structural phase transition has been rationalized as being due to a change in the structure from NaCl-type (B1 phase) to CsCl-type (B2 phase) [250, 327, 328, 345]. However, the other IVC occuring at about 30 to 35 GPa has never before been reproduced theoretically, and is not well understood, despite the fact that it was the first to have been discovered in 1972 [177]. In paper III, the use of local orbitals, rather than a plane wave basis set meant, that we could efficiently perform global hybrid functional calculations on the phases of EuO and treat explicitly and self-consistently a large set of electronic states in the valence basis set. As we show, this allowed us to reproduce for the first time all of the phase transitions in EuO and, together with the analysis of the associated one-electron properties, provide a rationale for their existence.

Figure 5.3 shows the evolution of some properties of EuO as a function of pressure. This figure is much like Figure 1 of the paper III manuscript, except that the top panel also includes data points for the calculated pressure-volume relation of the CsCl-type phase in the dashed black line to compare with the experimental data of Ref. [298] in the open blue circles. Otherwise, Figure 5.3 is identical to Figure 1 of paper III, with the solid black line in the top panel representing the calculated pressure-volume relation, and the coloured symbols representing three different sets of previously reported experimental data [157, 177, 298]. The middle and bottom panels report, respectively, the band-gap and population of d-type bands of Eu atoms in EuO for the phase in the NaCl-type structure. The middle panel confirms that the metallization of the system is associated with the first IVC at around 16 GPa, as was already understood. The bottom panel, on the other hand, provides new analysis, which shows that the second, previously elusive, metal-metal IVC is associated with an abrupt depopulation of the Eu d-type bands. Further analysis is provided in Figure 2 of the manuscript of paper III, which shows that the more stable Eu d-type orbitals of t_{2g} symmetry actually increase in population across the phase transition, and only the less stable Eu d-type orbitals of e_g symmetry are depopulated at the metal-metal IVC. This behaviour can be understood from the fact that as the EuO structure is being compressed, the splitting of the t_{2g} and e_g bands will increase as a result of the stronger

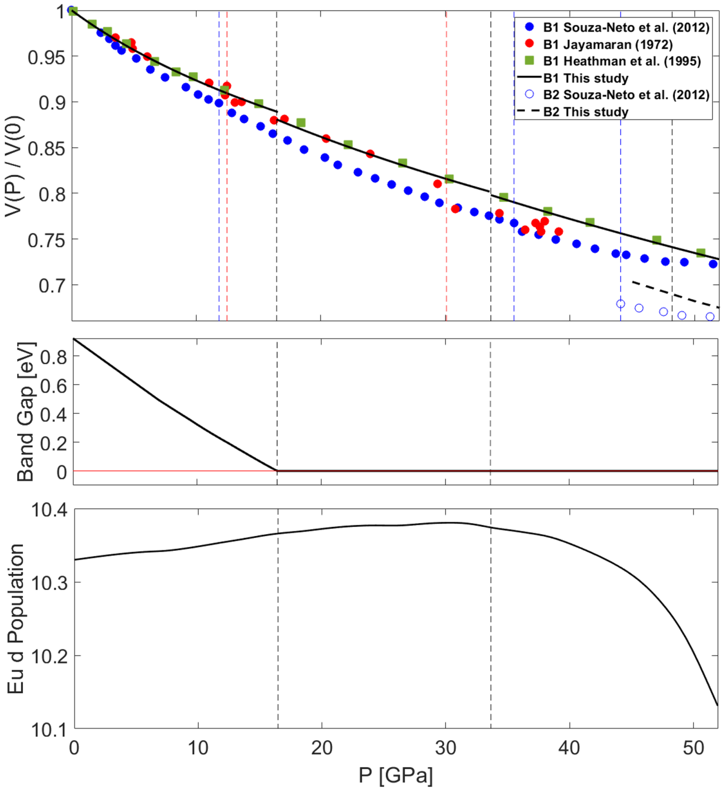

Figure 5.3: (Top panel) Pressure-volume equation-of-state of EuO as computed here (black solid line for NaCl-type structure and black dashed line for CsCl-type structure) and measured with three different previous X-ray diffraction experiments (coloured symbols) [157, 177, 298]. The transition pressured are denoted with dashed vertical lines of the corresponding colours. (Middle panel) Band-gap of EuO in the NaCl-type structure as a function of pressure. (Bottom panel) population of *d*-type bands of Eu atoms in NaCl-type structured EuO, as a function of pressure.

octahedral crystal field, thus destabilizing the Eu states of e_g symmetry.

Our interpretation that the onset of the metal-metal transition is due to an increased magnitude of the octahedral crystal field around the Eu center is somewhat in disagreement with the interpretation of Ref. [298]. These authors provided X-ray absorption near-edge structure (XANES) data, from which — by comparison to the XANES spectra of EuO and Eu_2O_3 at ambient pressure — the phase transition was inferred to be the result of a change in oxidation state from Eu^{2+} to Eu^{3+}. Such a change in oxidation state of Eu implies a change in the electronic configuration, from $[Xe]6s^0 4f^7$ to $[Xe]6s^0 4f^6$, and hence a depopulation of the f-states of Eu, instead of the d-states. Our analysis provides no evidence for such an interpretation, because the Eu f-states display no discontinuity in their behaviour across all of the phase transitions. The only discontinuity (or change in behaviour) is that of the Eu d-type states of e_g symmetry, as shown in Figures 2 and S1 of the manuscript.

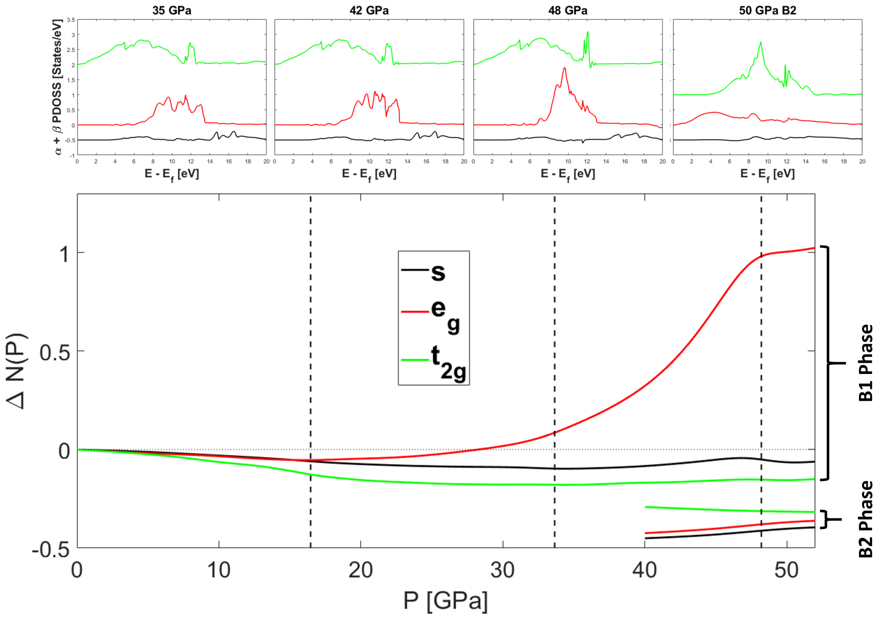

Figure 5.4: (Top panels) conduction band PDOSs of bands of t_{2g}, e_g and s symmetry at four pressures, for the B1 phase (first three panels) and the B2 phase (rightmost panel at 50 GPa). Populations of the Eu bands of t_{2g}, e_g and s symmetry (integral of the PDOSs) from 0 to 50 GPa, calculated as a difference with respect to the ambient pressure values.

It is however important to appreciate that while our interpretation of the results is different from that of Ref. [298], our calculations are in complete agreement with their reported experimental data. This is best evidenced in Figure 5.4, which reports the projected DOSs (PDOSs) of bands of t_{2g}, e_g and s symmetry (top panels) and the band populations (bottom panel), calculated as a difference w.r.t. the ambient pressure values. Indeed, the experiment reported in Ref. [298] was an Eu L_3 edge XANES measurement, which, (according to Fermi's golden rule for dipolar excitations) involves the excitation of an inner Eu p-state to a state of t_{2g}, e_g or s symmetry. So in a first order approximation, the transition probabilities are directly related to the PDOSs of bands of t_{2g}, e_g and s symmetry in the conduction band. It can be seen in Figure 5.4 that as pressure is increased beyond the metal-metal IVC at 33 GPa, a greater number of states of e_g symmetry become available in the conduction band, because of a strengthening of the octahedral crystal field around the Eu atoms, leading to an increased intensity of the XANES Eu L_3 edge. Then, at around 48 GPa, the structural transition to the B2 phase with the CsCl-type structure leads to a weaker square antiprismatic crystal field, and correspondingly a lower number of states of e_g symmetry being available in the conduction band, which is associated also to a decrease in the intensity of the XANES Eu L_3 edge.

In summary, our contribution in paper III provides the first calculation to reproduce all pressure-induced phase transitions in EuO, which is an important success for local orbital periodic KS-DFT theories. Our analyses provides new insight into these phase transitions, in particular, we show that they can be interpreted from simple arguments of crystal field theory, in a manner that is completely consistent with existing experimental data. Our study provides an important benchmark for studying the behaviour of lanthanides in materials at high pressure, and also highlights aspects which have caused confusion in previous interpretations of experiments at high pressure, with important implications for future work.

6 The Two-Component Self-Consistent Field Approach in a Finite Basis

6.1 The Periodic Roothaan-Hall Procedure

6.1.1 From the Roothaan-Hall Equation to an Eigenvalue Equation

We have seen from Eqs. (4.53) and (4.54) how to formulate the HF equations in reciprocal space, so that they can be written for infinite periodic systems. But we have not discussed yet explicitly how they can be practically solved self-consistently, that is the Roothaan-Hall procedure [149, 264]. Indeed, Eq. (4.53) is verified by the occupied valence orbitals, but before doing the calculation we don't know which of the orbitals will be occupied and which will be virtual. The start of the Roothaan-Hall procedure is thus to assume at the start that all orbitals are potentially occupied, and write:

$$\begin{bmatrix} \mathbf{F}^{\alpha\alpha}_{\{\mathbf{k}_i\}} & \mathbf{F}^{\alpha\beta}_{\{\mathbf{k}_i\}} \\ \mathbf{F}^{\beta\alpha}_{\{\mathbf{k}_i\}} & \mathbf{F}^{\beta\beta}_{\{\mathbf{k}_i\}} \end{bmatrix} \begin{bmatrix} \mathbf{c}^{\alpha}_{\{\mathbf{k}_i\}} \\ \mathbf{c}^{\beta}_{\{\mathbf{k}_i\}} \end{bmatrix} = \begin{bmatrix} \mathbf{S}^{\alpha\alpha}_{\{\mathbf{k}_i\}} & \mathbf{0} \\ \mathbf{0} & \mathbf{S}^{\beta\beta}_{\{\mathbf{k}_i\}} \end{bmatrix} \begin{bmatrix} \mathbf{c}^{\alpha}_{\{\mathbf{k}_i\}} \\ \mathbf{c}^{\beta}_{\{\mathbf{k}_i\}} \end{bmatrix} \epsilon_{\{\mathbf{k}_i\}} \ . \tag{6.1}$$

The difference between Eq. (6.1) and Eq. (4.53), is that now the subscript i is included instead of m, because the procedure now, in general, includes all orbitals. Eq. (6.1) is called the Roothaan-Hall equation. At this point, it is convenient to write Eq. (6.1) in the following compact form:

$$\underline{\mathbf{F}}_{\{\mathbf{k}_i\}} \underline{\mathbf{c}}_{\{\mathbf{k}_i\}} = \underline{\mathbf{S}}_{\{\mathbf{k}_i\}} \underline{\mathbf{c}}_{\{\mathbf{k}_i\}} \epsilon_{\{\mathbf{k}_i\}} \tag{6.2}$$

where the underlined matrices contain all of the corresponding spin-blocks of Eq. (6.1), for example:

$$\underline{\mathbf{F}}_{\{\mathbf{k}_i\}} = \begin{bmatrix} \mathbf{F}^{\alpha\alpha}_{\{\mathbf{k}_i\}} & \mathbf{F}^{\alpha\beta}_{\{\mathbf{k}_i\}} \\ \mathbf{F}^{\beta\alpha}_{\{\mathbf{k}_i\}} & \mathbf{F}^{\beta\beta}_{\{\mathbf{k}_i\}} \end{bmatrix} \tag{6.3}$$

We can transform Eq. (6.2) into a more convenient form by realizing that the orthogonality conditions of the COs of Eq. (4.4) implies the following generalized orthogonality relation in the basis of Bloch functions:

$$\underline{\mathbf{c}}^{\dagger}_{\{\mathbf{k}_i\}} \underline{\mathbf{S}}_{\{\mathbf{k}_i\}} \underline{\mathbf{c}}_{\{\mathbf{k}_i\}} = \mathbb{I} \ . \tag{6.4}$$

Then, multiplying both sides of Eq. (6.2) by the Hermitian-conjugate of the CO coefficient matrix, and then substituting in Eq. (6.4), we find the following expression for the one-electron energy levels:

$$\underline{\mathbf{c}}^{\dagger}_{\{\mathbf{k}_i\}} \underline{\mathbf{F}}_{\{\mathbf{k}_i\}} \underline{\mathbf{c}}_{\{\mathbf{k}_i\}} = \epsilon_{\{\mathbf{k}_i\}} \ . \tag{6.5}$$

So if the Fock matrix can be built, the transformation of Eq. (6.5) then permits to obtain the one-electron energy levels. More generally, let us apply a transformation to Eq. (6.2), using the generic matrix $\mathbf{X}$ and its inverse $\mathbf{X}^{-1}$, as follows:

$$\mathbf{X}^{\dagger} \underline{\mathbf{F}}_{\{\mathbf{k}_i\}} \mathbf{X} \mathbf{X}^{-1} \underline{\mathbf{c}}_{\{\mathbf{k}_i\}} = \mathbf{X}^{\dagger} \underline{\mathbf{S}}_{\{\mathbf{k}_i\}} \mathbf{X} \mathbf{X}^{-1} \underline{\mathbf{c}}_{\{\mathbf{k}_i\}} \epsilon_{\{\mathbf{k}_i\}} \ . \tag{6.6}$$

In particular, if $\mathbf{X}$ were an orthogonal, unitary matrix (i.e. a matrix for which $\mathbf{X}^{-1} = \mathbf{X}^{\dagger}$ and $\mathbf{X}^{\dagger}\mathbf{X} = \mathbb{I}$), then the transformation applied in Eq. (6.6) would be called a similarity transformation. But Eq. (6.4) suggests that we should not look for unitary transformation matrices. Rather, we look for those matrices $\mathbf{X}$ which orthonormalize the Bloch function basis, as follows:

$$\mathbf{X}^{\dagger}\underline{\mathbf{S}}_{\{\mathbf{k}_i\}}\mathbf{X} = \mathbb{I} \; . \tag{6.7}$$

Substituting Eq. (6.7) in Eq. (6.6), we see that such a matrix $\mathbf{X}$ transforms the Roothaan-Hall equations into eigenvalue equations, with eigenvalues $\boldsymbol{\epsilon}_{\{\mathbf{k}_i\}}$ and eigenvectors $\underline{\mathbf{c}}'_{\{\mathbf{k}_i\}}$:

$$\underline{\mathbf{F}}'_{\{\mathbf{k}_i\}}\underline{\mathbf{c}}'_{\{\mathbf{k}_i\}} = \boldsymbol{\epsilon}_{\{\mathbf{k}_i\}}\underline{\mathbf{c}}'_{\{\mathbf{k}_i\}} \; , \tag{6.8a}$$

where in the above we have defined the transformed Fock matrix $\underline{\mathbf{F}}'_{\{\mathbf{k}_i\}}$, and CO coefficients which read as follows:

$$\underline{\mathbf{F}}'_{\{\mathbf{k}_i\}} = \mathbf{X}^{\dagger}\underline{\mathbf{F}}_{\{\mathbf{k}_i\}}\mathbf{X} \; , \tag{6.8b}$$

and:

$$\underline{\mathbf{c}}'_{\{\mathbf{k}_i\}} = \mathbf{X}^{-1}\underline{\mathbf{c}}_{\{\mathbf{k}_i\}} \; . \tag{6.8c}$$

There are different possible choices for the transformation matrix $\mathbf{X}$. One choice can be identified by comparing Eq. (6.4) with Eq. (6.7), from which it is clear that any previously calculated CO coefficient matrix is an appropriate transformation matrix $\mathbf{X} \Leftarrow \underline{\mathbf{c}}_{\{\mathbf{k}_i\}}$. But, generally at the start of the Roothaan-Hall procedure, the matrix $\underline{\mathbf{c}}_{\{\mathbf{k}_i\}}$ is not known. So we need another choice, at least for the beginning of the procedure. This other choice can be provided to us through the real, symmetric overlap matrix $\underline{\mathbf{S}}_{\{\mathbf{k}_i\}}$ itself, by noticing that [306]:

$$\left[\underline{\mathbf{S}}^{-\frac{1}{2}}_{\{\mathbf{k}_i\}}\right]^{\dagger}\underline{\mathbf{S}}_{\{\mathbf{k}_i\}}\underline{\mathbf{S}}^{-\frac{1}{2}}_{\{\mathbf{k}_i\}} = \underline{\mathbf{S}}^{-\frac{1}{2}}_{\{\mathbf{k}_i\}}\underline{\mathbf{S}}_{\{\mathbf{k}_i\}}\underline{\mathbf{S}}^{-\frac{1}{2}}_{\{\mathbf{k}_i\}} = \mathbb{I} \; . \tag{6.9}$$

Comparing Eq. (6.9) with Eq. (6.7) we see indeed that we can get an appropriate choice for the transformation matrix $\mathbf{X}$ from the overlap matrix, by setting $\mathbf{X} \Leftarrow \underline{\mathbf{S}}^{-\frac{1}{2}}_{\{\mathbf{k}_i\}}$. This procedure is known as symmetric orthogonalization [213, 306]. The $\underline{\mathbf{S}}^{-\frac{1}{2}}_{\{\mathbf{k}_i\}}$ can be calculated by realizing that the overlap matrix taken to an arbitrary power P can be calculated from the diagonal matrix of its eigenvalues $\underline{\mathbf{s}}_{\{\mathbf{k}_i\}}$ and the unitary matrix of its eigenvectors $\underline{\mathbf{W}}_{\{\mathbf{k}_i\}}$, as follows:

$$\underline{\mathbf{S}}^{P}_{\{\mathbf{k}_i\}} = \underline{\mathbf{W}}^{\dagger}_{\{\mathbf{k}_i\}}\underline{\mathbf{s}}^{P}_{\{\mathbf{k}_i\}}\underline{\mathbf{W}}_{\{\mathbf{k}_i\}} \; . \tag{6.10}$$

So according to the symmetric orthogonalization prescription, the corresponding transformation matrix $\mathbf{X}_{\text{symm-ortho}}$ reads:

$$\mathbf{X}_{\text{symm-ortho}} = \underline{\mathbf{S}}^{-\frac{1}{2}}_{\{\mathbf{k}_i\}} = \underline{\mathbf{W}}^{\dagger}_{\{\mathbf{k}_i\}}\underline{\mathbf{s}}^{-\frac{1}{2}}_{\{\mathbf{k}_i\}}\underline{\mathbf{W}}_{\{\mathbf{k}_i\}} \; . \tag{6.11}$$

The calculation of the matrix $\underline{\mathbf{s}}^{-\frac{1}{2}}_{\{\mathbf{k}_i\}}$ in Eq. (6.11) can become problematic if some of the Bloch functions are linearly dependent (or quasi-linearly dependent), because then some of the eigenvalues of the overlap matrix will vanish. A second way of using the overlap matrix to generate the transformation matrix allows to eventually deal with this problem. This second procedure is called canonical orthogonalization and consists of generating the corresponding transformation matrix $\mathbf{X}_{\text{can-ortho}}$ as follows [306]:

$$\mathbf{X}_{\text{can-ortho}} = \underline{\mathbf{W}}_{\{\mathbf{k}_i\}} \underline{\mathbf{s}}_{\{\mathbf{k}_i\}}^{-\frac{1}{2}} \ . \tag{6.12}$$

Substituting Eq. (6.12) in Eq. (6.7), we verify that $\mathbf{X}_{\text{can-ortho}}$ is indeed an appropriate choice for the transformation matrix [306]:

$$\mathbf{X}^{\dagger}_{\text{can-ortho}} \underline{\mathbf{S}}_{\{\mathbf{k}_i\}} \mathbf{X}_{\text{can-ortho}} = \underline{\mathbf{s}}_{\{\mathbf{k}_i\}}^{-\frac{1}{2}} \underline{\mathbf{W}}^{\dagger}_{\{\mathbf{k}_i\}} \underline{\mathbf{S}}_{\{\mathbf{k}_i\}} \underline{\mathbf{W}}_{\{\mathbf{k}_i\}} \underline{\mathbf{s}}_{\{\mathbf{k}_i\}}^{-\frac{1}{2}} = \underline{\mathbf{s}}_{\{\mathbf{k}_i\}}^{-\frac{1}{2}} \underline{\mathbf{s}}_{\{\mathbf{k}_i\}} \underline{\mathbf{s}}_{\{\mathbf{k}_i\}}^{-\frac{1}{2}} = \mathbb{I} \ . \tag{6.13}$$

In practice, we can use the canonical orthogonalization prescription to calculate the actual matrix $\mathbf{X}$ from the subset of linearly independent Bloch functions, as follows:

$$\mathbf{X} = \underline{\tilde{\mathbf{W}}}_{\{\mathbf{k}_i\}} \underline{\tilde{\mathbf{s}}}_{\{\mathbf{k}_i\}}^{-\frac{1}{2}} \tag{6.14}$$

in which the tilde over $\underline{\tilde{\mathbf{W}}}_{\{\mathbf{k}_i\}}$ and $\underline{\tilde{\mathbf{s}}}_{\{\mathbf{k}_i\}}^{-\frac{1}{2}}$ indicates that these matrices only contain those eigenvectors and eigenvalues of the overlap matrix which are associated to eigenvalues above a chosen threshold [212, 306]. So once the matrix $\mathbf{X}$ has been built according to Eq. (6.14), it can be used to transform the Roothaan-Hall equations to a set of eigenvalue problems, according to Eq. (6.8), which can be solved for the one-electron energies $\boldsymbol{\epsilon}_{\{\mathbf{k}_i\}}$ and CO coefficients $\underline{\mathbf{c}}_{\{\mathbf{k}_i\}}$. The only point that remains to be specified is how exactly to calculate the Fock matrix $\underline{\mathbf{F}}_{\{\mathbf{k}_i\}}$.

6.1.2 Constructing the Fock Matrix

It is convenient to have a representation of the Fock matrix in terms of AOs, because, given that these are local functions, their local character can be exploited to simplify the evaluation of integrals. This is achieved starting from Eq. (4.12) and then proceeding as in Eq. (5.6) to find the following Fourier transform relation:

$$F^{\sigma\sigma'}_{\mu\nu\{\mathbf{k}_i\}} = \sum_{\mathbf{g}} e^{i\mathbf{k}_i \cdot \mathbf{g}} F^{\sigma\sigma'}_{\mu\nu\{\mathbf{g}\}} \ , \tag{6.15}$$

in which $F^{\sigma\sigma'}_{\mu\nu\{\mathbf{g}\}}$ are the elements of the direct space Fock matrix in the AO basis:

$$F^{\sigma\sigma'}_{\mu\nu\{\mathbf{g}\}} = \int d\mathbf{r}_j \, \chi_\mu \left(\mathbf{r}_j - \mathbf{A}_\mu\right) F^{\sigma\sigma'} \chi_\nu \left(\mathbf{r}_j - \mathbf{A}_\nu - \mathbf{g}\right) \ , \tag{6.16}$$

where $F^{\sigma\sigma'}$ is the direct space Fock operator and reads as follows:

$$F^{\sigma\sigma'} = -\frac{\nabla_j^2}{2} + \tilde{V}_{eN}(j) + \tilde{V}_{NN}(j) + \sum_A \sum_{\mathbf{n}} \left[U^{AREP}\left(j, \mathbf{A} + \mathbf{n}\right) + U^{\sigma\sigma'}_{SOREP}\left(j, \mathbf{A} + \mathbf{n}\right)\right] + C^{\sigma\sigma'} - K^{\sigma\sigma'} \ . \tag{6.17}$$

Collecting the SR part of the Fock operator in a term called $h_0(j)$, we find:

$$F^{\sigma\sigma'} = h_0(j) + \sum_A \sum_{\mathbf{n}} U^{\sigma\sigma'}_{SOREP}(j, \mathbf{A} + \mathbf{n}) + C^{\sigma\sigma'} - K^{\sigma\sigma'} \ . \tag{6.18}$$

All of the operators in Eq. (6.18) have already been defined in section 2.6, except for the $C^{\sigma\sigma'}$ and $K^{\sigma\sigma'}$, which are the direct space representation of the Coulomb and Fock exchange operators of Eqs. (4.12b) and (4.12c), and read as follows:

$$C^{\sigma\sigma'} = \delta_{\sigma\sigma'} \sum_{\rho\omega} \sum_{\mathbf{n}} \mathrm{Re}\left[P^{\alpha\alpha\oplus\beta\beta}_{\rho\omega\{\mathbf{n}\}}\right] \sum_{\mathbf{h}} (\bullet\bullet|\rho^{\{\mathbf{h}\}}\omega^{\{\mathbf{h+n}\}}) \ , \tag{6.19}$$

and for the exchange operator:

$$K^{\sigma\sigma'} = \sum_{\rho\omega} \sum_{\mathbf{n}} P^{\sigma'\sigma}_{\omega\rho\{\mathbf{n}\}} \sum_{\mathbf{h}} (\bullet\rho^{\{\mathbf{h}\}}|\omega^{\{\mathbf{h+n}\}}\bullet) \ . \tag{6.20}$$

In Eqs. (6.19) and (6.20), the following abbreviated notation has been assumed for direct-space two-electron integrals in the AO basis:

$$\begin{aligned}(\mu^{\{\mathbf{0}\}}\nu^{\{\mathbf{g}\}}|\rho^{\{\mathbf{h}\}}\omega^{\{\mathbf{h+n}\}}) \ \equiv & \int d\mathbf{r}_j \, \chi^*_\mu\left(\mathbf{r}_j - \mathbf{A}_\mu\right)\chi_\nu\left(\mathbf{r}_j - \mathbf{A}_\nu - \mathbf{g}\right) \\ \times & \int d\mathbf{r}_i \, \chi^*_\rho\left(\mathbf{r}_i - \mathbf{A}_\rho - \mathbf{h}\right)\frac{1}{r_{ij}}\chi_\omega\left(\mathbf{r}_i - \mathbf{A}_\omega - \mathbf{h} - \mathbf{n}\right) \ .\end{aligned} \tag{6.21}$$

Since the AOs, as defined in Eq. (3.28), are purely real, it is clear from Eq. (6.21) that the two-electron integral $(\mu^{\{\mathbf{0}\}}\nu^{\{\mathbf{g}\}}|\rho^{\{\mathbf{h}\}}\omega^{\{\mathbf{h+n}\}})$ expressed in the AO basis is formally invariant to certain permutations of the AOs. The possible permutations of the AOs are as follows:

$$\mu^{\{\mathbf{0}\}} \leftrightarrow \nu^{\{\mathbf{g}\}} \quad \rho^{\{\mathbf{h}\}} \leftrightarrow \omega^{\{\mathbf{h+n}\}} \quad (\mu^{\{\mathbf{0}\}}\nu^{\{\mathbf{g}\}}) \leftrightarrow (\rho^{\{\mathbf{h}\}}\omega^{\{\mathbf{h+n}\}}) \ . \tag{6.22}$$

The permutations defined in Eq. (6.22) generate a set of 8 different orderings of the AOs in the two-electron integral. So formally, the calculation of one two-electron integral $(\mu^{\{\mathbf{0}\}}\nu^{\{\mathbf{g}\}}|\rho^{\{\mathbf{h}\}}\omega^{\{\mathbf{h+n}\}})$ generates the following set of integrals:

$$\begin{aligned}&(\mu^{\{\mathbf{0}\}}\nu^{\{\mathbf{g}\}}|\rho^{\{\mathbf{h}\}}\omega^{\{\mathbf{h+n}\}}),\ (\nu^{\{\mathbf{g}\}}\mu^{\{\mathbf{0}\}}|\rho^{\{\mathbf{h}\}}\omega^{\{\mathbf{h+n}\}}),\ (\mu^{\{\mathbf{0}\}}\nu^{\{\mathbf{g}\}}|\omega^{\{\mathbf{h+n}\}}\rho^{\{\mathbf{h}\}}) \\ &(\nu^{\{\mathbf{g}\}}\mu^{\{\mathbf{0}\}}|\omega^{\{\mathbf{h+n}\}}\rho^{\{\mathbf{h}\}}),\ (\rho^{\{\mathbf{h}\}}\omega^{\{\mathbf{h+n}\}}|\mu^{\{\mathbf{0}\}}\nu^{\{\mathbf{g}\}}),\ (\omega^{\{\mathbf{h+n}\}}\rho^{\{\mathbf{h}\}}|\mu^{\{\mathbf{0}\}}\nu^{\{\mathbf{g}\}}) \\ &\qquad (\rho^{\{\mathbf{h}\}}\omega^{\{\mathbf{h+n}\}}|\nu^{\{\mathbf{g}\}}\mu^{\{\mathbf{0}\}}),\ (\omega^{\{\mathbf{h+n}\}}\rho^{\{\mathbf{h}\}}|\nu^{\{\mathbf{g}\}}\mu^{\{\mathbf{0}\}}) \ .\end{aligned} \tag{6.23}$$

In practice, however, the need to truncate the infinite sums on $\mathbf{g}, \mathbf{h}$ and $\mathbf{n}$ in a generally non-balanced way (for example, maybe the sum over $\mathbf{h}$ vectors is pushed further than the one over $\mathbf{g}$ vectors) limits the use of the permutations described in Eq. (6.22). A detailed discussion on this topic is provided in Ref. [19].

It is also convenient to introduce the following abbreviated notation for one-electron integrals in the AO basis, involving a generic direct-space one-electron operator $O^{\{\mathbf{A}+\mathbf{n}\}}$ centered at position **A** in cell **n**:

$$(\mu^{\{\mathbf{0}\}}|O^{\{\mathbf{A}+\mathbf{n}\}}|\nu^{\{\mathbf{g}\}}) = \int d\mathbf{r}_j\, \chi_\mu\left(\mathbf{r}_j - \mathbf{A}_\mu\right) O(j, \mathbf{A}+\mathbf{n}) \chi_\nu\left(\mathbf{r}_j - \mathbf{A}_\nu - \mathbf{g}\right) \tag{6.24}$$

So according to Eqs. (6.18)-(6.21), the action of the operators $C^{\sigma\sigma'}$ and $K^{\sigma\sigma'}$ on a product of two AOs, evaluated in direct-space, produces terms of the following form:

$$\int d\mathbf{r}_j\, \chi_\mu\left(\mathbf{r}_j - \mathbf{A}_\mu\right) (\bullet\bullet|\rho^{\{\mathbf{h}\}}\omega^{\{\mathbf{h}+\mathbf{n}\}}) \chi_\nu\left(\mathbf{r}_j - \mathbf{A}_\nu - \mathbf{g}\right) = (\mu^{\{\mathbf{0}\}}\nu^{\{\mathbf{g}\}}|\rho^{\{\mathbf{h}\}}\omega^{\{\mathbf{h}+\mathbf{n}\}}) \,, \tag{6.25}$$

and:

$$\int d\mathbf{r}_j\, \chi_\mu\left(\mathbf{r}_j - \mathbf{A}_\mu\right) (\bullet\rho^{\{\mathbf{h}\}}|\omega^{\{\mathbf{h}+\mathbf{n}\}}\bullet) \chi_\nu\left(\mathbf{r}_j - \mathbf{A}_\nu - \mathbf{g}\right) = (\mu^{\{\mathbf{0}\}}\rho^{\{\mathbf{h}\}}|\omega^{\{\mathbf{h}+\mathbf{n}\}}\nu^{\{\mathbf{g}\}}) \,. \tag{6.26}$$

Starting from Eq. (4.13) and proceeding again as for Eq. (5.6), the total energy can then be expressed in the AO basis, in terms of the direct-space Fock operator as follows:

$$E = \frac{1}{2} \sum_{\sigma\sigma'} \sum_{\mu\nu} \sum_{\mathbf{g}} P^{\sigma\sigma'}_{\mu\nu\{\mathbf{g}\}} \left[(\mu^{\{\mathbf{0}\}}|h_0|\nu^{\{\mathbf{g}\}}) + F^{\sigma\sigma'}_{\mu\nu\{\mathbf{g}\}} + \sum_{A} \sum_{\mathbf{n}} (\mu^{\{\mathbf{0}\}}|U^{\sigma\sigma'\{\mathbf{A}+\mathbf{n}\}}_{SOREP}|\nu^{\{\mathbf{g}\}}) \right] . \tag{6.27}$$

Strategies for evaluating the Coulomb and Fock exchange terms in the non-periodic limit are discussed in Appendices C and D, respectively. Strategies to evaluate the total energy in the non-periodic limit are discussed in Appendix E. Appendix F provides a discussion on the treatment of the xc term for the KS-DFT in the non-periodic limit. Appendix G discusses some aspects on the generalization of the approach to periodic systems that are specific to the treatment of SOC. The discussion in Appendix G does not include aspects related to the treatment of periodic systems that are also common to the one-component periodic SCF procedure, because these are discussed elsewhere in the literature [54, 60, 88, 89, 90, 92, 93, 254]. Appendix H discusses an alternate strategy for the treatment of spin-related relativistic effects like SOC, in which the SR problem, described by Eq. (4.54) is initially solved, then the operator $\mathbf{U}_{SOREP}$ is treated as a perturbation, using an uncoupled-perturbed or coupled-perturbed approach of second, third or fourth order. The discussion in Appendix H starts from a treatment of the $\mathbf{U}_{SOREP}$ using conventional non-degenerate Rayleigh-Schrödinger perturbation theory, from which expressions are developed for the total energy, as well as the perturbed eigenvalues and density matrix. Then, expressions involving also contributions from degenerate states are developed using a non-canonical formulation, which is inspired by the work of Karna and Dupuis (who used a similar approach to treat electric fields as a perturbation) [183] and Maschio and Kirtman (who used a similar approach to treat basis sets as a perturbation) [223].

6.1.3 Statement of the Procedure

We now have all of the necessary ingredients to state the Roothaan-Hall procedure. To write the steps of the procedure, the direct-space Fock and density matrices, as well as the CO coefficients, at iteration k, for example, are denoted as $\underline{\mathbf{F}}_{\{\mathbf{g}\}}(k)$, $\underline{\mathbf{P}}_{\{\mathbf{g}\}}(k)$, and $\underline{\mathbf{c}}_{\{\mathbf{k}_i\}}(k)$, respectively. The statement of the periodic two-component Roothaan-Hall procedure is as follows:

1. Obtain the initial direct-space density matrix $\underline{\mathbf{P}}_{\{\mathbf{g}\}}(0)$ from a guess.
2. For all points $\mathbf{k}_i$ in the Monkhorst-Pack net, Do:
    (a) Obtain the initial transformation matrix $\mathbf{X}(0)$ from the eigenvectors of the overlap matrix according to Eq. (6.14).
    (b) Write the $\mathbf{X}(0)$ to disk.
3. Construct the direct-space Fock matrix $\underline{\mathbf{F}}_{\{\mathbf{g}\}}(0)$ from Eq. (6.18).
4. Calculate $E(0)$ using the $\underline{\mathbf{F}}_{\{\mathbf{g}\}}(0)$ from Eq. (6.27).
5. For all points $\mathbf{k}_i$ in the Monkhorst-Pack net, Do:
    (a) Fourier transform the Fock matrix to reciprocal space and obtain the $\underline{\mathbf{F}}_{\{\mathbf{k}_i\}}(0)$ from Eq. (6.15).
    (b) Read the $\mathbf{X}(0)$ from disk.
    (c) Construct the transformed Fock matrix $\underline{\mathbf{F}}'_{\{\mathbf{k}_i\}}(0)$ from Eq. (6.8) using $\mathbf{X}(0)$.
    (d) Diagonalize the transformed Fock matrix and solve for the one-electron energy levels $\boldsymbol{\epsilon}_{\{\mathbf{k}_i\}}(0)$ and CO coefficients $\underline{\mathbf{c}}_{\{\mathbf{k}_i\}}(1)$ according to Eq. (6.8).
    (e) Write $\underline{\mathbf{c}}_{\{\mathbf{k}_i\}}(1)$ to disk.
6. Use all of the $\boldsymbol{\epsilon}_{\{\mathbf{k}_i\}}(0)$ to determine the set of occupied bands from the *aufbau* principle (see discussion below for more specific details).
7. Set $k = 1$
8. begin iteration on k:
    (a) For all points $\mathbf{k}_m$ in the Monkhorst-Pack net, Do:
        i. Read the $\underline{\mathbf{c}}_{\{\mathbf{k}_m\}}(k)$ from disk.
        ii. Calculate the reciprocal space density matrix $\underline{\mathbf{P}}_{\{\mathbf{k}_j\}}(k)$ using the occupied $\underline{\mathbf{c}}_{\{\mathbf{k}_m\}}(k)$ from Eq. (5.1).
        iii. Add the contribution of $\underline{\mathbf{P}}_{\{\mathbf{k}_j\}}(k)$ to the Fourier transform expression of Eq. (5.3) in an effort to obtain the direct space density matrix $\underline{\mathbf{P}}_{\{\mathbf{g}\}}(k)$.
    (b) Check for convergence on $E(k-1)$ and/or the $\underline{\mathbf{P}}_{\{\mathbf{g}\}}(k)$. If convergence satisfied, go to step 9. Otherwise, continue to step 8c.
    (c) Construct the direct-space Fock matrix $\underline{\mathbf{F}}_{\{\mathbf{g}\}}(k)$ from Eq. (6.18), using $\underline{\mathbf{P}}_{\{\mathbf{g}\}}(k)$.
    (d) Calculate $E(k)$ using $\underline{\mathbf{F}}_{\{\mathbf{g}\}}(k)$ from Eq. (6.27).
    (e) For all points $\mathbf{k}_i$ in the Monkhorst-Pack net, Do:

        i. Fourier transform the Fock matrix to reciprocal space and obtain $\underline{\mathbf{F}}_{\{\mathbf{k}_i\}}(k)$ from Eq. (6.15).
        ii. Read $\underline{\mathbf{c}}_{\{\mathbf{k}_i\}}(k)$ from disk.
        iii. Set $\mathbf{X}(k) = \underline{\mathbf{c}}_{\{\mathbf{k}_i\}}(k)$
        iv. Construct the transformed Fock matrix $\underline{\mathbf{F}}'_{\{\mathbf{k}_i\}}(k)$ from Eq. (6.8) using $\mathbf{X}(k)$.
        v. Diagonalize the transformed Fock matrix and solve for the one-electron energy levels $\boldsymbol{\epsilon}_{\{\mathbf{k}_i\}}(k)$ and CO coefficients $\underline{\mathbf{c}}_{\{\mathbf{k}_i\}}(k+1)$ according to Eq. (6.8).
        vi. Write $\underline{\mathbf{c}}_{\{\mathbf{k}_i\}}(k+1)$ to disk.
    (f) Use all of the $\boldsymbol{\epsilon}_{\{\mathbf{k}_i\}}(k+1)$ to determine the set of occupied bands from the *aufbau* principle (see discussion below for more specific details).
    (g) Set $k \to k+1$ and go back to step 8a.

9. Write the direct-space density matrix $\underline{\mathbf{P}}_{\{\mathbf{g}\}}(k)$ to disk.

10. All done! ☺

It is appropriate at this point to provide some specifications on the above procedure. With regards to step 1, in the Crystal program, the guess density matrix is provided by a superposition of non-interacting atomic densities, which are calculated from a non- or scalar-relativistic atomic HF calculation using an approach described in Ref. [61]. A strategy to appropriately modify such a guess density matrix for two-component relativistic calculations is described in paper IV. With respect to step 9, the direct-space density matrix is written to allow the future calculation of one-electron properties from the solution of the SCF. In the Crystal program, an additional set of arrays are also written to disk for this purpose. These include, notably, the vectors PAR and INF, as well as the direct-space Fock matrix. The vector PAR contains useful constants to perform the calculation, like for example the number π, amongst others. The vector INF contains most of the system specific integers that are required to perform the calculation, like for example the number of symmetry operators of the system, the number of atoms in the primitive cell, the number of basis functions, etc ... The direct-space Fock matrix is written to disk for the prospect of calculating the band structure of the system (i.e. the $\boldsymbol{\epsilon}_{\{\mathbf{k}_i\}}$) on a dense set of points in the FBZ. It is not strictly necessary to write the Fock matrix, but it means that future calculation of the band structure can be done by reading it from disk, instead of having to reconstruct it, by recalculating the integrals.

With regards to steps 6 and 8f, the term *aufbau* principle is used in the sense that the one-electron energy levels are occupied according to the subset of lowest energy bands. For metallic systems, in which there is a partially occupied band that crosses the Fermi energy ϵ_F, the ϵ_F must also be determined to allow the construction of the reciprocal space density matrix from Eq. (5.1). This is achieved by representing the number of valence electrons in terms of the following numerical quadrature of the Heaviside step function over the volume of the FBZ:

$$N_v = \frac{1}{\Omega_r} \sum_j \int_{\Omega_r} d\mathbf{k}_j \, \frac{1}{N_{m\{\mathbf{k}_m\}}} \theta\left[\epsilon_F - \epsilon_{\{\mathbf{k}_j\}}\right] \ . \tag{6.28}$$

Eq. (6.28) can be applied iteratively for different values of ϵ_F, until the correct number of valence electrons N_v is obtained.

In general, the presence of the Heaviside step function in Eqs. (5.1) and (6.28) means that for metallic systems, the accurate calculation of integrals in reciprocal space will require a relatively dense Monkhorst-Pack net. This poses no formal challenges, but can make the calculation expensive. A strategy to reduce the cost of the calculation is to replace the $\frac{1}{N_{m\{\mathbf{k}_m\}}}\theta\left[\epsilon_F - \epsilon_{\{\mathbf{k}_j\}}\right]$ in Eqs. (5.1) and (6.28) by the smoother Fermi-Dirac function, according to the following scheme:

$$\frac{1}{N_{m\{\mathbf{k}_m\}}}\theta\left[\epsilon_F - \epsilon_{\{\mathbf{k}_j\}}\right] \rightarrow \theta_F\left[\epsilon_F - \epsilon_{\{\mathbf{k}_j\}}\right] , \tag{6.29}$$

where the Fermi-Dirac function θ_F reads as follows:

$$\theta_F\left[\epsilon_F - \epsilon_{\{\mathbf{k}_j\}}\right] = \left[1 + \exp\left(\frac{\epsilon_{\{\mathbf{k}_j\}} - \epsilon_F}{k_b T}\right)\right]^{-1} , \tag{6.30}$$

and $k_b T$ is the “smearing width”, and is a parameter that must be chosen for numerical convenience. Strategies for the efficient evaluation of the required reciprocal space integrals are discussed in Ref. [254].

Finally, in the second part of Appendix G modifications to the Roothaan-Hall procedure are discussed, in which at each cycle k the direct-space density matrix is determined, not only from the occupied CO coefficients, but using also a linear combination of the density matrices from previous cycles. These methods belong to a class of approaches called the relaxed constraints algorithms (RCA). There are two variants of the RCA algorithms which are discussed. The first is the optimal damping algorithm of Karlström and Cancès, which is a fully analytical method [48, 50, 51, 182]. The second is the energy direct inversion in the iterative subspace (EDIIS) method of Cancès and friends, which involves numerically solving an indefinite quadratic programming problem [57, 200]. Here, the indefinite quadratic programming problem is solved using a FORTRAN translated version of Yinyu Ye’s original SOLQP MATLAB code [339, 340].

6.2 Some Example Benchmark Two-Component Periodic Calculations

The majority of the details of the new periodic two-component program are presented in papers IV-VII, as well as Appendices B-G. The papers also present a significant set of tests to confirm the correctness of the implementation. But the published tests are mostly on non-periodic (molecular) systems. Here, additional tests are presented on periodic systems to complement the documentation on the new program. The full input decks for these benchmark periodic two-component calculations are provided in Appendix I. Two-component KS-DFT calculations are provided with the standard GGA, for comparison to previous work of other authors. On the other hand, the author is not aware of any other program to treat SOC with a two-component periodic SCF in the framework of generalized KS-DFT (i.e. using hybrid functionals). Therefore, results of hybrid functional calculations are also provided to document the capability of the code.

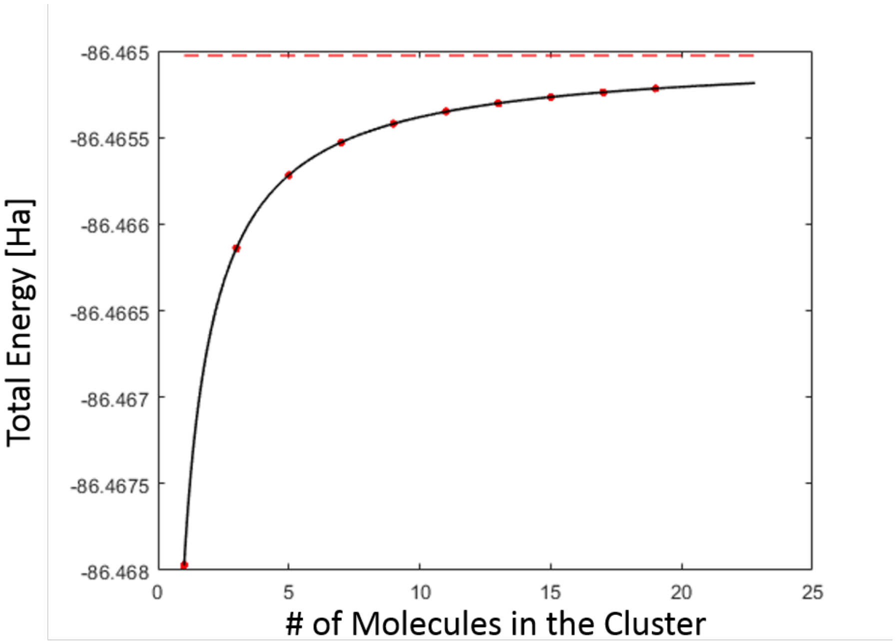

Figure 6.1: Total energy per elementary unit of the IO clusters as a function of chain length (red dots), fitted to an analytical function (solid black line), as compared to the energy of the fully periodic polymer (dashed red line). The periodic energy agrees with the energy extrapolated to infinite cluster size down to 2.028×10^{-06} Ha.

The first set of tests compares the total energy obtained from large clusters of molecules to that of the infinite system. Indeed, given that the correctness of the total energy for the molecular implementation is well established from the published tests, it is interesting to compare the energy of long chains of molecules to the fully periodic calculation, in order to also confirm the correctness of the latter. The tests were perfomed on an infinite chain of IO, with a cell parameter of 4 Å, and the IO units were oriented with the molecular axis perpendicular to the periodic direction, with a bond length of 2 Å. For the I centers, we use the ECP46MDF fully-relativistic ECP of Dolg and co-workers, which was fitted with multiconfigurational four-component HF calculations using the DCB Hamiltonian, as well as the associated $(6s6p)/[4s4p]$ basis set, as modified for periodic systems (see Appendix I) [301]. For O we use the basis set of Towler and co-workers [308]. The PBE0 hybrid GGA functional was used in its canonical non-collinear formulation [9, 78]. The obtained total energies for the molecular and periodic calculations are presented in Figure 6.1. The energy of the finite clusters are plotted with the red dots as a function of the number of IO units and have been fitted to an analytical function (solid black line) of the form $E = \frac{d}{x^3} + \frac{c}{x^2} + \frac{b}{x} + a$, where x is the number of IO units in the cluster and a, b, c, d are parameters obtained from the fitting. The total energy from the fully periodic calculation is plotted with the dashed red line at a value of $E_{per} = -86.465026$ H (H being the abbreviation for the Hartree atomic unit of energy). We can compare the periodic energy to the value of the fitted parameter a, which represents the energy of the cluster, as extrapolated to infinite chain length. This gives a difference of $E_{per} - a = 2.028 \times 10^{-06}$ Ha, which is very close to the convergence criteria on the energy of 1.000×10^{-07} Ha, thus confirming the correctness of the periodic calculation.

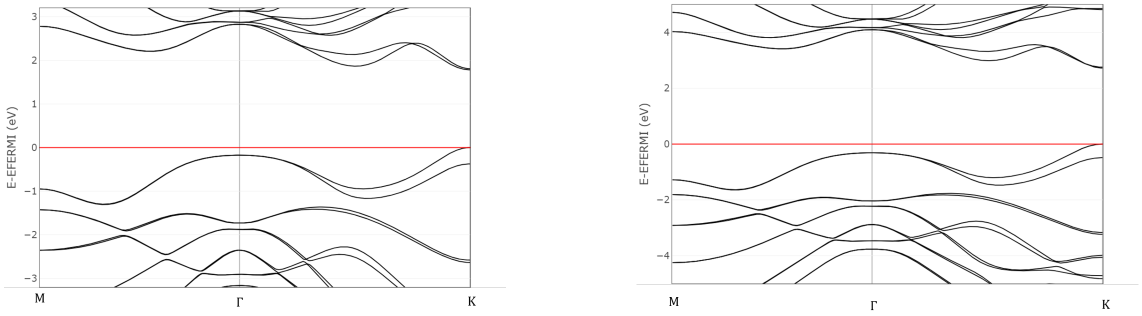

Figure 6.2: Electronic band structure of the dichalcogenide monolayer of WS_2, as obtained from a two-component SCF with the PBE (left) and PBE0 (right) functionals. This figure was generated the Crysplot plotting program [29].

The second set of tests, this time for a 2D periodic system, is on the dichalcogenide monolayer of WS_2, whose band structure has been reported to display "giant" SO-induced splitting [347]. The calculation was performed this time with both the PBE and PBE0 functionals [9, 246]. Here, for W we use the ECP60MDF fully-relativistic ECP of Dolg and co-workers, which was fitted with multiconfigurational four-component HF calculations using the DCB+QED Hamiltonian, with a modified version of the associated ecp-60-dhf-SVP basis set provided in the library of the Turbomole package (see Appendix I) [3, 121]. For S, we use the basis set of Lichanot and co-workers [207]. The obtained band structures with the PBE and PBE0 functionals are provided in Figure 6.2. The PBE result compares very well with the band structure published in Ref. [347]. As for the comparison of the results from the PBE and PBE0 functionals, the major difference in the two obtained band structures is the much larger band gap shown from the PBE0 calculation, as compared to the PBE one.

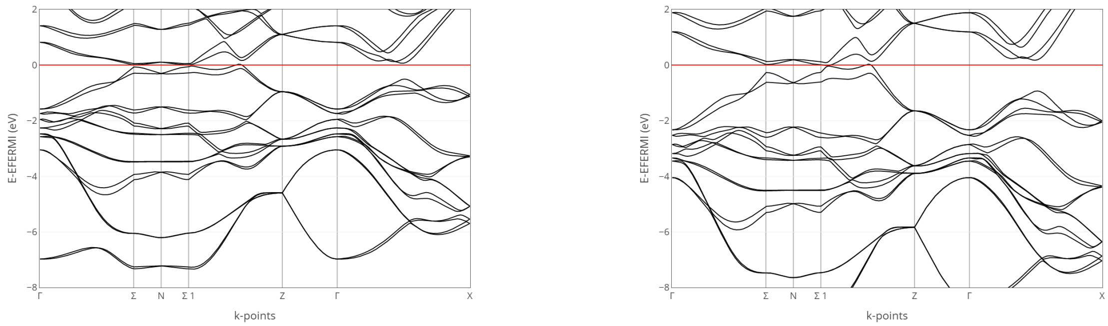

Figure 6.3: Electronic band structure of the TaAs Weyl semimetal, as obtained from a two-component SCF with the PBE functional. This figure was generated the Crysplot plotting program [29].

Finally, the third test is on a 3D periodic system, namely the TaAs Weyl semimetal. We use again for Ta the ECP60MDF fully-relativistic ECP of Dolg and co-workers, with a modified version of the ecp-60-dhf-

QZV basis set provided in the library of the Turbomole package (see Appendix I) [3, 121]. For As, we use the ECP28MDF fully-relativistic ECP (again obtained from fitting to multiconfigurational four-component HF calculations, this time with the DCB Hamiltonian) with the corresponding $(6s6p)/[4s4p]$ basis set of Dolg and co-workers [301]. The band structures obtained with the PBE and PBE0 functionals of the GGA are presented in Figures 6.3. The PBE result compares very well with the work of Ref. [168]. For the purposes of comparing the results obtained from the PBE and PBE0 functionals, here the PBE0 calculation displays a significantly larger spin-orbit splitting of the bands.

6.3 Significance of Contribution from Paper IV

Paper IV [77] was authored by (in this order) the present author of the thesis, Prof. Jean-Pierre Flament of the Université de Lille, France, and Prof. Alessandro Erba of the Università di Torino, Italy. The present author's contribution to Paper IV was most of the research and writing of the paper, because the other authors adopted a supervisory role. The present author would however like to stress the important contribution to this project from the other authors. In particular, the required SOC integral routines for calculating the matrix elements of the $\mathbf{U}_{SOREP}$ were modified from the ones provided to the author by Prof. Jean-Pierre Flament. These routines are those originally included in Profs. Valerie Vallet's and Jean-Pierre Flament's SO configuration-interaction program Epciso [316]. They are based on the ones kindly provided to Profs. Vallet and Flament by Prof. Russell Pitzer and described in Ref. [256]. Prof. Flament also implemented a two-component molecular HF SCF in his local version of the Hondo program, which allowed the present author to perform some very useful internal tests against his implementation in the Crystal program. On the other hand, Prof. Alessandro Erba was available every day for useful discussions with the present author with regards to this project, as well as the rest of this thesis.

Paper IV discusses the generalization of the Crystal program to a two-component SCF for HF calculations on molecular systems. The correctness, numerical stability and relative efficiency of the implementation is documented by comparison to previously existing similar ones in the NWchem, Dirac and Turbomole programs [1, 3, 15, 240, 315, 346]. The total energies, as calculated with all programs, are reported for a set of four closed-shell molecules and three open-shell molecules in Tables I and II of paper IV. The agreements of our implementation against all others are within reasonable bounds. The best agreement is against the implementation in the Dirac program (energy differences on the order of 10^{-10}-10^{-11} Ha), followed by the NWchem program (10^{-6}-10^{-10} Ha), and finally the Turbomole program (10^{-4}-10^{-7} Ha). In Table III of paper IV, the number of SCF cycles needed to converge these calculations are reported. Here it is seen that our implementation takes less cycles than the other ones (generally two thirds to half the amount of cycles, or better). The relative number of cycles of the other implementations follows the same order as for the total energy. That is to say, amongst the other implementations Dirac converges fastest, followed by NWchem and Turbomole. This suggests that the relative amount of cycles needed to converge the calculations might be directly related to the numerical stability of the implementations. Given that none of the authors of paper IV are developers of the NWchem, Dirac or Turbomole programs, it must however be appreciated that the numbers on the amount of SCF cycles represent merely our best efforts as users of these programs. It is possible that developpers of each program could obtain better results using their respective codes.

Apart from these important, yet rather technical details, paper IV presents a new approach to impose a specified noncollinear magnetization as a starting guess for the SCF procedure. In all of the tested cases, such an approach allowed us to better explore the rugged energy landscape of the molecules and find lower energy solutions. This approach for the noncollinear guess magnetization turned out to be also necessary to explore the energy landscape of the systems studied in papers V and VII.

In summary, paper IV was an important stepping stone to provide a program to perform generalized KS-DFT two-component calculations on periodic systems for two reasons. i) It represents the development of an apparently very numerically stable implementation for two-component calculations with exact non-local Fock exchange and ii) The new procedure for a noncollinear guess magnetization provides us with a means to find a desired solution.

6.4 Non-Collinear Density Functional Theory and Significance of Contribution from Paper V

Paper V [78] was authored by (in this order) the present author of the thesis, Prof. Jean-Pierre Flament of the Université de Lille, France, and Prof. Alessandro Erba of the Università di Torino, Italy. The present author's contribution to Paper V was most of the research and writing of the paper, because the other authors adopted a supervisory role. Paper V discussed strategies for the treatment of the xc term of the KS-DFT in a two-component spinor basis and its corresponding implementation in the Crystal program. The principal challenge in performing such two-component fully-relativistic KS-DFT calculations is the need to generalize collinear xc functions (which only depend on the z-component of the magnetization m_z) to a non-collinear magnetization (to a functional that depends also on the other Cartesian components m_x and m_y). Indeed, if a SOC operator is included in the Hamiltonian, the usual collinear procedure does not result in rotational invariance of the total energy (meaning that the total energy, or practically any other property, loses physical meaning because it will depend on the choice of the orientation for the Cartesian frame). The only way to regain rotational invariance is to insert all Cartesian components of the magnetization in the functional. But since no explicitly relativistic functionals have been devised in this way, in practice it is necessary to modify existing one-component SR collinear functionals [15, 45, 72, 76, 105, 134, 141, 162, 175, 190, 194, 198, 224, 245, 252, 271, 284, 320]. Practically the modifications of the functionals are done through some kind of variable substitution. In the LDA, the original collinear xc functional F_{col}^{LDA} depends on the electron density n, and the m_z:

$$F_{col}^{LDA} = F_{col}^{LDA}\left[n, m_z\right] \ , \tag{6.31}$$

where the explicit dependence of n and m_z on the coordinates of an electron $\mathbf{r}_j$ has been dropped. In the GGA, the collinear functional F_{col}^{GGA} depends also on the gradients of n and m_z:

$$F_{col}^{GGA} = F_{col}^{GGA}\left[n, m_z, \boldsymbol{\nabla} n \cdot \boldsymbol{\nabla} n, \boldsymbol{\nabla} m_z \cdot \boldsymbol{\nabla} m_z, \boldsymbol{\nabla} n \cdot \boldsymbol{\nabla} m_z\right] \ . \tag{6.32}$$

The existing implementations of non-collinear KS-DFT follow one of two variable substitution schemes for including also the m_x and m_y in the functional. The first scheme is based on the original idea of Kübler and co-workers (called the canonical approach) [198], in which the variables in Eqs. (6.31) or (6.32) that depend on m_z are directly replaced by equivalent variables that depend on the modulus of the magnetization $m = |\mathbf{m}|$. Hence the non-collinear functional F^{LDA}_{ncol} is of the following form in the LDA:

$$F^{LDA}_{ncol} = F^{LDA}_{ncol}\left[n, m\right] \ . \tag{6.33}$$

and the functional F^{GGA}_{ncol} in the GGA reads:

$$F^{GGA}_{ncol} = F^{GGA}_{ncol}\left[n, m, \boldsymbol{\nabla} n \cdot \boldsymbol{\nabla} n, \boldsymbol{\nabla} m \cdot \boldsymbol{\nabla} m, \boldsymbol{\nabla} n \cdot \boldsymbol{\nabla} m\right] \ . \tag{6.34}$$

The second variable substitution scheme is that developed by Scalmani and Frisch (SF) [271]. The method of SF coincides with the canonical one in the LDA, such that the SF xc functional reads exactly as in Eq. (6.33) in the LDA, but is more complicated in the GGA. Here we only cite that one of the SF GGA variables g_{mm} replacing the one containing the gradient of m_z in Eq. (6.32) reads as follows:

$$g_{mm} = \boldsymbol{\nabla}\mathbf{m} \cdot \circ \boldsymbol{\nabla}\mathbf{m} = \sum_{i=x,y,z} \boldsymbol{\nabla} m_i \cdot \boldsymbol{\nabla} m_i \ . \tag{6.35}$$

So the symbol $\circ$ is the dot product over the components of the vector $\mathbf{m}$, while the $\cdot$ is the dot product of the components of $\boldsymbol{\nabla}$. The full details on the formulation of SF can be found in paper V or Appendix F.

In summary, paper V represents a second important stepping stone towards providing a code to perform generalized KS-DFT two-component periodic calculations because it provides strategies (and their corresponding implementation) for evaluating the xc term in a rotationally invariant way.

6.5 On the Treatment of Orbital Currents and Significance of Contribution from Paper VI

Paper VI [78] was authored by (in this order) the present author of the thesis, Prof. Jean-Pierre Flament of the Université de Lille, France, and Prof. Alessandro Erba of the Università di Torino, Italy. The present author's contribution to Paper VI was most of the research and writing of the paper, because the other authors adopted a supervisory role. The author would like to acknowledge that Prof. Jean-Pierre Flament performed however the SO configuration-interaction calculation reported in this paper with his program Epciso [316].

From the previous section we have seen how to include the electron density n, and the three Cartesian components of the magnetization m_x, m_y and m_z into the xc functional. But according to the discussion in section 4.2 on the density variables in two-component relativistic KS-DFT, we are still missing a dependence on the orbital-current density $\mathbf{j}$ and the spin-current densities $\mathbf{J}_x$, $\mathbf{J}_y$ and $\mathbf{J}_z$. The manner in which $\mathbf{j}$ can be practically included in relativistic KS-DFT calculations is the subject of paper VI. The $\mathbf{j}$ is a current of charges that is induced by the SOC effect in time-reversal symmetry broken (TRSB) systems (for example, systems with an uneven number of electrons) and can couple and evolve jointly with the magnetization. The importance of including the orbital-current density $\mathbf{j}$ in the calculation procedure can be understood from Eqs. (5.6), (5.9) and (5.11). These show that the n, m_x, m_y and m_z include a dependence on most blocks of the density matrix , but not the diagonal imaginary spin-blocks $\mathrm{Im}\left[\mathbf{P}^{\alpha\alpha}_{\{\mathbf{g}\}}\right]$ and $\mathrm{Im}\left[\mathbf{P}^{\beta\beta}_{\{\mathbf{g}\}}\right]$ and these are exactly the blocks which define $\mathbf{j}$. As a matter of fact it turns out that KS-DFT calculations with standard (i.e. non-hybrid) functionals based on collinear or non-collinear formulations introduce no dependence on these imaginary diagonal spin-blocks of the density matrix because of their lack of dependence on the orbital-current density $\mathbf{j}$, as summarized in Figure 1 of paper VI.

One way of including the dependence on $\mathbf{j}$ in practical KS-DFT calculations can be realized by considering Eq. (6.20), which shows us that the imaginary diagonal spin-blocks of the Fock exchange operator do instead introduce the proper dependence of the corresponding spin-blocks of the density matrix that define $\mathbf{j}$. This identifies the crucial role of the Fock exchange operator, as included in hybrid xc functionals, for treating SOC in TRSB systems, because it provides a means to include $\mathbf{j}$ in the two-electron potential.

Figure 2 of paper VI compares the orbital-current density $\mathbf{j}$ as obtained from KS-DFT calculations against an accurate reference SO configuration-interaction calculation for the I_2^+ molecule. This figure shows that while the non-hybrid KS-DFT calculation completely fails at properly coupling the orbital-current density with its magnetization, the hybrid functional result matches the one from the SO configuration-interaction calculation.

In summary, paper VI provides strong formal arguments for the importance of including Fock exchange in relativistic calculations on TRSB molecular systems. In particular, this provides a means to include a dependence of the two-electron potential on $\mathbf{j}$. But this turns out to be even more important in periodic TRSB systems, as explained below, in the following section.

6.6 The Periodic Two-Component Approach and Significance of Contribution from Paper VII

Paper VII [79] was authored by (in this order) the present author of the thesis, Prof. Jean-Pierre Flament of the Université de Lille, France, and Prof. Alessandro Erba of the Università di Torino, Italy. The present author's contribution to Paper VII was most of the research and writing of the paper, because the other authors adopted a supervisory role. Paper VII describes the generalization to periodic systems of the approaches discussed in papers IV, V, and VI for a two-component self-consistent treatment of SOC, and their implementation in the Crystal code. This represents, to the author's knowledge, the first implementation for a self-consistent two-component treatment of SOC with the generalized KS-DFT (i.e. with hybrid functionals including a fraction of Fock exchange). While, previous implementations allow in some way also for a treatment of SOC with hybrid functionals, these are based on the second-variational approach [5, 7, 46, 147, 191]. In such a treatment, the SR problem (potentially including Fock exchange) is first solved in a one-component basis, then the fully-relativistic Hamiltonian matrix (now including SOC) is subsequently diagonalized in a basis consisting of a subset of the previously determined SR states. Paper VII discusses a variety of formal advantages that arise from the simultaneous and self-consistent treatment of SOC with Fock exchange in a two-component spinor basis, which would not be described using the previous, more approximate treatments of existing implementations. Paper VII also generalizes the discussion in paper VI on how the inclusion of a fraction of Fock exchange can be used as a means to include not only the orbital-current density $\mathbf{j}$, but also the spin-current densities $\mathbf{J}_x$, $\mathbf{J}_y$ and $\mathbf{J}_z$ into the two-electron potential.

The formal advantages of including the non-local Fock exchange operator are the following:

1. The non-local Fock exchange operator imparts a local magnetic torque to the two-electron potential. That is to say, it imparts the ability to the two-electron potential to locally rotate the magnetization in an effort to minimize the total energy. In paper VII we show examples where for non-hybrid functionals, in the absence of Fock exchange, the lack of local magnetic torque means that different initial guesses for the magnetization result in different final solutions. In contrast, with hybrid functionals that contain a fraction of Fock exchange, we are always able to find the magnetization distribution that yields the lowest energy, regardless of the starting guess.

2. The local magnetic torque afforded by the presence of the Fock exchange operator improves the rotational invariance of non-collinear GGA calculations.

3. The presence of the Fock exchange operator allows for treating the orbital relaxation contribution to the orbital-current density $\mathbf{j}$ and spin-current densities $\mathbf{J}_x$, $\mathbf{J}_y$ and $\mathbf{J}_z$, thus permitting them to couple with the magnetization. This allows to yield physically meaningful solutions for both the current densities and the magnetization.

4. For TRSB periodic systems that lack a center of inversion, we derive a sum rule, linking the electronic band structure at opposite points in the FBZ ($\mathbf{k}_j$ and $-\mathbf{k}_j$) for non-hybrid functional calculations. This sum rule shows that standard collinear or non-collinear KS-DFT calculations (i.e. without a fraction of Fock exchange) do not even allow for a full breaking of time-reversal symmetry in reciprocal space. On the other hand, hybrid functional calculations are not constrained by such a sum rule.

All of these formal advantages originate from a simultaneous and self-consistent treatment of SOC with Fock exchange in a spinor two-component basis. Paper VII therefore provides a practical methodology for a proper treatment of these effects and its corresponding implementation.

The inclusion of the current densities $\mathbf{j}$, $\mathbf{J}_x$, $\mathbf{J}_y$ and $\mathbf{J}_z$ only from the Fock exchange operator but not in the approximate functional F_{xc} is not only a practical recipe, as shown in paper VII, but is also formally the correct recipe in the GGA or LDA of the SCDFT, as will be shown below.

Following Eq. (4.24), we can write the exchange energy E_x of the system in the SCDFT from the following adiabatic-connection expression:

$$E_x\left[n,\mathbf{m},\mathbf{j},\mathbf{J}_x,\mathbf{J}_y,\mathbf{J}_z\right] \approx (1-a)\int d\mathbf{r}_j F_x\left[n,\mathbf{m},\mathbf{j},\mathbf{J}_x,\mathbf{J}_y,\mathbf{J}_z\right] + aE_{Fock}\left[n,\mathbf{m},\mathbf{j},\mathbf{J}_x,\mathbf{J}_y,\mathbf{J}_z\right] \ , \tag{6.36}$$

where E_{Fock} is the energy contribution from the non-local Fock exchange operator of Eq. (6.20). Returning to Eqs. (5.6), (5.9), (5.11) and (5.13), it is clear that all of the density variables n, m_x, m_y, m_z, $\mathbf{j}$, $\mathbf{J}_x$, $\mathbf{J}_y$ and $\mathbf{J}_z$ each depend on one of the eight distinct spin-blocks of the complex single-particle density matrix.

The important point is that while all of these spin-blocks enter into the definition of E_{Fock} in a consistent and uniform way, they do not for F_{xc}. Indeed, Tao and Perdew [174] have shown from their study on the homogeneous electron gas subject to an external magnetic field, that the field-induced $\mathbf{j}$ only enters into the functional as its square $\mathbf{j}\cdot\mathbf{j}$. From Eq. (5.11), the calculation of $\mathbf{j}\cdot\mathbf{j}$ involves determining the second derivatives of the "density":

$$\sum_{\mu\nu}\sum_{\mathbf{g}} \mathrm{Im}\left[P^{\alpha\alpha\oplus\beta\beta}_{\mu\nu\{\mathbf{g}\}}\right]\chi_{\mu}\left(\mathbf{r}_j-\mathbf{A}_{\mu}\right)\chi_{\nu}\left(\mathbf{r}_j-\mathbf{A}_{\nu}-\mathbf{g}\right)\ . \tag{6.37}$$

These second derivatives only enter into meta-GGA approximations to F_{xc}, but not LDA or GGA ones.

Similar results were found by Pittalis, Vignale and Eich [255] in their study of the short-range behaviour of the exchange hole in the SCDFT, such that it was found that the $\mathbf{j}$, $\mathbf{J}_x$, $\mathbf{J}_y$ and $\mathbf{J}_z$ only enter into meta-GGA approximations of the exchange functional F_x. This means that in the LDA or GGA of the SCDFT, the functional will only depend on n and $\mathbf{m}$ and we can rewrite Eq. (6.36) as follows:

$$E_x\left[n,\mathbf{m},\mathbf{j},\mathbf{J}_x,\mathbf{J}_y,\mathbf{J}_z\right]\approx(1-a)\int d\mathbf{r}_j F_x\left[n,\mathbf{m}\right]+aE_{Fock}\left[n,\mathbf{m},\mathbf{j},\mathbf{J}_x,\mathbf{J}_y,\mathbf{J}_z\right]\ . \tag{6.38}$$

Hence the treatment of current densities solely from the Fock exchange operator is justified from the adiabatic-connection of the LDA and GGA of the SCDFT, according to Eq. (6.38).

It is worth appreciating that while a non-vanishing $\mathbf{j}$ only occurs in TRSB systems, the $\mathbf{J}_x, \mathbf{J}_y, \mathbf{J}_z$ can be large in any system with significant SOC. This means that the use of a Fock exchange operator in the self-consistent calculation is important for a proper treatment of SOC, also in systems that maintain time-reversal symmetry.

7 Conclusion

This thesis has investigated the development of first-principles approaches for the study of heavy-element containing periodic systems and their application, particularly to highly-correlated crystalline lanthanide oxides. In a scalar-relativistic context, the generalized Kohn-Sham Density Functional Theory (KS-DFT) approach (i.e. using hybrid functionals, containing a fraction of non-local Fock exchange) has proven to represent an efficient and accurate means to correct for the infamous self-interaction error that plague conventional local or semi-local density functional approximations (DFAs). This approach has permitted for a detailed characterization of the electronic and magnetic structure of the lanthanide sesquioxide series, and (finally) provide a rationale for the existence of all known pressure-induced electronic and structural phase transitions in the europium monoxide EuO. But the non-local Fock exchange term turned out to be even more important in the second part of the thesis, when fully relativistic theories and algorithms (including not only scalar-relativistic effects, but also spin-orbit coupling, SOC) were developped, following a periodic two-component self-consistent field (2c-SCF) approach.

The importance of the Fock exchange term for 2c-SCF calculations arises, on the one hand, because it allows for treating the orbital relaxation contribution to the orbital- and spin-current densities $\mathbf{j}$, $\mathbf{J}_x$, $\mathbf{J}_y$ and $\mathbf{J}_z$. This means that it allows $\mathbf{j}$ and the $\mathbf{J}_x$, $\mathbf{J}_y$ and $\mathbf{J}_z$ to properly couple with the magnetization $\mathbf{m}$ and thus yield physically meaningful solutions for both $\mathbf{m}$ and the current densities in time-reversal symmetry broken (TRSB) systems. The Fock exchange operator also imparts a local-magnetic torque to the two-electron potential, which practically means that the final solution for $\mathbf{m}$, $\mathbf{j}$, $\mathbf{J}_x$, $\mathbf{J}_y$ and $\mathbf{J}_z$ no longer just depend on the starting guess of the calculation. The local-magnetic torque afforded by the Fock exchange operator can also improve the rotational invariance of the calculation. In TRSB periodic systems that lack an inversion center, the Fock exchange operator also allows for a full breaking of time-reversal symmetry. This is because, in calculations using non-hybrid DFAs (or even those in which Fock exchange is treated in a one-component basis, using the popular second-variational approach), the electronic band structure is constrained by a sum rule linking the energy levels at opposite points in the first Brillouin zone ($\mathbf{k}_j$ and $-\mathbf{k}_j$). Including a fraction of Fock exchange is also important for treating SOC self-consistently in systems that maintain time-reversal symmetry, for a proper treatment of the orbital relaxation of the spin-current densities $\mathbf{J}_x$, $\mathbf{J}_y$ and $\mathbf{J}_z$.

One research direction that was initiated during the course of this thesis and which appears to be particularly promissing is the perturbative treatment of SOC according to the scheme discussed in Appendix H. Such a scheme permits to calculate the energy contribution of SOC, as well as the pertubed band structure and density matrix, without necessarily needing non-collinear formulations of the KS-DFT, and at very little computational cost. With this perturbative approach, calculation of the SOC contribution to the total energy is essentially free, both from the points of view of calculation time and memory requirements, because it only requires calculation of one-electron integrals. On the other hand, determining the perturbed band structure and density matrix involves memory requirements that are similar to the 2c-SCF, although calculation times could be greatly diminished. The perturbative approach also provides a means to obtain an improved density matrix as a starting guess for the 2c-SCF. The development and implementation of this perturbative approach represents an interesting research direction for the immediate future. Other such directions include the following:

1. Finishing to refine and test the periodic 2c-SCF relaxed constraints algorithms discussed in the second part of Appendix G
2. Development of basis set libraries for periodic 2c-SCF calculations
3. Development of algorithms for the calculation of analytical energy gradients and mechanical properties with the periodic 2c-SCF and their applications

Future work in the longer term could include the development and applications of the following:

1. Methods for calculating response properties in periodic systems from a fully relativistic framework
2. Approaches for treating correlation in periodic systems from wavefunction methods
3. All-electron periodic relativistic methods
4. Exploitation of time-reversal and double-group symmetries in the 2c-SCF
5. Implementation of the analytical Hessian of the total energy using the formulas of Appendix B

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Appendices

A On the Use of Dirac's Bra-ket Notation

The use of the bra-ket notation in Eq. (2.41) and as propagated in section 2.6 with Eqs. (2.42), (2.47) and (2.48), is an abuse of Dirac's original notation [83]. They were only written in this way for consistency with the literature on pseudopotentials and ECPs. For sake of brevity, the proper use of the notation is only outlined here taking as an example kets that resemble closely those of Eq. (2.48), but are somewhat simpler in form for the purposes of this demonstration. These are namely the $|\widetilde{l,m}\rangle$, rather than the $|l,m\rangle$ of Eq. (2.48), because the $|\widetilde{l,m}\rangle$ can be represented in terms of complex spherical harmonics $\mathcal{Y}_l^m$, rather than real spherical harmonics $\mathcal{X}_l^m$.

The $|\widetilde{l,m}\rangle$ are related to the $|l,m\rangle$ as follows:

$$\begin{aligned} |l,0\rangle &= |\widetilde{l,0}\rangle \\ |l,-|m|\rangle &= \frac{i}{2}\left(|\widetilde{l,-|m|}\rangle - |\widetilde{l,|m|}\rangle\right) \\ |l,|m|\rangle &= \frac{1}{2}\left(|\widetilde{l,-|m|}\rangle + |\widetilde{l,|m|}\rangle\right) \ . \end{aligned} \tag{A.1}$$

Formally, the $|\widetilde{l,m}\rangle$ is an element of an abstract Hilbert space, which is only defined, firstly by the following orthogonality condition, involving the normalization constant $N_{l,m}^{l',m'}$:

$$\langle\widetilde{l',m'}|\widetilde{l,m}\rangle = N_{l,m}^{l',m'}\,\delta_{l'l}\delta_{m'm} \ , \tag{A.2a}$$

and by a certain set of rules developed through operator algebra, involving the angular momentum $\mathbf{L}$ operator, its z-component L_z, as well as the angular momentum ladder operators $L_\pm = L_x \pm iL_y$, as follows:

$$\mathbf{L}^2|\widetilde{l,m}\rangle = \hbar^2 l\,(l+1)\ |\widetilde{l,m}\rangle \quad l \in [0,1,2,\dots] \ , \tag{A.2b}$$

and for the z-component angular momentum L_z:

$$L_z|\widetilde{l,m}\rangle = \hbar m\ |\widetilde{l,m}\rangle \quad m \in [-l,-l+1,\dots,l] \ . \tag{A.2c}$$

Finally, for the ladder operators $L_\pm$:

$$L_\pm|\widetilde{l,m}\rangle = \hbar\sqrt{l(l+1)-m(m\pm 1)}\ |\widetilde{l,m\pm 1}\rangle \tag{A.2d}$$

An operator $P_{\tilde{l}}(\Omega_{Ai})$, analogous to the one of Eq. (2.47) is formally defined in terms of the abstract states $|\widetilde{l,m}\rangle$ by representing them in the basis of solid angles $|\Omega_{Ai}\rangle$, that is to say:

$$P_{\tilde{l}}(\Omega_{Ai}) = \sum_{m=-l}^{l}\langle\Omega_{Ai}|\widetilde{l,m}\rangle\langle\widetilde{l,m}|\Omega_{Ai}\rangle \ , \tag{A.3}$$

in which, we define the representation of the abstract state $\langle\widetilde{l,m}|$ onto the basis of solid angles $\langle\widetilde{l,m}|\Omega_{Ai}\rangle$, in terms of complex spherical harmonics $\mathcal{Y}_l^m$, as follows:

$$\langle \widetilde{l,m} | \Omega_{Ai} \rangle \equiv \left[\mathcal{Y}_l^m \left(\Omega_{Ai} \right) \right]^* \ , \tag{A.4a}$$

and:

$$\langle \Omega_{Ai} | \widetilde{l,m} \rangle \equiv \mathcal{Y}_l^m \left(\Omega_{Ai} \right) \ . \tag{A.4b}$$

The action of $|\widetilde{l,m}\rangle$ on an abstract one-electron state $|\phi\rangle$ can be evaluated by then also defining:

$$\langle \Omega_{Ai} | \phi \rangle \equiv \phi(\mathbf{r}_i) \ . \tag{A.5}$$

Then, the product $\langle \widetilde{l,m} | \phi \rangle$ can be evaluated in the basis of solid angles by defining the following resolution of the identity:

$$1 \equiv \int d\Omega_{Ai} | \Omega_{Ai} \rangle \langle \Omega_{Ai} | \ , \tag{A.6}$$

such that, using Eqs. (A.4a), (A.5) and (A.6):

$$\langle \widetilde{l,m} | \phi \rangle = \int d\Omega_{Ai} \langle \widetilde{l,m} | \Omega_{Ai} \rangle \langle \Omega_{Ai} | \phi \rangle = \int d\Omega_{Ai} \left[\mathcal{Y}_l^m \left(\Omega_{Ai} \right) \right]^* \phi(\mathbf{r}_i) \ . \tag{A.7}$$

B Gradients and Hessians Within the McMurchie-Davidson-Saunders Algorithm

B.1 Basics and Basis Functions

The McMurchie-Davidson algorithm [225] evaluates mono- and bi-electronic integrals starting from a cartesian Gaussian-type function (CGTF) basis, defined as follows:

$$C(\alpha, \mathbf{r}-\mathbf{A}, t, u, v) = (r_x - A_x)^t (r_y - A_y)^u (r_z - A_z)^v exp(-\alpha|\mathbf{r}-\mathbf{A}|^2) \tag{B.1}$$

The CGTF are expanded as linear combinations of Hermite Gaussian-type functions, defined as:

$$\Lambda(\alpha, \mathbf{r}-\mathbf{A}, t, u, v) = \Big(\frac{\partial}{\partial A_x}\Big)^t \Big(\frac{\partial}{\partial A_y}\Big)^u \Big(\frac{\partial}{\partial A_z}\Big)^v exp(-\alpha|\mathbf{r}-\mathbf{A}|^2) \tag{B.2}$$

Although the McMurchie Davidson algorithm works with CGTF, modern quantum chemistry codes based on gaussians work in a real spherical Gaussian-type function (RSGTF) basis. So the application of the McMurchie Davidson algorithm requires an additional transformation from the RSGTF to the CGTF bases.

Instead, Saunders [268] suggested another procedure, which evaluates the integrals directly starting from the RSGTF basis. This method turns out to be more efficient than approaches which require transformation from the RSGTF to the CGTF bases.

Unnormalized complex spherical Gaussian-type functions (CSGTF) are defined in polar coordinates as:

$$\begin{aligned} S(\alpha, \mathbf{r}-\mathbf{A}, n, l, m) &= |\mathbf{r}-\mathbf{A}|^{2n+l} P_l^{|m|}(cos\theta) exp(im\phi) exp(-\alpha|\mathbf{r}-\mathbf{A}|^2) \\ &= Y_l^m(\mathbf{r}-\mathbf{A}) exp(-\alpha|\mathbf{r}-\mathbf{A}|^2) \end{aligned} \tag{B.3}$$

with $P_l^{|m|}$ being the Legendre function and Y_l^m a unnormalized complex solid spherical harmonic. The RSGTF can be obtained from CSGTF as follows:

$$R(\alpha, \mathbf{r}-\mathbf{A}, n, l, 0) = S(\alpha, \mathbf{r}-\mathbf{A}, n, l, 0) \tag{B.4a}$$

$$R(\alpha, \mathbf{r}-\mathbf{A}, n, l, |m|) = \text{Re }\, S(\alpha, \mathbf{r}-\mathbf{A}, n, l, |m|) \tag{B.4b}$$

$$R(\alpha, \mathbf{r}-\mathbf{A}, n, l, -|m|) = \text{Im }\, S(\alpha, \mathbf{r}-\mathbf{A}, n, l, |m|) \tag{B.4c}$$

CRYSTAL uses RSGTF with $n = 0$, however RSGTF with $n \neq 0$ are used in the process of evaluating kinetic energy integrals [254]. Formulae are derived in this document within the CSGTF basis, however these can be transformed to the RSGTF basis using equations 4a-c.

The RSGTF also admit the following representation in a Cartesian set of variables [254]:

$$R(\alpha, \mathbf{r} - \mathbf{A}, n, l, m) = X_l^m(\mathbf{r} - \mathbf{A}) exp(-\alpha|\mathbf{r} - \mathbf{A}|^2) \tag{B.5a}$$

$$X_l^m(\mathbf{r} - \mathbf{A}) = \sum_{tuv}^{(t+u+v=l)} D_l^m(t, u, v)(r_x - A_x)^t (r_y - A_y)^u (r_z - A_z)^v \tag{B.5b}$$

where $X_l^m(\mathbf{r} - \mathbf{A})$ is an unnormalized real solid spherical harmonic and $D_l^m(t, u, v)$ are coefficients whose values are provided in [254].

In the context of the McMurchie-Davidson-Saunders algorithm, a CSGTF pair is expanded in a linear combination of HGTF, as follows:

$$S(\alpha, \mathbf{r} - \mathbf{A}, n, l, m) S(\beta, \mathbf{r} - \mathbf{B}, \tilde{n}, \tilde{l}, \tilde{m}) = \sum_{tuv} E[n, l, m, \tilde{n}, \tilde{l}, \tilde{m}, t, u, v] \Lambda(\gamma, \mathbf{r} - \mathbf{P}, t, u, v) \tag{B.6}$$

where $\gamma = \alpha + \beta$ and $\mathbf{P} = \frac{\alpha\mathbf{A} + \beta\mathbf{B}}{\gamma}$. The coefficients E can be generated from four recurrence relations which can be easily derived from the properties of spherical harmonics and hermite polynomials [268]. The recurrences are as follows [268]:

B.1.1 Recursions in n

$$\begin{aligned}
E[n+1, l, m, \tilde{n}, \tilde{l}, \tilde{m}, t, u, v] = \Big(&E[n, l, m, \tilde{n}, \tilde{l}, \tilde{m}, t-2, u, v] + E[n+1, l, m, \tilde{n}, \tilde{l}, \tilde{m}, t, u-2, v] \\
&E[n, l, m, \tilde{n}, \tilde{l}, \tilde{m}, t, u, v-2]\Big)/(2\gamma)^2 + \Big((P_x - A_x)E[n, l, m, \tilde{n}, \tilde{l}, \tilde{m}, t-1, u, v] \\
&+(P_y - A_y)E[n, l, m, \tilde{n}, \tilde{l}, \tilde{m}, t, u-1, v] + (P_z - A_z)E[n, l, m, \tilde{n}, \tilde{l}, \tilde{m}, t, u, v-1]\Big)/\gamma \\
&+\Big(|\mathbf{P} - \mathbf{A}|^2 + \frac{1}{\gamma}(t + u + v + \frac{3}{2})\Big)E[n, l, m, \tilde{n}, \tilde{l}, \tilde{m}, t, u, v] \\
&+2(P_x - A_x)(t+1)E[n, l, m, \tilde{n}, \tilde{l}, \tilde{m}, t+1, u, v] + 2(P_y - A_y)(u+1)E[n, l, m, \tilde{n}, \tilde{l}, \tilde{m}, t, u+1, v] \\
&+2(P_z - A_z)(v+1)E[n, l, m, \tilde{n}, \tilde{l}, \tilde{m}, t, u, v+1] + (t+2)(t+1)E[n, l, m, \tilde{n}, \tilde{l}, \tilde{m}, t+2, u, v] \\
&+(u+2)(u+1)E[n, l, m, \tilde{n}, \tilde{l}, \tilde{m}, t, u+2, v] + (v+2)(v+1)E[n, l, m, \tilde{n}, \tilde{l}, \tilde{m}, t, u, v+2]
\end{aligned} \tag{B.7}$$

From now on the indices n and $\tilde{n}$ are omitted from equations when dealing with recursions in other quantum numbers.

B.1.2 Recursions in l

$$
\begin{aligned}
E[l+1,m,\tilde{l},\tilde{m},t,u,v] = {} & \frac{(2l+1)}{(l-|m|+1)}\Big\{\frac{1}{2\gamma}E[l,m,\tilde{l},\tilde{m},t,u,v-1] \\
& +(P_z-A_z)E[l,m,\tilde{l},\tilde{m},t,u,v] + (v+1)E[l,m,\tilde{l},\tilde{m},t,u,v+1]\Big\} \\
& -\frac{(l+|m|)}{(l-|m|+1)}\Big\{\frac{1}{(2\gamma)^2}\Big(E[l-1,m,\tilde{l},\tilde{m},t-2,u,v] + E[l-1,m,\tilde{l},\tilde{m},t,u-2,v] \\
& +E[l-1,m,\tilde{l},\tilde{m},t,u,v-2]\Big) + \frac{1}{\gamma}\Big((P_x-A_x)E[l,m,\tilde{l},\tilde{m},t-1,u,v] \\
& +(P_y-A_y)E[l-1,m,\tilde{l},\tilde{m},t,u-1,v] + (P_z-A_z)E[l-1,m,\tilde{l},\tilde{m},t,u,v-1]\Big) \\
& +\Big(|\mathbf{P}-\mathbf{A}|^2 + \frac{1}{\gamma}(t+u+v+\frac{3}{2})\Big) \\
& \times E[l-1,m,\tilde{l},\tilde{m},t,u,v] + 2(t+1)(P_x-A_x)E[l-1,m,\tilde{l},\tilde{m},t+1,u,v] \\
& +2(u+1)(P_y-A_y)E[l-1,m,\tilde{l},\tilde{m},t,u+1,v] + 2(v+1)(P_z-A_z)E[l-1,m,\tilde{l},\tilde{m},t,u,v+1] \\
& +(t+2)(t+1)E[l-1,m,\tilde{l},\tilde{m},t+2,u,v] + (u+2)(u+1)E[l-1,m,\tilde{l},\tilde{m},t,u+2,v] + \\
& (v+2)(v+1)E[l-1,m,\tilde{l},\tilde{m},t,u,v+2]\Big\}
\end{aligned}
\tag{B.8}
$$

B.1.3 Recursions in l and m

$$
\begin{aligned}
E[l+1,l+1,\tilde{l},\tilde{m},t,u,v] = {} & (2l+1)\Big(\frac{1}{2\gamma}E[l,l,\tilde{l},\tilde{m},t-1,u,v] + (t+1)E[l,l,\tilde{l},\tilde{m},t+1,u,v] \\
& +(P_x-A_x)E[l,l,\tilde{l},\tilde{m},t,u,v] + i\frac{1}{2\gamma}E[l,l,\tilde{l},\tilde{m},t,u-1,v] \\
& +i(u+1)E[l,l,\tilde{l},\tilde{m},t,u+1,v] + i(P_y-A_y)E[l,l,\tilde{l},\tilde{m},t,u,v]\Big)
\end{aligned}
\tag{B.9}
$$

B.1.4 Recursions in l and $-m$

$$\begin{aligned}E[l+1,-l-1,\tilde{l},\tilde{m},t,u,v] = (2l+1)\Big(&\frac{1}{2\gamma}E[l,-l,\tilde{l},\tilde{m},t-1,u,v] + (t+1)E[l,-l,\tilde{l},\tilde{m},t+1,u,v]\\ &+(P_x-A_x)E[l,-l,\tilde{l},\tilde{m},t,u,v] - i\frac{1}{2\gamma}E[l,-l,\tilde{l},\tilde{m},t,u-1,v]\\ &-i(u+1)E[l,-l,\tilde{l},\tilde{m},t,u+1,v] - i(P_y-A_y)E[l,-l,\tilde{l},\tilde{m},t,u,v]\Big)\end{aligned} \tag{B.10}$$

Equations 6-10 are understood in the sense that the E coefficients are non-zero for $t+u+v \leq 2n+2\tilde{n}+l+\tilde{l}$, $t \geq 0, u \geq 0, v \geq 0$. As well, the convention $\forall\ E[...,-0,...] = 0$ is understood for any index in the square bracket. Finally, equations 6-10 are invariant to simultaneous permutations of n, l, m for $\tilde{n}, \tilde{l}, \tilde{m}$. The starting point of the recurrences is:

$$E[0,0,0,0,0,0,0,0,0] = exp\Big(-\frac{\alpha\beta}{\gamma}|\mathbf{B}-\mathbf{A}|\Big)$$

Equations 7-10 can be transformed from the CSGTF basis to the RSGTF basis by mapping $i \to -1$ and $m \to -m$ in the imaginary part of these expressions.

B.2 Gradient Recurrences

Doll et al. (2001) [89] provides formulas for the expansion coefficients of the derivative in x of a CSGTF pair. Here I derive the formulas for the derivatives in y and z. More details on how these coefficients can be used to calculate the gradient of the total energy can be found in [89].

The derivatives of the CSGTF pair are expressed as:

$$\begin{aligned}&\frac{\partial}{\partial A_j}\Big(S(\alpha,\mathbf{r}-\mathbf{A},n,l,m)S(\beta,\mathbf{r}-\mathbf{B},\tilde{n},\tilde{l},\tilde{m})\Big) = \\ &\sum_{tuv} G^A_j[n,l,m,\tilde{n},\tilde{l},\tilde{m},t,u,v]\Lambda(\gamma,\mathbf{r}-\mathbf{P},t,u,v)\end{aligned} \tag{B.11}$$

where the upper index in G^A_j indicates that the derivate is taken with respect to center A and $j = x, y, z$. From the properties of HGTF, it is easy to show that [89]:

$$G_j^A[n,l,m,\tilde{n},\tilde{l},\tilde{m},t,u,v] = \frac{\partial}{\partial A_j}E[n,l,m,\tilde{n},\tilde{l},\tilde{m},t,u,v] \\ +\frac{\alpha}{\gamma}E[n,l,m,\tilde{n},\tilde{l},\tilde{m},t-\delta_{jx},u-\delta_{jy},v-\delta_{jz}] \tag{B.12}$$

where δ_{jk} is the kronecker delta. From the previous, the following starting point for the gradient recurrence relations can be derived [89]:

$$G_j^A[0,0,0,0,0,0,0,0,0] = 2\frac{\alpha\beta}{\gamma}(B_j - A_j)E[0,0,0,0,0,0,0,0,0] \tag{B.13}$$

$$G_j^A[0,0,0,0,0,0,\delta_{jx},\delta_{jy},\delta_{jz}] = \frac{\alpha}{\gamma}E[0,0,0,0,0,0,0,0,0] \tag{B.14}$$

All of the other $G_j^A[0,0,0,0,0,0,t,u,v]$ being zero. As well, derivatives with respect to center B can be conveniently calculated from other coefficients as follows [89]:

$$G_j^B[n,l,m,\tilde{n},\tilde{l},\tilde{m},t,u,v] = E[n,l,m,\tilde{n},\tilde{l},\tilde{m},t-\delta_{jx},u-\delta_{jy},v-\delta_{jz}] \\ -G_j^A[n,l,m,\tilde{n},\tilde{l},\tilde{m},t,u,v] \tag{B.15}$$

The use of the recurrence formulas for the G_j^A coefficients are similar to the strategy for the E coefficients, except that now the G_j^A are zero for $t+u+v \le 2n+2\tilde{n}+l+\tilde{l}+1,\ t \ge 0, u \ge 0, v \ge 0$ and formulas similar to those for the E coefficients are used when increasing quantum numbers on center B, while different formulas (shown below) are used for increasing the quantum numbers on center A.

B.2.1 Recursions in l and m: Derivative in y

From the properties of CSGTF:

$$S(\alpha,\mathbf{r}-\mathbf{A},l+1,l+1) = (2l+1)((x-A_x)+i(y-A_y))S(\alpha,\mathbf{r}-\mathbf{A},l,l) \tag{B.16}$$

So taking the derivative of the Gaussian pair:

$$\frac{\partial}{\partial A_y}S(\alpha,\mathbf{r}-\mathbf{A},l+1,l+1)S(\beta,\mathbf{r}-\mathbf{B},\tilde{l},\tilde{m}) = (2l+1)\frac{\partial}{\partial A_y}\Bigg(\sum_{tuv}E[l,l,\tilde{l},\tilde{m},t,u,v] \\ ((x-A_x)+i(y-A_y))\Lambda(\gamma,\mathbf{r}-\mathbf{P},t,u,v)\Bigg) \tag{B.17a}$$

Rearranging terms:

$$\frac{\partial}{\partial A_y}S(\alpha,\mathbf{r}-\mathbf{A},l+1,l+1)S(\beta,\mathbf{r}-\mathbf{B},\tilde{l},\tilde{m}) = (2l+1)\Bigg(\sum_{tuv} -iE[l,l,\tilde{l},\tilde{m},t,u,v]\Lambda(\gamma,\mathbf{r}-\mathbf{P},t,u,v)$$
$$+((x-A_x)+i(y-A_y))\frac{\partial}{\partial A_y}(E[l,l,\tilde{l},\tilde{m},t,u,v]\Lambda(\gamma,\mathbf{r}-\mathbf{P},t,u,v))\Bigg) \quad \text{(B.17b)}$$

Using the defintion of the G_y^A coefficients:

$$\frac{\partial}{\partial A_y}S(\alpha,\mathbf{r}-\mathbf{A},l+1,l+1)S(\beta,\mathbf{r}-\mathbf{B},\tilde{l},\tilde{m}) = (2l+1)\Bigg(\sum_{tuv} -iE[l,l,\tilde{l},\tilde{m},t,u,v]\Lambda(\gamma,\mathbf{r}-\mathbf{P},t,u,v)$$
$$+((x-A_x)+i(y-A_y))G_y^A[l,l,\tilde{l},\tilde{m},t,u,v]\Lambda(\gamma,\mathbf{r}-\mathbf{P},t,u,v)\Bigg)$$
$$\equiv \sum_{tuv} G_y^A[l+1,l+1,\tilde{l},\tilde{m},t,u,v]\Lambda(\gamma,\mathbf{r}-\mathbf{P},t,u,v) \quad \text{(B.17c)}$$

Now consider the recursions for HGTF:

$$\begin{aligned}(j-P_j)\Lambda(\gamma,\mathbf{r}-\mathbf{P},t,u,v) &= \frac{1}{2\gamma}\Lambda(\gamma,\mathbf{r}-\mathbf{P},t+\delta_{jx},u+\delta_{jy},v+\delta_{jz})\\ &+ w\Lambda(\gamma,\mathbf{r}-\mathbf{P},t-\delta_{jx},u-\delta_{jy},v-\delta_{jz}),\end{aligned} \quad \text{(B.18)}$$

where $w = t,u,v$. Two applications of equation (18) allow us to derive the following shifted recursion relations:

$$\begin{aligned}(j-A_j)\Lambda(\gamma,\mathbf{r}-\mathbf{P},t,u,v) &= \frac{1}{2\gamma}\Lambda(\gamma,\mathbf{r}-\mathbf{P},t+\delta_{jx},u+\delta_{jy},v+\delta_{jz})\\ &+ (P_j-A_j)\Lambda(\gamma,\mathbf{r}-\mathbf{P},t,u,v)\\ &+ w\Lambda(\gamma,\mathbf{r}-\mathbf{P},t-\delta_{jx},u-\delta_{jy},v-\delta_{jz})\end{aligned} \quad \text{(B.19a)}$$

$$\begin{aligned}(j-A_j)^2\Lambda(\gamma,\mathbf{r}-\mathbf{P},t,u,v) &= \frac{1}{(2\gamma)^2}\Lambda(\gamma,\mathbf{r}-\mathbf{P},t+2\delta_{jx},u+2\delta_{jy},v+2\delta_{jz})\\ &+ \frac{(P_j-A_j)}{\gamma}\Lambda(\gamma,\mathbf{r}-\mathbf{P},t+\delta_{jx},u+\delta_{jy},v+\delta_{jz})\\ &+ \Big(\frac{2w+1}{2\gamma}+(P_j-A_j)^2\Big)\Lambda(\gamma,\mathbf{r}-\mathbf{P},t,u,v)\\ &+ 2w(P_j-A_j)\Lambda(\gamma,\mathbf{r}-\mathbf{P},t-\delta_{jx},u-\delta_{jy},v-\delta_{jz})+w(w-1)\\ &\times \Lambda(\gamma,\mathbf{r}-\mathbf{P},t-2\delta_{jx},u-2\delta_{jy},v-2\delta_{jz}),\end{aligned} \quad \text{(B.19b)}$$

where equation (19b) will be useful later on.

Substituting equation (19a) in (17c):

$$\begin{aligned}\sum_{tuv} G_y^A[l+1,l+1,\tilde{l},\tilde{m},t,u,v]\Lambda(\gamma,\mathbf{r}-\mathbf{P},t,u,v) &= (2l+1)\Bigg(\sum_{tuv} -iE[l,l,\tilde{l},\tilde{m},t,u,v]\Lambda(\gamma,\mathbf{r}-\mathbf{P},t,u,v)\\ &+\Big\{(P_x-A_x)\Lambda(\gamma,\mathbf{r}-\mathbf{P},t,u,v)+\frac{1}{2\gamma}\Lambda(\gamma,\mathbf{r}-\mathbf{P},t+1,u,v)+t\Lambda(\gamma,\mathbf{r}-\mathbf{P},t-1,u,v)\\ &+i\Big((P_y-A_y)\Lambda(\gamma,\mathbf{r}-\mathbf{P},t,u,v)+\frac{1}{2\gamma}\Lambda(\gamma,\mathbf{r}-\mathbf{P},t,u+1,v)+u\Lambda(\gamma,\mathbf{r}-\mathbf{P},t,u-1,v)\Big)\Big\}\\ &\times G_y^A[l,l,\tilde{l},\tilde{m},t,u,v]\Bigg)\end{aligned}\tag{B.20}$$

From equation (20) we deduce the following recursion relation:

$$\begin{aligned}G_y^A[l+1,l+1,\tilde{l},\tilde{m},t,u,v] &= (2l+1)\Big(-iE[l,l,\tilde{l},\tilde{m},t,u,v]+\frac{1}{2\gamma}G_y^A[l,l,\tilde{l},\tilde{m},t-1,u,v]\\ &+(t+1)G_y^A[l,l,\tilde{l},\tilde{m},t+1,u,v]+(P_x-A_x)G_y^A[l,l,\tilde{l},\tilde{m},t,u,v]+i\frac{1}{2\gamma}G_y^A[l,l,\tilde{l},\tilde{m},t,u-1,v]\\ &+i(u+1)G_y^A[l,l,\tilde{l},\tilde{m},t,u+1,v]+i(P_y-A_y)G_y^A[l,l,\tilde{l},\tilde{m},t,u,v]\Big)\end{aligned}\tag{B.21}$$

B.2.2 Recursions in *l* and *m*: Derivative in *z*

Now for the derivative in *z*, we obtain from equation (16):

$$\begin{aligned}&\frac{\partial}{\partial A_z}S(\alpha,\mathbf{r}-\mathbf{A},l+1,l+1)S(\beta,\mathbf{r}-\mathbf{B},\tilde{l},\tilde{m})\\ &=(2l+1)((x-A_x)+i(y-A_y))\frac{\partial}{\partial A_z}\Big(\sum_{tuv}E[l,l,\tilde{l},\tilde{m},t,u,v]\Lambda(\gamma,\mathbf{r}-\mathbf{P},t,u,v)\Big)\\ &=(2l+1)((x-A_x)+i(y-A_y))\sum_{tuv}G_z^A[l,l,\tilde{l},\tilde{m},t,u,v]\Lambda(\gamma,\mathbf{r}-\mathbf{P},t,u,v)\\ &\equiv\sum_{tuv}G_z^A[l+1,l+1,\tilde{l},\tilde{m},t,u,v]\Lambda(\gamma,\mathbf{r}-\mathbf{P},t,u,v)\end{aligned}\tag{B.22}$$

So the derivative in *z* does not generate any additional terms in the expression for the Gaussian pair. The recurrences for the derivative in *z* are therefore similar to those for the *E*[...] coefficients. Proceeding similarly as in equations (18-21), we obtain:

$$\begin{aligned}G_z^A[l+1,l+1,\tilde{l},\tilde{m},t,u,v] &= (2l+1)\Big(\frac{1}{2\gamma}G_z^A[l,l,\tilde{l},\tilde{m},t-1,u,v]+(t+1)G_z^A[l,l,\tilde{l},\tilde{m},t+1,u,v]\\ &+(P_x-A_x)G_z^A[l,l,\tilde{l},\tilde{m},t,u,v]+i\frac{1}{2\gamma}G_z^A[l,l,\tilde{l},\tilde{m},t,u-1,v]\\ &+i(u+1)G_z^A[l,l,\tilde{l},\tilde{m},t,u+1,v]+i(P_y-A_y)G_z^A[l,l,\tilde{l},\tilde{m},t,u,v]\Big)\end{aligned}\tag{B.23}$$

B.2.3 Recursions in l and $-m$: Derivative in y

From the properties of complex spherical Gaussians:

$$S(\alpha, \mathbf{r} - \mathbf{A}, l+1, -l-1) = (2l+1)((x - A_x) - i(y - A_y))S(\alpha, \mathbf{r} - \mathbf{A}, l, -l) \tag{B.24}$$

Equation (24) is very similar to equation (16), apart from a change of sign of the last index of the complex spherical Gaussian and a change of sign in the imaginary part of the term in the large round brackets. So, proceeding as above, this effect is carried all the way through and we generate very similar recurrence relations, as follows:

$$\begin{aligned}
G_y^A[l+1, -l-1, \tilde{l}, \tilde{m}, t, u, v] = (2l+1)\Big(& iE[l, -l, \tilde{l}, \tilde{m}, t, u, v] + \frac{1}{2\gamma}G_y^A[l, -l, \tilde{l}, \tilde{m}, t-1, u, v] \\
& + (t+1)G_y^A[l, -l, \tilde{l}, \tilde{m}, t+1, u, v] + (P_x - A_x)G_y^A[l, -l, \tilde{l}, \tilde{m}, t, u, v] - i\frac{1}{2\gamma}G_y^A[l, -l, \tilde{l}, \tilde{m}, t, u-1, v] \\
& - i(u+1)G_y^A[l, -l, \tilde{l}, \tilde{m}, t, u+1, v] - i(P_y - A_y)G_y^A[l, -l, \tilde{l}, \tilde{m}, t, u, v]\Big)
\end{aligned} \tag{B.25}$$

B.2.4 Recursions in l and $-m$: Derivative in z

$$\begin{aligned}
G_z^A[l+1, -l-1, \tilde{l}, \tilde{m}, t, u, v] = (2l+1)\Big(& \frac{1}{2\gamma}G_z^A[l, -l, \tilde{l}, \tilde{m}, t-1, u, v] + (t+1)G_z^A[l, -l, \tilde{l}, \tilde{m}, t+1, u, v] \\
& + (P_x - A_x)G_z^A[l, -l, \tilde{l}, \tilde{m}, t, u, v] - i\frac{1}{2\gamma}G_z^A[l, -l, \tilde{l}, \tilde{m}, t, u-1, v] \\
& - i(u+1)G_z^A[l, -l, \tilde{l}, \tilde{m}, t, u+1, v] - i(P_y - A_y)G_z^A[l, -l, \tilde{l}, \tilde{m}, t, u, v]\Big)
\end{aligned} \tag{B.26}$$

B.2.5 Recursions in l: Derivative in y

From the properties of complex spherical Gaussians:

$$\begin{aligned}
S(\alpha, \mathbf{r} - \mathbf{A}, l+1, m) = & \frac{(2l+1)}{(l - |m| + 1)}(z - A_z)S(\alpha, \mathbf{r} - \mathbf{A}, l, m) \\
& - \frac{(l + |m|)}{(l - |m| + 1)}((x - A_x)^2 + (y - A_y)^2 + (z - A_z)^2)S(\alpha, \mathbf{r} - \mathbf{A}, l-1, m)
\end{aligned} \tag{B.27}$$

So taking the derivative of the Gaussian pair:

$$
\begin{aligned}
\frac{\partial}{\partial A_y} S(\alpha, \mathbf{r}-\mathbf{A}, l+1, m) S(\beta, \mathbf{r}-\mathbf{B}, \tilde{l}, \tilde{m}) &= \frac{(2l+1)}{(l-|m|+1)}(z-A_z) \\
&\times \frac{\partial}{\partial A_y} \sum_{tuv} E[l, m, \tilde{l}, \tilde{m}, t, u, v] \Lambda(\gamma, \mathbf{r}-\mathbf{P}, t, u, v) \\
&- \frac{(l+|m|)}{(l-|m|+1)} \frac{\partial}{\partial A_y} \Big(((x-A_x)^2 + (y-A_y)^2 + (z-A_z)^2) \\
&\times \sum_{tuv} E[l-1, m, \tilde{l}, \tilde{m}, t, u, v] \Lambda(\gamma, \mathbf{r}-\mathbf{P}, t, u, v) \Big)
\end{aligned}
$$

$$
\begin{aligned}
&= \frac{(2l+1)}{(l-|m|+1)}(z-A_z) \sum_{tuv} G_y^A[l, m, \tilde{l}, \tilde{m}, t, u, v] \Lambda(\gamma, \mathbf{r}-\mathbf{P}, t, u, v) \\
&- \frac{(l+|m|)}{(l-|m|+1)} \Big(-2(y-A_y) \sum_{tuv} E[l, m, \tilde{l}, \tilde{m}, t, u, v] \Lambda(\gamma, \mathbf{r}-\mathbf{P}, t, u, v) \\
&+ \big((x-A_x)^2 + (y-A_y)^2 + (z-A_z)^2\big) \sum_{tuv} G_y^A[l-1, m, \tilde{l}, \tilde{m}, t, u, v] \Lambda(\gamma, \mathbf{r}-\mathbf{P}, t, u, v) \Big) \\
&\equiv \sum_{tuv} G_y^A[l+1, m, \tilde{l}, \tilde{m}, t, u, v] \Lambda(\gamma, \mathbf{r}-\mathbf{P}, t, u, v) \qquad \text{(B.28)}
\end{aligned}
$$

Substituting equations (19a) and (19b) in equation (28):

$$
\begin{aligned}
&\sum_{tuv} G_y^A[l+1, m, \tilde{l}, \tilde{m}, t, u, v]\Lambda(\gamma, \mathbf{r}-\mathbf{P}, t, u, v) = \\
&\frac{(2l+1)}{(l-|m|+1)} \sum_{tuv} G_y^A[l, m, \tilde{l}, \tilde{m}, t, u, v]\Big\{\frac{1}{2\gamma}\Lambda(\gamma, \mathbf{r}-\mathbf{P}, t, u, v+1) \\
&\quad +(P_z-A_z)\Lambda(\gamma, \mathbf{r}-\mathbf{P}, t, u, v) + v\Lambda(\gamma, \mathbf{r}-\mathbf{P}, t, u, v-1)\Big\} \\
&+2\frac{(l+|m|)}{(l-|m|+1)} \sum_{tuv} E[l-1, m, \tilde{l}, \tilde{m}, t, u, v]\Big\{\frac{1}{2\gamma}\Lambda(\gamma, \mathbf{r}-\mathbf{P}, t, u+1, v) \\
&\quad +(P_y-A_y)\Lambda(\gamma, \mathbf{r}-\mathbf{P}, t, u, v) + u\Lambda(\gamma, \mathbf{r}-\mathbf{P}, t, u-1, v)\Big\} \\
&-\frac{(l+|m|)}{(l-|m|+1)} \sum_{tuv} G_y^A[l-1, m, \tilde{l}, \tilde{m}, t, u, v]\Big\{\frac{1}{(2\gamma)^2}\Lambda(\gamma, \mathbf{r}-\mathbf{P}, t+2, u, v) \\
&+\frac{P_x-A_x}{\gamma}\Lambda(\gamma, \mathbf{r}-\mathbf{P}, t+1, u, v) + \Big(\frac{2t+1}{2\gamma} + (P_x-A_x)^2\Big)\Lambda(\gamma, \mathbf{r}-\mathbf{P}, t, u, v) \\
&\quad +2t(P_x-A_x)\Lambda(\gamma, \mathbf{r}-\mathbf{P}, t-1, u, v) + t(t-1)\Lambda(\gamma, \mathbf{r}-\mathbf{P}, t-2, u, v)\Big\} \\
&-\frac{(l+|m|)}{(l-|m|+1)} \sum_{tuv} G_y^A[l-1, m, \tilde{l}, \tilde{m}, t, u, v]\Big\{\frac{1}{(2\gamma)^2}\Lambda(\gamma, \mathbf{r}-\mathbf{P}, t, u+2, v) \\
&+\frac{P_y-A_y}{\gamma}\Lambda(\gamma, \mathbf{r}-\mathbf{P}, t, u+1, v) + \Big(\frac{2u+1}{2\gamma} + (P_y-A_y)^2\Big)\Lambda(\gamma, \mathbf{r}-\mathbf{P}, t, u, v) \\
&\quad +2u(P_y-A_y)\Lambda(\gamma, \mathbf{r}-\mathbf{P}, t, u-1, v) + u(u-1)\Lambda(\gamma, \mathbf{r}-\mathbf{P}, t, u-2, v)\Big\} \\
&-\frac{(l+|m|)}{(l-|m|+1)} \sum_{tuv} G_y^A[l-1, m, \tilde{l}, \tilde{m}, t, u, v]\Big\{\frac{1}{(2\gamma)^2}\Lambda(\gamma, \mathbf{r}-\mathbf{P}, t, u, v+2) \\
&+\frac{P_z-A_z}{\gamma}\Lambda(\gamma, \mathbf{r}-\mathbf{P}, t, u, v+1) + \Big(\frac{2v+1}{2\gamma} + (P_z-A_z)^2\Big)\Lambda(\gamma, \mathbf{r}-\mathbf{P}, t, u, v) \\
&\quad +2v(P_z-A_z)\Lambda(\gamma, \mathbf{r}-\mathbf{P}, t, u, v-1) + v(v-1)\Lambda(\gamma, \mathbf{r}-\mathbf{P}, t, u, v-2)\Big\}
\end{aligned}
\tag{B.29}
$$

From equation (29) we determine the following recursion relation:

$$\begin{aligned}
G_y^A[l+1,m,\tilde{l},\tilde{m},t,u,v] = \frac{(2l+1)}{(l-|m|+1)}\Big\{&\frac{1}{2\gamma}G_y^A[l,m,\tilde{l},\tilde{m},t,u,v-1] \\
&+(P_z-A_z)G_y^A[l,m,\tilde{l},\tilde{m},t,u,v] + (v+1)G_y^A[l,m,\tilde{l},\tilde{m},t,u,v+1]\Big\} \\
&-\frac{(l+|m|)}{(l-|m|+1)}\Big\{\frac{1}{(2\gamma)^2}\Big(G_y^A[l-1,m,\tilde{l},\tilde{m},t-2,u,v] \\
&+G_y^A[l-1,m,\tilde{l},\tilde{m},t,u-2,v] + G_y^A[l-1,m,\tilde{l},\tilde{m},t,u,v-2]\Big) \\
&+\frac{1}{\gamma}\Big((P_x-A_x)G_y^A[l-1,m,\tilde{l},\tilde{m},t-1,u,v] - E[l-1,m,\tilde{l},\tilde{m},t,u-1,v] \\
&+(P_y-A_y)G_y^A[l-1,m,\tilde{l},\tilde{m},t,u-1,v] + (P_z-A_z)G_y^A[l-1,m,\tilde{l},\tilde{m},t,u,v-1]\Big) \\
&+\Big(|\mathbf{P}-\mathbf{A}|^2 + \frac{1}{\gamma}(t+u+v+\frac{3}{2})\Big)G_y^A[l-1,m,\tilde{l},\tilde{m},t,u,v] \\
&-2(P_y-A_y)E[l-1,m,\tilde{l},\tilde{m},t,u,v] + 2(t+1)(P_x-A_x)G_y^A[l-1,m,\tilde{l},\tilde{m},t+1,u,v] \\
&+2(u+1)(P_y-A_y)G_y^A[l-1,m,\tilde{l},\tilde{m},t,u+1,v] + 2(v+1)(P_z-A_z)G_y^A[l-1,m,\tilde{l},\tilde{m},t,u,v+1] \\
&-2(u+1)E[l-1,m,\tilde{l},\tilde{m},t,u+1,v] + (t+2)(t+1)G_y^A[l-1,m,\tilde{l},\tilde{m},t+2,u,v] \\
&+(u+2)(u+1)G_y^A[l-1,m,\tilde{l},\tilde{m},t,u+2,v] + (v+2)(v+1)G_y^A[l-1,m,\tilde{l},\tilde{m},t,u,v+2]\Big\}
\end{aligned} \tag{B.30}$$

B.2.6 Recursions in *l*: Derivative in *z*

Taking the derivative in *z* of the Gaussian pair from equation (22):

$$\begin{aligned}
&\frac{\partial}{\partial A_z}S(\alpha,\mathbf{r}-\mathbf{A},l+1,m)S(\beta,\mathbf{r}-\mathbf{B},\tilde{l},\tilde{m}) = \\
&-\frac{(2l+1)}{(l-|m|+1)}\sum_{tuv}E[l,m,\tilde{l},\tilde{m},t,u,v]\Lambda(\gamma,\mathbf{r}-\mathbf{P},t,u,v) \\
&+\frac{(2l+1)}{(l-|m|+1)}(z-A_z)\sum_{tuv}G_z^A[l,m,\tilde{l},\tilde{m},t,u,v]\Lambda(\gamma,\mathbf{r}-\mathbf{P},t,u,v) \\
&+2\frac{(l+|m|)}{(l-|m|+1)}(z-A_z)\sum_{tuv}E[l-1,m,\tilde{l},\tilde{m},t,u,v]\Lambda(\gamma,\mathbf{r}-\mathbf{P},t,u,v) \\
&-\frac{(l+|m|)}{(l-|m|+1)}((x-A_x)^2+(y-A_y)^2+(z-A_z)^2) \\
&\sum_{tuv}G_z^A[l-1,m,\tilde{l},\tilde{m},t,u,v]\Lambda(\gamma,\mathbf{r}-\mathbf{P},t,u,v) \\
&\equiv \sum_{tuv}G_z^A[l+1,m,\tilde{l},\tilde{m},t,u,v]\Lambda(\gamma,\mathbf{r}-\mathbf{P},t,u,v)
\end{aligned} \tag{B.31}$$

Substituting equations (19a) and (19b) in equation (31):

$$
\begin{aligned}
&\sum_{tuv} G_z^A[l+1, m, \tilde{l}, \tilde{m}, t, u, v]\Lambda(\gamma, \mathbf{r}-\mathbf{P}, t, u, v) = \\
&-\frac{(2l+1)}{(l-|m|+1)} \sum_{tuv} E[l, m, \tilde{l}, \tilde{m}, t, u, v]\Lambda(\gamma, \mathbf{r}-\mathbf{P}, t, u, v) \\
&\frac{(2l+1)}{(l-|m|+1)} \sum_{tuv} G_z^A[l, m, \tilde{l}, \tilde{m}, t, u, v]\Big\{\frac{1}{2\gamma}\Lambda(\gamma, \mathbf{r}-\mathbf{P}, t, u, v+1) \\
&+(P_z - A_z)\Lambda(\gamma, \mathbf{r}-\mathbf{P}, t, u, v) + v\Lambda(\gamma, \mathbf{r}-\mathbf{P}, t, u, v-1)\Big\} \\
&+2\frac{(2l+1)}{(l-|m|+1)} \sum_{tuv} E[l-1, m, \tilde{l}, \tilde{m}, t, u, v]\Big\{\frac{1}{2\gamma}\Lambda(\gamma, \mathbf{r}-\mathbf{P}, t, u, v+1) \\
&+(P_z - A_z)\Lambda(\gamma, \mathbf{r}-\mathbf{P}, t, u, v) + v\Lambda(\gamma, \mathbf{r}-\mathbf{P}, t, u, v-1)\Big\} \\
&-\frac{(l+|m|)}{(l-|m|+1)} \sum_{tuv} G_z^A[l-1, m, \tilde{l}, \tilde{m}, t, u, v]\Big\{\frac{1}{(2\gamma)^2}\Lambda(\gamma, \mathbf{r}-\mathbf{P}, t+2, u, v) \\
&+\frac{P_x - A_x}{\gamma}\Lambda(\gamma, \mathbf{r}-\mathbf{P}, t+1, u, v) + \Big(\frac{2t+1}{2\gamma} + (P_x - A_x)^2\Big)\Lambda(\gamma, \mathbf{r}-\mathbf{P}, t, u, v) \\
&+2t(P_x - A_x)\Lambda(\gamma, \mathbf{r}-\mathbf{P}, t-1, u, v) + t(t-1)\Lambda(\gamma, \mathbf{r}-\mathbf{P}, t-2, u, v)\Big\} \\
&-\frac{(l+|m|)}{(l-|m|+1)} \sum_{tuv} G_z^A[l-1, m, \tilde{l}, \tilde{m}, t, u, v]\Big\{\frac{1}{(2\gamma)^2}\Lambda(\gamma, \mathbf{r}-\mathbf{P}, t, u+2, v) \\
&+\frac{P_y - A_y}{\gamma}\Lambda(\gamma, \mathbf{r}-\mathbf{P}, t, u+1, v) + \Big(\frac{2u+1}{2\gamma} + (P_y - A_y)^2\Big)\Lambda(\gamma, \mathbf{r}-\mathbf{P}, t, u, v) \\
&+2u(P_y - A_y)\Lambda(\gamma, \mathbf{r}-\mathbf{P}, t, u-1, v) + u(u-1)\Lambda(\gamma, \mathbf{r}-\mathbf{P}, t, u-2, v)\Big\} \\
&-\frac{(l+|m|)}{(l-|m|+1)} \sum_{tuv} G_z^A[l-1, m, \tilde{l}, \tilde{m}, t, u, v]\Big\{\frac{1}{(2\gamma)^2}\Lambda(\gamma, \mathbf{r}-\mathbf{P}, t, u, v+2) \\
&+\frac{P_z - A_z}{\gamma}\Lambda(\gamma, \mathbf{r}-\mathbf{P}, t, u, v+1) + \Big(\frac{2v+1}{2\gamma} + (P_z - A_z)^2\Big)\Lambda(\gamma, \mathbf{r}-\mathbf{P}, t, u, v) \\
&+2v(P_z - A_z)\Lambda(\gamma, \mathbf{r}-\mathbf{P}, t, u, v-1) + v(v-1)\Lambda(\gamma, \mathbf{r}-\mathbf{P}, t, u, v-2)\Big\}
\end{aligned}
\tag{B.32}
$$

From equation (32), we deduce the following recursion relation:

$$
\begin{aligned}
G_z^A[l+1,m,\tilde{l},\tilde{m},t,u,v] = \frac{(2l+1)}{(l-|m|+1)}\Big\{\frac{1}{2\gamma}G_z^A[l,m,\tilde{l},\tilde{m},t,u,v-1] \\
-E[l,m,\tilde{l},\tilde{m},t,u,v] + (P_z-A_z)G_z^A[l,m,\tilde{l},\tilde{m},t,u,v] \\
+(v+1)G_z^A[l,m,\tilde{l},\tilde{m},t,u,v+1]\Big\} - \frac{(l+|m|)}{(l-|m|+1)}\Big\{\frac{1}{(2\gamma)^2}\Big(G_z^A[l-1,m,\tilde{l},\tilde{m},t-2,u,v] \\
+G_z^A[l-1,m,\tilde{l},\tilde{m},t,u-2,v] + G_z^A[l-1,m,\tilde{l},\tilde{m},t,u,v-2]\Big) \\
+\frac{1}{\gamma}\Big((P_x-A_x)G_z^A[l-1,m,\tilde{l},\tilde{m},t-1,u,v] - E[l-1,m,\tilde{l},\tilde{m},t,u,v-1] \\
+(P_y-A_y)G_z^A[l-1,m,\tilde{l},\tilde{m},t,u-1,v] + (P_z-A_z)G_z^A[l-1,m,\tilde{l},\tilde{m},t,u,v-1]\Big) \\
+\Big(|\mathbf{P}-\mathbf{A}|^2 + \frac{1}{\gamma}(t+u+v+\frac{3}{2})\Big)G_z^A[l-1,m,\tilde{l},\tilde{m},t,u,v] \\
-2(P_z-A_z)E[l-1,m,\tilde{l},\tilde{m},t,u,v] + 2(t+1)(P_x-A_x)G_z^A[l-1,m,\tilde{l},\tilde{m},t+1,u,v] \\
+2(u+1)(P_y-A_y)G_z^A[l-1,m,\tilde{l},\tilde{m},t,u+1,v] + 2(v+1)(P_z-A_z)G_z^A[l-1,m,\tilde{l},\tilde{m},t,u,v+1] \\
-2(v+1)E[l-1,m,\tilde{l},\tilde{m},t,u,v+1] + (t+2)(t+1)G_z^A[l-1,m,\tilde{l},\tilde{m},t+2,u,v] \\
+(u+2)(u+1)G_z^A[l-1,m,\tilde{l},\tilde{m},t,u+2,v] + (v+2)(v+1)G_z^A[l-1,m,\tilde{l},\tilde{m},t,u,v+2]\Big\}
\end{aligned}
\tag{B.33}
$$

B.2.7 Recursions in n: Derivative in y

From the properties of CSGTF:

$$
S(\alpha,\mathbf{r}-\mathbf{A},n+1,l,m) = ((x-A_x)^2 + (y-A_y)^2 + (z-A_z)^2)S(\alpha,\mathbf{r}-\mathbf{A},n,l,m) \tag{B.34}
$$

So for the derivative of a CSGTF pair, we have:

$$
\begin{aligned}
\frac{\partial}{\partial A_y}S(\alpha,\mathbf{r}-\mathbf{A},n+1,l,m)S(\beta,\mathbf{r}-\mathbf{B},\tilde{n},\tilde{l},\tilde{m}) = \\
-2(y-A_y)\sum_{tuv}E[n,l,m,\tilde{n},\tilde{l},\tilde{m},t,u,v]\Lambda(\gamma,\mathbf{r}-\mathbf{P},t,u,v) \\
|\mathbf{r}-\mathbf{A}|^2\sum_{tuv}G_y^A[n,l,m,\tilde{n},\tilde{l},\tilde{m},t,u,v]\Lambda(\gamma,\mathbf{r}-\mathbf{P},t,u,v) \\
\equiv \sum_{tuv}G_y^A[n+1,l,m,\tilde{n},\tilde{l},\tilde{m},t,u,v]\Lambda(\gamma,\mathbf{r}-\mathbf{P},t,u,v)
\end{aligned}
\tag{B.35}
$$

Substituting equations (19a-b) in (35), we have:

$$\begin{aligned}
&\sum_{tuv} G^A_y[n+1,l,m,\tilde{n},\tilde{l},\tilde{m},t,u,v]\Lambda(\gamma,\mathbf{r}-\mathbf{P},t,u,v) = \\
&-2\sum_{tuv} E[n,l,m,\tilde{n},\tilde{l},\tilde{m},t,u,v]\Big\{\frac{1}{2\gamma}\Lambda(\gamma,\mathbf{r}-\mathbf{P},t,u+1,v) \\
&+(P_y-A_y)\Lambda(\gamma,\mathbf{r}-\mathbf{P},t,u,v)+u\Lambda(\gamma,\mathbf{r}-\mathbf{P},t,u-1,v)\Big\} \\
&+\sum_{tuv} G^A_y[n,l,m,\tilde{n},\tilde{l},\tilde{m},t,u,v]\Big\{\frac{1}{(2\gamma)^2}\Lambda(\gamma,\mathbf{r}-\mathbf{P},t+2,u,v) \\
&+\frac{P_x-A_x}{\gamma}\Lambda(\gamma,\mathbf{r}-\mathbf{P},t+1,u,v)+\Big(\frac{2t+1}{2\gamma}+(P_x-A_x)^2\Big)\Lambda(\gamma,\mathbf{r}-\mathbf{P},t,u,v) \\
&+2t(P_x-A_x)\Lambda(\gamma,\mathbf{r}-\mathbf{P},t-1,u,v)+t(t-1)\Lambda(\gamma,\mathbf{r}-\mathbf{P},t-2,u,v)\Big\} \\
&-\frac{(l+|m|)}{(l-|m|+1)}\sum_{tuv} G^A_y[n,l,m,\tilde{n},\tilde{l},\tilde{m},t,u,v]\Big\{\frac{1}{(2\gamma)^2}\Lambda(\gamma,\mathbf{r}-\mathbf{P},t,u+2,v) \\
&+\frac{P_y-A_y}{\gamma}\Lambda(\gamma,\mathbf{r}-\mathbf{P},t,u+1,v)+\Big(\frac{2u+1}{2\gamma}+(P_y-A_y)^2\Big)\Lambda(\gamma,\mathbf{r}-\mathbf{P},t,u,v) \\
&+2u(P_y-A_y)\Lambda(\gamma,\mathbf{r}-\mathbf{P},t,u-1,v)+u(u-1)\Lambda(\gamma,\mathbf{r}-\mathbf{P},t,u-2,v)\Big\} \\
&-\frac{(l+|m|)}{(l-|m|+1)}\sum_{tuv} G^A_y[n,l,m,\tilde{n},\tilde{l},\tilde{m},t,u,v]\Big\{\frac{1}{(2\gamma)^2}\Lambda(\gamma,\mathbf{r}-\mathbf{P},t,u,v+2) \\
&+\frac{P_z-A_z}{\gamma}\Lambda(\gamma,\mathbf{r}-\mathbf{P},t,u,v+1)+\Big(\frac{2v+1}{2\gamma}+(P_z-A_z)^2\Big)\Lambda(\gamma,\mathbf{r}-\mathbf{P},t,u,v) \\
&+2v(P_z-A_z)\Lambda(\gamma,\mathbf{r}-\mathbf{P},t,u,v-1)+v(v-1)\Lambda(\gamma,\mathbf{r}-\mathbf{P},t,u,v-2)
\end{aligned} \tag{B.36}$$

which implies the following recurrence relation:

$$\begin{aligned}
G^A_y[n+1,l,m,\tilde{n},\tilde{l},\tilde{m},t,u,v] &= \frac{1}{(2\gamma)^2}\Big(G^A_y[n,l,m,\tilde{n},\tilde{l},\tilde{m},t-2,u,v] \\
&+G^A_y[n,l,m,\tilde{n},\tilde{l},\tilde{m},t,u-2,v]+G^A_y[n,l,m,\tilde{n},\tilde{l},\tilde{m},t,u,v-2]\Big) \\
&+\frac{1}{\gamma}\Big(-E[n,l,m,\tilde{n},\tilde{l},\tilde{m},t,u-1,v]+(P_x-A_x)G^A_y[n,l,m,\tilde{n},\tilde{l},\tilde{m},t-1,u,v] \\
&+(P_y-A_y)G^A_y[n,l,m,\tilde{n},\tilde{l},\tilde{m},t,u-1,v]+(P_z-A_z)G^A_y[n,l,m,\tilde{n},\tilde{l},\tilde{m},t,u,v-1]\Big) \\
&+\Big(|\mathbf{P}-\mathbf{A}|^2+\frac{1}{\gamma}(t+u+v+\frac{3}{2})\Big)G^A_y[n,l,m,\tilde{n},\tilde{l},\tilde{m},t,u,v] \\
&-2(P_y-A_y)E[n,l,m,\tilde{n},\tilde{l},\tilde{m},t,u,v]+2(t+1)(P_x-A_x)G^A_y[n,l,m,\tilde{n},\tilde{l},\tilde{m},t+1,u,v] \\
&+2(u+1)(P_y-A_y)G^A_y[n,l,m,\tilde{n},\tilde{l},\tilde{m},t,u+1,v]+2(v+1)(P_z-A_z)G^A_y[n,l,m,\tilde{n},\tilde{l},\tilde{m},t,u,v+1] \\
&-2(u+1)E[n,l,m,\tilde{n},\tilde{l},\tilde{m},t,u+1,v]+(t+2)(t+1)G^A_y[n,l,m,\tilde{n},\tilde{l},\tilde{m},t+2,u,v] \\
&+(u+2)(u+1)G^A_y[n,l,m,\tilde{n},\tilde{l},\tilde{m},t,u+2,v]+(v+2)(v+1)G^A_y[n,l,m,\tilde{n},\tilde{l},\tilde{m},t,u,v+2]
\end{aligned} \tag{B.37}$$

B.2.8 Recursions in n: Derivative in z

Since equation (34) is radially symmetric, derivatives generate similar recurrences in n for x, y and z. So the recurrence in n for derivatives in z is very similar to that for derivatives in y:

$$
\begin{aligned}
G_z^A[n+1,l,m,\tilde{n},\tilde{l},\tilde{m},t,u,v] = \frac{1}{(2\gamma)^2}\Big(G_z^A[n,l,m,\tilde{n},\tilde{l},\tilde{m},t-2,u,v] \\
+G_z^A[n,l,m,\tilde{n},\tilde{l},\tilde{m},t,u-2,v] + G_z^A[n,l,m,\tilde{n},\tilde{l},\tilde{m},t,u,v-2]\Big) \\
+\frac{1}{\gamma}\Big(-E[n,l,m,\tilde{n},\tilde{l},\tilde{m},t,u,v-1] + (P_x-A_x)G_z^A[n,l,m,\tilde{n},\tilde{l},\tilde{m},t-1,u,v] \\
+(P_y-A_y)G_z^A[n,l,m,\tilde{n},\tilde{l},\tilde{m},t,u-1,v] + (P_z-A_z)G_z^A[n,l,m,\tilde{n},\tilde{l},\tilde{m},t,u,v-1]\Big) \\
+\Big(|\mathbf{P}-\mathbf{A}|^2 + \frac{1}{\gamma}(t+u+v+\frac{3}{2})\Big)G_z^A[n,l,m,\tilde{n},\tilde{l},\tilde{m},t,u,v] \\
-2(P_z-A_z)E[n,l,m,\tilde{n},\tilde{l},\tilde{m},t,u,v] + 2(t+1)(P_x-A_x)G_z^A[n,l,m,\tilde{n},\tilde{l},\tilde{m},t+1,u,v] \\
+2(u+1)(P_y-A_y)G_z^A[n,l,m,\tilde{n},\tilde{l},\tilde{m},t,u+1,v] + 2(v+1)(P_z-A_z)G_z^A[n,l,m,\tilde{n},\tilde{l},\tilde{m},t,u,v+1] \\
-2(v+1)E[n,l,m,\tilde{n},\tilde{l},\tilde{m},t,u,v+1] + (t+2)(t+1)G_z^A[n,l,m,\tilde{n},\tilde{l},\tilde{m},t+2,u,v] \\
+(u+2)(u+1)G_z^A[n,l,m,\tilde{n},\tilde{l},\tilde{m},t,u+2,v] + (v+2)(v+1)G_z^A[n,l,m,\tilde{n},\tilde{l},\tilde{m},t,u,v+2]
\end{aligned}
\tag{B.38}
$$

B.3 Hessian Recurrences

I now derive the recurrence relations for the second derivatives of the CSGTF pair. The starting point of the recurrences can be obtained by first considering the derivative of the gradient expression in equation (11):

$$
\begin{aligned}
&\frac{\partial}{\partial I_i}\frac{\partial}{\partial J_j}\Big(S(\alpha,\mathbf{r}-\mathbf{A},n,l,m)S(\beta,\mathbf{r}-\mathbf{B},\tilde{n},\tilde{l},\tilde{m})\Big) = \\
&\frac{\partial}{\partial I_i}\sum_{tuv} G_j^J[n,l,m,\tilde{n},\tilde{l},\tilde{m},t,u,v]\Lambda(\gamma,\mathbf{r}-\mathbf{P},t,u,v) \\
&\equiv \sum_{tuv} F_{ij}^{IJ}[n,l,m,\tilde{n},\tilde{l},\tilde{m},t,u,v]\Lambda(\gamma,\mathbf{r}-\mathbf{P},t,u,v)
\end{aligned}
\tag{B.39}
$$

where $I = A, B$ and $J = A, B$. Distributing the derivative, we have:

$$\begin{aligned}\sum_{tuv} F^{IJ}_{ij}[n, l, m, \tilde{n}, \tilde{l}, \tilde{m}, t, u, v]\Lambda(\gamma, \mathbf{r} - \mathbf{P}, t, u, v) = \\ \sum_{tuv} \frac{\partial}{\partial I_i} G^J_j[n, l, m, \tilde{n}, \tilde{l}, \tilde{m}, t, u, v]\Lambda(\gamma, \mathbf{r} - \mathbf{P}, t, u, v) \\ + \frac{\zeta_I}{\gamma} G^J_j[n, l, m, \tilde{n}, \tilde{l}, \tilde{m}, t, u, v]\Lambda(\gamma, \mathbf{r} - \mathbf{P}, t + \delta_{ix}, u + \delta_{iy}, v + \delta_{iz})\end{aligned} \tag{B.40}$$

where $\zeta_I = \alpha$ for $I = A$ and $\zeta_I = \beta$ for $I = B$. As well, we have used the identity:

$$\begin{aligned}\frac{\partial}{\partial I_i}\Lambda(\alpha, \mathbf{r} - \mathbf{P}, t, u, v) &= \frac{\partial}{\partial I_i}\Big(\frac{\partial}{\partial P_x}\Big)^t\Big(\frac{\partial}{\partial P_y}\Big)^u\Big(\frac{\partial}{\partial P_z}\Big)^v exp(-\alpha|\mathbf{r} - \mathbf{P}|^2) \\ &= \frac{\partial P_i}{\partial I_i}\Big(\frac{\partial}{\partial P_x}\Big)^{t+\delta_{ix}}\Big(\frac{\partial}{\partial P_y}\Big)^{u+\delta_{iy}}\Big(\frac{\partial}{\partial P_z}\Big)^{v+\delta_{iz}} exp(-\alpha|\mathbf{r} - \mathbf{P}|^2) \\ &= \frac{\zeta_I}{\gamma}\Big(\frac{\partial}{\partial P_x}\Big)^{t+\delta_{ix}}\Big(\frac{\partial}{\partial P_y}\Big)^{u+\delta_{iy}}\Big(\frac{\partial}{\partial P_z}\Big)^{v+\delta_{iz}} exp(-\alpha|\mathbf{r} - \mathbf{P}|^2)\end{aligned} \tag{B.41}$$

From equation (40), we deduce the following relation:

$$\begin{aligned}F^{IJ}_{ij}[n, l, m, \tilde{n}, \tilde{l}, \tilde{m}, t, u, v] &= \frac{\partial}{\partial I_i} G^J_j[n, l, m, \tilde{n}, \tilde{l}, \tilde{m}, t, u, v] \\ &+ \frac{\zeta_I}{\gamma} G^J_j[n, l, m, \tilde{n}, \tilde{l}, \tilde{m}, t - \delta_{ix}, u - \delta_{iy}, v - \delta_{iz}]\end{aligned} \tag{B.42}$$

From equation (42) we can develop expressions for the starting point of the recurrence relations. These expressions will be derived for the F^{AA}_{ij}. Later, transformations from the F^{AA}_{ij} to the F^{AB}_{ij}, F^{BA}_{ij} and F^{BB}_{ij} will be provided. These transformations are analogous to that for the gradient coefficients (equation (15)).

To obtain the starting point of the recurrences, let us substitute equation (13) and (15) in (41):

$$\begin{aligned}F^{AA}_{ij}[0, 0, 0, 0, 0, 0, 0, 0, 0] &= \frac{\partial}{\partial A_i} G^A_j[0, 0, 0, 0, 0, 0, 0, 0, 0] \\ &+ \frac{\alpha}{\gamma} G^A_j[0, 0, 0, 0, 0, 0, -\delta_{ix}, -\delta_{iy}, -\delta_{iz}]\end{aligned} \tag{B.43a}$$

$$\begin{aligned}F^{AA}_{ij}[0, 0, 0, 0, 0, 0, 0, 0, 0] &= \frac{\partial}{\partial A_i} 2\frac{\alpha\beta}{\gamma}(B_j - A_j) exp\Big(-\frac{\alpha\beta}{\gamma}|\mathbf{B} - \mathbf{A}|\Big) \\ &= 2\frac{\alpha\beta}{\gamma}\Big\{2\frac{\alpha\beta}{\gamma}(B_i - A_i)(B_j - A_j) - \delta_{ij}\Big\} E[0, 0, 0, 0, 0, 0, 0, 0, 0]\end{aligned} \tag{B.43b}$$

As well:

$$F_{ij}^{AA}[0,0,0,0,0,0,\delta_{jx},\delta_{jy},\delta_{jz}] = \frac{\partial}{\partial A_i} G_j^A[0,0,0,0,0,0,\delta_{jx},\delta_{jy},\delta_{jz}] \\ +\frac{\alpha}{\gamma} G_j^A[0,0,0,0,0,0,\delta_{jx}-\delta_{ix},\delta_{jy}-\delta_{iy},\delta_{jz}-\delta_{iz}] \tag{B.44a}$$

$$F_{ij}^{AA}[0,0,0,0,0,0,\delta_{jx},\delta_{jy},\delta_{jz}] = \frac{\alpha}{\gamma}\Big(2\frac{\alpha\beta}{\gamma}(B_i - A_i)E[0,0,0,0,0,0,0,0,0] \\ +\delta_{ij} G_j^A[0,0,0,0,0,0,0,0,0]\Big) \tag{B.44b}$$

in addition:

$$F_{ij}^{AA}[0,0,0,0,0,0,\delta_{ix},\delta_{iy},\delta_{iz}] = \frac{\partial}{\partial A_i} G_j^A[0,0,0,0,0,0,\delta_{ix},\delta_{iy},\delta_{iz}] \\ +\frac{\alpha}{\gamma} G_j^A[0,0,0,0,0,0,0,0,0] \tag{B.45a}$$

$$F_{ij}^{AA}[0,0,0,0,0,0,\delta_{ix},\delta_{iy},\delta_{iz}] = \frac{\alpha}{\gamma}\Big(2\delta_{ij}\frac{\alpha\beta}{\gamma}(B_i - A_i)E[0,0,0,0,0,0,0,0,0] \\ +G_j^A[0,0,0,0,0,0,0,0,0]\Big) \tag{B.45b}$$

and:

$$F_{ij}^{AA}[0,0,0,0,0,0,2\delta_{jx},2\delta_{jy},2\delta_{jz}] = \frac{\partial}{\partial A_i} G_j^A[0,0,0,0,0,0,2\delta_{jx},2\delta_{jy},2\delta_{jz}] \\ +\frac{\alpha}{\gamma} G_j^A[0,0,0,0,0,0,2\delta_{jx}-\delta_{ix},2\delta_{jy}-\delta_{iy},2\delta_{jz}-\delta_{iz}] \tag{B.46a}$$

$$F_{ij}^{AA}[0,0,0,0,0,0,2\delta_{jx},2\delta_{jy},2\delta_{jz}] = \delta_{ij}\frac{\alpha}{\gamma} G_j^A[0,0,0,0,0,0,\delta_{jx},\delta_{jy},\delta_{jz}] \tag{B.46b}$$

Finally:

$$F_{ij}^{AA}[0,0,0,0,0,0,2\delta_{ix},2\delta_{iy},2\delta_{iz}] = \frac{\partial}{\partial A_i} G_j^A[0,0,0,0,0,0,2\delta_{ix},2\delta_{iy},2\delta_{iz}] \\ +\frac{\alpha}{\gamma} G_j^A[0,0,0,0,0,0,\delta_{ix},\delta_{iy},\delta_{iz}] \tag{B.47a}$$

$$F_{ij}^{AA}[0,0,0,0,0,0,2\delta_{ix},2\delta_{iy},2\delta_{iz}] = \frac{\alpha}{\gamma} G_j^A[0,0,0,0,0,0,\delta_{ix},\delta_{iy},\delta_{iz}] \tag{B.47b}$$

Derivatives with respect to center B can be obtained as follows. First, it is easy to show that [89]:

$$\frac{\partial}{\partial A_i} + \frac{\partial}{\partial B_i} = \frac{\partial}{\partial P_i} \tag{B.48}$$

So from equation (40):

$$\begin{aligned}
&\frac{\partial}{\partial B_i} \sum_{tuv} G_j^A[n, l, m, \tilde{n}, \tilde{l}, \tilde{m}, t, u, v] \Lambda(\gamma, \mathbf{r} - \mathbf{P}, t, u, v) \\
&= \Big(\frac{\partial}{\partial P_i} - \frac{\partial}{\partial A_i}\Big) \sum_{tuv} G_j^A[n, l, m, \tilde{n}, \tilde{l}, \tilde{m}, t, u, v] \Lambda(\gamma, \mathbf{r} - \mathbf{P}, t, u, v) \\
&= \sum_{tuv} G_j^A[n, l, m, \tilde{n}, \tilde{l}, \tilde{m}, t, u, v] \Lambda(\gamma, \mathbf{r} - \mathbf{P}, t + \delta_{ix}, u + \delta_{iy}, v + \delta_{iz}) \\
&\qquad - F_{ij}^{AA}[n, l, m, \tilde{n}, \tilde{l}, \tilde{m}, t, u, v] \Lambda(\gamma, \mathbf{r} - \mathbf{P}, t, u, v)
\end{aligned} \tag{B.49}$$

From which we deduce the relation:

$$\begin{aligned}
&F_{ij}^{AB}[n, l, m, \tilde{n}, \tilde{l}, \tilde{m}, t, u, v] = F_{ji}^{BA}[n, l, m, \tilde{n}, \tilde{l}, \tilde{m}, t, u, v] \\
&= G_j^A[n, l, m, \tilde{n}, \tilde{l}, \tilde{m}, t - \delta_{ix}, u - \delta_{iy}, v - \delta_{iz}] - F_{ij}^{AA}[n, l, m, \tilde{n}, \tilde{l}, \tilde{m}, t, u, v]
\end{aligned} \tag{B.50}$$

where the first equality above comes from the symmetric property of the Hessian matrix. For calculating coefficients related to double derivatives in B, we have:

$$\begin{aligned}
&\frac{\partial}{\partial B_i} \frac{\partial}{\partial B_j} \sum_{tuv} E[n, l, m, \tilde{n}, \tilde{l}, \tilde{m}, t, u, v] \Lambda(\gamma, \mathbf{r} - \mathbf{P}, t, u, v) \\
&= \Big(\frac{\partial}{\partial P_i} - \frac{\partial}{\partial A_i}\Big)\Big(\frac{\partial}{\partial P_j} - \frac{\partial}{\partial A_j}\Big) \sum_{tuv} E[n, l, m, \tilde{n}, \tilde{l}, \tilde{m}, t, u, v] \\
&\qquad \times \Lambda(\gamma, \mathbf{r} - \mathbf{P}, t, u, v) \\
&= \Big(\frac{\partial}{\partial P_i} - \frac{\partial}{\partial A_i}\Big) \sum_{tuv} E[n, l, m, \tilde{n}, \tilde{l}, \tilde{m}, t, u, v] \Lambda(\gamma, \mathbf{r} - \mathbf{P}, t + \delta_{jx}, u + \delta_{jy}, v + \delta_{jz}) \\
&\qquad - G_j^A[n, l, m, \tilde{n}, \tilde{l}, \tilde{m}, t, u, v] \Lambda(\gamma, \mathbf{r} - \mathbf{P}, t, u, v) \\
&= \sum_{tuv} E[n, l, m, \tilde{n}, \tilde{l}, \tilde{m}, t, u, v] \Lambda(\gamma, \mathbf{r} - \mathbf{P}, t + \delta_{jx} + \delta_{ix}, u + \delta_{jy} + \delta_{iy}, v + \delta_{jz} + \delta_{iz}) \\
&\qquad - G_i^A[n, l, m, \tilde{n}, \tilde{l}, \tilde{m}, t, u, v] \Lambda(\gamma, \mathbf{r} - \mathbf{P}, t + \delta_{jx}, u + \delta_{jy}, v + \delta_{jz}) \\
&\qquad - G_j^A[n, l, m, \tilde{n}, \tilde{l}, \tilde{m}, t, u, v] \Lambda(\gamma, \mathbf{r} - \mathbf{P}, t + \delta_{ix}, u + \delta_{iy}, v + \delta_{iz}) \\
&\qquad + F_{ij}^{AA}[n, l, m, \tilde{n}, \tilde{l}, \tilde{m}, t, u, v] \Lambda(\gamma, \mathbf{r} - \mathbf{P}, t, u, v)
\end{aligned} \tag{B.51}$$

From equation (51), we deduce the following relation:

$$\begin{aligned}
F_{ij}^{BB}[n,l,m,\tilde{n},\tilde{l},\tilde{m},t,u,v] &= F_{ij}^{AA}[n,l,m,\tilde{n},\tilde{l},\tilde{m},t,u,v] \\
+E[n,l,m,\tilde{n},\tilde{l},\tilde{m},t-\delta_{jx}-\delta_{ix},u-\delta_{jy}-\delta_{iy},v-\delta_{jz}-\delta_{iz}] \\
-G_i^A[n,l,m,\tilde{n},\tilde{l},\tilde{m},t-\delta_{jx},u-\delta_{jy},v-\delta_{jz}] \\
-G_j^A[n,l,m,\tilde{n},\tilde{l},\tilde{m},t-\delta_{ix},u-\delta_{iy},v-\delta_{iz}]
\end{aligned} \tag{B.52}$$

The above equations suggest that the use of the recurrence formulas for the F_{ij}^{IJ} coefficients are similar to the strategy for the E and G_j^J coefficients, except that now the F_{ij}^{IJ} are zero for $t+u+v \le 2n+2\tilde{n}+l+\tilde{l}+2,\ t \ge 0, u \ge 0, v \ge 0$. Formulas similar to those for the E coefficients are used when increasing quantum numbers on center B for the F_{ij}^{AA} or for increasing quantum numbers on center A for the F_{ij}^{BB}. Formulas similar to those for the G_j^J coefficients are used for increasing both quantum numbers for the F_{ij}^{AB} and the F_{ij}^{BA}. New formulas are needed only for increasing quantum numbers on center A for the F_{ij}^{AA} or for increasing the quantum numbers on center B for the F_{ij}^{BB}. There are six independant derivative components for any F_{ij}^{IJ} and there are four types of recurrence relations. So a total of $6 \times 4 = 24$ new formulas need to be derived. These formulae can be derived by proceeding similarly as in the case of the gradient formulas above, except that an extra derivative is taken in the expression for the CSGTF pair. In the following the procedure is not repeated and only the final result is shown.

B.3.1 Recursions in l and m: Derivative in xx

$$\begin{aligned}
F_{xx}^{AA}[l+1,l+1,\tilde{l},\tilde{m},t,u,v] &= (2l+1)\Big(-G_x^A[l,l,\tilde{l},\tilde{m},t,u,v] + \frac{1}{2\gamma}F_{xx}^{AA}[l,l,\tilde{l},\tilde{m},t-1,u,v] \\
&+(t+1)F_{xx}^{AA}[l,l,\tilde{l},\tilde{m},t+1,u,v] - G_x^A[l,l,\tilde{l},\tilde{m},t,u,v] \\
&+(P_x-A_x)F_{xx}^{AA}[l,l,\tilde{l},\tilde{m},t,u,v] + i\frac{1}{2\gamma}F_{xx}^{AA}[l,l,\tilde{l},\tilde{m},t,u-1,v] \\
&+i(u+1)F_{xx}^{AA}[l,l,\tilde{l},\tilde{m},t,u+1,v] + i(P_y-A_y)F_{xx}^{AA}[l,l,\tilde{l},\tilde{m},t,u,v]\Big)
\end{aligned} \tag{B.53}$$

B.3.2 Recursions in l and m: Derivative in xy

$$\begin{aligned}
F_{xy}^{AA}[l+1,l+1,\tilde{l},\tilde{m},t,u,v] &= (2l+1)\Big(-G_y^A[l,l,\tilde{l},\tilde{m},t,u,v] + \frac{1}{2\gamma}F_{xy}^{AA}[l,l,\tilde{l},\tilde{m},t-1,u,v] \\
&+(t+1)F_{xy}^{AA}[l,l,\tilde{l},\tilde{m},t+1,u,v] - iG_y^A[l,l,\tilde{l},\tilde{m},t,u,v] \\
&+(P_x-A_x)F_{xy}^{AA}[l,l,\tilde{l},\tilde{m},t,u,v] + i\frac{1}{2\gamma}F_{xy}^{AA}[l,l,\tilde{l},\tilde{m},t,u-1,v] \\
&+i(u+1)F_{xy}^{AA}[l,l,\tilde{l},\tilde{m},t,u+1,v] + i(P_y-A_y)F_{xy}^{AA}[l,l,\tilde{l},\tilde{m},t,u,v]\Big)
\end{aligned} \tag{B.54}$$

B.3.3 Recursions in *l* and *m*: Derivative in *xz*

$$\begin{aligned}F_{xz}^{AA}[l+1,l+1,\tilde{l},\tilde{m},t,u,v] &= (2l+1)\Big(-G_z^{A}[l,l,\tilde{l},\tilde{m},t,u,v]+\frac{1}{2\gamma}F_{xz}^{AA}[l,l,\tilde{l},\tilde{m},t-1,u,v]\\ &+(t+1)F_{xz}^{AA}[l,l,\tilde{l},\tilde{m},t+1,u,v]+(P_x-A_x)F_{xz}^{AA}[l,l,\tilde{l},\tilde{m},t,u,v]+i\frac{1}{2\gamma}F_{xz}^{AA}[l,l,\tilde{l},\tilde{m},t,u-1,v]\\ &+i(u+1)F_{xz}^{AA}[l,l,\tilde{l},\tilde{m},t,u+1,v]+i(P_y-A_y)F_{xz}^{AA}[l,l,\tilde{l},\tilde{m},t,u,v]\Big)\end{aligned}\tag{B.55}$$

B.3.4 Recursions in *l* and *m*: Derivative in *yy*

$$\begin{aligned}F_{yy}^{AA}[l+1,l+1,\tilde{l},\tilde{m},t,u,v] &= (2l+1)\Big(-iG_y^{A}[l,l,\tilde{l},\tilde{m},t,u,v]+\frac{1}{2\gamma}F_{yy}^{AA}[l,l,\tilde{l},\tilde{m},t-1,u,v]\\ &+(t+1)F_{yy}^{AA}[l,l,\tilde{l},\tilde{m},t+1,u,v]+(P_x-A_x)F_{yy}^{AA}[l,l,\tilde{l},\tilde{m},t,u,v]+i\frac{1}{2\gamma}F_{yy}^{AA}[l,l,\tilde{l},\tilde{m},t,u-1,v]\\ &+i(u+1)F_{yy}^{AA}[l,l,\tilde{l},\tilde{m},t,u+1,v]-iG_y^{A}[l,l,\tilde{l},\tilde{m},t,u,v]+i(P_y-A_y)F_{yy}^{AA}[l,l,\tilde{l},\tilde{m},t,u,v]\Big)\end{aligned}\tag{B.56}$$

B.3.5 Recursions in *l* and *m*: Derivative in *yz*

$$\begin{aligned}F_{yz}^{AA}[l+1,l+1,\tilde{l},\tilde{m},t,u,v] &= (2l+1)\Big(-iG_z^{A}[l,l,\tilde{l},\tilde{m},t,u,v]+\frac{1}{2\gamma}F_{yz}^{AA}[l,l,\tilde{l},\tilde{m},t-1,u,v]\\ &+(t+1)F_{yz}^{AA}[l,l,\tilde{l},\tilde{m},t+1,u,v]+(P_x-A_x)F_{yz}^{AA}[l,l,\tilde{l},\tilde{m},t,u,v]+i\frac{1}{2\gamma}F_{yz}^{AA}[l,l,\tilde{l},\tilde{m},t,u-1,v]\\ &+i(u+1)F_{yz}^{AA}[l,l,\tilde{l},\tilde{m},t,u+1,v]+i(P_y-A_y)F_{yz}^{AA}[l,l,\tilde{l},\tilde{m},t,u,v]\Big)\end{aligned}\tag{B.57}$$

B.3.6 Recursions in *l* and *m*: Derivative in *zz*

$$\begin{aligned}F_{zz}^{AA}[l+1,l+1,\tilde{l},\tilde{m},t,u,v] &= (2l+1)\Big(\frac{1}{2\gamma}F_{zz}^{AA}[l,l,\tilde{l},\tilde{m},t-1,u,v]+(t+1)F_{zz}^{AA}[l,l,\tilde{l},\tilde{m},t+1,u,v]\\ &+(P_x-A_x)F_{zz}^{AA}[l,l,\tilde{l},\tilde{m},t,u,v]+i\frac{1}{2\gamma}F_{zz}^{AA}[l,l,\tilde{l},\tilde{m},t,u-1,v]\\ &+i(u+1)F_{zz}^{AA}[l,l,\tilde{l},\tilde{m},t,u+1,v]+i(P_y-A_y)F_{zz}^{AA}[l,l,\tilde{l},\tilde{m},t,u,v]\Big)\end{aligned}\tag{B.58}$$

B.3.7 Recursions in l and $-m$: Derivative in xx

$$\begin{aligned}F^{AA}_{xx}[l+1,-l-1,\tilde{l},\tilde{m},t,u,v] = (2l+1)\Big(&-G^{A}_{x}[l,-l,\tilde{l},\tilde{m},t,u,v] + \frac{1}{2\gamma}F^{AA}_{xx}[l,-l,\tilde{l},\tilde{m},t-1,u,v]\\ &+(t+1)F^{AA}_{xx}[l,-l,\tilde{l},\tilde{m},t+1,u,v] - G^{A}_{x}[l,-l,\tilde{l},\tilde{m},t,u,v]\\ &+(P_x-A_x)F^{AA}_{xx}[l,-l,\tilde{l},\tilde{m},t,u,v] - i\frac{1}{2\gamma}F^{AA}_{xx}[l,-l,\tilde{l},\tilde{m},t,u-1,v]\\ &-i(u+1)F^{AA}_{xx}[l,-l,\tilde{l},\tilde{m},t,u+1,v] - i(P_y-A_y)F^{AA}_{xx}[l,-l,\tilde{l},\tilde{m},t,u,v]\Big)\end{aligned} \tag{B.59}$$

B.3.8 Recursions in l and $-m$: Derivative in xy

$$\begin{aligned}F^{AA}_{xy}[l+1,-l-1,\tilde{l},\tilde{m},t,u,v] = (2l+1)\Big(&-G^{A}_{y}[l,-l,\tilde{l},\tilde{m},t,u,v] + \frac{1}{2\gamma}F^{AA}_{xy}[l,-l,\tilde{l},\tilde{m},t-1,u,v]\\ &+(t+1)F^{AA}_{xy}[l,-l,\tilde{l},\tilde{m},t+1,u,v] + iG^{A}_{y}[l,-l,\tilde{l},\tilde{m},t,u,v]\\ &+(P_x-A_x)F^{AA}_{xy}[l,-l,\tilde{l},\tilde{m},t,u,v] - i\frac{1}{2\gamma}F^{AA}_{xy}[l,-l,\tilde{l},\tilde{m},t,u-1,v]\\ &-i(u+1)F^{AA}_{xy}[l,-l,\tilde{l},\tilde{m},t,u+1,v] - i(P_y-A_y)F^{AA}_{xy}[l,-l,\tilde{l},\tilde{m},t,u,v]\Big)\end{aligned} \tag{B.60}$$

B.3.9 Recursions in l and $-m$: Derivative in xz

$$\begin{aligned}F^{AA}_{xz}[l+1,-l-1,\tilde{l},\tilde{m},t,u,v] = (2l+1)\Big(&-G^{A}_{z}[l,-l,\tilde{l},\tilde{m},t,u,v] + \frac{1}{2\gamma}F^{AA}_{xz}[l,-l,\tilde{l},\tilde{m},t-1,u,v]\\ +(t+1)F^{AA}_{xz}[l,-l,\tilde{l},\tilde{m},t+1,u,v] &+ (P_x-A_x)F^{AA}_{xz}[l,-l,\tilde{l},\tilde{m},t,u,v] - i\frac{1}{2\gamma}F^{AA}_{xz}[l,-l,\tilde{l},\tilde{m},t,u-1,v]\\ &-i(u+1)F^{AA}_{xz}[l,-l,\tilde{l},\tilde{m},t,u+1,v] - i(P_y-A_y)F^{AA}_{xz}[l,-l,\tilde{l},\tilde{m},t,u,v]\Big)\end{aligned} \tag{B.61}$$

B.3.10 Recursions in l and $-m$: Derivative in yy

$$\begin{aligned}F^{AA}_{yy}[l+1,-l-1,\tilde{l},\tilde{m},t,u,v] = (2l+1)\Big(&iG^{A}_{y}[l,-l,\tilde{l},\tilde{m},t,u,v] + \frac{1}{2\gamma}F^{AA}_{yy}[l,-l,\tilde{l},\tilde{m},t-1,u,v]\\ &+(t+1)F^{AA}_{yy}[l,-l,\tilde{l},\tilde{m},t+1,u,v] + iG^{A}_{y}[l,-l,\tilde{l},\tilde{m},t,u,v]\\ &+(P_x-A_x)F^{AA}_{yy}[l,-l,\tilde{l},\tilde{m},t,u,v] - i\frac{1}{2\gamma}F^{AA}_{yy}[l,-l,\tilde{l},\tilde{m},t,u-1,v]\\ &-i(u+1)F^{AA}_{yy}[l,-l,\tilde{l},\tilde{m},t,u+1,v] - i(P_y-A_y)F^{AA}_{yy}[l,-l,\tilde{l},\tilde{m},t,u,v]\Big)\end{aligned} \tag{B.62}$$

B.3.11 Recursions in l and $-m$: Derivative in yz

$$\begin{aligned}F_{yz}^{AA}[l+1,-l-1,\tilde{l},\tilde{m},t,u,v] = (2l+1)\Big(iG_z^{A}[l,-l,\tilde{l},\tilde{m},t,u,v] + \frac{1}{2\gamma}F_{yz}^{AA}[l,-l,\tilde{l},\tilde{m},t-1,u,v] \\ +(t+1)F_{yz}^{AA}[l,-l,\tilde{l},\tilde{m},t+1,u,v] + (P_x-A_x)F_{yz}^{AA}[l,-l,\tilde{l},\tilde{m},t,u,v] - i\frac{1}{2\gamma}F_{yz}^{AA}[l,-l,\tilde{l},\tilde{m},t,u-1,v] \\ -i(u+1)F_{yz}^{AA}[l,-l,\tilde{l},\tilde{m},t,u+1,v] - i(P_y-A_y)F_{yz}^{AA}[l,-l,\tilde{l},\tilde{m},t,u,v]\Big)\end{aligned} \tag{B.63}$$

B.3.12 Recursions in l and $-m$: Derivative in zz

$$\begin{aligned}F_{zz}^{AA}[l+1,-l-1,\tilde{l},\tilde{m},t,u,v] = (2l+1)\Big(\frac{1}{2\gamma}F_{zz}^{AA}[l,-l,\tilde{l},\tilde{m},t-1,u,v] \\ +(t+1)F_{zz}^{AA}[l,-l,\tilde{l},\tilde{m},t+1,u,v] \\ +(P_x-A_x)F_{zz}^{AA}[l,-l,\tilde{l},\tilde{m},t,u,v] - i\frac{1}{2\gamma}F_{zz}^{AA}[l,-l,\tilde{l},\tilde{m},t,u-1,v] \\ -i(u+1)F_{zz}^{AA}[l,-l,\tilde{l},\tilde{m},t,u+1,v] - i(P_y-A_y)F_{zz}^{AA}[l,-l,\tilde{l},\tilde{m},t,u,v]\Big)\end{aligned} \tag{B.64}$$

B.3.13 Recursions in l: Derivative in xx

$$
\begin{aligned}
F^{AA}_{xx}[l+1,m,\tilde{l},\tilde{m},t,u,v] = \frac{(2l+1)}{(l-|m|+1)}\Big\{\frac{1}{2\gamma}F^{AA}_{xx}[l,m,\tilde{l},\tilde{m},t,u,v-1] \\
+(P_z-A_z)F^{AA}_{xx}[l,m,\tilde{l},\tilde{m},t,u,v] + (v+1)F^{AA}_{xx}[l,m,\tilde{l},\tilde{m},t,u,v+1]\Big\} \\
-\frac{(l+|m|)}{(l-|m|+1)}\Big\{\frac{1}{(2\gamma)^2}\Big(F^{AA}_{xx}[l-1,m,\tilde{l},\tilde{m},t-2,u,v] \\
+F^{AA}_{xx}[l-1,m,\tilde{l},\tilde{m},t,u-2,v] + F^{AA}_{xx}[l-1,m,\tilde{l},\tilde{m},t,u,v-2]\Big) \\
+\frac{1}{\gamma}\Big((P_x-A_x)F^{AA}_{xx}[l-1,m,\tilde{l},\tilde{m},t-1,u,v] - G^{A}_{x}[l-1,m,\tilde{l},\tilde{m},t-1,u,v] \\
-G^{A}_{x}[l-1,m,\tilde{l},\tilde{m},t-1,u,v] + (P_y-A_y)F^{AA}_{xx}[l-1,m,\tilde{l},\tilde{m},t,u-1,v] \\
+(P_z-A_z)F^{AA}_{xx}[l-1,m,\tilde{l},\tilde{m},t,u,v-1]\Big) + \Big(|\mathbf{P}-\mathbf{A}|^2 + \frac{1}{\gamma}(t+u+v+\frac{3}{2})\Big) \\
\times F^{AA}_{xx}[l-1,m,\tilde{l},\tilde{m},t,u,v] - 2(P_x-A_x)G^{A}_{x}[l-1,m,\tilde{l},\tilde{m},t,u,v] \\
-2(P_x-A_x)G^{A}_{x}[l-1,m,\tilde{l},\tilde{m},t,u,v+2E[l-1,m,\tilde{l},\tilde{m},t,u,v] \\
+2(t+1)(P_x-A_x)F^{AA}_{xx}[l-1,m,\tilde{l},\tilde{m},t+1,u,v] \\
+2(u+1)(P_y-A_y)F^{AA}_{xx}[l-1,m,\tilde{l},\tilde{m},t,u+1,v] \\
+2(v+1)(P_z-A_z)F^{AA}_{xx}[l-1,m,\tilde{l},\tilde{m},t,u,v+1] \\
-2(t+1)G^{A}_{x}[l-1,m,\tilde{l},\tilde{m},t+1,u,v] - 2(t+1)G^{A}_{x}[l-1,m,\tilde{l},\tilde{m},t+1,u,v] \\
+(t+2)(t+1)F^{AA}_{xx}[l-1,m,\tilde{l},\tilde{m},t+2,u,v] \\
+(u+2)(u+1)F^{AA}_{xx}[l-1,m,\tilde{l},\tilde{m},t,u+2,v] + \\
(v+2)(v+1)F^{AA}_{xx}[l-1,m,\tilde{l},\tilde{m},t,u,v+2]\Big\}
\end{aligned}
\tag{B.65}
$$

B.3.14 Recursions in l: Derivative in xy

$$
\begin{aligned}
F_{xy}^{AA}[l+1,m,\tilde{l},\tilde{m},t,u,v] = \frac{(2l+1)}{(l-|m|+1)}\Big\{\frac{1}{2\gamma}F_{xy}^{AA}[l,m,\tilde{l},\tilde{m},t,u,v-1] \\
+(P_z-A_z)F_{xy}^{AA}[l,m,\tilde{l},\tilde{m},t,u,v]+(v+1)F_{xy}^{AA}[l,m,\tilde{l},\tilde{m},t,u,v+1]\Big\} \\
-\frac{(l+|m|)}{(l-|m|+1)}\Big\{\frac{1}{(2\gamma)^2}\Big(F_{xy}^{AA}[l-1,m,\tilde{l},\tilde{m},t-2,u,v] \\
+F_{xy}^{AA}[l-1,m,\tilde{l},\tilde{m},t,u-2,v]+F_{xy}^{AA}[l-1,m,\tilde{l},\tilde{m},t,u,v-2]\Big) \\
+\frac{1}{\gamma}\Big((P_x-A_x)F_{xy}^{AA}[l-1,m,\tilde{l},\tilde{m},t-1,u,v]-G_x^{A}[l-1,m,\tilde{l},\tilde{m},t,u-1,v] \\
-G_y^{A}[l-1,m,\tilde{l},\tilde{m},t-1,u,v]+(P_y-A_y)F_{xy}^{AA}[l-1,m,\tilde{l},\tilde{m},t,u-1,v] \\
+(P_z-A_z)F_{xy}^{AA}[l-1,m,\tilde{l},\tilde{m},t,u,v-1]\Big)+\Big(|\mathbf{P}-\mathbf{A}|^2+\frac{1}{\gamma}(t+u+v+\frac{3}{2})\Big) \\
\times F_{xy}^{AA}[l-1,m,\tilde{l},\tilde{m},t,u,v]-2(P_x-A_x)G_y^{A}[l-1,m,\tilde{l},\tilde{m},t,u,v] \\
-2(P_y-A_y)G_x^{A}[l-1,m,\tilde{l},\tilde{m},t,u,v]+2(t+1)(P_x-A_x)F_{xy}^{AA}[l-1,m,\tilde{l},\tilde{m},t+1,u,v] \\
+2(u+1)(P_y-A_y)F_{xy}^{AA}[l-1,m,\tilde{l},\tilde{m},t,u+1,v] \\
+2(v+1)(P_z-A_z)F_{xy}^{AA}[l-1,m,\tilde{l},\tilde{m},t,u,v+1] \\
-2(t+1)G_y^{A}[l-1,m,\tilde{l},\tilde{m},t+1,u,v]-2(u+1)G_x^{A}[l-1,m,\tilde{l},\tilde{m},t,u+1,v] \\
+(t+2)(t+1)F_{xy}^{AA}[l-1,m,\tilde{l},\tilde{m},t+2,u,v] \\
+(u+2)(u+1)F_{xy}^{AA}[l-1,m,\tilde{l},\tilde{m},t,u+2,v]+ \\
(v+2)(v+1)F_{xy}^{AA}[l-1,m,\tilde{l},\tilde{m},t,u,v+2]\Big\} \qquad \text{(B.66)}
\end{aligned}
$$

B.3.15 Recursions in l: Derivative in xz

$$\begin{aligned}
F^{AA}_{xz}[l+1,m,\tilde{l},\tilde{m},t,u,v] = {}& \frac{(2l+1)}{(l-|m|+1)}\Big\{\frac{1}{2\gamma}F^{AA}_{xz}[l,m,\tilde{l},\tilde{m},t,u,v-1] \\
& -G^{A}_{x}[l,m,\tilde{l},\tilde{m},t,u,v] + (P_z-A_z)F^{AA}_{xz}[l,m,\tilde{l},\tilde{m},t,u,v] \\
& +(v+1)F^{AA}_{xz}[l,m,\tilde{l},\tilde{m},t,u,v+1]\Big\} \\
& -\frac{(l+|m|)}{(l-|m|+1)}\Big\{\frac{1}{(2\gamma)^2}\Big(F^{AA}_{xz}[l-1,m,\tilde{l},\tilde{m},t-2,u,v] \\
& +F^{AA}_{xz}[l-1,m,\tilde{l},\tilde{m},t,u-2,v] + F^{AA}_{xz}[l-1,m,\tilde{l},\tilde{m},t,u,v-2]\Big) \\
& +\frac{1}{\gamma}\Big((P_x-A_x)F^{AA}_{xz}[l-1,m,\tilde{l},\tilde{m},t-1,u,v] - G^{A}_{z}[l-1,m,\tilde{l},\tilde{m},t-1,u,v] \\
& +(P_y-A_y)F^{AA}_{xz}[l-1,m,\tilde{l},\tilde{m},t,u-1,v] - G^{A}_{x}[l-1,m,\tilde{l},\tilde{m},t,u,v-1] \\
& +(P_z-A_z)F^{AA}_{xz}[l-1,m,\tilde{l},\tilde{m},t,u,v-1]\Big) + \Big(|\mathbf{P}-\mathbf{A}|^2 + \frac{1}{\gamma}(t+u+v+\frac{3}{2})\Big) \\
& F^{AA}_{xz}[l-1,m,\tilde{l},\tilde{m},t,u,v] - 2(P_z-A_z)G^{A}_{x}[l-1,m,\tilde{l},\tilde{m},t,u,v] \\
& -2(P_x-A_x)G^{A}_{z}[l-1,m,\tilde{l},\tilde{m},t,u,v] \\
& +2(t+1)(P_x-A_x)F^{AA}_{xz}[l-1,m,\tilde{l},\tilde{m},t+1,u,v] \\
& +2(u+1)(P_y-A_y)F^{AA}_{xz}[l-1,m,\tilde{l},\tilde{m},t,u+1,v] \\
& -2(v+1)G^{A}_{x}[l-1,m,\tilde{l},\tilde{m},t,u,v+1] \\
& +2(v+1)(P_z-A_z)F^{AA}_{xz}[l-1,m,\tilde{l},\tilde{m},t,u,v+1] \\
& -2(t+1)G^{A}_{z}[l-1,m,\tilde{l},\tilde{m},t+1,u,v] \\
& +(t+2)(t+1)F^{AA}_{xz}[l-1,m,\tilde{l},\tilde{m},t+2,u,v] \\
& +(u+2)(u+1)F^{AA}_{xz}[l-1,m,\tilde{l},\tilde{m},t,u+2,v] \\
& +(v+2)(v+1)F^{AA}_{xz}[l-1,m,\tilde{l},\tilde{m},t,u,v+2]\Big\}
\end{aligned} \tag{B.67}$$

B.3.16 Recursions in l: Derivative in yy

$$
\begin{aligned}
F_{yy}^{AA}[l+1,m,\tilde{l},\tilde{m},t,u,v] = \frac{(2l+1)}{(l-|m|+1)}\Big\{&\frac{1}{2\gamma}F_{yy}^{AA}[l,m,\tilde{l},\tilde{m},t,u,v-1]\\
&+(P_z-A_z)F_{yy}^{AA}[l,m,\tilde{l},\tilde{m},t,u,v]+(v+1)F_{yy}^{AA}[l,m,\tilde{l},\tilde{m},t,u,v+1]\Big\}\\
&-\frac{(l+|m|)}{(l-|m|+1)}\Big\{\frac{1}{(2\gamma)^2}\Big(F_{yy}^{AA}[l-1,m,\tilde{l},\tilde{m},t-2,u,v]\\
&+F_{yy}^{AA}[l-1,m,\tilde{l},\tilde{m},t,u-2,v]+F_{yy}^{AA}[l-1,m,\tilde{l},\tilde{m},t,u,v-2]\Big)\\
&+\frac{1}{\gamma}\Big((P_x-A_x)F_{yy}^{AA}[l-1,m,\tilde{l},\tilde{m},t-1,u,v]-G_y[l-1,m,\tilde{l},\tilde{m},t,u-1,v]\\
&-G_y[l-1,m,\tilde{l},\tilde{m},t,u-1,v]+(P_y-A_y)F_{yy}^{AA}[l-1,m,\tilde{l},\tilde{m},t,u-1,v]\\
&+(P_z-A_z)F_{yy}^{AA}[l-1,m,\tilde{l},\tilde{m},t,u,v-1]\Big)+\Big(|\mathbf{P}-\mathbf{A}|^2+\frac{1}{\gamma}(t+u+v+\frac{3}{2})\Big)\\
&\times F_{yy}^{AA}[l-1,m,\tilde{l},\tilde{m},t,u,v]-2(P_y-A_y)G_y^A[l-1,m,\tilde{l},\tilde{m},t,u,v]\\
&+2E[l-1,m,\tilde{l},\tilde{m},t,u,v]-2(P_y-A_y)G_y^A[l-1,m,\tilde{l},\tilde{m},t,u,v]\\
&+2(t+1)(P_x-A_x)F_{yy}^{AA}[l-1,m,\tilde{l},\tilde{m},t+1,u,v]\\
&+2(u+1)(P_y-A_y)F_{yy}^{AA}[l-1,m,\tilde{l},\tilde{m},t,u+1,v]\\
&+2(v+1)(P_z-A_z)F_{yy}^{AA}[l-1,m,\tilde{l},\tilde{m},t,u,v+1]\\
&-2(u+1)G_y^A[l-1,m,\tilde{l},\tilde{m},t,u+1,v]-2(u+1)G_y^A[l-1,m,\tilde{l},\tilde{m},t,u+1,v]\\
&+(t+2)(t+1)F_{yy}^{AA}[l-1,m,\tilde{l},\tilde{m},t+2,u,v]\\
&+(u+2)(u+1)F_{yy}^{AA}[l-1,m,\tilde{l},\tilde{m},t,u+2,v]\\
&+(v+2)(v+1)F_{yy}^{AA}[l-1,m,\tilde{l},\tilde{m},t,u,v+2]\Big\}
\end{aligned}
\tag{B.68}
$$

B.3.17 Recursions in l: Derivative in yz

$$
\begin{aligned}
F_{yz}^{AA}[l+1,m,\tilde{l},\tilde{m},t,u,v] = \frac{(2l+1)}{(l-|m|+1)}\Big\{ & \frac{1}{2\gamma}F_{yz}^{AA}[l,m,\tilde{l},\tilde{m},t,u,v-1] \\
& -G_y^{A}[l,m,\tilde{l},\tilde{m},t,u,v] + (P_z-A_z)F_{yz}^{AA}[l,m,\tilde{l},\tilde{m},t,u,v] \\
& +(v+1)F_{yz}^{AA}[l,m,\tilde{l},\tilde{m},t,u,v+1]\Big\} \\
& -\frac{(l+|m|)}{(l-|m|+1)}\Big\{\frac{1}{(2\gamma)^2}\Big(F_{yz}^{AA}[l-1,m,\tilde{l},\tilde{m},t-2,u,v] \\
& +F_{yz}^{AA}[l-1,m,\tilde{l},\tilde{m},t,u-2,v] + F_{yz}^{AA}[l-1,m,\tilde{l},\tilde{m},t,u,v-2]\Big) \\
& +\frac{1}{\gamma}\Big((P_x-A_x)F_{yz}^{AA}[l-1,m,\tilde{l},\tilde{m},t-1,u,v] - G_z^{A}[l-1,m,\tilde{l},\tilde{m},t,u-1,v] \\
& +(P_y-A_y)F_{yz}^{AA}[l-1,m,\tilde{l},\tilde{m},t,u-1,v] - G_y^{A}[l-1,m,\tilde{l},\tilde{m},t,u,v-1] \\
& +(P_z-A_z)F_{yz}^{AA}[l-1,m,\tilde{l},\tilde{m},t,u,v-1]\Big) + \Big(|\mathbf{P}-\mathbf{A}|^2 + \frac{1}{\gamma}(t+u+v+\frac{3}{2})\Big) \\
& F_{yz}^{AA}[l-1,m,\tilde{l},\tilde{m},t,u,v] - 2(P_z-A_z)G_y^{A}[l-1,m,\tilde{l},\tilde{m},t,u,v] \\
& -2(P_y-A_y)G_z^{A}[l-1,m,\tilde{l},\tilde{m},t,u,v] \\
& +2(t+1)(P_x-A_x)F_{yz}^{AA}[l-1,m,\tilde{l},\tilde{m},t+1,u,v] \\
& +2(u+1)(P_y-A_y)F_{yz}^{AA}[l-1,m,\tilde{l},\tilde{m},t,u+1,v] \\
& -2(v+1)G_y^{A}[l-1,m,\tilde{l},\tilde{m},t,u,v+1] \\
& +2(v+1)(P_z-A_z)F_{yz}^{AA}[l-1,m,\tilde{l},\tilde{m},t,u,v+1] \\
& -2(u+1)G_z^{A}[l-1,m,\tilde{l},\tilde{m},t,u+1,v] \\
& +(t+2)(t+1)F_{yz}^{AA}[l-1,m,\tilde{l},\tilde{m},t+2,u,v] \\
& +(u+2)(u+1)F_{yz}^{AA}[l-1,m,\tilde{l},\tilde{m},t,u+2,v] \\
& +(v+2)(v+1)F_{yz}^{AA}[l-1,m,\tilde{l},\tilde{m},t,u,v+2]\Big\}
\end{aligned}
\tag{B.69}
$$

B.3.18 Recursions in l: Derivative in zz

$$
\begin{aligned}
F_{zz}^{AA}[l+1,m,\tilde{l},\tilde{m},t,u,v] &= \frac{(2l+1)}{(l-|m|+1)}\Big\{\frac{1}{2\gamma}F_{zz}^{AA}[l,m,\tilde{l},\tilde{m},t,u,v-1] \\
&\quad -G_{z}^{A}[l,m,\tilde{l},\tilde{m},t,u,v]-G_{z}^{A}[l,m,\tilde{l},\tilde{m},t,u,v] \\
&\quad +(P_z-A_z)F_{zz}^{AA}[l,m,\tilde{l},\tilde{m},t,u,v]+(v+1)F_{zz}^{AA}[l,m,\tilde{l},\tilde{m},t,u,v+1]\Big\} \\
&\quad -\frac{(l+|m|)}{(l-|m|+1)}\Big\{\frac{1}{(2\gamma)^2}\Big(F_{zz}^{AA}[l-1,m,\tilde{l},\tilde{m},t-2,u,v] \\
&\quad +F_{zz}^{AA}[l-1,m,\tilde{l},\tilde{m},t,u-2,v]+F_{zz}^{AA}[l-1,m,\tilde{l},\tilde{m},t,u,v-2]\Big) \\
&\quad +\frac{1}{\gamma}\Big((P_x-A_x)F_{zz}^{AA}[l-1,m,\tilde{l},\tilde{m},t-1,u,v]-G_{z}^{A}[l-1,m,\tilde{l},\tilde{m},t,u,v-1] \\
&\quad -G_{z}^{A}[l-1,m,\tilde{l},\tilde{m},t,u,v-1]+(P_y-A_y)F_{zz}^{AA}[l-1,m,\tilde{l},\tilde{m},t,u-1,v] \\
&\quad +(P_z-A_z)F_{zz}^{AA}[l-1,m,\tilde{l},\tilde{m},t,u,v-1]\Big) \\
&\quad +\Big(|\mathbf{P}-\mathbf{A}|^2+\frac{1}{\gamma}(t+u+v+\frac{3}{2})\Big) \\
&\quad \times F_{zz}^{AA}[l-1,m,\tilde{l},\tilde{m},t,u,v]-2(P_z-A_z)G_{z}^{A}[l-1,m,\tilde{l},\tilde{m},t,u,v] \\
&\quad +2E[l-1,m,\tilde{l},\tilde{m},t,u,v]-2(P_z-A_z)G_{z}^{A}[l-1,m,\tilde{l},\tilde{m},t,u,v] \\
&\quad +2(t+1)(P_x-A_x)F_{zz}^{AA}[l-1,m,\tilde{l},\tilde{m},t+1,u,v] \\
&\quad +2(u+1)(P_y-A_y)F_{zz}^{AA}[l-1,m,\tilde{l},\tilde{m},t,u+1,v] \\
&\quad -2(v+1)G_{z}^{A}[l-1,m,\tilde{l},\tilde{m},t,u,v+1] \\
&\quad +2(v+1)(P_z-A_z)F_{zz}^{AA}[l-1,m,\tilde{l},\tilde{m},t,u,v+1] \\
&\quad -2(v+1)G_{z}^{A}[l-1,m,\tilde{l},\tilde{m},t,u,v+1] \\
&\quad +(t+2)(t+1)F_{zz}^{AA}[l-1,m,\tilde{l},\tilde{m},t+2,u,v] \\
&\quad +(u+2)(u+1)F_{zz}^{AA}[l-1,m,\tilde{l},\tilde{m},t,u+2,v] \\
&\quad +(v+2)(v+1)F_{zz}^{AA}[l-1,m,\tilde{l},\tilde{m},t,u,v+2]\Big\}
\end{aligned}
\tag{B.70}
$$

B.3.19 Recursions in n: Derivative in xx

$$\begin{aligned}
F^{AA}_{xx}[n+1,l,m,\tilde{n},\tilde{l},\tilde{m},t,u,v] &= \frac{1}{(2\gamma)^2}\Big(F^{AA}_{xx}[n,l,m,\tilde{n},\tilde{l},\tilde{m},t-2,u,v] \\
&+F^{AA}_{xx}[n,l,m,\tilde{n},\tilde{l},\tilde{m},t,u-2,v] + F^{AA}_{xx}[n,l,m,\tilde{n},\tilde{l},\tilde{m},t,u,v-2]\Big) \\
&+\frac{1}{\gamma}\Big(-G^{A}_{x}[n,l,m,\tilde{n},\tilde{l},\tilde{m},t-1,u,v] - G^{A}_{x}[n,l,m,\tilde{n},\tilde{l},\tilde{m},t-1,u,v] \\
&+(P_x-A_x)F^{AA}_{xx}[n,l,m,\tilde{n},\tilde{l},\tilde{m},t-1,u,v] + (P_y-A_y)F^{AA}_{xx}[n,l,m,\tilde{n},\tilde{l},\tilde{m},t,u-1,v] \\
&+(P_z-A_z)F^{AA}_{xx}[n,l,m,\tilde{n},\tilde{l},\tilde{m},t,u,v-1]\Big) + \Big(|\mathbf{P}-\mathbf{A}|^2 + \frac{1}{\gamma}(t+u+v+\frac{3}{2})\Big) \\
&F^{AA}_{xx}[n,l,m,\tilde{n},\tilde{l},\tilde{m},t,u,v] - 2E[n,l,m,\tilde{n},\tilde{l},\tilde{m},t,u,v] \\
&-2(P_x-A_x)G^{A}_{x}[n,l,m,\tilde{n},\tilde{l},\tilde{m},t,u,v] - 2(P_x-A_x)G^{A}_{x}[n,l,m,\tilde{n},\tilde{l},\tilde{m},t,u,v] \\
&+2(t+1)(P_x-A_x)F^{AA}_{xx}[n,l,m,\tilde{n},\tilde{l},\tilde{m},t+1,u,v] + 2(u+1)(P_y-A_y)F^{AA}_{xx}[n,l,m,\tilde{n},\tilde{l},\tilde{m},t,u+1,v] \\
&+2(v+1)(P_z-A_z)F^{AA}_{xx}[n,l,m,\tilde{n},\tilde{l},\tilde{m},t,u,v+1] - 2(t+1)G^{A}_{x}[n,l,m,\tilde{n},\tilde{l},\tilde{m},t+1,u,v] \\
&-2(t+1)G^{A}_{x}[n,l,m,\tilde{n},\tilde{l},\tilde{m},t+1,u,v] + (t+2)(t+1)F^{AA}_{xx}[n,l,m,\tilde{n},\tilde{l},\tilde{m},t+2,u,v] \\
&+(u+2)(u+1)F^{AA}_{xx}[n,l,m,\tilde{n},\tilde{l},\tilde{m},t,u+2,v] + (v+2)(v+1)F^{AA}_{xx}[n,l,m,\tilde{n},\tilde{l},\tilde{m},t,u,v+2]
\end{aligned} \tag{B.71}$$

B.3.20 Recursions in n: Derivative in xy

$$\begin{aligned}
F^{AA}_{xy}[n+1,l,m,\tilde{n},\tilde{l},\tilde{m},t,u,v] &= \frac{1}{(2\gamma)^2}\Big(F^{AA}_{xy}[n,l,m,\tilde{n},\tilde{l},\tilde{m},t-2,u,v] \\
&+F^{AA}_{xy}[n,l,m,\tilde{n},\tilde{l},\tilde{m},t,u-2,v] + F^{AA}_{xy}[n,l,m,\tilde{n},\tilde{l},\tilde{m},t,u,v-2]\Big) \\
&+\frac{1}{\gamma}\Big(-G^{A}_{x}[n,l,m,\tilde{n},\tilde{l},\tilde{m},t,u-1,v] - G^{A}_{y}[n,l,m,\tilde{n},\tilde{l},\tilde{m},t-1,u,v] \\
&+(P_x-A_x)F^{AA}_{xy}[n,l,m,\tilde{n},\tilde{l},\tilde{m},t-1,u,v] + (P_y-A_y)F^{AA}_{xy}[n,l,m,\tilde{n},\tilde{l},\tilde{m},t,u-1,v] \\
&+(P_z-A_z)F^{AA}_{xy}[n,l,m,\tilde{n},\tilde{l},\tilde{m},t,u,v-1]\Big) + \Big(|\mathbf{P}-\mathbf{A}|^2 + \frac{1}{\gamma}(t+u+v+\frac{3}{2})\Big) \\
&\times F^{AA}_{xy}[n,l,m,\tilde{n},\tilde{l},\tilde{m},t,u,v] - 2(P_y-A_y)G^{A}_{x}[n,l,m,\tilde{n},\tilde{l},\tilde{m},t,u,v] \\
&-2(P_x-A_x)G^{A}_{y}[n,l,m,\tilde{n},\tilde{l},\tilde{m},t,u,v] + 2(t+1)(P_x-A_x)F^{AA}_{xy}[n,l,m,\tilde{n},\tilde{l},\tilde{m},t+1,u,v] \\
&+2(u+1)(P_y-A_y)F^{AA}_{xy}[n,l,m,\tilde{n},\tilde{l},\tilde{m},t,u+1,v] + 2(v+1)(P_z-A_z)F^{AA}_{xy}[n,l,m,\tilde{n},\tilde{l},\tilde{m},t,u,v+1] \\
&-2(t+1)G^{A}_{y}[n,l,m,\tilde{n},\tilde{l},\tilde{m},t+1,u,v] - 2(u+1)G^{A}_{x}[n,l,m,\tilde{n},\tilde{l},\tilde{m},t,u+1,v] \\
&+(t+2)(t+1)F^{AA}_{xy}[n,l,m,\tilde{n},\tilde{l},\tilde{m},t+2,u,v] + (u+2)(u+1)F^{AA}_{xy}[n,l,m,\tilde{n},\tilde{l},\tilde{m},t,u+2,v] \\
&+(v+2)(v+1)F^{AA}_{xy}[n,l,m,\tilde{n},\tilde{l},\tilde{m},t,u,v+2]
\end{aligned} \tag{B.72}$$

B.3.21 Recursions in n: Derivative in xz

$$
\begin{aligned}
F_{xz}^{AA}[n+1,l,m,\tilde{n},\tilde{l},\tilde{m},t,u,v] = {} & \frac{1}{(2\gamma)^2}\Big(F_{xz}^{AA}[n,l,m,\tilde{n},\tilde{l},\tilde{m},t-2,u,v] \\
& +F_{xz}^{AA}[n,l,m,\tilde{n},\tilde{l},\tilde{m},t,u-2,v] + F_{xz}^{AA}[n,l,m,\tilde{n},\tilde{l},\tilde{m},t,u,v-2]\Big) \\
& +\frac{1}{\gamma}\Big(-G_x^{A}[n,l,m,\tilde{n},\tilde{l},\tilde{m},t,u,v-1] - G_z^{A}[n,l,m,\tilde{n},\tilde{l},\tilde{m},t-1,u,v] \\
& +(P_x-A_x)F_{xz}^{AA}[n,l,m,\tilde{n},\tilde{l},\tilde{m},t-1,u,v] + (P_y-A_y)F_{xz}^{AA}[n,l,m,\tilde{n},\tilde{l},\tilde{m},t,u-1,v] \\
& +(P_z-A_z)F_{xz}^{AA}[n,l,m,\tilde{n},\tilde{l},\tilde{m},t,u,v-1]\Big) + \Big(|\mathbf{P}-\mathbf{A}|^2 + \frac{1}{\gamma}(t+u+v+\frac{3}{2})\Big) \\
& \times F_{xz}^{AA}[n,l,m,\tilde{n},\tilde{l},\tilde{m},t,u,v] - 2(P_z-A_z)G_x^{A}[n,l,m,\tilde{n},\tilde{l},\tilde{m},t,u,v] \\
& -2(P_x-A_x)G_z^{A}[n,l,m,\tilde{n},\tilde{l},\tilde{m},t,u,v] + 2(t+1)(P_x-A_x)F_{xz}^{AA}[n,l,m,\tilde{n},\tilde{l},\tilde{m},t+1,u,v] \\
& +2(u+1)(P_y-A_y)F_{xz}^{AA}[n,l,m,\tilde{n},\tilde{l},\tilde{m},t,u+1,v] + 2(v+1)(P_z-A_z)F_{xz}^{AA}[n,l,m,\tilde{n},\tilde{l},\tilde{m},t,u,v+1] \\
& -2(t+1)G_z^{A}[n,l,m,\tilde{n},\tilde{l},\tilde{m},t+1,u,v] - 2(v+1)G_x^{A}[n,l,m,\tilde{n},\tilde{l},\tilde{m},t,u,v+1] \\
& +(t+2)(t+1)F_{xz}^{AA}[n,l,m,\tilde{n},\tilde{l},\tilde{m},t+2,u,v] + (u+2)(u+1)F_{xz}^{AA}[n,l,m,\tilde{n},\tilde{l},\tilde{m},t,u+2,v] \\
& +(v+2)(v+1)F_{xz}^{AA}[n,l,m,\tilde{n},\tilde{l},\tilde{m},t,u,v+2]
\end{aligned}
\tag{B.73}
$$

B.3.22 Recursions in n: Derivative in yy

$$
\begin{aligned}
F_{yy}^{AA}[n+1,l,m,\tilde{n},\tilde{l},\tilde{m},t,u,v] = {} & \frac{1}{(2\gamma)^2}\Big(F_{yy}^{AA}[n,l,m,\tilde{n},\tilde{l},\tilde{m},t-2,u,v] \\
& +F_{yy}^{AA}[n,l,m,\tilde{n},\tilde{l},\tilde{m},t,u-2,v] + F_{yy}^{AA}[n,l,m,\tilde{n},\tilde{l},\tilde{m},t,u,v-2]\Big) \\
& +\frac{1}{\gamma}\Big(-G_y^{A}[n,l,m,\tilde{n},\tilde{l},\tilde{m},t,u-1,v] - G_y^{A}[n,l,m,\tilde{n},\tilde{l},\tilde{m},t,u-1,v] \\
& +(P_x-A_x)F_{yy}^{AA}[n,l,m,\tilde{n},\tilde{l},\tilde{m},t-1,u,v] + (P_y-A_y)F_{yy}^{AA}[n,l,m,\tilde{n},\tilde{l},\tilde{m},t,u-1,v] \\
& +(P_z-A_z)F_{yy}^{AA}[n,l,m,\tilde{n},\tilde{l},\tilde{m},t,u,v-1]\Big) + \Big(|\mathbf{P}-\mathbf{A}|^2 + \frac{1}{\gamma}(t+u+v+\frac{3}{2})\Big) \\
& F_{yy}^{AA}[n,l,m,\tilde{n},\tilde{l},\tilde{m},t,u,v] - 2E[n,l,m,\tilde{n},\tilde{l},\tilde{m},t,u,v] \\
& -2(P_y-A_y)G_y^{A}[n,l,m,\tilde{n},\tilde{l},\tilde{m},t,u,v] - 2(P_y-A_y)G_y^{A}[n,l,m,\tilde{n},\tilde{l},\tilde{m},t,u,v] \\
& +2(t+1)(P_x-A_x)F_{yy}^{AA}[n,l,m,\tilde{n},\tilde{l},\tilde{m},t+1,u,v] + 2(u+1)(P_y-A_y)F_{yy}^{AA}[n,l,m,\tilde{n},\tilde{l},\tilde{m},t,u+1,v] \\
& +2(v+1)(P_z-A_z)F_{yy}^{AA}[n,l,m,\tilde{n},\tilde{l},\tilde{m},t,u,v+1] - 2(u+1)G_y^{A}[n,l,m,\tilde{n},\tilde{l},\tilde{m},t,u+1,v] \\
& -2(u+1)G_y^{A}[n,l,m,\tilde{n},\tilde{l},\tilde{m},t,u+1,v] + (t+2)(t+1)F_{yy}^{AA}[n,l,m,\tilde{n},\tilde{l},\tilde{m},t+2,u,v] \\
& +(u+2)(u+1)F_{yy}^{AA}[n,l,m,\tilde{n},\tilde{l},\tilde{m},t,u+2,v] + (v+2)(v+1)F_{yy}^{AA}[n,l,m,\tilde{n},\tilde{l},\tilde{m},t,u,v+2]
\end{aligned}
\tag{B.74}
$$

B.3.23 Recursions in n: Derivative in yz

$$
\begin{aligned}
F_{yz}^{AA}[n+1,l,m,\tilde{n},\tilde{l},\tilde{m},t,u,v] = \frac{1}{(2\gamma)^2}\Big(&F_{yz}^{AA}[n,l,m,\tilde{n},\tilde{l},\tilde{m},t-2,u,v] \\
&+F_{yz}^{AA}[n,l,m,\tilde{n},\tilde{l},\tilde{m},t,u-2,v] + F_{yz}^{AA}[n,l,m,\tilde{n},\tilde{l},\tilde{m},t,u,v-2]\Big) \\
&+\frac{1}{\gamma}\Big(- G_{y}^{A}[n,l,m,\tilde{n},\tilde{l},\tilde{m},t,u,v-1] - G_{z}^{A}[n,l,m,\tilde{n},\tilde{l},\tilde{m},t,u-1,v] \\
&+(P_x - A_x)F_{yz}^{AA}[n,l,m,\tilde{n},\tilde{l},\tilde{m},t-1,u,v] + (P_y - A_y)F_{yz}^{AA}[n,l,m,\tilde{n},\tilde{l},\tilde{m},t,u-1,v] \\
&+(P_z - A_z)F_{yz}^{AA}[n,l,m,\tilde{n},\tilde{l},\tilde{m},t,u,v-1]\Big) + \Big(|\mathbf{P}-\mathbf{A}|^2 + \frac{1}{\gamma}(t+u+v+\frac{3}{2})\Big) \\
&\times F_{yz}^{AA}[n,l,m,\tilde{n},\tilde{l},\tilde{m},t,u,v] - 2(P_z - A_z)G_{y}^{A}[n,l,m,\tilde{n},\tilde{l},\tilde{m},t,u,v] \\
&-2(P_y - A_y)G_{z}^{A}[n,l,m,\tilde{n},\tilde{l},\tilde{m},t,u,v] + 2(t+1)(P_x - A_x)F_{yz}^{AA}[n,l,m,\tilde{n},\tilde{l},\tilde{m},t+1,u,v] \\
&+2(u+1)(P_y - A_y)F_{yz}^{AA}[n,l,m,\tilde{n},\tilde{l},\tilde{m},t,u+1,v] + 2(v+1)(P_z - A_z)F_{yz}^{AA}[n,l,m,\tilde{n},\tilde{l},\tilde{m},t,u,v+1] \\
&-2(u+1)G_{z}^{A}[n,l,m,\tilde{n},\tilde{l},\tilde{m},t,u+1,v] - 2(v+1)G_{y}^{A}[n,l,m,\tilde{n},\tilde{l},\tilde{m},t,u,v+1] \\
&+(t+2)(t+1)F_{yz}^{AA}[n,l,m,\tilde{n},\tilde{l},\tilde{m},t+2,u,v] + (u+2)(u+1)F_{yz}^{AA}[n,l,m,\tilde{n},\tilde{l},\tilde{m},t,u+2,v] \\
&+(v+2)(v+1)F_{yz}^{AA}[n,l,m,\tilde{n},\tilde{l},\tilde{m},t,u,v+2]
\end{aligned} \tag{B.75}
$$

B.3.24 Recursions in n: Derivative in zz

$$
\begin{aligned}
F_{zz}^{AA}[n+1,l,m,\tilde{n},\tilde{l},\tilde{m},t,u,v] = \frac{1}{(2\gamma)^2}\Big(&F_{zz}^{AA}[n,l,m,\tilde{n},\tilde{l},\tilde{m},t-2,u,v] \\
&+F_{zz}^{AA}[n,l,m,\tilde{n},\tilde{l},\tilde{m},t,u-2,v] + F_{zz}^{AA}[n,l,m,\tilde{n},\tilde{l},\tilde{m},t,u,v-2]\Big) \\
&+\frac{1}{\gamma}\Big(- G_{z}^{A}[n,l,m,\tilde{n},\tilde{l},\tilde{m},t,u,v-1] - G_{z}^{A}[n,l,m,\tilde{n},\tilde{l},\tilde{m},t,u,v-1] \\
&+(P_x - A_x)F_{zz}^{AA}[n,l,m,\tilde{n},\tilde{l},\tilde{m},t-1,u,v] + (P_y - A_y)F_{zz}^{AA}[n,l,m,\tilde{n},\tilde{l},\tilde{m},t,u-1,v] \\
&+(P_z - A_z)F_{zz}^{AA}[n,l,m,\tilde{n},\tilde{l},\tilde{m},t,u,v-1]\Big) + \Big(|\mathbf{P}-\mathbf{A}|^2 + \frac{1}{\gamma}(t+u+v+\frac{3}{2})\Big) \\
&F_{zz}^{AA}[n,l,m,\tilde{n},\tilde{l},\tilde{m},t,u,v] - 2E[n,l,m,\tilde{n},\tilde{l},\tilde{m},t,u,v] \\
&-2(P_z - A_z)G_{z}^{A}[n,l,m,\tilde{n},\tilde{l},\tilde{m},t,u,v] - 2(P_z - A_z)G_{z}^{A}[n,l,m,\tilde{n},\tilde{l},\tilde{m},t,u,v] \\
&+2(t+1)(P_x - A_x)F_{zz}^{AA}[n,l,m,\tilde{n},\tilde{l},\tilde{m},t+1,u,v] + 2(u+1)(P_y - A_y)F_{zz}^{AA}[n,l,m,\tilde{n},\tilde{l},\tilde{m},t,u+1,v] \\
&+2(v+1)(P_z - A_z)F_{zz}^{AA}[n,l,m,\tilde{n},\tilde{l},\tilde{m},t,u,v+1] - 2(v+1)G_{z}^{A}[n,l,m,\tilde{n},\tilde{l},\tilde{m},t,u,v+1] \\
&-2(v+1)G_{z}^{A}[n,l,m,\tilde{n},\tilde{l},\tilde{m},t,u,v+1] + (t+2)(t+1)F_{zz}^{AA}[n,l,m,\tilde{n},\tilde{l},\tilde{m},t+2,u,v] \\
&+(u+2)(u+1)F_{zz}^{AA}[n,l,m,\tilde{n},\tilde{l},\tilde{m},t,u+2,v] + (v+2)(v+1)F_{zz}^{AA}[n,l,m,\tilde{n},\tilde{l},\tilde{m},t,u,v+2]
\end{aligned} \tag{B.76}
$$

C Calculating the Coulomb Term in a Two-Component SCF

The relativistic (Hermitian-complex) density matrix D has the form:

$$D = \begin{pmatrix} D^{\alpha\alpha} & D^{\alpha\beta} \\ D^{\beta\alpha} & D^{\beta\beta} \end{pmatrix}, \tag{C.1}$$

The matrix D is built from the occupied spin-orbitals:

$$D_{\mu\nu} = \sum_{i}^{occ} c^{*}_{\mu i} c_{\nu i} \tag{C.2}$$

The Hermitian-complex Fock matrix F has a similar structure:

$$F = \begin{pmatrix} F^{\alpha\alpha} & F^{\alpha\beta} \\ F^{\beta\alpha} & F^{\beta\beta} \end{pmatrix}, \tag{C.3}$$

An element of the Fock matrix $F_{\mu\nu}$ is built from mono-electronic contributions $h_{\mu\nu}$ and bielectronic contributions $B_{\mu\nu}$:

$$F_{\mu\nu} = h_{\mu\nu} + B_{\mu\nu} = h_{\mu\nu} + C_{\mu\nu} - X_{\mu\nu} = h_{\mu\nu} + \sum_{\sigma\rho} \{(\mu\nu|\sigma\rho) - (\mu\sigma|\nu\rho)\} D_{\sigma\rho} \tag{C.4}$$

where $(\mu\nu|\sigma\rho)$ and $(\mu\sigma|\nu\rho)$ are bielectronic integrals, and greek letters represents a combination of indices for spin-space coordinates. The two bielectronic terms above refer to Coulomb ($C_{\mu\nu}$) and exchange ($X_{\mu\nu}$) contributions, respectively. The integration over spin-coordinates results in only the following bielectronic integrals having non-zero contributions:

$$(\alpha\alpha|\beta\beta), (\alpha\alpha|\alpha\alpha), (\beta\beta|\beta\beta), (\beta\beta|\alpha\alpha) \tag{C.5}$$

Substituting (5) in (4) we find:

$$F^{\alpha\alpha}_{\mu\nu} = h^{\alpha\alpha}_{\mu\nu} + \sum_{\sigma\rho} (\mu\nu|\sigma\rho) \left(D^{\alpha\alpha}_{\sigma\rho} + D^{\beta\beta}_{\sigma\rho} \right) - \sum_{\sigma\rho} (\mu\sigma|\nu\rho) D^{\alpha\alpha}_{\sigma\rho} \tag{C.6}$$

$$F^{\beta\beta}_{\mu\nu} = h^{\beta\beta}_{\mu\nu} + \sum_{\sigma\rho} (\mu\nu|\sigma\rho) \left(D^{\alpha\alpha}_{\sigma\rho} + D^{\beta\beta}_{\sigma\rho} \right) - \sum_{\sigma\rho} (\mu\sigma|\nu\rho) D^{\beta\beta}_{\sigma\rho} \tag{C.7}$$

$$F^{\alpha\beta}_{\mu\nu} = h^{\alpha\beta}_{\mu\nu} - \sum_{\sigma\rho} (\mu\sigma|\nu\rho) D^{\beta\alpha}_{\sigma\rho} \tag{C.8}$$

$$F^{\beta\alpha}_{\mu\nu} = h^{\beta\alpha}_{\mu\nu} - \sum_{\sigma\rho} (\mu\sigma|\nu\rho) D^{\alpha\beta}_{\sigma\rho} \tag{C.9}$$

So the only surviving Coulomb contribution is the same second term appearing above in equations (6) and (7). All other terms in equations (6)-(9) are exchange contributions.

Let us now consider this Coulomb contribution:

$$C_{\mu\nu} = \sum_{\sigma\rho}(\mu\nu|\sigma\rho)(D^{\alpha\alpha}_{\sigma\rho} + D^{\beta\beta}_{\sigma\rho}) = \sum_{\sigma\rho} G_{\mu\nu\sigma\rho} D^{\alpha\alpha+\beta\beta}_{\sigma\rho} \tag{C.10}$$

Since $G_{\mu\nu\sigma\rho}$ is real, we have:

$$\mathrm{Re}[C_{\mu\nu}] = \sum_{\sigma\rho} G_{\mu\nu\sigma\rho}\mathrm{Re}[D^{\alpha\alpha+\beta\beta}_{\sigma\rho}] \tag{C.11}$$

$$\mathrm{Im}[C_{\mu\nu}] = \sum_{\sigma\rho} G_{\mu\nu\sigma\rho}\mathrm{Im}[D^{\alpha\alpha+\beta\beta}_{\sigma\rho}] \tag{C.12}$$

Let us first consider $\mathrm{Im}[C_{\mu\nu}]$:

$$\begin{aligned} \mathrm{Im}[C_{\mu\nu}] &= \sum_{\sigma}\sum_{\rho} G_{\mu\nu\sigma\rho}\mathrm{Im}[D^{\alpha\alpha+\beta\beta}_{\sigma\rho}] \\ &= \sum_{\sigma}\sum_{\rho<\sigma} G_{\mu\nu\sigma\rho}\mathrm{Im}[D^{\alpha\alpha+\beta\beta}_{\sigma\rho}] + \sum_{\sigma}\sum_{\rho>\sigma} G_{\mu\nu\sigma\rho}\mathrm{Im}[D^{\alpha\alpha+\beta\beta}_{\sigma\rho}], \end{aligned} \tag{C.13}$$

Now, using the Hermiticity of the $G_{\mu\nu}$ and D, we have:

$$G_{\mu\nu\sigma\rho} = G_{\mu\nu\rho\sigma}, \tag{C.14}$$

and

$$\mathrm{Im}[D^{\alpha\alpha+\beta\beta}_{\sigma\rho}] = -\mathrm{Im}[D^{\alpha\alpha+\beta\beta}_{\rho\sigma}] \tag{C.15}$$

Substituting (14) and (15) in (13):

$$\mathrm{Im}[C_{\mu\nu}] = \sum_{\sigma}\sum_{\rho<\sigma} G_{\mu\nu\sigma\rho}\mathrm{Im}[D^{\alpha\alpha+\beta\beta}_{\sigma\rho}] - \sum_{\sigma}\sum_{\rho>\sigma} G_{\mu\nu\rho\sigma}\mathrm{Im}[D^{\alpha\alpha+\beta\beta}_{\rho\sigma}] \tag{C.16}$$

Rearranging the order of the two sums in the second term above:

$$\mathrm{Im}[C_{\mu\nu}] = \sum_{\sigma}\sum_{\rho<\sigma} G_{\mu\nu\sigma\rho}\mathrm{Im}[D^{\alpha\alpha+\beta\beta}_{\sigma\rho}] - \sum_{\rho}\sum_{\sigma<\rho} G_{\mu\nu\rho\sigma}\mathrm{Im}[D^{\alpha\alpha+\beta\beta}_{\rho\sigma}] \tag{C.17}$$

Now interchanging variable names in the second term, we find:

$$\mathrm{Im}[C_{\mu\nu}] = \sum_{\sigma}\sum_{\rho<\sigma} G_{\mu\nu\sigma\rho}\mathrm{Im}[D^{\alpha\alpha+\beta\beta}_{\sigma\rho}] - \sum_{\sigma}\sum_{\rho<\sigma} G_{\mu\nu\sigma\rho}\mathrm{Im}[D^{\alpha\alpha+\beta\beta}_{\sigma\rho}] = 0 \tag{C.18}$$

Substituting (18) in (10), we conclude:

$$C_{\mu\nu} = \sum_{\sigma\rho}(\mu\nu|\sigma\rho)\mathrm{Re}(D^{\alpha\alpha}_{\sigma\rho} + D^{\beta\beta}_{\sigma\rho}) \tag{C.19}$$

So only the real part of the density matrix contributes to the Coulomb integral, similar to the non-relativistic case. The Fock matrix elements are therefore reduced to:

$$F_{\mu\nu}^{\alpha\alpha} = h_{\mu\nu}^{\alpha\alpha} + \sum_{\sigma\rho}(\mu\nu|\sigma\rho)\mathrm{Re}\Big(D_{\sigma\rho}^{\alpha\alpha} + D_{\sigma\rho}^{\beta\beta}\Big) - \sum_{\sigma\rho}(\mu\sigma|\nu\rho)D_{\sigma\rho}^{\alpha\alpha} \tag{C.20}$$

$$F_{\mu\nu}^{\beta\beta} = h_{\mu\nu}^{\beta\beta} + \sum_{\sigma\rho}(\mu\nu|\sigma\rho)\mathrm{Re}\Big(D_{\sigma\rho}^{\alpha\alpha} + D_{\sigma\rho}^{\beta\beta}\Big) - \sum_{\sigma\rho}(\mu\sigma|\nu\rho)D_{\sigma\rho}^{\beta\beta} \tag{C.21}$$

$$F_{\mu\nu}^{\alpha\beta} = h_{\mu\nu}^{\alpha\beta} - \sum_{\sigma\rho}(\mu\sigma|\nu\rho)D_{\sigma\rho}^{\beta\alpha} \tag{C.22}$$

$$F_{\mu\nu}^{\beta\alpha} = h_{\mu\nu}^{\beta\alpha} - \sum_{\sigma\rho}(\mu\sigma|\nu\rho)D_{\sigma\rho}^{\alpha\beta} \tag{C.23}$$

For calculating the Coulomb contribution to the energy in the relativistic case, we store $\mathrm{Re}(D_{\sigma\rho}^{\alpha\alpha} + D_{\sigma\rho}^{\beta\beta})$ in the variable PG_IRR in the routine named PDIG_SOC. The variable PG_IRR stores $\mathrm{Re}(D_{\sigma\rho}^{\alpha} + D_{\sigma\rho}^{\beta})$ in the non-relativistic case, so that the format is similar in both cases. PG_IRR is vectorized column-wise in shell-couple blocks. The lower-triangular half of the matrix is stored, but because it is vectorized in shell-couple blocks, PG_IRR also has upper-triangular elements in steps along the diagonal. The variable PG_IRR is then passed to the routine SHELLXCOUL, where the Coulomb contribution to the Fock matrix is calculated in the usual way.

D Calculating the Exchange Term in a Two-Component SCF

The action of the exchange operator on two Atomic-Orbitals (AOs) χ_μ and χ_ν is written as:

$$X_{\mu\nu} = \langle\chi_\mu|\hat{X}|\chi_\nu\rangle = -\frac{1}{2}\sum_{\sigma\rho}(\chi_\mu\chi_\sigma|\chi_\nu\chi_\rho)P_{\sigma\rho} \tag{D.1}$$

where:

$$(\chi_\mu\chi_\sigma|\chi_\nu\chi_\rho) = \iint \chi_\mu(\mathbf{r_1})\chi_\sigma(\mathbf{r_1})\frac{1}{|\mathbf{r_1}-\mathbf{r_2}|}\chi_\nu(\mathbf{r_2})\chi_\rho(\mathbf{r_2})\mathrm{d}\mathbf{r_1}\mathrm{d}\mathbf{r_2} \tag{D.2}$$

The matrix elements $X_{\mu\nu}$ are used in part to construct an element of the Fock matrix $F_{\mu\nu}$:

$$F_{\mu\nu} = h_{\mu\nu} + C_{\mu\nu} + X_{\mu\nu} = h_{\mu\nu} + \sum_{\sigma\rho}(\chi_\mu\chi_\nu|\chi_\sigma\chi_\rho)P_{\sigma\rho} - \frac{1}{2}\sum_{\sigma\rho}(\chi_\mu\chi_\sigma|\chi_\nu\chi_\rho)P_{\sigma\rho}, \tag{D.3}$$

where $h_{\mu\nu}$ and $C_{\mu\nu}$ are monoelectronic and Coulomb contributions, which we do not discuss here.

For calculating a matrix element $X_{\mu\nu}$, neglecting the role played by the lattice vectors, the following permutations are allowed from equation (2):

$$\chi_\mu \leftrightarrow \chi_\sigma, \quad \chi_\nu \leftrightarrow \chi_\rho \quad \text{and} \quad (\chi_\mu\chi_\sigma) \leftrightarrow (\chi_\nu\chi_\rho) \tag{D.4}$$

from an algorithmic point of view it proves convenient to contract AOs in shells. Correspondingly, the indices μ, ν, σ, ρ actually don't refer to AO indices, but rather to AO shell indices. This means that the quantity $X_{\mu\nu}$ is not a scalar, but rather a matrix of size $\{n_\mu \times n_\nu\}$, where n_μ is the # of AOs in the shell μ. Accordingly, from now on μ, ν, σ, ρ refer to AO shell indices.

The calculation of the $X_{\mu\nu}$ was historically performed in the CRYSTAL code using the SHELLXN subroutine, which calculated both the exchange and Coulomb contributions to the Fock matrix simultaneously, using the $\chi_\mu \leftrightarrow \chi_\sigma$ and $\chi_\nu \leftrightarrow \chi_\rho$ permutation relations. The SHELLXN routine, however did not use the $(\chi_\mu\chi_\sigma) \leftrightarrow (\chi_\nu\chi_\rho)$, relation as it is in general valid for the Coulomb contribution in the periodic case, but is still valid for the exchange contribution. It is nonetheless, still advantageous to calculate the Coulomb and exchange contributions simultaneously when the system has symmetry, because some Coulomb and exchange integrals can be related. However, if the system has little or no symmetry, it may become advantegeous instead to calculate the Coulomb and exchange contributions seperatly and make use of the $(\chi_\mu\chi_\sigma) \leftrightarrow (\chi_\nu\chi_\rho)$ permutation relation for the exchange part. Such a code was written in recent years, using the SHELLXCOUL SHELLEXCH subroutines to calculate the Coulomb and exchange contributions seperatly for systems with no symmetry.

The SHELLEXCH routine has 7 DO loops which extend until the end of the calculation, they are:

1. on the first shell couple sets $\chi_\mu\chi_\sigma$
2. on the stars of **h** vectors of equal length (useful for crystals, but irrelevant for molecules)

3. on the set of **h** irreducible vectors within a star (useful for crystals, but irrelevant for molecules)
4. on the second shell couple sets $\chi_\nu\chi_\rho$
5. on the daughters of the second shell couple set
6. on the stars of $\mathbf{g}'$ vectors of equal length (useful for crystals, but irrelevant for molecules)
7. on the set of $\mathbf{g}'$ irreducible vectors within a star (useful for crystals, but irrelevant for molecules)

The loop 1., on the first shell couple set scans the shell couples for which $\mu \geq \sigma$. The loop numbers 4. and 5. on the second couples scans the couples for which $\nu \geq \rho$, but also constrained to $[\mu\sigma] \geq [\nu\rho]$. Here, $[\mu\sigma] = \frac{\tilde{\mu}(\tilde{\mu}-1)}{2} + \tilde{\sigma}$, where $\tilde{\mu} = \max(\mu, \sigma)$ and $\tilde{\sigma} = \min(\mu, \sigma)$. A more expanded discussion on these inequalities is provided further on, making use of a simple example.

Each loop contains the instructions for screening of the integrals according to the T_3, T_4 and T_5 tolerances as well as calculation of preliminary quantities that are needed for the calculation of integrals (expansion in HGTF, and quantities needed for the Bipolar approximation). The integrals are then calculated either using the ATMOL or POPLE packages, or making use of the Bipolar approximation. The integrals are then multiplied with the density matrix and the result is added to the Fock matrix.

At this stage, we are inside loops over the two shell couples. In principle, the same integral could be utilized for several different elements of the Fock matrix, using the following permutation relations:

$$(\chi_\mu\chi_\sigma|\chi_\nu\chi_\rho)P_{\sigma\rho} \to F_{\mu\nu} \tag{D.5}$$

$$(\chi_\mu\chi_\sigma|\chi_\rho\chi_\nu)P_{\sigma\nu} \to F_{\mu\rho} \tag{D.6}$$

$$(\chi_\sigma\chi_\mu|\chi_\nu\chi_\rho)P_{\mu\rho} \to F_{\sigma\nu} \tag{D.7}$$

$$(\chi_\sigma\chi_\mu|\chi_\rho\chi_\nu)P_{\mu\nu} \to F_{\sigma\rho} \tag{D.8}$$

$$(\chi_\nu\chi_\rho|\chi_\mu\chi_\sigma)P_{\rho\sigma} \to F_{\nu\mu} \tag{D.9}$$

$$(\chi_\nu\chi_\rho|\chi_\sigma\chi_\mu)P_{\rho\mu} \to F_{\nu\sigma} \tag{D.10}$$

$$(\chi_\rho\chi_\nu|\chi_\mu\chi_\sigma)P_{\nu\sigma} \to F_{\rho\mu} \tag{D.11}$$

$$(\chi_\rho\chi_\nu|\chi_\sigma\chi_\mu)P_{\nu\mu} \to F_{\rho\sigma} \tag{D.12}$$

However, the code aims to build only the lower triangular half of the Fock matrix. For doing so, only the lower triangular elements of the density matrix are available. These restrictions provide additional constrains, so that only a subset of the permutation relations above are used, which are: a) relevant to calculating elements of the lower half of the Fock matrix; and b) involve elements of the lower half of the density matrix. The subset of permutation relations is as follows:

$$\begin{aligned}&\text{if}\quad \sigma \geq \rho\,(\text{utp})\quad : \\ &(\chi_\mu\chi_\sigma|\chi_\nu\chi_\rho)P_{\sigma\rho} \rightarrow F_{\mu\nu}\end{aligned} \tag{D.13}$$

$$\begin{aligned}&\text{if}\quad \sigma \geq \nu\,(\text{utp})\quad \text{and}\quad \nu \neq \rho\quad : \\ &(\chi_\mu\chi_\sigma|\chi_\rho\chi_\nu)P_{\sigma\nu} \rightarrow F_{\mu\rho}\end{aligned} \tag{D.14}$$

$$\begin{aligned}&\text{if}\quad \sigma \geq \nu\,(\text{utf})\quad \text{and}\quad \mu \neq \sigma\quad : \\ &(\chi_\sigma\chi_\mu|\chi_\nu\chi_\rho)P_{\mu\rho} \rightarrow F_{\sigma\nu}\end{aligned} \tag{D.15}$$

$$\begin{aligned}&\text{if}\quad \sigma \geq \rho\,(\text{utf})\quad \text{and}\quad \mu \neq \sigma\quad \text{and}\quad \nu \neq \rho\quad : \\ &(\chi_\sigma\chi_\mu|\chi_\rho\chi_\nu)P_{\mu\nu} \rightarrow F_{\sigma\rho}\end{aligned} \tag{D.16}$$

$$\begin{aligned}&\text{if}\quad \nu \geq \mu\,(\text{utf})\quad \text{and}\quad \rho \geq \sigma\,(\text{utp})\quad \text{and}\quad [\mu\sigma] \neq [\nu\rho]\quad : \\ &(\chi_\nu\chi_\rho|\chi_\mu\chi_\sigma)P_{\rho\sigma} \rightarrow F_{\nu\mu}\end{aligned} \tag{D.17}$$

where (utp) means that the inequality ensures that no upper-triangular elements of the density matrix are used. (utf) ensures that no upper-triangular elements of the Fock matrix are built.

If it so happens that an element of the upper half of the density matrix is needed to construct an element of the lower half of the Fock matrix, then an additional transformation is necessary, making use of the hermiticity of the required density and bielectronic integral blocks. These additional transformations are provided by the following relations:

$$\begin{aligned}&\text{if}\quad \rho > \sigma\,(\text{utp})\quad : \\ &\quad(\chi_\mu\chi_\sigma|\chi_\nu\chi_\rho)P_{\sigma\rho} = (\chi_\mu\chi_\sigma|\chi_\nu\chi_\rho)^{T_{\sigma\rho}}P_{\rho\sigma} \rightarrow F_{\mu\nu}\end{aligned} \tag{D.18}$$

$$\begin{aligned}&\text{if}\quad \nu \neq \rho\quad \text{and}\quad \nu > \sigma\,(\text{utp})\quad : \\ &\quad(\chi_\mu\chi_\sigma|\chi_\rho\chi_\nu)P_{\sigma\nu} = (\chi_\mu\chi_\sigma|\chi_\rho\chi_\nu)^{T_{\sigma\nu}}P_{\nu\sigma} \rightarrow F_{\mu\rho}\end{aligned} \tag{D.19}$$

$$\begin{aligned}&\text{if}\quad \nu \geq \mu\,(\text{utf})\quad \text{and}\quad \sigma > \rho\,(\text{utp})\quad \text{and}\quad [\mu\sigma] \neq [\nu\rho]\quad : \\ &\quad(\chi_\nu\chi_\rho|\chi_\mu\chi_\sigma)P_{\rho\sigma} = (\chi_\nu\chi_\rho|\chi_\mu\chi_\sigma)^{T_{\rho\sigma}}P_{\sigma\rho} \rightarrow F_{\nu\mu}\end{aligned} \tag{D.20}$$

where $T_{\mu\nu}$ means to take the transpose of all the $\{n_\mu \times n_\nu\}$ sized matrices in $(\chi_\mu\chi_\sigma|\chi_\nu\chi_\rho)$. Otherwise, in some cases the iteration is over shell couple pairs that would build an upper triangular element of the Fock matrix, using a lower triangular element of the density matrix. In such cases, this integral can still be used to build a lower triangular element of the Fock matrix, making use of the hermiticity of the relevant Fock and bielectronic integral blocks:

$$\begin{aligned} &\text{if} \quad \mu \neq \sigma \quad \text{and} \quad \nu \geq \sigma \,(\text{utf}) \quad \text{and} \quad [\mu\sigma] \neq [\nu\rho] \quad : \\ &(\chi_\sigma\chi_\mu|\chi_\nu\chi_\rho)P_{\mu\rho} = (\chi_\sigma\chi_\mu|\chi_\nu\chi_\rho)^{T_{\sigma\nu}}P_{\mu\rho} \rightarrow F_{\nu\sigma} \end{aligned} \tag{D.21}$$

$$\begin{aligned} &\text{if} \quad \nu \neq \rho \quad \text{and} \quad \rho \geq \mu \,(\text{utf}) \quad \text{and} \quad \sigma > \nu \,(\text{utp}) \quad \text{and} \quad [\mu\sigma] \neq [\nu\rho] \quad : \\ &(\chi_\mu\chi_\sigma|\chi_\rho\chi_\nu)P_{\sigma\nu} = (\chi_\mu\chi_\sigma|\chi_\rho\chi_\nu)^{T_{\mu\rho}}P_{\sigma\nu} \rightarrow F_{\rho\mu} \end{aligned} \tag{D.22}$$

$$\begin{aligned} &\text{if} \quad \mu \neq \sigma \quad \text{and} \quad \nu \neq \rho \quad \text{and} \quad \rho \geq \sigma \,(\text{utf}) \quad \text{and} \quad [\mu\sigma] \neq [\nu\rho] \quad : \\ &(\chi_\sigma\chi_\mu|\chi_\rho\chi_\nu)P_{\mu\nu} = (\chi_\sigma\chi_\mu|\chi_\rho\chi_\nu)^{T_{\sigma\rho}}P_{\mu\nu} \rightarrow F_{\rho\sigma} \end{aligned} \tag{D.23}$$

Finally, it is also possible that the iteration is over shell couple pairs that would build an upper triangular element of the Fock matrix using an upper triangular element of the density matrix. In this case, the additional transformation makes use of the hermiticity of all three of the Fock, density and bielectronic integral matrices:

$$\begin{aligned} &\text{if} \quad \nu \neq \rho \quad \text{and} \quad \rho \geq \mu \,(\text{utf}) \quad \text{and} \quad \nu \geq \sigma \,(\text{utp}) \quad \text{and} \quad [\mu\sigma] \neq [\nu\rho] \quad : \\ &(\chi_\mu\chi_\sigma|\chi_\rho\chi_\nu)P_{\sigma\nu} = (\chi_\mu\chi_\sigma|\chi_\rho\chi_\nu)^{T_{\mu\rho}T_{\sigma\nu}}P_{\nu\sigma} \rightarrow F_{\rho\mu} \end{aligned} \tag{D.24}$$

The multiplication of the density and bielectronic integral AO blocks is achieved using a call to MXMB. For the molecular case (neglecting the role of lattice vectors), this multiplication involves first extracting a block of the density matrix corresponding to the relevant shell-shell atomic orbital block and multiplying it by the corresponding block of integrals. The density matrix is stored in such a way that the multiplication is carried out for the $\alpha+\beta$ component and then the $\alpha-\beta$ component. Equations (13-24) appear in the code in the order (13,18,14,19,15,16,20,17,21,22,24,23).

Let us now consider a simple example of an LiH molecule. The Li is treated with a relativistic effective core potential, so that there is only one s function in the valence of the Li and one s function on the H, for a total of two functions in the system. Remembering that in the SHELLEXCH routine, the loops on the shell couples are constrained by $\mu \geq \sigma$, $\nu \geq \rho$ and $[\mu\sigma] \geq [\nu\rho]$, the explored shell couple pairs are as follows (in order of μ, σ, ν, ρ):

$$\begin{array}{cccc} \mu & \sigma & \nu & \rho \\ 1 & 1 & 1 & 1 \\ 2 & 1 & 1 & 1 \\ 2 & 1 & 2 & 1 \\ 2 & 2 & 1 & 1 \\ 2 & 2 & 2 & 1 \\ 2 & 2 & 2 & 2 \end{array} \tag{D.25}$$

With the removal of the restriction $[\mu\sigma] \geq [\nu\rho]$, the explored shell couple pairs would be:

$$\begin{array}{cccc} \mu & \sigma & \nu & \rho \\ 1 & 1 & 1 & 1 \\ 1 & 1 & 2 & 1 \\ 1 & 1 & 2 & 2 \\ 2 & 1 & 1 & 1 \\ 2 & 1 & 2 & 1 \\ 2 & 1 & 2 & 2 \\ 2 & 2 & 1 & 1 \\ 2 & 2 & 2 & 1 \\ 2 & 2 & 2 & 2 \end{array} \tag{D.26}$$

where the red shell couple pairs would be explicitly iterated because of the removal of $[\mu\sigma] \geq [\nu\rho]$. However, this is still not the full list of shell couple pairs, because the code is still restricted by $\mu \geq \sigma$ and $\nu \geq \rho$. The full list of shell couple pairs is as follows:

$$
\begin{array}{cccc}
\mu & \sigma & \nu & \rho \\
1 & 1 & 1 & 1 \\
1 & 1 & 2 & 1 \\
1 & 1 & 1 & 2 \\
1 & 1 & 2 & 2 \\
2 & 1 & 1 & 1 \\
2 & 1 & 2 & 1 \\
2 & 1 & 1 & 2 \\
2 & 1 & 2 & 2, \\
1 & 2 & 1 & 1 \\
1 & 2 & 2 & 1 \\
1 & 2 & 1 & 2 \\
1 & 2 & 2 & 2 \\
2 & 2 & 1 & 1 \\
2 & 2 & 2 & 1 \\
2 & 2 & 1 & 2 \\
2 & 2 & 2 & 2
\end{array}
\tag{D.27}
$$

where the green shell couple pairs would be the new ones explcitly iterated because of the removal of the restrictions $\mu \geq \sigma$ and $\nu \geq \rho$. Nonetheless, it is not necessary to iterate over the full list of shell couple pairs in equations (26) and (27), because the additional green and red shell couple pairs can be generated from the black ones using the permutation relations in equations (13-24), as shown below (assuming that the expored shell couple pairs are as in equation 25):

$\mu \ \sigma \ \nu \ \rho$

1 1 1 1 $(11|11)P_{11} \rightarrow F_{11}$ (eq. 13) a.

no permutations allowed

2 1 1 1 $(21|11)P_{11} \rightarrow F_{21}$ (eq. 13) b.

1 2 1 1 $(12|11)P_{21} \rightarrow F_{11}$ (eq. 15) c.

1 2 1 1 $(12|11)P_{21} = (12|11)^{T_{11}}P_{21} \rightarrow F_{11}$ (eq. 21) d.

1 1 2 1 [2]

1 1 1 2 none of (eq. 13-24) permit this permutation

2 1 2 1 $(21|21)P_{11} \rightarrow F_{22}$ (eq. 13) e.

---

[2] eq. 17 not $\nu \geq \mu$ (utf) ; eq. 20 not $\nu \geq \mu$ (utf) and not $\sigma > \rho$ (utp)

2 1 1 2 $(21|12)P_{12} = (21|12)^{T_{12}}P_{21} \rightarrow F_{21}$ (eq. 19) f.

1 2 1 2 $(12|12)P_{22} \rightarrow F_{11}$ (eq. 16) g.

1 2 2 1 eq. 15 not $\sigma \geq \nu$ (utf)

2 2 1 1 $(22|11)P_{21} \rightarrow F_{21}$ (eq. 13) h.

1 1 2 2 [3]

2 2 2 1 $(22|21)P_{21} \rightarrow F_{22}$ (eq. 13) i.

2 2 1 2 $(22|12)P_{21} \rightarrow F_{21}$ (eq. 14) j.

2 1 2 2 $(21|22)P_{12} = (21|22)^{T_{12}}P_{21} \rightarrow F_{22}$ (eq. 20) k.

1 2 2 2 none of (eq. 13-24) permit this permutation

2 2 2 2 $(22|22)P_{22} \rightarrow F_{22}$ (eq. 13) l.

no permutations allowed

where the red shell couple pairs indicate allowed permutations, that however arent performed, either because they contribute only to the upper triangular part of the Fock matrix, or because they yield a contribution which has already been accounted for using the hermiticity of the density matrix. For the shell couple pairs that have contributions which are added to the Fock matrix, I provide the number of the equation, corresponding to which permutation relation above was used to generate the contribution, as well as a lower case letter a.-l., which labels the individual contributions. For shell couple pairs that do not have allowed contributions, I provide the reasoning as to why they aren't calculated, according to the associated criteria.

I now show how the contributions a.-l. can be used to calculate the exchange contribution for all elements of the lower triangular half of the Fock matrix. From equation (1), we have:

$$X_{11} = -\frac{1}{2}\{(11|11)P_{11} + (11|12)P_{12} + (12|11)P_{21} + (12|12)P_{22}\} \tag{D.28}$$

Using the hermiticity of the density matrix:

$$X_{11} = -\frac{1}{2}\{(11|11)P_{11} + (12|11)P_{21} + (12|11)P_{21} + (12|12)P_{22}\} \tag{D.29}$$

$$X_{11} = -\frac{1}{2}\{\text{a.} + \text{d.} + \text{c.} + \text{g.}\} \tag{D.30}$$

$$X_{21} = -\frac{1}{2}\{(21|11)P_{11} + (21|12)P_{12} + (22|11)P_{21} + (22|12)P_{22}\} \tag{D.31}$$

$$X_{21} = -\frac{1}{2}\{\text{b.} + \text{f.} + \text{h.} + \text{j.}\} \tag{D.32}$$

---

[3] eq. 17 not $\nu \geq \mu$ (utf) and not $\rho \geq \sigma$ (utp); eq. 20 not $\nu \geq \mu$ (utf)

$$X_{22} = -\frac{1}{2}\{(21|21)P_{11} + (21|22)P_{12} + (22|21)P_{21} + (22|22)P_{22}\} \tag{D.33}$$

$$X_{22} = -\frac{1}{2}\{\text{e.} + \text{k.} + \text{i.} + \text{l.}\} \tag{D.34}$$

E Calculating the Total Energy in a Two-Component SCF

The total Hartree-Fock energy can be expressed as:

$$E = \frac{1}{2}\Big\{\sum_{\mu,\nu} h_{\mu\nu}D_{\mu\nu} + \sum_{\mu,\nu} F_{\mu\nu}D_{\mu\nu}\Big\} = \frac{1}{2}\Big\{\mathrm{Tr}(hD^{\dagger}) + \mathrm{Tr}(FD^{\dagger})\Big\}, \tag{E.1}$$

where h is a mono-electronic operator of the form:

$$h = \begin{pmatrix} h_0 & 0 \\ 0 & h_0 \end{pmatrix} + \begin{pmatrix} LS^{\alpha\alpha} & LS^{\alpha\beta} \\ LS^{\alpha\beta\dagger} & -LS^{\alpha\alpha} \end{pmatrix}, \tag{E.2}$$

where:

$$LS^{\alpha\alpha} = \frac{i}{2}LS_z, \tag{E.3}$$

and:

$$LS^{\alpha\beta} = \frac{1}{2}LS_y + \frac{i}{2}LS_x, \tag{E.4}$$

$$LS_{x,y,z} = f(r)S_{x,y,z}L_{x,y,z}, \tag{E.5}$$

if $f(r)$ is a linear combination of fitted parameters from construction of the pseudopotential, $S_{x,y,z}$ and $L_{x,y,z}$ are Cartesian components of the spin and angular momentum operators. h_0 is the non-relativistic mono-electronic operator and D and F are the 4-component Hermitian-complex density and Fock matrices:

$$F = \begin{pmatrix} F^{\alpha\alpha} & F^{\alpha\beta} \\ F^{\beta\alpha} & F^{\beta\beta} \end{pmatrix}, \tag{E.6}$$

$$D = \begin{pmatrix} D^{\alpha\alpha} & D^{\alpha\beta} \\ D^{\beta\alpha} & D^{\beta\beta} \end{pmatrix}, \tag{E.7}$$

The matrix D is built from the occupied spin-orbitals, for example:

$$D^{\alpha\beta}_{\mu\nu} = \sum_{i}^{occ} \left[c^{\alpha}_{\mu i}\right]^{*} c^{\beta}_{\nu i} \tag{E.8}$$

The matrix F is built from mono- and bielectronic-operators:

$$F^{\alpha\alpha}_{\mu\nu} = h^{\alpha\alpha}_{\mu\nu} + \sum_{\sigma,\rho}(\mu\nu|\sigma\rho)\mathrm{Re}\Big(D^{\alpha\alpha}_{\sigma\rho} + D^{\beta\beta}_{\sigma\rho}\Big) - \sum_{\sigma,\rho}(\mu\sigma|\nu\rho)D^{\alpha\alpha}_{\sigma\rho} \tag{E.9}$$

$$F^{\beta\beta}_{\mu\nu} = h^{\beta\beta}_{\mu\nu} + \sum_{\sigma,\rho}(\mu\nu|\sigma\rho)\mathrm{Re}\Big(D^{\alpha\alpha}_{\sigma\rho} + D^{\beta\beta}_{\sigma\rho}\Big) - \sum_{\sigma,\rho}(\mu\sigma|\nu\rho)D^{\beta\beta}_{\sigma\rho} \tag{E.10}$$

$$F_{\mu\nu}^{\alpha\beta} = h_{\mu\nu}^{\alpha\beta} - \sum_{\sigma,\rho} (\mu\sigma|\nu\rho) D_{\sigma\rho}^{\beta\alpha} \tag{E.11}$$

$$F_{\mu\nu}^{\beta\alpha} = h_{\mu\nu}^{\beta\alpha} - \sum_{\sigma,\rho} (\mu\sigma|\nu\rho) D_{\sigma\rho}^{\alpha\beta} \tag{E.12}$$

The energy is calculated using the trace operator in equation (1) for $A = h$ or F as follows, for n being half of the dimension of the Fock and density matrices:

$$\mathrm{Tr}(AD^{\dagger}) = \sum_{\mu=1}^{n}\sum_{\nu=1}^{n} A_{\mu\nu}D_{\mu\nu} + \sum_{\mu=n+1}^{2n}\sum_{\nu=1}^{n} A_{\mu\nu}D_{\mu\nu} + \sum_{\mu=1}^{n}\sum_{\nu=n+1}^{2n} A_{\mu\nu}D_{\mu\nu} + \sum_{\mu=n+1}^{2n}\sum_{\nu=n+1}^{2n} A_{\mu\nu}D_{\mu\nu} \tag{E.13}$$

$$\mathrm{Tr}(AD^{\dagger}) = \sum_{\mu=1}^{n}\sum_{\nu=1}^{n} A_{\mu\nu}^{\alpha\alpha}D_{\mu\nu}^{\alpha\alpha} + \sum_{\mu=1}^{n}\sum_{\nu=1}^{n} A_{\mu\nu}^{\beta\alpha}D_{\mu\nu}^{\beta\alpha} + \sum_{\mu=1}^{n}\sum_{\nu=1}^{n} A_{\mu\nu}^{\alpha\beta}D_{\mu\nu}^{\alpha\beta} + \sum_{\mu=1}^{n}\sum_{\nu=1}^{n} A_{\mu\nu}^{\beta\beta}D_{\mu\nu}^{\beta\beta} \tag{E.14}$$

$$\mathrm{Tr}(AD^{\dagger}) = \mathrm{Tr}(A^{\alpha\alpha}D^{\alpha\alpha^{\dagger}}) + \mathrm{Tr}(A^{\beta\beta}D^{\beta\beta^{\dagger}}) + \mathrm{Tr}(A^{\alpha\beta}D^{\alpha\beta^{\dagger}}) + \mathrm{Tr}(A^{\beta\alpha}D^{\beta\alpha^{\dagger}}) \tag{E.15}$$

Using $D^{\alpha\beta}{=}D^{\beta\alpha^{\dagger}}$ and $A^{\beta\alpha}{=}A^{\alpha\beta^{\dagger}}$:

$$\mathrm{Tr}(AD^{\dagger}) = \mathrm{Tr}(A^{\alpha\alpha}D^{\alpha\alpha^{\dagger}}) + \mathrm{Tr}(A^{\beta\beta}D^{\beta\beta^{\dagger}}) + \mathrm{Tr}(A^{\alpha\beta}D^{\alpha\beta^{\dagger}}) + \mathrm{Tr}(A^{\alpha\beta^{\dagger}}D^{\alpha\beta}) \tag{E.16}$$

Using $\mathrm{Tr}(A^{T}D)$ $=\mathrm{Tr}(AD^{T})$:

$$\mathrm{Tr}(AD^{\dagger}) = \mathrm{Tr}(A^{\alpha\alpha}D^{\alpha\alpha^{\dagger}}) + \mathrm{Tr}(A^{\beta\beta}D^{\beta\beta^{\dagger}}) + \mathrm{Tr}(A^{\alpha\beta}D^{\alpha\beta^{T*}}) + \mathrm{Tr}(A^{\alpha\beta^{T*}}D^{\alpha\beta}) \tag{E.17}$$

$$\mathrm{Tr}(AD^{\dagger}) = \mathrm{Tr}(A^{\alpha\alpha}D^{\alpha\alpha^{\dagger}}) + \mathrm{Tr}(A^{\beta\beta}D^{\beta\beta^{\dagger}}) + \mathrm{Tr}(A^{\alpha\beta}D^{\alpha\beta^{*T}}) + \mathrm{Tr}(A^{\alpha\beta^{*}}D^{\alpha\beta^{T}}) \tag{E.18}$$

Using $\mathrm{Tr}(A^{*}D)$ $=\{\mathrm{Tr}(AD^{*})\}^{*}$:

$$\mathrm{Tr}(AD^{\dagger}) = \mathrm{Tr}(A^{\alpha\alpha}D^{\alpha\alpha^{\dagger}}) + \mathrm{Tr}(A^{\beta\beta}D^{\beta\beta^{\dagger}}) + \mathrm{Tr}(A^{\alpha\beta}D^{\alpha\beta^{*T}}) + \left\{\mathrm{Tr}(A^{\alpha\beta}D^{\alpha\beta^{*T}})\right\}^{*} \tag{E.19}$$

$$\mathrm{Tr}(AD^{\dagger}) = \mathrm{Tr}(A^{\alpha\alpha}D^{\alpha\alpha^{\dagger}}) + \mathrm{Tr}(A^{\beta\beta}D^{\beta\beta^{\dagger}}) + 2\,\mathrm{Re}\left\{\{\mathrm{Tr}(A^{\alpha\beta}D^{\alpha\beta^{\dagger}})\}\right\} \tag{E.20}$$

From which we deduce that:

$$\begin{aligned} \mathrm{Re}\left\{\{\mathrm{Tr}(AD^{\dagger})\}\right\} \quad &= \mathrm{Tr}(\mathrm{Re}\{A^{\alpha\alpha}\}\,\mathrm{Re}\left\{D^{\alpha\alpha^{\dagger}}\right\}) - \mathrm{Tr}(\mathrm{Im}\{A^{\alpha\alpha}\}\,\mathrm{Im}\left\{D^{\alpha\alpha^{\dagger}}\right\}) + \mathrm{Tr}(\mathrm{Re}\left\{A^{\beta\beta}\right\}\mathrm{Re}\left\{D^{\beta\beta^{\dagger}}\right\}) \\ &-\mathrm{Tr}(\mathrm{Im}\left\{A^{\beta\beta}\right\}\mathrm{Im}\left\{D^{\beta\beta^{\dagger}}\right\}) + 2\mathrm{Tr}(\mathrm{Re}\left\{A^{\alpha\beta}\right\}\mathrm{Re}\left\{D^{\alpha\beta^{\dagger}}\right\}) - 2\mathrm{Tr}(\mathrm{Im}\left\{A^{\alpha\beta}\right\}\mathrm{Im}\left\{D^{\alpha\beta^{\dagger}}\right\}) \end{aligned} \tag{E.21}$$

and

$$\begin{aligned} \mathrm{Im}\left\{\{\mathrm{Tr}(AD^{\dagger})\}\right\} \quad &= \mathrm{Tr}(\mathrm{Re}\{A^{\alpha\alpha}\}\,\mathrm{Im}\left\{D^{\alpha\alpha^{\dagger}}\right\}) + \mathrm{Tr}(\mathrm{Im}\{A^{\alpha\alpha}\}\,\mathrm{Re}\left\{D^{\alpha\alpha^{\dagger}}\right\}) \\ &+\mathrm{Tr}(\mathrm{Re}\left\{A^{\beta\beta}\right\}\mathrm{Im}\left\{D^{\beta\beta^{\dagger}}\right\}) + \mathrm{Tr}(\mathrm{Im}\left\{A^{\beta\beta}\right\}\mathrm{Re}\left\{D^{\beta\beta^{\dagger}}\right\}) \end{aligned} \tag{E.22}$$

We now show that $\mathrm{Im}\Big\{\{\mathrm{Tr}(AD^\dagger)\}\Big\} = 0$, so that as expected, the energy is purely real. The proof is as follows. Using the definition of the trace operator in equation (1):

$$\begin{aligned}\mathrm{Im}\Big\{\{\mathrm{Tr}(AD^\dagger)\}\Big\} &= \sum_\mu\sum_\nu \mathrm{Re}\Big\{A^{\alpha\alpha}_{\mu\nu}\Big\}\mathrm{Im}\Big\{D^{\alpha\alpha}_{\mu\nu}\Big\} + \sum_\mu\sum_\nu \mathrm{Im}\Big\{A^{\alpha\alpha}_{\mu\nu}\Big\}\mathrm{Re}\Big\{D^{\alpha\alpha}_{\mu\nu}\Big\} \\ &+ \sum_\mu\sum_\nu \mathrm{Re}\Big\{A^{\beta\beta}_{\mu\nu}\Big\}\mathrm{Im}\Big\{D^{\beta\beta}_{\mu\nu}\Big\} + \sum_\mu\sum_\nu \mathrm{Im}\Big\{A^{\beta\beta}_{\mu\nu}\Big\}\mathrm{Re}\Big\{D^{\beta\beta}_{\mu\nu}\Big\} \end{aligned} \tag{E.23}$$

$$\begin{aligned}\mathrm{Im}\Big\{\{\mathrm{Tr}(AD^\dagger)\}\Big\} &= \sum_\mu\sum_{\nu\le\mu} \mathrm{Re}\Big\{A^{\alpha\alpha}_{\mu\nu}\Big\}\mathrm{Im}\Big\{D^{\alpha\alpha}_{\mu\nu}\Big\} + \sum_\mu\sum_{\nu>\mu} \mathrm{Re}\Big\{A^{\alpha\alpha}_{\mu\nu}\Big\}\mathrm{Im}\Big\{D^{\alpha\alpha}_{\mu\nu}\Big\} + \sum_\mu\sum_{\nu\le\mu} \mathrm{Im}\Big\{A^{\alpha\alpha}_{\mu\nu}\Big\}\mathrm{Re}\Big\{D^{\alpha\alpha}_{\mu\nu}\Big\} \\ &+ \sum_\mu\sum_{\nu>\mu} \mathrm{Im}\Big\{A^{\alpha\alpha}_{\mu\nu}\Big\}\mathrm{Re}\Big\{D^{\alpha\alpha}_{\mu\nu}\Big\} + \sum_\mu\sum_{\nu\le\mu} \mathrm{Re}\Big\{A^{\beta\beta}_{\mu\nu}\Big\}\mathrm{Im}\Big\{D^{\beta\beta}_{\mu\nu}\Big\} + \sum_\mu\sum_{\nu>\mu} \mathrm{Re}\Big\{A^{\beta\beta}_{\mu\nu}\Big\}\mathrm{Im}\Big\{D^{\beta\beta}_{\mu\nu}\Big\} \\ &+ \sum_\mu\sum_{\nu\le\mu} \mathrm{Im}\Big\{A^{\beta\beta}_{\mu\nu}\Big\}\mathrm{Re}\Big\{D^{\beta\beta}_{\mu\nu}\Big\} + \sum_\mu\sum_{\nu>\mu} \mathrm{Im}\Big\{A^{\beta\beta}_{\mu\nu}\Big\}\mathrm{Re}\Big\{D^{\beta\beta}_{\mu\nu}\Big\} \end{aligned} \tag{E.24}$$

Now from the hermiticity of D and A, the $A^{\alpha\alpha}, D^{\alpha\alpha}$ and $A^{\beta\beta}, D^{\beta\beta}$ blocks must also be Hermitian, so all off-diagonal contribution cancel and we are left with the diagonal terms:

$$\begin{aligned}\mathrm{Im}\Big\{\{\mathrm{Tr}(AD^\dagger)\}\Big\} &= \sum_\mu\sum_{\nu=\mu} \mathrm{Re}\Big\{A^{\alpha\alpha}_{\mu\mu}\Big\}\mathrm{Im}\Big\{D^{\alpha\alpha}_{\mu\mu}\Big\} + \sum_\mu\sum_{\nu=\mu} \mathrm{Im}\Big\{A^{\alpha\alpha}_{\mu\mu}\Big\}\mathrm{Re}\Big\{D^{\alpha\alpha}_{\mu\mu}\Big\} \\ &+ \sum_\mu\sum_{\nu=\mu} \mathrm{Re}\Big\{A^{\beta\beta}_{\mu\mu}\Big\}\mathrm{Im}\Big\{D^{\beta\beta}_{\mu\mu}\Big\} + \sum_\mu\sum_{\nu=\mu} \mathrm{Im}\Big\{A^{\beta\beta}_{\mu\mu}\Big\}\mathrm{Re}\Big\{D^{\beta\beta}_{\mu\mu}\Big\} \end{aligned} \tag{E.25}$$

But since A and D are hermitian the diagonal terms are purely real. Since all contributions above involve the imaginary part of a diagonal element of A and D, we deduce immediately that:

$$\mathrm{Im}\Big\{\{\mathrm{Tr}(AD^\dagger)\}\Big\} = 0 \tag{E.26}$$

So, substituting equation (26) and (21) in equation (1):

$$E = \frac{1}{2}\Big\{\mathrm{Re}\Big\{[\mathrm{Tr}(hD^\dagger)]\Big\} + \mathrm{Re}\Big\{[\mathrm{Tr}(FD^\dagger)]\Big\}\Big\} \tag{E.27}$$

Now splitting the second term (the Fock matrix term) in monoelectronic (h) and bielectronic (G) contributions:

$$E = \mathrm{Re}\Big\{[\mathrm{Tr}(hD^\dagger)]\Big\} + \frac{1}{2}\mathrm{Re}\Big\{[\mathrm{Tr}(GD^\dagger)]\Big\} \tag{E.28}$$

The bielectronic contributions to the energy can be directly calculated from equation (21) with $A = G$. The monoelectronic contribution is calculated as follows, using equation (2):

$$\mathrm{Re}\Big\{[\mathrm{Tr}(hD^\dagger)]\Big\} = \mathrm{Re}\Big\{[\mathrm{Tr}(h_0D^\dagger)]\Big\} + \mathrm{Re}\Big\{[\mathrm{Tr}(LS\,D^\dagger)]\Big\} \tag{E.29}$$

where the second LSD term is the relativistic contribution to the energy, while the first term is the non-relativistic monoelectronic operator. Again from equation (2) and equation (21):

$$\begin{aligned}\mathrm{Re}\left\{[\mathrm{Tr}(h_0 D^{\dagger})]\right\} &= \mathrm{Tr}(\mathrm{Re}\left\{h_0^{\alpha\alpha}\right\}\mathrm{Re}\left\{D^{\alpha\alpha^{\dagger}}\right\}) - \mathrm{Tr}(\mathrm{Im}\left\{h_0^{\alpha\alpha}\right\}\mathrm{Im}\left\{D^{\alpha\alpha^{\dagger}}\right\}) \\ &\quad +\mathrm{Tr}(\mathrm{Re}\left\{h_0^{\beta\beta}\right\}\mathrm{Re}\left\{D^{\beta\beta^{\dagger}}\right\}) - \mathrm{Tr}(\mathrm{Im}\left\{h_0^{\beta\beta}\right\}\mathrm{Im}\left\{D^{\beta\beta^{\dagger}}\right\})\end{aligned} \tag{E.30}$$

and:

$$\begin{aligned}\mathrm{Re}\left\{[\mathrm{Tr}(LS\,D^{\dagger})]\right\} &= \mathrm{Tr}(\mathrm{Re}\{LS^{\alpha\alpha}\}\mathrm{Re}\left\{D^{\alpha\alpha^{\dagger}}\right\}) - \mathrm{Tr}(\mathrm{Im}\{LS^{\alpha\alpha}\}\mathrm{Im}\left\{D^{\alpha\alpha^{\dagger}}\right\}) \\ &\quad -\mathrm{Tr}(\mathrm{Re}\{LS^{\alpha\alpha}\}\mathrm{Re}\left\{D^{\beta\beta^{\dagger}}\right\}) + \mathrm{Tr}(\mathrm{Im}\{LS^{\alpha\alpha}\}\mathrm{Im}\left\{D^{\beta\beta^{\dagger}}\right\}) \\ &\quad +2\mathrm{Tr}(\mathrm{Re}\left\{LS^{\alpha\beta}\right\}\mathrm{Re}\left\{D^{\alpha\beta^{\dagger}}\right\}) + 2\mathrm{Tr}(\mathrm{Im}\left\{LS^{\alpha\beta}\right\}\mathrm{Im}\left\{D^{\alpha\beta^{\dagger}}\right\})\end{aligned} \tag{E.31}$$

So we have, finally

$$\begin{aligned}\mathrm{Re}\left\{[\mathrm{Tr}(LS\,D^{\dagger})]\right\} &= \mathrm{Tr}\Big(\mathrm{Re}\{LS^{\alpha\alpha}\}[\mathrm{Re}\left\{D^{\alpha\alpha^{\dagger}}\right\} - \mathrm{Re}\left\{D^{\beta\beta^{\dagger}}\right\}]\Big) \\ &- \mathrm{Tr}\Big(\mathrm{Im}\{LS^{\alpha\alpha}\}[\mathrm{Im}\left\{D^{\alpha\alpha^{\dagger}}\right\} - \mathrm{Im}\left\{D^{\beta\beta^{\dagger}}\right\}]\Big) \\ &+ 2\mathrm{Tr}(\mathrm{Re}\left\{LS^{\alpha\beta}\right\}\mathrm{Re}\left\{D^{\alpha\beta^{\dagger}}\right\}) \\ &- 2\mathrm{Tr}(\mathrm{Im}\left\{LS^{\alpha\beta}\right\}\mathrm{Im}\left\{D^{\alpha\beta^{\dagger}}\right\})\end{aligned} \tag{E.32}$$

F The Non-Collinear Density Functional Theory

F.1 General Formulas

We write the generalized spin-density matrix in the non-collinear case as:

$$\bar{\mathbf{n}}(\mathbf{r}) = \frac{1}{2}\left[n(\mathbf{r})\boldsymbol{\sigma}_0 + \sum_{c=x,y,z} m_c(\mathbf{r})\boldsymbol{\sigma}_c\right] \tag{F.1}$$

where $\boldsymbol{\sigma}_0$ is a unit matrix, $\mathbf{m}(\mathbf{r})$ is the spin magnetization vector, whose Cartesian components are defined in terms of complex 2-component spinors $\boldsymbol{\Psi}_i(\mathbf{r})$ as:

$$m_c(\mathbf{r}) = \sum_i^{occ} \boldsymbol{\Psi}_i^\dagger(\mathbf{r})\boldsymbol{\sigma}_c\boldsymbol{\Psi}_i(\mathbf{r}) \tag{F.2}$$

The spinors are defined in terms of the spin-orbitals as:

$$\boldsymbol{\Psi}_i(\mathbf{r}) = \begin{pmatrix} \psi_i^\alpha(\mathbf{r}) \\ \psi_i^\beta(\mathbf{r}) \end{pmatrix} \tag{F.3}$$

and the spin-orbitals $\psi_i^\sigma(\mathbf{r})$ are individually expanded in a linear-combination of atomic-orbitals:

$$\psi_i^\sigma(\mathbf{r}) = \sum_\mu c_{\mu i}^\sigma \chi_\mu(\mathbf{r}) \tag{F.4}$$

The $\boldsymbol{\sigma}_c$ are the Pauli matrices:

$$\boldsymbol{\sigma}_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad \boldsymbol{\sigma}_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \quad \boldsymbol{\sigma}_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \tag{F.5}$$

Now expanding the magnetization components $m_c(\mathbf{r})$ in equation (F.2) we find, for example for $c = x$:

$$\begin{aligned}
m_x(\mathbf{r}) &= \sum_i^{occ} \begin{pmatrix} \psi_i^{\alpha^*}(\mathbf{r}) & \psi_i^{\beta^*}(\mathbf{r}) \end{pmatrix} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} \psi_i^\alpha(\mathbf{r}) \\ \psi_i^\beta(\mathbf{r}) \end{pmatrix} && \text{(F.6)} \\
&= \sum_i^{occ} \begin{pmatrix} \psi_i^{\beta^*}(\mathbf{r}) & \psi_i^{\alpha^*}(\mathbf{r}) \end{pmatrix} \begin{pmatrix} \psi_i^\alpha(\mathbf{r}) \\ \psi_i^\beta(\mathbf{r}) \end{pmatrix} && \text{(F.7)} \\
&= \sum_i^{occ} \psi_i^{\beta^*}(\mathbf{r})\psi_i^\alpha(\mathbf{r}) + \psi_i^{\alpha^*}(\mathbf{r})\psi_i^\beta(\mathbf{r}) \\
&= \sum_i^{occ} \sum_{\mu,\nu} \left(c_{\mu i}^{\beta^*} c_{\nu i}^\alpha + c_{\mu i}^{\alpha^*} c_{\nu i}^\beta\right)\chi_\mu(\mathbf{r})\chi_\nu(\mathbf{r}) && \text{(F.8)}
\end{aligned}$$

For $c = y$:

$$\begin{aligned}
m_y(\mathbf{r}) &= \sum_i^{occ} \begin{pmatrix} \psi_i^{\alpha^*}(\mathbf{r}) & \psi_i^{\beta^*}(\mathbf{r}) \end{pmatrix} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \begin{pmatrix} \psi_i^{\alpha}(\mathbf{r}) \\ \psi_i^{\beta}(\mathbf{r}) \end{pmatrix} && \text{(F.9)} \\
&= \sum_i^{occ} \begin{pmatrix} i\psi_i^{\beta^*}(\mathbf{r}) & -i\psi_i^{\alpha^*}(\mathbf{r}) \end{pmatrix} \begin{pmatrix} \psi_i^{\alpha}(\mathbf{r}) \\ \psi_i^{\beta}(\mathbf{r}) \end{pmatrix} && \text{(F.10)} \\
&= \sum_i^{occ} i \left(\psi_i^{\beta^*}(\mathbf{r}) \psi_i^{\alpha}(\mathbf{r}) - \psi_i^{\alpha^*}(\mathbf{r}) \psi_i^{\beta}(\mathbf{r}) \right) \\
&= \sum_i^{occ} \sum_{\mu,\nu} i \left(c_{\mu i}^{\beta^*} c_{\nu i}^{\alpha} - c_{\mu i}^{\alpha^*} c_{\nu i}^{\beta} \right) \chi_\mu(\mathbf{r}) \chi_\nu(\mathbf{r}) && \text{(F.11)}
\end{aligned}$$

For $c = z$:

$$\begin{aligned}
m_z(\mathbf{r}) &= \sum_i^{occ} \begin{pmatrix} \psi_i^{\alpha^*}(\mathbf{r}) & \psi_i^{\beta^*}(\mathbf{r}) \end{pmatrix} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} \psi_i^{\alpha}(\mathbf{r}) \\ \psi_i^{\beta}(\mathbf{r}) \end{pmatrix} && \text{(F.12)} \\
&= \sum_i^{occ} \begin{pmatrix} \psi_i^{\alpha^*}(\mathbf{r}) & -\psi_i^{\beta^*}(\mathbf{r}) \end{pmatrix} \begin{pmatrix} \psi_i^{\alpha}(\mathbf{r}) \\ \psi_i^{\beta}(\mathbf{r}) \end{pmatrix} && \text{(F.13)} \\
&= \sum_i^{occ} \psi_i^{\alpha^*}(\mathbf{r}) \psi_i^{\alpha}(\mathbf{r}) - \psi_i^{\beta^*}(\mathbf{r}) \psi_i^{\beta}(\mathbf{r}) \\
&= \sum_i^{occ} \sum_{\mu,\nu} \left(c_{\mu i}^{\alpha^*} c_{\nu i}^{\alpha} - c_{\mu i}^{\beta^*} c_{\nu i}^{\beta} \right) \chi_\mu(\mathbf{r}) \chi_\nu(\mathbf{r}) && \text{(F.14)}
\end{aligned}$$

So from equations (F.7), (F.11) and (F.14), we have:

$$\begin{aligned}
m_x(\mathbf{r}) &= \sum_{\mu,\nu} \left(P_{\mu\nu}^{\alpha\beta} + P_{\mu\nu}^{\beta\alpha} \right) \chi_\mu(\mathbf{r}) \chi_\nu(\mathbf{r}) && \text{(F.15)} \\
m_y(\mathbf{r}) &= -\sum_{\mu,\nu} i \left(P_{\mu\nu}^{\alpha\beta} - P_{\mu\nu}^{\beta\alpha} \right) \chi_\mu(\mathbf{r}) \chi_\nu(\mathbf{r}) && \text{(F.16)} \\
m_z(\mathbf{r}) &= \sum_{\mu,\nu} \left(P_{\mu\nu}^{\alpha\alpha} - P_{\mu\nu}^{\beta\beta} \right) \chi_\mu(\mathbf{r}) \chi_\nu(\mathbf{r}) && \text{(F.17)}
\end{aligned}$$

Using the hermiticity of the density matrix P (i.e. $P_{\mu\nu}^{\alpha\beta} = P_{\nu\mu}^{\beta\alpha^*}$ and $P_{\mu\nu}^{\sigma\sigma} = P_{\nu\mu}^{\sigma\sigma^*}$):

$$\begin{aligned}
m_x(\mathbf{r}) &= \sum_{\mu,\nu} \left(\operatorname{Re} P_{\mu\nu}^{\alpha\beta} + \operatorname{Re} P_{\mu\nu}^{\beta\alpha} \right) \chi_\mu(\mathbf{r}) \chi_\nu(\mathbf{r}) && \text{(F.18)} \\
m_y(\mathbf{r}) &= \sum_{\mu,\nu} \left(\operatorname{Im} P_{\mu\nu}^{\alpha\beta} - \operatorname{Im} P_{\mu\nu}^{\beta\alpha} \right) \chi_\mu(\mathbf{r}) \chi_\nu(\mathbf{r}) && \text{(F.19)} \\
m_z(\mathbf{r}) &= \sum_{\mu,\nu} \left(\operatorname{Re} P_{\mu\nu}^{\alpha\alpha} - \operatorname{Re} P_{\mu\nu}^{\beta\beta} \right) \chi_\mu(\mathbf{r}) \chi_\nu(\mathbf{r}) && \text{(F.20)}
\end{aligned}$$

It can also be noticed that while $P^{\alpha\beta}$ and $P^{\beta\alpha}$ are individually not Hermitian, their sums and differences that appear above are symmetric, which means that once they are constructed as such, there is no further need to seriously modify the existing 1-c UKS code for constructing $m_x(\mathbf{r})$ and $m_y(\mathbf{r})$.

Finally $n(\mathbf{r})$ is the total density:

$$n(\mathbf{r}) = \sum_{i}^{occ} \mathbf{\Psi}_i^\dagger(\mathbf{r})\mathbf{\Psi}_i(\mathbf{r}) \tag{F.21}$$

$$n(\mathbf{r}) = \sum_{\mu,\nu} \left(\operatorname{Re} P_{\mu\nu}^{\alpha\alpha} + \operatorname{Re} P_{\mu\nu}^{\beta\beta}\right)\chi_\mu(\mathbf{r})\chi_\nu(\mathbf{r}) \tag{F.22}$$

It is also convenient to define the variables:

$$n_{\sigma\sigma'}^{\mathrm{Re}}(\mathbf{r}) = \sum_{\mu,\nu} \operatorname{Re}\left(P_{\mu\nu}^{\sigma\sigma'}\right)\chi_\mu(\mathbf{r})\chi_\nu(\mathbf{r}) \tag{F.23}$$

$$n_{\sigma\sigma'}^{\mathrm{Im}}(\mathbf{r}) = \sum_{\mu,\nu} \operatorname{Im}\left(P_{\mu\nu}^{\sigma\sigma'}\right)\chi_\mu(\mathbf{r})\chi_\nu(\mathbf{r}) \tag{F.24}$$

In terms of equations (F.18), (F.19) and (F.20) this gives:

$$m_x(\mathbf{r}) = n_{\alpha\beta}^{\mathrm{Re}}(\mathbf{r}) + n_{\beta\alpha}^{\mathrm{Re}}(\mathbf{r}) \tag{F.25}$$

$$m_y(\mathbf{r}) = n_{\alpha\beta}^{\mathrm{Im}}(\mathbf{r}) - n_{\beta\alpha}^{\mathrm{Im}}(\mathbf{r}) \tag{F.26}$$

$$m_z(\mathbf{r}) = n_{\alpha\alpha}^{\mathrm{Re}}(\mathbf{r}) - n_{\beta\beta}^{\mathrm{Re}}(\mathbf{r}) \tag{F.27}$$

$$n(\mathbf{r}) = n_{\alpha\alpha}^{\mathrm{Re}}(\mathbf{r}) + n_{\beta\beta}^{\mathrm{Re}}(\mathbf{r}) \tag{F.28}$$

According to the definitions above, we may rewrite the generalized density matrix $\bar{\mathbf{n}}(\mathbf{r})$ from equation (F.1) as follows:

$$\bar{\mathbf{n}}(\mathbf{r}) = \frac{1}{2}\begin{pmatrix} n(\mathbf{r}) + m_z(\mathbf{r}) & m_x(\mathbf{r}) - im_y(\mathbf{r}) \\ m_x(\mathbf{r}) + im_y(\mathbf{r}) & n(\mathbf{r}) - m_z(\mathbf{r}) \end{pmatrix} \overset{diag}{\rightarrow} \begin{pmatrix} n_+(\mathbf{r}) & 0 \\ 0 & n_-(\mathbf{r}) \end{pmatrix} \tag{F.29}$$

where in the last passage above, a unitary transformation on $n(\mathbf{r})$ has been performed to diagonalize the matrix. The eigenvalues $n_\pm(\mathbf{r})$ are:

$$n_\pm(\mathbf{r}) = \frac{1}{2}(n(\mathbf{r}) \pm \sqrt{m_x^2(\mathbf{r}) + m_y^2(\mathbf{r}) + m_z^2(\mathbf{r})}) = \frac{1}{2}(n(\mathbf{r}) \pm m(\mathbf{r})) \tag{F.30}$$

The exchange-correlation (xc) potential matrix $\mathbf{V}_{xc}(\mathbf{r})$ is the functional derivative of the xc Energy E_{xc} with respect to the generalized density $\bar{\mathbf{n}}(\mathbf{r})$:

$$\mathbf{V}_{xc}(\mathbf{r}) = \frac{\delta E_{xc}}{\delta \bar{\mathbf{n}}(\mathbf{r})} \tag{F.31}$$

The energy is itself expressed using the xc functional:

$$E_{xc} = \int F_{xc}[\bar{\mathbf{n}}(\mathbf{r})]d\mathbf{r} \tag{F.32}$$

expanding $\bar{\mathbf{n}}(\mathbf{r})$ in the independant variables $n(\mathbf{r})$, $m_x(\mathbf{r}), m_y(\mathbf{r}), m_z(\mathbf{r})$, using equation (F.1):

$$\mathbf{V}_{xc}(\mathbf{r}) = \left(\frac{\delta E_{xc}}{\delta n(\mathbf{r})}\boldsymbol{\sigma}_0 + \sum_c \frac{\delta E_{xc}}{\delta m_c(\mathbf{r})}\boldsymbol{\sigma}_c \right) \tag{F.33}$$

It can be noticed from the above that the $\boldsymbol{\sigma}$ will direct the various terms of the xc components into the correct blocks of the Fock matrix ($\alpha\alpha, \alpha\beta$ and so on).

The variations above w.r.t. $m_c(\mathbf{r})$ are reformulated as:

$$\begin{aligned} \frac{\delta E_{xc}}{\delta m_c(\mathbf{r})} &= \frac{\delta E_{xc}}{\delta m(\mathbf{r})}\frac{\partial m(\mathbf{r})}{\partial m_c(\mathbf{r})} \\ &= \frac{\delta E_{xc}}{\delta m(\mathbf{r})}\frac{m_c(\mathbf{r})}{m(\mathbf{r})} \end{aligned} \tag{F.34}$$

For the purpose of the following derivation, we express the derivatives in terms of $n(\mathbf{r})$ and $m(\mathbf{r})$. Later these will be transformed to $n_+(\mathbf{r})$ and $n_-(\mathbf{r})$. Substituting (F.34) into (F.33), we obtain:

$$\mathbf{V}_{xc}(\mathbf{r}) = \left(\frac{\delta E_{xc}}{\delta n(\mathbf{r})}\boldsymbol{\sigma}_0 + \frac{\delta E_{xc}}{\delta m(\mathbf{r})} \sum_c \frac{m_c(\mathbf{r})}{m(\mathbf{r})}\boldsymbol{\sigma}_c \right) \tag{F.35}$$

It can be noticed from the above that the variable $m(\mathbf{r})$ plays the role of the spin density $m_z(\mathbf{r}) = n_\alpha(\mathbf{r}) - n_\beta(\mathbf{r})$ and the variable $n(\mathbf{r})$ plays the role of the total density $n(\mathbf{r}) = n_\alpha(\mathbf{r}) + n_\beta(\mathbf{r})$ in the 1-c UKS case. For the LSDA, the variation of the energy can be replaced by a partial derivative of the functional

F.2 Application to the LSDA

F.2.1 Exchange

Two different means of deriving the 2-c LSDA potential will be shown below. The first method starts from the 1-c functional which is subsequently transformed to the 2-c functional, in part by replacing m_z by m. Then, the derivatives of the 2-c functional are calculated to build the 2-c potential. The second method instead starts directly from the 1-c potential and applies a transformation to build directly the 2-c potential. The 2 approaches are summarized as follows:

1) start from $F^{1c}[n, m_z]$ then $m_z \leftrightarrow m \rightarrow F^{2c}[n, m] \rightarrow V^{2c}$
2) start from $V^{1c}[n, m_z] \rightarrow$ apply tranformation $\rightarrow V^{2c}[n, m]$

F.2.2 Exchange: First Strategy

Let us start by applying the first approach to the exchange part of the potential. We wish to re-express the functional in terms of the new variables $n(\mathbf{r})$ and $m(\mathbf{r})$. For the particular case of the exchange part of the LSDA in the 1-c UKS, we have:

$$F_x^{1c}[n_{\alpha\alpha}^{\mathrm{Re}}(\mathbf{r}), n_{\beta\beta}^{\mathrm{Re}}(\mathbf{r})] = A\left({n_{\alpha\alpha}^{\mathrm{Re}}}^{4/3}(\mathbf{r}) + {n_{\beta\beta}^{\mathrm{Re}}}^{4/3}(\mathbf{r})\right) + B \tag{F.36}$$

where A and B are constants that depend on the particular implementation of the LSDA.

We first re-express the above in terms of the total and spin densities familiar to the 1-c UKS case:

$$F_x^{1c}[n(\mathbf{r}), m_z(\mathbf{r})] = 2^{-4/3}A\left((n(\mathbf{r}) + m_z(\mathbf{r}))^{4/3} + (n(\mathbf{r}) - m_z(\mathbf{r}))^{4/3}\right) + B \tag{F.37}$$

This yields the following 1-c UKS exchange potential $\mathbf{V}_x^{1c}(\mathbf{r})$:

$$\mathbf{V}_x^{1c}(\mathbf{r}) = \begin{pmatrix} \frac{\partial}{\partial n_{\alpha\alpha}^{\mathrm{Re}}(\mathbf{r})} \\ \frac{\partial}{\partial n_{\beta\beta}^{\mathrm{Re}}(\mathbf{r})} \end{pmatrix} F_x^{1c}[n(\mathbf{r}), m_z(\mathbf{r})] \tag{F.38}$$

$$\mathbf{V}_x^{1c}(\mathbf{r}) = \frac{4}{3}A\begin{pmatrix} {n_{\alpha\alpha}^{\mathrm{Re}}}^{1/3}(\mathbf{r}) \\ {n_{\beta\beta}^{\mathrm{Re}}}^{1/3}(\mathbf{r}) \end{pmatrix} = \frac{2^{5/3}}{3}A\begin{pmatrix} (n(\mathbf{r}) + m_z(\mathbf{r}))^{1/3} \\ (n(\mathbf{r}) - m_z(\mathbf{r}))^{1/3} \end{pmatrix} \tag{F.39}$$

For the 2-component generalization we simply replace the $m_z(\mathbf{r})$ by $m(\mathbf{r})$ in equation (F.37):

$$F_x^{2c}[n(\mathbf{r}), m(\mathbf{r})] = 2^{-4/3}A\left((n(\mathbf{r}) + m(\mathbf{r}))^{4/3} + (n(\mathbf{r}) - m(\mathbf{r}))^{4/3}\right) + B \tag{F.40}$$

To evaluate the exchange potential $\mathbf{V}_x(\mathbf{r})$ we require the following derivatives(see equation (F.33)):

$$\frac{\partial F_x^{2c}[\bar{\mathbf{n}}(\mathbf{r})]}{\partial n(\mathbf{r})} = \frac{2^{2/3}}{3}A\left((n(\mathbf{r}) + m(\mathbf{r}))^{1/3} + (n(\mathbf{r}) - m(\mathbf{r}))^{1/3}\right) \tag{F.41}$$

$$\frac{\partial F_x^{2c}[\bar{\mathbf{n}}(\mathbf{r})]}{\partial m(\mathbf{r})} = \frac{2^{2/3}}{3}A\left((n(\mathbf{r}) + m(\mathbf{r}))^{1/3} - (n(\mathbf{r}) - m(\mathbf{r}))^{1/3}\right) \tag{F.42}$$

Substituting (F.41) in (F.35) we obtain the 2-c LSDA exchange potential:

$$\begin{aligned} \mathbf{V}_x^{2c}(\mathbf{r}) = \frac{2^{2/3}}{3}A\Big[&\left((n(\mathbf{r}) + m(\mathbf{r}))^{1/3} + (n(\mathbf{r}) - m(\mathbf{r}))^{1/3}\right)\boldsymbol{\sigma}_0 \\ &+ \left((n(\mathbf{r}) + m(\mathbf{r}))^{1/3} - (n(\mathbf{r}) - m(\mathbf{r}))^{1/3}\right)\sum_c \frac{m_c(\mathbf{r})}{m(\mathbf{r})}\boldsymbol{\sigma}_c\Big] \end{aligned} \tag{F.43}$$

Finally expressing the above in terms of the eigenvalues $n_+(\mathbf{r})$ and $n_-(\mathbf{r})$:

$$\mathbf{V}_x^{2c}(\mathbf{r}) = \frac{2}{3}A\left[\left(n_+^{1/3}(\mathbf{r}) + n_-^{1/3}(\mathbf{r})\right)\boldsymbol{\sigma}_0 + \left(n_+^{1/3}(\mathbf{r}) - n_-^{1/3}(\mathbf{r})\right)\sum_c \frac{m_c(\mathbf{r})}{m(\mathbf{r})}\boldsymbol{\sigma}_c\right] \tag{F.44}$$

Now adopting the more compact notation:

$$\mathbf{V}_x^{2c}(\mathbf{r}) = V_x^1(\mathbf{r})\boldsymbol{\sigma}_0 + V_x^2(\mathbf{r})\sum_c \frac{m_c(\mathbf{r})}{m(\mathbf{r})}\boldsymbol{\sigma}_c \tag{F.45}$$

the 2-c LSDA exchange potential finds the following matrix representation:

$$\mathbf{V}_x^{2c} = \begin{pmatrix} V_x^{\alpha\alpha} & V_x^{\alpha\beta} \\ V_x^{\beta\alpha} & V_x^{\beta\beta} \end{pmatrix} = \begin{pmatrix} V_x^1 + V_x^2\frac{m_z}{m} & V_x^2\frac{1}{m}\left[m_x - im_y\right] \\ V_x^2\frac{1}{m}\left[m_x + im_y\right] & V_x^1 - V_x^2\frac{m_z}{m} \end{pmatrix} \tag{F.46}$$

where in the matrix above, the dependence on the coordinates of the electrons $\mathbf{r}$ is made implicit. The V_x^1 and V_x^2 are defined explicitly as:

$$V_x^1(\mathbf{r}) = \frac{2}{3}A\left(n_+^{1/3}(\mathbf{r}) + n_-^{1/3}(\mathbf{r})\right) \tag{F.47}$$

$$V_x^2(\mathbf{r}) = \frac{2}{3}A\left(n_+^{1/3}(\mathbf{r}) - n_-^{1/3}(\mathbf{r})\right) \tag{F.48}$$

F.2.3 Exchange: Second Strategy

Now let us apply the second approach for deriving the 2-c exchange potential. This time, we start directly from the 1-c potential of equation (F.39) and apply a variable transformation. A difference is that the derivative operator that is applied to the functional is different from equation (F.38) in the 2-c case. The 2-c derivative operator is as follows. Expanding equation (F.33) in matrix form:

$$\mathbf{V}_x^{2c} = \begin{pmatrix} \frac{\partial}{\partial n} + \frac{m_z}{m}\frac{\partial}{\partial m} & \frac{1}{m}\left[m_x - im_y\right]\frac{\partial}{\partial m} \\ \frac{1}{m}\left[m_x + im_y\right]\frac{\partial}{\partial m} & \frac{\partial}{\partial n} - \frac{m_z}{m}\frac{\partial}{\partial m} \end{pmatrix} F_x^{2c} \tag{F.49}$$

where above and in the following, the dependence on the electron coordinates are again made implicit. Another difference is that the 1-c UKS code works in terms of $n_{\alpha\alpha}^{\mathrm{Re}}$, $n_{\beta\beta}^{\mathrm{Re}}$ and $\zeta = \frac{n}{m_z}$, while for the 2-c formalism, we want to work in terms of n and the m_c. A generalization of the existing code therefore requires the use of the following variable transformations:

$$n_{\alpha\alpha}^{\mathrm{Re}} \rightarrow \frac{n+m}{2} \equiv n_+ \quad n_{\beta\beta}^{\mathrm{Re}} \rightarrow \frac{n-m}{2} \equiv n_- \quad \zeta \rightarrow \frac{m}{n} \tag{F.50}$$

After these transformations are performed, the effect on the 1-c UKS code will be to calculate derivatives of the functional in the following way:

$$\frac{\partial}{\partial n^{\text{Re}}_{\alpha\alpha}} F^{1c}_x[n^{\text{Re}}_{\alpha\alpha}, n^{\text{Re}}_{\beta\beta}] \rightarrow \frac{\partial}{\partial n_+} F^{2c}_x[n, m] \tag{F.51}$$

$$\frac{\partial}{\partial n^{\text{Re}}_{\beta\beta}} F^{1c}_x[n^{\text{Re}}_{\alpha\alpha}, n^{\text{Re}}_{\beta\beta}] \rightarrow \frac{\partial}{\partial n_-} F^{2c}_x[n, m] \tag{F.52}$$

These derivatives can then be transformed to the desired derivatives w.r.t n and the m_c, using the chain-rule as follows:

$$\frac{\partial}{\partial n} F^{2c}_x[n, m] = \left(\frac{\partial n_+}{\partial n} \frac{\partial}{\partial n_+} + \frac{\partial n_-}{\partial n} \frac{\partial}{\partial n_-} \right) F^{2c}_x[n, m] \tag{F.53}$$

and for $c = x, y, z$:

$$\frac{\partial}{\partial m_c} F^{2c}_x[n, m] = \left(\frac{\partial n_+}{\partial m_c} \frac{\partial}{\partial n_+} + \frac{\partial n_-}{\partial m_c} \frac{\partial}{\partial n_-} \right) F^{2c}_x[n, m] \tag{F.54}$$

From equation (F.1):

$$\begin{aligned} \frac{\partial n_+}{\partial n} &= \frac{1}{2}\left[1 + \frac{\partial m}{\partial n}\right] \\ &= \frac{1}{2} \end{aligned} \tag{F.55}$$

and

$$\begin{aligned} \frac{\partial n_-}{\partial n} &= \frac{1}{2}\left[1 - \frac{\partial m}{\partial n}\right] \\ &= \frac{1}{2} \end{aligned} \tag{F.56}$$

for $c = x, y, z$

$$\begin{aligned} \frac{\partial n_-}{\partial m_c} &= -\frac{1}{2}\left[\frac{\partial m}{\partial m_c} - \frac{\partial n}{\partial m_c}\right] \\ &= -\frac{1}{2}\frac{m_c}{m} \end{aligned} \tag{F.57}$$

and similarly:

$$\begin{aligned} \frac{\partial n_+}{\partial m_c} &= \frac{1}{2}\left[\frac{\partial m}{\partial m_c} + \frac{\partial n}{\partial m_c}\right] \\ &= \frac{1}{2}\frac{m_c}{m} \end{aligned} \tag{F.58}$$

These terms are then gathered in equation (F.49) to give:

$$\mathbf{V}_x^{2c}[n,m] =$$

$$\begin{pmatrix} \frac{1}{2}\left(\frac{\partial}{\partial n_+} + \frac{\partial}{\partial n_-}\right) + \frac{1}{2}\frac{m_z}{m}\left(\frac{\partial}{\partial n_+} - \frac{\partial}{\partial n_-}\right) & \frac{1}{2m}\left[m_x - im_y\right]\left(\frac{\partial}{\partial n_+} - \frac{\partial}{\partial n_-}\right) \\ \frac{1}{2m}\left[m_x + im_y\right]\left(\frac{\partial}{\partial n_+} - \frac{\partial}{\partial n_-}\right) & \frac{1}{2}\left(\frac{\partial}{\partial n_+} + \frac{\partial}{\partial n_-}\right) - \frac{1}{2}\frac{m_z}{m}\left(\frac{\partial}{\partial n_+} - \frac{\partial}{\partial n_-}\right) \end{pmatrix} \times$$

$$F_x^{2c}[n,m] \tag{F.59}$$

Applying the above operator to the 1-c UKS functional of equations (F.37), using the variable transformations specified in equation (F.50), we obtain the same 2-c exchange potential as in equation (F.44).

F.2.4 Correlation

Now for the correlation part of the functional, I take for example the Vosko-Wilk-Nusair parametrization. In this case, the correlation energy is written as:

$$E_c^{1c,VWN} = \int n(\mathbf{r}) F_c^{1c,VWN}[n_{\alpha\alpha}^{\mathrm{Re}}(\mathbf{r}), n_{\beta\beta}^{\mathrm{Re}}(\mathbf{r})] d\mathbf{r} \tag{F.60}$$

and the correlation functional $F_c^{1c,VWN}[n_{\alpha\alpha}^{\mathrm{Re}}(\mathbf{r}), n_{\beta\beta}^{\mathrm{Re}}(\mathbf{r})]$ is build starting from:

$$F_{c,i}^{1c}[r_s(\mathbf{r})] = A_i \Bigg\{ \ln \frac{x^2(\mathbf{r})}{X_i(x(\mathbf{r}))} + \frac{2b_i}{Q_i} \arctan \frac{Q_i}{2x(\mathbf{r}) + b_i} - \frac{b_i x_{0,i}}{X_i\left(x_{0,i}\right)} \\ \left[\ln \frac{(x(\mathbf{r}) - x_{0,i})^2}{X_i(x(\mathbf{r}))} + \frac{2\left(2x_{0,i} + b_i\right)}{Q_i} \arctan \frac{Q_i}{2x(\mathbf{r}) + b_i} \right] \Bigg\} \tag{F.61}$$

where $x(\mathbf{r}) = r_s^{1/2}(\mathbf{r})$, if $r_s(\mathbf{r}) = \left(\frac{3}{4\pi n(\mathbf{r})}\right)^{1/3}$ is the Wigner-Seitz radius, $X_i(x(\mathbf{r})) = x^2(\mathbf{r}) + b_i x(\mathbf{r}) + c_i$, $Q_i = (4c_i - b_i^2)^{1/2}$ and A_i, b_i, c_i and $x_{0,i}$ are parameters. The subscript $i = P, F$ where P and F stand for Para- and Ferromagnetic, are end-member cases of the general open-shell functional. The end-member cases are identified using the relative spin-polarization $\zeta(\mathbf{r}) = \frac{m_z(\mathbf{r})}{n(\mathbf{r})}$. For $i = P$, we have $\zeta(\mathbf{r}) = 0$ and for $i = F$, we have $\zeta(\mathbf{r}) = 1$. The two functionals $F_{c,P}^{1c}[r_s(\mathbf{r})]$ and $F_{c,F}^{1c}[r_s(\mathbf{r})]$ are built using the same formula above (F.61), but with different values for the parameters A_i, b_i, c_i and $x_{0,i}$. The general open-shell functional is then build from the $F_{c,P}^{1c}[r_s(\mathbf{r})]$ and $F_{c,F}^{1c}[r_s(\mathbf{r})]$ using an interpolation formula of the form:

$$F_c^{1c,VWN}[n_{\alpha\alpha}^{\mathrm{Re}}(\mathbf{r}), n_{\beta\beta}^{\mathrm{Re}}(\mathbf{r})] \equiv F_c^{1c,VWN}[r_s(\mathbf{r}), \zeta(\mathbf{r})] = F_{c,P}^{1c}[r_s(\mathbf{r})] + \alpha_c(r_s(\mathbf{r})) \times \\ \left[\frac{f(\zeta(\mathbf{r}))}{f''(0)}\right](1 - \zeta^4(\mathbf{r})) + \left[F_{c,F}^{1c}[r_s(\mathbf{r})] - F_{c,P}^{1c}[r_s(\mathbf{r})]\right] f(\zeta(\mathbf{r}))\zeta^4(\mathbf{r}) \tag{F.62}$$

where $f(\zeta(\mathbf{r}))$ is the LSDA exchange interpolation function:

$$f(\zeta(\mathbf{r})) = \frac{1}{2}\frac{\left[(1+\zeta(\mathbf{r}))^{4/3} + (1-\zeta(\mathbf{r}))^{4/3} - 2\right]}{2^{1/3}-1} \tag{F.63}$$

and $\alpha_c(r_s(\mathbf{r}))$ is the "spin-stiffness", formally defined as:

$$\alpha_c(r_s(\mathbf{r})) = \left[\frac{\partial^2 F_c^{1c}[r_s(\mathbf{r}),\zeta(\mathbf{r})]}{\partial\zeta^2(\mathbf{r})}\right]_{\zeta(\mathbf{r})=0} \tag{F.64}$$

In practice, however $\alpha_c(r_s(\mathbf{r}))$ is fitted using numerical derivatives of different parametrizations of equation (F.61), above.

The 1-component VWN correlation potential is then defined using the derivatives of the VWN functional:

$$\mathbf{V}_c^{1c,VWN}[n_{\alpha\alpha}^{\text{Re}}, n_{\beta\beta}^{\text{Re}}] = \begin{pmatrix} \frac{\partial}{\partial n_{\alpha\alpha}^{\text{Re}}(\mathbf{r})} \\ \frac{\partial}{\partial n_{\beta\beta}^{\text{Re}}(\mathbf{r})} \end{pmatrix} \left(n(\mathbf{r}) F_c^{1c,VWN}[n_{\alpha\alpha}^{\text{Re}}(\mathbf{r}), n_{\beta\beta}^{\text{Re}}(\mathbf{r})]\right) \tag{F.65}$$

The generalization of this correlation potential to the 2-component case involves again simply replacing $m_z(\mathbf{r})$ by $m(\mathbf{r})$ in formulae (F.62) and (F.63) and further by replacing the derivative operators above (following equation (F.35)) as follows:

$$\begin{gathered} \mathbf{V}^{2c}[n(\mathbf{r}), m(\mathbf{r})] = \\ \begin{pmatrix} \frac{\partial}{\partial n} + \frac{m_z}{m}\frac{\partial}{\partial m} & \frac{1}{m}\left[m_x - i m_y\right]\frac{\partial}{\partial m} \\ \frac{1}{m}\left[m_x + i m_y\right]\frac{\partial}{\partial m} & \frac{\partial}{\partial n} - \frac{m_z}{m}\frac{\partial}{\partial m} \end{pmatrix} \left(n(\mathbf{r}) F^{2c}[n(\mathbf{r}), m(\mathbf{r})]\right) \end{gathered} \tag{F.66}$$

where again, in the matrix above the dependence on the coordinates of the electrons $\mathbf{r}$ is made implicit. For the case of the correlation functional, only the second approach is used to derive the potential as a result of the fact that the functional is more complicated. Using the same variable transformations as in the exchange potential case, we arrive to an analogous equation to equation (F.2.3) but this time applied to the correlation functional:

$$\begin{gathered} \mathbf{V}_c^{2c,VWN}[n(\mathbf{r}), m(\mathbf{r})] = \\ \begin{pmatrix} \frac{1}{2}\left(\frac{\partial}{\partial n_+} + \frac{\partial}{\partial n_-}\right) + \frac{1}{2}\frac{m_z}{m}\left(\frac{\partial}{\partial n_+} - \frac{\partial}{\partial n_-}\right) & \frac{1}{2m}\left[m_x - i m_y\right]\left(\frac{\partial}{\partial n_+} - \frac{\partial}{\partial n_-}\right) \\ \frac{1}{2m}\left[m_x + i m_y\right]\left(\frac{\partial}{\partial n_+} - \frac{\partial}{\partial n_-}\right) & \frac{1}{2}\left(\frac{\partial}{\partial n_+} + \frac{\partial}{\partial n_-}\right) - \frac{1}{2}\frac{m_z}{m}\left(\frac{\partial}{\partial n_+} - \frac{\partial}{\partial n_-}\right) \end{pmatrix} \times \\ \times \left(n(\mathbf{r}) F_c^{2c,VWN}[n(\mathbf{r}), m(\mathbf{r})]\right) \end{gathered} \tag{F.67}$$

The formula above is also applicable to other LSDA functionals in the code, as all 1-c UKS LSDA functionals.

F.3 Application to GGA

F.3.1 Potential in the Collinear Theory

For the 1-c UKS case, we are interested in xc energy contributions arising from functionals of the form (dependence on the electron coordinates is dropped):

$$E_{xc} = \int F[n^{\text{Re}}_{\alpha\alpha}, n^{\text{Re}}_{\beta\beta}, \left|\nabla n^{\text{Re}}_{\alpha\alpha}\right|^2, \left|\nabla n^{\text{Re}}_{\beta\beta}\right|^2, \nabla n^{\text{Re}}_{\alpha\alpha} \cdot \nabla n^{\text{Re}}_{\beta\beta}]d\mathbf{r} \tag{F.68}$$

Finding the expression for the potential involves taking the first variation of the energy:

$$\begin{aligned} dE_{xc} &= E_{xc}(n^{\text{Re}}_{\alpha\alpha} + \delta n^{\text{Re}}_{\alpha\alpha}, n^{\text{Re}}_{\beta\beta} + \delta n^{\text{Re}}_{\beta\beta}) - E_{xc}(n^{\text{Re}}_{\alpha\alpha}, n^{\text{Re}}_{\beta\beta}) \\ &= \int \left(\frac{\delta E_{xc}}{\delta n^{\text{Re}}_{\alpha\alpha}} \delta n^{\text{Re}}_{\alpha\alpha} + \frac{\delta E_{xc}}{\delta n^{\text{Re}}_{\beta\beta}} \delta n^{\text{Re}}_{\beta\beta} \right) d\mathbf{r} - E_{xc}(n^{\text{Re}}_{\alpha\alpha}, n^{\text{Re}}_{\beta\beta}) \\ &= \int \left(V^{\alpha\alpha}_{xc} \delta n^{\text{Re}}_{\alpha\alpha} + V^{\beta\beta}_{xc} \delta n^{\text{Re}}_{\beta\beta} \right) d\mathbf{r} - E_{xc}(n^{\text{Re}}_{\alpha\alpha}, n^{\text{Re}}_{\beta\beta}) \end{aligned} \tag{F.69}$$

The variation of the energy is expanded in first order as:

$$\begin{aligned} dE_{xc} = \int \Bigg[F &+ \frac{\partial F}{\partial n^{\text{Re}}_{\alpha\alpha}} \delta n^{\text{Re}}_{\alpha\alpha} + \frac{\partial F}{\partial n^{\text{Re}}_{\beta\beta}} \delta n^{\text{Re}}_{\beta\beta} + \frac{\partial F}{\partial \left|\nabla n^{\text{Re}}_{\alpha\alpha}\right|^2} \delta \left|\nabla n^{\text{Re}}_{\alpha\alpha}\right|^2 \\ &+ \frac{\partial F}{\partial \left|\nabla n^{\text{Re}}_{\beta\beta}\right|^2} \delta \left|\nabla n^{\text{Re}}_{\beta\beta}\right|^2 + \frac{\partial F}{\partial \nabla n^{\text{Re}}_{\alpha\alpha} \cdot \nabla n^{\text{Re}}_{\beta\beta}} \delta \left(\nabla n^{\text{Re}}_{\alpha\alpha} \cdot \nabla n^{\text{Re}}_{\beta\beta} \right) \Bigg] d\mathbf{r} \end{aligned} \tag{F.70}$$

Using $\delta \left|\nabla n^{\text{Re}}_{\sigma\sigma}\right|^2 = 2\nabla n^{\text{Re}}_{\sigma\sigma} \cdot \delta \nabla n^{\text{Re}}_{\sigma\sigma}$, as well as $\delta \left(\nabla n^{\text{Re}}_{\alpha\alpha} \cdot \nabla n^{\text{Re}}_{\beta\beta} \right) = \nabla n^{\text{Re}}_{\alpha\alpha} \cdot \delta \nabla n^{\text{Re}}_{\beta\beta} + \nabla n^{\text{Re}}_{\beta\beta} \cdot \delta \nabla n^{\text{Re}}_{\alpha\alpha}$, we have:

$$\begin{aligned} dE_{xc} = \int \Bigg[F &+ \frac{\partial F}{\partial n^{\text{Re}}_{\alpha\alpha}} \delta n^{\text{Re}}_{\alpha\alpha} + \frac{\partial F}{\partial n^{\text{Re}}_{\beta\beta}} \delta n^{\text{Re}}_{\beta\beta} + \\ &\frac{\partial F}{\partial \left|\nabla n^{\text{Re}}_{\alpha\alpha}\right|^2} 2\nabla n^{\text{Re}}_{\alpha\alpha} \cdot \delta \nabla n^{\text{Re}}_{\alpha\alpha} + \frac{\partial F}{\partial \left|\nabla n^{\text{Re}}_{\beta\beta}\right|^2} 2\nabla n^{\text{Re}}_{\beta\beta} \cdot \delta \nabla n^{\text{Re}}_{\beta\beta} \\ &+ \frac{\partial F}{\partial \nabla n^{\text{Re}}_{\alpha\alpha} \cdot \nabla n^{\text{Re}}_{\beta\beta}} \left(\nabla n^{\text{Re}}_{\alpha\alpha} \cdot \delta \nabla n^{\text{Re}}_{\beta\beta} + \nabla n^{\text{Re}}_{\beta\beta} \cdot \delta \nabla n^{\text{Re}}_{\alpha\alpha} \right) \Bigg] d\mathbf{r} \end{aligned} \tag{F.71}$$

Now given a generic vector $\mathbf{F}$ and scalar ϕ, the product rule for the divergence operator says that $(\nabla\phi) \cdot \mathbf{F} = \nabla \cdot (\phi\mathbf{F}) - \phi(\nabla \cdot \mathbf{F})$ applying this to the above, with the scalar being the $\delta n_{\sigma\sigma}$, and using (in first order)

$\nabla \delta n_{\sigma\sigma} = \delta \nabla n_{\sigma\sigma}$:

$$\begin{aligned}
dE_{xc} = \int \Bigg[F + \frac{\partial F}{\partial n^{\mathrm{Re}}_{\alpha\alpha}} \delta n^{\mathrm{Re}}_{\alpha\alpha} + \frac{\partial F}{\partial n^{\mathrm{Re}}_{\beta\beta}} \delta n^{\mathrm{Re}}_{\beta\beta} + \\
2\nabla \cdot \left(\frac{\partial F}{\partial \left| \nabla n^{\mathrm{Re}}_{\alpha\alpha} \right|^2} \nabla n^{\mathrm{Re}}_{\alpha\alpha} \delta n^{\mathrm{Re}}_{\alpha\alpha} \right) - 2\nabla \cdot \left(\frac{\partial F}{\partial \left| \nabla n^{\mathrm{Re}}_{\alpha\alpha} \right|^2} \nabla n^{\mathrm{Re}}_{\alpha\alpha} \right) \delta n^{\mathrm{Re}}_{\alpha\alpha} \\
+2\nabla \cdot \left(\frac{\partial F}{\partial \left| \nabla n^{\mathrm{Re}}_{\beta\beta} \right|^2} \nabla n^{\mathrm{Re}}_{\beta\beta} \delta n^{\mathrm{Re}}_{\beta\beta} \right) - 2\nabla \cdot \left(\frac{\partial F}{\partial \left| \nabla n^{\mathrm{Re}}_{\beta\beta} \right|^2} \nabla n^{\mathrm{Re}}_{\beta\beta} \right) \delta n^{\mathrm{Re}}_{\beta\beta} \\
+\nabla \cdot \left(\frac{\partial F}{\partial \nabla n^{\mathrm{Re}}_{\alpha\alpha} \cdot \nabla n^{\mathrm{Re}}_{\beta\beta}} \nabla n^{\mathrm{Re}}_{\alpha\alpha} \delta n^{\mathrm{Re}}_{\beta\beta} \right) - \nabla \cdot \left(\frac{\partial F}{\partial \nabla n^{\mathrm{Re}}_{\alpha\alpha} \cdot \nabla n^{\mathrm{Re}}_{\beta\beta}} \nabla n^{\mathrm{Re}}_{\alpha\alpha} \right) \delta n^{\mathrm{Re}}_{\beta\beta} \\
+\nabla \cdot \left(\frac{\partial F}{\partial \nabla n^{\mathrm{Re}}_{\alpha\alpha} \cdot \nabla n^{\mathrm{Re}}_{\beta\beta}} \nabla n^{\mathrm{Re}}_{\beta\beta} \delta n^{\mathrm{Re}}_{\alpha\alpha} \right) - \nabla \cdot \left(\frac{\partial F}{\partial \nabla n^{\mathrm{Re}}_{\alpha\alpha} \cdot \nabla n^{\mathrm{Re}}_{\beta\beta}} \nabla n^{\mathrm{Re}}_{\beta\beta} \right) \delta n^{\mathrm{Re}}_{\alpha\alpha} \Bigg] d\mathbf{r}
\end{aligned} \tag{F.72}$$

Integrating some of the terms:

$$\begin{aligned}
dE_{xc} = \int \left[F + \frac{\partial F}{\partial n^{\mathrm{Re}}_{\alpha\alpha}} \delta n^{\mathrm{Re}}_{\alpha\alpha} + \frac{\partial F}{\partial n^{\mathrm{Re}}_{\beta\beta}} \delta n^{\mathrm{Re}}_{\beta\beta} \right] d\mathbf{r} \\
+2 \left. \frac{\partial F}{\partial \left| \nabla n^{\mathrm{Re}}_{\alpha\alpha} \right|^2} \nabla n^{\mathrm{Re}}_{\alpha\alpha} \delta n^{\mathrm{Re}}_{\alpha\alpha} \right|_{-\infty}^{\infty} - 2 \int \left[\nabla \cdot \left(\frac{\partial F}{\partial \left| \nabla n^{\mathrm{Re}}_{\alpha\alpha} \right|^2} \nabla n^{\mathrm{Re}}_{\alpha\alpha} \right) \delta n^{\mathrm{Re}}_{\alpha\alpha} \right] d\mathbf{r} \\
+2 \left. \frac{\partial F}{\partial \left| \nabla n^{\mathrm{Re}}_{\beta\beta} \right|^2} \nabla n^{\mathrm{Re}}_{\beta\beta} \delta n^{\mathrm{Re}}_{\beta\beta} \right|_{-\infty}^{\infty} - 2 \int \left[\nabla \cdot \left(\frac{\partial F}{\partial \left| \nabla n^{\mathrm{Re}}_{\beta\beta} \right|^2} \nabla n^{\mathrm{Re}}_{\beta\beta} \right) \delta n^{\mathrm{Re}}_{\beta\beta} \right] d\mathbf{r} \\
+ \left. \frac{\partial F}{\partial \nabla n^{\mathrm{Re}}_{\alpha\alpha} \cdot \nabla n^{\mathrm{Re}}_{\beta\beta}} \nabla n^{\mathrm{Re}}_{\alpha\alpha} \delta n^{\mathrm{Re}}_{\beta\beta} \right|_{-\infty}^{\infty} - \int \left[\nabla \cdot \left(\frac{\partial F}{\partial \nabla n^{\mathrm{Re}}_{\alpha\alpha} \cdot \nabla n^{\mathrm{Re}}_{\beta\beta}} \nabla n^{\mathrm{Re}}_{\alpha\alpha} \right) \delta n^{\mathrm{Re}}_{\beta\beta} \right] d\mathbf{r} \\
+ \left. \frac{\partial F}{\partial \nabla n^{\mathrm{Re}}_{\alpha\alpha} \cdot \nabla n^{\mathrm{Re}}_{\beta\beta}} \nabla n^{\mathrm{Re}}_{\beta\beta} \delta n^{\mathrm{Re}}_{\alpha\alpha} \right|_{\infty}^{\infty} - \int \left[\nabla \cdot \left(\frac{\partial F}{\partial \nabla n^{\mathrm{Re}}_{\alpha\alpha} \cdot \nabla n^{\mathrm{Re}}_{\beta\beta}} \nabla n^{\mathrm{Re}}_{\beta\beta} \right) \delta n^{\mathrm{Re}}_{\alpha\alpha} \right] d\mathbf{r}
\end{aligned} \tag{F.73}$$

Now provided that the derivatives of the functional are bound at infinity, the terms outside the integral vanish, and we are left with:

$$\begin{aligned}
dE_{xc} = \int \left[F + \frac{\partial F}{\partial n^{\mathrm{Re}}_{\alpha\alpha}} \delta n^{\mathrm{Re}}_{\alpha\alpha} + \frac{\partial F}{\partial n^{\mathrm{Re}}_{\beta\beta}} \delta n^{\mathrm{Re}}_{\beta\beta} \right] d\mathbf{r} - 2 \int \left[\nabla \cdot \left(\frac{\partial F}{\partial \left| \nabla n^{\mathrm{Re}}_{\alpha\alpha} \right|^2} \nabla n^{\mathrm{Re}}_{\alpha\alpha} \right) \delta n^{\mathrm{Re}}_{\alpha\alpha} \right] d\mathbf{r} \\
-2 \int \left[\nabla \cdot \left(\frac{\partial F}{\partial \left| \nabla n^{\mathrm{Re}}_{\beta\beta} \right|^2} \nabla n^{\mathrm{Re}}_{\beta\beta} \right) \delta n^{\mathrm{Re}}_{\beta\beta} \right] d\mathbf{r} - \int \left[\nabla \cdot \left(\frac{\partial F}{\partial \nabla n^{\mathrm{Re}}_{\alpha\alpha} \cdot \nabla n^{\mathrm{Re}}_{\beta\beta}} \nabla n^{\mathrm{Re}}_{\alpha\alpha} \right) \delta n^{\mathrm{Re}}_{\beta\beta} \right] d\mathbf{r} \\
- \int \left[\nabla \cdot \left(\frac{\partial F}{\partial \nabla n^{\mathrm{Re}}_{\alpha\alpha} \cdot \nabla n^{\mathrm{Re}}_{\beta\beta}} \nabla n^{\mathrm{Re}}_{\beta\beta} \right) \delta n^{\mathrm{Re}}_{\alpha\alpha} \right] d\mathbf{r}
\end{aligned} \tag{F.74}$$

Comparing the former with equation (F.69), we see immediately that:

$$V_{xc}^{\alpha\alpha} = \frac{\partial F}{\partial n_{\alpha\alpha}^{\mathrm{Re}}} - 2\nabla \cdot \left(\frac{\partial F}{\partial \left| \nabla n_{\alpha\alpha}^{\mathrm{Re}} \right|^2} \nabla n_{\alpha\alpha}^{\mathrm{Re}} \right) - \nabla \cdot \left(\frac{\partial F}{\partial \nabla n_{\alpha\alpha}^{\mathrm{Re}} \cdot \nabla n_{\beta\beta}^{\mathrm{Re}}} \nabla n_{\beta\beta}^{\mathrm{Re}} \right) \tag{F.75}$$

and:

$$V_{xc}^{\beta\beta} = \frac{\partial F}{\partial n_{\beta\beta}^{\mathrm{Re}}} - 2\nabla \cdot \left(\frac{\partial F}{\partial \left| \nabla n_{\beta\beta}^{\mathrm{Re}} \right|^2} \nabla n_{\beta\beta}^{\mathrm{Re}} \right) - \nabla \cdot \left(\frac{\partial F}{\partial \nabla n_{\alpha\alpha}^{\mathrm{Re}} \cdot \nabla n_{\beta\beta}^{\mathrm{Re}}} \nabla n_{\alpha\alpha}^{\mathrm{Re}} \right) \tag{F.76}$$

Matrix elements of the xc potential are, for example for the $\alpha\alpha$ block:

$$\begin{aligned} \left\langle \chi_\mu \middle| V_{xc}^{\alpha\alpha} \middle| \chi_\nu \right\rangle = \int \chi_\mu V_{xc}^{\alpha\alpha} \chi_\nu d\mathbf{r} = \int \chi_\mu \chi_\nu \frac{\partial F}{\partial n_{\alpha\alpha}^{\mathrm{Re}}} d\mathbf{r} \\ -2 \int \nabla \cdot \left(\frac{\partial F}{\partial \left| \nabla n_{\alpha\alpha}^{\mathrm{Re}} \right|^2} \nabla n_{\alpha\alpha}^{\mathrm{Re}} \right) \chi_\mu \chi_\nu d\mathbf{r} - \int \nabla \cdot \left(\frac{\partial F}{\partial \nabla n_{\alpha\alpha}^{\mathrm{Re}} \cdot \nabla n_{\beta\beta}^{\mathrm{Re}}} \nabla n_{\beta\beta}^{\mathrm{Re}} \right) \chi_\mu \chi_\nu d\mathbf{r} \end{aligned} \tag{F.77}$$

Integrating the last two terms by parts:

$$\left\langle \chi_\mu \middle| V_{xc}^{\alpha\alpha} \middle| \chi_\nu \right\rangle = \int \left[\chi_\mu \chi_\nu \frac{\partial F}{\partial n_{\alpha\alpha}^{\mathrm{Re}}} + \left(2 \frac{\partial F}{\partial \left| \nabla n_{\alpha\alpha}^{\mathrm{Re}} \right|^2} \nabla n_{\alpha\alpha}^{\mathrm{Re}} + \frac{\partial F}{\partial \nabla n_{\alpha\alpha}^{\mathrm{Re}} \cdot \nabla n_{\beta\beta}^{\mathrm{Re}}} \nabla n_{\beta\beta}^{\mathrm{Re}} \right) \cdot \nabla \left(\chi_\mu \chi_\nu \right) \right] d\mathbf{r} \tag{F.78}$$

F.3.2 Generalization to Non-Collinear Densities

The 1-c UKS GGA functionals are of the general form:

$$F_{xc}^{GGA,1c}[n_{\alpha\alpha}^{\mathrm{Re}}, n_{\beta\beta}^{\mathrm{Re}}, \left| \nabla n_{\alpha\alpha}^{\mathrm{Re}} \right|^2, \left| \nabla n_{\beta\beta}^{\mathrm{Re}} \right|^2, \nabla n_{\alpha\alpha}^{\mathrm{Re}} \cdot \nabla n_{\beta\beta}^{\mathrm{Re}}]$$

A generalization of the existing 1-c UKS code to the non-collinear density can be achieved using the second strategy outlined above for the LSDA case. A variable transformation similar to that in equation F.50 is used for GGA functionals, except that now the transformation is also applied to gradient variables (explicit dependence on the electron coordinates is dropped in the following):

$$n_{\alpha\alpha}^{\mathrm{Re}} \to n_+ \quad n_{\beta\beta}^{\mathrm{Re}} \to n_- \quad \zeta \to \frac{m}{n}$$

$$\left| \nabla n_{\alpha\alpha}^{\mathrm{Re}} \right| \to |\nabla n_+| \quad \left| \nabla n_{\beta\beta}^{\mathrm{Re}} \right| \to |\nabla n_-|$$

$$\nabla n_{\alpha\alpha}^{\mathrm{Re}} \cdot \nabla n_{\beta\beta}^{\mathrm{Re}} \to \nabla n_+ \cdot \nabla n_- \tag{F.79}$$

The effect of these variable transformation on the existing 1-c UKS code will be to calculate derivatives of the functional in the following way:

$$\frac{\partial}{\partial n_{\alpha\alpha}^{\mathrm{Re}}} F_{xc}^{1c,GGA} \quad \rightarrow \quad \frac{\partial}{\partial n_+} F_{xc}^{2c,GGA} \tag{F.80}$$

$$\frac{\partial}{\partial n_{\beta\beta}^{\mathrm{Re}}} F_{xc}^{1c,GGA} \quad \rightarrow \quad \frac{\partial}{\partial n_-} F_{xc}^{2c,GGA} \tag{F.81}$$

$$\frac{\partial}{\partial \left|\nabla n_{\alpha\alpha}^{\mathrm{Re}}\right|^2} F_{xc}^{1c,GGA} \quad \rightarrow \quad \frac{\partial}{\partial |\nabla n_+|^2} F_{xc}^{2c,GGA} \tag{F.82}$$

$$\frac{\partial}{\partial \left|\nabla n_{\beta\beta}^{\mathrm{Re}}\right|^2} F_{xc}^{1c,GGA} \quad \rightarrow \quad \frac{\partial}{\partial |\nabla n_-|^2} F_{xc}^{2c,GGA} \tag{F.83}$$

$$\frac{\partial}{\partial \nabla n_{\alpha\alpha}^{\mathrm{Re}} \cdot \nabla n_{\beta\beta}^{\mathrm{Re}}} F_{xc}^{1c,GGA} \quad \rightarrow \quad \frac{\partial}{\partial \nabla n_+ \cdot \nabla n_-} F_{xc}^{2c,GGA} \tag{F.84}$$

Applying the variable transformation (F.3.2) to equation (F.74), we find the first variation of the xc Energy for non-collinear densities (the superscript $2c, GGA$ is dropped in the following):

$$\begin{aligned} dE_{xc} = \int \left[F + \frac{\partial F}{\partial n_+}\delta n_+ + \frac{\partial F}{\partial n_-}\delta n_- \right] d\mathbf{r} - 2\int \left[\nabla \cdot \left(\frac{\partial F}{\partial |\nabla n_+|^2} \nabla n_+ \right) \delta n_+ \right] d\mathbf{r} \\ -2\int \left[\nabla \cdot \left(\frac{\partial F}{\partial |\nabla n_-|^2} \nabla n_- \right) \delta n_- \right] d\mathbf{r} - \int \left[\nabla \cdot \left(\frac{\partial F}{\partial \nabla n_+ \cdot \nabla n_-} \nabla n_+ \right) \delta n_- \right] d\mathbf{r} \\ - \int \left[\nabla \cdot \left(\frac{\partial F}{\partial \nabla n_+ \cdot \nabla n_-} \nabla n_- \right) \delta n_+ \right] d\mathbf{r} \end{aligned} \tag{F.85}$$

Now substituting $n_\pm = \frac{1}{2}(n \pm m)$ in the variations of $n_\pm$ above:

$$\begin{aligned} dE_{xc} = \frac{1}{2}\Bigg\{ \int \left[F + \frac{\partial F}{\partial n_+}\delta n + \frac{\partial F}{\partial n_+}\delta m + \frac{\partial F}{\partial n_-}\delta n - \frac{\partial F}{\partial n_-}\delta m \right] d\mathbf{r} \\ -2\int \left[\nabla \cdot \left(\frac{\partial F}{\partial |\nabla n_+|^2} \nabla n_+ \right) \delta n + \nabla \cdot \left(\frac{\partial F}{\partial |\nabla n_+|^2} \nabla n_+ \right) \delta m \right] d\mathbf{r} \\ -2\int \left[\nabla \cdot \left(\frac{\partial F}{\partial |\nabla n_-|^2} \nabla n_- \right) \delta n - \nabla \cdot \left(\frac{\partial F}{\partial |\nabla n_-|^2} \nabla n_- \right) \delta m \right] d\mathbf{r} \\ - \int \left[\nabla \cdot \left(\frac{\partial F}{\partial \nabla n_+ \cdot \nabla n_-} \nabla n_+ \right) \delta n - \nabla \cdot \left(\frac{\partial F}{\partial \nabla n_+ \cdot \nabla n_-} \nabla n_+ \right) \delta m \right] d\mathbf{r} \\ - \int \left[\nabla \cdot \left(\frac{\partial F}{\partial \nabla n_+ \cdot \nabla n_-} \nabla n_- \right) \delta n + \nabla \cdot \left(\frac{\partial F}{\partial \nabla n_+ \cdot \nabla n_-} \nabla n_- \right) \delta m \right] d\mathbf{r} \Bigg\} \end{aligned} \tag{F.86}$$

This yields:

$$\frac{\delta E_{xc}}{\delta n} = \frac{1}{2}\left\{\frac{\partial F}{\partial n_+} + \frac{\partial F}{\partial n_-} - \nabla\cdot\left[2\frac{\partial F}{\partial|\nabla n_+|^2}\nabla n_+ + 2\frac{\partial F}{\partial|\nabla n_-|^2}\nabla n_- \right.\right.$$
$$\left.\left. + \frac{\partial F}{\partial \nabla n_+\cdot\nabla n_-}\nabla n_+ + \frac{\partial F}{\partial \nabla n_+\cdot\nabla n_-}\nabla n_-\right]\right\} \tag{F.87}$$

and:

$$\frac{\delta E_{xc}}{\delta m} = \frac{1}{2}\left\{\frac{\partial F}{\partial n_+} - \frac{\partial F}{\partial n_-} - \nabla\cdot\left[2\frac{\partial F}{\partial|\nabla n_+|^2}\nabla n_+ - 2\frac{\partial F}{\partial|\nabla n_-|^2}\nabla n_- \right.\right.$$
$$\left.\left. - \frac{\partial F}{\partial \nabla n_+\cdot\nabla n_-}\nabla n_+ + \frac{\partial F}{\partial \nabla n_+\cdot\nabla n_-}\nabla n_-\right]\right\} \tag{F.88}$$

Now substituting $\nabla n_\pm = \frac{1}{2}\nabla(n \pm m)$ in the above, we obtain:

$$\frac{\delta E_{xc}}{\delta n} = \frac{1}{2}\left\{\frac{\partial F}{\partial n_+} + \frac{\partial F}{\partial n_-} - \nabla\cdot\left[\left(\frac{\partial F}{\partial|\nabla n_+|^2} + \frac{\partial F}{\partial|\nabla n_-|^2} + \right.\right.\right.$$
$$\left.\left.\left.\frac{\partial F}{\partial \nabla n_+\cdot\nabla n_-}\right)\nabla n + \left(\frac{\partial F}{\partial|\nabla n_+|^2} - \frac{\partial F}{\partial|\nabla n_-|^2}\right)\nabla m\right]\right\} \tag{F.89}$$

and:

$$\frac{\delta E_{xc}}{\delta m} = \frac{1}{2}\left\{\frac{\partial F}{\partial n_+} - \frac{\partial F}{\partial n_-} - \nabla\cdot\left[\left(\frac{\partial F}{\partial|\nabla n_+|^2} - \frac{\partial F}{\partial|\nabla n_-|^2}\right)\nabla n\right.\right.$$
$$\left.\left. + \left(\frac{\partial F}{\partial|\nabla n_+|^2} + \frac{\partial F}{\partial|\nabla n_-|^2} - \frac{\partial F}{\partial \nabla n_+\cdot\nabla n_-}\right)\nabla m\right]\right\} \tag{F.90}$$

The two equations above are equivalent to equations (25) and (26) of the TURBOMOLE paper. However, for our purposes it is easier to extend the existing code by working in terms of equations (F.87) and (F.88) instead.

From equations (F.35) and (F.33), as well as (F.87) and (F.88), the matrix elements of the xc potential have the form:

$$\left\langle\chi_\mu\middle|\mathbf{V_{xc}}\middle|\chi_\nu\right\rangle = \frac{1}{2}\boldsymbol{\sigma_0}\left\{\int \chi_\mu\chi_\nu\left(\frac{\partial F}{\partial n_+} + \frac{\partial F}{\partial n_-}\right)d\mathbf{r} - \nabla\cdot\int\left[2\frac{\partial F}{\partial|\nabla n_+|^2}\nabla n_+\right.\right.$$
$$\left.\left. +2\frac{\partial F}{\partial|\nabla n_-|^2}\nabla n_- + \frac{\partial F}{\partial \nabla n_+\cdot\nabla n_-}\nabla n_+ + \frac{\partial F}{\partial \nabla n_+\cdot\nabla n_-}\nabla n_-\right]\chi_\mu\chi_\nu d\mathbf{r}\right\}$$
$$+\frac{1}{2}\left(\sum_{c=x,y,z}\frac{m_c}{m}\boldsymbol{\sigma_c}\right)\left\{\int \chi_\mu\chi_\nu\left(\frac{\partial F}{\partial n_+} - \frac{\partial F}{\partial n_-}\right)d\mathbf{r} - \nabla\cdot\int\left[2\frac{\partial F}{\partial|\nabla n_+|^2}\nabla n_+\right.\right.$$
$$\left.\left. -2\frac{\partial F}{\partial|\nabla n_-|^2}\nabla n_- - \frac{\partial F}{\partial \nabla n_+\cdot\nabla n_-}\nabla n_+ + \frac{\partial F}{\partial \nabla n_+\cdot\nabla n_-}\nabla n_-\right]\chi_\mu\chi_\nu d\mathbf{r}\right\} \tag{F.91}$$

Integrating by parts the terms which contain the divergence of derivatives of the functional (second and fourth integrals in the above):

$$\begin{aligned}\left\langle\chi_\mu\middle|\mathbf{V_{xc}}\middle|\chi_\nu\right\rangle = \frac{1}{2}\boldsymbol{\sigma_0}\Bigg\{\int\chi_\mu\chi_\nu\left(\frac{\partial F}{\partial n_+}+\frac{\partial F}{\partial n_-}\right)d\mathbf{r}+\int\Bigg[2\frac{\partial F}{\partial|\nabla n_+|^2}\nabla n_+ \\ +2\frac{\partial F}{\partial|\nabla n_-|^2}\nabla n_- + \frac{\partial F}{\partial\nabla n_+\cdot\nabla n_-}\nabla n_+ + \frac{\partial F}{\partial\nabla n_+\cdot\nabla n_-}\nabla n_-\Bigg]\cdot\nabla\left(\chi_\mu\chi_\nu\right)d\mathbf{r}\Bigg\} \\ +\frac{1}{2}\left(\sum_{c=x,y,z}\frac{m_c}{m}\boldsymbol{\sigma_c}\right)\Bigg\{\int\chi_\mu\chi_\nu\left(\frac{\partial F}{\partial n_+}-\frac{\partial F}{\partial n_-}\right)d\mathbf{r}+\int\Bigg[2\frac{\partial F}{\partial|\nabla n_+|^2}\nabla n_+ \\ -2\frac{\partial F}{\partial|\nabla n_-|^2}\nabla n_- - \frac{\partial F}{\partial\nabla n_+\cdot\nabla n_-}\nabla n_+ + \frac{\partial F}{\partial\nabla n_+\cdot\nabla n_-}\nabla n_-\Bigg]\cdot\nabla\left(\chi_\mu\chi_\nu\right)d\mathbf{r}\Bigg\}\end{aligned} \tag{F.92}$$

Using the compact notation:

$$\begin{aligned}N_{xc} = \frac{1}{2}\Bigg\{\int\chi_\mu\chi_\nu\left(\frac{\partial F}{\partial n_+}+\frac{\partial F}{\partial n_-}\right)d\mathbf{r}+\int\Bigg[2\frac{\partial F}{\partial|\nabla n_+|^2}\nabla n_+ \\ +2\frac{\partial F}{\partial|\nabla n_-|^2}\nabla n_- + \frac{\partial F}{\partial\nabla n_+\cdot\nabla n_-}\nabla n_+ + \frac{\partial F}{\partial\nabla n_+\cdot\nabla n_-}\nabla n_-\Bigg]\cdot\nabla\left(\chi_\mu\chi_\nu\right)d\mathbf{r}\Bigg\}\end{aligned} \tag{F.93}$$

and:

$$\begin{aligned}B_{xc} = \frac{1}{2}\Bigg\{\int\chi_\mu\chi_\nu\left(\frac{\partial F}{\partial n_+}-\frac{\partial F}{\partial n_-}\right)d\mathbf{r}+\int\Bigg[2\frac{\partial F}{\partial|\nabla n_+|^2}\nabla n_+ \\ -2\frac{\partial F}{\partial|\nabla n_-|^2}\nabla n_- - \frac{\partial F}{\partial\nabla n_+\cdot\nabla n_-}\nabla n_+ + \frac{\partial F}{\partial\nabla n_+\cdot\nabla n_-}\nabla n_-\Bigg]\cdot\nabla\left(\chi_\mu\chi_\nu\right)d\mathbf{r}\Bigg\}\end{aligned} \tag{F.94}$$

we obtain for the elements of the xc potential matrix in spin-space:

$$\left\langle\chi_\mu\middle|V_{xc}^{\alpha\alpha}\middle|\chi_\nu\right\rangle = N_{xc}+\frac{m_z}{m}B_{xc} \tag{F.95}$$

$$\left\langle\chi_\mu\middle|V_{xc}^{\alpha\beta}\middle|\chi_\nu\right\rangle = \frac{1}{m}\left[m_x-im_y\right]B_{xc} \tag{F.96}$$

$$\left\langle\chi_\mu\middle|V_{xc}^{\beta\alpha}\middle|\chi_\nu\right\rangle = \frac{1}{m}\left[m_x+im_y\right]B_{xc} \tag{F.97}$$

$$\left\langle\chi_\mu\middle|V_{xc}^{\beta\beta}\middle|\chi_\nu\right\rangle = N_{xc}-\frac{m_z}{m}B_{xc} \tag{F.98}$$

F.4 Building the Kohn-Sham Matrix

Once the xc potential has been calculated at different points in space, as sketched above, the xc contribution needs to be added to the Kohn-Sham matrix in the appropriate way. The Kohn-Sham matrix has the following general structure:

$$F_{\mu\nu}^{\alpha\alpha} = h_{\mu\nu}^{\alpha\alpha}+\sum_{\sigma,\rho}(\chi_\mu\chi_\nu|\chi_\sigma\chi_\rho)\mathrm{Re}\left(P_{\sigma\rho}^{\alpha\alpha}+P_{\sigma\rho}^{\beta\beta}\right)+\left\langle\chi_\mu\middle|V_{xc}^{\alpha\alpha}\middle|\chi_\nu\right\rangle \tag{F.99}$$

$$F^{\beta\beta}_{\mu\nu} = h^{\beta\beta}_{\mu\nu} + \sum_{\sigma,\rho}(\chi_\mu\chi_\nu|\chi_\sigma\chi_\rho)\mathrm{Re}\left(P^{\alpha\alpha}_{\sigma\rho} + P^{\beta\beta}_{\sigma\rho}\right) + \left\langle\chi_\mu\middle|V^{\beta\beta}_{xc}\middle|\chi_\nu\right\rangle \tag{F.100}$$

$$F^{\alpha\beta}_{\mu\nu} = h^{\alpha\beta}_{\mu\nu} + \left\langle\chi_\mu\middle|V^{\alpha\beta}_{xc}\middle|\chi_\nu\right\rangle \tag{F.101}$$

$$F^{\beta\alpha}_{\mu\nu} = h^{\beta\alpha}_{\mu\nu} + \left\langle\chi_\mu\middle|V^{\beta\alpha}_{xc}\middle|\chi_\nu\right\rangle \tag{F.102}$$

where the first and second terms ($h^{\sigma\sigma'}_{\mu\nu}$ and the ones containing the sum over σ and ρ) represent mono-electronic and Coulomb contributions, while the last terms $\left\langle\chi_\mu\middle|V^{\sigma\sigma'}_{xc}\middle|\chi_\nu\right\rangle$ represent xc contributions. Finally the following symmetries of the xc potential term can be exploited, as is evident from the above, as well as equations (F.46) and (F.66):

$$\mathrm{Re}\left\langle\chi_\mu\middle|V^{\alpha\beta}_{xc}\middle|\chi_\nu\right\rangle = \mathrm{Re}\left\langle\chi_\mu\middle|V^{\beta\alpha}_{xc}\middle|\chi_\nu\right\rangle \tag{F.103}$$

$$\mathrm{Im}\left\langle\chi_\mu\middle|V^{\alpha\beta}_{xc}\middle|\chi_\nu\right\rangle = -\mathrm{Im}\left\langle\chi_\mu\middle|V^{\beta\alpha}_{xc}\middle|\chi_\nu\right\rangle \tag{F.104}$$

What is more, unlike the full Kohn-Sham matrix, all of the matrices $\left\langle\chi_\mu\middle|V^{\sigma\sigma'}_{xc}\middle|\chi_\nu\right\rangle$ are symmetric with respect to permutation of the spatial part of the orbitals. The $V^{\alpha\alpha}_{xc}$ and $V^{\beta\beta}_{xc}$ blocks are real-Hermitian, while the $V^{\alpha\beta}_{xc}$ and $V^{\beta\alpha}_{xc}$ are complex-symmetric:

$$\mathrm{Re}\left\langle\chi_\mu\middle|V^{\alpha\alpha}_{xc}\middle|\chi_\nu\right\rangle = \mathrm{Re}\left\langle\chi_\nu\middle|V^{\alpha\alpha}_{xc}\middle|\chi_\mu\right\rangle \tag{F.105}$$

$$\mathrm{Re}\left\langle\chi_\mu\middle|V^{\beta\beta}_{xc}\middle|\chi_\nu\right\rangle = \mathrm{Re}\left\langle\chi_\nu\middle|V^{\beta\beta}_{xc}\middle|\chi_\mu\right\rangle \tag{F.106}$$

$$\mathrm{Re}\left\langle\chi_\mu\middle|V^{\alpha\beta}_{xc}\middle|\chi_\nu\right\rangle = \mathrm{Re}\left\langle\chi_\nu\middle|V^{\alpha\beta}_{xc}\middle|\chi_\mu\right\rangle \tag{F.107}$$

$$\mathrm{Im}\left\langle\chi_\mu\middle|V^{\alpha\beta}_{xc}\middle|\chi_\nu\right\rangle = \mathrm{Im}\left\langle\chi_\nu\middle|V^{\alpha\beta}_{xc}\middle|\chi_\mu\right\rangle \tag{F.108}$$

$$\mathrm{Re}\left\langle\chi_\mu\middle|V^{\beta\alpha}_{xc}\middle|\chi_\nu\right\rangle = \mathrm{Re}\left\langle\chi_\nu\middle|V^{\beta\alpha}_{xc}\middle|\chi_\mu\right\rangle \tag{F.109}$$

$$\mathrm{Im}\left\langle\chi_\mu\middle|V^{\beta\alpha}_{xc}\middle|\chi_\nu\right\rangle = \mathrm{Im}\left\langle\chi_\nu\middle|V^{\beta\alpha}_{xc}\middle|\chi_\mu\right\rangle \tag{F.110}$$

This means that only the lower triangular half of $\mathrm{Re}\left\langle\chi_\mu\middle|V^{\alpha\alpha}_{xc}\middle|\chi_\nu\right\rangle$, $\mathrm{Re}\left\langle\chi_\mu\middle|V^{\beta\beta}_{xc}\middle|\chi_\nu\right\rangle$, $\mathrm{Re}\left\langle\chi_\mu\middle|V^{\alpha\beta}_{xc}\middle|\chi_\nu\right\rangle$ and $\mathrm{Im}\left\langle\chi_\mu\middle|V^{\alpha\beta}_{xc}\middle|\chi_\nu\right\rangle$ need to be calculated explicitly.

F.5 Non-Collinear Guess

The result of the non-collinear calculation depends strongly on the starting guess for the distribution of the magnetization. This is because the only term in the Fock which changes the direction of the magnetization is the spin-orbit operator. Without spin-orbit there is no coupling between the geometry and spin. So the dependence of the total energy on the orientation of the magnetization is weak, especially if the spin-orbit coupling contribution is not very big. As a result there is no guarantee that the scf procedure will converge to the correct magnetization without a proper guess. To manipulate the starting guess, we define polar θ and azimuthal ϕ angles which allow to orient the magnetization vector at a given point in space. Then, the components of the vector take the form:

$$\mathbf{m}(\mathbf{r}) = m(\mathbf{r})\mathbf{v}(\mathbf{r}) \tag{F.111}$$

$$\mathbf{v}(\mathbf{r}) = [\sin(\theta)\sin(\phi), \sin(\theta)\cos(\phi), \cos(\theta)] \tag{F.112}$$

So the relative magntitude of the Cartesian components of **m** are determined by the vector **v**. From equations (F.18), (F.19) and (F.20), the components m_x and m_y depend on the real and imaginary parts, respectively of the off-diagonal blocks of the density matrix in spin space (the $\alpha\beta$ and $\beta\alpha$ blocks). The component m_z instead depends on the real part of the diagonal blocks of the density in spin space (the $\alpha\alpha$ and $\beta\beta$ blocks). So given a generic spin-density matrix P_{spin} determined, for example as a superposition of atomic spin-densities, the relative magnitude of the Cartesian components of **m** can be determined by applying **v** to the appropriate blocks of the density matrix:

$$\operatorname{Re} P^{\alpha\beta} = \sin(\theta)\sin(\phi)P_{\text{spin}} \tag{F.113}$$

$$\operatorname{Im} P^{\alpha\beta} = \sin(\theta)\cos(\phi)P_{\text{spin}} \tag{F.114}$$

$$\operatorname{Re} P^{\alpha\alpha} = \cos(\theta)P_{\text{spin}} \tag{F.115}$$

Once these have been assigned, the relative magnitude of m_x, m_y and m_z are correctly determined through the angles θ and ϕ using equations (F.18), (F.19) and (F.20). If P_{spin} is an atomic spin-density, then different angles θ and ϕ can be given to the different atoms in the system to yield the desired magnetization distribution.

F.6 Theory of Scalmani and Frisch

Scalmani and Frisch offered another choice of non-collinear variables. Here we show how the matrix elements can be obtained using their set of variables. The choice is as follows:

$$F^{LDA} = F^{LDA}[n, m] \tag{F.116}$$

$$F^{GGA} = F^{GGA}[n_+, n_-, \gamma_+, \gamma_-, \gamma_{+-}] \tag{F.117}$$

So the F^{LDA} is the same as in the canonical theory, and the new GGA variables are given as:

$$\gamma_\pm = \frac{1}{4}\left[\boldsymbol{\nabla} n \cdot \boldsymbol{\nabla} n + \boldsymbol{\nabla}\mathbf{m} \cdot \circ \boldsymbol{\nabla}\mathbf{m}\right] \pm \frac{f_{\nabla}}{2}\left[(\boldsymbol{\nabla} n \cdot \boldsymbol{\nabla}\mathbf{m}) \circ (\boldsymbol{\nabla} n \cdot \boldsymbol{\nabla}\mathbf{m})\right]^{1/2} \tag{F.118}$$

and:

$$\gamma_{+-} = \frac{1}{4}\left[\boldsymbol{\nabla} n \cdot \boldsymbol{\nabla} n - \boldsymbol{\nabla}\mathbf{m} \cdot \circ \boldsymbol{\nabla}\mathbf{m}\right] \tag{F.119}$$

where the $\cdot$ indicates a contraction over the Cartesian components of the gradient (product in direct space) and the $\circ$ indicates a contration over the Cartesian components of the magnetisation (product in spin-space).

In Eq (F.118), the f_∇ corresponds to the following:

$$f_\nabla = \operatorname{sgn}\left(\boldsymbol{\nabla} n \cdot [\boldsymbol{\nabla}\mathbf{m}] \circ \mathbf{m}\right) \tag{F.120}$$

The LDA matrix elements are the same as in the collinear theory, because for LDA, the theory of Scalmani and Frisch coincides with the canonical theory. So the matrix elements only need to be derived for GGA. From Eq (F.69), the xc energy is expanded in first order as follows:

$$dE_{xc} = \int \left[F + \frac{\partial F}{\partial n_+}\delta n_+ + \frac{\partial F}{\partial n_-}\delta n_- + \frac{\partial F}{\partial \gamma_+}\delta \gamma_+ + \frac{\partial F}{\partial \gamma_-}\delta \gamma_- + \frac{\partial F}{\partial \gamma_{+-}}\delta \gamma_{+-} \right] d\mathbf{r} \tag{F.121}$$

Using:

$$\begin{aligned} n_\pm &= \frac{1}{2}\left(n \pm [\mathbf{m} \circ \mathbf{m}]^{1/2}\right) \\ \delta n_\pm &= \frac{1}{2}\left(\delta n \pm [\mathbf{m} \circ \mathbf{m}]^{-1/2}[\mathbf{m} \circ \delta\mathbf{m}]\right) \end{aligned}$$

We find:

$$\begin{aligned} dE_{xc} &= \int \left[F + \frac{1}{2}\left(\frac{\partial F}{\partial n_+} + \frac{\partial F}{\partial n_-}\right)\delta n + \frac{1}{2}[\mathbf{m} \circ \mathbf{m}]^{-1/2}\left(\frac{\partial F}{\partial n_+} - \frac{\partial F}{\partial n_-}\right)[\mathbf{m} \circ \delta\mathbf{m}] \right. \\ &+ \left. \frac{\partial F}{\partial \gamma_+}\delta\gamma_+ + \frac{\partial F}{\partial \gamma_-}\delta\gamma_- + \frac{\partial F}{\partial \gamma_{+-}}\delta\gamma_{+-} \right] d\mathbf{r} \end{aligned} \tag{F.122}$$

The variation of the xc energy requires the variation of the $\gamma_\pm$ and γ_{+-}. Starting with $\gamma_\pm$, from Eq. (F.118):

$$\begin{aligned} \delta\gamma_\pm &= \frac{1}{2}\boldsymbol{\nabla} n \cdot \delta(\boldsymbol{\nabla} n) + \frac{1}{2}\boldsymbol{\nabla}\mathbf{m} \cdot \circ\delta(\boldsymbol{\nabla}\mathbf{m}) \\ &\pm [(\boldsymbol{\nabla} n \cdot \boldsymbol{\nabla}\mathbf{m}) \circ (\boldsymbol{\nabla} n \cdot \boldsymbol{\nabla}\mathbf{m})]^{1/2}\, \delta_{irac}(\boldsymbol{\nabla} n \cdot \boldsymbol{\nabla}\mathbf{m} \circ \mathbf{m})\, \delta(\boldsymbol{\nabla} n \cdot \boldsymbol{\nabla}\mathbf{m} \circ \mathbf{m}) \\ &\pm \frac{f_\nabla}{4}[(\boldsymbol{\nabla} n \cdot \boldsymbol{\nabla}\mathbf{m}) \circ (\boldsymbol{\nabla} n \cdot \boldsymbol{\nabla}\mathbf{m})]^{-1/2}\, \delta\{(\boldsymbol{\nabla} n \cdot \boldsymbol{\nabla}\mathbf{m}) \circ (\boldsymbol{\nabla} n \cdot \boldsymbol{\nabla}\mathbf{m})\} \end{aligned} \tag{F.123}$$

where δ_{irac} is the dirac-delta function. Expanding the above differentials:

$$\begin{aligned} \delta\gamma_\pm &= \frac{1}{2}\boldsymbol{\nabla} n \cdot \delta(\boldsymbol{\nabla} n) + \frac{1}{2}\boldsymbol{\nabla}\mathbf{m} \cdot \circ\delta(\boldsymbol{\nabla}\mathbf{m}) \\ &\pm [(\boldsymbol{\nabla} n \cdot \boldsymbol{\nabla}\mathbf{m}) \circ (\boldsymbol{\nabla} n \cdot \boldsymbol{\nabla}\mathbf{m})]^{1/2} \\ &\times \delta_{irac}(\boldsymbol{\nabla} n \cdot \boldsymbol{\nabla}\mathbf{m} \circ \mathbf{m})\, [\boldsymbol{\nabla} n \cdot \delta(\boldsymbol{\nabla}\mathbf{m} \circ \mathbf{m}) + \boldsymbol{\nabla}\mathbf{m} \circ \mathbf{m} \cdot \delta(\boldsymbol{\nabla} n)] \\ &\pm \frac{f_\nabla}{2}[(\boldsymbol{\nabla} n \cdot \boldsymbol{\nabla}\mathbf{m}) \circ (\boldsymbol{\nabla} n \cdot \boldsymbol{\nabla}\mathbf{m})]^{-1/2}(\boldsymbol{\nabla} n \cdot \boldsymbol{\nabla}\mathbf{m}) \circ [\boldsymbol{\nabla} n \cdot \delta(\boldsymbol{\nabla}\mathbf{m}) + \boldsymbol{\nabla}\mathbf{m} \cdot \delta(\boldsymbol{\nabla} n)] \end{aligned} \tag{F.124}$$

Now given a generic vector $\mathbf{F}$ and scalar ϕ, the product rule for the divergence operator says that $(\nabla\phi) \cdot \mathbf{F} = \nabla \cdot (\phi\mathbf{F}) - \phi(\nabla \cdot \mathbf{F})$ applying this to the above, with the scalar being the argument of the differential, and using (in first order) $\boldsymbol{\nabla}\delta n = \delta\boldsymbol{\nabla} n$:

$$\begin{aligned}
\delta\gamma_{\pm} &= \frac{1}{2}\boldsymbol{\nabla}\cdot(\boldsymbol{\nabla} n\delta n) - \frac{1}{2}\boldsymbol{\nabla}\cdot(\boldsymbol{\nabla} n)\,\delta n + \frac{1}{2}\boldsymbol{\nabla}\cdot(\boldsymbol{\nabla}\mathbf{m}\circ\delta\mathbf{m}) - \frac{1}{2}\boldsymbol{\nabla}\cdot(\boldsymbol{\nabla}\mathbf{m})\circ\delta\mathbf{m} \\
&\pm [(\boldsymbol{\nabla} n\cdot\boldsymbol{\nabla}\mathbf{m})\circ(\boldsymbol{\nabla} n\cdot\boldsymbol{\nabla}\mathbf{m})]^{1/2}\,\delta_{irac}\,(\boldsymbol{\nabla} n\cdot\boldsymbol{\nabla}\mathbf{m}\circ\mathbf{m}) \\
&\times \Big[\boldsymbol{\nabla}\cdot\{\boldsymbol{\nabla} n\delta\,(\mathbf{m}\circ\mathbf{m})\} - \boldsymbol{\nabla}\cdot\{\boldsymbol{\nabla} n\}\,\delta\,(\mathbf{m}\circ\mathbf{m}) \\
&+ \boldsymbol{\nabla}\cdot(\boldsymbol{\nabla}\mathbf{m}\circ\mathbf{m}\delta n) - \boldsymbol{\nabla}\cdot(\boldsymbol{\nabla}\mathbf{m}\circ\mathbf{m})\,\delta n\Big] \\
&\pm \frac{f_{\nabla}}{2}\,[(\boldsymbol{\nabla} n\cdot\boldsymbol{\nabla}\mathbf{m})\circ(\boldsymbol{\nabla} n\cdot\boldsymbol{\nabla}\mathbf{m})]^{-1/2} \\
&\times (\boldsymbol{\nabla} n\cdot\boldsymbol{\nabla}\mathbf{m})\circ\Big[\boldsymbol{\nabla}\cdot(\boldsymbol{\nabla} n\delta\mathbf{m}) - \boldsymbol{\nabla}\cdot(\boldsymbol{\nabla} n)\,\delta\mathbf{m} \\
&+ \boldsymbol{\nabla}\cdot(\boldsymbol{\nabla}\mathbf{m}\delta n) - \boldsymbol{\nabla}\cdot(\boldsymbol{\nabla}\mathbf{m})\,\delta n\Big] \qquad \text{(F.125)}
\end{aligned}$$

Similarly, the variation of γ_{+-} yields, from Eq. (F.119):

$$\begin{aligned}
\delta\gamma_{+-} &= \frac{1}{2}\boldsymbol{\nabla}\cdot(\boldsymbol{\nabla} n\delta n) - \frac{1}{2}\boldsymbol{\nabla}\cdot(\boldsymbol{\nabla} n)\,\delta n \\
&- \frac{1}{2}\boldsymbol{\nabla}\cdot(\boldsymbol{\nabla}\mathbf{m}\circ\delta\mathbf{m}) + \frac{1}{2}\boldsymbol{\nabla}\cdot(\boldsymbol{\nabla}\mathbf{m})\circ\delta\mathbf{m} \qquad \text{(F.126)}
\end{aligned}$$

Substituting Eq. (F.125) and (F.126) in Eq. (F.121):

$$
\begin{aligned}
dE_{xc} &= \int\left[F + \frac{1}{2}\left(\frac{\partial F}{\partial n_+} + \frac{\partial F}{\partial n_-}\right)\delta n + \frac{1}{2}\left[\mathbf{m}\circ\mathbf{m}\right]^{-1/2}\left(\frac{\partial F}{\partial n_+} - \frac{\partial F}{\partial n_-}\right)\left[\mathbf{m}\circ\delta\mathbf{m}\right]\right]d\mathbf{r} \\
&+ \int \frac{1}{2}\boldsymbol{\nabla}\cdot\left[\frac{\partial F}{\partial \gamma_+}\boldsymbol{\nabla} n\delta n\right]d\mathbf{r} - \int \frac{1}{2}\boldsymbol{\nabla}\cdot\left[\frac{\partial F}{\partial \gamma_+}\boldsymbol{\nabla} n\right]\delta n d\mathbf{r} \\
&+ \int \frac{1}{2}\boldsymbol{\nabla}\cdot\left[\frac{\partial F}{\partial \gamma_+}\boldsymbol{\nabla}\mathbf{m}\circ\delta\mathbf{m}\right]d\mathbf{r} - \int \frac{1}{2}\boldsymbol{\nabla}\cdot\left[\frac{\partial F}{\partial \gamma_+}\boldsymbol{\nabla}\mathbf{m}\right]\circ\delta\mathbf{m}d\mathbf{r} \\
&+ \int\left\{\left[(\boldsymbol{\nabla} n\cdot\boldsymbol{\nabla}\mathbf{m})\circ(\boldsymbol{\nabla} n\cdot\boldsymbol{\nabla}\mathbf{m})\right]^{1/2}\delta_{irac}\left(\boldsymbol{\nabla} n\cdot\boldsymbol{\nabla}\mathbf{m}\circ\mathbf{m}\right)\right. \\
&\times \left(\boldsymbol{\nabla}\cdot\left[\frac{\partial F}{\partial \gamma_+}\boldsymbol{\nabla} n\delta\left(\mathbf{m}\circ\mathbf{m}\right)\right] - \boldsymbol{\nabla}\cdot\left[\frac{\partial F}{\partial \gamma_+}\boldsymbol{\nabla} n\right]\delta\left(\mathbf{m}\circ\mathbf{m}\right)\right. \\
&+ \left.\left.\boldsymbol{\nabla}\cdot\left[\frac{\partial F}{\partial \gamma_+}\boldsymbol{\nabla}\mathbf{m}\circ\mathbf{m}\delta n\right] - \boldsymbol{\nabla}\cdot\left[\frac{\partial F}{\partial \gamma_+}\boldsymbol{\nabla}\mathbf{m}\circ\mathbf{m}\right]\delta n\right)\right\}d\mathbf{r} \\
&+ \int\left\{\frac{f_{\nabla}}{2}\left[(\boldsymbol{\nabla} n\cdot\boldsymbol{\nabla}\mathbf{m})\circ(\boldsymbol{\nabla} n\cdot\boldsymbol{\nabla}\mathbf{m})\right]^{-1/2}\right. \\
&\times \left.(\boldsymbol{\nabla} n\cdot\boldsymbol{\nabla}\mathbf{m})\circ\left[\boldsymbol{\nabla}\cdot\left(\frac{\partial F}{\partial \gamma_+}\boldsymbol{\nabla} n\delta\mathbf{m}\right)\right]\right\}d\mathbf{r} \\
&- \int\left\{\frac{f_{\nabla}}{2}\left[(\boldsymbol{\nabla} n\cdot\boldsymbol{\nabla}\mathbf{m})\circ(\boldsymbol{\nabla} n\cdot\boldsymbol{\nabla}\mathbf{m})\right]^{-1/2}\right. \\
&\times \left.(\boldsymbol{\nabla} n\cdot\boldsymbol{\nabla}\mathbf{m})\circ\left[\boldsymbol{\nabla}\cdot\left(\frac{\partial F}{\partial \gamma_+}\boldsymbol{\nabla} n\right)\delta\mathbf{m}\right]\right\}d\mathbf{r} \\
&+ \int\left\{\frac{f_{\nabla}}{2}\left[(\boldsymbol{\nabla} n\cdot\boldsymbol{\nabla}\mathbf{m})\circ(\boldsymbol{\nabla} n\cdot\boldsymbol{\nabla}\mathbf{m})\right]^{-1/2}\right. \\
&\times \left.(\boldsymbol{\nabla} n\cdot\boldsymbol{\nabla}\mathbf{m})\circ\left[\boldsymbol{\nabla}\cdot\left(\frac{\partial F}{\partial \gamma_+}\boldsymbol{\nabla}\mathbf{m}\delta n\right)\right]\right\}d\mathbf{r} \\
&- \int\left\{\frac{f_{\nabla}}{2}\left[(\boldsymbol{\nabla} n\cdot\boldsymbol{\nabla}\mathbf{m})\circ(\boldsymbol{\nabla} n\cdot\boldsymbol{\nabla}\mathbf{m})\right]^{-1/2}\right. \\
&\times \left.(\boldsymbol{\nabla} n\cdot\boldsymbol{\nabla}\mathbf{m})\circ\left[\boldsymbol{\nabla}\cdot\left(\frac{\partial F}{\partial \gamma_+}\boldsymbol{\nabla}\mathbf{m}\right)\delta n\right]\right\}d\mathbf{r} \\
&+ \int \frac{1}{2}\boldsymbol{\nabla}\cdot\left[\frac{\partial F}{\partial \gamma_-}\boldsymbol{\nabla} n\delta n\right]d\mathbf{r} - \int \frac{1}{2}\boldsymbol{\nabla}\cdot\left[\frac{\partial F}{\partial \gamma_-}\boldsymbol{\nabla} n\right]\delta n d\mathbf{r} \\
&+ \int \frac{1}{2}\boldsymbol{\nabla}\cdot\left[\frac{\partial F}{\partial \gamma_-}\boldsymbol{\nabla}\mathbf{m}\circ\delta\mathbf{m}\right]d\mathbf{r} - \int \frac{1}{2}\boldsymbol{\nabla}\cdot\left[\frac{\partial F}{\partial \gamma_-}\boldsymbol{\nabla}\mathbf{m}\right]\circ\delta\mathbf{m}d\mathbf{r} \\
&+ \int\left\{\left[(\boldsymbol{\nabla} n\cdot\boldsymbol{\nabla}\mathbf{m})\circ(\boldsymbol{\nabla} n\cdot\boldsymbol{\nabla}\mathbf{m})\right]^{1/2}\delta_{irac}\left(\boldsymbol{\nabla} n\cdot\boldsymbol{\nabla}\mathbf{m}\circ\mathbf{m}\right)\right.
\end{aligned}
$$

$$
\begin{aligned}
\times\quad & \Big(\boldsymbol{\nabla}\cdot\left[\frac{\partial F}{\partial\gamma_-}\boldsymbol{\nabla}n\delta\left(\mathbf{m}\circ\mathbf{m}\right)\right]-\boldsymbol{\nabla}\cdot\left[\frac{\partial F}{\partial\gamma_-}\boldsymbol{\nabla}n\right]\delta\left(\mathbf{m}\circ\mathbf{m}\right)\\
+\quad & \boldsymbol{\nabla}\cdot\left[\frac{\partial F}{\partial\gamma_-}\boldsymbol{\nabla}\mathbf{m}\circ\mathbf{m}\delta n\right]-\boldsymbol{\nabla}\cdot\left[\frac{\partial F}{\partial\gamma_-}\boldsymbol{\nabla}\mathbf{m}\circ\mathbf{m}\right]\delta n\Big)\Big\}d\mathbf{r}\\
-\quad & \int\Big\{\frac{f_\nabla}{2}\left[\left(\boldsymbol{\nabla}n\cdot\boldsymbol{\nabla}\mathbf{m}\right)\circ\left(\boldsymbol{\nabla}n\cdot\boldsymbol{\nabla}\mathbf{m}\right)\right]^{-1/2}\\
\times\quad & \left(\boldsymbol{\nabla}n\cdot\boldsymbol{\nabla}\mathbf{m}\right)\circ\left[\boldsymbol{\nabla}\cdot\left(\frac{\partial F}{\partial\gamma_-}\boldsymbol{\nabla}n\delta\mathbf{m}\right)\right]\Big\}d\mathbf{r}\\
+\quad & \int\Big\{\frac{f_\nabla}{2}\left[\left(\boldsymbol{\nabla}n\cdot\boldsymbol{\nabla}\mathbf{m}\right)\circ\left(\boldsymbol{\nabla}n\cdot\boldsymbol{\nabla}\mathbf{m}\right)\right]^{-1/2}\\
\times\quad & \left(\boldsymbol{\nabla}n\cdot\boldsymbol{\nabla}\mathbf{m}\right)\circ\left[\boldsymbol{\nabla}\cdot\left(\frac{\partial F}{\partial\gamma_-}\boldsymbol{\nabla}n\right)\delta\mathbf{m}\right]\Big\}d\mathbf{r}\\
-\quad & \int\Big\{\frac{f_\nabla}{2}\left[\left(\boldsymbol{\nabla}n\cdot\boldsymbol{\nabla}\mathbf{m}\right)\circ\left(\boldsymbol{\nabla}n\cdot\boldsymbol{\nabla}\mathbf{m}\right)\right]^{-1/2}\\
\times\quad & \left(\boldsymbol{\nabla}n\cdot\boldsymbol{\nabla}\mathbf{m}\right)\circ\left[\boldsymbol{\nabla}\cdot\left(\frac{\partial F}{\partial\gamma_-}\boldsymbol{\nabla}\mathbf{m}\delta n\right)\right]\Big\}d\mathbf{r}\\
+\quad & \int\Big\{\frac{f_\nabla}{2}\left[\left(\boldsymbol{\nabla}n\cdot\boldsymbol{\nabla}\mathbf{m}\right)\circ\left(\boldsymbol{\nabla}n\cdot\boldsymbol{\nabla}\mathbf{m}\right)\right]^{-1/2}\\
\times\quad & \left(\boldsymbol{\nabla}n\cdot\boldsymbol{\nabla}\mathbf{m}\right)\circ\left[\boldsymbol{\nabla}\cdot\left(\frac{\partial F}{\partial\gamma_-}\boldsymbol{\nabla}\mathbf{m}\right)\delta n\right]\Big\}d\mathbf{r}\\
+\quad & \int\frac{1}{2}\boldsymbol{\nabla}\cdot\left[\frac{\partial F}{\partial\gamma_{+-}}\boldsymbol{\nabla}n\delta n\right]d\mathbf{r}-\int\frac{1}{2}\boldsymbol{\nabla}\cdot\left[\frac{\partial F}{\partial\gamma_{+-}}\boldsymbol{\nabla}n\right]\delta n d\mathbf{r}\\
-\quad & \int\frac{1}{2}\boldsymbol{\nabla}\cdot\left[\frac{\partial F}{\partial\gamma_{+-}}\boldsymbol{\nabla}\mathbf{m}\circ\delta\mathbf{m}\right]d\mathbf{r}+\int\frac{1}{2}\boldsymbol{\nabla}\cdot\left[\frac{\partial F}{\partial\gamma_{+-}}\boldsymbol{\nabla}\mathbf{m}\right]\circ\delta\mathbf{m}d\mathbf{r}
\end{aligned}
\tag{F.127}
$$

Integrating out some of the terms:

$$
\begin{aligned}
dE_{xc} &= \int \left[F + \frac{1}{2}\left(\frac{\partial F}{\partial n_+} + \frac{\partial F}{\partial n_-}\right)\delta n + \frac{1}{2}\left[\mathbf{m}\circ\mathbf{m}\right]^{-1/2}\left(\frac{\partial F}{\partial n_+} - \frac{\partial F}{\partial n_-}\right)\left[\mathbf{m}\circ\delta\mathbf{m}\right]\right] d\mathbf{r} \\
&- \int \frac{1}{2}\boldsymbol{\nabla}\cdot\left[\frac{\partial F}{\partial\gamma_+}\boldsymbol{\nabla} n\right]\delta n d\mathbf{r} - \int \frac{1}{2}\boldsymbol{\nabla}\cdot\left[\frac{\partial F}{\partial\gamma_+}\boldsymbol{\nabla}\mathbf{m}\right]\circ\delta\mathbf{m} d\mathbf{r} \\
&+ \int \Bigg\{ \left[(\boldsymbol{\nabla} n\cdot\boldsymbol{\nabla}\mathbf{m})\circ(\boldsymbol{\nabla} n\cdot\boldsymbol{\nabla}\mathbf{m})\right]^{1/2}\delta_{irac}\left(\boldsymbol{\nabla} n\cdot\boldsymbol{\nabla}\mathbf{m}\circ\mathbf{m}\right) \\
&\times \Big(-\boldsymbol{\nabla}\cdot\left[\frac{\partial F}{\partial\gamma_+}\boldsymbol{\nabla} n\right]\delta\left(\mathbf{m}\circ\mathbf{m}\right) - \boldsymbol{\nabla}\cdot\left[\frac{\partial F}{\partial\gamma_+}\boldsymbol{\nabla}\mathbf{m}\circ\mathbf{m}\right]\delta n\Big)\Bigg\} d\mathbf{r} \\
&- \int \Bigg\{ \frac{f_{\nabla}}{2}\left[(\boldsymbol{\nabla} n\cdot\boldsymbol{\nabla}\mathbf{m})\circ(\boldsymbol{\nabla} n\cdot\boldsymbol{\nabla}\mathbf{m})\right]^{-1/2} \\
&\times (\boldsymbol{\nabla} n\cdot\boldsymbol{\nabla}\mathbf{m})\circ\left[\boldsymbol{\nabla}\cdot\left(\frac{\partial F}{\partial\gamma_+}\boldsymbol{\nabla} n\right)\delta\mathbf{m}\right]\Bigg\} d\mathbf{r} \\
&- \int \Bigg\{ \frac{f_{\nabla}}{2}\left[(\boldsymbol{\nabla} n\cdot\boldsymbol{\nabla}\mathbf{m})\circ(\boldsymbol{\nabla} n\cdot\boldsymbol{\nabla}\mathbf{m})\right]^{-1/2} \\
&\times (\boldsymbol{\nabla} n\cdot\boldsymbol{\nabla}\mathbf{m})\circ\left[\boldsymbol{\nabla}\cdot\left(\frac{\partial F}{\partial\gamma_+}\boldsymbol{\nabla}\mathbf{m}\right)\delta n\right]\Bigg\} d\mathbf{r} \\
&- \int \frac{1}{2}\boldsymbol{\nabla}\cdot\left[\frac{\partial F}{\partial\gamma_-}\boldsymbol{\nabla} n\right]\delta n d\mathbf{r} - \int \frac{1}{2}\boldsymbol{\nabla}\cdot\left[\frac{\partial F}{\partial\gamma_-}\boldsymbol{\nabla}\mathbf{m}\right]\circ\delta\mathbf{m} d\mathbf{r} \\
&+ \int \Bigg\{ \left[(\boldsymbol{\nabla} n\cdot\boldsymbol{\nabla}\mathbf{m})\circ(\boldsymbol{\nabla} n\cdot\boldsymbol{\nabla}\mathbf{m})\right]^{1/2}\delta_{irac}\left(\boldsymbol{\nabla} n\cdot\boldsymbol{\nabla}\mathbf{m}\circ\mathbf{m}\right) \\
&\times \Big(-\boldsymbol{\nabla}\cdot\left[\frac{\partial F}{\partial\gamma_-}\boldsymbol{\nabla} n\right]\delta\left(\mathbf{m}\circ\mathbf{m}\right) - \boldsymbol{\nabla}\cdot\left[\frac{\partial F}{\partial\gamma_-}\boldsymbol{\nabla}\mathbf{m}\circ\mathbf{m}\right]\delta n\Big)\Bigg\} d\mathbf{r} \\
&+ \int \Bigg\{ \frac{f_{\nabla}}{2}\left[(\boldsymbol{\nabla} n\cdot\boldsymbol{\nabla}\mathbf{m})\circ(\boldsymbol{\nabla} n\cdot\boldsymbol{\nabla}\mathbf{m})\right]^{-1/2} \\
&\times (\boldsymbol{\nabla} n\cdot\boldsymbol{\nabla}\mathbf{m})\circ\left[\boldsymbol{\nabla}\cdot\left(\frac{\partial F}{\partial\gamma_-}\boldsymbol{\nabla} n\right)\delta\mathbf{m}\right]\Bigg\} d\mathbf{r} \\
&+ \int \Bigg\{ \frac{f_{\nabla}}{2}\left[(\boldsymbol{\nabla} n\cdot\boldsymbol{\nabla}\mathbf{m})\circ(\boldsymbol{\nabla} n\cdot\boldsymbol{\nabla}\mathbf{m})\right]^{-1/2} \\
&\times (\boldsymbol{\nabla} n\cdot\boldsymbol{\nabla}\mathbf{m})\circ\left[\boldsymbol{\nabla}\cdot\left(\frac{\partial F}{\partial\gamma_-}\boldsymbol{\nabla}\mathbf{m}\right)\delta n\right]\Bigg\} d\mathbf{r} \\
&- \int \frac{1}{2}\boldsymbol{\nabla}\cdot\left[\frac{\partial F}{\partial\gamma_{+-}}\boldsymbol{\nabla} n\right]\delta n d\mathbf{r} + \int \frac{1}{2}\boldsymbol{\nabla}\cdot\left[\frac{\partial F}{\partial\gamma_{+-}}\boldsymbol{\nabla}\mathbf{m}\right]\circ\delta\mathbf{m} d\mathbf{r}
\end{aligned}
\tag{F.128}
$$

Now presuming that the perturbations δn and $\delta\mathbf{m}$ are small enough, such that in firsts order, the dirac-delta function terms can be neglected:

$$
\begin{aligned}
dE_{xc} &= \int\left[F+\frac{1}{2}\left(\frac{\partial F}{\partial n_+}+\frac{\partial F}{\partial n_-}\right)\delta n+\frac{1}{2}\left[\mathbf{m}\circ\mathbf{m}\right]^{-1/2}\left(\frac{\partial F}{\partial n_+}-\frac{\partial F}{\partial n_-}\right)\left[\mathbf{m}\circ\delta\mathbf{m}\right]\right]d\mathbf{r}\\
&- \int\frac{1}{2}\boldsymbol{\nabla}\cdot\left[\frac{\partial F}{\partial\gamma_+}\boldsymbol{\nabla}n\right]\delta n d\mathbf{r}-\int\frac{1}{2}\boldsymbol{\nabla}\cdot\left[\frac{\partial F}{\partial\gamma_+}\boldsymbol{\nabla}\mathbf{m}\right]\circ\delta\mathbf{m}d\mathbf{r}\\
&- \int\left\{\frac{f_\nabla}{2}\left[(\boldsymbol{\nabla}n\cdot\boldsymbol{\nabla}\mathbf{m})\circ(\boldsymbol{\nabla}n\cdot\boldsymbol{\nabla}\mathbf{m})\right]^{-1/2}\right.\\
&\times \left.(\boldsymbol{\nabla}n\cdot\boldsymbol{\nabla}\mathbf{m})\circ\left[\boldsymbol{\nabla}\cdot\left(\frac{\partial F}{\partial\gamma_+}\boldsymbol{\nabla}n\right)\delta\mathbf{m}\right]\right\}d\mathbf{r}\\
&- \int\left\{\frac{f_\nabla}{2}\left[(\boldsymbol{\nabla}n\cdot\boldsymbol{\nabla}\mathbf{m})\circ(\boldsymbol{\nabla}n\cdot\boldsymbol{\nabla}\mathbf{m})\right]^{-1/2}\right.\\
&\times \left.(\boldsymbol{\nabla}n\cdot\boldsymbol{\nabla}\mathbf{m})\circ\left[\boldsymbol{\nabla}\cdot\left(\frac{\partial F}{\partial\gamma_+}\boldsymbol{\nabla}\mathbf{m}\right)\delta n\right]\right\}d\mathbf{r}\\
&- \int\frac{1}{2}\boldsymbol{\nabla}\cdot\left[\frac{\partial F}{\partial\gamma_-}\boldsymbol{\nabla}n\right]\delta n d\mathbf{r}-\int\frac{1}{2}\boldsymbol{\nabla}\cdot\left[\frac{\partial F}{\partial\gamma_-}\boldsymbol{\nabla}\mathbf{m}\right]\circ\delta\mathbf{m}d\mathbf{r}\\
&+ \int\left\{\frac{f_\nabla}{2}\left[(\boldsymbol{\nabla}n\cdot\boldsymbol{\nabla}\mathbf{m})\circ(\boldsymbol{\nabla}n\cdot\boldsymbol{\nabla}\mathbf{m})\right]^{-1/2}\right.\\
&\times \left.(\boldsymbol{\nabla}n\cdot\boldsymbol{\nabla}\mathbf{m})\circ\left[\boldsymbol{\nabla}\cdot\left(\frac{\partial F}{\partial\gamma_-}\boldsymbol{\nabla}n\right)\delta\mathbf{m}\right]\right\}d\mathbf{r}\\
&+ \int\left\{\frac{f_\nabla}{2}\left[(\boldsymbol{\nabla}n\cdot\boldsymbol{\nabla}\mathbf{m})\circ(\boldsymbol{\nabla}n\cdot\boldsymbol{\nabla}\mathbf{m})\right]^{-1/2}\right.\\
&\times \left.(\boldsymbol{\nabla}n\cdot\boldsymbol{\nabla}\mathbf{m})\circ\left[\boldsymbol{\nabla}\cdot\left(\frac{\partial F}{\partial\gamma_-}\boldsymbol{\nabla}\mathbf{m}\right)\delta n\right]\right\}d\mathbf{r}\\
&- \int\frac{1}{2}\boldsymbol{\nabla}\cdot\left[\frac{\partial F}{\partial\gamma_{+-}}\boldsymbol{\nabla}n\right]\delta n d\mathbf{r}+\int\frac{1}{2}\boldsymbol{\nabla}\cdot\left[\frac{\partial F}{\partial\gamma_{+-}}\boldsymbol{\nabla}\mathbf{m}\right]\circ\delta\mathbf{m}d\mathbf{r}
\end{aligned}
\tag{F.129}
$$

From the above, the following relations can be immediately deduced:

$$
\begin{aligned}
\frac{\delta E_{xc}}{\delta n} &= \frac{1}{2}\left(\frac{\partial F}{\partial n_+}+\frac{\partial F}{\partial n_-}\right)-\frac{1}{2}\boldsymbol{\nabla}\cdot\left[\left(\frac{\partial F}{\partial\gamma_+}+\frac{\partial F}{\partial\gamma_-}+\frac{\partial F}{\partial\gamma_{+-}}\right)\boldsymbol{\nabla}n\right.\\
&+ \left.\left(\frac{\partial F}{\partial\gamma_+}-\frac{\partial F}{\partial\gamma_-}\right)f_\nabla\left[(\boldsymbol{\nabla}n\cdot\boldsymbol{\nabla}\mathbf{m})\circ(\boldsymbol{\nabla}n\cdot\boldsymbol{\nabla}\mathbf{m})\right]^{-1/2}(\boldsymbol{\nabla}n\cdot\boldsymbol{\nabla}\mathbf{m})\circ\boldsymbol{\nabla}\mathbf{m}\right]
\end{aligned}
\tag{F.130}
$$

and:

$$\begin{aligned}
\frac{\delta E_{xc}}{\delta m_c} &= \frac{1}{2} m_c [\mathbf{m} \circ \mathbf{m}]^{-1/2} \left(\frac{\partial F}{\partial n_+} - \frac{\partial F}{\partial n_-} \right) - \frac{1}{2} \boldsymbol{\nabla} \cdot \left[\left(\frac{\partial F}{\partial \gamma_+} + \frac{\partial F}{\partial \gamma_-} - \frac{\partial F}{\partial \gamma_{+-}} \right) \boldsymbol{\nabla} m_c \right. \\
&+ \left. \left(\frac{\partial F}{\partial \gamma_+} - \frac{\partial F}{\partial \gamma_-} \right) f_{\nabla} \left[(\boldsymbol{\nabla} n \cdot \boldsymbol{\nabla} \mathbf{m}) \circ (\boldsymbol{\nabla} n \cdot \boldsymbol{\nabla} \mathbf{m}) \right]^{-1/2} (\boldsymbol{\nabla} n \cdot \boldsymbol{\nabla} m_c) \, \boldsymbol{\nabla} n \right] \qquad \text{(F.131)}
\end{aligned}$$

The matrix elements are therefore as follows, through integration by parts:

$$\begin{aligned}
\langle \chi_\mu | \frac{\delta E_{xc}}{\delta n} | \chi_\nu \rangle &= \frac{1}{2} \int \left(\frac{\partial F}{\partial n_+} + \frac{\partial F}{\partial n_-} \right) \chi_\mu \chi_\nu d\mathbf{r} + \frac{1}{2} \int \left[\left(\frac{\partial F}{\partial \gamma_+} + \frac{\partial F}{\partial \gamma_-} + \frac{\partial F}{\partial \gamma_{+-}} \right) \boldsymbol{\nabla} n \right. \\
&+ \left. \left(\frac{\partial F}{\partial \gamma_+} - \frac{\partial F}{\partial \gamma_-} \right) f_{\nabla} \left[(\boldsymbol{\nabla} n \cdot \boldsymbol{\nabla} \mathbf{m}) \circ (\boldsymbol{\nabla} n \cdot \boldsymbol{\nabla} \mathbf{m}) \right]^{-1/2} (\boldsymbol{\nabla} n \cdot \boldsymbol{\nabla} \mathbf{m}) \circ \boldsymbol{\nabla} \mathbf{m} \right] \cdot \boldsymbol{\nabla} \left(\chi_\mu \chi_\nu \right) d\mathbf{r}
\end{aligned}$$

(F.132)

and:

$$\begin{aligned}
\langle \chi_\mu | \frac{\delta E_{xc}}{\delta \mathbf{m}} | \chi_\nu \rangle &= \frac{1}{2} \int \mathbf{m} [\mathbf{m} \circ \mathbf{m}]^{-1/2} \left(\frac{\partial F}{\partial n_+} - \frac{\partial F}{\partial n_-} \right) \chi_\mu \chi_\nu + \frac{1}{2} \int \left[\left(\frac{\partial F}{\partial \gamma_+} + \frac{\partial F}{\partial \gamma_-} - \frac{\partial F}{\partial \gamma_{+-}} \right) \boldsymbol{\nabla} \mathbf{m} \right. \\
&+ \left. \left(\frac{\partial F}{\partial \gamma_+} - \frac{\partial F}{\partial \gamma_-} \right) f_{\nabla} \left[(\boldsymbol{\nabla} n \cdot \boldsymbol{\nabla} \mathbf{m}) \circ (\boldsymbol{\nabla} n \cdot \boldsymbol{\nabla} \mathbf{m}) \right]^{-1/2} (\boldsymbol{\nabla} n \cdot \boldsymbol{\nabla} \mathbf{m}) \, \boldsymbol{\nabla} n \right] \cdot \boldsymbol{\nabla} \left(\chi_\mu \chi_\nu \right) d\mathbf{r}
\end{aligned}$$

(F.133)

G Aspects Related to the Treatment of the Lattice and Acceleration of the SCF

G.1 Symmetry Properties of the Matrix Elements

G.1.1 Spin-Orbit Integrals

We are concerned with the symmetry properties of matrix elements for SOC integrals which have the following form. For molecular systems:

$$\left[h_{\mathrm{SO}}^{\sigma\sigma'}\right]_{\mu\nu} = \sum_{a\in\lambda} \langle \chi_\mu^\sigma | \hat{h}_{\mathrm{SO}}(\mathbf{A}_a) | \chi_\nu^{\sigma'} \rangle \tag{G.1}$$

and for periodic systems:

$$\left[h_{\mathrm{SO}}^{\sigma\sigma'}\right]_{\mu[\mathbf{0}]\nu[\mathbf{g}]} = \sum_{\mathbf{n}=-\infty}^{\infty} \sum_{a\in\lambda} \langle \chi_\mu^{\sigma[\mathbf{0}]} | \hat{h}_{\mathrm{SO}}(\mathbf{n}-\mathbf{A}_a) | \chi_\nu^{\sigma'[\mathbf{g}]} \rangle \tag{G.2}$$

where $\hat{h}_{\mathrm{SO}}$ is the spin-orbit operator centered at site $\mathbf{A}_a$ in cell $\mathbf{n}$. The summation over $\mathbf{n}$ extends to the infinite set of lattice vectors, and that over $\mathbf{A}_a$, extends to all sites in the lattice $\boldsymbol{\lambda}$. The $\chi_\mu^{\sigma[\mathbf{0}]}$ is an atomic spin-orbital centered at site $\mathbf{A}_\mu$ in cell $\mathbf{0}$ and with spin $\sigma = \alpha$ or β. The matrix elements can be written more explicitly as:

$$\left[h_{\mathrm{SO}}^{\sigma\sigma'}\right]_{\mu[\mathbf{0}]\nu[\mathbf{g}]} = \sum_{\mathbf{n}=-\infty}^{\infty} \sum_{a\in\lambda} \sum_{l=1}^{L-1} \int d\mathbf{r} \chi_\mu^\sigma(\mathbf{r}-\mathbf{A}_\mu) \hat{\xi}_l(|\mathbf{r}-\mathbf{n}-\mathbf{A}_a|) \mathbf{L}\cdot\mathbf{S} \chi_\nu^{\sigma'}(\mathbf{r}-\mathbf{g}-\mathbf{A}_\nu) \tag{G.3}$$

where the spin-orbit operator has been written above as a sum of radial functions $\hat{\xi}_l$ and the angular-momentum $\mathbf{L}$ and spin $\mathbf{S}$ operators. Actually, the $\mathbf{L}$ shares the same center as $\hat{\xi}_l$, but this dependance is supressed to shorten the notation.

The action of the spin-operator on the atomic spin-orbitals results in the following representations for the different spin-blocks of the matrix elements. For the purely-imaginary $\alpha\alpha$ spin block:

$$\left[h_{\mathrm{SO}}^{\alpha\alpha}\right]_{\mu[\mathbf{0}]\nu[\mathbf{g}]} = \frac{1}{2} \sum_{\mathbf{n}=-\infty}^{\infty} \sum_{a\in\lambda} \sum_{l=1}^{L-1} \langle \chi_\mu^{[\mathbf{0}]} | \hat{\xi}_l(\mathbf{n}-\mathbf{A}_a) L_z | \chi_\nu^{[\mathbf{g}]} \rangle \tag{G.4}$$

For the $\beta\beta$ spin block:

$$\left[h_{\mathrm{SO}}^{\beta\beta}\right]_{\mu[\mathbf{0}]\nu[\mathbf{g}]} = -\frac{1}{2} \sum_{\mathbf{n}=-\infty}^{\infty} \sum_{a\in\lambda} \sum_{l=1}^{L-1} \langle \chi_\mu^{[\mathbf{0}]} | \hat{\xi}_l(\mathbf{n}-\mathbf{A}_a) L_z | \chi_\nu^{[\mathbf{g}]} \rangle = -\left[h_{\mathrm{SO}}^{\alpha\alpha}\right]_{\mu[\mathbf{0}]\nu[\mathbf{g}]} \tag{G.5}$$

For the $\alpha\beta$ spin block:

$$\left[h_{\mathrm{SO}}^{\alpha\beta}\right]_{\mu[\mathbf{0}]\nu[\mathbf{g}]} = \frac{1}{2} \sum_{\mathbf{n}=-\infty}^{\infty} \sum_{a\in\lambda} \sum_{l=1}^{L-1} \langle \chi_\mu^{[\mathbf{0}]} | \hat{\xi}_l(\mathbf{n}-\mathbf{A}_a) L_- | \chi_\nu^{[\mathbf{g}]} \rangle \tag{G.6}$$

and for the $\beta\alpha$ spin block:

$$\left[h^{\beta\alpha}_{\mathrm{SO}}\right]_{\mu[\mathbf{0}]\nu[\mathbf{g}]} = \frac{1}{2}\sum_{\mathbf{n}=-\infty}^{\infty}\sum_{a\in\lambda}\sum_{l=1}^{L-1}\langle\chi^{[\mathbf{0}]}_{\mu}|\hat{\xi}_l(\mathbf{n}-\mathbf{A}_a)L_{+}|\chi^{[\mathbf{g}]}_{\nu}\rangle \tag{G.7}$$

Now since $L_{\pm} = L_x \pm iL_y$ and L_x and L_y are imaginary-Hermitian, it follows that:

$$\left[h^{\alpha\beta}_{\mathrm{SO}}\right]_{\mu[\mathbf{0}]\nu[\mathbf{g}]} = -\left[h^{\alpha\beta}_{\mathrm{SO}}\right]_{\nu[\mathbf{g}]\mu[\mathbf{0}]} \tag{G.8}$$

and:

$$\left[h^{\beta\alpha}_{\mathrm{SO}}\right]_{\mu[\mathbf{0}]\nu[\mathbf{g}]} = -\left[h^{\beta\alpha}_{\mathrm{SO}}\right]_{\nu[\mathbf{g}]\mu[\mathbf{0}]} \tag{G.9}$$

It is useful to modify equations (G.8) and (G.9) such that a **[0]** is used as an index in the bra-, because this is the convention used in the code. This can be done by exploiting the translational invariance of the matrix elements, as shown below.

From equation (G.3), for the generic case $\left[h^{\sigma\sigma'}_{\mathrm{SO}}\right]_{\mu[\mathbf{g}]\nu[\mathbf{m}]}$ can be written as:

$$\left[h^{\sigma\sigma'}_{\mathrm{SO}}\right]_{\mu[\mathbf{g}]\nu[\mathbf{m}]} = \sum_{\mathbf{n}=-\infty}^{\infty}\sum_{a\in\lambda}\sum_{l=1}^{L-1}\int d\mathbf{r}\chi^{\sigma}_{\mu}(\mathbf{r}-\mathbf{g}-\mathbf{A}_{\mu})\hat{\xi}_l(|\mathbf{r}-\mathbf{n}-\mathbf{A}_a|)\mathbf{L}\cdot\mathbf{S}\chi^{\sigma'}_{\nu}(\mathbf{r}-\mathbf{m}-\mathbf{A}_{\nu}) \tag{G.10}$$

Since the result of the integral only depends on the relative distance of the centers we may shift each term in the integral by **g**, as follows:

$$\left[h^{\sigma\sigma'}_{\mathrm{SO}}\right]_{\mu[\mathbf{g}]\nu[\mathbf{m}]} = \sum_{\mathbf{n}=-\infty}^{\infty}\sum_{a\in\lambda}\sum_{l=1}^{L-1}\int d\mathbf{r}\chi^{\sigma}_{\mu}(\mathbf{r}-\mathbf{A}_{\mu})\hat{\xi}_l(|\mathbf{r}-\mathbf{n}+\mathbf{g}-\mathbf{A}_a|)\mathbf{L}\cdot\mathbf{S}\chi^{\sigma'}_{\nu}(\mathbf{r}-\mathbf{m}+\mathbf{g}-\mathbf{A}_{\nu}) \tag{G.11}$$

and since **n** is arbitrary, we can redefine the first index of summation to **n** + **g** ⇒ **n** and write:

$$\left[h^{\sigma\sigma'}_{\mathrm{SO}}\right]_{\mu[\mathbf{g}]\nu[\mathbf{m}]} = \sum_{\mathbf{n}=-\infty}^{\infty}\sum_{a\in\lambda}\sum_{l=1}^{L-1}\int d\mathbf{r}\chi^{\sigma}_{\mu}(\mathbf{r}-\mathbf{A}_{\mu})\hat{\xi}_l(|\mathbf{r}-\mathbf{n}-\mathbf{A}_a|)\mathbf{L}\cdot\mathbf{S}\chi^{\sigma'}_{\nu}(\mathbf{r}-\mathbf{m}+\mathbf{g}-\mathbf{A}_{\nu}) \tag{G.12}$$

At which point it becomes immediately evident that:

$$\left[h^{\sigma\sigma'}_{\mathrm{SO}}\right]_{\mu[\mathbf{g}]\nu[\mathbf{m}]} = \left[h^{\sigma\sigma'}_{\mathrm{SO}}\right]_{\mu[\mathbf{0}]\nu[\mathbf{m}-\mathbf{g}]} \tag{G.13}$$

Combining equations (G.13) with (G.8) and (G.9), we have:

$$\left[h^{\alpha\beta}_{\mathrm{SO}}\right]_{\mu[\mathbf{0}]\nu[\mathbf{g}]} = -\left[h^{\alpha\beta}_{\mathrm{SO}}\right]_{\nu[\mathbf{0}]\mu[-\mathbf{g}]} \tag{G.14}$$

and:

$$\left[h^{\beta\alpha}_{\mathrm{SO}}\right]_{\mu[\mathbf{0}]\nu[\mathbf{g}]} = -\left[h^{\beta\alpha}_{\mathrm{SO}}\right]_{\nu[\mathbf{0}]\mu[-\mathbf{g}]} \tag{G.15}$$

Moreover, the Hermiticity of the spin orbit operator guarantees that:

$$\left[h_{\mathrm{SO}}^{\sigma\sigma'}\right]_{\mu[\mathbf{g}]\nu[\mathbf{m}]} = \left[h_{\mathrm{SO}}^{\sigma'\sigma}\right]^*_{\nu[\mathbf{m}]\mu[\mathbf{g}]} \tag{G.16}$$

Combining equations (G.14) and (G.15) with (G.16), gives the full relations for the off-diagonal spin blocks:

$$\left[h_{\mathrm{SO}}^{\alpha\beta}\right]_{\mu[\mathbf{0}]\nu[\mathbf{g}]} = -\left[h_{\mathrm{SO}}^{\alpha\beta}\right]_{\nu[\mathbf{0}]\mu[-\mathbf{g}]} = \left[h_{\mathrm{SO}}^{\beta\alpha}\right]^*_{\nu[\mathbf{0}]\mu[-\mathbf{g}]} = -\left[h_{\mathrm{SO}}^{\beta\alpha}\right]^*_{\mu[\mathbf{0}]\nu[\mathbf{g}]} \tag{G.17}$$

For the purely-imaginary diagonal spin-blocks, combining equation (G.5) with (G.16):

$$\left[h_{\mathrm{SO}}^{\alpha\alpha}\right]_{\mu[\mathbf{0}]\nu[\mathbf{g}]} = -\left[h_{\mathrm{SO}}^{\alpha\alpha}\right]_{\nu[\mathbf{0}]\mu[-\mathbf{g}]} = -\left[h_{\mathrm{SO}}^{\beta\beta}\right]_{\mu[\mathbf{0}]\nu[\mathbf{g}]} = \left[h_{\mathrm{SO}}^{\beta\beta}\right]_{\nu[\mathbf{0}]\mu[-\mathbf{g}]} \tag{G.18}$$

G.1.2 Other Integrals

We now derive likewise the symmetry properties of the other matrix elements. For the scalar-relativistic mono-electronic part $\mathbf{h}_0^{\mathbf{g}}$, the spin-structure is as follows:

$$\mathbf{h}_0^{\mathbf{g}} = \begin{pmatrix} \mathbf{h}_0^{\mathbf{g}\alpha\alpha} & \mathbf{0} \\ \mathbf{0} & \mathbf{h}_0^{\mathbf{g}\beta\beta} \end{pmatrix} \tag{G.19}$$

and since the scalar-relativistic operator does not depend on spin:

$$\mathbf{h}_0^{\mathbf{g}\alpha\alpha} = \mathbf{h}_0^{\mathbf{g}\beta\beta} \tag{G.20}$$

Furthermore, this operator is real-Hermitian, so that:

$$\left[h_0^{\alpha\alpha}\right]_{\mu[\mathbf{0}]\nu[\mathbf{g}]} = \left[h_0^{\alpha\alpha}\right]_{\nu[\mathbf{0}]\mu[-\mathbf{g}]} = \left[h_0^{\beta\beta}\right]_{\mu[\mathbf{0}]\nu[\mathbf{g}]} = \left[h_0^{\beta\beta}\right]_{\nu[\mathbf{0}]\mu[-\mathbf{g}]} \tag{G.21}$$

The Coulomb part $\mathbf{C}^{\mathbf{g}}$ has a similar spin-structure to $\mathbf{h}_0^{\mathbf{g}}$. That is:

$$\mathbf{C}^{\mathbf{g}} = \begin{pmatrix} \mathbf{C}^{\mathbf{g}\alpha\alpha} & \mathbf{0} \\ \mathbf{0} & \mathbf{C}^{\mathbf{g}\beta\beta} \end{pmatrix} \tag{G.22}$$

and likewise, the Coulomb operator also does not depend on spin and is real-Hermitian, so that again:

$$\left[C^{\alpha\alpha}\right]_{\mu[\mathbf{0}]\nu[\mathbf{g}]} = \left[C^{\alpha\alpha}\right]_{\nu[\mathbf{0}]\mu[-\mathbf{g}]} = \left[C^{\beta\beta}\right]_{\mu[\mathbf{0}]\nu[\mathbf{g}]} = \left[C^{\beta\beta}\right]_{\nu[\mathbf{0}]\mu[-\mathbf{g}]} \tag{G.23}$$

Finally, the exchange operator is complex-Hermitian:

$$\left[K^{\sigma\sigma'}\right]_{\mu[\mathbf{0}]\nu[\mathbf{g}]} = \left[K^{\sigma'\sigma}\right]^*_{\nu[\mathbf{0}]\mu[-\mathbf{g}]} \tag{G.24}$$

On the other hand, for the DFT exchange-correlation potential, for the real diagonal spin-blocks:

$$[V_{xc}^{\sigma\sigma}]_{\mu[\mathbf{0}]\nu[\mathbf{g}]} = [V_{xc}^{\sigma\sigma}]_{\nu[\mathbf{0}]\mu[-\mathbf{g}]} \tag{G.25}$$

$$\mathrm{Im}\,[V_{xc}^{\sigma\sigma}]_{\mu[\mathbf{0}]\nu[\mathbf{g}]} = 0 \tag{G.26}$$

and for the complex off-diagonal spin-blocks:

$$\left[V_{xc}^{\sigma\sigma'}\right]_{\mu[\mathbf{0}]\nu[\mathbf{g}]} = \left[V_{xc}^{\sigma\sigma'}\right]_{\nu[\mathbf{0}]\mu[-\mathbf{g}]} = \left[V_{xc}^{\sigma'\sigma}\right]^{*}_{\nu[\mathbf{0}]\mu[-\mathbf{g}]} = \left[V_{xc}^{\sigma'\sigma}\right]^{*}_{\mu[\mathbf{0}]\nu[\mathbf{g}]} \tag{G.27}$$

G.1.3 The Fock Matrix

The complete Fock operator is likewise also complex-Hermitian:

$$\left[F^{\sigma\sigma'}\right]_{\mu[\mathbf{0}]\nu[\mathbf{g}]} = \left[F^{\sigma'\sigma}\right]^{*}_{\nu[\mathbf{0}]\mu[-\mathbf{g}]} \tag{G.28}$$

The relations above are different than the corresponding ones from the scalar-relativistic code. In that case, since all matrix elements are real, Hermiticity guarantees that any element of the scalar-relativistic Fock matrix $\mathbf{F}_0^{\mathbf{g}}$ obeys the following relation:

$$\left[F_0^{\sigma}\right]_{\mu[\mathbf{0}]\nu[\mathbf{g}]} = \left[F_0^{\sigma}\right]_{\nu[\mathbf{0}]\mu[-\mathbf{g}]} \tag{G.29}$$

G.2 Inverse Fourier Transform of the Fock Matrix

We now introduce the simplified notation:

$$F_{\mu\nu\mathbf{g}}^{\sigma 0} \equiv \left[F_0^{\sigma}\right]_{\mu[\mathbf{0}]\nu[\mathbf{g}]} \tag{G.30}$$

and for the fully relativistic case:

$$F_{\mu\nu\mathbf{g}}^{\sigma\sigma'} \equiv \left[F^{\sigma\sigma'}\right]_{\mu[\mathbf{0}]\nu[\mathbf{g}]} \tag{G.31}$$

where it is assumed henceforth that the **g** refers to the center of the function associated to the second index.

G.2.1 The Scalar-Relativistic Case

For the inverse Fourier transform of the Fock matrix, we have in the scalar-relativistic case and for say the lower triangular part of the matrix ($\mu > \nu$):

$$\mathcal{F}_{\mu\nu\mathbf{k}}^{\sigma 0} = \sum_{\mathbf{g}=-\infty}^{\infty} F_{\mu\nu\mathbf{g}}^{\sigma 0} e^{i\mathbf{k}\cdot\mathbf{g}} \tag{G.32}$$

Restricting the sum to positive $\mathbf{g}$ values:

$$\mathcal{F}^{\sigma 0}_{\mu\nu\mathbf{k}} = F^{\sigma 0}_{\mu\nu\mathbf{0}} + \sum_{\mathbf{g}>\mathbf{0}} \left\{ F^{\sigma 0}_{\mu\nu\mathbf{g}} e^{i\mathbf{k}\cdot\mathbf{g}} + F^{\sigma 0}_{\mu\nu-\mathbf{g}} e^{-i\mathbf{k}\cdot\mathbf{g}} \right\} \tag{G.33}$$

G.2.2 The Fully Relativistic Case

Now for the fully relativistic case, starting with the lower triangular part of a given spin-block:

$$\mathcal{F}^{\sigma\sigma'}_{\mu\nu\mathbf{k}} = \sum_{\mathbf{g}=-\infty}^{\infty} F^{\sigma\sigma'}_{\mu\nu\mathbf{g}} e^{i\mathbf{k}\cdot\mathbf{g}} \tag{G.34}$$

Restricting the sum to positive $\mathbf{g}$ values:

$$\mathcal{F}^{\sigma\sigma'}_{\mu\nu\mathbf{k}} = F^{\sigma\sigma'}_{\mu\nu\mathbf{0}} + \sum_{\mathbf{g}>\mathbf{0}} \left\{ F^{\sigma\sigma'}_{\mu\nu\mathbf{g}} e^{i\mathbf{k}\cdot\mathbf{g}} + F^{\sigma\sigma'}_{\mu\nu-\mathbf{g}} e^{-i\mathbf{k}\cdot\mathbf{g}} \right\} \tag{G.35}$$

It is useful to write the expression for the inverse Fourier transform in terms of the individually transformed real and imaginary parts of the Fock matrix, because this simplifies the generalization of the scalar relativistic code, as in this way the code may be written using real algebra. From equation (G.34) , splitting the real and imaginary components:

$$\begin{aligned} \mathcal{F}^{\sigma\sigma'}_{\mu\nu\mathbf{k}} &= {}^{\mathcal{R}}\mathcal{F}^{\sigma\sigma'}_{\mu\nu\mathbf{k}} + i\, {}^{\mathcal{I}}\mathcal{F}^{\sigma\sigma'}_{\mu\nu\mathbf{k}} \\ &= \sum_{\mathbf{g}=-\infty}^{\infty} \left(\mathrm{Re}\left[F^{\sigma\sigma'}_{\mu\nu\mathbf{g}}\right] + i\,\mathrm{Im}\left[F^{\sigma\sigma'}_{\mu\nu\mathbf{g}}\right] \right) e^{i\mathbf{k}\cdot\mathbf{g}} \end{aligned} \tag{G.36}$$

where the $\mathrm{Re}\left[F^{\sigma\sigma'}_{\mu\nu\mathbf{g}}\right]$ and $\mathrm{Im}\left[F^{\sigma\sigma'}_{\mu\nu\mathbf{g}}\right]$ denote the real and imaginary parts of the Fock matrix in direct-space, and:

$$ {}^{\mathcal{R}}\mathcal{F}^{\sigma\sigma'}_{\mu\nu\mathbf{k}} = \sum_{\mathbf{g}=-\infty}^{\infty} \mathrm{Re}\left[F^{\sigma\sigma'}_{\mu\nu\mathbf{g}}\right] e^{i\mathbf{k}\cdot\mathbf{g}} \tag{G.37}$$

$$ {}^{\mathcal{I}}\mathcal{F}^{\sigma\sigma'}_{\mu\nu\mathbf{k}} = \sum_{\mathbf{g}=-\infty}^{\infty} \mathrm{Im}\left[F^{\sigma\sigma'}_{\mu\nu\mathbf{g}}\right] e^{i\mathbf{k}\cdot\mathbf{g}} \tag{G.38}$$

are the inverse Fourier tranforms of $\mathrm{Re}\left[F^{\sigma\sigma'}_{\mu\nu\mathbf{g}}\right]$ and $\mathrm{Im}\left[F^{\sigma\sigma'}_{\mu\nu\mathbf{g}}\right]$. Note that both ${}^{\mathcal{R}}\mathcal{F}^{\sigma\sigma'}_{\mu\nu\mathbf{k}}$ and ${}^{\mathcal{I}}\mathcal{F}^{\sigma\sigma'}_{\mu\nu\mathbf{k}}$ are complex quantities, because of the presence of the $e^{i\mathbf{k}\cdot\mathbf{g}}$ factors.

We now want to obtain expressions for the real and imaginary parts of the full matrix $\mathcal{F}^{\sigma\sigma'}_{\mu\nu\mathbf{k}}$, in terms of the individually transformed quantities ${}^{\mathcal{R}}\mathcal{F}^{\sigma\sigma'}_{\mu\nu\mathbf{k}}$ and ${}^{\mathcal{I}}\mathcal{F}^{\sigma\sigma'}_{\mu\nu\mathbf{k}}$, because this makes it easier to generalize the existing procedure in the scalar-relatvistic code. This can be done as follows, from equation (G.36):

$$\begin{aligned} \mathcal{F}^{\sigma\sigma'}_{\mu\nu\mathbf{k}} &= \left(\mathrm{Re}\left[{}^{\mathcal{R}}\mathcal{F}^{\sigma\sigma'}_{\mu\nu\mathbf{k}}\right] + i\,\mathrm{Im}\left[{}^{\mathcal{R}}\mathcal{F}^{\sigma\sigma'}_{\mu\nu\mathbf{k}}\right]\right) \\ &+ i\left(\mathrm{Re}\left[{}^{\mathcal{I}}\mathcal{F}^{\sigma\sigma'}_{\mu\nu\mathbf{k}}\right] + i\,\mathrm{Im}\left[{}^{\mathcal{I}}\mathcal{F}^{\sigma\sigma'}_{\mu\nu\mathbf{k}}\right]\right) \qquad \text{(G.39)} \end{aligned}$$

So that:

$$\mathrm{Re}\left[\mathcal{F}^{\sigma\sigma'}_{\mu\nu\mathbf{k}}\right] = \mathrm{Re}\left[{}^{\mathcal{R}}\mathcal{F}^{\sigma\sigma'}_{\mu\nu\mathbf{k}}\right] - \mathrm{Im}\left[{}^{\mathcal{I}}\mathcal{F}^{\sigma\sigma'}_{\mu\nu\mathbf{k}}\right] \qquad \text{(G.40)}$$

$$\mathrm{Im}\left[\mathcal{F}^{\sigma\sigma'}_{\mu\nu\mathbf{k}}\right] = \mathrm{Im}\left[{}^{\mathcal{R}}\mathcal{F}^{\sigma\sigma'}_{\mu\nu\mathbf{k}}\right] + \mathrm{Re}\left[{}^{\mathcal{I}}\mathcal{F}^{\sigma\sigma'}_{\mu\nu\mathbf{k}}\right] \qquad \text{(G.41)}$$

G.2.3 Hermitizing the Fock Matrix in Fourier Space

We now discuss the problem of generating the elements of the lower triangular block of the matrix in reciprocal space. We start with the scalar-relativistic case:

$$\mathcal{F}^{\sigma 0}_{\nu\mu\mathbf{k}} = \sum_{\mathbf{g}=-\infty}^{\infty} F^{\sigma 0}_{\nu\mu\mathbf{g}} e^{i\mathbf{k}\cdot\mathbf{g}} \qquad \text{(G.42)}$$

Exploiting hermiticity, by substituting equation (G.29) in the above:

$$\mathcal{F}^{\sigma 0}_{\nu\mu\mathbf{k}} = \sum_{\mathbf{g}=-\infty}^{\infty} F^{\sigma 0}_{\mu\nu-\mathbf{g}} e^{i\mathbf{k}\cdot\mathbf{g}} \qquad \text{(G.43)}$$

and since **g** is arbitrary, we may redefine **g** ⇔ **−g**, such that:

$$\mathcal{F}^{\sigma 0}_{\nu\mu\mathbf{k}} = \sum_{\mathbf{g}=-\infty}^{\infty} F^{\sigma 0}_{\mu\nu\mathbf{g}} e^{-i\mathbf{k}\cdot\mathbf{g}} = \mathcal{F}^{\sigma 0}_{\mu\nu-\mathbf{k}} \qquad \text{(G.44)}$$

Furthermore, from the above if $F^{\sigma 0}_{\mu\nu\mathbf{g}}$ is purely real as in the scalar relativistic case, then:

$$\mathcal{F}^{\sigma 0}_{\mu\nu-\mathbf{k}} = \left[\mathcal{F}^{\sigma 0}_{\mu\nu\mathbf{k}}\right]^* \qquad \text{(G.45)}$$

So that finally:

$$\mathcal{F}^{\sigma 0}_{\nu\mu\mathbf{k}} = \left[\mathcal{F}^{\sigma 0}_{\mu\nu\mathbf{k}}\right]^* \qquad \text{(G.46)}$$

For the fully-relativistic case, proceeding similarly, first for the ${}^{\mathcal{R}}\mathcal{F}^{\sigma\sigma'}_{\nu\mu\mathbf{k}}$:

$$\begin{aligned} {}^{\mathcal{R}}\mathcal{F}^{\sigma\sigma'}_{\nu\mu\mathbf{k}} &= \sum_{\mathbf{g}=-\infty}^{\infty} \mathrm{Re}\left[F^{\sigma\sigma'}_{\nu\mu\mathbf{g}}\right] e^{i\mathbf{k}\cdot\mathbf{g}} = \sum_{\mathbf{g}=-\infty}^{\infty} \mathrm{Re}\left[F^{\sigma'\sigma}_{\mu\nu-\mathbf{g}}\right] e^{i\mathbf{k}\cdot\mathbf{g}} \\ &= \sum_{\mathbf{g}=-\infty}^{\infty} \mathrm{Re}\left[F^{\sigma'\sigma}_{\mu\nu\mathbf{g}}\right] e^{-i\mathbf{k}\cdot\mathbf{g}} = {}^{\mathcal{R}}\mathcal{F}^{\sigma'\sigma}_{\mu\nu-\mathbf{k}} = \left[{}^{\mathcal{R}}\mathcal{F}^{\sigma'\sigma}_{\mu\nu\mathbf{k}}\right]^* \qquad \text{(G.47)} \end{aligned}$$

and now similarly for the ${}^{\mathcal{I}}\mathcal{F}^{\sigma\sigma'}_{\nu\mu\mathbf{k}}$:

$$\begin{aligned} {}^{\mathcal{I}}\mathcal{F}^{\sigma\sigma'}_{\nu\mu\mathbf{k}} &= \sum_{\mathbf{g}=-\infty}^{\infty} \mathrm{Im}\left[F^{\sigma\sigma'}_{\nu\mu\mathbf{g}}\right] e^{i\mathbf{k}\cdot\mathbf{g}} = -\sum_{\mathbf{g}=-\infty}^{\infty} \mathrm{Im}\left[F^{\sigma'\sigma}_{\mu\nu-\mathbf{g}}\right] e^{i\mathbf{k}\cdot\mathbf{g}} \\ &= -\sum_{\mathbf{g}=-\infty}^{\infty} \mathrm{Im}\left[F^{\sigma'\sigma}_{\mu\nu\mathbf{g}}\right] e^{-i\mathbf{k}\cdot\mathbf{g}} = -\,{}^{\mathcal{I}}\mathcal{F}^{\sigma'\sigma}_{\mu\nu-\mathbf{k}} = -\left[{}^{\mathcal{I}}\mathcal{F}^{\sigma'\sigma}_{\mu\nu\mathbf{k}}\right]^{*} \end{aligned} \tag{G.48}$$

Combining equations (G.40), (G.41), (G.47) and (G.48), we find:

$$\mathrm{Re}\left[\mathcal{F}^{\sigma\sigma'}_{\nu\mu\mathbf{k}}\right] = \mathrm{Re}\left[{}^{\mathcal{R}}\mathcal{F}^{\sigma'\sigma}_{\mu\nu\mathbf{k}}\right] - \mathrm{Im}\left[{}^{\mathcal{I}}\mathcal{F}^{\sigma'\sigma}_{\mu\nu\mathbf{k}}\right] \tag{G.49}$$

$$\mathrm{Im}\left[\mathcal{F}^{\sigma\sigma'}_{\nu\mu\mathbf{k}}\right] = -\,\mathrm{Im}\left[{}^{\mathcal{R}}\mathcal{F}^{\sigma'\sigma}_{\mu\nu\mathbf{k}}\right] - \mathrm{Re}\left[{}^{\mathcal{I}}\mathcal{F}^{\sigma'\sigma}_{\mu\nu\mathbf{k}}\right] \tag{G.50}$$

So that finally, comparing the above with equations (G.40) and (G.41):

$$\mathcal{F}^{\sigma\sigma'}_{\nu\mu\mathbf{k}} = \left[\mathcal{F}^{\sigma'\sigma}_{\mu\nu\mathbf{k}}\right]^{*} \tag{G.51}$$

G.2.4 The Fully Relativistic Algorithm

The strategy for building the Fock matrix is therefore as follows. First we calculate the integrals in direct space for one of the triangles of the matrix (say $\mu > \nu$) for both positive and negative $\mathbf{g}$. The only integrals that would need to be explicitly calculated for the upper triangular ($\nu > \mu$) block are the $\alpha\beta$ integrals, of which there are two types (namely, spin-orbit and exchange). Actually, for the spin-orbit ones, substituting Eq. (G.17) in Eq. (G.34):

$$[h^{\alpha\beta}_{SO}]_{\nu\mu\{\mathbf{k}\}} = \sum_{\mathbf{g}=-\infty}^{\infty} [h^{\alpha\beta}_{SO}]_{\nu\mu[\mathbf{g}]} e^{i\mathbf{k}\cdot\mathbf{g}} \tag{G.52}$$

$$= -\sum_{\mathbf{g}=-\infty}^{\infty} [h^{\alpha\beta}_{SO}]_{\mu\nu[-\mathbf{g}]} e^{i\mathbf{k}\cdot\mathbf{g}} \tag{G.53}$$

$$= -\sum_{\mathbf{g}=-\infty}^{\infty} [h^{\alpha\beta}_{SO}]_{\mu\nu[\mathbf{g}]} e^{-i\mathbf{k}\cdot\mathbf{g}} \tag{G.54}$$

As a result, the only integrals which need to be explicitly calculated are the $\alpha\beta$ exchange integrals. For the upper triangular exchange integrals, we calculate them for the opposite lattice vector of the lower triangular integrals. So for the inverse Fourier transaform, we proceed as follows:

$$[K^{\alpha\beta}]_{\nu\mu\{\mathbf{k}\}} = \sum_{\mathbf{g}=-\infty}^{\infty} [K^{\alpha\beta}]_{\nu\mu[\mathbf{g}]} e^{i\mathbf{k}\cdot\mathbf{g}} \tag{G.55}$$

$$= \sum_{\mathbf{g}=-\infty}^{\infty} [K^{\alpha\beta}]_{\nu\mu[-\mathbf{g}]} e^{-i\mathbf{k}\cdot\mathbf{g}} \tag{G.56}$$

So a complex conjugate must be included in the Fourier monomial for transforming the upper triangular exchange integrals.

The real and imaginary parts of all of the lower triangular integrals are instead individually transformed using Eqs. (G.37) and (G.38). The reciprocal space integrals are then combined and hermitized using Eqs. (G.40), (G.41) and (G.51).

G.3 On the Need for Breaking Time-Reversal Symmetry in Reciprocal Space

The time-reversal symmetry operator is a mapping of the time-dependent wavefunction $\Psi(t) \mapsto \Psi(-t)$. The reversal of time has a well-established effect on, for example, position, electron momentum and spin, as follows:

$$\mathbf{r} \mapsto \mathbf{r} \tag{G.57}$$

$$\mathbf{k} \mapsto -\mathbf{k} \tag{G.58}$$

$$\alpha \mapsto \beta \tag{G.59}$$

$$\beta \mapsto -\alpha \tag{G.60}$$

In a two-component spinor basis, the time-reversal operator can be expressed as:

$$-i\sigma_y K = \begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix} K \tag{G.61}$$

where K represents the complex-conjugation operator.

So time reversal symmetry acts on the diagonal blocks of the Fock matrix as follows:

$$[F^{\alpha\alpha}]_{\mu\nu\{\mathbf{k}\}} \mapsto [F^{\beta\beta}]^*_{\mu\nu\{-\mathbf{k}\}} \tag{G.62}$$

Supposing in the scalar-relativistic case that the Hamiltonian is invariant to time-reversal (i.e. the Hamiltonian commutes with the operator of time reversal), this means that:

$$[F^{\alpha 0}]_{\mu\nu\{\mathbf{k}\}} = [F^{\beta 0}]^*_{\mu\nu\{-\mathbf{k}\}} \tag{G.63}$$

Clearly this condition is not obeyed in open-shell systems, where Fock matrix elements for α cannot be related to those for β. So in general time-reversal symmetry does not hold for open-shell systems. In the absence of time-reversal symmetry, matrix elements need in general to be calculated for all spins and for **k** and −**k**. However, in the scalar-relativistic case, given that the Fock matrix in direct-space is purely real, we can write:

$$\begin{aligned} [F^{\sigma 0}]_{\mu\nu\{-\mathbf{k}\}} &= \sum_{\mathbf{g}=-\infty}^{\infty} F^{\sigma 0}_{\mu\nu\mathbf{g}} e^{-i\mathbf{k}\cdot\mathbf{g}} \\ &= \left[\sum_{\mathbf{g}=-\infty}^{\infty} F^{\sigma 0}_{\mu\nu\mathbf{g}} e^{i\mathbf{k}\cdot\mathbf{g}} \right]^* = [F^{\sigma 0}]^*_{\mu\nu\{\mathbf{k}\}} \end{aligned} \tag{G.64}$$

So that the eigenvalues at $-\mathbf{k}$ and $\mathbf{k}$ are equivalent, and the eigenvectors are complex conjugates of each other. As a result in the scalar-relativistic case, even for open-shell systems where time-reversal symmetry is broken, the Fock matrix needs only be diagonalized at either $\mathbf{k}$ or $-\mathbf{k}$.

The situation is different for the fully relativistic case, where the Fock matrix in direct space is already complex, in such a case we have:

$$\begin{aligned} [F^{\sigma\sigma'}]_{\mu\nu\{-\mathbf{k}\}} &= \sum_{\mathbf{g}=-\infty}^{\infty} F^{\sigma\sigma'}_{\mu\nu\mathbf{g}} e^{-i\mathbf{k}\cdot\mathbf{g}} \\ &= \left[\sum_{\mathbf{g}=-\infty}^{\infty} [F^{\sigma\sigma'}]^*_{\mu\nu\mathbf{g}} e^{i\mathbf{k}\cdot\mathbf{g}} \right]^* \neq [F^{\sigma\sigma'}]^*_{\mu\nu\{\mathbf{k}\}} \end{aligned} \tag{G.65}$$

So no relation can be established between the Fock matrix elements (or their eigenvalues and eigenvectors) at $\mathbf{k}$ and $-\mathbf{k}$. This means that in general, for a fully relativistic description of open-shell systems (where the Hamiltonian does not commute with the operator of time-reversal) the Fock matrix needs to be diagonalized explicitly at $\mathbf{k}$ and $-\mathbf{k}$.

G.4 The Density Matrix

We now discuss the construction of the density matrix in direct space, obtained as a Fourier transform of the matrix in reciprocal space:

$$[P^{\sigma\sigma'}]_{\mu\nu[\mathbf{g}]} = \int d\mathbf{k} [P^{\sigma\sigma'}]_{\mu\nu\{\mathbf{k}\}} e^{i\mathbf{k}\cdot\mathbf{g}} \tag{G.66}$$

$$= \int d\mathbf{k} \sum_i [a^{\sigma}]^*_{\mu i}(\mathbf{k}) [a^{\sigma'}]_{\nu i}(\mathbf{k}) \theta(\epsilon_F - \epsilon_i(\mathbf{k})) e^{-i\mathbf{k}\cdot\mathbf{g}} \tag{G.67}$$

where the $[a^{\sigma}]_{\mu i}(\mathbf{k})$ are the eigenvectors of the Fock matrix, and the $\epsilon_i(\mathbf{k})$ its eigenvalues. The ϵ_F is the calculated Fermi energy and θ is the Heaviside step-on function.

Using Euler's formula $\left(e^{\pm i\theta} = \cos(\theta) \pm i\sin(\theta)\right)$, we can write explicit expressions for the real and imaginary parts of the density matrix:

$$\mathrm{Re}[P^{\sigma\sigma'}]_{\mu\nu[\mathbf{g}]} = \int d\mathbf{k} \sum_i \Big\{ \cos(\mathbf{k}\cdot\mathbf{g}) \Big(\mathrm{Re}[a^{\sigma}]_{\mu i}(\mathbf{k})\, \mathrm{Re}[a^{\sigma'}]_{\nu i}(\mathbf{k}) + \mathrm{Im}[a^{\sigma}]_{\mu i}(\mathbf{k})\, \mathrm{Im}[a^{\sigma'}]_{\nu i}(\mathbf{k}) \Big) \\ - \sin(\mathbf{k}\cdot\mathbf{g}) \Big(\mathrm{Re}[a^{\sigma}]_{\mu i}(\mathbf{k})\, \mathrm{Im}[a^{\sigma'}]_{\nu i}(\mathbf{k}) - \mathrm{Im}[a^{\sigma}]_{\mu i}(\mathbf{k})\, \mathrm{Re}[a^{\sigma'}]_{\nu i}(\mathbf{k}) \Big) \Big\} \theta(\epsilon_F - \epsilon_i(\mathbf{k})) \tag{G.68}$$

and:

$$\mathrm{Im}[P^{\sigma\sigma'}]_{\mu\nu[\mathbf{g}]} = \int d\mathbf{k} \sum_i \Big\{ \cos(\mathbf{k}\cdot\mathbf{g}) \Big(\mathrm{Re}[a^{\sigma}]_{\mu i}(\mathbf{k})\, \mathrm{Im}[a^{\sigma'}]_{\nu i}(\mathbf{k}) - \mathrm{Im}[a^{\sigma}]_{\mu i}(\mathbf{k})\, \mathrm{Re}[a^{\sigma'}]_{\nu i}(\mathbf{k}) \Big) \\ + \sin(\mathbf{k}\cdot\mathbf{g}) \Big(\mathrm{Re}[a^{\sigma}]_{\mu i}(\mathbf{k})\, \mathrm{Re}[a^{\sigma'}]_{\nu i}(\mathbf{k}) + \mathrm{Im}[a^{\sigma}]_{\mu i}(\mathbf{k})\, \mathrm{Im}[a^{\sigma'}]_{\nu i}(\mathbf{k}) \Big) \Big\} \theta(\epsilon_F - \epsilon_i(\mathbf{k})) \tag{G.69}$$

For the off-diagonal spin-blocks, the upper portion ($[P^{\alpha\beta}]_{\mu\nu[\mathbf{g}]}$) is built for the opposite vector to the lower triangular portion ($[P^{\alpha\beta}]_{\nu\mu[-\mathbf{g}]}$)

G.5 Acceleration of the SCF through Karlström Extrapolation

G.5.1 General Remarks

We now discuss how the SCF can be solved using the extrapolation method for the density matrix, following the approach first described by Karlström. This approach is also called relaxed constraints algorithm (RCA) or optimal damping algorithm (ODA) in the papers of Cancès.

We start the algorithm by performing a regular SCF cycle from the guess density matrix $\mathbf{P}_0$, and one further diagonalization in the following cycle to obtain a second density matrix $\mathbf{P}_1$. The method then consists of finding the optimal mixing parameter x to combine $\mathbf{P}_0$ and $\mathbf{P}_1$ to form the new density matrix $\mathbf{P}$, which will be used for constructing the Fock matrix at the following cycle:

$$\mathbf{P} = \mathbf{P}_0 + x\,(\mathbf{P}_1 - \mathbf{P}_0) = \mathbf{P}_0 + x\boldsymbol{\Delta} \tag{G.70}$$

where here all density matrices are expressed in direct space. The optimal mixing parameter x is determined by a steepest-descent step to find the minimum of the energy as a function of x. For Hartree-Fock the steepest descent can be done analytically. For DFT, there is no analytical formula, so it can be done numerically, but Cancès found that it is not worth the trouble, and he suggests using the analytical HF expression also for accelerating the DFT SCF. So for now we only discuss the HF case.

The steepest-descent step guarantees that the energy goes down at every cycle. What is more, Cancès showed that if x is limited in the range $[0, 1]$, then the algorithm guarantees that $\mathbf{P}$ stays in the convex set of density matrices that satisfy:

$$P_{\mu\nu} = P^*_{\nu\mu} \qquad \text{(Hermiticity)} \tag{G.71}$$

$$\mathrm{Tr}\,(\mathbf{SP}) = N \qquad \text{(Conservation of particles)} \tag{G.72}$$

$$\mathbf{PSP} = \mathbf{P} \qquad \text{(Idempotency)} \tag{G.73}$$

Actually these constraints are guaranteed to be obeyed at convergence, but in general at a non-converged cycle, instead of the Idempotency one, we have the relaxed constraint:

$$\mathbf{PSP} \leq \mathbf{P} \tag{G.74}$$

This is why he calls it the relaxed-constraints algorithm.

In essence, what the above means is that so long as x is limited in the range $[0, 1]$, $\mathbf{P}$ is guaranteed to be a solution of the Hartree-Fock equations (but not necessarily the lowest energy solution!). However, because the energy is guaranteed to always go down, at convergence $\mathbf{P}$ can be at worst a local-minimum of the Hartree-Fock equations.

G.5.2 Expressing the Energy in Terms of the Damping Parameter

Now we discuss the derivation for the expression of the optimal mixing parameter x. The derivation turns out to be general for both the one- and two-component cases. We start with the expression for the HF energy, in terms of the optimally mixed density-matrix $\mathbf{P}$:

$$\begin{aligned} E &= \frac{1}{2}\sum_{\mathbf{g}}\sum_{\mu\nu}\left[h^{\mathbf{g}}_{\mu\nu}P^{\mathbf{g}}_{\mu\nu} + F^{\mathbf{g}}_{\mu\nu}P^{\mathbf{g}}_{\mu\nu}\right] \\ &= \sum_{\mathbf{g}}\sum_{\mu\nu} h^{\mathbf{g}}_{\mu\nu}P^{\mathbf{g}}_{\mu\nu} + \frac{1}{2}\sum_{\mathbf{g},\mathbf{h},\mathbf{n}}\sum_{\mu\nu}\sum_{\rho\sigma} P^{\mathbf{g}}_{\mu\nu}G^{\mathbf{0},\mathbf{g},\mathbf{h},\mathbf{n}}_{\mu\nu\rho\sigma}P^{\mathbf{n}}_{\rho\sigma} \end{aligned} \tag{G.75}$$

where $G^{\mathbf{0},\mathbf{g},\mathbf{h},\mathbf{n}}_{\mu\nu\rho\sigma}$ represents the bi-electronic Coulomb and exchange integrals:

$$G^{\mathbf{0},\mathbf{g},\mathbf{h},\mathbf{n}}_{\mu\nu\rho\sigma} = \left(\chi^{\mathbf{0}}_{\mu}\chi^{\mathbf{g}}_{\nu}|\chi^{\mathbf{h}}_{\rho}\chi^{\mathbf{h}+\mathbf{n}}_{\sigma}\right) - \frac{1}{2}\left(\chi^{\mathbf{0}}_{\mu}\chi^{\mathbf{h}}_{\rho}|\chi^{\mathbf{g}}_{\nu}\chi^{\mathbf{h}+\mathbf{n}}_{\sigma}\right) \tag{G.76}$$

Substituting Eq. (G.70) in Eq. (G.75) we obtain an expression for E as a function of x:

$$\begin{aligned} E &= \sum_{\mathbf{g}}\sum_{\mu\nu} h^{\mathbf{g}}_{\mu\nu}P^{\mathbf{g}}_{0\mu\nu} + x\sum_{\mathbf{g}}\sum_{\mu\nu} h^{\mathbf{g}}_{\mu\nu}\Delta^{\mathbf{g}}_{\mu\nu} \\ &+ \frac{1}{2}\sum_{\mathbf{g},\mathbf{h},\mathbf{n}}\sum_{\mu\nu}\sum_{\rho\sigma}\left(P^{\mathbf{g}}_{0\mu\nu} + x\Delta^{\mathbf{g}}_{\mu\nu}\right)G^{\mathbf{0},\mathbf{g},\mathbf{h},\mathbf{n}}_{\mu\nu\rho\sigma}\left(P^{\mathbf{n}}_{0\rho\sigma} + x\Delta^{\mathbf{n}}_{\rho\sigma}\right) \end{aligned} \tag{G.77}$$

Regrouping the terms:

$$\begin{aligned} E &= \sum_{\mathbf{g}} \sum_{\mu\nu} h^{\mathbf{g}}_{\mu\nu} P^{\mathbf{g}}_{0\mu\nu} + \frac{1}{2} \sum_{\mathbf{g},\mathbf{h},\mathbf{n}} \sum_{\mu\nu} \sum_{\rho\sigma} P^{\mathbf{g}}_{0\mu\nu} G^{\mathbf{0},\mathbf{g},\mathbf{h},\mathbf{n}}_{\mu\nu\rho\sigma} P^{\mathbf{n}}_{0\mu\nu} \\ &+ x \sum_{\mathbf{g}} \sum_{\mu\nu} h^{\mathbf{g}}_{\mu\nu} \Delta^{\mathbf{g}}_{\mu\nu} + \frac{x}{2} \sum_{\mathbf{g},\mathbf{h},\mathbf{n}} \sum_{\mu\nu} \sum_{\rho\sigma} P^{\mathbf{g}}_{0\mu\nu} G^{\mathbf{0},\mathbf{g},\mathbf{h},\mathbf{n}}_{\mu\nu\rho\sigma} \Delta^{\mathbf{n}}_{\rho\sigma} \\ &+ \frac{x}{2} \sum_{\mathbf{g},\mathbf{h},\mathbf{n}} \sum_{\mu\nu} \sum_{\rho\sigma} \Delta^{\mathbf{g}}_{\mu\nu} G^{\mathbf{0},\mathbf{g},\mathbf{h},\mathbf{n}}_{\mu\nu\rho\sigma} P^{\mathbf{n}}_{0\rho\sigma} \\ &+ \frac{x^2}{2} \sum_{\mathbf{g},\mathbf{h},\mathbf{n}} \sum_{\mu\nu} \sum_{\rho\sigma} \Delta^{\mathbf{g}}_{\mu\nu} G^{\mathbf{0},\mathbf{g},\mathbf{h},\mathbf{n}}_{\mu\nu\rho\sigma} \Delta^{\mathbf{n}}_{\rho\sigma} \end{aligned} \tag{G.78}$$

G.5.3 Permutation Symmetries and the Integral Tolerances

We discuss the treatment of the fourth and fifth terms in the above Eq. (G.78):

$$\frac{x}{2} \sum_{\mathbf{g},\mathbf{h},\mathbf{n}} \sum_{\mu\nu} \sum_{\rho\sigma} P^{\mathbf{g}}_{0\mu\nu} G^{\mathbf{0},\mathbf{g},\mathbf{h},\mathbf{n}}_{\mu\nu\rho\sigma} \Delta^{\mathbf{n}}_{\rho\sigma} + \frac{x}{2} \sum_{\mathbf{g},\mathbf{h},\mathbf{n}} \sum_{\mu\nu} \sum_{\rho\sigma} \Delta^{\mathbf{g}}_{\mu\nu} G^{\mathbf{0},\mathbf{g},\mathbf{h},\mathbf{n}}_{\mu\nu\rho\sigma} P^{\mathbf{n}}_{0\rho\sigma} \tag{G.79}$$

In the molecular case, these two terms are equivalent to each other. To see this, we drop the lattice vector notation:

$$\frac{x}{2} \sum_{\mu\nu} \sum_{\rho\sigma} P_{0\mu\nu} G_{\mu\nu\rho\sigma} \Delta_{\rho\sigma} + \frac{x}{2} \sum_{\mu\nu} \sum_{\rho\sigma} \Delta_{\mu\nu} G_{\mu\nu\rho\sigma} P_{0\rho\sigma} \tag{G.80}$$

Then, using the fact that the bielectronic integral is invariant to global permutations of the form $\chi_\mu\chi_\nu \leftrightarrow \chi_\rho\chi_\sigma$, we have:

$$\begin{aligned} \frac{x}{2} \sum_{\mu\nu} \sum_{\rho\sigma} P_{0\mu\nu} G_{\mu\nu\rho\sigma} \Delta_{\rho\sigma} + \frac{x}{2} \sum_{\mu\nu} \sum_{\rho\sigma} \Delta_{\mu\nu} G_{\mu\nu\rho\sigma} P_{0\rho\sigma} = \\ x \sum_{\mu\nu} \sum_{\rho\sigma} P_{0\mu\nu} G_{\mu\nu\rho\sigma} \Delta_{\rho\sigma} \end{aligned} \tag{G.81}$$

For periodic systems, on the other hand, the permutation $\chi_\mu\chi_\nu \leftrightarrow \chi_\rho\chi_\sigma$ also involves lattice vectors, and is only satisfied exactly in the limit where the T2 tolerance on Coulomb integrals is infinite. This is because the T2 tolerance involves expanding approximately only the two functions on the right of the bielectronic integral (those carrying the indices ν and σ) in a multipole expansion, but not those on the left of the bielectronic integral (not μ and ρ). (A short discussion on this is given in Jacopo's thesis.) So the required permutation is lost for small values of T2. It is still possible to generate the required analytical expression for x without using the permutation $\chi_\mu\chi_\nu \leftrightarrow \chi_\rho\chi_\sigma$, but the expression we get would be significantly more costly and difficult to program. For now, we assume for periodic systems that T2 is sufficiently high such that the effect of breaking this permutation symmetry is small. Further on we derive the general case.

G.5.4 Case 1: Infinite T2 Tolerance

We first assume that T2 is sufficiently high, so that the fourth and fifth terms in Eq. (G.78) are equivalent to each other. So we have:

$$\begin{aligned} E &= \sum_{\mathbf{g}} \sum_{\mu\nu} h^{\mathbf{g}}_{\mu\nu} P^{\mathbf{g}}_{0\mu\nu} + \frac{1}{2} \sum_{\mathbf{g},\mathbf{h},\mathbf{n}} \sum_{\mu\nu} \sum_{\rho\sigma} P^{\mathbf{g}}_{0\mu\nu} G^{\mathbf{0},\mathbf{g},\mathbf{h},\mathbf{n}}_{\mu\nu\rho\sigma} P^{\mathbf{n}}_{0\mu\nu} \\ &+ x \sum_{\mathbf{g}} \sum_{\mu\nu} h^{\mathbf{g}}_{\mu\nu} \Delta^{\mathbf{g}}_{\mu\nu} + x \sum_{\mathbf{g},\mathbf{h},\mathbf{n}} \sum_{\mu\nu} \sum_{\rho\sigma} P^{\mathbf{g}}_{0\mu\nu} G^{\mathbf{0},\mathbf{g},\mathbf{h},\mathbf{n}}_{\mu\nu\rho\sigma} \Delta^{\mathbf{n}}_{\rho\sigma} \\ &+ \frac{x^2}{2} \sum_{\mathbf{g},\mathbf{h},\mathbf{n}} \sum_{\mu\nu} \sum_{\rho\sigma} \Delta^{\mathbf{g}}_{\mu\nu} G^{\mathbf{0},\mathbf{g},\mathbf{h},\mathbf{n}}_{\mu\nu\rho\sigma} \Delta^{\mathbf{n}}_{\rho\sigma} \end{aligned} \tag{G.82}$$

The first two terms above in Eq. (G.82) are just the energy calculated at cycle 0:

$$E_0 = \sum_{\mathbf{g}} \sum_{\mu\nu} h^{\mathbf{g}}_{\mu\nu} P^{\mathbf{g}}_{0\mu\nu} + \frac{1}{2} \sum_{\mathbf{g},\mathbf{h},\mathbf{n}} \sum_{\mu\nu} \sum_{\rho\sigma} P^{\mathbf{g}}_{0\mu\nu} G^{\mathbf{0},\mathbf{g},\mathbf{h},\mathbf{n}}_{\mu\nu\rho\sigma} P^{\mathbf{n}}_{0\mu\nu} \tag{G.83}$$

The third and fourth terms in Eq. (G.82) can be re-written using the Fock matrix at cycle 0 $\mathbf{F}_0$ and the $\boldsymbol{\Delta}$ matrix:

$$\sum_{\mathbf{g}} \sum_{\mu\nu} F^{\mathbf{g}}_{0\mu\nu} \Delta^{\mathbf{g}}_{\mu\nu} = \sum_{\mathbf{g}} \sum_{\mu\nu} h^{\mathbf{g}}_{\mu\nu} \Delta^{\mathbf{g}}_{\mu\nu} + \sum_{\mathbf{g},\mathbf{h},\mathbf{n}} \sum_{\mu\nu} \sum_{\rho\sigma} P^{\mathbf{g}}_{0\mu\nu} G^{\mathbf{0},\mathbf{g},\mathbf{h},\mathbf{n}}_{\mu\nu\rho\sigma} \Delta^{\mathbf{n}}_{\rho\sigma} \tag{G.84}$$

The last term can be re-written in terms of differencess of Fock matrices at cycles 1 and 0, with the $\boldsymbol{\Delta}$ matrix:

$$\sum_{\mathbf{g}} \sum_{\mu\nu} \left(F^{\mathbf{g}}_{1\mu\nu} - F^{\mathbf{g}}_{0\mu\nu}\right) \Delta^{\mathbf{g}}_{\mu\nu} = \sum_{\mathbf{g},\mathbf{h},\mathbf{n}} \sum_{\mu\nu} \sum_{\rho\sigma} \Delta^{\mathbf{g}}_{\mu\nu} G^{\mathbf{0},\mathbf{g},\mathbf{h},\mathbf{n}}_{\mu\nu\rho\sigma} \Delta^{\mathbf{n}}_{\rho\sigma} \tag{G.85}$$

Substituting Eqs. (G.83), (G.84) and G.85 in Eq. (G.82):

$$E = E_0 + x \sum_{\mathbf{g}} \sum_{\mu\nu} F^{\mathbf{g}}_{0\mu\nu} \Delta^{\mathbf{g}}_{\mu\nu} + \frac{x^2}{2} \sum_{\mathbf{g}} \sum_{\mu\nu} \left(F^{\mathbf{g}}_{1\mu\nu} - F^{\mathbf{g}}_{0\mu\nu}\right) \Delta^{\mathbf{g}}_{\mu\nu} \tag{G.86}$$

If E is a minimum w.r.t. x, then its first derivative must vanish:

$$\frac{\mathrm{d}E}{\mathrm{d}x} = \sum_{\mathbf{g}} \sum_{\mu\nu} F^{\mathbf{g}}_{0\mu\nu} \Delta^{\mathbf{g}}_{\mu\nu} + x \sum_{\mathbf{g}} \sum_{\mu\nu} \left(F^{\mathbf{g}}_{1\mu\nu} - F^{\mathbf{g}}_{0\mu\nu}\right) \Delta^{\mathbf{g}}_{\mu\nu} = 0 \tag{G.87}$$

Isolating x:

$$x = -\frac{\sum_{\mathbf{g}} \sum_{\mu\nu} F^{\mathbf{g}}_{0\mu\nu} \Delta^{\mathbf{g}}_{\mu\nu}}{\sum_{\mathbf{g}} \sum_{\mu\nu} \left(F^{\mathbf{g}}_{1\mu\nu} - F^{\mathbf{g}}_{0\mu\nu}\right) \Delta^{\mathbf{g}}_{\mu\nu}} \tag{G.88}$$

In the paper of Cancès, they go on to simplify this expression in terms of the eigenvalues and mono- and bi-electronic contributions to the energy. However, for the periodic case, it is not easy to seperate the mono- and bi-electronic energy contributions. The way in which to express the quantities above in terms of the eigenvalues obtained in reciprocal space would also need to be re-thought for the periodic case. So for now

I coded the expression above, and not the simplified expression of Cancès.

G.5.5 Case 2: Finite T2 Tolerance

We now discuss the case of finite T2 tolerance, where the fourth and fifth terms in Eq. (G.78) cannot be combined.

In this case, we proceed as in Case 1 for the other terms, but leave untouched the terms carrying x (i.e. the third, fourth and fifth terms in Eq. (G.78)):

$$\begin{aligned} E &= E_0 + x\Bigg(\sum_{\mathbf{g}} \sum_{\mu\nu} h^{\mathbf{g}}_{\mu\nu} \Delta^{\mathbf{g}}_{\mu\nu} + \frac{1}{2} \sum_{\mathbf{g},\mathbf{h},\mathbf{n}} \sum_{\mu\nu} \sum_{\rho\sigma} P^{\mathbf{g}}_{0\mu\nu} G^{\mathbf{0},\mathbf{g},\mathbf{h},\mathbf{n}}_{\mu\nu\rho\sigma} \Delta^{\mathbf{n}}_{\rho\sigma} \\ &+ \frac{1}{2} \sum_{\mathbf{g},\mathbf{h},\mathbf{n}} \sum_{\mu\nu} \sum_{\rho\sigma} \Delta^{\mathbf{g}}_{\mu\nu} G^{\mathbf{0},\mathbf{g},\mathbf{h},\mathbf{n}}_{\mu\nu\rho\sigma} P^{\mathbf{n}}_{0\rho\sigma} \Bigg) \\ &+ \frac{x^2}{2} \sum_{\mathbf{g}} \sum_{\mu\nu} \left(F^{\mathbf{g}}_{1\mu\nu} - F^{\mathbf{g}}_{0\mu\nu} \right) \Delta^{\mathbf{g}}_{\mu\nu} \end{aligned} \tag{G.89}$$

The first and third terms in the large parenthesis in the above Eq. (G.89) can be written in terms of a Fock matrix calculated using a half density matrix at cycle 0:

$$\sum_{\mathbf{g}} \sum_{\mu\nu} F^{\mathbf{g}}_{\mu\nu}(P_0/2) \Delta^{\mathbf{g}}_{\mu\nu} = \sum_{\mathbf{g}} \sum_{\mu\nu} h^{\mathbf{g}}_{\mu\nu} \Delta^{\mathbf{g}}_{\mu\nu} + \frac{1}{2} \sum_{\mathbf{g},\mathbf{h},\mathbf{n}} \sum_{\mu\nu} \sum_{\rho\sigma} \Delta^{\mathbf{g}}_{\mu\nu} G^{\mathbf{0},\mathbf{g},\mathbf{h},\mathbf{n}}_{\mu\nu\rho\sigma} P^{\mathbf{n}}_{0\rho\sigma} \tag{G.90}$$

where $F^{\mathbf{g}}_{\mu\nu}(P_0/2)$ denotes an element of the Fock matrix, where the bi-electronic term is calculated using $P^{\mathbf{n}}_{0\rho\sigma}/2$ elements instead of $P^{\mathbf{n}}_{0\rho\sigma}$ elements.

The second term in the large parenthsis in Eq. (G.89) can be written in terms of differences of Fock matrices calculated at cycles 0 and 1:

$$\sum_{\mathbf{g}} \sum_{\mu\nu} \left(F^{\mathbf{g}}_{1\mu\nu} - F^{\mathbf{g}}_{0\mu\nu} \right) P^{\mathbf{g}}_{0\mu\nu} = \sum_{\mathbf{g},\mathbf{h},\mathbf{n}} \sum_{\mu\nu} \sum_{\rho\sigma} P^{\mathbf{g}}_{0\mu\nu} G^{\mathbf{0},\mathbf{g},\mathbf{h},\mathbf{n}}_{\mu\nu\rho\sigma} \Delta^{\mathbf{n}}_{\rho\sigma} \tag{G.91}$$

Substituting Eqs. (G.90) and (G.91) in Eq. (G.89):

$$\begin{aligned} E &= E_0 + x\Bigg(\sum_{\mathbf{g}} \sum_{\mu\nu} F^{\mathbf{g}}_{\mu\nu}(P_0/2) \Delta^{\mathbf{g}}_{\mu\nu} + \frac{1}{2} \sum_{\mathbf{g}} \sum_{\mu\nu} \left(F^{\mathbf{g}}_{1\mu\nu} - F^{\mathbf{g}}_{0\mu\nu} \right) P^{\mathbf{g}}_{0\mu\nu} \Bigg) \\ &+ \frac{x^2}{2} \sum_{\mathbf{g}} \sum_{\mu\nu} \left(F^{\mathbf{g}}_{1\mu\nu} - F^{\mathbf{g}}_{0\mu\nu} \right) \Delta^{\mathbf{g}}_{\mu\nu} \end{aligned} \tag{G.92}$$

Setting the derivative of E to zero and isolating for x like in Case 1, we obtain:

$$x = -\frac{\sum_{\mathbf{g}} \sum_{\mu\nu} F^{\mathbf{g}}_{\mu\nu}(P_0/2) \Delta^{\mathbf{g}}_{\mu\nu} + \frac{1}{2} \sum_{\mathbf{g}} \sum_{\mu\nu} \left(F^{\mathbf{g}}_{1\mu\nu} - F^{\mathbf{g}}_{0\mu\nu} \right) P^{\mathbf{g}}_{0\mu\nu}}{\sum_{\mathbf{g}} \sum_{\mu\nu} \left(F^{\mathbf{g}}_{1\mu\nu} - F^{\mathbf{g}}_{0\mu\nu} \right) \Delta^{\mathbf{g}}_{\mu\nu}} \tag{G.93}$$

G.6 The Algorithm According to Karlström and Cancès

In accordance with the notation of Cancès, density matrices (and their derived Focks) obtained from extrapolation is denoted with a tilde, while density matrices (and their Focks) obtained from regular diagonalization are denoted without a tilde. So Eq. (G.88) can be written as:

$$x_k = -\frac{\sum_{\mathbf{g}} \sum_{\mu\nu} \tilde{F}^{\mathbf{g}}_{k-1\mu\nu} \left(P^{\mathbf{g}}_{k\mu\nu} - \tilde{P}^{\mathbf{g}}_{k-1\mu\nu} \right)}{\sum_{\mathbf{g}} \sum_{\mu\nu} \left(F^{\mathbf{g}}_{k\mu\nu} - \tilde{F}^{\mathbf{g}}_{k-1\mu\nu} \right) \left(P^{\mathbf{g}}_{k\mu\nu} - \tilde{P}^{\mathbf{g}}_{k-1\mu\nu} \right)} \tag{G.94}$$

The complete Karlström algorithm therefore proceeds as follows.

1. Obtain $\mathbf{P}_0$ from a guess
2. Construct $\mathbf{F}_0$
3. Set $\tilde{\mathbf{F}}_0 = \mathbf{F}_0$ and $\tilde{\mathbf{P}}_0 = \mathbf{P}_0$
4. Save $\tilde{\mathbf{P}}_0$ and $\tilde{\mathbf{F}}_0$ to disk
5. Diagonalize $\mathbf{F}_0$
6. Construct $\mathbf{P}_1$ by aufbau
7. Set $k = 1$
8. Begin iteration on k:
    (a) Construct $\mathbf{F}_k = \mathbf{F}(\mathbf{P}_k)$
    (b) Calculate Energy $E = \frac{1}{2}\mathrm{Tr}(\mathbf{h}\mathbf{P}_k) + \frac{1}{2}\mathrm{Tr}(\mathbf{F}_k\mathbf{P}_k)$
    (c) Read $\tilde{\mathbf{P}}_{k-1}$ and $\tilde{\mathbf{F}}_{k-1}$ from disk
    (d) Calculate the optimal mixing fraction x_k from Eq. (G.94) using $\mathbf{P}_k$, $\mathbf{F}_k$, $\tilde{\mathbf{P}}_{k-1}$ and $\tilde{\mathbf{F}}_{k-1}$
    (e) if $x_k < 0$ or $x_k > 1$, set $x_k = 1$
    (f) Calculate $\tilde{\mathbf{P}}_k = \tilde{\mathbf{P}}_{k-1} + x_k \left(\mathbf{P}_k - \tilde{\mathbf{P}}_{k-1} \right)$
    (g) Calculate $\tilde{\mathbf{F}}_k = \tilde{\mathbf{F}}_{k-1} + x_k \left(\mathbf{F}_k - \tilde{\mathbf{F}}_{k-1} \right)$
    (h) Write $\tilde{\mathbf{P}}_k$ and $\tilde{\mathbf{F}}_k$ to disk
    (i) Diagonalize $\tilde{\mathbf{F}}_k$
    (j) Construct $\mathbf{P}_{k+1}$ from aufbau
    (k) Check for convergence
    (l) If not converged, set $k = k + 1$ and return to a.

G.6.1 Modified Method for Slowly Varying Density

The algorithm described in the previous section works well when there are large changes in $\mathbf{P}^{\mathbf{g}}_{k}$ and $\tilde{\mathbf{P}}^{\mathbf{g}}_{k-1}$, such that the SCF would otherwise oscillate between two states. In this case, the generation of the new density matrix by mixing of the $\mathbf{P}^{\mathbf{g}}_{k}$ and $\tilde{\mathbf{P}}^{\mathbf{g}}_{k-1}$ damps the oscillations. However, in the situation where the density varies slowly, such that the difference $\mathbf{\Delta}^{\mathbf{g}}_{k} = \mathbf{P}^{\mathbf{g}}_{k} - \tilde{\mathbf{P}}^{\mathbf{g}}_{k-1}$ is small, both the numerator and the denominator in Eq. (G.94) are small in absolute value, and x_k is unstable and can easily take values way outside the allowed range $[0, 1]$. In this case, we always take $x_k = 1$ and the Karlström algorithm reduces to the regular Hartree-Fock Roothaan procedure. In such cases, it is useful to instead modify the original algorithm to provide some form of acceleration for the case of slowly varying density.

We proceed as follows, assuming that the density is slowly varying:

$$\mathbf{P}_k - \tilde{\mathbf{P}}_{k-1} \approx \mathbf{P}_{k+1} - \mathbf{P}_k \tag{G.95}$$

Substituting the above in Eq. (G.94), we have:

$$\frac{-\sum_{\mathbf{g}}\sum_{\mu\nu}\tilde{F}^{\mathbf{g}}_{k-1\mu\nu}\left(P^{\mathbf{g}}_{k\mu\nu} - \tilde{P}^{\mathbf{g}}_{k-1\mu\nu}\right)}{\sum_{\mathbf{g}}\sum_{\mu\nu}\left(F^{\mathbf{g}}_{k\mu\nu} - \tilde{F}^{\mathbf{g}}_{k-1\mu\nu}\right)\left(P^{\mathbf{g}}_{k\mu\nu} - \tilde{P}^{\mathbf{g}}_{k-1\mu\nu}\right)} \approx \frac{-\sum_{\mathbf{g}}\sum_{\mu\nu}\tilde{F}^{\mathbf{g}}_{k-1\mu\nu}\left(P^{\mathbf{g}}_{k+1\mu\nu} - P^{\mathbf{g}}_{k\mu\nu}\right)}{\sum_{\mathbf{g}}\sum_{\mu\nu}\left(\tilde{F}^{\mathbf{g}}_{k\mu\nu} - \tilde{F}^{\mathbf{g}}_{k-1\mu\nu}\right)\left(P^{\mathbf{g}}_{k+1\mu\nu} - P^{\mathbf{g}}_{k\mu\nu}\right)}$$

These expressions are formally equivalent in the limit of slowly varying density, but in practice the r.h.s. one might be more useful, because it combines information from three cycles (cycles $k-1$, k and $k+1$), instead of two cycles, at the same cost of the original algorithm. The density matrix $\mathbf{P}^{\mathbf{g}}_{k+1}$ is available at cycle k, right after the diagonalization of $\mathbf{F}^{\mathbf{k}}_{k}$. So we may use the r.h.s. of the above equation to calculate x_{k+1} at the end of cycle k. That is to say:

$$x_{k+1} = \frac{-\sum_{\mathbf{g}}\sum_{\mu\nu}\tilde{F}^{\mathbf{g}}_{k-1\mu\nu}\left(P^{\mathbf{g}}_{k+1\mu\nu} - P^{\mathbf{g}}_{k\mu\nu}\right)}{\sum_{\mathbf{g}}\sum_{\mu\nu}\left(\tilde{F}^{\mathbf{g}}_{k\mu\nu} - \tilde{F}^{\mathbf{g}}_{k-1\mu\nu}\right)\left(P^{\mathbf{g}}_{k+1\mu\nu} - P^{\mathbf{g}}_{k\mu\nu}\right)} \tag{G.96}$$

The modified algorithm therefore proceeds as follows:

1. Obtain $\mathbf{P}_0$ from a guess
2. Construct $\mathbf{F}_0$
3. Set $\tilde{\mathbf{F}}_0 = \mathbf{F}_0$
4. Save $\tilde{\mathbf{F}}_0$ to disk
5. Diagonalize $\tilde{\mathbf{F}}_0$
6. Construct $\mathbf{P}_1$ by aufbau
7. Save $\mathbf{P}_1$ to disk
8. Set $\tilde{\mathbf{P}}_1 = \mathbf{P}_1$

9. Set $k = 1$

10. Begin iteration on k:

    (a) Construct $\tilde{\mathbf{F}}_k = \tilde{\mathbf{F}}(\tilde{\mathbf{P}}_k)$

    (b) Calculate Energy $E = \frac{1}{2}\mathrm{Tr}(\mathbf{h}\tilde{\mathbf{P}}_k) + \frac{1}{2}\mathrm{Tr}(\tilde{\mathbf{F}}_k\tilde{\mathbf{P}}_k)$

    (c) Save $\tilde{\mathbf{F}}_k$ to disk

    (d) Diagonalize $\tilde{\mathbf{F}}_k$

    (e) Construct $\mathbf{P}_{k+1}$ from aufbau

    (f) Read $\mathbf{P}_k$, $\tilde{\mathbf{F}}_k$ and $\tilde{\mathbf{F}}_{k-1}$ from disk

    (g) Calculate the optimal mixing fraction x_{k+1} from Eq. (G.96) using $\mathbf{P}_{k+1}$, $\tilde{\mathbf{F}}_k$, $\mathbf{P}_k$ and $\tilde{\mathbf{F}}_{k-1}$

    (h) if $x_k < 0$ or $x_k > 1$, set $x_k = 1$

    (i) Calculate $\tilde{\mathbf{P}}_{k+1} = \tilde{\mathbf{P}}_k + x_{k+1}\left(\mathbf{P}_{k+1} - \tilde{\mathbf{P}}_k\right)$

    (j) Write $\mathbf{P}_{k+1}$ to disk

    (k) Check for convergence

    (l) If not converged, set $k = k + 1$ and return to a.

G.7 The EDIIS Method of Cancès

G.7.1 Relation with the Method of Karlström

We discuss an improvement on the Karlström method suggested by Cancès. Recalling the Karlström expression from Eq. (G.86), at iteration $k = 1$:

$$E = E_0 + x\sum_{\mathbf{g}}\sum_{\mu\nu} F^{\mathbf{g}}_{0\mu\nu}\left(P^{\mathbf{g}}_{1\mu\nu} - P^{\mathbf{g}}_{0\mu\nu}\right) + \frac{x^2}{2}\sum_{\mathbf{g}}\sum_{\mu\nu}\left(F^{\mathbf{g}}_{1\mu\nu} - F^{\mathbf{g}}_{0\mu\nu}\right)\left(P^{\mathbf{g}}_{1\mu\nu} - P^{\mathbf{g}}_{0\mu\nu}\right) \tag{G.97}$$

Or, taking the trace notation:

$$E = E_0 + x\mathrm{Tr}\left[\mathbf{F}_0\left(\mathbf{P}_1 - \mathbf{P}_0\right)\right] + \frac{x^2}{2}\mathrm{Tr}\left[\left(\mathbf{F}_1 - \mathbf{F}_0\right)\left(\mathbf{P}_1 - \mathbf{P}_0\right)\right] \tag{G.98}$$

Cancès suggests to improve this method by including the density matrix from all cycles up to the current iteration k, instead of only cycles $k - 1$ and k. The resulting method still maintains the desirable formal advantages discussed in section G.5.1. The expression for the energy then becomes (see next sections for derivation of this expression):

$$E = \sum_{i=0}^{k} c_i E_i - \frac{1}{4}\sum_{i,j=0}^{k} c_i c_j \mathrm{Tr}\left[\left(\mathbf{F}_i - \mathbf{F}_j\right)\left(\mathbf{P}_i - \mathbf{P}_j\right)\right] \tag{G.99}$$

The resulting method is called EDIIS (energy-DIIS i.e. energy direct inversion in the iterative subspace). This method is used in part in the Gaussian code as the default convergence accelerator.

We show the equivalence of Eqs. (G.98) and (G.99), when only two cycles are included. The proof starts by setting the conditions for the intialization of the Karlström algorithm. Namely, $c_1 = x$ and $c_0 = 1 - x$, then showing that Eq. (G.99) reduces to Eq. (G.98) for $k = 1$.

Setting $c_1 = x$ and $c_0 = 1 - x$:

$$\begin{aligned} E &= (1-x)E_0 + xE_1 - \frac{1}{4}(1-x)^2 \mathrm{Tr}\left[(\mathbf{F}_0 - \mathbf{F}_0)(\mathbf{P}_0 - \mathbf{P}_0)\right] - \frac{1}{4}x^2 \mathrm{Tr}\left[(\mathbf{F}_1 - \mathbf{F}_1)(\mathbf{P}_1 - \mathbf{P}_1)\right] \\ &- \frac{1}{2}x(1-x)\mathrm{Tr}\left[(\mathbf{F}_1 - \mathbf{F}_0)(\mathbf{P}_1 - \mathbf{P}_0)\right] \\ &= (1-x)E_0 + xE_1 - \frac{1}{2}x(1-x)\mathrm{Tr}\left[(\mathbf{F}_1 - \mathbf{F}_0)(\mathbf{P}_1 - \mathbf{P}_0)\right] \\ &= E_0 + x\left(E_1 - E_0 - \frac{1}{2}\mathrm{Tr}\left[(\mathbf{F}_1 - \mathbf{F}_0)(\mathbf{P}_1 - \mathbf{P}_0)\right]\right) + x^2\left(\frac{1}{2}\mathrm{Tr}\left[(\mathbf{F}_1 - \mathbf{F}_0)(\mathbf{P}_1 - \mathbf{P}_0)\right]\right) \end{aligned} \tag{G.100}$$

The term multiplying x^2 and the E_0 already have the right expression, when compared to Eq. (G.98), so all that remains in the proof is showing that the term multiplying x reduces also to the right expression.

Taking the coefficient multiplying x in Eq. (G.100):

$$\begin{aligned} x &:: \\ E_1 &- E_0 - \frac{1}{2}\mathrm{Tr}\left[(\mathbf{F}_1 - \mathbf{F}_0)(\mathbf{P}_1 - \mathbf{P}_0)\right] \\ &= \frac{1}{2}\mathrm{Tr}\left[\mathbf{h}\mathbf{P}_1\right] + \frac{1}{2}\mathrm{Tr}\left[\mathbf{F}_1\mathbf{P}_1\right] - \frac{1}{2}\mathrm{Tr}\left[\mathbf{h}\mathbf{P}_0\right] - \frac{1}{2}\mathrm{Tr}\left[\mathbf{F}_0\mathbf{P}_0\right] \\ &- \frac{1}{2}\mathrm{Tr}\left[\mathbf{F}_1\mathbf{P}_1\right] - \frac{1}{2}\mathrm{Tr}\left[\mathbf{F}_0\mathbf{P}_0\right] + \frac{1}{2}\mathrm{Tr}\left[\mathbf{F}_1\mathbf{P}_0\right] + \frac{1}{2}\mathrm{Tr}\left[\mathbf{F}_0\mathbf{P}_1\right] \\ &= \frac{1}{2}\mathrm{Tr}\left[\mathbf{h}\mathbf{P}_1\right] - \frac{1}{2}\mathrm{Tr}\left[\mathbf{h}\mathbf{P}_0\right] - \mathrm{Tr}\left[\mathbf{F}_0\mathbf{P}_0\right] + \frac{1}{2}\mathrm{Tr}\left[\mathbf{F}_1\mathbf{P}_0\right] + \frac{1}{2}\mathrm{Tr}\left[\mathbf{F}_0\mathbf{P}_1\right] \end{aligned} \tag{G.101}$$

To further reduce Eq. (G.101), we note that from the permutational invariance of the bielectronic integrals:

$$\mathrm{Tr}\left[(\mathbf{F}_0 - \mathbf{h})\,\mathbf{P}_1\right] = \mathrm{Tr}\left[(\mathbf{F}_1 - \mathbf{h})\,\mathbf{P}_0\right] \tag{G.102}$$

From which it follows that:

$$\begin{aligned} \mathrm{Tr}\left[\mathbf{F}_0\mathbf{P}_1\right] - \mathrm{Tr}\left[\mathbf{F}_1\mathbf{P}_0\right] &= \mathrm{Tr}\left[\mathbf{h}\,(\mathbf{P}_1 - \mathbf{P}_0)\right] \\ \mathrm{Tr}\left[\mathbf{F}_0\mathbf{P}_1\right] + \mathrm{Tr}\left[\mathbf{F}_1\mathbf{P}_0\right] &= 2\mathrm{Tr}\left[\mathbf{F}_0\mathbf{P}_1\right] - \mathrm{Tr}\left[\mathbf{h}\mathbf{P}_1\right] + \mathrm{Tr}\left[\mathbf{h}\mathbf{P}_0\right] \end{aligned} \tag{G.103}$$

Substituting Eq. (G.103) in (G.101), we find:

$$
\begin{aligned}
x &:: \\
\tfrac{1}{2} & \mathrm{Tr}\left[\mathbf{h}\mathbf{P}_1\right] - \frac{1}{2}\mathrm{Tr}\left[\mathbf{h}\mathbf{P}_0\right] - \mathrm{Tr}\left[\mathbf{F}_0\mathbf{P}_0\right] + \frac{1}{2}\mathrm{Tr}\left[\mathbf{F}_1\mathbf{P}_0\right] + \frac{1}{2}\mathrm{Tr}\left[\mathbf{F}_0\mathbf{P}_1\right] \\
= & \frac{1}{2}\mathrm{Tr}\left[\mathbf{h}\mathbf{P}_1\right] - \frac{1}{2}\mathrm{Tr}\left[\mathbf{h}\mathbf{P}_0\right] - \mathrm{Tr}\left[\mathbf{F}_0\mathbf{P}_0\right] + \mathrm{Tr}\left[\mathbf{F}_0\mathbf{P}_1\right] - \frac{1}{2}\mathrm{Tr}\left[\mathbf{h}\mathbf{P}_1\right] + \frac{1}{2}\mathrm{Tr}\left[\mathbf{h}\mathbf{P}_0\right] \\
= & -\mathrm{Tr}\left[\mathbf{F}_0\mathbf{P}_0\right] + \mathrm{Tr}\left[\mathbf{F}_0\mathbf{P}_1\right] \\
= & \mathrm{Tr}\left[\mathbf{F}_0\left(\mathbf{P}_1 - \mathbf{P}_0\right)\right] \qquad \text{(G.104)}
\end{aligned}
$$

G.7.2 Derivation of the Method

We recall the energy expression from Eq. (G.75):

$$
\begin{aligned}
E &= \frac{1}{2}\sum_{\mathbf{g}}\sum_{\mu\nu}\left[h^{\mathbf{g}}_{\mu\nu}P^{\mathbf{g}}_{\mu\nu} + F^{\mathbf{g}}_{\mu\nu}P^{\mathbf{g}}_{\mu\nu}\right] \\
&= \sum_{\mathbf{g}}\sum_{\mu\nu} h^{\mathbf{g}}_{\mu\nu}P^{\mathbf{g}}_{\mu\nu} + \frac{1}{2}\sum_{\mathbf{g},\mathbf{h},\mathbf{n}}\sum_{\mu\nu}\sum_{\rho\sigma} P^{\mathbf{g}}_{\mu\nu}G^{\mathbf{0},\mathbf{g},\mathbf{h},\mathbf{n}}_{\mu\nu\rho\sigma}P^{\mathbf{n}}_{\rho\sigma} \\
&= \mathrm{Tr}\left[\mathbf{h}\mathbf{P}\right] + \frac{1}{2}\mathrm{Tr}\left[\mathbf{J}\mathbf{P}\right], \qquad \text{(G.105)}
\end{aligned}
$$

where in the last passage the notation:

$$
J^{\mathbf{n}}_{\mu\nu} = \sum_{\mathbf{g},\mathbf{h}}\sum_{\rho\sigma} P^{\mathbf{g}}_{\mu\nu}G^{\mathbf{0},\mathbf{g},\mathbf{h},\mathbf{n}}_{\mu\nu\rho\sigma} \qquad \text{(G.106)}
$$

has been introduced. We then write the density-matrix at the current iteration as a linear-combination of those from the previous cycles:

$$
\tilde{\mathbf{P}}^{\mathbf{g}} = \sum_{i=0}^{k} c_i\mathbf{P}^{\mathbf{g}}_i, \quad \sum_{i=0}^{k} c_i = 1, \quad c_i \geq 0, \qquad \text{(G.107)}
$$

where the constraints on the c_i guarantees to stay in the convex-set of density-matrices permissible by the RCA algorithm. Substituting Eq. (G.107) in Eq. (G.105), we find:

$$
E = \sum_{i=0}^{k} c_i\,\mathrm{Tr}\left[\mathbf{h}\mathbf{P}_i\right] + \frac{1}{2}\sum_{i,j=0}^{k} c_ic_j\,\mathrm{Tr}\left[\mathbf{J}_i\mathbf{P}_j\right] \qquad \text{(G.108)}
$$

Developping the bielectronic term:

$$\begin{aligned}
E &= \sum_{i=0}^{k} c_i \operatorname{Tr}\left[\mathbf{h}\mathbf{P}_i\right] + \frac{1}{2}\sum_{i,j=0}^{k} c_i c_j \operatorname{Tr}\left[\mathbf{J}_i \mathbf{P}_j\right] \\
&= \sum_{i=0}^{k} c_i \operatorname{Tr}\left[\mathbf{h}\mathbf{P}_i\right] + \frac{1}{4}\sum_{i,j=0}^{k} c_i c_j \operatorname{Tr}\left[\left(\mathbf{J}_i \mathbf{P}_j\right) + \left(\mathbf{J}_j \mathbf{P}_i\right)\right] \\
&= \sum_{i=0}^{k} c_i \operatorname{Tr}\left[\mathbf{h}\mathbf{P}_i\right] + \frac{1}{2}\sum_{i=0}^{k} c_i \operatorname{Tr}\left[\left(\mathbf{J}_i \mathbf{P}_i\right)\right] - \frac{1}{4}\sum_{i,j=0}^{k} c_i c_j \operatorname{Tr}\left[\left(\mathbf{J}_i - \mathbf{J}_j\right)\left(\mathbf{P}_i - \mathbf{P}_j\right)\right] \\
&= \sum_{i=0}^{k} c_i E_i - \frac{1}{4}\sum_{i,j=0}^{k} c_i c_j \operatorname{Tr}\left[\left(\mathbf{J}_i - \mathbf{J}_j\right)\left(\mathbf{P}_i - \mathbf{P}_j\right)\right] \\
&= \sum_{i=0}^{k} c_i E_i - \frac{1}{4}\sum_{i,j=0}^{k} c_i c_j \operatorname{Tr}\left[\left(\mathbf{F}_i - \mathbf{F}_j\right)\left(\mathbf{P}_i - \mathbf{P}_j\right)\right] \qquad \text{(G.109)}
\end{aligned}$$

For numerical reasons, it is beneficial to scale the first term on the same order as the second term in Eq. (G.109), by exploiting the property $\sum_{i=0}^{k} c_i = 1$, as follows:

$$E = E_0 + \sum_{i=0}^{k} c_i \left(E_i - E_0\right) - \frac{1}{4}\sum_{i,j=0}^{k} c_i c_j \operatorname{Tr}\left[\left(\mathbf{F}_i - \mathbf{F}_j\right)\left(\mathbf{P}_i - \mathbf{P}_j\right)\right] \qquad \text{(G.110)}$$

The EDIIS problem can then be stated as follows:

$$\begin{aligned}
\text{min} :: \quad & f_{EDIIS} = E_0 + \sum_{i=0}^{k} c_i \left(E_i - E_0\right) - \frac{1}{4}\sum_{i,j=0}^{k} c_i c_j \operatorname{Tr}\left[\left(\mathbf{F}_i - \mathbf{F}_j\right)\left(\mathbf{P}_i - \mathbf{P}_j\right)\right] \\
\text{s.t.} :: \quad & \sum_{i=0}^{k} c_i = 1, \quad c_i \geq 0 \qquad \text{(G.111)}
\end{aligned}$$

The above problem has the general form of an indefinite quadratic programming problem, which we solve using Yinyu Ye's SOLQP code, that I was able to translate to FORTRAN. Once the optimal set of c_i are obtained, they are used to form the Fock matrix at the current iteration:

$$\tilde{\mathbf{F}}^{\mathbf{g}} = \sum_{i=0}^{k} c_i \mathbf{F}_i^{\mathbf{g}} \qquad \text{(G.112)}$$

The EDIIS algorithm therefore proceeds as follows:

1. Obtain $\mathbf{P}_0$ from a guess
2. Construct $\mathbf{F}_0$
3. Calculate Calculate Energy $E_0 = \frac{1}{2}\text{Tr}(\mathbf{h}\mathbf{P}_0) + \frac{1}{2}\text{Tr}(\mathbf{F}_0\mathbf{P}_0)$

4. Write $\mathbf{F}_0$, $\mathbf{P}_0$ and E_0 to disk
5. Set $\tilde{\mathbf{F}}_0 = \mathbf{F}_0$ and $\tilde{\mathbf{P}}_0 = \mathbf{P}_0$
6. Diagonalize $\tilde{\mathbf{F}}_0$
7. Construct $\mathbf{P}_1$ by aufbau
8. Set $k = 1$
9. Begin iteration on k:
    - (a) Construct $\mathbf{F}_k = \mathbf{F}(\mathbf{P}_k)$
    - (b) Calculate Energy $E_k = \frac{1}{2}\mathrm{Tr}(\mathbf{h}\mathbf{P}_k) + \frac{1}{2}\mathrm{Tr}(\mathbf{F}_k\mathbf{P}_k)$
    - (c) Write $\mathbf{F}_k$, $\mathbf{P}_k$ and E_k to disk
    - (d) Read $\mathbf{P}_{k-1}, \mathbf{P}_{k-2}, ..., \mathbf{P}_0$, $\mathbf{F}_{k-1}, \mathbf{F}_{k-2}, ..., \mathbf{F}_0$ and $E_{k-1}, E_{k-2}, ..., E_0$ from disk
    - (e) Calculate the optimal set of c_i by minimizing f_{EDIIS} through solving the quadratic programming problem described by Eq. (G.111)
    - (f) Calculate $\tilde{\mathbf{F}}_k = \sum_{i=0}^{k} c_i \mathbf{F}_i$
    - (g) Diagonalize $\tilde{\mathbf{F}}_k$
    - (h) Construct $\mathbf{P}_{k+1}$ from aufbau
    - (i) Check for convergence
    - (j) If not converged, set $k = k + 1$ and return to a.

H Perturbative Treatment of Spin-Orbit Coupling

H.1 Non-Degenerate Rayleigh-Schrödinger Perturbation Theory

We write the fully relativistic (FR) Hamiltonian $\hat{H}$ as a sum of a scalar-relativistic (SR) part $\hat{H}^{(0)}$ and a spin-orbit coupling (SOC) part $\hat{h}_{SO}$:

$$\hat{H} = \hat{H}^{(0)} + \hat{h}_{SO} \tag{H.1}$$

We assume that the SR problem has already been solved, so that all eigenstates $|\psi_i^{(0)}\rangle$ of the SR Hamiltonian (as well as their energies $E_i^{(0)}$) are known:

$$\hat{H}^{(0)}|\psi_i^{(0)}\rangle = E_i^{(0)}|\psi_i^{(0)}\rangle \tag{H.2a}$$

We also suppose that the calculated SR states have been orthonormalized:

$$\langle\psi_j^{(0)}|\psi_i^{(0)}\rangle = \delta_{ij} \tag{H.2b}$$

This does not represent a loss of generality, since the $|\psi_i^{(0)}\rangle$ are necessarily orthonormalized if they yield different E_i, while degenerate states can always be orthonormalized. We then use the $|\psi_i^{(0)}\rangle$ as a starting point to find the exact states $|\Psi_i\rangle$ of the FR Hamiltonian:

$$\hat{H}|\Psi_i\rangle = E_i|\Psi_i\rangle \tag{H.3}$$

Instead of solving directly Eq. (H.3), the $|\Psi_i\rangle$ and E_i are determined by expanding them in orders of the perturbation $\hat{h}_{SO}$, choosing $|\psi_i^{(0)}\rangle$ and $E_i^{(0)}$ as the corresponding zeroth-order approximations:

$$|\Psi_i\rangle = \sum_{k=0}^{\infty} \lambda^k |\psi_i^{(k)}\rangle \tag{H.4a}$$

$$E_i = \sum_{k=0}^{\infty} \lambda^k E_i^{(k)} \tag{H.4b}$$

$$\hat{H} = \sum_{k=0}^{\infty} \lambda^k H^{(k)} \tag{H.4c}$$

where λ is a sufficiently small dimensionless perturbation parameter and the hat has been dropped from the $H^{(k)}$. The $\psi_i^{(0)}$ and $E_i^{(0)}$ are of course already known from Eq. (H.2) and the higher-order terms are determined by substituting Eqs. (H.4a-H.4c) into Eq. (H.3):

$$\left(\sum_{k=0}^{\infty} \lambda^k H^{(k)}\right) \sum_{k=0}^{\infty} \lambda^k |\psi_i^{(k)}\rangle = \left(\sum_{k=0}^{\infty} \lambda^k E_i^{(k)}\right) \sum_{k=0}^{\infty} \lambda^k |\psi_i^{(k)}\rangle \tag{H.5}$$

Collecting terms with like powers of λ, we have:

$$\begin{aligned}
0 &= \lambda^0 \left\{H^{(0)}|\psi_i^{(0)}\rangle - E_i^{(0)}|\psi_i^{(0)}\rangle\right\} \\
&+ \lambda^1 \left\{H^{(1)}|\psi_i^{(0)}\rangle - E_i^{(0)}|\psi_i^{(1)}\rangle + H^{(0)}|\psi_i^{(1)}\rangle - E_i^{(1)}|\psi_i^{(0)}\rangle\right\} \\
&+ \lambda^2 \left\{H^{(0)}|\psi_i^{(2)}\rangle + H^{(1)}|\psi_i^{(1)}\rangle + H^{(2)}|\psi_i^{(0)}\rangle - E_i^{(0)}|\psi_i^{(2)}\rangle - E_i^{(1)}|\psi_i^{(1)}\rangle - E_i^{(2)}|\psi_i^{(0)}\rangle\right\} \\
&+ \lambda^3 \Big\{H^{(0)}|\psi_i^{(3)}\rangle + H^{(1)}|\psi_i^{(2)}\rangle + H^{(2)}|\psi_i^{(1)}\rangle + H^{(3)}|\psi_i^{(0)}\rangle - E_i^{(0)}|\psi_i^{(3)}\rangle - E_i^{(1)}|\psi_i^{(2)}\rangle \\
&- E_i^{(2)}|\psi_i^{(1)}\rangle - E_i^{(3)}|\psi_i^{(0)}\rangle\Big\} + \ldots\ldots
\end{aligned} \tag{H.6}$$

and since λ is arbitrary, every term in the curly brackets must equal zero, so we end up with the following set of equations:

$$\begin{aligned}
\left(H^{(0)} - E_i^{(0)}\right)|\psi_i^{(0)}\rangle &= 0 \\
\left(H^{(0)} - E_i^{(0)}\right)|\psi_i^{(1)}\rangle &= -\left(H^{(1)} - E_i^{(1)}\right)|\psi_i^{(0)}\rangle \\
\left(H^{(0)} - E_i^{(0)}\right)|\psi_i^{(2)}\rangle &= -\left(H^{(2)} - E_i^{(2)}\right)|\psi_i^{(0)}\rangle - \left(H^{(1)} - E_i^{(1)}\right)|\psi_i^{(1)}\rangle \\
\left(H^{(0)} - E_i^{(0)}\right)|\psi_i^{(3)}\rangle &= -\left(H^{(3)} - E_i^{(3)}\right)|\psi_i^{(0)}\rangle - \left(H^{(2)} - E_i^{(2)}\right)|\psi_i^{(1)}\rangle - \left(H^{(1)} - E_i^{(1)}\right)|\psi_i^{(2)}\rangle \\
&\cdots \\
&\cdots \\
\left(H^{(0)} - E_i^{(0)}\right)|\psi_i^{(n)}\rangle &= -\sum_{k=1}^{n}\left(H^{(k)} - E_i^{(k)}\right)|\psi_i^{(n-k)}\rangle
\end{aligned} \tag{H.7}$$

Eq. (H.7) permits to express the perturbed states $|\psi_i^{(n)}\rangle$ and energies $E_i^{(n)}$ at order n in terms of all the lower-order quantities. We note that Eq. (H.7) does not however determine the component of $|\psi_i^{(0)}\rangle$ in $|\psi_i^{(n)}\rangle$, because for any real number a:

$$\left(H^{(0)} - E_i^{(0)}\right)\left(|\psi_i^{(n)}\rangle + a|\psi_i^{(0)}\rangle\right) = \left(H^{(0)} - E_i^{(0)}\right)|\psi_i^{(n)}\rangle \tag{H.8}$$

This means that there is an ambiguity in the determination of $|\psi_i^{(n)}\rangle$ from Eq. (H.7). The ambiguity is resolved by enforcing the following orthonormality conditions with respect to the zeroth-order states:

$$\langle\psi_i^{(0)}|\psi_i^{(k)}\rangle = \delta_{k0} \tag{H.9}$$

Substituting Eq. (H.9) in (H.7), we find:

$$E_i^{(n)} = \sum_{k=1}^{n}\langle\psi_i^{(0)}|H^{(k)}|\psi_i^{(n-k)}\rangle \tag{H.10}$$

Eq. (H.10) gives us a means to find the perturbed energy to arbitrary order through the perturbed states $|\psi_i^{(k)}\rangle$. To find also an expression for the perturbed states, we first expand the $|\psi_i^{(k)}\rangle$ in a basis consisting of the states

$|\psi_m^{(0)}\rangle$ of the SR Hamiltonian:

$$|\psi_i^{(k)}\rangle = \sum_m{}' c_{mi}^{(k)} |\psi_m^{(0)}\rangle \tag{H.11}$$

where the prime over the m summation indicates that it extends over all values of m which satisfy $E_m^{(0)} \neq E_i^{(0)}$ for $m \neq i$. The exclusion of the terms $E_m^{(0)} = E_i^{(0)}$ represents an approximation in the expansion of the $|\psi_i^{(k)}\rangle$. These terms are dealt with using degenerate perturbation theory.

Bracketing both sides of Eq. (H.11) by $\langle\psi_j^{(0)}|$ and taking into account Eq. (H.2b), we find:

$$c_{mi}^{(k)} = \langle\psi_m^{(0)}|\psi_i^{(k)}\rangle \tag{H.12}$$

Then bracketing Eq. (H.7) by $\langle\psi_j^{(0)}|$ and substituting in Eq. (H.12), we have:

$$c_{ji}^{(n)} = \frac{1}{E_i^{(0)} - E_j^{(0)}} \langle\psi_j^{(0)}| \sum_{k=1}^{n} \left(H^{(k)} - E_i^{(k)}\right) |\psi_i^{(n-k)}\rangle \tag{H.13}$$

Substituting Eq. (H.13) in Eq. (H.11)

$$|\psi_i^{(n)}\rangle = \sum_j{}' \left(\frac{\sum_{k=1}^{n} \langle\psi_j^{(0)}| \left(H^{(k)} - E_i^{(k)}\right) |\psi_i^{(n-k)}\rangle}{E_i^{(0)} - E_j^{(0)}} \right) |\psi_j^{(0)}\rangle \tag{H.14}$$

which provides a recurrence relation for finding the higher-order perturbed states from the lower order ones.

H.1.1 Example for Low Order

In the following, we provide expressions for the $|\psi_i^{(k)}\rangle$ and $E_i^{(k)}$ for low values of k. Since the perturbation parameter λ is arbitrary, we choose $\lambda = 1$, then from equations (H.4a-H.4c):

$$|\Psi_i\rangle = |\psi_i^{(0)}\rangle + |\psi_i^{(1)}\rangle + |\psi_i^{(2)}\rangle + ... \tag{H.15a}$$

$$E_i = E_i^{(0)} + E_i^{(1)} + E_i^{(2)} + ... \tag{H.15b}$$

$$\hat{H} = H^{(0)} + H^{(1)} + H^{(2)} + ... \equiv H^{(0)} + \hat{h}_{SO} \tag{H.15c}$$

For the Hamiltonian, we limit our approximation to first order in the perturbation, so that:

$$\hat{h}_{SO} \approx H^{(1)} \tag{H.16}$$

Later we will provide insight into the meaning of the approximation introduced by Eq. (H.16) for practical calculations. Application of Eq. (H.14) for $n = 1$ gives:

$$\begin{aligned} |\psi_i^{(1)}\rangle &= \sum_j{}' \left(\frac{\langle\psi_j^{(0)}|H^{(1)}|\psi_i^{(0)}\rangle}{E_i^{(0)} - E_j^{(0)}} \right) |\psi_j^{(0)}\rangle \\ &\approx \sum_j{}' \left(\frac{\langle\psi_j^{(0)}|\hat{h}_{SO}|\psi_i^{(0)}\rangle}{E_i^{(0)} - E_j^{(0)}} \right) |\psi_j^{(0)}\rangle \end{aligned} \tag{H.17}$$

For the energy, from Eq. (H.10), again for $n = 1$:

$$E_i^{(1)} = \langle\psi_i^{(0)}|H^{(1)}|\psi_i^{(0)}\rangle \approx \langle\psi_i^{(0)}|\hat{h}_{SO}|\psi_i^{(0)}\rangle \tag{H.18}$$

Now for $n = 2$, Substituting Eqs. (H.17) and (H.18) in Eq. (H.10):

$$E_i^{(2)} = \langle\psi_i^{(0)}|H^{(1)}|\psi_i^{(1)}\rangle + \langle\psi_i^{(0)}|H^{(2)}|\psi_i^{(0)}\rangle \tag{H.19a}$$

$$E_i^{(2)} = \langle\psi_i^{(0)}|H^{(2)}|\psi_i^{(0)}\rangle + \sum_j{}' \frac{\langle\psi_i^{(0)}|H^{(1)}|\psi_j^{(0)}\rangle\langle\psi_j^{(0)}|H^{(1)}|\psi_i^{(0)}\rangle}{E_i^{(0)} - E_j^{(0)}} \tag{H.19b}$$

$$E_i^{(2)} \approx \sum_j{}' \frac{\langle\psi_i^{(0)}|\hat{h}_{SO}|\psi_j^{(0)}\rangle\langle\psi_j^{(0)}|\hat{h}_{SO}|\psi_i^{(0)}\rangle}{E_i^{(0)} - E_j^{(0)}} \tag{H.19c}$$

So that finally, substituting Eqs. (H.18) and (H.19c) in Eq. (H.15b), the approximation for the energies of the FR problem are written as:

$$E_i \approx E_i^{(0)} + \langle\psi_i^{(0)}|\hat{h}_{SO}|\psi_i^{(0)}\rangle + \sum_j{}' \frac{\langle\psi_i^{(0)}|\hat{h}_{SO}|\psi_j^{(0)}\rangle\langle\psi_j^{(0)}|\hat{h}_{SO}|\psi_i^{(0)}\rangle}{E_i^{(0)} - E_j^{(0)}} \tag{H.20}$$

Proceeding similarly for $E_i^{(3)}$, we find:

$$\begin{aligned} E_i^{(3)} &\approx \sum_{jk}{}' \frac{\langle\psi_i^{(0)}|\hat{h}_{SO}|\psi_j^{(0)}\rangle\langle\psi_j^{(0)}|\hat{h}_{SO}|\psi_k^{(0)}\rangle\langle\psi_k^{(0)}|\hat{h}_{SO}|\psi_i^{(0)}\rangle}{\left(E_i^{(0)} - E_j^{(0)}\right)\left(E_i^{(0)} - E_k^{(0)}\right)} \\ &- E_i^{(1)} \sum_j{}' \frac{\langle\psi_i^{(0)}|\hat{h}_{SO}|\psi_j^{(0)}\rangle\langle\psi_j^{(0)}|\hat{h}_{SO}|\psi_i^{(0)}\rangle}{\left(E_i^{(0)} - E_j^{(0)}\right)^2} \end{aligned} \tag{H.21}$$

and for $E_i^{(4)}$:

$$\begin{aligned}
E_i^{(4)} \approx \; & \sum_{jkl}{}' \frac{\langle\psi_i^{(0)}|\hat{h}_{SO}|\psi_j^{(0)}\rangle\langle\psi_j^{(0)}|\hat{h}_{SO}|\psi_k^{(0)}\rangle\langle\psi_k^{(0)}|\hat{h}_{SO}|\psi_l^{(0)}\rangle\langle\psi_l^{(0)}|\hat{h}_{SO}|\psi_i^{(0)}\rangle}{\left(E_i^{(0)} - E_j^{(0)}\right)\left(E_i^{(0)} - E_k^{(0)}\right)\left(E_i^{(0)} - E_l^{(0)}\right)} \\
- \; & E_i^{(1)} \sum_{jk}{}' \frac{\langle\psi_i^{(0)}|\hat{h}_{SO}|\psi_j^{(0)}\rangle\langle\psi_j^{(0)}|\hat{h}_{SO}|\psi_k^{(0)}\rangle\langle\psi_k^{(0)}|\hat{h}_{SO}|\psi_i^{(0)}\rangle}{\left(E_i^{(0)} - E_j^{(0)}\right)\left(E_i^{(0)} - E_k^{(0)}\right)^2} \\
- \; & E_i^{(1)} \sum_{jk}{}' \frac{\langle\psi_i^{(0)}|\hat{h}_{SO}|\psi_j^{(0)}\rangle\langle\psi_j^{(0)}|\hat{h}_{SO}|\psi_k^{(0)}\rangle\langle\psi_k^{(0)}|\hat{h}_{SO}|\psi_i^{(0)}\rangle}{\left(E_i^{(0)} - E_j^{(0)}\right)^2\left(E_i^{(0)} - E_k^{(0)}\right)} \\
+ \; & \left(E_i^{(1)}\right)^2 \sum_{j}{}' \frac{\langle\psi_i^{(0)}|\hat{h}_{SO}|\psi_j^{(0)}\rangle\langle\psi_j^{(0)}|\hat{h}_{SO}|\psi_i^{(0)}\rangle}{\left(E_i^{(0)} - E_j^{(0)}\right)^3} \\
- \; & E_i^{(2)} \sum_{j}{}' \frac{\langle\psi_i^{(0)}|\hat{h}_{SO}|\psi_j^{(0)}\rangle\langle\psi_j^{(0)}|\hat{h}_{SO}|\psi_i^{(0)}\rangle}{\left(E_i^{(0)} - E_j^{(0)}\right)^2}
\end{aligned} \tag{H.22}$$

H.2 Degenerate Rayleigh-Schrödinger Perturbation Theory

The previous section considered the perturbative expansion of quantities depending on $\hat{h}_{SO}$ in terms of states from the SR problem $|\psi_i^{(0)}\rangle$ and $|\psi_j^{(0)}\rangle$, where $E_i^{(0)} \neq E_j^{(0)}$. Here we discuss how to also include contributions from degenerate states $|\psi_i^{(0)}\rangle$ and $|\psi_j^{(0)}\rangle$,where now $E_i^{(0)} = E_j^{(0)}$. We assume that there are $u = 1, 2, ..., n_i$ states from the SR problem $|\psi_{iu}^{(0)}\rangle$, each of which have the same energy $E_i^{(0)}$, that is to say there are n_i equations for which:

$$H^{(0)}|\psi_{iu}^{(0)}\rangle = E_i^{(0)}|\psi_{iu}^{(0)}\rangle \tag{H.23}$$

We assume that it is possible to define suitably symmetrized states $|\varphi_{it}^{(0)}\rangle$ for $t = 1, 2, ..., n_i$ as linear combinations of the n_i degenerate states $|\psi_{iu}^{(0)}\rangle$ as an initial guess for the purposes of solving the FR problem:

$$|\varphi_{it}^{(0)}\rangle = \sum_{u=1}^{n_i} c_{ut}|\psi_{iu}^{(0)}\rangle \tag{H.24}$$

As in Eqs. (H.4a-H.4c) we write:

$$|\Psi_{it}\rangle = |\varphi_{it}^{(0)}\rangle + \lambda|\varphi_{it}^{(1)}\rangle + \lambda^2|\varphi_{it}^{(2)}\rangle + ... \tag{H.25a}$$

$$\hat{H} = H^{(0)} + \lambda H^{(1)} + \lambda^2 H^{(2)} + ... \tag{H.25b}$$

$$E_{it} = E_i^{(0)} + \lambda E_{it}^{(1)} + \lambda^2 E_{it}^{(2)} + ... \tag{H.25c}$$

where the following convention has been used for all perturbative orders $m > 0$:

$$|\varphi_{it}^{(m)}\rangle = |\psi_{it}^{(m)}\rangle \tag{H.26}$$

The index t has been included in the $E_{it}^{(m)}$ for $m > 0$ because the perturbation may or may not break the degeneracies.

Then following Eqs. (H.5)-(H.7) we insert Eq. (H.25) into Eq. (H.3) and obtain the following set of equations:

$$\left(H^{(0)} - E_i^{(0)}\right)|\varphi_{it}^{(n)}\rangle = -\sum_{k=1}^{n}\left(H^{(k)} - E_{it}^{(k)}\right)|\varphi_{it}^{(n-k)}\rangle \tag{H.27}$$

Inspired by Eq. (H.11), we expand the perturbed states $|\varphi_{it}^{(k)}\rangle$ now in terms of all states of the SR problem (whether degenerate or non-degenerate):

$$|\varphi_{it}^{(k)}\rangle = \sum_{j}\sum_{u=1}^{n_i} c_{ju,it}^{(k)}|\psi_{ju}^{(0)}\rangle \tag{H.28}$$

Comparing Eq. (H.24) to (H.28), we find:

$$c_{ju,it}^{(0)} = c_{ut}\delta_{ji} \tag{H.29}$$

Substituting Eq. (H.28) into Eq. (H.27):

$$\begin{aligned}\sum_{j}\sum_{u=1}^{n_i} c_{ju,it}^{(n)}\left(E_j^{(0)} - E_i^{(0)}\right)|\psi_{ju}^{(0)}\rangle = \\ -\sum_{k=1}^{n}\sum_{j}\sum_{u=1}^{n_i} c_{ju,it}^{(n-k)}\left(H^{(k)} - E_{it}^{(k)}\right)|\psi_{ju}^{(0)}\rangle\end{aligned} \tag{H.30}$$

Left multypling both sides of Eq. (H.30) by $\langle\psi_{ip}^{(0)}|$:

$$\begin{aligned}\sum_{j}\sum_{u=1}^{n_i} c_{ju,it}^{(n)}\left(E_j^{(0)} - E_i^{(0)}\right)\langle\psi_{ip}^{(0)}|\psi_{ju}^{(0)}\rangle = \\ -\sum_{k=1}^{n}\sum_{j}\sum_{u=1}^{n_i} c_{ju,it}^{(n-k)}\left(\langle\psi_{ip}^{(0)}|H^{(k)}|\psi_{ju}^{(0)}\rangle - E_{it}^{(k)}\langle\psi_{ip}^{(0)}|\psi_{ju}^{(0)}\rangle\right)\end{aligned} \tag{H.31}$$

Defining the overlap $\mathbb{S}_{ip,ju}$ and Hamiltonian $\mathbb{H}_{ip,ju}^{(k)}$ matrix-element notation:

$$\mathbb{S}_{ip,ju} = \langle\psi_{ip}^{(0)}|\psi_{ju}^{(0)}\rangle \tag{H.32a}$$

and:

$$\mathbb{H}_{ip,ju}^{(k)} = \langle\psi_{ip}^{(0)}|H^{(k)}|\psi_{ju}^{(0)}\rangle \tag{H.32b}$$

We obtain:

$$\sum_{j}\sum_{u=1}^{n_i} c_{ju,it}^{(n)} \left(E_j^{(0)} - E_i^{(0)}\right) \mathbb{S}_{ip,ju} =$$
$$-\sum_{k=1}^{n}\sum_{j}\sum_{u=1}^{n_i} c_{ju,it}^{(n-k)} \left(\mathbb{H}_{ip,ju}^{(k)} - E_{it}^{(k)} \mathbb{S}_{ip,ju}\right) \tag{H.33}$$

We note, from Eq. (H.2b) that the matrix elements $\mathbb{S}_{ip,ju}$ are reduced to:

$$\mathbb{S}_{ip,ju} = \delta_{ij} \tag{H.34}$$

Substituting Eq. (H.34) in Eq. (H.33):

$$\sum_{k=1}^{n}\sum_{j}\sum_{u=1}^{n_i} c_{iu,it}^{(n-k)} \left(\mathbb{H}_{ip,iu}^{(k)} - E_{it}^{(k)}\right) = 0 \tag{H.35}$$

H.2.1 Example for Low Order

Similarly to section H.1.1 we here apply the general Eq. (H.35) here for $n = 1$ and approximate the perturbation from Eq. (H.16). That is to say, we set:

$$\mathbb{H}_{ip,ju}^{(1)} \approx \langle \psi_{ip}^{(0)} | h_{SO} | \psi_{ju}^{(0)} \rangle \equiv \mathbb{B}_{ip,ju} \tag{H.36}$$

Substituting Eq. (H.36) in Eq. (H.35) for $n = 1$:

$$\sum_{j}\sum_{u=1}^{n_i} \left(\mathbb{B}_{ip,iu} - E_{it}^{(1)}\right) c_{iu,it}^{(0)} = 0 \tag{H.37}$$

Substituting Eq. (H.29) in Eq. (H.37):

$$\sum_{u=1}^{n_i} \left(\mathbb{B}_{ip,iu} - E_{it}^{(1)}\right) c_{ut} = 0 \tag{H.38}$$

Eq. (H.38) represents an eigenvalue problem (with eigenvectors $\boldsymbol{c}_t$ and eigenvalues $E_{it}^{(1)}$). The $E_{it}^{(1)}$ can be obtained by solving the following secular equation:

$$\det\left|\mathbb{B} - \mathbb{I}E^{(1)}\right| = 0 \tag{H.39}$$

where $\mathbb{B}$ is the matrix of the $\mathbb{B}_{ip,iu}$, $E^{(1)}$ is the vector of the $E_i^{(1)}$ and $\mathbb{I}$ is the identity matrix. Once the $E_{it}^{(1)}$ have been obtained, the eigenvectors $\boldsymbol{c}_t$ can be found by solving Eq. (H.38).

H.2.2 How to get the Correction to the Wavefunction from Lifted Degeneracies by Combining the Degenerate and Non-Degenerate Theories

We assume that we have solved Eq. (H.38) for the $E_{it}^{(1)}$ and c_{ut}, for u and $t = 1, 2, ..., n_i$ and the degeneracies between the n_i states are lifted. We can construct the functions $|\varphi_{it}^{(0)}\rangle$ using the c_{ut} from Eq. (H.24).

In order to get the first-order correction to the wavefunction, we re-define the zeroth order approximation of the non-degenerate perturbation problem, no longer as the quantities obtained from the SR problem, but now as the quantities obtained from Eq. (H.38). That is to say, we set:

$$E_i^{(0)} + E_{it}^{(1)} \rightarrow \mathcal{E}_{i+t-1}^{(0)} \tag{H.40}$$

and:

$$|\varphi_{it}^{(0)}\rangle \rightarrow |\varphi_{i+t-1}^{(0)}\rangle \tag{H.41}$$

where the re-indexing has been achieved to reflect the fact that the n_i states are no longer degenerate. We then expand the FR energies E_g and wavefunction $|\Psi_g\rangle$ starting from the $\mathcal{E}_g^{(0)}$ and $|\varphi_g^{(0)}\rangle$, where $g \in G = \{i, i+1, ..., i+n_i-1\}$. Hence:

$$E_g = \mathcal{E}_g^{(0)} + \lambda\mathcal{E}_g^{(1)} + \lambda^2\mathcal{E}_g^{(2)} + ... \tag{H.42}$$

and for the wavefunction:

$$|\Psi_g\rangle = |\varphi_g^{(0)}\rangle + \lambda|\varphi_g^{(1)}\rangle + \lambda^2|\varphi_g^{(2)}\rangle + ... \tag{H.43}$$

or, according to Eq. (H.26):

$$|\Psi_g\rangle = |\varphi_g^{(0)}\rangle + \lambda|\psi_g^{(1)}\rangle + \lambda^2|\psi_g^{(2)}\rangle + ... \tag{H.44}$$

Then, proceeding as in section H.1 we obtain a similar expression to Eq. (H.17):

$$|\psi_g^{(1)}\rangle \approx \sum_j^{\notin G} \left(\frac{\langle\psi_j^{(0)}|\hat{h}_{SO}|\varphi_g^{(0)}\rangle}{\mathcal{E}_g^{(0)} - E_j^{(0)}} \right) |\psi_j^{(0)}\rangle \tag{H.45}$$

H.3 Application of Canonical Non-Degenerate Perturbation Theory to a Scalar-Relativistic Self-Consistent Reference

H.3.1 Energy

We apply the formulas from section H.1.1 to the calculation of the FR energy, starting from reference wavefunctions $|\psi_i^{(0)}\rangle$ obtained from a self-consistent SR calculation (either from Hartree-Fock, HF, or Kohn-Sham density-functional theory, KS-DFT). We are interested in the ground-state wavefunction $|\psi\rangle$ and the subscript i and superscript (0) are dropped. In the case of HF, the reference wavefunctions are anti-symmetrized (i.e. antti-symmetrized for finnish readers!) products of one-electron functions (Slater determinants). In the case of KS-DFT, we choose a fictitious reference non-interacting fermionic system (which can also be represented by a Slater determinant wavefunction) which gives the same density as the actual (interacting) system at every point in space. So in both the HF and KS-DFT cases, we have for a system with d electrons:

$$|\psi\rangle = |\phi_1\rangle \otimes |\phi_2\rangle \otimes \ ... \ \otimes |\phi_d\rangle \tag{H.46a}$$

$$\begin{aligned} \langle \mathbf{x}_1, \mathbf{x}_2, ..., \mathbf{x}_d | \psi \rangle \ &\equiv \ \psi\,(\mathbf{x}_1, \mathbf{x}_2, ..., \mathbf{x}_d) = \mathcal{A}\,(\ \langle \mathbf{x}_1|\phi_1\rangle \times \langle \mathbf{x}_2|\phi_2\rangle \times \ ... \ \times \langle \mathbf{x}_d|\phi_d\rangle \ ) \\ &= \ \frac{1}{\sqrt{d!}} \begin{vmatrix} \phi_1(\mathbf{x}_1) & \phi_2(\mathbf{x}_1) & \dots & \phi_d(\mathbf{x}_1) \\ \phi_1(\mathbf{x}_2) & \phi_2(\mathbf{x}_2) & \dots & \phi_d(\mathbf{x}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_1(\mathbf{x}_d) & \phi_2(\mathbf{x}_d) & \dots & \phi_d(\mathbf{x}_d) \end{vmatrix} \end{aligned} \tag{H.46b}$$

where the ϕ_i are the one-electron functions (the spin-orbitals), $\mathbf{x}_i = [\mathbf{r}_i, \sigma_i]$ are the space-spin coordinates of the electrons and $\mathcal{A}$ is an anti-symmetrizer (whose action creates the determinant expression from the product of one-electron functions). For molecules, the ϕ_i are the molecular orbitals (MOs), which are expanded in a linear combination of atomic-orbitals (AOs). For periodic systems, the ϕ_i are the crystalline orbitals (COs), which are expanded using Bloch functions. The Bloch functions are themselves in turn expanded in a set of AOs.

A Slater determinant which differs from $|\psi\rangle$ by one $|\psi_m^p\rangle$ or two $|\psi_{mn}^{pq}\rangle$ spin-orbitals is denoted as:

$$\begin{aligned} & \psi\,(\mathbf{x}_1, \mathbf{x}_2, ..., \mathbf{x}_d) \\ = \ & \mathcal{A}\,(\ \langle \mathbf{x}_1|\phi_1\rangle \times \langle \mathbf{x}_2|\phi_2\rangle \times \ ... \ \times \langle \mathbf{x}_d|\phi_d\rangle \ ) \end{aligned} \tag{H.47a}$$

$$\begin{aligned} & \psi_m^p\,(\mathbf{x}_1, \mathbf{x}_2, ..., \mathbf{x}_d) \\ = \ & \mathcal{A}\Big(\ \langle \mathbf{x}_1|\phi_1\rangle \times \langle \mathbf{x}_2|\phi_2\rangle \times \ ... \ \times \langle \mathbf{x}_m|\phi_p\rangle \times \ ... \ \times \langle \mathbf{x}_n|\phi_n\rangle \times \ ... \ \times \langle \mathbf{x}_d|\phi_d\rangle \ \Big) \end{aligned} \tag{H.47b}$$

$$\begin{aligned} & \psi_{mn}^{pq}\,(\mathbf{x}_1, \mathbf{x}_2, ..., \mathbf{x}_d) \\ = \ & \mathcal{A}\Big(\ \langle \mathbf{x}_1|\phi_1\rangle \times \langle \mathbf{x}_2|\phi_2\rangle \times \ ... \ \times \langle \mathbf{x}_m|\phi_p\rangle \times \ ... \ \times \langle \mathbf{x}_n|\phi_q\rangle \times \ ... \ \times \langle \mathbf{x}_d|\phi_d\rangle \ \Big) \end{aligned} \tag{H.47c}$$

In the above and throughout the rest of this text, the letters m, n label occupied SR spin-orbitals, p, q label virtual SR spin-orbitals and i, j, k label generic (both occupied or virtual) SR spin-orbitals. The capital letters M, N, P, Q and I, J, K label the corresponding FR spin-orbitals. In an actual HF or KS-DFT calculation, there are d singly occupied MOs and the number of unoccupied ones actually depends on the size of the basis-set expansion. In the following, we adopt the simplified notation $|\phi_i\rangle = |i\rangle$. The variational condition with imposed orthonormality of the $|i\rangle$ leads to the associated Euler-Lagrange equation (which corresponds either to the Roothan-Hall equation for HF or the Kohn-Sham equation for KS-DFT):

$$\hat{F}|i\rangle = \epsilon_i|i\rangle \tag{H.48}$$

where $\hat{F}$ is the SR Fock (or Kohn-Sham Hamiltonian) operator. For the FR problem:

$$\hat{\mathcal{F}}|I\rangle = \epsilon_I|I\rangle \tag{H.49}$$

where $\hat{\mathcal{F}}$ is the FR Fock (or Kohn-Sham Hamiltonian) operator, that is to say $\hat{\mathcal{F}} = \hat{F} + \hat{h}_{SO}$.

To evaluate the required matrix-elements in Eq. (H.20) between Slater determinants, we make use of the Slater-Condon rules. This allows us to express the matrix-elements of a generic many-electron operator in terms of integrals depending on the coordinates of at most two electrons. The two-electron integrals for a generic two-electron operator $\hat{O}(\mathbf{x}_i, \mathbf{x}_j)$ are denoted as:

$$(mp|\hat{O}|nq) \equiv \int d\mathbf{x}_i \int d\mathbf{x}_j\ \phi_m^*(\mathbf{x}_i)\phi_p(\mathbf{x}_i)\ \hat{O}(\mathbf{x}_i, \mathbf{x}_j)\ \phi_n^*(\mathbf{x}_j)\phi_q(\mathbf{x}_j) \tag{H.50}$$

We assume that the perturbation operator $\hat{h}_{SO}$ can be written as a sum of operators which depend individually on the coordinates of one electron $\hat{h}_{SO[1]}$ or two electrons $\hat{h}_{SO[2]}$:

$$\hat{h}_{SO}\,(\mathbf{x}_1, \mathbf{x}_2, ..., \mathbf{x}_d) = \sum_i \hat{h}_{SO[1]}(\mathbf{x}_i) + \frac{1}{2}\sum_i\sum_{j\neq i}\hat{h}_{SO[2]}(\mathbf{x}_i, \mathbf{x}_j) \tag{H.51}$$

The rules for evaluating matrix-elements of such an operator are as follows.

If a matrix-element is calculated between two-determinants that are identical:

$$\langle\psi|\hat{h}_{SO}|\psi\rangle = \sum_m^{\in occ}\langle m|\hat{h}_{SO[1]}|m\rangle + \frac{1}{2}\sum_m^{\in occ}\sum_n^{\in occ}\left[(mm|\hat{h}_{SO[2]}|nn) - (mn|\hat{h}_{SO[2]}|nm)\right] \tag{H.52a}$$

where *occ* indicates the set of occupied states in the SR reference. Similarly, in the following *virt* will label the set of virtual states of the SR reference. For us, the $\hat{h}_{SO}$ is treated using relativistic effective-core potentials. In this case, *occ* and *virt* actually only label the set of occupied and virtual valence states.

If the determinants differ by one spin-orbital:

$$\langle\psi|\hat{h}_{SO}|\psi_m^p\rangle = \langle m|\hat{h}_{SO[1]}|p\rangle + \sum_n^{\in occ}\left[(mp|\hat{h}_{SO[2]}|nn) - (mn|\hat{h}_{SO[2]}|np)\right] \tag{H.52b}$$

If the determinants differ by two spin-orbitals:

$$\langle\psi|\hat{h}_{SO}|\psi_{mn}^{pq}\rangle = (mp|\hat{h}_{SO[2]}|nq) - (mq|\hat{h}_{SO[2]}|np) \tag{H.52c}$$

Finally, if the determinants differ by more than two spin-orbitals:

$$\langle\psi|\hat{h}_{SO}|\psi^{pqr...}_{mno...}\rangle = 0 \tag{H.52d}$$

The perturbation operator $\hat{h}_{SO}$ corresponds to the difference between the SR Hamiltonian and the FR Hamiltonian:

$$\hat{h}_{SO} = \hat{\mathcal{F}} - \hat{F} \tag{H.53}$$

We represent the mono-electronic part of $\hat{h}_{SO}$ using relativistic effective core-potentials.

$$\hat{h}_{SO} = \hat{h}_{SO[1]} \tag{H.54}$$

and:

$$\hat{h}_{SO[2]} = 0 \tag{H.55}$$

Substituting Eqs. (H.54) and (H.55) in Eq.(H.52), we find the following expressions. For two determinants that are identical:

$$\langle\psi|\hat{h}_{SO}|\psi\rangle = \sum_{m}^{\in occ}\langle m|\hat{h}_{SO}|m\rangle \tag{H.56a}$$

For determinants differing by one spin-orbital:

$$\langle\psi|\hat{h}_{SO}|\psi^{p}_{m}\rangle = \langle m|\hat{h}_{SO}|p\rangle \tag{H.56b}$$

For determinants differing by two or more spin-orbitals:

$$\langle\psi|\hat{h}_{SO}|\psi^{pq...}_{mn...}\rangle = 0 \tag{H.56c}$$

Substituting Eq. (H.56) in Eq. (H.20):

$$E \approx E^{(0)} + \sum_{m}^{\in occ}\langle m|\hat{h}_{SO}|m\rangle + \sum_{m}^{\in occ}\sum_{p}^{\in virt}\frac{\langle m|\hat{h}_{SO}|p\rangle\langle p|\hat{h}_{SO}|m\rangle}{\epsilon_m - \epsilon_p} \tag{H.57}$$

The second term on the r.h.s. of Eq. (H.57) comes directly by applying Eq. (H.56a) to the Slater determinant containing only the occupied states. The numerator of the third term in Eq. (H.58) comes from Eq. (H.56b), by considering all possible mono-excitations from the ground-state, which substitute all virtuals for each occupied state in the matrix-elements. The denominator of the third term in Eq. (H.57) follows directly from Eq. (H.48).

We note that for the specific case of the $\hat{h}_{SO}$ since for two functions of like spin it is a purely imaginary and Hermitian operator, the diagonal elements go to zero and we obtain:

$$E \approx E^{(0)} + \sum_{m}^{\in occ}\sum_{p}^{\in virt}\frac{\langle m|\hat{h}_{SO}|p\rangle\langle p|\hat{h}_{SO}|m\rangle}{\epsilon_m - \epsilon_p} \tag{H.58}$$

Proceeding similarly for $E^{(3)}$ from Eq. (H.21), we write the expression in terms of all singly-excited determinants with non-vanishing contributions:

$$\begin{aligned} E^{(3)} &\approx \sum_{m}^{\in occ} \sum_{pq}^{\in virt} \frac{\langle\psi|\hat{h}_{SO}|\psi_m^p\rangle\langle\psi_m^p|\hat{h}_{SO}|\psi_m^q\rangle\langle\psi_m^q|\hat{h}_{SO}|\psi\rangle}{\left(E - E_m^p\right)\left(E - E_m^q\right)} \\ &+ \sum_{mn}^{\in occ} \sum_{p}^{\in virt} \frac{\langle\psi|\hat{h}_{SO}|\psi_m^p\rangle\langle\psi_m^p|\hat{h}_{SO}|\psi_n^p\rangle\langle\psi_n^p|\hat{h}_{SO}|\psi\rangle}{\left(E - E_m^p\right)\left(E - E_n^p\right)} \end{aligned} \tag{H.59a}$$

Expressing the determinants in Eq. (H.59a) in terms of one-electron orbitals:

$$\begin{aligned} E^{(3)} &\approx \sum_{m}^{\in occ} \sum_{pq}^{\in virt} \frac{\langle m|\hat{h}_{SO}|p\rangle\langle p|\hat{h}_{SO}|q\rangle\langle q|\hat{h}_{SO}|m\rangle}{\left(\epsilon_m - \epsilon_p\right)\left(\epsilon_m - \epsilon_q\right)} \\ &- \sum_{mn}^{\in occ} \sum_{p}^{\in virt} \frac{\langle m|\hat{h}_{SO}|p\rangle\langle n|\hat{h}_{SO}|m\rangle\langle p|\hat{h}_{SO}|n\rangle}{\left(\epsilon_m - \epsilon_p\right)\left(\epsilon_n - \epsilon_p\right)} \end{aligned} \tag{H.59b}$$

For $E^{(4)}$, let us first write the expression starting from Eq. (H.22) in terms of all singly- and doubly-excited determinants with non-vanishing contributions:

$$
\begin{aligned}
E^{(4)} \approx\ & \sum_{m}^{\in occ}\sum_{pqr}^{\in virt} \frac{\langle\psi|\hat{h}_{SO}|\psi_m^p\rangle\langle\psi_m^p|\hat{h}_{SO}|\psi_m^q\rangle\langle\psi_m^q|\hat{h}_{SO}|\psi_m^r\rangle\langle\psi_m^r|\hat{h}_{SO}|\psi\rangle}{(E-E_m^p)(E-E_m^q)(E-E_m^r)} \\
+\ & \sum_{mn}^{\in occ}\sum_{pq}^{\in virt} \frac{\langle\psi|\hat{h}_{SO}|\psi_m^p\rangle\langle\psi_m^p|\hat{h}_{SO}|\psi_n^p\rangle\langle\psi_n^p|\hat{h}_{SO}|\psi_n^q\rangle\langle\psi_n^q|\hat{h}_{SO}|\psi\rangle}{(E-E_m^p)(E-E_n^p)(E-E_n^q)} \\
+\ & \sum_{mn}^{\in occ}\sum_{pq}^{\in virt} \frac{\langle\psi|\hat{h}_{SO}|\psi_m^p\rangle\langle\psi_m^p|\hat{h}_{SO}|\psi_m^q\rangle\langle\psi_m^q|\hat{h}_{SO}|\psi_n^q\rangle\langle\psi_n^q|\hat{h}_{SO}|\psi\rangle}{(E-E_m^p)(E-E_m^q)(E-E_n^q)} \\
+\ & \sum_{mno}^{\in occ}\sum_{p}^{\in virt} \frac{\langle\psi|\hat{h}_{SO}|\psi_m^p\rangle\langle\psi_m^p|\hat{h}_{SO}|\psi_n^p\rangle\langle\psi_n^p|\hat{h}_{SO}|\psi_o^p\rangle\langle\psi_o^p|\hat{h}_{SO}|\psi\rangle}{(E-E_m^p)(E-E_n^p)(E-E_o^p)} \\
-\ & E^{(2)}\sum_{m}^{\in occ}\sum_{p}^{\in virt} \frac{\langle\psi|\hat{h}_{SO}|\psi_m^p\rangle\langle\psi_m^p|\hat{h}_{SO}|\psi\rangle}{(E-E_m^p)^2} \\
+\ & \sum_{mn}^{\in occ}{}^{>>}\sum_{pq}^{\in virt}{}^{>>} \frac{\langle\psi|\hat{h}_{SO}|\psi_m^p\rangle\langle\psi_m^p|\hat{h}_{SO}|\psi_{mn}^{pq}\rangle\langle\psi_{mn}^{pq}|\hat{h}_{SO}|\psi_m^p\rangle\langle\psi_m^p|\hat{h}_{SO}|\psi\rangle}{(E-E_m^p)(E-E_{mn}^{pq})(E-E_m^p)} \\
+\ & \sum_{mn}^{\in occ}{}^{>>}\sum_{pq}^{\in virt}{}^{>>} \frac{\langle\psi|\hat{h}_{SO}|\psi_m^p\rangle\langle\psi_m^p|\hat{h}_{SO}|\psi_{mn}^{pq}\rangle\langle\psi_{mn}^{pq}|\hat{h}_{SO}|\psi_n^p\rangle\langle\psi_n^p|\hat{h}_{SO}|\psi\rangle}{(E-E_m^p)(E-E_{mn}^{pq})(E-E_n^p)} \\
+\ & \sum_{mn}^{\in occ}{}^{>>}\sum_{pq}^{\in virt}{}^{>>} \frac{\langle\psi|\hat{h}_{SO}|\psi_m^p\rangle\langle\psi_m^p|\hat{h}_{SO}|\psi_{mn}^{pq}\rangle\langle\psi_{mn}^{pq}|\hat{h}_{SO}|\psi_m^q\rangle\langle\psi_m^q|\hat{h}_{SO}|\psi\rangle}{(E-E_m^p)(E-E_{mn}^{pq})(E-E_m^q)} \\
+\ & \sum_{mn}^{\in occ}{}^{>>}\sum_{pq}^{\in virt}{}^{>>} \frac{\langle\psi|\hat{h}_{SO}|\psi_m^p\rangle\langle\psi_m^p|\hat{h}_{SO}|\psi_{mn}^{pq}\rangle\langle\psi_{mn}^{pq}|\hat{h}_{SO}|\psi_n^q\rangle\langle\psi_n^q|\hat{h}_{SO}|\psi\rangle}{(E-E_m^p)(E-E_{mn}^{pq})(E-E_n^q)} \\
+\ & \sum_{mn}^{\in occ}{}^{>>}\sum_{pq}^{\in virt}{}^{>>} \frac{\langle\psi|\hat{h}_{SO}|\psi_n^p\rangle\langle\psi_n^p|\hat{h}_{SO}|\psi_{mn}^{pq}\rangle\langle\psi_{mn}^{pq}|\hat{h}_{SO}|\psi_m^p\rangle\langle\psi_m^p|\hat{h}_{SO}|\psi\rangle}{(E-E_n^p)(E-E_{mn}^{pq})(E-E_m^p)} \\
+\ & \sum_{mn}^{\in occ}{}^{>>}\sum_{pq}^{\in virt}{}^{>>} \frac{\langle\psi|\hat{h}_{SO}|\psi_n^p\rangle\langle\psi_n^p|\hat{h}_{SO}|\psi_{mn}^{pq}\rangle\langle\psi_{mn}^{pq}|\hat{h}_{SO}|\psi_n^p\rangle\langle\psi_n^p|\hat{h}_{SO}|\psi\rangle}{(E-E_n^p)(E-E_{mn}^{pq})(E-E_n^p)} \\
+\ & \sum_{mn}^{\in occ}{}^{>>}\sum_{pq}^{\in virt}{}^{>>} \frac{\langle\psi|\hat{h}_{SO}|\psi_n^p\rangle\langle\psi_n^p|\hat{h}_{SO}|\psi_{mn}^{pq}\rangle\langle\psi_{mn}^{pq}|\hat{h}_{SO}|\psi_m^q\rangle\langle\psi_m^q|\hat{h}_{SO}|\psi\rangle}{(E-E_n^p)(E-E_{mn}^{pq})(E-E_m^q)} \\
+\ & \sum_{mn}^{\in occ}{}^{>>}\sum_{pq}^{\in virt}{}^{>>} \frac{\langle\psi|\hat{h}_{SO}|\psi_n^p\rangle\langle\psi_n^p|\hat{h}_{SO}|\psi_{mn}^{pq}\rangle\langle\psi_{mn}^{pq}|\hat{h}_{SO}|\psi_n^q\rangle\langle\psi_n^q|\hat{h}_{SO}|\psi\rangle}{(E-E_n^p)(E-E_{mn}^{pq})(E-E_n^q)} \\
+\ & \sum_{mn}^{\in occ}{}^{>>}\sum_{pq}^{\in virt}{}^{>>} \frac{\langle\psi|\hat{h}_{SO}|\psi_m^q\rangle\langle\psi_m^q|\hat{h}_{SO}|\psi_{mn}^{pq}\rangle\langle\psi_{mn}^{pq}|\hat{h}_{SO}|\psi_m^p\rangle\langle\psi_m^p|\hat{h}_{SO}|\psi\rangle}{(E-E_m^q)(E-E_{mn}^{pq})(E-E_m^p)} \\
+\ & \sum_{mn}^{\in occ}{}^{>>}\sum_{pq}^{\in virt}{}^{>>} \frac{\langle\psi|\hat{h}_{SO}|\psi_m^q\rangle\langle\psi_m^q|\hat{h}_{SO}|\psi_{mn}^{pq}\rangle\langle\psi_{mn}^{pq}|\hat{h}_{SO}|\psi_n^p\rangle\langle\psi_n^p|\hat{h}_{SO}|\psi\rangle}{(E-E_m^q)(E-E_{mn}^{pq})(E-E_n^p)} \\
+\ & \sum_{mn}^{\in occ}{}^{>>}\sum_{pq}^{\in virt}{}^{>>} \frac{\langle\psi|\hat{h}_{SO}|\psi_m^q\rangle\langle\psi_m^q|\hat{h}_{SO}|\psi_{mn}^{pq}\rangle\langle\psi_{mn}^{pq}|\hat{h}_{SO}|\psi_m^q\rangle\langle\psi_m^q|\hat{h}_{SO}|\psi\rangle}{(E-E_m^q)(E-E_{mn}^{pq})(E-E_m^q)} \\
+\ & \sum_{mn}^{\in occ}{}^{>>}\sum_{pq}^{\in virt}{}^{>>} \frac{\langle\psi|\hat{h}_{SO}|\psi_m^q\rangle\langle\psi_m^q|\hat{h}_{SO}|\psi_{mn}^{pq}\rangle\langle\psi_{mn}^{pq}|\hat{h}_{SO}|\psi_n^q\rangle\langle\psi_n^q|\hat{h}_{SO}|\psi\rangle}{(E-E_m^q)(E-E_{mn}^{pq})(E-E_n^q)} \\
+\ & \sum_{mn}^{\in occ}{}^{>>}\sum_{pq}^{\in virt}{}^{>>} \frac{\langle\psi|\hat{h}_{SO}|\psi_n^q\rangle\langle\psi_n^q|\hat{h}_{SO}|\psi_{mn}^{pq}\rangle\langle\psi_{mn}^{pq}|\hat{h}_{SO}|\psi_m^p\rangle\langle\psi_m^p|\hat{h}_{SO}|\psi\rangle}{(E-E_n^q)(E-E_{mn}^{pq})(E-E_m^p)} \\
+\ & \sum_{mn}^{\in occ}{}^{>>}\sum_{pq}^{\in virt}{}^{>>} \frac{\langle\psi|\hat{h}_{SO}|\psi_n^q\rangle\langle\psi_n^q|\hat{h}_{SO}|\psi_{mn}^{pq}\rangle\langle\psi_{mn}^{pq}|\hat{h}_{SO}|\psi_n^p\rangle\langle\psi_n^p|\hat{h}_{SO}|\psi\rangle}{(E-E_n^q)(E-E_{mn}^{pq})(E-E_n^p)} \\
+\ & \sum_{mn}^{\in occ}{}^{>>}\sum_{pq}^{\in virt}{}^{>>} \frac{\langle\psi|\hat{h}_{SO}|\psi_n^q\rangle\langle\psi_n^q|\hat{h}_{SO}|\psi_{mn}^{pq}\rangle\langle\psi_{mn}^{pq}|\hat{h}_{SO}|\psi_m^q\rangle\langle\psi_m^q|\hat{h}_{SO}|\psi\rangle}{(E-E_n^q)(E-E_{mn}^{pq})(E-E_m^q)} \\
+\ & \sum_{mn}^{\in occ}{}^{>>}\sum_{pq}^{\in virt}{}^{>>} \frac{\langle\psi|\hat{h}_{SO}|\psi_n^q\rangle\langle\psi_n^q|\hat{h}_{SO}|\psi_{mn}^{pq}\rangle\langle\psi_{mn}^{pq}|\hat{h}_{SO}|\psi_n^q\rangle\langle\psi_n^q|\hat{h}_{SO}|\psi\rangle}{(E-E_n^q)(E-E_{mn}^{pq})(E-E_n^q)}
\end{aligned}
\tag{H.60}
$$

So the first five terms in Eq. (H.60) involve only singly-excited determinants, while the sixteen terms involves all of the doubly-excited determinants that give non-vanishing contributions to the energy. The symbol $\sum_{m,n}^{\in occ} {}^{>}$ means that the sum is taken over all values of $m \in occ$ and all values of $n < m$, as a means to avoid double-counting of the doubly-excited configurations. Similarly, the symbol $\sum_{p,q}^{\in virt} {}^{>}$ means that the sum is taken over all values of $p \in virt$ and all values of $q < p$. Expanding the determinants in one-electron orbitals:

$$\begin{aligned}
E^{(4)} \approx\ & \sum_{m}^{\in occ}\sum_{pqr}^{\in virt} \frac{\langle m|\hat{h}_{SO}|p\rangle\langle p|\hat{h}_{SO}|q\rangle\langle q|\hat{h}_{SO}|r\rangle\langle r|\hat{h}_{SO}|m\rangle}{\left(\epsilon_m-\epsilon_p\right)\left(\epsilon_m-\epsilon_q\right)\left(\epsilon_m-\epsilon_r\right)} \\
- & \sum_{mn}^{\in occ}\sum_{pq}^{\in virt} \frac{\langle m|\hat{h}_{SO}|p\rangle\langle n|\hat{h}_{SO}|m\rangle\langle p|\hat{h}_{SO}|q\rangle\langle q|\hat{h}_{SO}|n\rangle}{\left(\epsilon_m-\epsilon_p\right)\left(\epsilon_n-\epsilon_p\right)\left(\epsilon_n-\epsilon_q\right)} \\
- & \sum_{mn}^{\in occ}\sum_{pq}^{\in virt} \frac{\langle m|\hat{h}_{SO}|p\rangle\langle p|\hat{h}_{SO}|q\rangle\langle n|\hat{h}_{SO}|m\rangle\langle q|\hat{h}_{SO}|n\rangle}{\left(\epsilon_m-\epsilon_p\right)\left(\epsilon_m-\epsilon_q\right)\left(\epsilon_n-\epsilon_q\right)} \\
+ & \sum_{mno}^{\in occ}\sum_{p}^{\in virt} \frac{\langle m|\hat{h}_{SO}|p\rangle\langle n|\hat{h}_{SO}|m\rangle\langle o|\hat{h}_{SO}|n\rangle\langle p|\hat{h}_{SO}|o\rangle}{\left(\epsilon_m-\epsilon_p\right)\left(\epsilon_n-\epsilon_p\right)\left(\epsilon_o-\epsilon_p\right)} \\
- & E_i^{(2)}\sum_{m}^{\in occ}\sum_{p}^{\in virt} \frac{\langle m|\hat{h}_{SO}|p\rangle\langle p|\hat{h}_{SO}|m\rangle}{\left(\epsilon_m-\epsilon_p\right)^2} \\
+ & \sum_{mn}^{\in occ}{}^{>>}\sum_{pq}^{\in virt}{}^{>>} \frac{\langle m|\hat{h}_{SO}|p\rangle\langle n|\hat{h}_{SO}|q\rangle\langle q|\hat{h}_{SO}|n\rangle\langle p|\hat{h}_{SO}|m\rangle}{\left(\epsilon_m-\epsilon_p\right)\left(\epsilon_m+\epsilon_n-\epsilon_p-\epsilon_q\right)\left(\epsilon_m-\epsilon_p\right)} \\
- & \sum_{mn}^{\in occ}{}^{>>}\sum_{pq}^{\in virt}{}^{>>} \frac{\langle m|\hat{h}_{SO}|p\rangle\langle n|\hat{h}_{SO}|q\rangle\langle q|\hat{h}_{SO}|m\rangle\langle p|\hat{h}_{SO}|n\rangle}{\left(\epsilon_m-\epsilon_p\right)\left(\epsilon_m+\epsilon_n-\epsilon_p-\epsilon_q\right)\left(\epsilon_n-\epsilon_p\right)} \\
- & \sum_{mn}^{\in occ}{}^{>>}\sum_{pq}^{\in virt}{}^{>>} \frac{\langle m|\hat{h}_{SO}|p\rangle\langle n|\hat{h}_{SO}|q\rangle\langle p|\hat{h}_{SO}|n\rangle\langle q|\hat{h}_{SO}|m\rangle}{\left(\epsilon_m-\epsilon_p\right)\left(\epsilon_m+\epsilon_n-\epsilon_p-\epsilon_q\right)\left(\epsilon_m-\epsilon_q\right)} \\
+ & \sum_{mn}^{\in occ}{}^{>>}\sum_{pq}^{\in virt}{}^{>>} \frac{\langle m|\hat{h}_{SO}|p\rangle\langle n|\hat{h}_{SO}|q\rangle\langle p|\hat{h}_{SO}|m\rangle\langle q|\hat{h}_{SO}|n\rangle}{\left(\epsilon_m-\epsilon_p\right)\left(\epsilon_m+\epsilon_n-\epsilon_p-\epsilon_q\right)\left(\epsilon_n-\epsilon_q\right)} \\
- & \sum_{mn}^{\in occ}{}^{>>}\sum_{pq}^{\in virt}{}^{>>} \frac{\langle n|\hat{h}_{SO}|p\rangle\langle m|\hat{h}_{SO}|q\rangle\langle q|\hat{h}_{SO}|n\rangle\langle p|\hat{h}_{SO}|m\rangle}{\left(\epsilon_n-\epsilon_p\right)\left(\epsilon_m+\epsilon_n-\epsilon_p-\epsilon_q\right)\left(\epsilon_m-\epsilon_p\right)} \\
+ & \sum_{mn}^{\in occ}{}^{>>}\sum_{pq}^{\in virt}{}^{>>} \frac{\langle n|\hat{h}_{SO}|p\rangle\langle m|\hat{h}_{SO}|q\rangle\langle q|\hat{h}_{SO}|m\rangle\langle p|\hat{h}_{SO}|n\rangle}{\left(\epsilon_n-\epsilon_p\right)\left(\epsilon_m+\epsilon_n-\epsilon_p-\epsilon_q\right)\left(\epsilon_n-\epsilon_p\right)} \\
+ & \sum_{mn}^{\in occ}{}^{>>}\sum_{pq}^{\in virt}{}^{>>} \frac{\langle n|\hat{h}_{SO}|p\rangle\langle m|\hat{h}_{SO}|q\rangle\langle p|\hat{h}_{SO}|n\rangle\langle q|\hat{h}_{SO}|m\rangle}{\left(\epsilon_n-\epsilon_p\right)\left(\epsilon_m+\epsilon_n-\epsilon_p-\epsilon_q\right)\left(\epsilon_m-\epsilon_q\right)} \\
- & \sum_{mn}^{\in occ}{}^{>>}\sum_{pq}^{\in virt}{}^{>>} \frac{\langle n|\hat{h}_{SO}|p\rangle\langle m|\hat{h}_{SO}|q\rangle\langle p|\hat{h}_{SO}|m\rangle\langle q|\hat{h}_{SO}|n\rangle}{\left(\epsilon_n-\epsilon_p\right)\left(\epsilon_m+\epsilon_n-\epsilon_p-\epsilon_q\right)\left(\epsilon_n-\epsilon_q\right)} \\
- & \sum_{mn}^{\in occ}{}^{>>}\sum_{pq}^{\in virt}{}^{>>} \frac{\langle m|\hat{h}_{SO}|q\rangle\langle n|\hat{h}_{SO}|p\rangle\langle q|\hat{h}_{SO}|n\rangle\langle p|\hat{h}_{SO}|m\rangle}{\left(\epsilon_m-\epsilon_q\right)\left(\epsilon_m+\epsilon_n-\epsilon_p-\epsilon_q\right)\left(\epsilon_m-\epsilon_p\right)} \\
+ & \sum_{mn}^{\in occ}{}^{>>}\sum_{pq}^{\in virt}{}^{>>} \frac{\langle m|\hat{h}_{SO}|q\rangle\langle n|\hat{h}_{SO}|p\rangle\langle q|\hat{h}_{SO}|m\rangle\langle p|\hat{h}_{SO}|n\rangle}{\left(\epsilon_m-\epsilon_q\right)\left(\epsilon_m+\epsilon_n-\epsilon_p-\epsilon_q\right)\left(\epsilon_n-\epsilon_p\right)} \\
+ & \sum_{mn}^{\in occ}{}^{>>}\sum_{pq}^{\in virt}{}^{>>} \frac{\langle m|\hat{h}_{SO}|q\rangle\langle n|\hat{h}_{SO}|p\rangle\langle p|\hat{h}_{SO}|n\rangle\langle q|\hat{h}_{SO}|m\rangle}{\left(\epsilon_m-\epsilon_q\right)\left(\epsilon_m+\epsilon_n-\epsilon_p-\epsilon_q\right)\left(\epsilon_m-\epsilon_q\right)} \\
- & \sum_{mn}^{\in occ}{}^{>>}\sum_{pq}^{\in virt}{}^{>>} \frac{\langle m|\hat{h}_{SO}|q\rangle\langle n|\hat{h}_{SO}|p\rangle\langle p|\hat{h}_{SO}|m\rangle\langle q|\hat{h}_{SO}|n\rangle}{\left(\epsilon_m-\epsilon_q\right)\left(\epsilon_m+\epsilon_n-\epsilon_p-\epsilon_q\right)\left(\epsilon_n-\epsilon_q\right)} \\
+ & \sum_{mn}^{\in occ}{}^{>>}\sum_{pq}^{\in virt}{}^{>>} \frac{\langle n|\hat{h}_{SO}|q\rangle\langle m|\hat{h}_{SO}|p\rangle\langle q|\hat{h}_{SO}|n\rangle\langle p|\hat{h}_{SO}|m\rangle}{\left(\epsilon_n-\epsilon_q\right)\left(\epsilon_m+\epsilon_n-\epsilon_p-\epsilon_q\right)\left(\epsilon_m-\epsilon_p\right)} \\
- & \sum_{mn}^{\in occ}{}^{>>}\sum_{pq}^{\in virt}{}^{>>} \frac{\langle n|\hat{h}_{SO}|q\rangle\langle m|\hat{h}_{SO}|p\rangle\langle q|\hat{h}_{SO}|m\rangle\langle p|\hat{h}_{SO}|n\rangle}{\left(\epsilon_n-\epsilon_q\right)\left(\epsilon_m+\epsilon_n-\epsilon_p-\epsilon_q\right)\left(\epsilon_n-\epsilon_p\right)} \\
- & \sum_{mn}^{\in occ}{}^{>>}\sum_{pq}^{\in virt}{}^{>>} \frac{\langle n|\hat{h}_{SO}|q\rangle\langle m|\hat{h}_{SO}|p\rangle\langle p|\hat{h}_{SO}|n\rangle\langle q|\hat{h}_{SO}|m\rangle}{\left(\epsilon_n-\epsilon_q\right)\left(\epsilon_m+\epsilon_n-\epsilon_p-\epsilon_q\right)\left(\epsilon_m-\epsilon_q\right)} \\
+ & \sum_{mn}^{\in occ}{}^{>>}\sum_{pq}^{\in virt}{}^{>>} \frac{\langle n|\hat{h}_{SO}|q\rangle\langle m|\hat{h}_{SO}|p\rangle\langle p|\hat{h}_{SO}|m\rangle\langle q|\hat{h}_{SO}|n\rangle}{\left(\epsilon_n-\epsilon_q\right)\left(\epsilon_m+\epsilon_n-\epsilon_p-\epsilon_q\right)\left(\epsilon_n-\epsilon_q\right)}
\end{aligned} \tag{H.61}$$

We can expand the sums involving doubly-excited determinants in Eq. (H.61) over all values of m, n and p, q by realizing that the different contributions cancel each other for the cases $m = n$ or $p = q$, such that we can write:

$$
\begin{aligned}
E^{(4)} \approx\ & \sum_{m}^{\in occ}\sum_{pqr}^{\in virt} \frac{\langle m|\hat{h}_{SO}|p\rangle\langle p|\hat{h}_{SO}|q\rangle\langle q|\hat{h}_{SO}|r\rangle\langle r|\hat{h}_{SO}|m\rangle}{\left(\epsilon_m-\epsilon_p\right)\left(\epsilon_m-\epsilon_q\right)(\epsilon_m-\epsilon_r)} \\
-\ & \sum_{mn}^{\in occ}\sum_{pq}^{\in virt} \frac{\langle m|\hat{h}_{SO}|p\rangle\langle n|\hat{h}_{SO}|m\rangle\langle p|\hat{h}_{SO}|q\rangle\langle q|\hat{h}_{SO}|n\rangle}{\left(\epsilon_m-\epsilon_p\right)\left(\epsilon_n-\epsilon_p\right)\left(\epsilon_n-\epsilon_q\right)} \\
-\ & \sum_{mn}^{\in occ}\sum_{pq}^{\in virt} \frac{\langle m|\hat{h}_{SO}|p\rangle\langle p|\hat{h}_{SO}|q\rangle\langle n|\hat{h}_{SO}|m\rangle\langle q|\hat{h}_{SO}|n\rangle}{\left(\epsilon_m-\epsilon_p\right)\left(\epsilon_m-\epsilon_q\right)\left(\epsilon_n-\epsilon_q\right)} \\
+\ & \sum_{mno}^{\in occ}\sum_{p}^{\in virt} \frac{\langle m|\hat{h}_{SO}|p\rangle\langle n|\hat{h}_{SO}|m\rangle\langle o|\hat{h}_{SO}|n\rangle\langle p|\hat{h}_{SO}|o\rangle}{\left(\epsilon_m-\epsilon_p\right)\left(\epsilon_n-\epsilon_p\right)\left(\epsilon_o-\epsilon_p\right)} \\
-\ & E_i^{(2)}\sum_{m}^{\in occ}\sum_{p}^{\in virt} \frac{\langle m|\hat{h}_{SO}|p\rangle\langle p|\hat{h}_{SO}|m\rangle}{\left(\epsilon_m-\epsilon_p\right)^2} \\
+\ & \frac{1}{4}\sum_{mn}^{\in occ}\sum_{pq}^{\in virt} \frac{\langle m|\hat{h}_{SO}|p\rangle\langle n|\hat{h}_{SO}|q\rangle\langle q|\hat{h}_{SO}|n\rangle\langle p|\hat{h}_{SO}|m\rangle}{\left(\epsilon_m-\epsilon_p\right)\left(\epsilon_m+\epsilon_n-\epsilon_p-\epsilon_q\right)\left(\epsilon_m-\epsilon_p\right)} \\
-\ & \frac{1}{4}\sum_{mn}^{\in occ}\sum_{pq}^{\in virt} \frac{\langle m|\hat{h}_{SO}|p\rangle\langle n|\hat{h}_{SO}|q\rangle\langle q|\hat{h}_{SO}|m\rangle\langle p|\hat{h}_{SO}|n\rangle}{\left(\epsilon_m-\epsilon_p\right)\left(\epsilon_m+\epsilon_n-\epsilon_p-\epsilon_q\right)\left(\epsilon_n-\epsilon_p\right)} \\
-\ & \frac{1}{4}\sum_{mn}^{\in occ}\sum_{pq}^{\in virt} \frac{\langle m|\hat{h}_{SO}|p\rangle\langle n|\hat{h}_{SO}|q\rangle\langle p|\hat{h}_{SO}|n\rangle\langle q|\hat{h}_{SO}|m\rangle}{\left(\epsilon_m-\epsilon_p\right)\left(\epsilon_m+\epsilon_n-\epsilon_p-\epsilon_q\right)\left(\epsilon_m-\epsilon_q\right)} \\
+\ & \frac{1}{4}\sum_{mn}^{\in occ}\sum_{pq}^{\in virt} \frac{\langle m|\hat{h}_{SO}|p\rangle\langle n|\hat{h}_{SO}|q\rangle\langle p|\hat{h}_{SO}|m\rangle\langle q|\hat{h}_{SO}|n\rangle}{\left(\epsilon_m-\epsilon_p\right)\left(\epsilon_m+\epsilon_n-\epsilon_p-\epsilon_q\right)\left(\epsilon_n-\epsilon_q\right)} \\
-\ & \frac{1}{4}\sum_{mn}^{\in occ}\sum_{pq}^{\in virt} \frac{\langle n|\hat{h}_{SO}|p\rangle\langle m|\hat{h}_{SO}|q\rangle\langle q|\hat{h}_{SO}|n\rangle\langle p|\hat{h}_{SO}|m\rangle}{\left(\epsilon_n-\epsilon_p\right)\left(\epsilon_m+\epsilon_n-\epsilon_p-\epsilon_q\right)\left(\epsilon_m-\epsilon_p\right)} \\
+\ & \frac{1}{4}\sum_{mn}^{\in occ}\sum_{pq}^{\in virt} \frac{\langle n|\hat{h}_{SO}|p\rangle\langle m|\hat{h}_{SO}|q\rangle\langle q|\hat{h}_{SO}|m\rangle\langle p|\hat{h}_{SO}|n\rangle}{\left(\epsilon_n-\epsilon_p\right)\left(\epsilon_m+\epsilon_n-\epsilon_p-\epsilon_q\right)\left(\epsilon_n-\epsilon_p\right)} \\
+\ & \frac{1}{4}\sum_{mn}^{\in occ}\sum_{pq}^{\in virt} \frac{\langle n|\hat{h}_{SO}|p\rangle\langle m|\hat{h}_{SO}|q\rangle\langle p|\hat{h}_{SO}|n\rangle\langle q|\hat{h}_{SO}|m\rangle}{\left(\epsilon_n-\epsilon_p\right)\left(\epsilon_m+\epsilon_n-\epsilon_p-\epsilon_q\right)\left(\epsilon_m-\epsilon_q\right)} \\
-\ & \frac{1}{4}\sum_{mn}^{\in occ}\sum_{pq}^{\in virt} \frac{\langle n|\hat{h}_{SO}|p\rangle\langle m|\hat{h}_{SO}|q\rangle\langle p|\hat{h}_{SO}|m\rangle\langle q|\hat{h}_{SO}|n\rangle}{\left(\epsilon_n-\epsilon_p\right)\left(\epsilon_m+\epsilon_n-\epsilon_p-\epsilon_q\right)\left(\epsilon_n-\epsilon_q\right)} \\
-\ & \frac{1}{4}\sum_{mn}^{\in occ}\sum_{pq}^{\in virt} \frac{\langle m|\hat{h}_{SO}|q\rangle\langle n|\hat{h}_{SO}|p\rangle\langle q|\hat{h}_{SO}|n\rangle\langle p|\hat{h}_{SO}|m\rangle}{\left(\epsilon_m-\epsilon_q\right)\left(\epsilon_m+\epsilon_n-\epsilon_p-\epsilon_q\right)\left(\epsilon_m-\epsilon_p\right)} \\
+\ & \frac{1}{4}\sum_{mn}^{\in occ}\sum_{pq}^{\in virt} \frac{\langle m|\hat{h}_{SO}|q\rangle\langle n|\hat{h}_{SO}|p\rangle\langle q|\hat{h}_{SO}|m\rangle\langle p|\hat{h}_{SO}|n\rangle}{\left(\epsilon_m-\epsilon_q\right)\left(\epsilon_m+\epsilon_n-\epsilon_p-\epsilon_q\right)\left(\epsilon_n-\epsilon_p\right)} \\
+\ & \frac{1}{4}\sum_{mn}^{\in occ}\sum_{pq}^{\in virt} \frac{\langle m|\hat{h}_{SO}|q\rangle\langle n|\hat{h}_{SO}|p\rangle\langle p|\hat{h}_{SO}|n\rangle\langle q|\hat{h}_{SO}|m\rangle}{\left(\epsilon_m-\epsilon_q\right)\left(\epsilon_m+\epsilon_n-\epsilon_p-\epsilon_q\right)\left(\epsilon_m-\epsilon_q\right)} \\
-\ & \frac{1}{4}\sum_{mn}^{\in occ}\sum_{pq}^{\in virt} \frac{\langle m|\hat{h}_{SO}|q\rangle\langle n|\hat{h}_{SO}|p\rangle\langle p|\hat{h}_{SO}|m\rangle\langle q|\hat{h}_{SO}|n\rangle}{\left(\epsilon_m-\epsilon_q\right)\left(\epsilon_m+\epsilon_n-\epsilon_p-\epsilon_q\right)\left(\epsilon_n-\epsilon_q\right)} \\
+\ & \frac{1}{4}\sum_{mn}^{\in occ}\sum_{pq}^{\in virt} \frac{\langle n|\hat{h}_{SO}|q\rangle\langle m|\hat{h}_{SO}|p\rangle\langle q|\hat{h}_{SO}|n\rangle\langle p|\hat{h}_{SO}|m\rangle}{\left(\epsilon_n-\epsilon_q\right)\left(\epsilon_m+\epsilon_n-\epsilon_p-\epsilon_q\right)\left(\epsilon_m-\epsilon_p\right)} \\
-\ & \frac{1}{4}\sum_{mn}^{\in occ}\sum_{pq}^{\in virt} \frac{\langle n|\hat{h}_{SO}|q\rangle\langle m|\hat{h}_{SO}|p\rangle\langle q|\hat{h}_{SO}|m\rangle\langle p|\hat{h}_{SO}|n\rangle}{\left(\epsilon_n-\epsilon_q\right)\left(\epsilon_m+\epsilon_n-\epsilon_p-\epsilon_q\right)\left(\epsilon_n-\epsilon_p\right)} \\
-\ & \frac{1}{4}\sum_{mn}^{\in occ}\sum_{pq}^{\in virt} \frac{\langle n|\hat{h}_{SO}|q\rangle\langle m|\hat{h}_{SO}|p\rangle\langle p|\hat{h}_{SO}|n\rangle\langle q|\hat{h}_{SO}|m\rangle}{\left(\epsilon_n-\epsilon_q\right)\left(\epsilon_m+\epsilon_n-\epsilon_p-\epsilon_q\right)\left(\epsilon_m-\epsilon_q\right)} \\
+\ & \frac{1}{4}\sum_{mn}^{\in occ}\sum_{pq}^{\in virt} \frac{\langle n|\hat{h}_{SO}|q\rangle\langle m|\hat{h}_{SO}|p\rangle\langle p|\hat{h}_{SO}|m\rangle\langle q|\hat{h}_{SO}|n\rangle}{\left(\epsilon_n-\epsilon_q\right)\left(\epsilon_m+\epsilon_n-\epsilon_p-\epsilon_q\right)\left(\epsilon_n-\epsilon_q\right)}
\end{aligned}
\tag{H.62}
$$

Grouping the terms 1,4,13,16 then 2,3,14,15 and 5,8,9,12 then 6,7,10,11 that originate from doubly-excited determinants in Eq. (H.62):

$$\begin{aligned}
E^{(4)} &\approx \sum_{m}^{\in occ}\sum_{pqr}^{\in virt} \frac{\langle m|\hat{h}_{SO}|p\rangle\langle p|\hat{h}_{SO}|q\rangle\langle q|\hat{h}_{SO}|r\rangle\langle r|\hat{h}_{SO}|m\rangle}{\left(\epsilon_m-\epsilon_p\right)\left(\epsilon_m-\epsilon_q\right)\left(\epsilon_m-\epsilon_r\right)} \\
&- \sum_{mn}^{\in occ}\sum_{pq}^{\in virt} \frac{\langle m|\hat{h}_{SO}|p\rangle\langle n|\hat{h}_{SO}|m\rangle\langle p|\hat{h}_{SO}|q\rangle\langle q|\hat{h}_{SO}|n\rangle}{\left(\epsilon_m-\epsilon_p\right)\left(\epsilon_n-\epsilon_p\right)\left(\epsilon_n-\epsilon_q\right)} \\
&- \sum_{mn}^{\in occ}\sum_{pq}^{\in virt} \frac{\langle m|\hat{h}_{SO}|p\rangle\langle p|\hat{h}_{SO}|q\rangle\langle n|\hat{h}_{SO}|m\rangle\langle q|\hat{h}_{SO}|n\rangle}{\left(\epsilon_m-\epsilon_p\right)\left(\epsilon_m-\epsilon_q\right)\left(\epsilon_n-\epsilon_q\right)} \\
&+ \sum_{mno}^{\in occ}\sum_{p}^{\in virt} \frac{\langle m|\hat{h}_{SO}|p\rangle\langle n|\hat{h}_{SO}|m\rangle\langle o|\hat{h}_{SO}|n\rangle\langle p|\hat{h}_{SO}|o\rangle}{\left(\epsilon_m-\epsilon_p\right)\left(\epsilon_n-\epsilon_p\right)\left(\epsilon_o-\epsilon_p\right)} \\
&- E_i^{(2)}\sum_{m}^{\in occ}\sum_{p}^{\in virt} \frac{\langle m|\hat{h}_{SO}|p\rangle\langle p|\hat{h}_{SO}|m\rangle}{\left(\epsilon_m-\epsilon_p\right)^2} \\
&+ \sum_{mn}^{\in occ}\sum_{pq}^{\in virt} \frac{\langle m|\hat{h}_{SO}|p\rangle\langle n|\hat{h}_{SO}|q\rangle\langle q|\hat{h}_{SO}|n\rangle\langle p|\hat{h}_{SO}|m\rangle}{\left(\epsilon_m+\epsilon_n-\epsilon_p-\epsilon_q\right)} \\
&\times \left\{\frac{1}{4\left(\epsilon_m-\epsilon_p\right)\left(\epsilon_m-\epsilon_p\right)}+\frac{1}{4\left(\epsilon_m-\epsilon_p\right)\left(\epsilon_n-\epsilon_q\right)}+\frac{1}{4\left(\epsilon_m-\epsilon_p\right)\left(\epsilon_n-\epsilon_q\right)}+\frac{1}{4\left(\epsilon_n-\epsilon_q\right)\left(\epsilon_n-\epsilon_q\right)}\right\} \\
&- \sum_{mn}^{\in occ}\sum_{pq}^{\in virt} \frac{\langle m|\hat{h}_{SO}|p\rangle\langle n|\hat{h}_{SO}|q\rangle\langle q|\hat{h}_{SO}|m\rangle\langle p|\hat{h}_{SO}|n\rangle+\langle p|\hat{h}_{SO}|m\rangle\langle q|\hat{h}_{SO}|n\rangle\langle m|\hat{h}_{SO}|q\rangle\langle n|\hat{h}_{SO}|p\rangle}{\left(\epsilon_m+\epsilon_n-\epsilon_p-\epsilon_q\right)} \\
&\times \left\{\frac{1}{4\left(\epsilon_m-\epsilon_p\right)\left(\epsilon_n-\epsilon_p\right)}+\frac{1}{4\left(\epsilon_m-\epsilon_p\right)\left(\epsilon_m-\epsilon_q\right)}+\frac{1}{4\left(\epsilon_n-\epsilon_q\right)\left(\epsilon_n-\epsilon_p\right)}+\frac{1}{4\left(\epsilon_n-\epsilon_q\right)\left(\epsilon_m-\epsilon_q\right)}\right\} \\
&+ \sum_{mn}^{\in occ}\sum_{pq}^{\in virt} \frac{\langle n|\hat{h}_{SO}|p\rangle\langle m|\hat{h}_{SO}|q\rangle\langle q|\hat{h}_{SO}|m\rangle\langle p|\hat{h}_{SO}|n\rangle}{\left(\epsilon_m+\epsilon_n-\epsilon_p-\epsilon_q\right)} \\
&\times \left\{\frac{1}{4\left(\epsilon_n-\epsilon_p\right)\left(\epsilon_n-\epsilon_p\right)}+\frac{1}{4\left(\epsilon_n-\epsilon_p\right)\left(\epsilon_m-\epsilon_q\right)}+\frac{1}{4\left(\epsilon_m-\epsilon_q\right)\left(\epsilon_n-\epsilon_p\right)}+\frac{1}{4\left(\epsilon_m-\epsilon_q\right)\left(\epsilon_m-\epsilon_q\right)}\right\}
\end{aligned} \tag{H.63}$$

Exploiting the invariance of the sixth term in Eq. (H.63) to a simultaneous permutation of $m, p \leftrightarrow n, q$, as well as the invariance of the seventh and eighth terms to a simultaneous permutation of $n, p \leftrightarrow m, q$, we find:

$$
\begin{aligned}
E^{(4)} \approx\ & \sum_{m}^{\in occ}\sum_{pqr}^{\in virt} \frac{\langle m|\hat{h}_{SO}|p\rangle\langle p|\hat{h}_{SO}|q\rangle\langle q|\hat{h}_{SO}|r\rangle\langle r|\hat{h}_{SO}|m\rangle}{\left(\epsilon_m - \epsilon_p\right)\left(\epsilon_m - \epsilon_q\right)\left(\epsilon_m - \epsilon_r\right)} \\
- & \sum_{mn}^{\in occ}\sum_{pq}^{\in virt} \frac{\langle m|\hat{h}_{SO}|p\rangle\langle n|\hat{h}_{SO}|m\rangle\langle p|\hat{h}_{SO}|q\rangle\langle q|\hat{h}_{SO}|n\rangle}{\left(\epsilon_m - \epsilon_p\right)\left(\epsilon_n - \epsilon_p\right)\left(\epsilon_n - \epsilon_q\right)} \\
- & \sum_{mn}^{\in occ}\sum_{pq}^{\in virt} \frac{\langle m|\hat{h}_{SO}|p\rangle\langle p|\hat{h}_{SO}|q\rangle\langle n|\hat{h}_{SO}|m\rangle\langle q|\hat{h}_{SO}|n\rangle}{\left(\epsilon_m - \epsilon_p\right)\left(\epsilon_m - \epsilon_q\right)\left(\epsilon_n - \epsilon_q\right)} \\
+ & \sum_{mno}^{\in occ}\sum_{p}^{\in virt} \frac{\langle m|\hat{h}_{SO}|p\rangle\langle n|\hat{h}_{SO}|m\rangle\langle o|\hat{h}_{SO}|n\rangle\langle p|\hat{h}_{SO}|o\rangle}{\left(\epsilon_m - \epsilon_p\right)\left(\epsilon_n - \epsilon_p\right)\left(\epsilon_o - \epsilon_p\right)} \\
- & E_i^{(2)}\sum_{m}^{\in occ}\sum_{p}^{\in virt} \frac{\langle m|\hat{h}_{SO}|p\rangle\langle p|\hat{h}_{SO}|m\rangle}{\left(\epsilon_m - \epsilon_p\right)^2} \\
+ & \frac{1}{2}\sum_{mn}^{\in occ}\sum_{pq}^{\in virt} \frac{\langle m|\hat{h}_{SO}|p\rangle\langle n|\hat{h}_{SO}|q\rangle\langle q|\hat{h}_{SO}|n\rangle\langle p|\hat{h}_{SO}|m\rangle}{\left(\epsilon_m - \epsilon_p\right)\left(\epsilon_n - \epsilon_q\right)\left(\epsilon_m - \epsilon_p\right)} \\
+ & \frac{1}{2}\sum_{mn}^{\in occ}\sum_{pq}^{\in virt} \frac{\langle n|\hat{h}_{SO}|p\rangle\langle m|\hat{h}_{SO}|q\rangle\langle q|\hat{h}_{SO}|m\rangle\langle p|\hat{h}_{SO}|n\rangle}{\left(\epsilon_n - \epsilon_p\right)\left(\epsilon_m - \epsilon_q\right)\left(\epsilon_n - \epsilon_p\right)} \\
- & \sum_{mn}^{\in occ}\sum_{pq}^{\in virt} \frac{\mathcal{R}\left[\langle m|\hat{h}_{SO}|p\rangle\langle n|\hat{h}_{SO}|q\rangle\langle q|\hat{h}_{SO}|m\rangle\langle p|\hat{h}_{SO}|n\rangle\right]}{\left(\epsilon_m - \epsilon_p\right)\left(\epsilon_m - \epsilon_q\right)\left(\epsilon_n - \epsilon_q\right)}
\end{aligned}
\tag{H.64}
$$

Now interchanging the indices $m \leftrightarrow n$ in the seventh term of Eq. (H.64) and substituting the expression for $E^{(2)}$ in the fifth term from the expresssion found in Eq. (H.58):

$$
\begin{aligned}
E^{(4)} \approx\ & \sum_{m}^{\in occ}\sum_{pqr}^{\in virt} \frac{\langle m|\hat{h}_{SO}|p\rangle\langle p|\hat{h}_{SO}|q\rangle\langle q|\hat{h}_{SO}|r\rangle\langle r|\hat{h}_{SO}|m\rangle}{\left(\epsilon_m - \epsilon_p\right)\left(\epsilon_m - \epsilon_q\right)\left(\epsilon_m - \epsilon_r\right)} \\
- & \sum_{mn}^{\in occ}\sum_{pq}^{\in virt} \frac{\langle m|\hat{h}_{SO}|p\rangle\langle n|\hat{h}_{SO}|m\rangle\langle p|\hat{h}_{SO}|q\rangle\langle q|\hat{h}_{SO}|n\rangle}{\left(\epsilon_m - \epsilon_p\right)\left(\epsilon_n - \epsilon_p\right)\left(\epsilon_n - \epsilon_q\right)} \\
- & \sum_{mn}^{\in occ}\sum_{pq}^{\in virt} \frac{\langle m|\hat{h}_{SO}|p\rangle\langle p|\hat{h}_{SO}|q\rangle\langle n|\hat{h}_{SO}|m\rangle\langle q|\hat{h}_{SO}|n\rangle}{\left(\epsilon_m - \epsilon_p\right)\left(\epsilon_m - \epsilon_q\right)\left(\epsilon_n - \epsilon_q\right)} \\
+ & \sum_{mno}^{\in occ}\sum_{p}^{\in virt} \frac{\langle m|\hat{h}_{SO}|p\rangle\langle n|\hat{h}_{SO}|m\rangle\langle o|\hat{h}_{SO}|n\rangle\langle p|\hat{h}_{SO}|o\rangle}{\left(\epsilon_m - \epsilon_p\right)\left(\epsilon_n - \epsilon_p\right)\left(\epsilon_o - \epsilon_p\right)} \\
- & \sum_{mn}^{\in occ}\sum_{pq}^{\in virt} \frac{\mathcal{R}\left[\langle m|\hat{h}_{SO}|p\rangle\langle n|\hat{h}_{SO}|q\rangle\langle q|\hat{h}_{SO}|m\rangle\langle p|\hat{h}_{SO}|n\rangle\right]}{\left(\epsilon_m - \epsilon_p\right)\left(\epsilon_m - \epsilon_q\right)\left(\epsilon_n - \epsilon_q\right)}
\end{aligned}
\tag{H.65}
$$

We can re-write Eq. (H.58) as follows to extend the summations over all states:

$$E \approx E^{(0)} + \sum_i \sum_j{}' f_i[1 - f_j] \frac{\langle i|\hat{h}_{SO}|j\rangle\langle j|\hat{h}_{SO}|i\rangle}{\epsilon_i - \epsilon_j} \tag{H.66}$$

where the $f_i = 1$ for an occupied state and $f_i = 0$ for a virtual state. A natural extension of Eq. (H.66) to fractional occupation numbers is to allow values $0 \leq f_i \leq 1$, according to the Fermi function:

$$f_i = \left(1 + \exp\left\{\frac{\epsilon_i - \epsilon_F}{k_b T}\right\}\right)^{-1} \tag{H.67}$$

where ϵ_F is the calculated Fermi energy and $k_b T$ is the chosen smearing width.

Eqs. (H.58) and (H.66) exclude the contribution to the energy from the term $\epsilon_j = \epsilon_i$ with $j \neq i$, whose treatment would require degenerate perturbation theory. The term $\epsilon_j = \epsilon_i$ with $j \neq i$ can have contributions if there are degenerate states exactly at the Fermi level ϵ_F. This can occur, in periodic systems, for example in metals.

H.3.2 Eigenstates and Eigenvalues

We now apply Eqs. (H.17) and (H.20) to the determination of the perturbed eigenvalues $\epsilon_i^{(2)}$ and perturbed eigenstates $|i^{(1)}\rangle$, choosing those of Eq. (H.48) as the corresponding zeroth-order approximation. From Eq. (H.17) and (H.20), we have:

$$|i^{(1)}\rangle \approx \sum_j{}' \left(\frac{\langle j|\hat{h}_{SO}|i\rangle}{\epsilon_i - \epsilon_j}\right)|j\rangle \tag{H.68}$$

and for the eigenvalues, the perturbative correction to first and second order are:

$$\epsilon_i^{(1)} \approx \langle i|\hat{h}_{SO}|i\rangle = 0 \tag{H.69}$$

and:

$$\epsilon_i^{(2)} \approx \sum_j{}' \frac{\langle i|\hat{h}_{SO}|j\rangle\langle j|\hat{h}_{SO}|i\rangle}{\epsilon_i - \epsilon_j} \tag{H.70}$$

where, again the $\epsilon_i^{(1)}$ go to zero because for two functions of equal spin, the SO operator is purely imaginary and Hermitian. We can then write the second-order approximation to the FR eigenvalues ϵ_I as follows:

$$\epsilon_I = \epsilon_i + \lambda\epsilon_i^{(1)} + \lambda^2\epsilon_i^{(2)} + \ldots \underset{\lambda\to1}{\approx} \epsilon_i + \sum_j{}' \frac{\langle i|\hat{h}_{SO}|j\rangle\langle j|\hat{h}_{SO}|i\rangle}{\epsilon_i - \epsilon_j} \tag{H.71}$$

and the FR eigenstates:

$$|I\rangle = |i\rangle + \lambda|i^{(1)}\rangle + \ldots \underset{\lambda\to1}{\approx} |i\rangle + \sum_j{}' \left(\frac{\langle j|\hat{h}_{SO}|i\rangle}{\epsilon_i - \epsilon_j}\right)|j\rangle \tag{H.72}$$

H.4 Molecular Systems

H.4.1 Energy

For calculating the energy of a molecular system, Eq. (H.66) must first be recast into the *real* AO basis $|\mu,\sigma\rangle$ upon which the eigenstates $|i\rangle$ are expanded. The $|i\rangle$ are expanded in Pauli spinor AOs, as follows:

$$|i\rangle = \sum_{\mu} c^{\alpha}_{\mu i}|\mu,\alpha\rangle + c^{\beta}_{\mu i}|\mu,\beta\rangle \tag{H.73}$$

where $c^{\alpha}_{\mu i}$, and $c^{\beta}_{\mu i}$ are the (generally) complex coefficients of the MOs. The AO basis is represented as:

$$|\mu,\sigma\rangle = |\mu\rangle \otimes |\sigma\rangle \tag{H.74}$$

where $|\sigma\rangle = |\alpha\rangle$ or $|\beta\rangle$ are functions defined in spin space. The projection of the AO onto the spin and position basis is defined as:

$$\langle r,\boldsymbol{\sigma}|\mu,\sigma\rangle = \langle r|\mu\rangle \cdot \langle\boldsymbol{\sigma}|\sigma\rangle \tag{H.75}$$

in which $\langle r|\mu\rangle$ is the representation of the functions $|\mu\rangle$ in the position basis and calculated as a linear combination of Gaussian functions.

The projection of the functions $|\sigma\rangle = |\alpha\rangle$ or $|\beta\rangle$ onto the spin basis are evaluated as follows:

$$\langle\alpha|\boldsymbol{\sigma}\rangle = \boldsymbol{\alpha}^T \quad \langle\beta|\boldsymbol{\sigma}\rangle = \boldsymbol{\beta}^T \tag{H.76}$$

in which $\langle\boldsymbol{\sigma}|$ indicates the projection onto the spin basis and $\boldsymbol{\alpha}$ and $\boldsymbol{\beta}$ are the simultaneous eigenfunctions of the one-electron spin operators $\hat{S}_z$ and $\hat{\mathbf{S}}^2$:

$$\boldsymbol{\alpha} = \begin{pmatrix}1\\0\end{pmatrix} \quad \text{and} \quad \boldsymbol{\beta} = \begin{pmatrix}0\\1\end{pmatrix} \tag{H.77}$$

Similarly, for the FR states:

$$|I\rangle = \sum_{\mu} c^{\alpha}_{\mu I}|\mu,\alpha\rangle + c^{\beta}_{\mu I}|\mu,\beta\rangle \tag{H.78}$$

where, for $\sigma = \alpha$ or β:

$$\begin{aligned} c^{\sigma}_{\mu I} &= c^{\sigma}_{\mu i} + \lambda c^{\sigma(1)}_{\mu i} + \lambda^2 c^{\sigma(2)}_{\mu i} + ... \\ &\underset{\lambda\to 1}{\approx} c^{\sigma}_{\mu i} + c^{\sigma(1)}_{\mu i} \end{aligned} \tag{H.79}$$

From Eq. (H.73), the $|i\rangle$ can be written as a sum over pure spin MOs $|i,\alpha\rangle$ and $|i,\beta\rangle$:

$$|i\rangle = |i,\alpha\rangle + |i,\beta\rangle \tag{H.80}$$

The pure spin MOs are defined as follows, for $\sigma = \alpha$ or β:

$$\begin{aligned} |i,\sigma\rangle &= \sum_{\mu} c^{\sigma}_{\mu i}|\mu,\sigma\rangle \\ \langle r,\boldsymbol{\sigma}|i,\sigma\rangle &= i^{\sigma}\boldsymbol{\sigma} \qquad \text{(H.81a)} \end{aligned}$$

The i^{σ} can be expressed in matrix notation, as follows:

$$i^{\sigma} = \left[\mathbf{c}^{\sigma}_{i}\right]^{T}\boldsymbol{\mu} \tag{H.82}$$

in which $\mathbf{c}^{\sigma}_{i}$ is a column vector whose elements are the $c^{\sigma}_{\mu i}$ and $\boldsymbol{\mu}$ is a column vector, whose elements are the $\langle r|\mu\rangle$.

For an SR reference, each MO is a pure spin MO, that is to say:

$$\begin{aligned} |i\rangle &= |i,\sigma\rangle \qquad \text{(H.83a)} \\ f_i &= f_{i\sigma} \qquad \text{(H.83b)} \\ \epsilon_i &= \epsilon^{\sigma}_{i} \qquad \text{(H.83c)} \end{aligned}$$

From now on the index i in $|i,\sigma\rangle$, i^{σ}, $f_{i\sigma}$ and ϵ^{σ}_{i}, as well as the index j in $|j,\sigma\rangle$, j^{σ}, $f_{j\sigma}$ and ϵ^{σ}_{j}runs from 1 to half the number of electrons (that is to say $i, j = 1, 2, ..., d/2$).

Substituting Eqs. (H.73)-(H.83), we can write the FR energy to second-order in the AO basis as follows:

$$E \approx E^{(0)} + \sum_{\sigma\sigma'}\sum_{i}\sum_{j}{}' \frac{f_{i\sigma}[1 - f_{j\sigma'}]}{\epsilon^{\sigma}_{i} - \epsilon^{\sigma'}_{j}} \left|\sum_{\mu\nu}\left[c^{\sigma}_{\mu i}\right]^{*} c^{\sigma'}_{\nu j}\langle\mu,\sigma|\hat{h}_{SO}|\nu,\sigma'\rangle\right|^{2} \tag{H.84}$$

Introducing the compact matrix-element notation:

$$b^{\sigma\sigma'}_{\mu\nu} = \langle\mu,\sigma|\hat{h}_{SO}|\nu,\sigma'\rangle \tag{H.85}$$

we obtain:

$$E \approx E^{(0)} + \sum_{\sigma\sigma'}\sum_{i}\sum_{j}{}' \frac{f_{i\sigma}[1 - f_{j\sigma'}]}{\epsilon^{\sigma}_{i} - \epsilon^{\sigma'}_{j}} \left|\sum_{\mu\nu}\left[c^{\sigma}_{\mu i}\right]^{*} c^{\sigma'}_{\nu j} b^{\sigma\sigma'}_{\mu\nu}\right|^{2} \tag{H.86}$$

H.4.2 Eigenvalues and Eigenstates

The perturbed eigenvalues are written as:

$$\epsilon_I = \epsilon^{\alpha}_{I} \text{ or } \epsilon^{\beta}_{I} \tag{H.87}$$

in which ϵ^{σ}_{I} is the state obtained by perturbing ϵ^{σ}_{i}, and $I = 1, 2, ..., d/2$. Likewise, for the perturbed eigenstates:

$$|I\rangle = |I^{\alpha}\rangle \text{ or } |I^{\beta}\rangle \tag{H.88}$$

where $|I^{\sigma}\rangle$ are the states obtained by perturbing $|i^{\sigma}\rangle$.

Substituting Eqs. (H.73)-(H.83) in Eq. (H.71), we write the FR eigenvalues to second-order in the AO basis, as follows:

$$\epsilon_I^{\sigma} \approx \epsilon_i^{\sigma} + \sum_{\sigma'} \sum_{j}{}' \frac{1}{\epsilon_i^{\sigma} - \epsilon_j^{\sigma'}} \left| \sum_{\mu\nu} \left[c_{\mu i}^{\sigma}\right]^* c_{\nu j}^{\sigma'} b_{\mu\nu}^{\sigma\sigma'} \right|^2 \tag{H.89}$$

and for the FR eigenstates, to first-order:

$$|I^{\sigma}\rangle \approx |i,\sigma\rangle + \sum_{\sigma'} \sum_{j}{}' \left(\sum_{\mu\nu} \frac{\left[c_{\nu j}^{\sigma'}\right]^* c_{\mu i}^{\sigma} b_{\nu\mu}^{\sigma'\sigma}}{\epsilon_i^{\sigma} - \epsilon_j^{\sigma'}} \right) |j,\sigma'\rangle \tag{H.90}$$

We note that even though the index σ is used as a superscript over ϵ_I^{σ} and $|I^{\sigma}\rangle$ in Eqs. (H.89) and (H.90), these quantities are nonetheless no longer pure spin states. This is because the sums over σ' in Eqs. (H.89) and (H.90) mix spin components. The superscript indeed only labels the spin component of the corresponding SR problem from which the FR states are expanded.

To display the mixed spin character of the calculated FR states we extend explicitly the sum over σ' in Eq. (H.90), using the notation introduced in Eq. (H.81). For the states perturbed starting from the SR α ones:

$$\langle r,\boldsymbol{\sigma}|I^{\alpha}\rangle \approx i^{\alpha}\boldsymbol{\alpha} + \sum_{j}{}' \left(\sum_{\mu\nu} \frac{\left[c_{\nu j}^{\alpha}\right]^* c_{\mu i}^{\alpha} b_{\nu\mu}^{\alpha\alpha}}{\epsilon_i^{\alpha} - \epsilon_j^{\alpha}} \right) j^{\alpha}\boldsymbol{\alpha} + \sum_{j}{}' \left(\sum_{\mu\nu} \frac{\left[c_{\nu j}^{\beta}\right]^* c_{\mu i}^{\alpha} b_{\nu\mu}^{\beta\alpha}}{\epsilon_i^{\alpha} - \epsilon_j^{\beta}} \right) j^{\beta}\boldsymbol{\beta} \tag{H.91}$$

and for the states perturbed starting from the SR β ones:

$$\langle r,\boldsymbol{\sigma}|I^{\beta}\rangle \approx i^{\beta}\boldsymbol{\beta} + \sum_{j}{}' \left(\sum_{\mu\nu} \frac{\left[c_{\nu j}^{\alpha}\right]^* c_{\mu i}^{\beta} b_{\nu\mu}^{\alpha\beta}}{\epsilon_i^{\beta} - \epsilon_j^{\alpha}} \right) j^{\alpha}\boldsymbol{\alpha} + \sum_{j}{}' \left(\sum_{\mu\nu} \frac{\left[c_{\nu j}^{\beta}\right]^* c_{\mu i}^{\beta} b_{\nu\mu}^{\beta\beta}}{\epsilon_i^{\beta} - \epsilon_j^{\beta}} \right) j^{\beta}\boldsymbol{\beta} \tag{H.92}$$

H.4.3 The Orbital Rotation Matrix

We define the quantities $I_{\sigma'}^{\sigma}$ as the σ' component of the FR state obtained from perturbation of the σ SR state. That is to say:

$$\langle r,\boldsymbol{\sigma}|I^{\alpha}\rangle = \boldsymbol{\alpha} I_{\alpha}^{\alpha} + \boldsymbol{\beta} I_{\beta}^{\alpha} = \begin{pmatrix} I_{\alpha}^{\alpha} \\ \\ I_{\beta}^{\alpha} \end{pmatrix} \tag{H.93}$$

and:

$$\langle r,\boldsymbol{\sigma}|I^{\beta}\rangle = \boldsymbol{\alpha} I_{\alpha}^{\beta} + \boldsymbol{\beta} I_{\beta}^{\beta} = \begin{pmatrix} I_{\alpha}^{\beta} \\ \\ I_{\beta}^{\beta} \end{pmatrix} \tag{H.94}$$

Combining Eqs. (H.93) and (H.94), we have:

$$\langle r, \boldsymbol{\sigma} | I^{\sigma} \rangle = \sum_{\sigma'} \boldsymbol{\sigma}' I^{\sigma}_{\sigma'} \tag{H.95}$$

Substituting Eqs. (H.91) and (H.92) in Eq. (H.95):

$$\begin{aligned} I^{\sigma}_{\sigma'} &\approx i^{\sigma}\delta_{\sigma\sigma'} + \sum_j{}' \left(\sum_{\mu\nu} \frac{\left[c^{\sigma'}_{\nu j}\right]^* c^{\sigma}_{\mu i} b^{\sigma'\sigma}_{\nu\mu}}{\epsilon^{\sigma}_i - \epsilon^{\sigma'}_j} \right) j^{\sigma'} \\ &\equiv i^{\sigma}\delta_{\sigma\sigma'} + I^{\sigma(1)}_{\sigma'} \end{aligned} \tag{H.96}$$

where we define:

$$I^{\sigma(1)}_{\sigma'} = \sum_j{}' \left(\sum_{\mu\nu} \frac{\left[c^{\sigma'}_{\nu j}\right]^* c^{\sigma}_{\mu i} b^{\sigma'\sigma}_{\nu\mu}}{\epsilon^{\sigma}_i - \epsilon^{\sigma'}_j} \right) j^{\sigma'} \tag{H.97}$$

Following Eqs. (H.78), (H.79) and (H.83), we can write the $I^{\sigma}_{\sigma'}$ in the AO basis, as follows:

$$I^{\sigma}_{\sigma'} = \sum_{\mu} c^{\sigma'\sigma}_{\mu I} \langle r|\mu\rangle \approx \sum_{\mu} \left[c^{\sigma}_{\mu i}\delta_{\sigma\sigma'} + c^{\sigma'\sigma(1)}_{\mu i} \right] \langle r|\mu\rangle \tag{H.98}$$

and for $I^{\sigma(1)}_{\sigma'}$:

$$I^{\sigma(1)}_{\sigma'} = \sum_{\mu} c^{\sigma'\sigma(1)}_{\mu i} \langle r|\mu\rangle \tag{H.99}$$

The coefficients $c^{\sigma'\sigma}_{\mu I}$ are defined in Eq. (H.98) through the following relations:

$$c^{\sigma'\sigma}_{\mu I} = c^{\sigma}_{\mu i}\delta_{\sigma\sigma'} + \lambda c^{\sigma'\sigma(1)}_{\mu i} + \lambda^2 c^{\sigma'\sigma(2)}_{\mu i} + \ldots \underset{\lambda\to 1}{\approx} c^{\sigma}_{\mu i}\delta_{\sigma\sigma'} + c^{\sigma'\sigma(1)}_{\mu i} \tag{H.100}$$

We can express Eqs. (H.98) in vector notation, as follows:

$$I^{\sigma}_{\sigma'} = \left[\mathbf{c}^{\sigma'\sigma}_I\right]^T \boldsymbol{\mu} \tag{H.101}$$

where $\mathbf{c}^{\sigma'\sigma}_I$ is a column vector whose elements are $c^{\sigma'\sigma}_{\mu I}$.

The vector notation version of Eq. (H.99) reads:

$$I^{\sigma(1)}_{\sigma'} = \left[\mathbf{c}^{\sigma'\sigma(1)}_i\right]^T \boldsymbol{\mu} \tag{H.102}$$

where $\mathbf{c}^{\sigma'\sigma(1)}_i$ is a column vector whose elements are the $c^{\sigma'\sigma(1)}_{\mu i}$. Substituting Eqs. (H.82) and (H.102) in Eq. (H.97), we have:

$$\left[\mathbf{c}^{\sigma'\sigma(1)}_i\right]^T \boldsymbol{\mu} = \sum_j{}' \left(\sum_{\eta\nu} \frac{\left[c^{\sigma'}_{\nu j}\right]^* c^{\sigma}_{\eta i} b^{\sigma'\sigma}_{\nu\eta}}{\epsilon^{\sigma}_i - \epsilon^{\sigma'}_j} \right) \left[\mathbf{c}^{\sigma'}_j\right]^T \boldsymbol{\mu} \tag{H.103}$$

Since $\boldsymbol{\mu}$ is an arbitrary basis, we must conclude:

$$\mathbf{c}_i^{\sigma'\sigma(1)} = \sum_j{}' \left(\sum_{\eta\nu} \frac{\left[c_{\nu j}^{\sigma'}\right]^* c_{\eta i}^{\sigma} b_{\nu\eta}^{\sigma'\sigma}}{\epsilon_i^{\sigma} - \epsilon_j^{\sigma'}} \right) \mathbf{c}_j^{\sigma'} \tag{H.104}$$

Let us now define the matrix:

$$G_{ji}^{\sigma'\sigma(1)} = \sum_{\eta\nu} \left[c_{\nu j}^{\sigma'}\right]^* c_{\eta i}^{\sigma} b_{\nu\eta}^{\sigma'\sigma} = \left[G_{ij}^{\sigma\sigma'(1)}\right]^* \tag{H.105}$$

where the Hermiticity of $G_{ji}^{\sigma'\sigma(1)}$ follows from the Hermiticity of the spin-orbit matrix elements. Through Eq. (H.105), we may define the matrix of orbital rotations:

$$U_{ji}^{\sigma'\sigma(1)} = \frac{G_{ji}^{\sigma'\sigma(1)}}{\epsilon_i^{\sigma} - \epsilon_j^{\sigma'}} = -\left[U_{ij}^{\sigma\sigma'(1)}\right]^* \tag{H.106}$$

Substituting Eqs. (H.105) and (H.106) in Eq. (H.104), we have:

$$\mathbf{c}_i^{\sigma'\sigma(1)} = \sum_j{}' \mathbf{c}_j^{\sigma'} U_{ji}^{\sigma'\sigma(1)} = -\sum_j{}' \left[U_{ij}^{\sigma\sigma'(1)}\right]^* \mathbf{c}_j^{\sigma'} \tag{H.107}$$

In summary, once the $\mathbf{c}_i^{\sigma'\sigma(1)}$ have been obtained from Eq. (H.107), the $\mathbf{c}_I^{\sigma'\sigma}$ can be obtained according to Eq. (H.100) as:

$$\mathbf{c}_I^{\sigma'\sigma} \approx \mathbf{c}_i^{\sigma} \delta_{\sigma\sigma'} + \mathbf{c}_i^{\sigma'\sigma(1)} \tag{H.108}$$

In homage to Eq. (H.107), we may define more generally, for arbitrary perturbative order t:

$$\mathbf{c}_i^{\sigma'\sigma(t)} = \sum_j{}' \mathbf{c}_j^{\sigma'} U_{ji}^{\sigma'\sigma(t)} \tag{H.109}$$

It is useful to re-write Eq.(H.109) in matrix notation, as follows:

$$\mathbf{c}^{\sigma'\sigma(t)} = \mathbf{c}^{\sigma'} \mathbf{U}^{\sigma'\sigma(t)} \tag{H.110}$$

where $\mathbf{c}^{\sigma'\sigma(t)}$ and $\mathbf{c}^{\sigma'}$ are matrices which contain the vectors $\mathbf{c}_i^{\sigma'\sigma(t)}$ and $\mathbf{c}_j^{\sigma'}$.

H.4.4 Energy and Eigenvalues in Terms of the Orbital Rotation Matrix

Substituting Eqs. (H.105) and (H.106) in Eq. (H.86), we have a simple expression for the energy in terms of the newly defined matrices:

$$E \approx E^{(0)} + \sum_{\sigma\sigma'} \sum_i \sum_j{}' f_{i\sigma}[1 - f_{j\sigma'}] U_{ji}^{\sigma'\sigma(1)} G_{ij}^{\sigma\sigma'(1)} \tag{H.111}$$

Now substituting Eqs. (H.105) and (H.106) in Eq. (H.89), we find for the eigenvalues:

$$\epsilon_I^{\sigma} \approx \epsilon_i^{\sigma} + \sum_{\sigma'} \sum_{j}{}' U_{ji}^{\sigma'\sigma(1)} G_{ij}^{\sigma\sigma'(1)} \tag{H.112}$$

H.4.5 The Perturbed Density Matrix

Returning to Eq. (H.100), we write, for example the states perturbed from $|i, \alpha\rangle$:

$$\begin{aligned} c_{\mu I}^{\sigma\alpha} f_{i\alpha} \left[c_{\nu I}^{\sigma'\alpha}\right]^* &= \left(c_{\mu i}^{\alpha}\delta_{\alpha\sigma} + \lambda c_{\mu i}^{\sigma\alpha(1)} + \lambda^2 c_{\mu i}^{\sigma\alpha(2)} + \lambda^3 c_{\mu i}^{\sigma\alpha(3)} + ...\right) f_{i\alpha} \\ &\times \left(\left[c_{\nu i}^{\alpha}\right]^* \delta_{\alpha\sigma'} + \lambda \left[c_{\nu i}^{\sigma'\alpha(1)}\right]^* + \lambda^2 \left[c_{\nu i}^{\sigma'\alpha(2)}\right]^* + \lambda^3 \left[c_{\nu i}^{\sigma'\alpha(3)}\right]^* + ...\right) \end{aligned} \tag{H.113}$$

and for the states perturbed from $|i, \beta\rangle$:

$$\begin{aligned} c_{\mu I}^{\sigma\beta} f_{i\beta} \left[c_{\nu I}^{\sigma'\beta}\right]^* &= \left(c_{\mu i}^{\beta}\delta_{\beta\sigma} + \lambda c_{\mu i}^{\sigma\beta(1)} + \lambda^2 c_{\mu i}^{\sigma\beta(2)} + \lambda^2 c_{\mu i}^{\sigma\beta(2)} + \lambda^3 c_{\mu i}^{\sigma\beta(3)} + ...\right) f_{i\beta} \\ &\times \left(\left[c_{\nu i}^{\beta}\right]^* \delta_{\beta\sigma'} + \lambda \left[c_{\nu i}^{\sigma'\beta(1)}\right]^* + \lambda^2 \left[c_{\nu i}^{\sigma'\beta(2)}\right]^* + \lambda^3 \left[c_{\nu i}^{\sigma'\beta(3)}\right]^* + ...\right) \end{aligned} \tag{H.114}$$

Carrying out the multiplication and collecting terms of like order in Eq. (H.113):

$$\begin{aligned} c_{\mu I}^{\sigma\alpha} f_{i\alpha} \left[c_{\nu I}^{\sigma'\alpha}\right]^* &= c_{\mu i}^{\alpha}\delta_{\alpha\sigma}\delta_{\alpha\sigma'} f_{i\alpha} \left[c_{\nu i}^{\alpha}\right]^* \\ &+ \lambda \left(c_{\mu i}^{\alpha}\delta_{\alpha\sigma} f_{i\alpha} \left[c_{\nu i}^{\sigma'\alpha(1)}\right]^* + c_{\mu i}^{\sigma\alpha(1)}\delta_{\alpha\sigma'} f_{i\alpha} \left[c_{\nu i}^{\alpha}\right]^*\right) \\ &+ \lambda^2 \left(c_{\mu i}^{\alpha}\delta_{\alpha\sigma} f_{i\alpha} \left[c_{\nu i}^{\sigma'\alpha(2)}\right]^* + c_{\mu i}^{\sigma\alpha(2)}\delta_{\alpha\sigma'} f_{i\alpha} \left[c_{\nu i}^{\alpha}\right]^* + c_{\mu i}^{\sigma\alpha(1)} f_{i\alpha} \left[c_{\nu i}^{\sigma'\alpha(1)}\right]^*\right) \\ &+ \lambda^3 \left(c_{\mu i}^{\alpha}\delta_{\alpha\sigma} f_{i\alpha} \left[c_{\nu i}^{\sigma'\alpha(3)}\right]^* + c_{\mu i}^{\sigma\alpha(3)}\delta_{\alpha\sigma'} f_{i\alpha} \left[c_{\nu i}^{\alpha}\right]^* + c_{\mu i}^{\sigma\alpha(2)} f_{i\alpha} \left[c_{\nu i}^{\sigma'\alpha(1)}\right]^* + c_{\mu i}^{\sigma\alpha(1)} f_{i\alpha} \left[c_{\nu i}^{\sigma'\alpha(2)}\right]^*\right) \\ &+ \ldots \end{aligned} \tag{H.115}$$

and similarly collecting terms of like order in Eq. (H.114):

$$\begin{aligned} c_{\mu I}^{\sigma\beta} f_{i\beta} \left[c_{\nu I}^{\sigma'\beta}\right]^* &= c_{\mu i}^{\beta}\delta_{\beta\sigma}\delta_{\beta\sigma'} f_{i\beta} \left[c_{\nu i}^{\beta}\right]^* \\ &+ \lambda \left(c_{\mu i}^{\beta}\delta_{\beta\sigma} f_{i\beta} \left[c_{\nu i}^{\sigma'\beta(1)}\right]^* + c_{\mu i}^{\sigma\beta(1)}\delta_{\beta\sigma'} f_{i\beta} \left[c_{\nu i}^{\beta}\right]^*\right) \\ &+ \lambda^2 \left(c_{\mu i}^{\beta}\delta_{\beta\sigma} f_{i\beta} \left[c_{\nu i}^{\sigma'\beta(2)}\right]^* + c_{\mu i}^{\sigma\beta(2)}\delta_{\beta\sigma'} f_{i\beta} \left[c_{\nu i}^{\beta}\right]^* + c_{\mu i}^{\sigma\beta(1)} f_{i\beta} \left[c_{\nu i}^{\sigma'\beta(1)}\right]^*\right) \\ &+ \lambda^3 \left(c_{\mu i}^{\beta}\delta_{\beta\sigma} f_{i\beta} \left[c_{\nu i}^{\sigma'\beta(3)}\right]^* + c_{\mu i}^{\sigma\beta(3)}\delta_{\beta\sigma'} f_{i\beta} \left[c_{\nu i}^{\beta}\right]^* + c_{\mu i}^{\sigma\beta(2)} f_{i\beta} \left[c_{\nu i}^{\sigma'\beta(1)}\right]^* + c_{\mu i}^{\sigma\beta(1)} f_{i\beta} \left[c_{\nu i}^{\sigma'\beta(2)}\right]^*\right) \\ &+ \ldots \end{aligned} \tag{H.116}$$

Summing both sides of Eqs. (H.115) and (H.116) over all states, we define the FR density matrix:

$$\begin{aligned}
\mathbb{P}^{\sigma\sigma'}_{\mu\nu} &= \sum_i c^{\sigma\alpha}_{\mu I} f_{i\alpha} \left[c^{\sigma'\alpha}_{\nu I}\right]^* + c^{\sigma\beta}_{\mu I} f_{i\beta} \left[c^{\sigma'\beta}_{\nu I}\right]^* \\
&= \sum_i c^{\alpha}_{\mu i} \delta_{\alpha\sigma} \delta_{\alpha\sigma'} f_{i\alpha} \left[c^{\alpha}_{\nu i}\right]^* + c^{\beta}_{\mu i} \delta_{\beta\sigma} \delta_{\beta\sigma'} f_{i\beta} \left[c^{\beta}_{\nu i}\right]^* \\
&+ \lambda \sum_i \Big(c^{\alpha}_{\mu i} \delta_{\alpha\sigma} f_{i\alpha} \left[c^{\sigma'\alpha(1)}_{\nu i}\right]^* + c^{\beta}_{\mu i} \delta_{\beta\sigma} f_{i\beta} \left[c^{\sigma'\beta(1)}_{\nu i}\right]^* \\
&+ c^{\sigma\alpha(1)}_{\mu i} \delta_{\alpha\sigma'} f_{i\alpha} \left[c^{\alpha}_{\nu i}\right]^* + c^{\sigma\beta(1)}_{\mu i} \delta_{\beta\sigma'} f_{i\beta} \left[c^{\beta}_{\nu i}\right]^* \Big) \\
&+ \lambda^2 \sum_i \Big(c^{\alpha}_{\mu i} \delta_{\alpha\sigma} f_{i\alpha} \left[c^{\sigma'\alpha(2)}_{\nu i}\right]^* + c^{\beta}_{\mu i} \delta_{\beta\sigma} f_{i\beta} \left[c^{\sigma'\beta(2)}_{\nu i}\right]^* \\
&+ c^{\sigma\alpha(2)}_{\mu i} \delta_{\alpha\sigma'} f_{i\alpha} \left[c^{\alpha}_{\nu i}\right]^* + c^{\sigma\beta(2)}_{\mu i} \delta_{\beta\sigma'} f_{i\beta} \left[c^{\beta}_{\nu i}\right]^* \\
&+ c^{\sigma\alpha(1)}_{\mu i} f_{i\alpha} \left[c^{\sigma'\alpha(1)}_{\nu i}\right]^* + c^{\sigma\beta(1)}_{\mu i} f_{i\beta} \left[c^{\sigma'\beta(1)}_{\nu i}\right]^* \Big) \\
&+ \lambda^3 \sum_i \Big(c^{\alpha}_{\mu i} \delta_{\alpha\sigma} f_{i\alpha} \left[c^{\sigma'\alpha(3)}_{\nu i}\right]^* + c^{\beta}_{\mu i} \delta_{\beta\sigma} f_{i\beta} \left[c^{\sigma'\beta(3)}_{\nu i}\right]^* \\
&+ c^{\sigma\alpha(3)}_{\mu i} \delta_{\alpha\sigma'} f_{i\alpha} \left[c^{\alpha}_{\nu i}\right]^* + c^{\sigma\beta(3)}_{\mu i} \delta_{\beta\sigma'} f_{i\beta} \left[c^{\beta}_{\nu i}\right]^* \\
&+ c^{\sigma\alpha(2)}_{\mu i} f_{i\alpha} \left[c^{\sigma'\alpha(1)}_{\nu i}\right]^* + c^{\sigma\beta(2)}_{\mu i} f_{i\beta} \left[c^{\sigma'\beta(1)}_{\nu i}\right]^* \\
&+ c^{\sigma\alpha(1)}_{\mu i} f_{i\alpha} \left[c^{\sigma'\alpha(2)}_{\nu i}\right]^* + c^{\sigma\beta(1)}_{\mu i} f_{i\beta} \left[c^{\sigma'\beta(2)}_{\nu i}\right]^* \Big) \\
&+ \ldots
\end{aligned} \tag{H.117}$$

then setting $\lambda = 1$ and collecting terms of like order, it is possible to define the perturbed density matrix elements:

$$\mathbb{P}^{\sigma\sigma'}_{\mu\nu} \underset{\lambda\to 1}{=} P^{\sigma\sigma'}_{\mu\nu} + \mathbb{P}^{\sigma\sigma'(1)}_{\mu\nu} + \mathbb{P}^{\sigma\sigma'(2)}_{\mu\nu} + \ldots \tag{H.118a}$$

and:

$$\begin{aligned} P^{\sigma\sigma'}_{\mu\nu} &= \sum_i f_{i\alpha} c^{\alpha}_{\mu i}\delta_{\alpha\sigma}\delta_{\alpha\sigma'}\left[c^{\alpha}_{\nu i}\right]^* + f_{i\beta} c^{\beta}_{\mu i}\delta_{\beta\sigma}\delta_{\beta\sigma'}\left[c^{\beta}_{\nu i}\right]^* \end{aligned} \tag{H.118b}$$

$$\begin{aligned} \mathbb{P}^{\sigma\sigma'(1)}_{\mu\nu} &= \sum_i f_{i\alpha}\left(c^{\alpha}_{\mu i}\delta_{\alpha\sigma}\left[c^{\sigma'\alpha(1)}_{\nu i}\right]^* + c^{\sigma\alpha(1)}_{\mu i}\delta_{\alpha\sigma'}\left[c^{\alpha}_{\nu i}\right]^*\right) \\ &+ f_{i\beta}\left(c^{\beta}_{\mu i}\delta_{\beta\sigma}\left[c^{\sigma'\beta(1)}_{\nu i}\right]^* + c^{\sigma\beta(1)}_{\mu i}\delta_{\beta\sigma'}\left[c^{\beta}_{\nu i}\right]^*\right) \end{aligned} \tag{H.118c}$$

$$\begin{aligned} \mathbb{P}^{\sigma\sigma'(2)}_{\mu\nu} &= \sum_i f_{i\alpha}\left(c^{\alpha}_{\mu i}\delta_{\alpha\sigma}\left[c^{\sigma'\alpha(2)}_{\nu i}\right]^* + c^{\sigma\alpha(2)}_{\mu i}\delta_{\alpha\sigma'}\left[c^{\alpha}_{\nu i}\right]^*\right) \\ &+ f_{i\beta}\left(c^{\beta}_{\mu i}\delta_{\beta\sigma}\left[c^{\sigma'\beta(2)}_{\nu i}\right]^* + c^{\sigma\beta(2)}_{\mu i}\delta_{\beta\sigma'}\left[c^{\beta}_{\nu i}\right]^*\right) \\ &+ c^{\sigma\alpha(1)}_{\mu i} f_{i\alpha}\left[c^{\sigma'\alpha(1)}_{\nu i}\right]^* + c^{\sigma\beta(1)}_{\mu i} f_{i\beta}\left[c^{\sigma'\beta(1)}_{\nu i}\right]^* \end{aligned} \tag{H.118d}$$

$$\begin{aligned} \mathbb{P}^{\sigma\sigma'(3)}_{\mu\nu} &= \sum_i f_{i\alpha}\left(c^{\alpha}_{\mu i}\delta_{\alpha\sigma}\left[c^{\sigma'\alpha(3)}_{\nu i}\right]^* + c^{\sigma\alpha(3)}_{\mu i}\delta_{\alpha\sigma'}\left[c^{\alpha}_{\nu i}\right]^*\right) \\ &+ f_{i\beta}\left(c^{\beta}_{\mu i}\delta_{\beta\sigma}\left[c^{\sigma'\beta(3)}_{\nu i}\right]^* + c^{\sigma\beta(3)}_{\mu i}\delta_{\beta\sigma'}\left[c^{\beta}_{\nu i}\right]^*\right) \\ &+ c^{\sigma\alpha(2)}_{\mu i} f_{i\alpha}\left[c^{\sigma'\alpha(1)}_{\nu i}\right]^* + c^{\sigma\beta(2)}_{\mu i} f_{i\beta}\left[c^{\sigma'\beta(1)}_{\nu i}\right]^* \\ &+ c^{\sigma\alpha(1)}_{\mu i} f_{i\alpha}\left[c^{\sigma'\alpha(2)}_{\nu i}\right]^* + c^{\sigma\beta(1)}_{\mu i} f_{i\beta}\left[c^{\sigma'\beta(2)}_{\nu i}\right]^* \\ &\cdots \end{aligned} \tag{H.118e}$$

Defining $\mathbf{f}_\alpha$ and $\mathbf{f}_\beta$ as the diagonal matrices containing the elements $f_{i\alpha}$ and $f_{i\beta}$, we can write Eqs. (H.118b)-(H.118d) in matrix form, as follows:

$$\mathbf{P}^{\sigma\sigma'} = \delta_{\sigma\sigma'}\mathbf{c}^{\sigma}\mathbf{f}_{\sigma}\left[\mathbf{c}^{\sigma}\right]^{\dagger} \tag{H.119a}$$

$$\mathbb{P}^{\sigma\sigma'(1)} = \mathbf{c}^{\sigma}\mathbf{f}_{\sigma}\left[\mathbf{c}^{\sigma\sigma'(1)}\right]^{\dagger} + \mathbf{c}^{\sigma\sigma'(1)}\mathbf{f}_{\sigma'}\left[\mathbf{c}^{\sigma'}\right]^{\dagger} \tag{H.119b}$$

$$\begin{aligned} \mathbb{P}^{\sigma\sigma'(2)} &= \mathbf{c}^{\sigma}\mathbf{f}_{\sigma}\left[\mathbf{c}^{\sigma\sigma'(2)}\right]^{\dagger} + \mathbf{c}^{\sigma\sigma'(2)}\mathbf{f}_{\sigma'}\left[\mathbf{c}^{\sigma'}\right]^{\dagger} \\ &+ \mathbf{c}^{\sigma\alpha(1)}\mathbf{f}_{\alpha}\left[\mathbf{c}^{\alpha\sigma'(1)}\right]^{\dagger} + \mathbf{c}^{\sigma\beta(1)}\mathbf{f}_{\beta}\left[\mathbf{c}^{\beta\sigma'(1)}\right]^{\dagger} \\ \mathbb{P}^{\sigma\sigma'(3)} &= \mathbf{c}^{\sigma}\mathbf{f}_{\sigma}\left[\mathbf{c}^{\sigma\sigma'(3)}\right]^{\dagger} + \mathbf{c}^{\sigma\sigma'(3)}\mathbf{f}_{\sigma'}\left[\mathbf{c}^{\sigma'}\right]^{\dagger} \\ &+ \mathbf{c}^{\sigma\alpha(2)}\mathbf{f}_{\alpha}\left[\mathbf{c}^{\alpha\sigma'(1)}\right]^{\dagger} + \mathbf{c}^{\sigma\beta(2)}\mathbf{f}_{\beta}\left[\mathbf{c}^{\beta\sigma'(1)}\right]^{\dagger} \\ &+ \mathbf{c}^{\sigma\alpha(1)}\mathbf{f}_{\alpha}\left[\mathbf{c}^{\alpha\sigma'(2)}\right]^{\dagger} + \mathbf{c}^{\sigma\beta(1)}\mathbf{f}_{\beta}\left[\mathbf{c}^{\beta\sigma'(2)}\right]^{\dagger} \\ &\cdots \end{aligned} \tag{H.119c}$$

We can calculate the $P^{\sigma\sigma'}_{\mu\nu}$ from Eq. (H.118b) and $\mathbb{P}^{\sigma\sigma'(1)}_{\mu\nu}$ through the matrix $U^{\sigma'\sigma(1)}_{ji}$ from Eq. (H.107). However, it is not immediately obvious how to calculate $\mathbb{P}^{\sigma\sigma'(2)}_{\mu\nu}$, because it depends on $c^{\alpha\sigma'(2)}_{\mu i}$ and $c^{\beta\sigma'(2)}_{\mu i}$

(and hence $U_{ji}^{\alpha\sigma'(2)}$ and $U_{ji}^{\beta\sigma'(2)}$), which we do not yet know how to calculate.

In order to simplify the expression for $\mathbb{P}_{\mu\nu}^{\sigma\sigma'(2)}$, we expand the orthogonality conditions:

$$\begin{aligned}\sum_{\sigma}\left[\mathbf{c}^{\sigma'\sigma}\right]^{\dagger}\mathbf{S}^{\sigma\sigma}\mathbf{c}^{\sigma\sigma''} &= \sum_{\sigma}\left(\left[\mathbf{c}^{\sigma'}\right]^{\dagger}\delta_{\sigma\sigma'}+\lambda\left[\mathbf{c}^{\sigma'\sigma(1)}\right]^{\dagger}+\lambda^{2}\left[\mathbf{c}^{\sigma'\sigma(2)}\right]^{\dagger}+\lambda^{3}\left[\mathbf{c}^{\sigma'\sigma(3)}\right]^{\dagger}+...\right)\mathbf{S}^{\sigma\sigma}\\ &\times\left(\mathbf{c}^{\sigma''}\delta_{\sigma\sigma''}+\lambda\mathbf{c}^{\sigma\sigma''(1)}+\lambda^{2}\mathbf{c}^{\sigma\sigma''(2)}+\lambda^{3}\mathbf{c}^{\sigma\sigma''(3)}+...\right)=\boldsymbol{\delta}_{\sigma'\sigma''}\end{aligned} \tag{H.120}$$

where $\mathbf{S}^{\sigma\sigma'}$ is the overlap matrix in the AO basis. Then, for arbitrary perturbative order $t > 0$, taking the derivative to order t of Eq. (H.120) and setting $\lambda = 0$, we obtain a set of equations:

$$[\mathbf{c}^{\sigma}]^{\dagger}\mathbf{S}^{\sigma\sigma'}\mathbf{c}^{\sigma'} = \boldsymbol{\delta}_{\sigma\sigma'} \tag{H.121a}$$

$$\sum_{\sigma}\left[\mathbf{c}^{\sigma'\sigma(1)}\right]^{\dagger}\mathbf{S}^{\sigma\sigma}\delta_{\sigma\sigma''}\mathbf{c}^{\sigma''}+\left[\mathbf{c}^{\sigma'}\right]^{\dagger}\delta_{\sigma\sigma'}\mathbf{S}^{\sigma\sigma}\mathbf{c}^{\sigma\sigma''(1)} = \mathbf{0} \tag{H.121b}$$

$$\sum_{\sigma}\left[\mathbf{c}^{\sigma'\sigma(2)}\right]^{\dagger}\mathbf{S}^{\sigma\sigma}\delta_{\sigma\sigma''}\mathbf{c}^{\sigma''}+\left[\mathbf{c}^{\sigma'}\right]^{\dagger}\delta_{\sigma\sigma'}\mathbf{S}^{\sigma\sigma}\mathbf{c}^{\sigma\sigma''(2)}+\left[\mathbf{c}^{\sigma'\sigma(1)}\right]^{\dagger}\mathbf{S}^{\sigma\sigma}\mathbf{c}^{\sigma\sigma''(1)} = \mathbf{0} \tag{H.121c}$$

$$\sum_{\sigma}\left[\mathbf{c}^{\sigma'\sigma(3)}\right]^{\dagger}\mathbf{S}^{\sigma\sigma}\delta_{\sigma\sigma''}\mathbf{c}^{\sigma''}+\left[\mathbf{c}^{\sigma'}\right]^{\dagger}\delta_{\sigma\sigma'}\mathbf{S}^{\sigma\sigma}\mathbf{c}^{\sigma\sigma''(3)}+\left[\mathbf{c}^{\sigma'\sigma(2)}\right]^{\dagger}\mathbf{S}^{\sigma\sigma}\mathbf{c}^{\sigma\sigma''(1)}+\left[\mathbf{c}^{\sigma'\sigma(1)}\right]^{\dagger}\mathbf{S}^{\sigma\sigma}\mathbf{c}^{\sigma\sigma''(2)} = \mathbf{0} \tag{H.121d}$$

$$\cdots$$

Now substituting Eq. (H.110) in Eq. (H.121b):

$$\sum_{\sigma}\left[\mathbf{U}^{\sigma'\sigma(1)}\right]^{\dagger}[\mathbf{c}^{\sigma}]^{\dagger}\mathbf{S}^{\sigma\sigma}\delta_{\sigma\sigma''}\mathbf{c}^{\sigma''}+\left[\mathbf{c}^{\sigma'}\right]^{\dagger}\delta_{\sigma\sigma'}\mathbf{S}^{\sigma\sigma}\mathbf{c}^{\sigma}\mathbf{U}^{\sigma\sigma''(1)} = \mathbf{0} \tag{H.122}$$

Evaluating the delta functions, we find:

$$\left[\mathbf{U}^{\sigma'\sigma''(1)}\right]^{\dagger}\left[\mathbf{c}^{\sigma''}\right]^{\dagger}\mathbf{S}^{\sigma''\sigma''}\mathbf{c}^{\sigma''}+\left[\mathbf{c}^{\sigma'}\right]^{\dagger}\mathbf{S}^{\sigma'\sigma'}\mathbf{c}^{\sigma'}\mathbf{U}^{\sigma'\sigma''(1)} = \mathbf{0} \tag{H.123a}$$

Substituting Eq. (H.121a) in Eq. (H.123a) we find:

$$\mathbf{U}^{\sigma'\sigma''(1)} = -\left[\mathbf{U}^{\sigma'\sigma''(1)}\right]^{\dagger} \tag{H.123b}$$

We now pass to the second-order orthogonality conditions and substitute Eq. (H.110) in Eq. (H.121c):

$$\begin{aligned}\mathbf{0} &= \sum_{\sigma}\left[\mathbf{U}^{\sigma'\sigma(2)}\right]^{\dagger}[\mathbf{c}^{\sigma}]^{\dagger}\mathbf{S}^{\sigma\sigma}\delta_{\sigma\sigma''}\mathbf{c}^{\sigma''}+\left[\mathbf{c}^{\sigma'}\right]^{\dagger}\delta_{\sigma\sigma'}\mathbf{S}^{\sigma\sigma}\mathbf{c}^{\sigma}\mathbf{U}^{\sigma\sigma''(2)}\\ &+ \left[\mathbf{U}^{\sigma'\sigma(1)}\right]^{\dagger}[\mathbf{c}^{\sigma}]^{\dagger}\mathbf{S}^{\sigma\sigma}\mathbf{c}^{\sigma}\mathbf{U}^{\sigma\sigma''(1)}\end{aligned} \tag{H.124}$$

Evaluating the delta functions:

$$\begin{aligned}
\mathbf{0} \;&=\; \left[\mathbf{U}^{\sigma'\sigma''(2)}\right]^{\dagger}\left[\mathbf{c}^{\sigma''}\right]^{\dagger}\mathbf{S}^{\sigma''\sigma''}\mathbf{c}^{\sigma''} + \left[\mathbf{c}^{\sigma'}\right]^{\dagger}\mathbf{S}^{\sigma'\sigma'}\mathbf{c}^{\sigma'}\mathbf{U}^{\sigma'\sigma''(2)} \\
&+\; \sum_{\sigma}\left[\mathbf{U}^{\sigma'\sigma(1)}\right]^{\dagger}\left[\mathbf{c}^{\sigma}\right]^{\dagger}\mathbf{S}^{\sigma\sigma}\mathbf{c}^{\sigma}\mathbf{U}^{\sigma\sigma''(1)}
\end{aligned} \tag{H.125}$$

Substituting Eq. (H.121a) in Eq. (H.125), we have finally:

$$\left[\mathbf{U}^{\sigma'\sigma''(2)}\right]^{\dagger} + \mathbf{U}^{\sigma'\sigma''(2)} = -\sum_{\sigma}\left[\mathbf{U}^{\sigma'\sigma(1)}\right]^{\dagger}\mathbf{U}^{\sigma\sigma''(1)} \tag{H.126}$$

Proceeding now to the third-order orthogonality conditions and substituting Eq. (H.110) in Eq. (H.121c):

$$\begin{aligned}
\mathbf{0} \;&=\; \left[\mathbf{U}^{\sigma'\sigma''(3)}\right]^{\dagger}\left[\mathbf{c}^{\sigma''}\right]^{\dagger}\mathbf{S}^{\sigma''\sigma''}\mathbf{c}^{\sigma''} + \left[\mathbf{c}^{\sigma'}\right]^{\dagger}\mathbf{S}^{\sigma'\sigma'}\mathbf{c}^{\sigma'}\mathbf{U}^{\sigma'\sigma''(3)} \\
&+\; \sum_{\sigma}\left\{\left[\mathbf{U}^{\sigma'\sigma(2)}\right]^{\dagger}\left[\mathbf{c}^{\sigma}\right]^{\dagger}\mathbf{S}^{\sigma\sigma}\mathbf{c}^{\sigma}\mathbf{U}^{\sigma\sigma''(1)} + \left[\mathbf{U}^{\sigma'\sigma(1)}\right]^{\dagger}\left[\mathbf{c}^{\sigma}\right]^{\dagger}\mathbf{S}^{\sigma\sigma}\mathbf{c}^{\sigma}\mathbf{U}^{\sigma\sigma''(2)}\right\}
\end{aligned} \tag{H.127}$$

Substituting Eq. (H.121a) in Eq. (H.125), we find an expression for the third order orbital rotation matrix in terms of the lower order ones:

$$\left[\mathbf{U}^{\sigma'\sigma''(3)}\right]^{\dagger} + \mathbf{U}^{\sigma'\sigma''(3)} = -\sum_{\sigma}\left\{\left[\mathbf{U}^{\sigma'\sigma(2)}\right]^{\dagger}\mathbf{U}^{\sigma\sigma''(1)} + \left[\mathbf{U}^{\sigma'\sigma(1)}\right]^{\dagger}\mathbf{U}^{\sigma\sigma''(2)}\right\} \tag{H.128}$$

We now show how to calculate the remaining terms involving $\mathbf{U}^{\sigma'\sigma(2)}$ in Eq. (H.119c). In order to do this, an expression must be found for the $\mathbf{U}^{\sigma'\sigma(2)}$.

The Roothaan-Hall or Kohn-Sham equations in the AO basis are expanded in orders of the perturbation, as follows:

$$\begin{aligned}
&\left(\underline{\mathbf{F}} + \lambda\underline{\mathbb{F}}^{(1)} + \lambda^{2}\underline{\mathbb{F}}^{(2)} + \lambda^{3}\underline{\mathbb{F}}^{(3)} + ...\right)\left(\underline{\mathbf{c}} + \lambda\underline{\mathbf{c}}^{(1)} + \lambda^{2}\underline{\mathbf{c}}^{(2)} + \lambda^{3}\underline{\mathbf{c}}^{(3)} + ...\right) = \\
&\quad\underline{\mathbf{S}}\left(\underline{\mathbf{c}} + \lambda\underline{\mathbf{c}}^{(1)} + \lambda^{2}\underline{\mathbf{c}}^{(2)} + \lambda^{3}\underline{\mathbf{c}}^{(3)} + ...\right)\left(\underline{\boldsymbol{\epsilon}} + \lambda\underline{\boldsymbol{\epsilon}}^{(1)} + \lambda^{2}\underline{\boldsymbol{\epsilon}}^{(2)} + \lambda^{3}\underline{\boldsymbol{\epsilon}}^{(3)} + ...\right)
\end{aligned} \tag{H.129}$$

where the underlined notation denotes matrices, like for example:

$$\underline{\mathbb{F}} = \begin{pmatrix} \mathbb{F}^{\alpha\alpha} & \mathbb{F}^{\alpha\beta} \\ \mathbb{F}^{\beta\alpha} & \mathbb{F}^{\beta\beta} \end{pmatrix} \tag{H.130}$$

Collecting terms of like order in Eq. (H.129) and setting $\lambda \to 1$, we obtain the following set of equations:

$$\underline{\mathbf{F}}\,\underline{\mathbf{c}} = \underline{\mathbf{S}}\,\underline{\mathbf{c}}\,\underline{\boldsymbol{\epsilon}} \tag{H.131a}$$

$$\underline{\mathbb{F}}^{(1)}\,\underline{\mathbf{c}} + \underline{\mathbf{F}}\,\underline{\mathbf{c}}^{(1)} = \underline{\mathbf{S}}\,\underline{\mathbf{c}}^{(1)}\,\underline{\boldsymbol{\epsilon}} + \underline{\mathbf{S}}\,\underline{\mathbf{c}}\,\underline{\boldsymbol{\epsilon}}^{(1)} \tag{H.131b}$$

$$\underline{\mathbb{F}}^{(2)}\,\underline{\mathbf{c}} + \underline{\mathbb{F}}^{(1)}\,\underline{\mathbf{c}}^{(1)} + \underline{\mathbf{F}}\,\underline{\mathbf{c}}^{(2)} = \underline{\mathbf{S}}\,\underline{\mathbf{c}}^{(2)}\,\underline{\boldsymbol{\epsilon}} + \underline{\mathbf{S}}\,\underline{\mathbf{c}}^{(1)}\,\underline{\boldsymbol{\epsilon}}^{(1)} + \underline{\mathbf{S}}\,\underline{\mathbf{c}}\,\underline{\boldsymbol{\epsilon}}^{(2)} \tag{H.131c}$$

$$\underline{\mathbb{F}}^{(3)}\,\underline{\mathbf{c}} + \underline{\mathbb{F}}^{(2)}\,\underline{\mathbf{c}}^{(1)} + \underline{\mathbb{F}}^{(1)}\,\underline{\mathbf{c}}^{(2)} + \underline{\mathbf{F}}\,\underline{\mathbf{c}}^{(3)} = \underline{\mathbf{S}}\,\underline{\mathbf{c}}^{(3)}\,\underline{\boldsymbol{\epsilon}} + \underline{\mathbf{S}}\,\underline{\mathbf{c}}^{(2)}\,\underline{\boldsymbol{\epsilon}}^{(1)} + \underline{\mathbf{S}}\,\underline{\mathbf{c}}^{(1)}\,\underline{\boldsymbol{\epsilon}}^{(2)} + \underline{\mathbf{S}}\,\underline{\mathbf{c}}\,\underline{\boldsymbol{\epsilon}}^{(3)} \tag{H.131d}$$

$$\ldots$$

Let us now define the matrices:

$$\underline{\mathbf{G}}^{(n)} = \left[\underline{\mathbf{c}}\right]^{\dagger}\;\underline{\mathbb{F}}^{(n)}\,\underline{\mathbf{c}} \tag{H.132}$$

Left multiplying Eq. (H.131) by $\left[\underline{\mathbf{c}}\right]^{\dagger}$ and then substituting Eq. (H.110) and Eq. (H.132), we obtain:

$$\underline{\mathbf{G}}^{(0)} = \underline{\boldsymbol{\epsilon}} \tag{H.133a}$$

$$\underline{\mathbf{G}}^{(1)} + \underline{\boldsymbol{\epsilon}}\,\underline{\mathbf{U}}^{(1)} = \underline{\mathbf{U}}^{(1)}\,\underline{\boldsymbol{\epsilon}} + \underline{\boldsymbol{\epsilon}}^{(1)} \tag{H.133b}$$

$$\underline{\mathbf{G}}^{(2)} + \underline{\boldsymbol{\epsilon}}\,\underline{\mathbf{U}}^{(2)} + \underline{\mathbf{G}}^{(1)}\,\underline{\mathbf{U}}^{(1)} = \underline{\mathbf{U}}^{(2)}\,\underline{\boldsymbol{\epsilon}} + \underline{\mathbf{U}}^{(1)}\,\underline{\boldsymbol{\epsilon}}^{(1)} + \underline{\boldsymbol{\epsilon}}^{(2)} \tag{H.133c}$$

$$\underline{\mathbf{G}}^{(3)} + \underline{\mathbf{G}}^{(2)}\,\underline{\mathbf{U}}^{(1)} + \underline{\mathbf{G}}^{(1)}\,\underline{\mathbf{U}}^{(2)} + \underline{\boldsymbol{\epsilon}}\,\underline{\mathbf{U}}^{(3)} = \underline{\mathbf{U}}^{(3)}\,\underline{\boldsymbol{\epsilon}} + \underline{\mathbf{U}}^{(2)}\,\underline{\boldsymbol{\epsilon}}^{(1)} + \underline{\mathbf{U}}^{(1)}\,\underline{\boldsymbol{\epsilon}}^{(2)} + \underline{\boldsymbol{\epsilon}}^{(3)} \tag{H.133d}$$

$$\ldots$$

We now recall that from Eqs. (H.105) and (H.132), neglecting the orbital-relaxation contribution equates to setting:

$$\underline{\mathbf{G}}^{(1)} = \left[\underline{\mathbf{c}}\right]^{\dagger}\;\underline{\mathbf{b}}\,\underline{\mathbf{c}} \tag{H.134}$$

and:

$$\underline{\mathbf{G}}^{(2)} = \mathbf{0} \tag{H.135}$$

$$\underline{\mathbf{G}}^{(3)} = \mathbf{0} \tag{H.136}$$

Substituting Eqs. (H.134) and (H.135) in Eqs. (H.133c) and (H.133d), we find:

$$U_{ji}^{\sigma'\sigma(2)} = \frac{1}{\epsilon_j^{\sigma'} - \epsilon_i^{\sigma}} \Big(\sum_{\sigma''} \sum_k{}' U_{jk}^{\sigma'\sigma''(1)} \epsilon_{ki}^{\sigma''\sigma(1)} - \sum_{\sigma''} \sum_k{}' G_{jk}^{\sigma'\sigma''(1)} U_{ki}^{\sigma''\sigma(1)} + \epsilon_{ji}^{\sigma'\sigma(2)} \Big) \tag{H.137}$$

$$\begin{aligned} U_{ji}^{\sigma'\sigma(3)} &= \frac{1}{\epsilon_j^{\sigma'} - \epsilon_i^{\sigma}} \Big(\sum_{\sigma''} \sum_k{}' U_{jk}^{\sigma'\sigma''(2)} \epsilon_{ki}^{\sigma''\sigma(1)} - \sum_{\sigma''} \sum_k{}' G_{jk}^{\sigma'\sigma''(1)} U_{ki}^{\sigma''\sigma(2)} \\ &+ \sum_{\sigma''} \sum_k{}' U_{jk}^{\sigma'\sigma''(1)} \epsilon_{ki}^{\sigma''\sigma(2)} + \epsilon_{ji}^{\sigma'\sigma(3)} \Big) \end{aligned} \tag{H.138}$$

On the other hand, if orbital-relaxation is taken into account, then we set:

$$\underline{\mathbf{G}}^{(1)} = \left[\underline{\mathbf{c}}\right]^{\dagger} \underline{\mathbb{F}}^{(1)} \underline{\mathbf{c}} = \left[\underline{\mathbf{c}}\right]^{\dagger} \left(\underline{\mathbf{b}} + \underline{\mathbb{C}}^{(1)} - \underline{\mathbb{K}}^{(1)}\right) \underline{\mathbf{c}} \tag{H.139}$$

where the $\underline{\mathbb{C}}^{(n)}$ and $\underline{\mathbb{K}}^{(n)}$ are the perturbed Coulomb and Fock exchange matrices, defined in terms of the perturbed density matrix:

$$\mathbb{C}_{\mu\nu}^{\sigma\sigma'(n)} = \delta_{\sigma\sigma'} \sum_{\tau\omega} \mathrm{Re}\left[\mathbb{P}_{\tau\omega}^{\alpha\alpha(n)} + \mathbb{P}_{\tau\omega}^{\beta\beta(n)}\right] (\mu\nu|\tau\omega) \tag{H.140a}$$

$$\mathbb{K}_{\mu\nu}^{\sigma\sigma'(n)} = \sum_{\tau\omega} \mathbb{P}_{\tau\omega}^{\sigma\sigma'(n)} (\mu\tau|\omega\nu) \tag{H.140b}$$

and:

$$\underline{\mathbf{G}}^{(2)} = \left[\underline{\mathbf{c}}\right]^{\dagger} \underline{\mathbb{F}}^{(2)} \underline{\mathbf{c}} = \left[\underline{\mathbf{c}}\right]^{\dagger} \left(\underline{\mathbb{C}}^{(2)} - \underline{\mathbb{K}}^{(2)}\right) \underline{\mathbf{c}} \tag{H.141a}$$

$$\underline{\mathbf{G}}^{(3)} = \left[\underline{\mathbf{c}}\right]^{\dagger} \underline{\mathbb{F}}^{(3)} \underline{\mathbf{c}} = \left[\underline{\mathbf{c}}\right]^{\dagger} \left(\underline{\mathbb{C}}^{(3)} - \underline{\mathbb{K}}^{(3)}\right) \underline{\mathbf{c}} \tag{H.141b}$$

For the specific case of Eq. (H.139), given that the diagonal spin-blocks of the first-order perturbed-density matrix are purely imaginary, it is clear from Eq. (H.140a) that:

$$\underline{\mathbb{C}}^{(1)} = 0 \tag{H.142}$$

Substituting Eq. (H.142) in Eq. (H.139), we find:

$$\underline{\mathbf{G}}^{(1)} = \left[\underline{\mathbf{c}}\right]^{\dagger} \left(\underline{\mathbf{b}} - \underline{\mathbb{K}}^{(1)}\right) \underline{\mathbf{c}} \tag{H.143}$$

Substituting Eqs. (H.141a)-(H.143) into Eqs. (H.133c) and (H.133d), the corresponding expressions are found for $\underline{\mathbf{U}}^{(2)}$ and $\underline{\mathbf{U}}^{(3)}$ according to the coupled-perturbed approach:

$$
\begin{aligned}
U_{ji}^{\sigma'\sigma(2)} &= \frac{1}{\epsilon_j^{\sigma'} - \epsilon_i^{\sigma}} \Big(\sum_{\sigma''} \sum_k{}' U_{jk}^{\sigma'\sigma''(1)} \epsilon_{ki}^{\sigma''\sigma(1)} - \sum_{\sigma''} \sum_k{}' G_{jk}^{\sigma'\sigma''(1)} U_{ki}^{\sigma''\sigma(1)} + \epsilon_{ji}^{\sigma'\sigma(2)} - G_{ji}^{\sigma'\sigma(2)} \Big) \qquad \text{(H.144)} \\
U_{ji}^{\sigma'\sigma(3)} &= \frac{1}{\epsilon_j^{\sigma'} - \epsilon_i^{\sigma}} \Big(\sum_{\sigma''} \sum_k{}' U_{jk}^{\sigma'\sigma''(2)} \epsilon_{ki}^{\sigma''\sigma(1)} - \sum_{\sigma''} \sum_k{}' G_{jk}^{\sigma'\sigma''(1)} U_{ki}^{\sigma''\sigma(2)} \\
&+ \sum_{\sigma''} \sum_k{}' U_{jk}^{\sigma'\sigma''(1)} \epsilon_{ki}^{\sigma''\sigma(2)} + \epsilon_{ji}^{\sigma'\sigma(3)} - G_{ji}^{\sigma'\sigma(3)} - \sum_{\sigma''} \sum_k{}' G_{jk}^{\sigma'\sigma''(2)} U_{ki}^{\sigma''\sigma(1)} \Big) \qquad \text{(H.145)}
\end{aligned}
$$

H.5 The Non-Canonical Formulation

The expressions for the perturbed eigenvalues, eigenstates and density matrix from the previous section H.3 are approximate because, so far, they exclude contributions from degenerate states. The contribution from degenerate states further introduces an inconvenience when implementing them in a computer program, because a numerical tolerance on differences in the ϵ_i^{σ} would be needed to determine if the states are degenerate. In principle, the contributions from degenerate states could then be included, using the degenerate theory of section H.2, but this would considerably complicate the calculation procedure. It is thus advantegeous to re-formulate the expressions, as much as possible, in a manner that contributions from degenerate states naturally goes to zero. In order to do this, we note that the definition of the $\underline{\mathbf{U}}^{(t)}$ from Eq. (H.110) is not unique, because the only constraints on the $\underline{\mathbf{U}}^{(t)}$ are those provided from the orthogonality conditions and the perturbation equations, that is to say Eqs. (H.123b), (H.126), and (H.133). We can exploit this non-uniqueness to simplify the calculation procedure.

Let us start with the first order perturbation equation from Eq. (H.133b). we enforce that the occupied-virtual blocks of the Lagrange multiplier matrix are zero. That is to say:

$$\epsilon_{mp}^{\sigma\sigma'(1)} = \epsilon_{pm}^{\sigma'\sigma(1)} = 0 \qquad \text{(H.146)}$$

and:

$$\epsilon_{mp}^{\sigma\sigma'(2)} = \epsilon_{pm}^{\sigma'\sigma(2)} = 0 \qquad \text{(H.147)}$$

$$\epsilon_{mp}^{\sigma\sigma'(3)} = \epsilon_{pm}^{\sigma'\sigma(3)} = 0 \qquad \text{(H.148)}$$

H.5.1 The Orbital Rotation Matrices

Inserting Eq. (H.146) in Eq. (H.133b), we then find the expression for the occupied-virtual blocks of $\underline{\mathbf{U}}^{(1)}$:

$$U_{mp}^{\sigma'\sigma(1)} = \frac{G_{mp}^{\sigma'\sigma(1)}}{\epsilon_p^{\sigma} - \epsilon_m^{\sigma'}} = -\left[U_{pm}^{\sigma\sigma'(1)}\right]^* \qquad \text{(H.149)}$$

where the anti-Hermitian character of the occupied-virtual blocks of $\underline{\mathbf{U}}^{(1)}$ is consistent with Eq. (H.123b), as well as from the Hermiticity of $\underline{\mathbf{G}}^{(1)}$.

For the occupied-occupied and virtual-virtual blocks of $\underline{\mathbf{U}}^{(1)}$, we make the simplest choice which satisfies Eq. (H.123b) and enforce:

$$U_{mn}^{\sigma'\sigma(1)} = 0 \tag{H.150}$$

and:

$$U_{pq}^{\sigma'\sigma(1)} = 0 \tag{H.151}$$

Given that the occupied-occupied and virtual-virtual blocks of $\underline{\mathbf{U}}^{(1)}$ vanish, it follows from Eq. (H.133b) that:

$$\epsilon_{mn}^{\sigma\sigma'(1)} = G_{mn}^{\sigma\sigma'(1)} \tag{H.152}$$

and:

$$\epsilon_{pq}^{\sigma\sigma'(1)} = G_{pq}^{\sigma\sigma'(1)} \tag{H.153}$$

Substituting Eqs. (H.149) and (H.152) in Eq. (H.144), we find:

$$U_{pm}^{\sigma'\sigma(2)} = \frac{1}{\epsilon_p^{\sigma'} - \epsilon_m^{\sigma}} \Big(\sum_{\sigma''} \sum_{n}^{\in occ} U_{pn}^{\sigma'\sigma''(1)} G_{nm}^{\sigma''\sigma(1)} - \sum_{\sigma''} \sum_{q}^{\in virt} G_{pq}^{\sigma'\sigma''(1)} U_{qm}^{\sigma''\sigma(1)} - G_{pm}^{\sigma'\sigma(2)} \Big) \tag{H.154}$$

Eq. (H.154) gives an expression for the occupied-virtual blocks of $\underline{\mathbf{U}}^{(2)}$, now with no prime over the summations, because they naturally do not use terms involving degenerate states.

In order to find whether occupied-virtual blocks of $\underline{\mathbf{U}}^{(2)}$ are Hermitian or anti-Hermitian, let us return to Eq. (H.126):

$$\left[U_{mp}^{\sigma''\sigma'(2)} \right]^* + U_{pm}^{\sigma'\sigma''(2)} = - \sum_{\sigma} {\sum_{k}}' \left[U_{kp}^{\sigma\sigma'(1)} \right]^* U_{km}^{\sigma\sigma''(1)} \tag{H.155}$$

From Eqs. (H.150) (H.151), the r.h.s. of Eq. (H.155) goes to zero and we find:

$$U_{pm}^{\sigma'\sigma''(2)} = - \left[U_{mp}^{\sigma''\sigma'(2)} \right]^* \tag{H.156}$$

Eqs. (H.154) and (H.156) tell us how to build the occupied-virtual blocks of $\underline{\mathbf{U}}^{(2)}$.

To find an expression for the occupied-occupied and virtual-virtual blocks of $\underline{\mathbf{U}}^{(2)}$ we return to Eq. (H.126) and find:

$$U_{nm}^{\sigma'\sigma''(2)} = -\frac{1}{2} \sum_{\sigma} \sum_{p}^{\in virt} \left[U_{pn}^{\sigma\sigma'(1)} \right]^* U_{pm}^{\sigma\sigma''(1)} \tag{H.157a}$$

and for the virtual-virtual block:

$$U_{pq}^{\sigma'\sigma''(2)} = -\frac{1}{2} \sum_{\sigma} \sum_{n}^{\in occ} \left[U_{np}^{\sigma\sigma'(1)} \right]^* U_{nq}^{\sigma\sigma''(1)} \tag{H.157b}$$

Eqs. (H.157a) and (H.157b) are valid under the choice that the occupied-occupied and virtual-virtual blocks of $\underline{\mathbf{U}}^{(2)}$ are Hermitian:

$$U_{nm}^{\sigma'\sigma''(2)} = \left[U_{mn}^{\sigma''\sigma'(2)} \right]^* \tag{H.158a}$$

and:

$$U_{pq}^{\sigma'\sigma''(2)} = \left[U_{qp}^{\sigma''\sigma'(2)}\right]^{*} \tag{H.158b}$$

The occupied-virtual blocks of $\underline{\mathbf{U}}^{(3)}$ are found by substituting Eqs. (H.149) and (H.152) and (H.148) in Eq. (H.144):

$$\begin{aligned} U_{pm}^{\sigma'\sigma(3)} &= \frac{1}{\epsilon_p^{\sigma'} - \epsilon_m^{\sigma}}\Big(\sum_{\sigma''}\sum_{n}^{\in occ} U_{pn}^{\sigma'\sigma''(2)} G_{nm}^{\sigma''\sigma(1)} - \sum_{\sigma''}\sum_{n}^{\in occ} G_{pn}^{\sigma'\sigma''(1)} U_{nm}^{\sigma''\sigma(2)} \\ &- \sum_{\sigma''}\sum_{q}^{\in virt} G_{pq}^{\sigma'\sigma''(1)} U_{qm}^{\sigma''\sigma(2)} + \sum_{\sigma''}\sum_{n}^{\in occ} U_{pn}^{\sigma'\sigma''(1)} \epsilon_{nm}^{\sigma''\sigma(2)} \\ &- \sum_{\sigma''}\sum_{q}^{\in virt} G_{pq}^{\sigma'\sigma''(2)} U_{qm}^{\sigma''\sigma(1)} - G_{pm}^{\sigma'\sigma(3)} \Big) \end{aligned} \tag{H.159}$$

Returning to Eq. (H.128), we find that the occ-virt blocks containing the $U_{pm}^{\sigma'\sigma(3)}$ are anti-Hermitian:

$$U_{pm}^{\sigma'\sigma(3)} = -\left[U_{mp}^{\sigma\sigma'(3)}\right]^{*} \tag{H.160}$$

To find an expression for the occ-occ and virt-virt blocks of $\underline{\mathbf{U}}^{(3)}$, we return to Eq. (H.128) and substitute in Eqs. (H.150) and (H.151) to find:

$$U_{nm}^{\sigma'\sigma''(3)} = -\frac{1}{2}\sum_{\sigma}\sum_{p}^{\in virt}\Big(\left[U_{pn}^{\sigma\sigma'(2)}\right]^{*} U_{pm}^{\sigma\sigma''(1)} + \left[U_{pn}^{\sigma\sigma'(1)}\right]^{*} U_{pm}^{\sigma\sigma''(2)}\Big) \tag{H.161a}$$

$$U_{nm}^{\sigma'\sigma''(3)} = \left[U_{mn}^{\sigma''\sigma'(3)}\right]^{*} \tag{H.161b}$$

and for the virtual-virtual block:

$$U_{pq}^{\sigma'\sigma''(3)} = -\frac{1}{2}\sum_{\sigma}\sum_{n}^{\in occ}\Big(\left[U_{np}^{\sigma\sigma'(2)}\right]^{*} U_{nq}^{\sigma\sigma''(1)} + \left[U_{np}^{\sigma\sigma'(1)}\right]^{*} U_{nq}^{\sigma\sigma''(2)}\Big) \tag{H.161c}$$

$$U_{pq}^{\sigma'\sigma''(3)} = \left[U_{qp}^{\sigma''\sigma'(3)}\right]^{*} \tag{H.161d}$$

H.5.2 The Eigenvalues

We now concentrate on finding an expression for the second-order Langrange multiplier matrix $\underline{\boldsymbol{\epsilon}}^{(2)}$. Eq. (H.144) gives us the following general expression:

$$\begin{aligned} \epsilon_{ij}^{\sigma'\sigma''(2)} &= U_{ij}^{\sigma'\sigma''(2)}\left(\epsilon_i^{\sigma'} - \epsilon_j^{\sigma''}\right) - \sum_{\sigma}\sum_{k}{}' U_{ik}^{\sigma'\sigma(1)} \epsilon_{kj}^{\sigma\sigma''(1)} \\ &+ \sum_{\sigma}\sum_{k}{}' G_{ik}^{\sigma'\sigma(1)} U_{kj}^{\sigma\sigma''(1)} + G_{ij}^{\sigma'\sigma''(2)} \end{aligned} \tag{H.162}$$

We note that from Eq.(H.147) the occupied-virtual blocks of $\underline{\boldsymbol{\epsilon}}^{(2)}$ must vanish, so we can concentrate on the occupied-occupied and virtual-virtual blocks. For the occupied-occupied ones, substituting Eqs. (H.146), (H.150) and (H.157a) in Eq. (H.162):

$$\begin{aligned}\epsilon_{nm}^{\sigma'\sigma''(2)} &= -\frac{1}{2}\left(\epsilon_n^{\sigma'} - \epsilon_m^{\sigma''}\right)\sum_{\sigma}\sum_{p}^{\in virt}\left[U_{pn}^{\sigma\sigma'(1)}\right]^* U_{pm}^{\sigma\sigma''(1)} \\ &+ \sum_{\sigma}\sum_{p}^{\in virt} G_{np}^{\sigma'\sigma(1)} U_{pm}^{\sigma\sigma''(1)} + G_{nm}^{\sigma'\sigma''(2)} \qquad \text{(H.163)}\end{aligned}$$

So from the anti-Hermitian character of the occupied-virtual blocks of $\underline{\mathbf{U}}^{(1)}$, from Eq. (H.149), we obtain:

$$\begin{aligned}\epsilon_{nm}^{\sigma'\sigma''(2)} &= \frac{1}{2}\left(\epsilon_n^{\sigma'} - \epsilon_m^{\sigma''}\right)\sum_{\sigma}\sum_{p}^{\in virt} U_{np}^{\sigma'\sigma(1)} U_{pm}^{\sigma\sigma''(1)} \\ &+ \sum_{\sigma}\sum_{p}^{\in virt} G_{np}^{\sigma'\sigma(1)} U_{pm}^{\sigma\sigma''(1)} + G_{nm}^{\sigma'\sigma''(2)} \qquad \text{(H.164)}\end{aligned}$$

Eq. (H.164) can be further simplified by noting that from Eq. (H.149):

$$\sum_{\sigma}\sum_{p}^{\in virt} G_{np}^{\sigma'\sigma(1)} U_{pm}^{\sigma\sigma''(1)} = \sum_{\sigma}\sum_{p}^{\in virt}\left(\epsilon_p^{\sigma} - \epsilon_n^{\sigma'}\right) U_{np}^{\sigma'\sigma(1)} U_{pm}^{\sigma\sigma''(1)} \qquad \text{(H.165)}$$

Substituting Eq. (H.165) in Eq. (H.164):

$$\begin{aligned}\epsilon_{nm}^{\sigma'\sigma''(2)} &= \frac{1}{2}\left(\epsilon_n^{\sigma'} - \epsilon_m^{\sigma''}\right)\sum_{\sigma}\sum_{p}^{\in virt} U_{np}^{\sigma'\sigma(1)} U_{pm}^{\sigma\sigma''(1)} \\ &+ \sum_{\sigma}\sum_{p}^{\in virt}\left(\epsilon_p^{\sigma} - \epsilon_n^{\sigma'}\right) U_{np}^{\sigma'\sigma(1)} U_{pm}^{\sigma\sigma''(1)} + G_{nm}^{\sigma'\sigma''(2)} \qquad \text{(H.166)}\end{aligned}$$

Now for the virtual-virtual blocks of $\underline{\boldsymbol{\epsilon}}^{(2)}$, Substituting Eqs. (H.146), (H.149), (H.151) and (H.157b) in Eq. (H.162):

$$\begin{aligned}\epsilon_{qp}^{\sigma'\sigma''(2)} &= \frac{1}{2}\left(\epsilon_q^{\sigma'} - \epsilon_p^{\sigma''}\right)\sum_{\sigma}\sum_{m}^{\in occ} U_{qm}^{\sigma'\sigma(1)} U_{mp}^{\sigma\sigma''(1)} \\ &+ \sum_{\sigma}\sum_{m}^{\in occ} G_{qm}^{\sigma'\sigma(1)} U_{mp}^{\sigma\sigma''(1)} + G_{qp}^{\sigma'\sigma''(2)} \qquad \text{(H.167)}\end{aligned}$$

and finally, simplifying the term containing the $G_{qm}^{\sigma\sigma''(1)}$ as in Eq. (H.165), we obtain:

$$\begin{aligned}\epsilon_{qp}^{\sigma'\sigma''(2)} &= \frac{1}{2}\left(\epsilon_q^{\sigma'} - \epsilon_p^{\sigma''}\right)\sum_{\sigma}\sum_{m}^{\in occ} U_{qm}^{\sigma'\sigma(1)} U_{mp}^{\sigma\sigma''(1)} \\ &+ \sum_{\sigma}\sum_{m}^{\in occ}\left(\epsilon_m^{\sigma} - \epsilon_q^{\sigma'}\right) U_{qm}^{\sigma'\sigma(1)} U_{mp}^{\sigma\sigma''(1)} + G_{qp}^{\sigma'\sigma''(2)} \qquad \text{(H.168)}\end{aligned}$$

The second-order correction to the FR eigenvalues can thus be obtained by diagonalizing the occupied-occupied and virtual-virtual blocks of the second-order matrix of Lagrange multipliers obtained from Eqs. (H.166) and (H.168).

H.5.3 The Total Energy: Hartree Fock Formalism

The FR total energy $\mathcal{E}$ in the HF approximation is written as:

$$\mathcal{E} = \frac{1}{2}\mathcal{R}\,\mathrm{Tr}\left[\left(\underline{\mathbb{h}} + \underline{\mathbb{F}}\right)\underline{\mathbb{P}}\right] = \frac{1}{2}\sum_{\sigma\sigma'}\mathcal{R}\,\mathrm{Tr}\left[\mathbb{h}^{\sigma\sigma'}\mathbb{P}^{\sigma'\sigma}\right] + \frac{1}{2}\sum_{\sigma\sigma'}\mathcal{R}\,\mathrm{Tr}\left[\mathbb{F}^{\sigma\sigma'}\mathbb{P}^{\sigma'\sigma}\right] \qquad \text{(H.169)}$$

where $\mathcal{R}\,\mathrm{Tr}$ denotes the real part of the trace of the argument in square brackets, $\mathbf{h}^{\sigma\sigma'}$, $\mathbb{F}^{\sigma\sigma'}$ and $\mathbb{P}^{\sigma'\sigma}$ are the spin-blocks of the FR mono-electronic, Fock and density matrices. In Eq. (H.169) use has been made of the fact that the imaginary part of the trace operator goes to zero from the Hermiticity of $\underline{\mathbb{h}}$, $\underline{\mathbb{F}}$ and $\underline{\mathbb{P}}$.

In the following, use will be made of the block-diagonal character in spin space of the SR monoelectronic $\underline{\mathbf{h}}$, SR Fock $\underline{\mathbf{F}}$ and SR density $\underline{\mathbf{P}}$ matrices:

$$\underline{\mathbf{h}} = \begin{pmatrix}\mathbf{h}^{\alpha\alpha} & \mathbf{0}\\ \mathbf{0} & \mathbf{h}^{\beta\beta}\end{pmatrix} \qquad \text{(H.170a)}$$

$$\underline{\mathbf{F}} = \begin{pmatrix}\mathbf{F}^{\alpha\alpha} & \mathbf{0}\\ \mathbf{0} & \mathbf{F}^{\beta\beta}\end{pmatrix} \qquad \text{(H.170b)}$$

$$\underline{\mathbf{P}} = \begin{pmatrix}\mathbf{P}^{\alpha\alpha} & \mathbf{0}\\ \mathbf{0} & \mathbf{P}^{\beta\beta}\end{pmatrix} \qquad \text{(H.170c)}$$

Expanding all quantities in Eq. (H.169) in the perturbation:

$$\begin{aligned}E + \lambda E^{(1)} + \lambda^2 E^{(2)} + \dots &= \frac{1}{2}\sum_{\sigma}\mathcal{R}\,\mathrm{Tr}\left[\left(\mathbf{F}^{\sigma\sigma}\right) + \mathbf{h}^{\sigma\sigma}\left(\mathbf{P}^{\sigma\sigma} + \lambda\mathbb{P}^{\sigma\sigma(1)} + \lambda^2\mathbb{P}^{\sigma\sigma(2)} + \dots\right)\right] \\ &+ \frac{1}{2}\sum_{\sigma\sigma'}\mathcal{R}\,\mathrm{Tr}\left[\left\{\lambda\left(\mathbb{h}^{\sigma\sigma'(1)} + \mathbb{F}^{\sigma\sigma'(1)}\right) + \lambda^2\left(\mathbb{h}^{\sigma\sigma'(2)} + \mathbb{F}^{\sigma\sigma'(2)}\right) + \dots\right\}\right. \\ &\times \left.\left(\mathbf{P}^{\sigma'\sigma} + \lambda\mathbb{P}^{\sigma'\sigma(1)} + \lambda^2\mathbb{P}^{\sigma'\sigma(2)} + \dots\right)\right] \qquad \text{(H.171)}\end{aligned}$$

Then taking successively higher order derivatives of both sides of Eq. (H.171), collecting terms of like order and setting λ to zero, we find:

$$E = \frac{1}{2}\sum_{\sigma}\mathcal{R}\,\mathrm{Tr}\left[\left(\mathbf{h}^{\sigma\sigma}+\mathbf{F}^{\sigma\sigma}\right)\mathbf{P}^{\sigma\sigma}\right] \tag{H.172a}$$

$$\begin{aligned} E^{(1)} &= \frac{1}{2}\sum_{\sigma}\mathcal{R}\,\mathrm{Tr}\left[\left(\mathbf{h}^{\sigma\sigma}+\mathbf{F}^{\sigma\sigma}\right)\mathbb{P}^{\sigma\sigma(1)}\right]+\sum_{\sigma}\mathcal{R}\,\mathrm{Tr}\left[\mathbf{b}^{\sigma\sigma}\mathbf{P}^{\sigma\sigma}\right] \\ &- \frac{1}{2}\sum_{\sigma}\mathcal{R}\,\mathrm{Tr}\left[\mathbb{K}^{\sigma\sigma(1)}\mathbf{P}^{\sigma\sigma}\right] \end{aligned} \tag{H.172b}$$

$$\begin{aligned} E^{(2)} &= \frac{1}{2}\sum_{\sigma}\mathcal{R}\,\mathrm{Tr}\left[\left(\mathbf{h}^{\sigma\sigma}+\mathbf{F}^{\sigma\sigma}\right)\mathbb{P}^{\sigma\sigma(2)}\right]+\sum_{\sigma\sigma'}\mathcal{R}\,\mathrm{Tr}\left[\mathbf{b}^{\sigma\sigma'}\mathbb{P}^{\sigma'\sigma(1)}\right] \\ &- \frac{1}{2}\sum_{\sigma\sigma'}\mathcal{R}\,\mathrm{Tr}\left[\mathbb{K}^{\sigma\sigma'(1)}\mathbb{P}^{\sigma'\sigma(1)}\right]+\frac{1}{2}\sum_{\sigma}\mathcal{R}\,\mathrm{Tr}\left[\left(\mathbb{C}^{\sigma\sigma(2)}-\mathbb{K}^{\sigma\sigma(2)}\right)\mathbf{P}^{\sigma\sigma}\right] \end{aligned} \tag{H.172c}$$

$$\begin{aligned} E^{(3)} &= \frac{1}{2}\sum_{\sigma}\mathcal{R}\,\mathrm{Tr}\left[\left(\mathbf{h}^{\sigma\sigma}+\mathbf{F}^{\sigma\sigma}\right)\mathbb{P}^{\sigma\sigma(3)}\right]+\sum_{\sigma\sigma'}\mathcal{R}\,\mathrm{Tr}\left[\mathbf{b}^{\sigma\sigma'}\mathbb{P}^{\sigma'\sigma(2)}\right] \\ &- \frac{1}{2}\sum_{\sigma\sigma'}\mathcal{R}\,\mathrm{Tr}\left[\mathbb{K}^{\sigma\sigma'(1)}\mathbb{P}^{\sigma'\sigma(2)}\right]+\frac{1}{2}\sum_{\sigma\sigma'}\mathcal{R}\,\mathrm{Tr}\left[\left(\mathbb{C}^{\sigma\sigma'(2)}-\mathbb{K}^{\sigma\sigma'(2)}\right)\mathbf{P}^{\sigma'\sigma(1)}\right] \\ &+ \frac{1}{2}\sum_{\sigma}\mathcal{R}\,\mathrm{Tr}\left[\left(\mathbb{C}^{\sigma\sigma(3)}-\mathbb{K}^{\sigma\sigma(3)}\right)\mathbf{P}^{\sigma\sigma}\right] \end{aligned} \tag{H.172d}$$

$$\ldots$$

where use has been made of the block-diagonal character of the SR density and Fock matrices, from Eq. (H.170c) and (H.170b)

Let us first discuss the first-order contribution to the energy. Given that the $\mathbf{b}^{\sigma\sigma}$ and $\mathbb{K}^{\sigma\sigma(1)}$ are purely imaginary, and that the SR density matrix is purely real, we find immediately:

$$\sum_{\sigma}\mathcal{R}\,\mathrm{Tr}\left[\mathbf{b}^{\sigma\sigma}\mathbf{P}^{\sigma\sigma}\right]=0 \tag{H.173}$$

and:

$$\sum_{\sigma}\mathcal{R}\,\mathrm{Tr}\left[\mathbb{K}^{\sigma\sigma(1)}\mathbf{P}^{\sigma\sigma}\right]=0 \tag{H.174}$$

So the only possible first-order contribution to the energy is from the first term in Eq. (H.172b). Substituting Eqs. (H.110) and (H.119b) in Eq. (H.172b):

$$\begin{aligned} \frac{1}{2}\sum_{\sigma}\mathcal{R}\,\mathrm{Tr}\left[\left(\mathbf{h}^{\sigma\sigma}+\mathbf{F}^{\sigma\sigma}\right)\mathbb{P}^{\sigma\sigma(1)}\right] &= \frac{1}{2}\sum_{\sigma}\mathcal{R}\,\mathrm{Tr}\Bigg[\left(\mathbf{h}^{\sigma\sigma}+\mathbf{F}^{\sigma\sigma}\right) \\ &\times \left(\mathbf{c}^{\sigma}\mathbf{f}_{\sigma}\left[\mathbf{U}^{\sigma\sigma(1)}\right]^{\dagger}\left[\mathbf{c}^{\sigma}\right]^{\dagger}+\mathbf{c}^{\sigma}\mathbf{U}^{\sigma\sigma(1)}\mathbf{f}_{\sigma}\left[\mathbf{c}^{\sigma}\right]^{\dagger}\right)\Bigg] \end{aligned} \tag{H.175}$$

Then using the fact that the trace is invarient to a cyclic permutation of the matrices for both terms in Eq. (H.175) and using the anti-hermiticity of $\underline{\mathbf{U}}^{(1)}$ from Eq. (H.123b):

$$\frac{1}{2}\sum_{\sigma}\mathcal{R}\,\mathrm{Tr}\left[\left(\mathbf{h}^{\sigma\sigma}+\mathbf{F}^{\sigma\sigma}\right)\mathbb{P}^{\sigma\sigma(1)}\right]=\frac{1}{2}\sum_{\sigma}\mathcal{R}\,\mathrm{Tr}\left[\boldsymbol{\Theta}^{\sigma\sigma}\left(\mathbf{U}^{\sigma\sigma(1)}\mathbf{f}_{\sigma}-\mathbf{f}_{\sigma}\mathbf{U}^{\sigma\sigma(1)}\right)\right] \tag{H.176}$$

where $\boldsymbol{\Theta}^{\sigma\sigma}=[\mathbf{c}^{\sigma}]^{\dagger}\left(\mathbf{h}^{\sigma\sigma}+\mathbf{F}^{\sigma\sigma}\right)\mathbf{c}^{\sigma}$ Then, substituting Eqs. (H.150) and (H.151) in Eq. (H.176) the occ-occ and virt-virt blocks of $\underline{\mathbf{U}}^{(1)}$ are null, so we find:

$$\frac{1}{2}\sum_{\sigma}\mathcal{R}\,\mathrm{Tr}\left[\left(\mathbf{h}^{\sigma\sigma}+\mathbf{F}^{\sigma\sigma}\right)\mathbb{P}^{\sigma\sigma(1)}\right]=\frac{1}{2}\sum_{\sigma}\sum_{m}^{\in occ}\sum_{p}^{\in virt}\Theta_{mp}^{\sigma\sigma}\mathcal{R}\left[U_{pm}^{\sigma\sigma(1)}\right]f_{\sigma m}-\Theta_{pm}^{\sigma\sigma}f_{\sigma m}\mathcal{R}\left[U_{mp}^{\sigma\sigma(1)}\right] \tag{H.177}$$

and since the matrix $\boldsymbol{\Theta}^{\sigma\sigma}$ is real Hermitian, while from Eq. (H.123b) $\underline{\mathbf{U}}^{(1)}$ is anti-Hermitian, we find:

$$\frac{1}{2}\sum_{\sigma}\mathcal{R}\,\mathrm{Tr}\left[\left(\mathbf{h}^{\sigma\sigma}+\mathbf{F}^{\sigma\sigma}\right)\mathbb{P}^{\sigma\sigma(1)}\right]=\sum_{\sigma}\sum_{m}^{\in occ}\sum_{p}^{\in virt}f_{\sigma m}\Theta_{mp}^{\sigma\sigma}\mathcal{R}\left[U_{pm}^{\sigma\sigma(1)}\right] \tag{H.178}$$

Substituting Eqs. (H.174) and (H.178) in (H.172b), we obtain:

$$E^{(1)}=\sum_{\sigma}\sum_{m}^{\in occ}\sum_{p}^{\in virt}f_{\sigma m}\Theta_{mp}^{\sigma\sigma}\mathcal{R}\left[U_{pm}^{\sigma\sigma(1)}\right]=0 \tag{H.179}$$

We now consider the second-order contribution to the total energy. Proceeding as in Eqs. (H.175) and (H.176) we find:

$$\begin{aligned}\frac{1}{2}\sum_{\sigma}\mathcal{R}\,\mathrm{Tr}\left[\left(\mathbf{h}^{\sigma\sigma}+\mathbf{F}^{\sigma\sigma}\right)\mathbb{P}^{\sigma\sigma(2)}\right] &= \frac{1}{2}\sum_{\sigma}\mathcal{R}\,\mathrm{Tr}\Big[\boldsymbol{\Theta}^{\sigma\sigma}\Big(\mathbf{U}^{\sigma\sigma(2)}\mathbf{f}_{\sigma}+\mathbf{f}_{\sigma}\left[\mathbf{U}^{\sigma\sigma(2)}\right]^{\dagger}\\ &- \sum_{\sigma''}\mathbf{U}^{\sigma\sigma''(1)}\mathbf{f}_{\sigma''}\mathbf{U}^{\sigma''\sigma(1)}\Big)\Big]\end{aligned} \tag{H.180}$$

Expanding the trace operator in Eq. (H.180) and exploiting the real-Hermitian character of the matrix $\boldsymbol{\Theta}^{\sigma\sigma}$:

$$\begin{aligned}\frac{1}{2}\sum_{\sigma}\mathcal{R}\,\mathrm{Tr}\left[\left(\mathbf{h}^{\sigma\sigma}+\mathbf{F}^{\sigma\sigma}\right)\mathbb{P}^{\sigma\sigma(2)}\right] &= \frac{1}{2}\sum_{\sigma}\sum_{m}^{\in occ}\sum_{p}^{\in virt}f_{\sigma m}\Theta_{mp}^{\sigma\sigma}\left(\mathcal{R}\left[U_{pm}^{\sigma\sigma(2)}\right]-\mathcal{R}\left[U_{mp}^{\sigma\sigma(2)}\right]\right)\\ &+ \frac{1}{2}\sum_{\sigma}\sum_{m}^{\in occ}\sum_{n}^{\in occ}\Theta_{mn}^{\sigma\sigma}f_{\sigma m}\left(\mathcal{R}\left[U_{nm}^{\sigma\sigma(2)}\right]+\mathcal{R}\left[U_{nm}^{\sigma\sigma(2)}\right]\right)\\ &- \frac{1}{2}\sum_{\sigma}\sum_{p}^{\in virt}\sum_{q}^{\in virt}\Theta_{pq}^{\sigma\sigma}\Big(\sum_{\sigma''}\sum_{m}^{\in occ}f_{\sigma'' m}\mathcal{R}\left[U_{qm}^{\sigma\sigma''(1)}U_{mp}^{\sigma''\sigma(1)}\right]\Big)\end{aligned} \tag{H.181}$$

From Eqs. (H.158a) and (H.156), the occ-occ and occ-virt blocks of $\underline{\mathbf{U}}^{(2)}$ are Hermitian and anti-Hermitian, respectively so that we find:

$$\begin{aligned}\frac{1}{2}\sum_{\sigma}\mathcal{R}\,\mathrm{Tr}\left[\left(\mathbf{h}^{\sigma\sigma}+\mathbf{F}^{\sigma\sigma}\right)\mathbb{P}^{\sigma\sigma(2)}\right] &= \sum_{\sigma}\sum_{m}^{\in occ}\sum_{p}^{\in virt} f_{\sigma m}\Theta_{mp}^{\sigma\sigma}\mathcal{R}\left[U_{pm}^{\sigma\sigma(2)}\right] \\ &+ \sum_{\sigma}\sum_{m}^{\in occ}\sum_{n}^{\in occ} f_{\sigma m}\Theta_{mn}^{\sigma\sigma}\mathcal{R}\left[U_{nm}^{\sigma\sigma(2)}\right] \\ &- \frac{1}{2}\sum_{\sigma}\sum_{p}^{\in virt}\sum_{q}^{\in virt}\Theta_{pq}^{\sigma\sigma}\Big(\sum_{\sigma''}\sum_{m}^{\in occ} f_{\sigma'' m}\mathcal{R}\left[U_{qm}^{\sigma\sigma''(1)}U_{mp}^{\sigma''\sigma(1)}\right]\Big)\end{aligned}\tag{H.182}$$

Then, substituting Eqs. (H.154)and (H.157a) in Eq. (H.182):

$$\begin{aligned}\frac{1}{2}\sum_{\sigma}\mathcal{R}\,\mathrm{Tr}\left[\left(\mathbf{h}^{\sigma\sigma}+\mathbf{F}^{\sigma\sigma}\right)\mathbb{P}^{\sigma\sigma(2)}\right] &= \sum_{\sigma}\sum_{m}^{\in occ}\sum_{p}^{\in virt} f_{\sigma m}\Theta_{mp}^{\sigma\sigma}\mathcal{R}\left[U_{pm}^{\sigma\sigma(2)}\right] \\ &- \frac{1}{2}\sum_{\sigma}\sum_{m}^{\in occ}\sum_{n}^{\in occ} f_{\sigma m}\Theta_{mn}^{\sigma\sigma}\Big(\sum_{\sigma'}\sum_{p}^{\in virt}\mathcal{R}\Big[\left[U_{pn}^{\sigma'\sigma(1)}\right]^{*}U_{pm}^{\sigma'\sigma(1)}\Big]\Big) \\ &- \frac{1}{2}\sum_{\sigma}\sum_{p}^{\in virt}\sum_{q}^{\in virt}\Theta_{pq}^{\sigma\sigma}\Big(\sum_{\sigma''}\sum_{m}^{\in occ} f_{\sigma'' m}\mathcal{R}\left[U_{qm}^{\sigma\sigma''(1)}U_{mp}^{\sigma''\sigma(1)}\right]\Big)\end{aligned}\tag{H.183}$$

We finally consider the second term in Eq. (H.172c). Proceeding again as in Eqs. (H.175) and (H.176) we find:

$$\sum_{\sigma\sigma'}\mathcal{R}\,\mathrm{Tr}\left[\mathbf{b}^{\sigma\sigma'}\mathbb{P}^{\sigma'\sigma(1)}\right]=\sum_{\sigma\sigma'}\mathcal{R}\,\mathrm{Tr}\left[\left[\mathbf{c}^{\sigma}\right]^{\dagger}\mathbf{b}^{\sigma\sigma'}\mathbf{c}^{\sigma'}\left(\mathbf{U}^{\sigma'\sigma(1)}\mathbf{f}_{\sigma}-\mathbf{f}_{\sigma'}\mathbf{U}^{\sigma'\sigma(1)}\right)\right]\tag{H.184}$$

Now expanding the trace operator in Eq. (H.184), remembering that from Eqs. (H.150) and (H.151) the occ-occ and virt-virt blocks of $\underline{\mathbf{U}}^{(1)}$ are null, so we find:

$$\begin{aligned}\sum_{\sigma\sigma'}\mathcal{R}\,\mathrm{Tr}\left[\mathbf{b}^{\sigma\sigma'}\mathbb{P}^{\sigma'\sigma(1)}\right] &= \sum_{\sigma\sigma'}\mathcal{R}\Bigg[\sum_{m}^{\in occ}\sum_{p}^{\in virt}\left(\left[\mathbf{c}^{\sigma}\right]^{\dagger}\mathbf{b}^{\sigma\sigma'}\mathbf{c}^{\sigma'}\right)_{mp}U_{pm}^{\sigma'\sigma(1)}f_{\sigma m} \\ &- \left(\left[\mathbf{c}^{\sigma}\right]^{\dagger}\mathbf{b}^{\sigma\sigma'}\mathbf{c}^{\sigma'}\right)_{pm}f_{\sigma' m}U_{mp}^{\sigma'\sigma(1)}\Bigg] \\ &= \sum_{\sigma\sigma'}\mathcal{R}\Bigg[\sum_{m}^{\in occ}\sum_{p}^{\in virt}G_{mp}^{\sigma\sigma'(1)}U_{pm}^{\sigma'\sigma(1)}f_{\sigma m} \\ &- G_{pm}^{\sigma\sigma'(1)}f_{\sigma' m}U_{mp}^{\sigma'\sigma(1)}\Bigg]\end{aligned}\tag{H.185}$$

and finally, taking the real part of the argument:

$$\sum_{\sigma\sigma'}\mathcal{R}\,\mathrm{Tr}\left[\mathbf{b}^{\sigma\sigma'}\mathbb{P}^{\sigma'\sigma(1)}\right] = 2\sum_{\sigma\sigma'}\sum_{m}^{\in occ}\sum_{p}^{\in virt}f_{\sigma m}\mathcal{R}\left[G_{mp}^{\sigma\sigma'(1)}U_{pm}^{\sigma'\sigma(1)}\right]\tag{H.186}$$

We now consider the third order contribution to the energy. Taking the second term in Eq. (H.172d) and proceeding as in Eq. (H.184) we find:

$$\begin{aligned}\sum_{\sigma\sigma'}\mathcal{R}\,\mathrm{Tr}\left[\mathbf{b}^{\sigma\sigma'}\mathbb{P}^{\sigma'\sigma(2)}\right] &= \sum_{\sigma\sigma'}\mathcal{R}\,\mathrm{Tr}\Bigg[\left[\mathbf{c}^{\sigma}\right]^{\dagger}\mathbf{b}^{\sigma\sigma'}\mathbf{c}^{\sigma'}\Bigg(\mathbf{U}^{\sigma'\sigma(2)}\mathbf{f}_{\sigma}+\mathbf{f}_{\sigma'}\left[\mathbf{U}^{\sigma'\sigma(2)}\right]^{\dagger}\\ &+ \sum_{\sigma''}\mathbf{U}^{\sigma'\sigma''(1)}\mathbf{f}_{\sigma''}\left[\mathbf{U}^{\sigma''\sigma(1)}\right]^{\dagger}\Bigg)\Bigg]\end{aligned}\tag{H.187}$$

Proceeding as in Eq. (H.185):

$$\begin{aligned}&\sum_{\sigma\sigma'}\mathcal{R}\,\mathrm{Tr}\left[\mathbf{b}^{\sigma\sigma'}\mathbb{P}^{\sigma'\sigma(2)}\right]=\\ &\sum_{\sigma\sigma'}\Bigg[\sum_{m}^{\in occ}\sum_{p}^{\in virt}\left(\mathcal{R}\left[G_{mp}^{\sigma\sigma'(1)}U_{pm}^{\sigma'\sigma(2)}\right]f_{\sigma m}+\mathcal{R}\left[G_{pm}^{\sigma\sigma'(1)}\left[U_{pm}^{\sigma\sigma'(2)}\right]^{*}\right]f_{\sigma' m}\right)\\ &+\sum_{m}^{\in occ}\sum_{n}^{\in occ}\left(\mathcal{R}\left[G_{mn}^{\sigma\sigma'(1)}U_{nm}^{\sigma'\sigma(2)}\right]f_{\sigma m}+\mathcal{R}\left[G_{nm}^{\sigma\sigma'(1)}\left[U_{nm}^{\sigma\sigma'(2)}\right]^{*}\right]f_{\sigma' m}\right)\\ &+\sum_{p}^{\in virt}\sum_{q}^{\in virt}\mathcal{R}\left[G_{pq}^{\sigma\sigma'(1)}\right]\left(\sum_{\sigma''}\sum_{m}^{\in occ}\mathcal{R}\left[U_{qm}^{\sigma'\sigma''(1)}\left[U_{pm}^{\sigma\sigma''(1)}\right]^{*}\right]f_{\sigma'' m}\right)\\ &-\sum_{p}^{\in virt}\sum_{q}^{\in virt}\mathcal{I}\left[G_{pq}^{\sigma\sigma'(1)}\right]\left(\sum_{\sigma''}\sum_{m}^{\in occ}\mathcal{I}\left[U_{qm}^{\sigma'\sigma''(1)}\left[U_{pm}^{\sigma\sigma''(1)}\right]^{*}\right]f_{\sigma'' m}\right)\Bigg]\end{aligned}\tag{H.188}$$

and finally, exploiting the anti-Hermiticity of the occ-virt blocks of $\underline{\mathbf{U}}^{(2)}$, we find:

$$\begin{aligned}&\sum_{\sigma\sigma'}\mathcal{R}\,\mathrm{Tr}\left[\mathbf{b}^{\sigma\sigma'}\mathbb{P}^{\sigma'\sigma(2)}\right]=\\ &\sum_{\sigma\sigma'}\Bigg[\sum_{m}^{\in occ}\sum_{n}^{\in occ}\left(\mathcal{R}\left[G_{mn}^{\sigma\sigma'(1)}U_{nm}^{\sigma'\sigma(2)}\right]f_{\sigma m}+\mathcal{R}\left[G_{nm}^{\sigma\sigma'(1)}\left[U_{nm}^{\sigma\sigma'(2)}\right]^{*}\right]f_{\sigma' m}\right)\\ &+\sum_{p}^{\in virt}\sum_{q}^{\in virt}\mathcal{R}\left[G_{pq}^{\sigma\sigma'(1)}\right]\left(\sum_{\sigma''}\sum_{m}^{\in occ}\mathcal{R}\left[U_{qm}^{\sigma'\sigma''(1)}\left[U_{pm}^{\sigma\sigma''(1)}\right]^{*}\right]f_{\sigma'' m}\right)\\ &-\sum_{p}^{\in virt}\sum_{q}^{\in virt}\mathcal{I}\left[G_{pq}^{\sigma\sigma'(1)}\right]\left(\sum_{\sigma''}\sum_{m}^{\in occ}\mathcal{I}\left[U_{qm}^{\sigma'\sigma''(1)}\left[U_{pm}^{\sigma\sigma''(1)}\right]^{*}\right]f_{\sigma'' m}\right)\Bigg]\end{aligned}\tag{H.189}$$

H.5.4 The Total Energy: Canonical Non-Collinear LDA Formalism

The FR exchange-correlation (xc) energy $\mathcal{E}_{xc}$ contribution has the following general form:

$$\mathcal{E}_{xc}=\int F_{xc}[\boldsymbol{Q}]d\mathbf{r}=\int F_{xc}[\boldsymbol{Q}+\lambda\boldsymbol{Q}^{(1)}+\lambda^{2}\boldsymbol{Q}^{(2)}+\ldots]d\mathbf{r}\tag{H.190}$$

where $\boldsymbol{Q}$ are the FR density variables on which the xc functional F_{xc} depends. In the canonical non-collinear local density approximation (LDA) formalism, the $\boldsymbol{Q}$ is built as follows:

$$\boldsymbol{Q} = [\mathbb{N}_+, \mathbb{N}_-] \tag{H.191}$$

where the $\mathbb{N}_\pm$ are written as:

$$\mathbb{N}_\pm = \mathbb{N} \pm \mathbb{M} \tag{H.192}$$

where $\mathbb{N}$ and $\mathbb{M}$ are the FR particle-number density and magnetization. The FR particle-number density is calculated from the diagonal spin-blocks of the FR density matrix in the AO basis, as follows:

$$\mathbb{N} = \sum_{\sigma} \sum_{\mu\nu} \left[\mathbb{P}^{\sigma\sigma}_{\mu\nu}\right]^* \chi_\mu \chi_\nu \tag{H.193}$$

and expanded in orders of the perturbation starting from the corresponding SR density, as follows:

$$\mathbb{N} = n + \lambda n^{(1)} + \lambda^2 n^{(2)} + \ldots \tag{H.194}$$

where the perturbed particle-number densities $n^{(t)}$ are calculated as follows from the corresponding perturbed density matrix:

$$n^{(t)} = \sum_{\sigma} \sum_{\mu\nu} \left[\mathbb{P}^{\sigma\sigma(t)}_{\mu\nu}\right]^* \chi_\mu \chi_\nu \tag{H.195}$$

On the other hand, the FR magnetization $\mathbb{M}$ is the modulus of the FR magnetization vector **m**, and is hence calculated from its Cartesian components $\mathbb{M}_c$ as:

$$\mathbb{M} = \left[\sum_{c=x,y,z} \mathbb{M}_c^2\right]^{\frac{1}{2}} \tag{H.196}$$

The FR magnetization vector Cartesian components are calculated from the FR density matrix as follows:

$$\mathbb{M}_x = \sum_{\mu\nu} \left[\mathcal{R}\mathbb{P}^{\alpha\beta}_{\mu\nu} + \mathcal{R}\mathbb{P}^{\beta\alpha}_{\mu\nu}\right] \chi_\mu \chi_\nu \tag{H.197a}$$

$$\mathbb{M}_y = \sum_{\mu\nu} \left[-\mathcal{I}\mathbb{P}^{\alpha\beta}_{\mu\nu} + \mathcal{I}\mathbb{P}^{\beta\alpha}_{\mu\nu}\right] \chi_\mu \chi_\nu \tag{H.197b}$$

$$\mathbb{M}_z = \sum_{\mu\nu} \left[\mathcal{R}\mathbb{P}^{\alpha\alpha}_{\mu\nu} - \mathcal{R}\mathbb{P}^{\beta\beta}_{\mu\nu}\right] \chi_\mu \chi_\nu \tag{H.197c}$$

Like the particle-number densities, the magnetization and magnetization vector Cartesian components are written starting from the corresponding SR quantities as follows:

$$\mathbb{M} = m + \lambda m^{(1)} + \lambda^2 m^{(2)} + \ldots \tag{H.198a}$$

$$\mathbb{M}_c = m_c + \lambda m_c^{(1)} + \lambda^2 m_c^{(2)} + \ldots \quad \forall c = x, y, z \tag{H.198b}$$

The perturbed magnetization vector Cartesian components $m_c^{(t)}$ are calculated from the corresponding blocks of the perturbed density matrix, as follows:

$$m_x^{(t)} = \sum_{\mu\nu} \left[\mathcal{R}\mathbb{P}_{\mu\nu}^{\alpha\beta(t)} + \mathcal{R}\mathbb{P}_{\mu\nu}^{\beta\alpha(t)}\right]\chi_\mu\chi_\nu \tag{H.199a}$$

$$m_y^{(t)} = \sum_{\mu\nu} \left[-\mathcal{I}\mathbb{P}_{\mu\nu}^{\alpha\beta(t)} + \mathcal{I}\mathbb{P}_{\mu\nu}^{\beta\alpha(t)}\right]\chi_\mu\chi_\nu \tag{H.199b}$$

$$m_z^{(t)} = \sum_{\mu\nu} \left[\mathcal{R}\mathbb{P}_{\mu\nu}^{\alpha\alpha(t)} - \mathcal{R}\mathbb{P}_{\mu\nu}^{\beta\beta(t)}\right]\chi_\mu\chi_\nu \tag{H.199c}$$

An expression for the perturbed magnetization $m^{(t)}$ can then be obtained, first by squaring both sides of Eq. (H.196) and inserting Eq. (H.198), such that:

$$\begin{aligned} &\left(m + \lambda m^{(1)} + \lambda^2 m^{(2)} + \dots\right)\left(m + \lambda m^{(1)} + \lambda^2 m^{(2)} + \dots\right) = \\ &\sum_{c=x,y,z} \left(m_c + \lambda m_c^{(1)} + \lambda^2 m_c^{(2)} + \dots\right)\left(m_c + \lambda m_c^{(1)} + \lambda^2 m_c^{(2)} + \dots\right) \end{aligned} \tag{H.200}$$

Then collecting terms of like order in Eq. (H.200) and setting λ to 1, we get the following set of equations:

$$m = \left[\sum_{c=x,y,z} (m_c)^2\right]^{\frac{1}{2}} \tag{H.201a}$$

$$m^{(1)} m = \sum_{c=x,y,z} m_c^{(1)} m_c \tag{H.201b}$$

$$m^{(1)} m^{(1)} + 2m^{(2)} m = \sum_{c=x,y,z} m_c^{(1)} m_c^{(1)} + 2m_c^{(2)} m_c$$

$$\dots$$

Combining Eqs. (H.201a)-(H.201c), we have finally for the first order perturbed magnetization:

$$m^{(1)} = \left[\sum_{c=x,y,z} (m_c)^2\right]^{-\frac{1}{2}} \sum_{c=x,y,z} m_c^{(1)} m_c \tag{H.202}$$

and for the second order perturbed magnetization:

$$m^{(2)} = \frac{1}{2}\left[\sum_{c=x,y,z} (m_c)^2\right]^{-\frac{1}{2}} \left[\sum_{c=x,y,z} \left(m_c^{(1)} m_c^{(1)} + 2m_c^{(2)} m_c\right) - \frac{\left(\sum_{c=x,y,z} m_c^{(1)} m_c\right)^2}{\sum_{c=x,y,z} (m_c)^2}\right] \tag{H.203}$$

The xc contribution to the FR total energy can thus be calculated to second order by inserting Eqs. (H.191)-(H.203) in Eq. (H.190).

H.5.5 More Explicit Expressions for Programming the Perturbed Density Matrix

The goal here is to develop more explicit expressions for the perturbed density matrix of Eqs. (H.119b) and (H.119c) by exploiting the relations of the orbital rotation matrices elaborated in section H.5.1. Let us start by writing explicitly the expressions for diagonal and off-diagonal spin-blocks, by substituting Eq. (H.110) in Eqs. (H.119b), (H.119c) and (H.119c):

$$\mathbb{P}^{\alpha\alpha(1)} = \mathbf{c}^{\alpha}\mathbf{f}_{\alpha}\left[\mathbf{U}^{\alpha\alpha(1)}\right]^{\dagger}\left[\mathbf{c}^{\alpha}\right]^{\dagger} + \mathbf{c}^{\alpha}\mathbf{U}^{\alpha\alpha(1)}\mathbf{f}_{\alpha}\left[\mathbf{c}^{\alpha}\right]^{\dagger} \tag{H.204a}$$

$$\mathbb{P}^{\alpha\beta(1)} = \mathbf{c}^{\alpha}\mathbf{f}_{\alpha}\left[\mathbf{U}^{\alpha\beta(1)}\right]^{\dagger}\left[\mathbf{c}^{\beta}\right]^{\dagger} + \mathbf{c}^{\alpha}\mathbf{U}^{\alpha\beta(1)}\mathbf{f}_{\beta}\left[\mathbf{c}^{\beta}\right]^{\dagger} \tag{H.204b}$$

$$\mathbb{P}^{\beta\alpha(1)} = \mathbf{c}^{\beta}\mathbf{f}_{\beta}\left[\mathbf{U}^{\beta\alpha(1)}\right]^{\dagger}\left[\mathbf{c}^{\alpha}\right]^{\dagger} + \mathbf{c}^{\beta}\mathbf{U}^{\beta\alpha(1)}\mathbf{f}_{\alpha}\left[\mathbf{c}^{\alpha}\right]^{\dagger} \tag{H.204c}$$

$$\mathbb{P}^{\beta\beta(1)} = \mathbf{c}^{\beta}\mathbf{f}_{\beta}\left[\mathbf{U}^{\beta\beta(1)}\right]^{\dagger}\left[\mathbf{c}^{\beta}\right]^{\dagger} + \mathbf{c}^{\beta}\mathbf{U}^{\beta\beta(1)}\mathbf{f}_{\beta}\left[\mathbf{c}^{\beta}\right]^{\dagger} \tag{H.204d}$$

$$\begin{aligned}\mathbb{P}^{\alpha\alpha(2)} &= \mathbf{c}^{\alpha}\mathbf{f}_{\alpha}\left[\mathbf{U}^{\alpha\alpha(2)}\right]^{\dagger}\left[\mathbf{c}^{\alpha}\right]^{\dagger} + \mathbf{c}^{\alpha}\mathbf{U}^{\alpha\alpha(2)}\mathbf{f}_{\alpha}\left[\mathbf{c}^{\alpha}\right]^{\dagger}\\ &+ \mathbf{c}^{\alpha}\mathbf{U}^{\alpha\alpha(1)}\mathbf{f}_{\alpha}\left[\mathbf{U}^{\alpha\alpha(1)}\right]^{\dagger}\left[\mathbf{c}^{\alpha}\right]^{\dagger} + \mathbf{c}^{\alpha}\mathbf{U}^{\alpha\beta(1)}\mathbf{f}_{\beta}\left[\mathbf{U}^{\beta\alpha(1)}\right]^{\dagger}\left[\mathbf{c}^{\alpha}\right]^{\dagger}\end{aligned} \tag{H.204e}$$

$$\begin{aligned}\mathbb{P}^{\alpha\beta(2)} &= \mathbf{c}^{\alpha}\mathbf{f}_{\alpha}\left[\mathbf{U}^{\alpha\beta(2)}\right]^{\dagger}\left[\mathbf{c}^{\beta}\right]^{\dagger} + \mathbf{c}^{\alpha}\mathbf{U}^{\alpha\beta(2)}\mathbf{f}_{\beta}\left[\mathbf{c}^{\beta}\right]^{\dagger}\\ &+ \mathbf{c}^{\alpha}\mathbf{U}^{\alpha\alpha(1)}\mathbf{f}_{\alpha}\left[\mathbf{U}^{\alpha\beta(1)}\right]^{\dagger}\left[\mathbf{c}^{\beta}\right]^{\dagger} + \mathbf{c}^{\alpha}\mathbf{U}^{\alpha\beta(1)}\mathbf{f}_{\beta}\left[\mathbf{U}^{\beta\beta(1)}\right]^{\dagger}\left[\mathbf{c}^{\beta}\right]^{\dagger}\end{aligned} \tag{H.204f}$$

$$\begin{aligned}\mathbb{P}^{\beta\alpha(2)} &= \mathbf{c}^{\beta}\mathbf{f}_{\beta}\left[\mathbf{U}^{\beta\alpha(2)}\right]^{\dagger}\left[\mathbf{c}^{\alpha}\right]^{\dagger} + \mathbf{c}^{\beta}\mathbf{U}^{\beta\alpha(2)}\mathbf{f}_{\alpha}\left[\mathbf{c}^{\alpha}\right]^{\dagger}\\ &+ \mathbf{c}^{\beta}\mathbf{U}^{\beta\alpha(1)}\mathbf{f}_{\alpha}\left[\mathbf{U}^{\alpha\alpha(1)}\right]^{\dagger}\left[\mathbf{c}^{\alpha}\right]^{\dagger} + \mathbf{c}^{\beta}\mathbf{U}^{\beta\beta(1)}\mathbf{f}_{\beta}\left[\mathbf{U}^{\beta\alpha(1)}\right]^{\dagger}\left[\mathbf{c}^{\alpha}\right]^{\dagger}\end{aligned} \tag{H.204g}$$

$$\begin{aligned}\mathbb{P}^{\beta\beta(2)} &= \mathbf{c}^{\beta}\mathbf{f}_{\beta}\left[\mathbf{U}^{\beta\beta(2)}\right]^{\dagger}\left[\mathbf{c}^{\beta}\right]^{\dagger} + \mathbf{c}^{\beta}\mathbf{U}^{\beta\beta(2)}\mathbf{f}_{\beta}\left[\mathbf{c}^{\beta}\right]^{\dagger}\\ &+ \mathbf{c}^{\beta}\mathbf{U}^{\beta\alpha(1)}\mathbf{f}_{\alpha}\left[\mathbf{U}^{\alpha\beta(1)}\right]^{\dagger}\left[\mathbf{c}^{\beta}\right]^{\dagger} + \mathbf{c}^{\beta}\mathbf{U}^{\beta\beta(1)}\mathbf{f}_{\beta}\left[\mathbf{U}^{\beta\beta(1)}\right]^{\dagger}\left[\mathbf{c}^{\beta}\right]^{\dagger}\end{aligned} \tag{H.204h}$$

$$\begin{aligned}\mathbb{P}^{\alpha\alpha(3)} &= \mathbf{c}^{\alpha}\mathbf{f}_{\alpha}\left[\mathbf{U}^{\alpha\alpha(3)}\right]^{\dagger}\left[\mathbf{c}^{\alpha}\right]^{\dagger} + \mathbf{c}^{\alpha}\mathbf{U}^{\alpha\alpha(3)}\mathbf{f}_{\alpha}\left[\mathbf{c}^{\alpha}\right]^{\dagger}\\ &+ \mathbf{c}^{\alpha}\mathbf{U}^{\alpha\alpha(2)}\mathbf{f}_{\alpha}\left[\mathbf{U}^{\alpha\alpha(1)}\right]^{\dagger}\left[\mathbf{c}^{\alpha}\right]^{\dagger} + \mathbf{c}^{\alpha}\mathbf{U}^{\alpha\beta(2)}\mathbf{f}_{\beta}\left[\mathbf{U}^{\beta\alpha(1)}\right]^{\dagger}\left[\mathbf{c}^{\alpha}\right]^{\dagger}\\ &+ \mathbf{c}^{\alpha}\mathbf{U}^{\alpha\alpha(1)}\mathbf{f}_{\alpha}\left[\mathbf{U}^{\alpha\alpha(2)}\right]^{\dagger}\left[\mathbf{c}^{\alpha}\right]^{\dagger} + \mathbf{c}^{\alpha}\mathbf{U}^{\alpha\beta(1)}\mathbf{f}_{\beta}\left[\mathbf{U}^{\beta\alpha(2)}\right]^{\dagger}\left[\mathbf{c}^{\alpha}\right]^{\dagger}\end{aligned} \tag{H.204i}$$

$$\begin{aligned}\mathbb{P}^{\alpha\beta(3)} &= \mathbf{c}^{\alpha}\mathbf{f}_{\alpha}\left[\mathbf{U}^{\alpha\beta(3)}\right]^{\dagger}\left[\mathbf{c}^{\beta}\right]^{\dagger} + \mathbf{c}^{\alpha}\mathbf{U}^{\alpha\beta(3)}\mathbf{f}_{\beta}\left[\mathbf{c}^{\beta}\right]^{\dagger}\\ &+ \mathbf{c}^{\alpha}\mathbf{U}^{\alpha\alpha(2)}\mathbf{f}_{\alpha}\left[\mathbf{U}^{\alpha\beta(1)}\right]^{\dagger}\left[\mathbf{c}^{\beta}\right]^{\dagger} + \mathbf{c}^{\alpha}\mathbf{U}^{\alpha\beta(2)}\mathbf{f}_{\beta}\left[\mathbf{U}^{\beta\beta(1)}\right]^{\dagger}\left[\mathbf{c}^{\beta}\right]^{\dagger}\\ &+ \mathbf{c}^{\alpha}\mathbf{U}^{\alpha\alpha(1)}\mathbf{f}_{\alpha}\left[\mathbf{U}^{\alpha\beta(2)}\right]^{\dagger}\left[\mathbf{c}^{\beta}\right]^{\dagger} + \mathbf{c}^{\alpha}\mathbf{U}^{\alpha\beta(1)}\mathbf{f}_{\beta}\left[\mathbf{U}^{\beta\beta(2)}\right]^{\dagger}\left[\mathbf{c}^{\beta}\right]^{\dagger}\end{aligned} \tag{H.204j}$$

$$\begin{aligned}\mathbb{P}^{\beta\alpha(3)} &= \mathbf{c}^{\beta}\mathbf{f}_{\beta}\left[\mathbf{U}^{\beta\alpha(3)}\right]^{\dagger}\left[\mathbf{c}^{\alpha}\right]^{\dagger} + \mathbf{c}^{\beta}\mathbf{U}^{\beta\alpha(3)}\mathbf{f}_{\alpha}\left[\mathbf{c}^{\alpha}\right]^{\dagger}\\ &+ \mathbf{c}^{\beta}\mathbf{U}^{\beta\alpha(2)}\mathbf{f}_{\alpha}\left[\mathbf{U}^{\alpha\alpha(1)}\right]^{\dagger}\left[\mathbf{c}^{\alpha}\right]^{\dagger} + \mathbf{c}^{\beta}\mathbf{U}^{\beta\beta(2)}\mathbf{f}_{\beta}\left[\mathbf{U}^{\beta\alpha(1)}\right]^{\dagger}\left[\mathbf{c}^{\alpha}\right]^{\dagger}\\ &+ \mathbf{c}^{\beta}\mathbf{U}^{\beta\alpha(1)}\mathbf{f}_{\alpha}\left[\mathbf{U}^{\alpha\alpha(2)}\right]^{\dagger}\left[\mathbf{c}^{\alpha}\right]^{\dagger} + \mathbf{c}^{\beta}\mathbf{U}^{\beta\beta(1)}\mathbf{f}_{\beta}\left[\mathbf{U}^{\beta\alpha(2)}\right]^{\dagger}\left[\mathbf{c}^{\alpha}\right]^{\dagger}\end{aligned} \tag{H.204k}$$

$$\begin{aligned}\mathbb{P}^{\beta\beta(3)} &= \mathbf{c}^{\beta}\mathbf{f}_{\beta}\left[\mathbf{U}^{\beta\beta(3)}\right]^{\dagger}\left[\mathbf{c}^{\beta}\right]^{\dagger} + \mathbf{c}^{\beta}\mathbf{U}^{\beta\beta(3)}\mathbf{f}_{\beta}\left[\mathbf{c}^{\beta}\right]^{\dagger}\\ &+ \mathbf{c}^{\beta}\mathbf{U}^{\beta\alpha(2)}\mathbf{f}_{\alpha}\left[\mathbf{U}^{\alpha\beta(1)}\right]^{\dagger}\left[\mathbf{c}^{\beta}\right]^{\dagger} + \mathbf{c}^{\beta}\mathbf{U}^{\beta\beta(2)}\mathbf{f}_{\beta}\left[\mathbf{U}^{\beta\beta(1)}\right]^{\dagger}\left[\mathbf{c}^{\beta}\right]^{\dagger}\\ &+ \mathbf{c}^{\beta}\mathbf{U}^{\beta\alpha(1)}\mathbf{f}_{\alpha}\left[\mathbf{U}^{\alpha\beta(2)}\right]^{\dagger}\left[\mathbf{c}^{\beta}\right]^{\dagger} + \mathbf{c}^{\beta}\mathbf{U}^{\beta\beta(1)}\mathbf{f}_{\beta}\left[\mathbf{U}^{\beta\beta(2)}\right]^{\dagger}\left[\mathbf{c}^{\beta}\right]^{\dagger}\end{aligned} \tag{H.204l}$$

The individual matrix-elements for the first-order perturbed density matrix are calculated as follows, using Eqs. (H.149), (H.150) and (H.151):

$$\begin{aligned}\mathbb{P}_{\mu\nu}^{\alpha\alpha(1)} &= \sum_{m}^{\in occ} c_{\mu m}^{\alpha} f_{\alpha m} \sum_{p}^{\in virt} \left[U_{pm}^{\alpha\alpha(1)}\right]^{*} \left[c_{\nu p}^{\alpha}\right]^{*} \\ &+ \sum_{p}^{\in virt} c_{\mu p}^{\alpha} \sum_{m}^{\in occ} U_{pm}^{\alpha\alpha(1)} f_{\alpha m} \left[c_{\nu m}^{\alpha}\right]^{*} \end{aligned} \tag{H.205a}$$

$$\begin{aligned}\mathbb{P}_{\mu\nu}^{\alpha\beta(1)} &= -\sum_{m}^{\in occ} c_{\mu m}^{\alpha} f_{\alpha m} \sum_{p}^{\in virt} U_{mp}^{\alpha\beta(1)} \left[c_{\nu p}^{\beta}\right]^{*} \\ &+ \sum_{p}^{\in virt} c_{\mu p}^{\alpha} \sum_{m}^{\in occ} U_{pm}^{\alpha\beta(1)} f_{\beta m} \left[c_{\nu m}^{\beta}\right]^{*} \end{aligned} \tag{H.205b}$$

$$\begin{aligned}\mathbb{P}_{\mu\nu}^{\beta\alpha(1)} &= \sum_{m}^{\in occ} c_{\mu m}^{\beta} f_{\beta m} \sum_{p}^{\in virt} \left[U_{pm}^{\alpha\beta(1)}\right]^{*} \left[c_{\nu p}^{\alpha}\right]^{*} \\ &- \sum_{p}^{\in virt} c_{\mu p}^{\beta} \sum_{m}^{\in occ} \left[U_{mp}^{\alpha\beta(1)}\right]^{*} f_{\alpha m} \left[c_{\nu m}^{\alpha}\right]^{*} \end{aligned} \tag{H.205c}$$

$$\begin{aligned}\mathbb{P}_{\mu\nu}^{\beta\beta(1)} &= \sum_{m}^{\in occ} c_{\mu m}^{\beta} f_{\beta m} \sum_{p}^{\in virt} \left[U_{pm}^{\beta\beta(1)}\right]^{*} \left[c_{\nu p}^{\beta}\right]^{*} \\ &+ \sum_{p}^{\in virt} c_{\mu p}^{\beta} \sum_{m}^{\in occ} U_{pm}^{\beta\beta(1)} f_{\beta m} \left[c_{\nu m}^{\beta}\right]^{*} \end{aligned} \tag{H.205d}$$

The real and imaginary parts of the diagonal spin-blocks therefore read as follows, using the fact that from an SR reference, the $c_{\mu i}^{\sigma}$ are purely real and the $U_{ij}^{\sigma\sigma(1)}$ are purely imaginary:

$$\mathrm{Re}\left[\mathbb{P}_{\mu\nu}^{\alpha\alpha(1)}\right] = 0 \tag{H.206a}$$

$$\begin{aligned}\mathrm{Im}\left[\mathbb{P}_{\mu\nu}^{\alpha\alpha(1)}\right] &= -\sum_{m}^{\in occ} c_{\mu m}^{\alpha} f_{\alpha m} \sum_{p}^{\in virt} \mathrm{Im}\left[U_{pm}^{\alpha\alpha(1)}\right] c_{\nu p}^{\alpha} \\ &+ \sum_{p}^{\in virt} c_{\mu p}^{\alpha} \sum_{m}^{\in occ} \mathrm{Im}\left[U_{pm}^{\alpha\alpha(1)}\right] f_{\alpha m} c_{\nu m}^{\alpha} \end{aligned} \tag{H.206b}$$

$$\mathrm{Re}\left[\mathbb{P}_{\mu\nu}^{\beta\beta(1)}\right] = 0 \tag{H.206c}$$

$$\begin{aligned}\mathrm{Im}\left[\mathbb{P}_{\mu\nu}^{\beta\beta(1)}\right] &= -\sum_{m}^{\in occ} c_{\mu m}^{\beta} f_{\beta m} \sum_{p}^{\in virt} \mathrm{Im}\left[U_{pm}^{\beta\beta(1)}\right] c_{\nu p}^{\beta} \\ &+ \sum_{p}^{\in virt} c_{\mu p}^{\beta} \sum_{m}^{\in occ} \mathrm{Im}\left[U_{pm}^{\beta\beta(1)}\right] f_{\beta m} c_{\nu m}^{\beta} \end{aligned} \tag{H.206d}$$

and for the off-diagonal blocks, the real and imaginary parts read:

$$\begin{aligned}
\mathrm{Re}\left[\mathbb{P}_{\mu\nu}^{\alpha\beta(1)}\right] &= -\sum_{m}^{\in occ} c_{\mu m}^{\alpha} f_{\alpha m} \sum_{p}^{\in virt} \mathrm{Re}\left[U_{mp}^{\alpha\beta(1)}\right] c_{\nu p}^{\beta} \\
&+ \sum_{p}^{\in virt} c_{\mu p}^{\alpha} \sum_{m}^{\in occ} \mathrm{Re}\left[U_{pm}^{\alpha\beta(1)}\right] f_{\beta m} c_{\nu m}^{\beta} && \text{(H.207a)} \\
\mathrm{Im}\left[\mathbb{P}_{\mu\nu}^{\alpha\beta(1)}\right] &= -\sum_{m}^{\in occ} c_{\mu m}^{\alpha} f_{\alpha m} \sum_{p}^{\in virt} \mathrm{Im}\left[U_{mp}^{\alpha\beta(1)}\right] c_{\nu p}^{\beta} \\
&+ \sum_{p}^{\in virt} c_{\mu p}^{\alpha} \sum_{m}^{\in occ} \mathrm{Im}\left[U_{pm}^{\alpha\beta(1)}\right] f_{\beta m} c_{\nu m}^{\beta} && \text{(H.207b)} \\
\mathrm{Re}\left[\mathbb{P}_{\mu\nu}^{\beta\alpha(1)}\right] &= \sum_{m}^{\in occ} c_{\mu m}^{\beta} f_{\beta m} \sum_{p}^{\in virt} \mathrm{Re}\left[U_{pm}^{\alpha\beta(1)}\right] c_{\nu p}^{\alpha} \\
&- \sum_{p}^{\in virt} c_{\mu p}^{\beta} \sum_{m}^{\in occ} \mathrm{Re}\left[U_{mp}^{\alpha\beta(1)}\right] f_{\alpha m} c_{\nu m}^{\alpha} && \text{(H.207c)} \\
\mathrm{Im}\left[\mathbb{P}_{\mu\nu}^{\beta\alpha(1)}\right] &= -\sum_{m}^{\in occ} c_{\mu m}^{\beta} f_{\beta m} \sum_{p}^{\in virt} \mathrm{Im}\left[U_{pm}^{\alpha\beta(1)}\right] c_{\nu p}^{\alpha} \\
&+ \sum_{p}^{\in virt} c_{\mu p}^{\beta} \sum_{m}^{\in occ} \mathrm{Im}\left[U_{mp}^{\alpha\beta(1)}\right] f_{\alpha m} c_{\nu m}^{\alpha} && \text{(H.207d)}
\end{aligned}$$

The matrix-elements of the second-order perturbed density matrix read, for the off-diagonal spin-blocks ($\sigma \neq \sigma'$):

$$\begin{aligned}
\mathbb{P}_{\mu\nu}^{\sigma\sigma'(2)} &= \sum_{m}^{\in occ} c_{\mu m}^{\sigma} f_{\sigma m} \left\{ \sum_{n}^{\in occ} \left[U_{nm}^{\sigma'\sigma(2)}\right]^{*} \left[c_{\nu n}^{\sigma'}\right]^{*} + \sum_{p}^{\in virt} \left[U_{pm}^{\sigma'\sigma(2)}\right]^{*} \left[c_{\nu p}^{\sigma'}\right]^{*} \right\} \\
&+ \sum_{m}^{\in occ} c_{\mu m}^{\sigma} \sum_{n}^{\in occ} U_{mn}^{\sigma\sigma'(2)} f_{\sigma' n} \left[c_{\nu n}^{\sigma'}\right]^{*} + \sum_{p}^{\in virt} c_{\mu p}^{\sigma} \sum_{n}^{\in occ} U_{pn}^{\sigma\sigma'(2)} f_{\sigma' n} \left[c_{\nu n}^{\sigma'}\right]^{*} \\
&+ \sum_{p}^{\in virt} c_{\mu p}^{\sigma} \sum_{m}^{\in occ} U_{pm}^{\sigma\sigma(1)} f_{\sigma m} \sum_{q}^{\in virt} \left[U_{qm}^{\sigma'\sigma(1)}\right]^{*} \left[c_{\nu q}^{\sigma'}\right]^{*} \\
&+ \sum_{p}^{\in virt} c_{\mu p}^{\sigma} \sum_{m}^{\in occ} U_{pm}^{\sigma\sigma'(1)} f_{\sigma' m} \sum_{q}^{\in virt} \left[U_{qm}^{\sigma'\sigma'(1)}\right]^{*} \left[c_{\nu q}^{\sigma'}\right]^{*} && \text{(H.208a)}
\end{aligned}$$

the corresponding real and imaginary parts read:

$$\begin{aligned}
\mathrm{Re}\left[\mathbb{P}_{\mu\nu}^{\sigma\sigma'(2)}\right] &= \sum_{m}^{\in occ} c_{\mu m}^{\sigma} f_{\sigma m} \left\{ \sum_{n}^{\in occ} \mathrm{Re}\left[U_{nm}^{\sigma'\sigma(2)}\right] c_{\nu n}^{\sigma'} + \sum_{p}^{\in virt} \mathrm{Re}\left[U_{pm}^{\sigma'\sigma(2)}\right] c_{\nu p}^{\sigma'} \right\} \\
&+ \sum_{m}^{\in occ} c_{\mu m}^{\sigma} \sum_{n}^{\in occ} \mathrm{Re}\left[U_{mn}^{\sigma\sigma'(2)}\right] f_{\sigma' n} c_{\nu n}^{\sigma'} + \sum_{p}^{\in virt} c_{\mu p}^{\sigma} \sum_{n}^{\in occ} \mathrm{Re}\left[U_{pn}^{\sigma\sigma'(2)}\right] f_{\sigma' n} c_{\nu n}^{\sigma'} \\
&+ \sum_{p}^{\in virt} c_{\mu p}^{\sigma} \sum_{m}^{\in occ} \mathrm{Im}\left[U_{pm}^{\sigma\sigma(1)}\right] f_{\sigma m} \sum_{q}^{\in virt} \mathrm{Im}\left[U_{qm}^{\sigma'\sigma(1)}\right] c_{\nu q}^{\sigma'} \\
&+ \sum_{p}^{\in virt} c_{\mu p}^{\sigma} \sum_{m}^{\in occ} \mathrm{Im}\left[U_{pm}^{\sigma\sigma'(1)}\right] f_{\sigma' m} \sum_{q}^{\in virt} \mathrm{Im}\left[U_{qm}^{\sigma'\sigma'(1)}\right] c_{\nu q}^{\sigma'} \qquad \text{(H.208b)}
\end{aligned}$$

$$\begin{aligned}
\mathrm{Im}\left[\mathbb{P}_{\mu\nu}^{\sigma\sigma'(2)}\right] &= -\sum_{m}^{\in occ} c_{\mu m}^{\sigma} f_{\sigma m} \left\{ \sum_{n}^{\in occ} \mathrm{Im}\left[U_{nm}^{\sigma'\sigma(2)}\right] c_{\nu n}^{\sigma'} + \sum_{p}^{\in virt} \mathrm{Im}\left[U_{pm}^{\sigma'\sigma(2)}\right] c_{\nu p}^{\sigma'} \right\} \\
&+ \sum_{m}^{\in occ} c_{\mu m}^{\sigma} \sum_{n}^{\in occ} \mathrm{Im}\left[U_{mn}^{\sigma\sigma'(2)}\right] f_{\sigma' n} c_{\nu n}^{\sigma'} + \sum_{p}^{\in virt} c_{\mu p}^{\sigma} \sum_{n}^{\in occ} \mathrm{Im}\left[U_{pn}^{\sigma\sigma'(2)}\right] f_{\sigma' n} c_{\nu n}^{\sigma'} \\
&+ \sum_{p}^{\in virt} c_{\mu p}^{\sigma} \sum_{m}^{\in occ} \mathrm{Im}\left[U_{pm}^{\sigma\sigma(1)}\right] f_{\sigma m} \sum_{q}^{\in virt} \mathrm{Re}\left[U_{qm}^{\sigma'\sigma(1)}\right] c_{\nu q}^{\sigma'} \\
&- \sum_{p}^{\in virt} c_{\mu p}^{\sigma} \sum_{m}^{\in occ} \mathrm{Re}\left[U_{pm}^{\sigma\sigma'(1)}\right] f_{\sigma' m} \sum_{q}^{\in virt} \mathrm{Im}\left[U_{qm}^{\sigma'\sigma'(1)}\right] c_{\nu q}^{\sigma'} \qquad \text{(H.208c)}
\end{aligned}$$

and for the diagonal spin-blocks:

$$\begin{aligned}
\mathbb{P}_{\mu\nu}^{\sigma\sigma(2)} &= \sum_{m}^{\in occ} c_{\mu m}^{\sigma} f_{\sigma m} \left\{ \sum_{n}^{\in occ} \left[U_{nm}^{\sigma\sigma(2)}\right]^{*} \left[c_{\nu n}^{\sigma}\right]^{*} + \sum_{p}^{\in virt} \left[U_{pm}^{\sigma\sigma(2)}\right]^{*} \left[c_{\nu p}^{\sigma}\right]^{*} \right\} \\
&+ \sum_{m}^{\in occ} c_{\mu m}^{\sigma} \sum_{n}^{\in occ} U_{mn}^{\sigma\sigma(2)} f_{\sigma n} \left[c_{\nu n}^{\sigma}\right]^{*} + \sum_{p}^{\in virt} c_{\mu p}^{\sigma} \sum_{n}^{\in occ} U_{pn}^{\sigma\sigma(2)} f_{\sigma n} \left[c_{\nu n}^{\sigma}\right]^{*} \\
&+ \sum_{p}^{\in virt} c_{\mu p}^{\sigma} \sum_{m}^{\in occ} U_{pm}^{\sigma\sigma(1)} f_{\sigma m} \sum_{q}^{\in virt} \left[U_{qm}^{\sigma\sigma(1)}\right]^{*} \left[c_{\nu q}^{\sigma}\right]^{*} \\
&+ \sum_{p}^{\in virt} c_{\mu p}^{\sigma} \sum_{m}^{\in occ} U_{pm}^{\sigma\sigma'(1)} f_{\sigma' m} \sum_{q}^{\in virt} \left[U_{qm}^{\sigma\sigma'(1)}\right]^{*} \left[c_{\nu q}^{\sigma}\right]^{*} \qquad \text{(H.208d)}
\end{aligned}$$

The real and imaginary parts of the diagonal spin-blocks read:

$$
\begin{aligned}
\mathrm{Re}\left[\mathbb{P}_{\mu\nu}^{\sigma\sigma(2)}\right] &= \sum_{m}^{\in occ} c_{\mu m}^{\sigma} f_{\sigma m} \left\{ \sum_{n}^{\in occ} \mathrm{Re}\left[U_{nm}^{\sigma\sigma(2)}\right] c_{\nu n}^{\sigma} + \sum_{p}^{\in virt} \mathrm{Re}\left[U_{pm}^{\sigma\sigma(2)}\right] c_{\nu p}^{\sigma} \right\} \\
&+ \sum_{m}^{\in occ} c_{\mu m}^{\sigma} \sum_{n}^{\in occ} \mathrm{Re}\left[U_{mn}^{\sigma\sigma(2)}\right] f_{\sigma n} c_{\nu n}^{\sigma} + \sum_{p}^{\in virt} c_{\mu p}^{\sigma} \sum_{n}^{\in occ} \mathrm{Re}\left[U_{pn}^{\sigma\sigma(2)}\right] f_{\sigma n} c_{\nu n}^{\sigma} \\
&+ \sum_{p}^{\in virt} c_{\mu p}^{\sigma} \sum_{m}^{\in occ} \mathrm{Im}\left[U_{pm}^{\sigma\sigma(1)}\right] f_{\sigma m} \sum_{q}^{\in virt} \mathrm{Im}\left[U_{qm}^{\sigma\sigma(1)}\right] c_{\nu q}^{\sigma} \\
&+ \sum_{p}^{\in virt} c_{\mu p}^{\sigma} \sum_{m}^{\in occ} \mathrm{Re}\left[U_{pm}^{\sigma\sigma'(1)}\right] f_{\sigma' m} \sum_{q}^{\in virt} \mathrm{Re}\left[U_{qm}^{\sigma\sigma'(1)}\right] c_{\nu q}^{\sigma} \\
&+ \sum_{p}^{\in virt} c_{\mu p}^{\sigma} \sum_{m}^{\in occ} \mathrm{Im}\left[U_{pm}^{\sigma\sigma'(1)}\right] f_{\sigma' m} \sum_{q}^{\in virt} \mathrm{Im}\left[U_{qm}^{\sigma\sigma'(1)}\right] c_{\nu q}^{\sigma} \qquad \text{(H.208e)}
\end{aligned}
$$

$$
\begin{aligned}
\mathrm{Im}\left[\mathbb{P}_{\mu\nu}^{\sigma\sigma(2)}\right] &= -\sum_{m}^{\in occ} c_{\mu m}^{\sigma} f_{\sigma m} \left\{ \sum_{n}^{\in occ} \mathrm{Im}\left[U_{nm}^{\sigma\sigma(2)}\right] c_{\nu n}^{\sigma} + \sum_{p}^{\in virt} \mathrm{Im}\left[U_{pm}^{\sigma\sigma(2)}\right] c_{\nu p}^{\sigma} \right\} \\
&+ \sum_{m}^{\in occ} c_{\mu m}^{\sigma} \sum_{n}^{\in occ} \mathrm{Im}\left[U_{mn}^{\sigma\sigma(2)}\right] f_{\sigma n} c_{\nu n}^{\sigma} + \sum_{p}^{\in virt} c_{\mu p}^{\sigma} \sum_{n}^{\in occ} \mathrm{Im}\left[U_{pn}^{\sigma\sigma(2)}\right] f_{\sigma n} c_{\nu n}^{\sigma} \\
&+ \sum_{p}^{\in virt} c_{\mu p}^{\sigma} \sum_{m}^{\in occ} \mathrm{Im}\left[U_{pm}^{\sigma\sigma'(1)}\right] f_{\sigma' m} \sum_{q}^{\in virt} \mathrm{Re}\left[U_{qm}^{\sigma\sigma'(1)}\right] c_{\nu q}^{\sigma} \\
&- \sum_{p}^{\in virt} c_{\mu p}^{\sigma} \sum_{m}^{\in occ} \mathrm{Re}\left[U_{pm}^{\sigma\sigma'(1)}\right] f_{\sigma' m} \sum_{q}^{\in virt} \mathrm{Im}\left[U_{qm}^{\sigma\sigma'(1)}\right] c_{\nu q}^{\sigma} \qquad \text{(H.208f)}
\end{aligned}
$$

The matrix-elements of the third-order perturbed density matrix read, for the off-diagonal spin-blocks ($\sigma \neq \sigma'$):

$$\begin{aligned}
\mathbb{P}^{\sigma\sigma'(3)}_{\mu\nu} &= \sum_{m}^{\in occ} c^{\sigma}_{\mu m} f_{\sigma m} \left\{ \sum_{n}^{\in occ} \left[U^{\sigma'\sigma(3)}_{nm} \right]^{*} \left[c^{\sigma'}_{\nu n} \right]^{*} + \sum_{p}^{\in virt} \left[U^{\sigma'\sigma(3)}_{pm} \right]^{*} \left[c^{\sigma'}_{\nu p} \right]^{*} \right\} \\
&+ \sum_{m}^{\in occ} c^{\sigma}_{\mu m} \sum_{n}^{\in occ} U^{\sigma\sigma'(3)}_{mn} f_{\sigma' n} \left[c^{\sigma'}_{\nu n} \right]^{*} + \sum_{p}^{\in virt} c^{\sigma}_{\mu p} \sum_{n}^{\in occ} U^{\sigma\sigma'(3)}_{pn} f_{\sigma' n} \left[c^{\sigma'}_{\nu n} \right]^{*} \\
&+ \sum_{m}^{\in occ} c^{\sigma}_{\mu m} \sum_{n}^{\in occ} U^{\sigma\sigma(2)}_{mn} f_{\sigma n} \sum_{p}^{\in virt} \left[U^{\sigma'\sigma(1)}_{pn} \right]^{*} \left[c^{\sigma'}_{\nu p} \right]^{*} \\
&+ \sum_{p}^{\in virt} c^{\sigma}_{\mu p} \sum_{m}^{\in occ} U^{\sigma\sigma(2)}_{pm} f_{\sigma m} \sum_{q}^{\in virt} \left[U^{\sigma'\sigma(1)}_{qm} \right]^{*} \left[c^{\sigma'}_{\nu q} \right]^{*} \\
&+ \sum_{m}^{\in occ} c^{\sigma}_{\mu m} \sum_{n}^{\in occ} U^{\sigma\sigma'(2)}_{mn} f_{\sigma' n} \sum_{p}^{\in virt} \left[U^{\sigma'\sigma'(1)}_{pn} \right]^{*} \left[c^{\sigma'}_{\nu p} \right]^{*} \\
&+ \sum_{p}^{\in virt} c^{\sigma}_{\mu p} \sum_{m}^{\in occ} U^{\sigma\sigma'(2)}_{pm} f_{\sigma' m} \sum_{q}^{\in virt} \left[U^{\sigma'\sigma'(1)}_{qm} \right]^{*} \left[c^{\sigma'}_{\nu q} \right]^{*} \\
&+ \sum_{p}^{\in virt} c^{\sigma}_{\mu p} \sum_{m}^{\in occ} U^{\sigma\sigma(1)}_{pm} f_{\sigma m} \left\{ \sum_{n}^{\in occ} \left[U^{\sigma'\sigma(2)}_{nm} \right]^{*} \left[c^{\sigma'}_{\nu n} \right]^{*} + \sum_{q}^{\in virt} \left[U^{\sigma'\sigma(2)}_{qm} \right]^{*} \left[c^{\sigma'}_{\nu q} \right]^{*} \right\} \\
&+ \sum_{p}^{\in virt} c^{\sigma}_{\mu p} \sum_{m}^{\in occ} U^{\sigma\sigma'(1)}_{pm} f_{\sigma' m} \left\{ \sum_{n}^{\in occ} \left[U^{\sigma'\sigma'(2)}_{nm} \right]^{*} \left[c^{\sigma'}_{\nu n} \right]^{*} + \sum_{q}^{\in virt} \left[U^{\sigma'\sigma'(2)}_{qm} \right]^{*} \left[c^{\sigma'}_{\nu q} \right]^{*} \right\} \qquad \text{(H.209a)}
\end{aligned}$$

The corresponding real and imaginary parts read:

$$\begin{aligned}
\mathrm{Re}\left[\mathbb{P}_{\mu\nu}^{\sigma\sigma'(3)}\right] &= \sum_{m}^{\in occ} c_{\mu m}^{\sigma} f_{\sigma m} \left\{ \sum_{n}^{\in occ} \mathrm{Re}\left[U_{nm}^{\sigma'\sigma(3)}\right] c_{\nu n}^{\sigma'} + \sum_{p}^{\in virt} \mathrm{Re}\left[U_{pm}^{\sigma'\sigma(3)}\right] c_{\nu p}^{\sigma'} \right\} \\
&+ \sum_{m}^{\in occ} c_{\mu m}^{\sigma} \sum_{n}^{\in occ} \mathrm{Re}\left[U_{mn}^{\sigma\sigma'(3)}\right] f_{\sigma' n} c_{\nu n}^{\sigma'} + \sum_{p}^{\in virt} c_{\mu p}^{\sigma} \sum_{n}^{\in occ} \mathrm{Re}\left[U_{pn}^{\sigma\sigma'(3)}\right] f_{\sigma' n} c_{\nu n}^{\sigma'} \\
&+ \sum_{m}^{\in occ} c_{\mu m}^{\sigma} \sum_{n}^{\in occ} \mathrm{Re}\left[U_{mn}^{\sigma\sigma(2)}\right] f_{\sigma n} \sum_{p}^{\in virt} \mathrm{Re}\left[U_{pn}^{\sigma'\sigma(1)}\right] c_{\nu p}^{\sigma'} \\
&+ \sum_{m}^{\in occ} c_{\mu m}^{\sigma} \sum_{n}^{\in occ} \mathrm{Im}\left[U_{mn}^{\sigma\sigma(2)}\right] f_{\sigma n} \sum_{p}^{\in virt} \mathrm{Im}\left[U_{pn}^{\sigma'\sigma(1)}\right] c_{\nu p}^{\sigma'} \\
&+ \sum_{p}^{\in virt} c_{\mu p}^{\sigma} \sum_{m}^{\in occ} \mathrm{Re}\left[U_{pm}^{\sigma\sigma(2)}\right] f_{\sigma m} \sum_{q}^{\in virt} \mathrm{Re}\left[U_{qm}^{\sigma'\sigma(1)}\right] c_{\nu q}^{\sigma'} \\
&+ \sum_{p}^{\in virt} c_{\mu p}^{\sigma} \sum_{m}^{\in occ} \mathrm{Im}\left[U_{pm}^{\sigma\sigma(2)}\right] f_{\sigma m} \sum_{q}^{\in virt} \mathrm{Im}\left[U_{qm}^{\sigma'\sigma(1)}\right] c_{\nu q}^{\sigma'} \\
&+ \sum_{m}^{\in occ} c_{\mu m}^{\sigma} \sum_{n}^{\in occ} \mathrm{Im}\left[U_{mn}^{\sigma\sigma'(2)}\right] f_{\sigma' n} \sum_{p}^{\in virt} \mathrm{Im}\left[U_{pn}^{\sigma'\sigma'(1)}\right] c_{\nu p}^{\sigma'} \\
&+ \sum_{p}^{\in virt} c_{\mu p}^{\sigma} \sum_{m}^{\in occ} \mathrm{Im}\left[U_{pm}^{\sigma\sigma'(2)}\right] f_{\sigma' m} \sum_{q}^{\in virt} \mathrm{Im}\left[U_{qm}^{\sigma'\sigma'(1)}\right] c_{\nu q}^{\sigma'} \\
&+ \sum_{p}^{\in virt} c_{\mu p}^{\sigma} \sum_{m}^{\in occ} \mathrm{Im}\left[U_{pm}^{\sigma\sigma(1)}\right] f_{\sigma m} \left\{ \sum_{n}^{\in occ} \mathrm{Im}\left[U_{nm}^{\sigma'\sigma(2)}\right] c_{\nu n}^{\sigma'} + \sum_{q}^{\in virt} \mathrm{Im}\left[U_{qm}^{\sigma'\sigma(2)}\right] c_{\nu q}^{\sigma'} \right\} \\
&+ \sum_{p}^{\in virt} c_{\mu p}^{\sigma} \sum_{m}^{\in occ} \mathrm{Re}\left[U_{pm}^{\sigma\sigma'(1)}\right] f_{\sigma' m} \left\{ \sum_{n}^{\in occ} \mathrm{Re}\left[U_{nm}^{\sigma'\sigma'(2)}\right] c_{\nu n}^{\sigma'} + \sum_{q}^{\in virt} \mathrm{Re}\left[U_{qm}^{\sigma'\sigma'(2)}\right] c_{\nu q}^{\sigma'} \right\} \\
&+ \sum_{p}^{\in virt} c_{\mu p}^{\sigma} \sum_{m}^{\in occ} \mathrm{Im}\left[U_{pm}^{\sigma\sigma'(1)}\right] f_{\sigma' m} \left\{ \sum_{n}^{\in occ} \mathrm{Im}\left[U_{nm}^{\sigma'\sigma'(2)}\right] c_{\nu n}^{\sigma'} + \sum_{q}^{\in virt} \mathrm{Im}\left[U_{qm}^{\sigma'\sigma'(2)}\right] c_{\nu q}^{\sigma'} \right\}
\end{aligned} \tag{H.209b}$$

and for the imaginary part:

$$
\begin{aligned}
\mathrm{Im}\left[\mathbb{P}^{\sigma\sigma'(3)}_{\mu\nu}\right] \;=\;& -\sum_{m}^{\in occ} c^{\sigma}_{\mu m} f_{\sigma m}\left\{\sum_{n}^{\in occ}\mathrm{Im}\left[U^{\sigma'\sigma(3)}_{nm}\right]c^{\sigma'}_{\nu n}+\sum_{p}^{\in virt}\mathrm{Im}\left[U^{\sigma'\sigma(3)}_{pm}\right]c^{\sigma'}_{\nu p}\right\}\\
&+\sum_{m}^{\in occ} c^{\sigma}_{\mu m}\sum_{n}^{\in occ}\mathrm{Im}\left[U^{\sigma\sigma'(3)}_{mn}\right]f_{\sigma' n}c^{\sigma'}_{\nu n}+\sum_{p}^{\in virt} c^{\sigma}_{\mu p}\sum_{n}^{\in occ}\mathrm{Im}\left[U^{\sigma\sigma'(3)}_{pn}\right]f_{\sigma' n}c^{\sigma'}_{\nu n}\\
&+\sum_{m}^{\in occ} c^{\sigma}_{\mu m}\sum_{n}^{\in occ}\mathrm{Im}\left[U^{\sigma\sigma(2)}_{mn}\right]f_{\sigma n}\sum_{p}^{\in virt}\mathrm{Re}\left[U^{\sigma'\sigma(1)}_{pn}\right]c^{\sigma'}_{\nu p}\\
&-\sum_{m}^{\in occ} c^{\sigma}_{\mu m}\sum_{n}^{\in occ}\mathrm{Re}\left[U^{\sigma\sigma(2)}_{mn}\right]f_{\sigma n}\sum_{p}^{\in virt}\mathrm{Im}\left[U^{\sigma'\sigma(1)}_{pn}\right]c^{\sigma'}_{\nu p}\\
&+\sum_{p}^{\in virt} c^{\sigma}_{\mu p}\sum_{m}^{\in occ}\mathrm{Im}\left[U^{\sigma\sigma(2)}_{pm}\right]f_{\sigma m}\sum_{q}^{\in virt}\mathrm{Re}\left[U^{\sigma'\sigma(1)}_{qm}\right]c^{\sigma'}_{\nu q}\\
&-\sum_{p}^{\in virt} c^{\sigma}_{\mu p}\sum_{m}^{\in occ}\mathrm{Re}\left[U^{\sigma\sigma(2)}_{pm}\right]f_{\sigma m}\sum_{q}^{\in virt}\mathrm{Im}\left[U^{\sigma'\sigma(1)}_{qm}\right]c^{\sigma'}_{\nu q}\\
&-\sum_{m}^{\in occ} c^{\sigma}_{\mu m}\sum_{n}^{\in occ}\mathrm{Re}\left[U^{\sigma\sigma'(2)}_{mn}\right]f_{\sigma' n}\sum_{p}^{\in virt}\mathrm{Im}\left[U^{\sigma'\sigma'(1)}_{pn}\right]c^{\sigma'}_{\nu p}\\
&-\sum_{p}^{\in virt} c^{\sigma}_{\mu p}\sum_{m}^{\in occ}\mathrm{Re}\left[U^{\sigma\sigma'(2)}_{pm}\right]f_{\sigma' m}\sum_{q}^{\in virt}\mathrm{Im}\left[U^{\sigma'\sigma'(1)}_{qm}\right]c^{\sigma'}_{\nu q}\\
&+\sum_{p}^{\in virt} c^{\sigma}_{\mu p}\sum_{m}^{\in occ}\mathrm{Im}\left[U^{\sigma\sigma(1)}_{pm}\right]f_{\sigma m}\left\{\sum_{n}^{\in occ}\mathrm{Re}\left[U^{\sigma'\sigma(2)}_{nm}\right]c^{\sigma'}_{\nu n}+\sum_{q}^{\in virt}\mathrm{Re}\left[U^{\sigma'\sigma(2)}_{qm}\right]c^{\sigma'}_{\nu q}\right\}\\
&+\sum_{p}^{\in virt} c^{\sigma}_{\mu p}\sum_{m}^{\in occ}\mathrm{Im}\left[U^{\sigma\sigma'(1)}_{pm}\right]f_{\sigma' m}\left\{\sum_{n}^{\in occ}\mathrm{Re}\left[U^{\sigma'\sigma'(2)}_{nm}\right]c^{\sigma'}_{\nu n}+\sum_{q}^{\in virt}\mathrm{Re}\left[U^{\sigma'\sigma'(2)}_{qm}\right]c^{\sigma'}_{\nu q}\right\}\\
&-\sum_{p}^{\in virt} c^{\sigma}_{\mu p}\sum_{m}^{\in occ}\mathrm{Re}\left[U^{\sigma\sigma'(1)}_{pm}\right]f_{\sigma' m}\left\{\sum_{n}^{\in occ}\mathrm{Im}\left[U^{\sigma'\sigma'(2)}_{nm}\right]c^{\sigma'}_{\nu n}+\sum_{q}^{\in virt}\mathrm{Im}\left[U^{\sigma'\sigma'(2)}_{qm}\right]c^{\sigma'}_{\nu q}\right\}
\end{aligned}
\tag{H.209c}
$$

Now for the diagonal spin-blocks of the third-order perturbed density matrix-elements:

$$\begin{aligned}
\mathbb{P}^{\sigma\sigma(3)}_{\mu\nu} &= \sum_{m}^{\in occ} c^{\sigma}_{\mu m} f_{\sigma m} \left\{ \sum_{n}^{\in occ} \left[U^{\sigma\sigma(3)}_{nm}\right]^{*} \left[c^{\sigma}_{\nu n}\right]^{*} + \sum_{p}^{\in virt} \left[U^{\sigma\sigma(3)}_{pm}\right]^{*} \left[c^{\sigma}_{\nu p}\right]^{*} \right\} \\
&+ \sum_{m}^{\in occ} c^{\sigma}_{\mu m} \sum_{n}^{\in occ} U^{\sigma\sigma(3)}_{mn} f_{\sigma n} \left[c^{\sigma}_{\nu n}\right]^{*} + \sum_{p}^{\in virt} c^{\sigma}_{\mu p} \sum_{n}^{\in occ} U^{\sigma\sigma(3)}_{pn} f_{\sigma n} \left[c^{\sigma}_{\nu n}\right]^{*} \\
&+ \sum_{m}^{\in occ} c^{\sigma}_{\mu m} \sum_{n}^{\in occ} U^{\sigma\sigma(2)}_{mn} f_{\sigma n} \sum_{p}^{\in virt} \left[U^{\sigma\sigma(1)}_{pn}\right]^{*} \left[c^{\sigma}_{\nu p}\right]^{*} \\
&+ \sum_{p}^{\in virt} c^{\sigma}_{\mu p} \sum_{m}^{\in occ} U^{\sigma\sigma(2)}_{pm} f_{\sigma m} \sum_{q}^{\in virt} \left[U^{\sigma\sigma(1)}_{qm}\right]^{*} \left[c^{\sigma}_{\nu q}\right]^{*} \\
&+ \sum_{m}^{\in occ} c^{\sigma}_{\mu m} \sum_{n}^{\in occ} U^{\sigma\sigma'(2)}_{mn} f_{\sigma' n} \sum_{p}^{\in virt} \left[U^{\sigma\sigma'(1)}_{pn}\right]^{*} \left[c^{\sigma}_{\nu p}\right]^{*} \\
&+ \sum_{p}^{\in virt} c^{\sigma}_{\mu p} \sum_{m}^{\in occ} U^{\sigma\sigma'(2)}_{pm} f_{\sigma' m} \sum_{q}^{\in virt} \left[U^{\sigma\sigma'(1)}_{qm}\right]^{*} \left[c^{\sigma}_{\nu q}\right]^{*} \\
&+ \sum_{p}^{\in virt} c^{\sigma}_{\mu p} \sum_{m}^{\in occ} U^{\sigma\sigma(1)}_{pm} f_{\sigma m} \left\{ \sum_{n}^{\in occ} \left[U^{\sigma\sigma(2)}_{nm}\right]^{*} \left[c^{\sigma}_{\nu n}\right]^{*} + \sum_{q}^{\in virt} \left[U^{\sigma\sigma(2)}_{qm}\right]^{*} \left[c^{\sigma}_{\nu q}\right]^{*} \right\} \\
&+ \sum_{p}^{\in virt} c^{\sigma}_{\mu p} \sum_{m}^{\in occ} U^{\sigma\sigma'(1)}_{pm} f_{\sigma' m} \left\{ \sum_{n}^{\in occ} \left[U^{\sigma\sigma'(2)}_{nm}\right]^{*} \left[c^{\sigma}_{\nu n}\right]^{*} + \sum_{q}^{\in virt} \left[U^{\sigma\sigma'(2)}_{qm}\right]^{*} \left[c^{\sigma}_{\nu q}\right]^{*} \right\}
\end{aligned} \tag{H.210a}$$

The corresponding real and imaginary parts read:

$$\begin{aligned}
\mathrm{Re}\left[\mathbb{P}^{\sigma\sigma(3)}_{\mu\nu}\right] &= \sum_{m}^{\in occ} c^{\sigma}_{\mu m} f_{\sigma m} \left\{ \sum_{n}^{\in occ} \mathrm{Re}\left[U^{\sigma\sigma(3)}_{nm}\right] c^{\sigma}_{\nu n} + \sum_{p}^{\in virt} \mathrm{Re}\left[U^{\sigma\sigma(3)}_{pm}\right] c^{\sigma}_{\nu p} \right\} \\
&+ \sum_{m}^{\in occ} c^{\sigma}_{\mu m} \sum_{n}^{\in occ} \mathrm{Re}\left[U^{\sigma\sigma(3)}_{mn}\right] f_{\sigma n} c^{\sigma}_{\nu n} + \sum_{p}^{\in virt} c^{\sigma}_{\mu p} \sum_{n}^{\in occ} \mathrm{Re}\left[U^{\sigma\sigma(3)}_{pn}\right] f_{\sigma n} c^{\sigma}_{\nu n} \\
&+ \sum_{m}^{\in occ} c^{\sigma}_{\mu m} \sum_{n}^{\in occ} \mathrm{Im}\left[U^{\sigma\sigma(2)}_{mn}\right] f_{\sigma n} \sum_{p}^{\in virt} \mathrm{Im}\left[U^{\sigma\sigma(1)}_{pn}\right] c^{\sigma}_{\nu p} \\
&+ \sum_{p}^{\in virt} c^{\sigma}_{\mu p} \sum_{m}^{\in occ} \mathrm{Im}\left[U^{\sigma\sigma(2)}_{pm}\right] f_{\sigma m} \sum_{q}^{\in virt} \mathrm{Im}\left[U^{\sigma\sigma(1)}_{qm}\right] c^{\sigma}_{\nu q} \\
&+ \sum_{m}^{\in occ} c^{\sigma}_{\mu m} \sum_{n}^{\in occ} \mathrm{Re}\left[U^{\sigma\sigma'(2)}_{mn}\right] f_{\sigma' n} \sum_{p}^{\in virt} \mathrm{Re}\left[U^{\sigma\sigma'(1)}_{pn}\right] c^{\sigma}_{\nu p} \\
&+ \sum_{m}^{\in occ} c^{\sigma}_{\mu m} \sum_{n}^{\in occ} \mathrm{Im}\left[U^{\sigma\sigma'(2)}_{mn}\right] f_{\sigma' n} \sum_{p}^{\in virt} \mathrm{Im}\left[U^{\sigma\sigma'(1)}_{pn}\right] c^{\sigma}_{\nu p} \\
&+ \sum_{p}^{\in virt} c^{\sigma}_{\mu p} \sum_{m}^{\in occ} \mathrm{Re}\left[U^{\sigma\sigma'(2)}_{pm}\right] f_{\sigma' m} \sum_{q}^{\in virt} \mathrm{Re}\left[U^{\sigma\sigma'(1)}_{qm}\right] c^{\sigma}_{\nu q} \\
&+ \sum_{p}^{\in virt} c^{\sigma}_{\mu p} \sum_{m}^{\in occ} \mathrm{Im}\left[U^{\sigma\sigma'(2)}_{pm}\right] f_{\sigma' m} \sum_{q}^{\in virt} \mathrm{Im}\left[U^{\sigma\sigma'(1)}_{qm}\right] c^{\sigma}_{\nu q} \\
&+ \sum_{p}^{\in virt} c^{\sigma}_{\mu p} \sum_{m}^{\in occ} \mathrm{Im}\left[U^{\sigma\sigma(1)}_{pm}\right] f_{\sigma m} \left\{ \sum_{n}^{\in occ} \mathrm{Im}\left[U^{\sigma\sigma(2)}_{nm}\right] c^{\sigma}_{\nu n} + \sum_{q}^{\in virt} \mathrm{Im}\left[U^{\sigma\sigma(2)}_{qm}\right] c^{\sigma}_{\nu q} \right\} \\
&+ \sum_{p}^{\in virt} c^{\sigma}_{\mu p} \sum_{m}^{\in occ} \mathrm{Re}\left[U^{\sigma\sigma'(1)}_{pm}\right] f_{\sigma' m} \left\{ \sum_{n}^{\in occ} \mathrm{Re}\left[U^{\sigma\sigma'(2)}_{nm}\right] c^{\sigma}_{\nu n} + \sum_{q}^{\in virt} \mathrm{Re}\left[U^{\sigma\sigma'(2)}_{qm}\right] c^{\sigma}_{\nu q} \right\} \\
&+ \sum_{p}^{\in virt} c^{\sigma}_{\mu p} \sum_{m}^{\in occ} \mathrm{Im}\left[U^{\sigma\sigma'(1)}_{pm}\right] f_{\sigma' m} \left\{ \sum_{n}^{\in occ} \mathrm{Im}\left[U^{\sigma\sigma'(2)}_{nm}\right] c^{\sigma}_{\nu n} + \sum_{q}^{\in virt} \mathrm{Im}\left[U^{\sigma\sigma'(2)}_{qm}\right] c^{\sigma}_{\nu q} \right\}
\end{aligned} \tag{H.210b}$$

and for the imaginary part:

$$
\begin{aligned}
\mathrm{Im}\left[\mathbb{P}_{\mu\nu}^{\sigma\sigma(3)}\right] \quad = \quad & -\sum_{m}^{\in occ} c_{\mu m}^{\sigma} f_{\sigma m} \left\{ \sum_{n}^{\in occ} \mathrm{Im}\left[U_{nm}^{\sigma\sigma(3)}\right] c_{\nu n}^{\sigma} + \sum_{p}^{\in virt} \mathrm{Im}\left[U_{pm}^{\sigma\sigma(3)}\right] c_{\nu p}^{\sigma} \right\} \\
+ \quad & \sum_{m}^{\in occ} c_{\mu m}^{\sigma} \sum_{n}^{\in occ} \mathrm{Im}\left[U_{mn}^{\sigma\sigma(3)}\right] f_{\sigma n} c_{\nu n}^{\sigma} + \sum_{p}^{\in virt} c_{\mu p}^{\sigma} \sum_{n}^{\in occ} \mathrm{Im}\left[U_{pn}^{\sigma\sigma(3)}\right] f_{\sigma n} c_{\nu n}^{\sigma} \\
- \quad & \sum_{m}^{\in occ} c_{\mu m}^{\sigma} \sum_{n}^{\in occ} \mathrm{Re}\left[U_{mn}^{\sigma\sigma(2)}\right] f_{\sigma n} \sum_{p}^{\in virt} \mathrm{Im}\left[U_{pn}^{\sigma\sigma(1)}\right] c_{\nu p}^{\sigma} \\
- \quad & \sum_{p}^{\in virt} c_{\mu p}^{\sigma} \sum_{m}^{\in occ} \mathrm{Re}\left[U_{pm}^{\sigma\sigma(2)}\right] f_{\sigma m} \sum_{q}^{\in virt} \mathrm{Im}\left[U_{qm}^{\sigma\sigma(1)}\right] c_{\nu q}^{\sigma} \\
+ \quad & \sum_{m}^{\in occ} c_{\mu m}^{\sigma} \sum_{n}^{\in occ} \mathrm{Im}\left[U_{mn}^{\sigma\sigma'(2)}\right] f_{\sigma' n} \sum_{p}^{\in virt} \mathrm{Re}\left[U_{pn}^{\sigma\sigma'(1)}\right] c_{\nu p}^{\sigma} \\
- \quad & \sum_{m}^{\in occ} c_{\mu m}^{\sigma} \sum_{n}^{\in occ} \mathrm{Re}\left[U_{mn}^{\sigma\sigma'(2)}\right] f_{\sigma' n} \sum_{p}^{\in virt} \mathrm{Im}\left[U_{pn}^{\sigma\sigma'(1)}\right] c_{\nu p}^{\sigma} \\
+ \quad & \sum_{p}^{\in virt} c_{\mu p}^{\sigma} \sum_{m}^{\in occ} \mathrm{Im}\left[U_{pm}^{\sigma\sigma'(2)}\right] f_{\sigma' m} \sum_{q}^{\in virt} \mathrm{Re}\left[U_{qm}^{\sigma\sigma'(1)}\right] c_{\nu q}^{\sigma} \\
- \quad & \sum_{p}^{\in virt} c_{\mu p}^{\sigma} \sum_{m}^{\in occ} \mathrm{Re}\left[U_{pm}^{\sigma\sigma'(2)}\right] f_{\sigma' m} \sum_{q}^{\in virt} \mathrm{Im}\left[U_{qm}^{\sigma\sigma'(1)}\right] c_{\nu q}^{\sigma} \\
+ \quad & \sum_{p}^{\in virt} c_{\mu p}^{\sigma} \sum_{m}^{\in occ} \mathrm{Im}\left[U_{pm}^{\sigma\sigma(1)}\right] f_{\sigma m} \left\{ \sum_{n}^{\in occ} \mathrm{Re}\left[U_{nm}^{\sigma\sigma(2)}\right] c_{\nu n}^{\sigma} + \sum_{q}^{\in virt} \mathrm{Re}\left[U_{qm}^{\sigma\sigma(2)}\right] c_{\nu q}^{\sigma} \right\} \\
+ \quad & \sum_{p}^{\in virt} c_{\mu p}^{\sigma} \sum_{m}^{\in occ} \mathrm{Im}\left[U_{pm}^{\sigma\sigma'(1)}\right] f_{\sigma' m} \left\{ \sum_{n}^{\in occ} \mathrm{Re}\left[U_{nm}^{\sigma\sigma'(2)}\right] c_{\nu n}^{\sigma} + \sum_{q}^{\in virt} \mathrm{Re}\left[U_{qm}^{\sigma\sigma'(2)}\right] c_{\nu q}^{\sigma} \right\} \\
- \quad & \sum_{p}^{\in virt} c_{\mu p}^{\sigma} \sum_{m}^{\in occ} \mathrm{Re}\left[U_{pm}^{\sigma\sigma'(1)}\right] f_{\sigma' m} \left\{ \sum_{n}^{\in occ} \mathrm{Im}\left[U_{nm}^{\sigma\sigma'(2)}\right] c_{\nu n}^{\sigma} + \sum_{q}^{\in virt} \mathrm{Im}\left[U_{qm}^{\sigma\sigma'(2)}\right] c_{\nu q}^{\sigma} \right\}
\end{aligned}
\tag{H.210c}
$$

H.6 Simultaneous Perturbative Treatment of Spin-Orbit Coupling and Correlation

We now consider the case for which both SOC and dynamic correlation are treated as perturbations to the SR HF wavefunction. The Hamiltonian is then written as:

$$\hat{H} = \hat{H}^{(0,0)} + \hat{H}^{(1,0)} + \hat{H}^{(0,1)} \tag{H.211}$$

For the SR HF problem, $\hat{H}^{(0,0)}$ is the sum of one-electron Fock operators, $\hat{H}^{(1,0)}$ is the sum of one-electron SOC operators and $\hat{H}^{(0,1)}$ is the two-electron correlation potential:

$$\hat{H}^{(0,0)} = \sum_i \hat{F}_i = \sum_i \left(\hat{h}_i + \hat{C}_i - \hat{K}_i\right) = \hat{h} + \hat{C} - \hat{K} \tag{H.212a}$$

$$\hat{H}^{(1,0)} = \sum_i \hat{h}_{SO,i} = \hat{h}_{SO} \tag{H.212b}$$

$$\hat{H}^{(0,1)} = \frac{1}{2}\sum_i \sum_j{}' \frac{1}{r_{ij}} - \sum_i \left(\hat{C}_i - \hat{K}_i\right) = \hat{V}_{ee} - \left(\hat{C} - \hat{K}\right) \tag{H.212c}$$

where in Eq. (H.212) above, the indices i and j label the coordinates of the electrons. The energy of the system perturbed both by SOC and correlation is written as:

$$E = E^{(0,0)} + E^{(1,0)} + E^{(0,1)} + E^{(1,1)} + E^{(2,0)} + E^{(0,2)} + E^{(2,1)} + E^{(1,2)} + E^{(3,0)} + \dots \tag{H.213}$$

The sum $E^{(0,0)} + E^{(0,1)}$ is just the already calculated SR HF total energy, and we have already determined that for an SR HF reference $E^{(1,0)} = 0$. Then, the contributions $E^{(2,0)}$ and $E^{(3,0)}$ can be calculated from the uncoupled-perturbed approach from the previous sections. On the other hand, the contributions $E^{(0,2)}$ and $E^{(1,2)}$ would involve calculating the Møller-Plesset perturbed wavefunction, which is likely to be expensive, so we will not consider these for now. Let us concentrate instead on the the first order terms in correlation $E^{(1,1)}$ and $E^{(2,1)}$. The $(1,1)$ RSPT equation is as follows:

$$\begin{aligned} &\left[\hat{H}^{(0,0)} - E^{(0,0)}\right]|\psi^{(1,1)}\rangle + \left[\hat{H}^{(1,0)} - E^{(1,0)}\right]|\psi^{(0,1)}\rangle \\ &\quad + \left[\hat{H}^{(0,1)} - E^{(0,1)}\right]|\psi^{(1,0)}\rangle - E^{(1,1)}|\psi^{(0,0)}\rangle = 0 \end{aligned} \tag{H.214}$$

Left-multiplying both sides of Eq. (H.214) by $\langle\psi^{(0,0)}|$ and using Eq. (H.9):

$$E^{(1,1)} = \langle\psi^{(0,0)}|\hat{H}^{(1,0)}|\psi^{(0,1)}\rangle + \langle\psi^{(0,0)}|\hat{H}^{(0,1)}|\psi^{(1,0)}\rangle \tag{H.215}$$

It is useful to consider removing the first term in Eq. (H.215) involving the Møller-Plesset perturbed wavefunction $|\psi^{(0,1)}\rangle$, because this term is likely to be difficult to calculate. We can do this by first considering the $(1,0)$ RSPT equation:

$$\left[\hat{H}^{(0,0)} - E^{(0,0)}\right]|\psi^{(1,0)}\rangle + \left[\hat{H}^{(1,0)} - E^{(1,0)}\right]|\psi^{(0,0)}\rangle = 0 \tag{H.216}$$

Left-multiplying both sides of Eq. (H.216) by $|\psi^{(0,1)}\rangle$:

$$\langle\psi^{(0,1)}|\hat{H}^{(0,0)} - E^{(0,0)}|\psi^{(1,0)}\rangle + \langle\psi^{(0,1)}|\hat{H}^{(1,0)}|\psi^{(0,0)}\rangle = 0 \tag{H.217}$$

Proceeding similarly for the $(0, 1)$ RSPT equation:

$$\langle\psi^{(1,0)}|\hat{H}^{(0,0)} - E^{(0,0)}|\psi^{(0,1)}\rangle + \langle\psi^{(1,0)}|\hat{H}^{(0,1)}|\psi^{(0,0)}\rangle = 0 \tag{H.218}$$

Then taking the total of Eq. (H.215) minus the conjugate-transpose of Eq. (H.217) plus Eq. (H.218), we find:

$$E^{(1,1)} = 2\mathcal{R}\left[\langle\psi^{(0,0)}|\hat{H}^{(0,1)}|\psi^{(1,0)}\rangle\right] \tag{H.219a}$$

An alternative expression for $E^{(1,1)}$ can be found by taking the total of Eq. (H.215) minus the conjugate-transpose of Eq. (H.218) plus Eq. (H.217):

$$E^{(1,1)} = 2\mathcal{R}\left[\langle\psi^{(0,0)}|\hat{H}^{(1,0)}|\psi^{(0,1)}\rangle\right] \tag{H.219b}$$

But, from Brillouin's theorem, only doubly-excited determinants contribute to $|\psi^{(0,1)}\rangle$, and since from Eq. (H.212), $\hat{H}^{(1,0)}$ consists of only monoelectronic operators, we find:

$$E^{(1,1)} = 0 \tag{H.220}$$

Let us now move on to finding an appropriate expression for $E^{(2,1)}$. Bracketing the $(2, 1)$ RSPT equation with $\langle\psi^{(0,0)}|$:

$$E^{(2,1)} = \langle\psi^{(0,0)}|\hat{H}^{(1,0)}|\psi^{(1,1)}\rangle + \langle\psi^{(0,0)}|\hat{H}^{(0,1)}|\psi^{(2,0)}\rangle \tag{H.221}$$

We look to eliminate the first term on the r.h.s. of Eq. (H.221) because it involves the first order Møller-Plesset perturbed wavefunction. Bracketing the $(1, 0)$ RSPT equation with $\langle\psi^{(1,1)}|$:

$$0 = \langle\psi^{(1,1)}|\hat{H}^{(0,0)} - E^{(0,0)}|\psi^{(1,0)}\rangle + \langle\psi^{(1,1)}|\hat{H}^{(1,0)}|\psi^{(0,0)}\rangle \tag{H.222}$$

Bracketing the $(1, 1)$ RSPT equation with $\langle\psi^{(1,0)}|$:

$$0 = \langle\psi^{(1,0)}|\hat{H}^{(0,0)} - E^{(0,0)}|\psi^{(1,1)}\rangle + \langle\psi^{(1,0)}|\hat{H}^{(1,0)}|\psi^{(0,1)}\rangle + \langle\psi^{(1,0)}|\hat{H}^{(0,1)} - E^{(0,1)}|\psi^{(1,0)}\rangle \tag{H.223}$$

Bracketing the $(2, 0)$ RSPT equation with $\langle\psi^{(0,1)}|$:

$$0 = \langle\psi^{(0,1)}|\hat{H}^{(0,0)} - E^{(0,0)}|\psi^{(2,0)}\rangle + \langle\psi^{(0,1)}|\hat{H}^{(1,0)}|\psi^{(1,0)}\rangle \tag{H.224}$$

Bracketing the $(0, 1)$ RSPT equation with $\langle\psi^{(2,0)}|$:

$$0 = \langle\psi^{(2,0)}|\hat{H}^{(0,0)} - E^{(0,0)}|\psi^{(0,1)}\rangle + \langle\psi^{(2,0)}|\hat{H}^{(0,1)}|\psi^{(0,0)}\rangle \tag{H.225}$$

Taking the sum of Eq. (H.221) minus the conjugate transpose of Eq. (H.222) plus Eq. (H.223) minus the conjugate transpose of Eq. (H.257) plus Eq. (H.225) we find:

$$E^{(2,1)} = 2\mathcal{R}\left[\langle\psi^{(0,0)}|\hat{H}^{(0,1)}|\psi^{(2,0)}\rangle\right] + \langle\psi^{(1,0)}|\hat{H}^{(0,1)} - E^{(0,1)}|\psi^{(1,0)}\rangle \tag{H.226}$$

Now expanding the $|\psi^{(2,0)}\rangle$ and $|\psi^{(1,0)}\rangle$ in Eq. (H.226) using Eq. (H.14) we find:

$$\begin{aligned} E^{(2,1)} &= 2\sum_{j}{}' \mathcal{R}\left[\langle\psi^{(0,0)}|\hat{H}^{(0,1)}|\psi_j^{(0,0)}\rangle \sum_{k}{}' \frac{\langle\psi_j^{(0,0)}|\hat{H}^{(1,0)}|\psi_k^{(0,0)}\rangle\langle\psi_k^{(0,0)}|\hat{H}^{(1,0)}|\psi^{(0,0)}\rangle}{\left(E^{(0,0)} - E_j^{(0,0)}\right)\left(E^{(0,0)} - E_k^{(0,0)}\right)}\right] \\ &+ \sum_{jk}{}' \langle\psi_j^{(0,0)}|\hat{H}^{(0,1)} - E^{(0,1)}|\psi_k^{(0,0)}\rangle \frac{\langle\psi^{(0,0)}|\hat{H}^{(1,0)}|\psi_j^{(0,0)}\rangle\langle\psi_k^{(0,0)}|\hat{H}^{(1,0)}|\psi^{(0,0)}\rangle}{\left(E^{(0,0)} - E_j^{(0,0)}\right)\left(E^{(0,0)} - E_k^{(0,0)}\right)} \end{aligned} \tag{H.227}$$

Writing Eq. (H.227) explicitly in terms of all doubly- and singly-excited determinants with non-vanishing contributions, and taking into account the form of the operators $\hat{H}^{(1,0)}$ and $\hat{H}^{(0,1)}$ from Eq. (H.212):

$$\begin{aligned} E^{(2,1)} &= 2\sum_{m,n}^{\in occ}{}^{>>}\sum_{p,q}^{\in virt}{}^{>>}\mathcal{R}\Bigg[\langle\psi|\hat{V}_{ee}|\psi_{mn}^{pq}\rangle\Bigg\{\frac{\langle\psi_{mn}^{pq}|\hat{h}_{SO}|\psi_m^p\rangle\langle\psi_m^p|\hat{h}_{SO}|\psi\rangle}{\left(E - E_{mn}^{pq}\right)\left(E - E_m^p\right)} + \frac{\langle\psi_{mn}^{pq}|\hat{h}_{SO}|\psi_n^p\rangle\langle\psi_n^p|\hat{h}_{SO}|\psi\rangle}{\left(E - E_{mn}^{pq}\right)\left(E - E_n^p\right)} \\ &+ \frac{\langle\psi_{mn}^{pq}|\hat{h}_{SO}|\psi_m^q\rangle\langle\psi_m^q|\hat{h}_{SO}|\psi\rangle}{\left(E - E_{mn}^{pq}\right)\left(E - E_m^q\right)} + \frac{\langle\psi_{mn}^{pq}|\hat{h}_{SO}|\psi_n^q\rangle\langle\psi_n^q|\hat{h}_{SO}|\psi\rangle}{\left(E - E_{mn}^{pq}\right)\left(E - E_n^q\right)}\Bigg\}\Bigg] \\ &+ 2\sum_{m,n}^{\in occ}{}''\sum_{p,q}^{\in virt}{}''\mathcal{R}\Bigg[\langle\psi|\hat{V}_{ee} - \left(\hat{C} - \hat{K}\right)|\psi_m^p\rangle\Bigg\{\frac{\langle\psi_m^p|\hat{h}_{SO}|\psi_m^q\rangle\langle\psi_m^q|\hat{h}_{SO}|\psi\rangle}{\left(E - E_m^p\right)\left(E - E_m^q\right)} + \frac{\langle\psi_m^p|\hat{h}_{SO}|\psi_n^p\rangle\langle\psi_n^p|\hat{h}_{SO}|\psi\rangle}{\left(E - E_m^p\right)\left(E - E_n^p\right)}\Bigg\}\Bigg] \\ &+ \sum_{m,n}^{\in occ}{}''\sum_{p,q}^{\in virt}{}''\langle\psi_m^p|\hat{V}_{ee}|\psi_n^q\rangle\frac{\langle\psi|\hat{h}_{SO}|\psi_m^p\rangle\langle\psi_n^q|\hat{h}_{SO}|\psi\rangle}{\left(E - E_m^p\right)\left(E - E_n^q\right)} \\ &+ \sum_{m}^{\in occ}\sum_{p,q}^{\in virt}{}''\langle\psi_m^p|\hat{V}_{ee} - \left(\hat{C} - \hat{K}\right)|\psi_m^q\rangle\frac{\langle\psi|\hat{h}_{SO}|\psi_m^p\rangle\langle\psi_m^q|\hat{h}_{SO}|\psi\rangle}{\left(E - E_m^p\right)\left(E - E_m^q\right)} \\ &+ \sum_{m,n}^{\in occ}{}''\sum_{p}^{\in virt}\langle\psi_m^p|\hat{V}_{ee} - \left(\hat{C} - \hat{K}\right)|\psi_n^p\rangle\frac{\langle\psi|\hat{h}_{SO}|\psi_m^p\rangle\langle\psi_n^p|\hat{h}_{SO}|\psi\rangle}{\left(E - E_m^p\right)\left(E - E_n^p\right)} \\ &+ \sum_{m}^{\in occ}\sum_{p}^{\in virt}\langle\psi_m^p|\hat{V}_{ee} - \left(\hat{C} - \hat{K}\right)|\psi_m^p\rangle\frac{\langle\psi|\hat{h}_{SO}|\psi_m^p\rangle\langle\psi_m^p|\hat{h}_{SO}|\psi\rangle}{\left(E - E_m^p\right)\left(E - E_m^p\right)} \\ &- E^{(0,1)}\sum_{m}^{\in occ}\sum_{p}^{\in virt}\frac{\langle\psi|\hat{h}_{SO}|\psi_m^p\rangle\langle\psi_m^p|\hat{h}_{SO}|\psi\rangle}{\left(E - E_m^p\right)\left(E - E_m^p\right)} \end{aligned} \tag{H.228}$$

where, the symbol $\sum_{m,n}^{\in occ}{}^{>}$ means that the sum is taken over all values of $m \in occ$ and all values of $n < m$, as a means to avoid double-counting of the doubly-excited configurations. Similarly, the symbol $\sum_{p,q}^{\in virt}{}^{>}$ means that the sum is taken over all values of $p \in virt$ and all values of $q < p$. The double prime above the sums denotes that $n \neq m$ and $q \neq p$. Evaluating all of the required matrix-elements involving the correlation potential:

$$
\begin{aligned}
\langle\psi|\hat{V}_{ee}|\psi_{mn}^{pq}\rangle &= (mp|nq) - (mq|np) && \text{(H.229a)} \\
\langle\psi|\hat{V}_{ee} - \left(\hat{C} - \hat{K}\right)|\psi_{m}^{p}\rangle &= 0 && \text{(H.229b)} \\
\langle\psi_{m}^{p}|\hat{V}_{ee}|\psi_{n}^{q}\rangle &= (pm|nq) - (pq|nm) && \text{(H.229c)} \\
\langle\psi_{m}^{p}|\hat{V}_{ee} - \left(\hat{C} - \hat{K}\right)|\psi_{m}^{q}\rangle &= -\left[(pq|mm) - (pm|mq)\right] && \text{(H.229d)} \\
\langle\psi_{m}^{p}|\hat{V}_{ee} - \left(\hat{C} - \hat{K}\right)|\psi_{n}^{p}\rangle &= -\left[(nm|pp) - (np|pm)\right] && \text{(H.229e)} \\
\langle\psi_{m}^{p}|\hat{V}_{ee} - \left(\hat{C} - \hat{K}\right)|\psi_{m}^{p}\rangle &= -\frac{1}{2}\sum_{n,o}^{\in occ}\left[(oo|nn) - (on|no)\right] \\
&\quad - \left[(pp|mm) - (pm|mp)\right] && \text{(H.229f)} \\
E^{(0,1)} = \langle\psi|\hat{V}_{ee} - \left(\hat{C} - \hat{K}\right)|\psi\rangle &= -\frac{1}{2}\sum_{m,n}^{\in occ}\left[(mm|nn) - (mn|nm)\right] && \text{(H.229g)}
\end{aligned}
$$

Substituting Eq. (H.229) in (H.228):

$$
\begin{aligned}
E^{(2,1)} &= 2\sum_{m,n}^{\in occ}{}^{>>}\sum_{p,q}^{\in virt}{}^{>>}\mathcal{R}\Bigg[\{(mp|nq) - (mq|np)\}\Bigg\{\frac{\langle q|\hat{h}_{SO}|n\rangle\langle p|\hat{h}_{SO}|m\rangle}{\left(\epsilon_m + \epsilon_n - \epsilon_p - \epsilon_q\right)\left(\epsilon_m - \epsilon_p\right)} \\
&- \frac{\langle q|\hat{h}_{SO}|m\rangle\langle p|\hat{h}_{SO}|n\rangle}{\left(\epsilon_m + \epsilon_n - \epsilon_p - \epsilon_q\right)\left(\epsilon_n - \epsilon_p\right)} - \frac{\langle p|\hat{h}_{SO}|n\rangle\langle q|\hat{h}_{SO}|m\rangle}{\left(\epsilon_m + \epsilon_n - \epsilon_p - \epsilon_q\right)\left(\epsilon_m - \epsilon_q\right)} + \frac{\langle p|\hat{h}_{SO}|m\rangle\langle q|\hat{h}_{SO}|n\rangle}{\left(\epsilon_m + \epsilon_n - \epsilon_p - \epsilon_q\right)\left(\epsilon_n - \epsilon_q\right)}\Bigg\}\Bigg] \\
&+ \sum_{m,n}^{\in occ}{}''\sum_{p,q}^{\in virt}{}''\{(pm|nq) - (pq|nm)\}\frac{\langle m|\hat{h}_{SO}|p\rangle\langle q|\hat{h}_{SO}|n\rangle}{\left(\epsilon_m - \epsilon_p\right)\left(\epsilon_n - \epsilon_q\right)} \\
&- \sum_{m}^{\in occ}\sum_{p,q}^{\in virt}{}''\left[(pq|mm) - (pm|mq)\right]\frac{\langle m|\hat{h}_{SO}|p\rangle\langle q|\hat{h}_{SO}|m\rangle}{\left(\epsilon_m - \epsilon_p\right)\left(\epsilon_m - \epsilon_q\right)} \\
&- \sum_{m,n}^{\in occ}{}''\sum_{p}^{\in virt}\left[(nm|pp) - (np|pm)\right]\frac{\langle m|\hat{h}_{SO}|p\rangle\langle p|\hat{h}_{SO}|n\rangle}{\left(\epsilon_m - \epsilon_p\right)\left(\epsilon_n - \epsilon_p\right)} \\
&- \sum_{m}^{\in occ}\sum_{p}^{\in virt}\left[(pp|mm) - (pm|mp)\right]\frac{\langle m|\hat{h}_{SO}|p\rangle\langle p|\hat{h}_{SO}|m\rangle}{\left(\epsilon_m - \epsilon_p\right)\left(\epsilon_m - \epsilon_p\right)} \\
&= E_D^{(2,1)} + E_S^{(2,1)} && \text{(H.230)}
\end{aligned}
$$

In the last passage, we split the $E^{(2,1)}$ into a contribution arising from doubly-excited determinants that interact through the correlation potential $E_D^{(2,1)}$:

$$\begin{aligned}
E_D^{(2,1)} &= 2\sum_{m,n}^{\in occ}{}^{>>}\sum_{p,q}^{\in virt}{}^{>>}\mathcal{R}\Bigg[\{(mp|nq)-(mq|np)\}\Bigg\{\frac{\langle q|\hat{h}_{SO}|n\rangle\langle p|\hat{h}_{SO}|m\rangle}{\left(\epsilon_m+\epsilon_n-\epsilon_p-\epsilon_q\right)\left(\epsilon_m-\epsilon_p\right)} \\
&- \frac{\langle q|\hat{h}_{SO}|m\rangle\langle p|\hat{h}_{SO}|n\rangle}{\left(\epsilon_m+\epsilon_n-\epsilon_p-\epsilon_q\right)\left(\epsilon_n-\epsilon_p\right)}-\frac{\langle p|\hat{h}_{SO}|n\rangle\langle q|\hat{h}_{SO}|m\rangle}{\left(\epsilon_m+\epsilon_n-\epsilon_p-\epsilon_q\right)\left(\epsilon_m-\epsilon_q\right)} \\
&+ \frac{\langle p|\hat{h}_{SO}|m\rangle\langle q|\hat{h}_{SO}|n\rangle}{\left(\epsilon_m+\epsilon_n-\epsilon_p-\epsilon_q\right)\left(\epsilon_n-\epsilon_q\right)}\Bigg\}\Bigg] \qquad \text{(H.231a)}
\end{aligned}$$

as well as the contribution $E_S^{(2,1)}$ that arises from singly-excited determinants that interact through the correlation potential:

$$\begin{aligned}
E_S^{(2.1)} &= \sum_{m,n}^{\in occ}{}''\sum_{p,q}^{\in virt}{}''\{(pm|nq)-(pq|nm)\}\frac{\langle m|\hat{h}_{SO}|p\rangle\langle q|\hat{h}_{SO}|n\rangle}{\left(\epsilon_m-\epsilon_p\right)\left(\epsilon_n-\epsilon_q\right)} \\
&- \sum_{m}^{\in occ}\sum_{p,q}^{\in virt}{}''[(pq|mm)-(pm|mq)]\frac{\langle m|\hat{h}_{SO}|p\rangle\langle q|\hat{h}_{SO}|m\rangle}{\left(\epsilon_m-\epsilon_p\right)\left(\epsilon_m-\epsilon_q\right)} \\
&- \sum_{m,n}^{\in occ}{}''\sum_{p}^{\in virt}[(nm|pp)-(np|pm)]\frac{\langle m|\hat{h}_{SO}|p\rangle\langle p|\hat{h}_{SO}|n\rangle}{\left(\epsilon_m-\epsilon_p\right)\left(\epsilon_n-\epsilon_p\right)} \\
&- \sum_{m}^{\in occ}\sum_{p}^{\in virt}[(pp|mm)-(pm|mp)]\frac{\langle m|\hat{h}_{SO}|p\rangle\langle p|\hat{h}_{SO}|m\rangle}{\left(\epsilon_m-\epsilon_p\right)\left(\epsilon_m-\epsilon_p\right)} \\
&= \sum_{m,n}^{\in occ}\sum_{p,q}^{\in virt}\{(pm|nq)-(pq|nm)\}\frac{\langle m|\hat{h}_{SO}|p\rangle\langle q|\hat{h}_{SO}|n\rangle}{\left(\epsilon_m-\epsilon_p\right)\left(\epsilon_n-\epsilon_q\right)} \qquad \text{(H.231b)}
\end{aligned}$$

We now proceed to simplifying the expression for the contribution from doubly excited determinants $E_D^{(2,1)}$ to $E^{(2,1)}$. From Eq. (H.231a) the sums over m, n, p, q can be extended to the full set of values by realizing that the contribution from the terms $m = n$ or $p = q$ is zero, so that:

$$\begin{aligned}
E_D^{(2,1)} &= \frac{1}{2}\sum_{m,n}^{\in occ}\sum_{p,q}^{\in virt}\mathcal{R}\Bigg[\{(mp|nq)-(mq|np)\}\Bigg\{\frac{\langle q|\hat{h}_{SO}|n\rangle\langle p|\hat{h}_{SO}|m\rangle}{\left(\epsilon_m+\epsilon_n-\epsilon_p-\epsilon_q\right)\left(\epsilon_m-\epsilon_p\right)} \\
&- \frac{\langle q|\hat{h}_{SO}|m\rangle\langle p|\hat{h}_{SO}|n\rangle}{\left(\epsilon_m+\epsilon_n-\epsilon_p-\epsilon_q\right)\left(\epsilon_n-\epsilon_p\right)}-\frac{\langle p|\hat{h}_{SO}|n\rangle\langle q|\hat{h}_{SO}|m\rangle}{\left(\epsilon_m+\epsilon_n-\epsilon_p-\epsilon_q\right)\left(\epsilon_m-\epsilon_q\right)} \\
&+ \frac{\langle p|\hat{h}_{SO}|m\rangle\langle q|\hat{h}_{SO}|n\rangle}{\left(\epsilon_m+\epsilon_n-\epsilon_p-\epsilon_q\right)\left(\epsilon_n-\epsilon_q\right)}\Bigg\}\Bigg] \qquad \text{(H.232)}
\end{aligned}$$

It is now useful to consider getting rid of the denominator $\left(\epsilon_m + \epsilon_n - \epsilon_p - \epsilon_q\right)$. In order to do this, we notice that upon interchanging the labels m and n, the bielectronic integrals transform as:

$$(mp|nq) - (mq|np) \Rightarrow (np|mq) - (nq|mp) = -\{(mp|nq) - (mq|np)\} \tag{H.233}$$

Interchanging the labels of m and n in the second and third terms of Eq. (H.232), we find:

$$\begin{aligned} E_D^{(2,1)} &= \sum_{m,n}^{\in occ}\sum_{p,q}^{\in virt} \mathcal{R}\Bigg[\{(mp|nq) - (mq|np)\}\, \langle q|\hat{h}_{SO}|n\rangle\langle p|\hat{h}_{SO}|m\rangle \\ &\times \left\{ \frac{1}{\left(\epsilon_m + \epsilon_n - \epsilon_p - \epsilon_q\right)\left(\epsilon_m - \epsilon_p\right)} + \frac{1}{\left(\epsilon_m + \epsilon_n - \epsilon_p - \epsilon_q\right)\left(\epsilon_n - \epsilon_q\right)} \right\}\Bigg] \end{aligned} \tag{H.234}$$

Then, expressing both terms in Eq. (H.234) with a common denominator, we find:

$$E_D^{(2,1)} = \sum_{m,n}^{\in occ}\sum_{p,q}^{\in virt} \mathcal{R}\left[\{(mp|nq) - (mq|np)\} \left\{ \frac{\langle q|\hat{h}_{SO}|n\rangle\langle p|\hat{h}_{SO}|m\rangle}{\left(\epsilon_n - \epsilon_q\right)\left(\epsilon_m - \epsilon_p\right)} \right\} \right] \tag{H.235}$$

So that taking the sum of Eqs. (H.231b) and (H.235) we find:

$$\begin{aligned} E^{(2,1)} &= E_S^{(2,1)} + E_D^{(2,1)} = \sum_{m,n}^{\in occ}\sum_{p,q}^{\in virt} \{(pm|nq) - (pq|nm)\} \frac{\langle m|\hat{h}_{SO}|p\rangle\langle q|\hat{h}_{SO}|n\rangle}{\left(\epsilon_m - \epsilon_p\right)\left(\epsilon_n - \epsilon_q\right)} \\ &+ \sum_{m,n}^{\in occ}\sum_{p,q}^{\in virt} \mathcal{R}\left[\{(mp|nq) - (mq|np)\} \frac{\langle p|\hat{h}_{SO}|m\rangle\langle q|\hat{h}_{SO}|n\rangle}{\left(\epsilon_m - \epsilon_p\right)\left(\epsilon_n - \epsilon_q\right)} \right] \end{aligned} \tag{H.236}$$

H.6.1 Equations in a Finite Basis: The Singles Contribution

We consider now reducing the Eq. (H.236) to an expression that can be efficiently evaluated in a finite basis. We start with the first term in Eq. (H.236) that involves the contribution $E_S^{(2,1)}$ to $E^{(2,1)}$ from singly-excited determinants that interact through the correlation potential:

$$\begin{aligned} E_S^{(2,1)} &= \sum_{m,n}^{\in occ}\sum_{p,q}^{\in virt} \{(pm|nq) - (pq|nm)\} \frac{\langle m|\hat{h}_{SO}|p\rangle\langle q|\hat{h}_{SO}|n\rangle}{\left(\epsilon_m - \epsilon_p\right)\left(\epsilon_n - \epsilon_q\right)} \\ &= \sum_{m,n}^{\in occ}\sum_{p,q}^{\in virt} (pm|nq) \frac{\langle m|\hat{h}_{SO}|p\rangle\langle q|\hat{h}_{SO}|n\rangle}{\left(\epsilon_m - \epsilon_p\right)\left(\epsilon_n - \epsilon_q\right)} - \sum_{m,n}^{\in occ}\sum_{p,q}^{\in virt} (pq|nm) \frac{\langle m|\hat{h}_{SO}|p\rangle\langle q|\hat{h}_{SO}|n\rangle}{\left(\epsilon_m - \epsilon_p\right)\left(\epsilon_n - \epsilon_q\right)} \\ &= E_{S,C}^{(2,1)} - E_{S,K}^{(2,1)} \end{aligned} \tag{H.237}$$

where $E_S^{(2,1)}$ has been split into a "Coulomb"-type term $E_{S,C}^{(2,1)}$ and an "exchange"-type term $E_{S,K}^{(2,1)}$. Let us start with the "Coulomb"-type term $E_{S,C}^{(2,1)}$:

$$E_{S,C}^{(2,1)} = \sum_{m,n}^{\in occ} \sum_{p,q}^{\in virt} (pm|nq) \frac{\langle m|\hat{h}_{SO}|p\rangle\langle q|\hat{h}_{SO}|n\rangle}{\left(\epsilon_m - \epsilon_p\right)\left(\epsilon_n - \epsilon_q\right)} \tag{H.238}$$

Expanding the singly-occupied MOs in terms of AOs and making use of Eqs. (H.105) and (H.106):

$$E_{S,C}^{(2,1)} = \sum_{\sigma} \sum_{\mu\nu} \left[M_{\mu\nu}^{\sigma\sigma(1)}\right]^* \sum_{\sigma'} \sum_{\tau\omega} M_{\omega\tau}^{\sigma'\sigma'(1)} (\mu\nu|\tau\omega) \tag{H.239}$$

where the elements of the matrix of $M_{\mu\nu}^{\sigma\sigma'(N)}$ for integer $N > 0$ are defined as follows:

$$M_{\mu\nu}^{\sigma\sigma'(N)} = \sum_{m}^{\in occ} \sum_{p}^{\in virt} c_{\mu p}^{\sigma} \left[c_{\nu m}^{\sigma'}\right]^* U_{pm}^{\sigma\sigma'(N)} \tag{H.240}$$

Proceeding as in Eq. (H.239) for the "exchange"-type term $E_{S,K}^{(2,1)}$, we find:

$$E_{S,K}^{(2,1)} = \sum_{\sigma\sigma'} \sum_{\mu\nu} \left[M_{\mu\nu}^{\sigma\sigma'(1)}\right]^* \sum_{\tau\omega} M_{\omega\tau}^{\sigma\sigma'(1)} (\mu\omega|\tau\nu) \tag{H.241}$$

We note that from Eq. (H.241) every contribution with $\left[M_{\mu\nu}^{\sigma\sigma'(1)}\right]^* M_{\omega\tau}^{\sigma\sigma'(1)}$ will carry an imaginary part that will cancel perfectly with the imaginary part from the contribution $\left[M_{\omega\tau}^{\sigma\sigma'(1)}\right]^* M_{\mu\nu}^{\sigma\sigma'(1)}$, so that we may write:

$$E_{S,K}^{(2,1)} = \sum_{\sigma\sigma'} \mathcal{R}\left[\sum_{\mu\nu} \left[M_{\mu\nu}^{\sigma\sigma'(1)}\right]^* \sum_{\tau\omega} M_{\omega\tau}^{\sigma\sigma'(1)} (\mu\omega|\tau\nu)\right] \tag{H.242}$$

It can also be seen from Eq. (H.239) that $E_{S,C}^{(2,1)}$ is also purely real, because the diagonal spin-block matrix-elements $M_{\mu\nu}^{\sigma\sigma(1)}$ are purely imaginary, so that we may also write:

$$E_{S,C}^{(2,1)} = \sum_{\sigma\sigma'} \mathcal{R}\left[\sum_{\mu\nu} \left[M_{\mu\nu}^{\sigma\sigma(1)}\right]^* \sum_{\tau\omega} M_{\omega\tau}^{\sigma'\sigma'(1)} (\mu\nu|\tau\omega)\right] \tag{H.243}$$

H.6.2 Equations in a Finite Basis: The Doubles Contribution

We now find the expression in the AO basis for the second term in Eq. (H.236), corresponding to the contribution $E_D^{(2,1)}$ from doubly-excited determinants to $E^{(2,1)}$. As was done previously for $E_S^{(2,1)}$, we likewise split $E_D^{(2,1)}$ into a "Coulomb"-type contribution $E_{D,C}^{(2,1)}$ and an "exchange"-type contribution $E_{D,K}^{(2,1)}$:

$$\begin{aligned} E_D^{(2,1)} &= E_{D,C}^{(2,1)} - E_{D,K}^{(2,1)} = \sum_{m,n}^{\in occ}\sum_{p,q}^{\in virt}\mathcal{R}\left[(mp|nq)\left\{\frac{\langle q|\hat{h}_{SO}|n\rangle\langle p|\hat{h}_{SO}|m\rangle}{\left(\epsilon_n-\epsilon_q\right)\left(\epsilon_m-\epsilon_p\right)}\right\}\right] \\ &- \sum_{m,n}^{\in occ}\sum_{p,q}^{\in virt}\mathcal{R}\left[(mq|np)\left\{\frac{\langle q|\hat{h}_{SO}|n\rangle\langle p|\hat{h}_{SO}|m\rangle}{\left(\epsilon_n-\epsilon_q\right)\left(\epsilon_m-\epsilon_p\right)}\right\}\right] \end{aligned} \tag{H.244}$$

Proceeding as we did for Eq. (H.239) we find the expression in the AO basis for $E_{D,C}^{(2,1)}$:

$$E_{D,C}^{(2,1)} = \sum_{\sigma\sigma'}\mathcal{R}\left[\sum_{\mu\nu}M_{\nu\mu}^{\sigma\sigma(1)}\sum_{\tau\omega}M_{\omega\tau}^{\sigma'\sigma'(1)}(\mu\nu|\tau\omega)\right] \tag{H.245}$$

and for the $E_{D,K}^{(2,1)}$:

$$E_{D,K}^{(2,1)} = \sum_{\sigma\sigma'}\mathcal{R}\left[\sum_{\mu\nu}M_{\nu\mu}^{\sigma'\sigma(1)}\sum_{\tau\omega}M_{\omega\tau}^{\sigma\sigma'(1)}(\mu\omega|\tau\nu)\right] \tag{H.246}$$

H.6.3 Equations in a Finite Basis: Putting it all Together

Taking the sum of Eqs. (H.242), (H.243), (H.245) and (H.246):

$$\begin{aligned} E^{(2,1)} &= E_{S,C}^{(2,1)} + E_{D,C}^{(2,1)} - E_{S,K}^{(2,1)} - E_{D,K}^{(2,1)} \\ &= \sum_{\sigma\sigma'}\mathcal{R}\left[\sum_{\mu\nu}\left\{\left[M_{\mu\nu}^{\sigma\sigma(1)}\right]^* + M_{\nu\mu}^{\sigma\sigma(1)}\right\}\sum_{\tau\omega}M_{\omega\tau}^{\sigma'\sigma'(1)}(\mu\nu|\tau\omega)\right] \\ &- \sum_{\sigma\sigma'}\mathcal{R}\left[\sum_{\mu\nu}\left\{\left[M_{\mu\nu}^{\sigma\sigma'(1)}\right]^* + M_{\nu\mu}^{\sigma'\sigma(1)}\right\}\sum_{\tau\omega}M_{\omega\tau}^{\sigma\sigma'(1)}(\mu\omega|\tau\nu)\right] \end{aligned} \tag{H.247}$$

Finally, comparing Eq. (H.205) with Eq. (H.240) we notice that:

$$\left[M_{\mu\nu}^{\sigma\sigma'(1)}\right]^* + M_{\nu\mu}^{\sigma'\sigma(1)} = \left[\mathbb{P}_{\mu\nu}^{\sigma\sigma'(1)}\right]^* \tag{H.248}$$

Substituting Eq. (H.248) in Eq. (H.247) we find:

$$\begin{aligned} E^{(2,1)} &= \sum_{\sigma\sigma'}\mathcal{R}\left[\sum_{\mu\nu}\left[\mathbb{P}_{\mu\nu}^{\sigma\sigma(1)}\right]^*\sum_{\tau\omega}M_{\omega\tau}^{\sigma'\sigma'(1)}(\mu\nu|\tau\omega)\right] \\ &- \sum_{\sigma\sigma'}\mathcal{R}\left[\sum_{\mu\nu}\left[\mathbb{P}_{\mu\nu}^{\sigma\sigma'(1)}\right]^*\sum_{\tau\omega}M_{\omega\tau}^{\sigma\sigma'(1)}(\mu\omega|\tau\nu)\right] \end{aligned} \tag{H.249}$$

H.6.4 The $E^{(3,1)}$ Contribution

We can improve on the uncoupled-perturbed treatment of SOC by including also the contribution $E^{(3,1)}$. The $(3, 1)$ RSPT equation is as follows:

$$\begin{aligned} 0 &= \left[H^{(0,0)} - E^{(0,0)}\right]|\psi^{(3,1)}\rangle + \left[H^{(1,0)} - E^{(1,0)}\right]|\psi^{(2,1)}\rangle + \left[H^{(0,1)} - E^{(0,1)}\right]|\psi^{(3,0)}\rangle \\ &- E^{(2,0)}|\psi^{(1,1)}\rangle - E^{(1,1)}|\psi^{(2,0)}\rangle - E^{(3,0)}|\psi^{(0,1)}\rangle - E^{(2,1)}|\psi^{(1,0)}\rangle - E^{(3,1)}|\psi^{(0,0)}\rangle \end{aligned} \tag{H.250}$$

In the following we utilize the fact that $E^{(1,0)} = 0$ and $E^{(1,1)} = 0$. Bracketing Eq. (H.250) with $|\psi^{(0,0)}\rangle$, we find:

$$E^{(3,1)} = \langle\psi^{(0,0)}|H^{(1,0)}|\psi^{(2,1)}\rangle + \langle\psi^{(0,0)}|H^{(0,1)}|\psi^{(3,0)}\rangle \tag{H.251}$$

Eq. (H.251) provides a first formula for calculating $E^{(3,1)}$. But it might be useful to consider eliminating those terms containing high-order perturbed wavefunctions, to simplify evaluation. For this purpose, we bracket the $(1, 0)$ RSPT equation with $|\psi^{(2,1)}\rangle$ and obtain:

$$0 = \langle\psi^{(2,1)}|H^{(0,0)} - E^{(0,0)}|\psi^{(1,0)}\rangle + \langle\psi^{(2,1)}|H^{(1,0)}|\psi^{(0,0)}\rangle \tag{H.252}$$

Then, bracketing the $(2, 1)$ RSPT equation with $|\psi^{(1,0)}\rangle$:

$$\begin{aligned} 0 &= \langle\psi^{(1,0)}|H^{(0,0)} - E^{(0,0)}|\psi^{(2,1)}\rangle + \langle\psi^{(1,0)}|H^{(1,0)}|\psi^{(1,1)}\rangle \\ &+ \langle\psi^{(1,0)}|H^{(0,1)} - E^{(0,1)}|\psi^{(2,0)}\rangle - E^{(2,0)}\langle\psi^{(1,0)}|\psi^{(0,1)}\rangle \end{aligned} \tag{H.253}$$

Now bracketing the $(0, 1)$ RSPT equation with $|\psi^{(3,0)}\rangle$:

$$0 = \langle\psi^{(3,0)}|H^{(0,0)} - E^{(0,0)}|\psi^{(0,1)}\rangle + \langle\psi^{(3,0)}|H^{(0,1)}|\psi^{(0,0)}\rangle \tag{H.254}$$

Then, bracketing the $(2, 0)$ RSPT equation with $|\psi^{(1,1)}\rangle$:

$$0 = \langle\psi^{(1,1)}|H^{(0,0)} - E^{(0,0)}|\psi^{(2,0)}\rangle + \langle\psi^{(1,1)}|H^{(1,0)}|\psi^{(1,0)}\rangle \tag{H.255}$$

Now bracketing the $(1, 1)$ RSPT equation with $|\psi^{(2,0)}\rangle$:

$$0 = \langle\psi^{(2,0)}|H^{(0,0)} - E^{(0,0)}|\psi^{(1,1)}\rangle + \langle\psi^{(2,0)}|H^{(1,0)}|\psi^{(0,1)}\rangle + \langle\psi^{(2,0)}|H^{(0,1)} - E^{(0,1)}|\psi^{(1,0)}\rangle \tag{H.256}$$

Finally, bracketing the $(3, 0)$ RSPT equation with $|\psi^{(0,1)}\rangle$:

$$0 = \langle\psi^{(0,1)}|H^{(0,0)} - E^{(0,0)}|\psi^{(3,0)}\rangle + \langle\psi^{(0,1)}|H^{(1,0)}|\psi^{(2,0)}\rangle - E^{(2,0)}\langle\psi^{(0,1)}|\psi^{(1,0)}\rangle \tag{H.257}$$

Taking Eq. (H.251) minus the conjugate transpose of Eq. (H.252) plus Eq. (H.253) minus the conjugate transposes of Eqs. (H.254) and (H.255) plus Eqs. (H.256) and (H.257), we find:

$$\begin{aligned} E^{(3,1)} &= 2\mathcal{R}\left[\langle\psi^{(1,0)}|H^{(0,1)} - E^{(0,1)}|\psi^{(2,0)}\rangle\right] + 2\mathcal{R}\left[\langle\psi^{(0,1)}|H^{(1,0)}|\psi^{(2,0)}\rangle\right] \\ &- 2\mathcal{R}\left[E^{(2,0)}\langle\psi^{(1,0)}|\psi^{(0,1)}\rangle\right] \end{aligned} \tag{H.258}$$

Finally, from Brillouin's theorem, the $|\psi^{(0,1)}\rangle$ will consist of only doubly-excited configurations, while since the SOC operator is monoelectronic, $|\psi^{(1,0)}\rangle$ consists of singly-excited configurations. We can therefore conclude that $\langle\psi^{(1,0)}|\psi^{(0,1)}\rangle = 0$ and $E^{(3,1)}$ is reduced to:

$$E^{(3,1)} = 2\mathcal{R}\left[\langle\psi^{(1,0)}|H^{(0,1)} - E^{(0,1)}|\psi^{(2,0)}\rangle\right] + 2\mathcal{R}\left[\langle\psi^{(0,1)}|H^{(1,0)}|\psi^{(2,0)}\rangle\right] \tag{H.259}$$

Now expanding the $|\psi^{(0,1)}\rangle$, $|\psi^{(1,0)}\rangle$ and $|\psi^{(2,0)}\rangle$ in terms of zeroth-order quantities by substituting Eq. (H.14) in Eq. (H.259), we obtain:

$$\begin{aligned} E^{(3,1)} &= \sum_{jkl}{}' 2\mathcal{R}\Bigg[\langle\psi_j^{(0,0)}|H^{(0,1)} - E^{(0,1)}|\psi_k^{(0,0)}\rangle \\ &\times \frac{\langle\psi^{(0,0)}|H^{(1,0)}|\psi_j^{(0,0)}\rangle\langle\psi_k^{(0,0)}|H^{(1,0)}|\psi_l^{(0,0)}\rangle\langle\psi_l^{(0,0)}|H^{(1,0)}|\psi^{(0,0)}\rangle}{\left(E - E_j\right)\left(E - E_k\right)\left(E - E_l\right)}\Bigg] \\ &+ \sum_{jkl}{}' 2\mathcal{R}\Bigg[\langle\psi_j^{(0,0)}|H^{(1,0)}|\psi_k^{(0,0)}\rangle \\ &\times \frac{\langle\psi^{(0,0)}|H^{(0,1)}|\psi_j^{(0,0)}\rangle\langle\psi_k^{(0,0)}|H^{(1,0)}|\psi_l^{(0,0)}\rangle\langle\psi_l^{(0,0)}|H^{(1,0)}|\psi^{(0,0)}\rangle}{\left(E - E_j\right)\left(E - E_k\right)\left(E - E_l\right)}\Bigg] \end{aligned} \tag{H.260}$$

Writing Eq. (H.260) explicitly in terms of all doubly- and singly-excited determinants with non-vanishing contributions, and taking into account the form of the operators $\hat{H}^{(1,0)}$ and $\hat{H}^{(0,1)}$ from Eq. (H.212):

$$E^{(3,1)} = E_S^{(3,1)} + E_D^{(3,1)} \tag{H.261}$$

in which $E_S^{(3,1)}$ is the contribution from singly-excited determinants to $E^{(3,1)}$, which arises from non-vanishing singles contributions from the first term in Eq. (H.260). $E_S^{(3,1)}$ involves a total of sixteen terms for each combination of the singly-excited determinants $|\psi_m^p\rangle$, $|\psi_m^q\rangle$, $|\psi_n^p\rangle$ and $|\psi_n^q\rangle$, such that:

$$
\begin{aligned}
E_S^{(3,1)} = {} & 2\sum_{m,n}^{\in occ}{}''\sum_{p,q,r}^{\in virt}{}''\mathcal{R}\left[\langle\psi_m^p|\hat{V}_{ee}|\psi_n^q\rangle\frac{\langle\psi|\hat{h}_{SO}|\psi_m^p\rangle\langle\psi_n^q|\hat{h}_{SO}|\psi_n^r\rangle\langle\psi_n^r|\hat{h}_{SO}|\psi\rangle}{(E-E_m^p)(E-E_n^q)(E-E_n^r)}\right] \\
+ {} & 2\sum_{m,n,o}^{\in occ}{}''\sum_{p,q}^{\in virt}{}''\mathcal{R}\left[\langle\psi_m^p|\hat{V}_{ee}|\psi_n^q\rangle\frac{\langle\psi|\hat{h}_{SO}|\psi_m^p\rangle\langle\psi_n^q|\hat{h}_{SO}|\psi_o^q\rangle\langle\psi_o^q|\hat{h}_{SO}|\psi\rangle}{(E-E_m^p)(E-E_n^q)(E-E_o^q)}\right] \\
+ {} & 2\sum_{m,n}^{\in occ}{}''\sum_{p,q}^{\in virt}{}''\mathcal{R}\left[\langle\psi_m^p|\hat{V}_{ee}|\psi_n^q\rangle\frac{\langle\psi|\hat{h}_{SO}|\psi_m^p\rangle\langle\psi_n^q|\hat{h}_{SO}|\psi_m^q\rangle\langle\psi_m^q|\hat{h}_{SO}|\psi\rangle}{(E-E_m^p)(E-E_n^q)(E-E_m^q)}\right] \\
+ {} & 2\sum_{m,n}^{\in occ}{}''\sum_{p,q}^{\in virt}{}''\mathcal{R}\left[\langle\psi_m^p|\hat{V}_{ee}|\psi_n^q\rangle\frac{\langle\psi|\hat{h}_{SO}|\psi_m^p\rangle\langle\psi_n^q|\hat{h}_{SO}|\psi_n^p\rangle\langle\psi_n^p|\hat{h}_{SO}|\psi\rangle}{(E-E_m^p)(E-E_n^q)(E-E_n^p)}\right] \\
+ {} & 2\sum_{m,n}^{\in occ}{}''\sum_{p,q}^{\in virt}{}''\mathcal{R}\left[\langle\psi_m^p|\hat{V}_{ee}|\psi_n^q\rangle\frac{\langle\psi|\hat{h}_{SO}|\psi_m^p\rangle\langle\psi_n^q|\hat{h}_{SO}|\psi_n^q\rangle\langle\psi_n^q|\hat{h}_{SO}|\psi\rangle}{(E-E_m^p)(E-E_n^q)(E-E_n^q)}\right] \\
+ {} & 2\sum_{m}^{\in occ}\sum_{p,q,r}^{\in virt}{}''\mathcal{R}\left[\langle\psi_m^p|\hat{V}_{ee}-\left(\hat{C}-\hat{K}\right)|\psi_m^q\rangle\frac{\langle\psi|\hat{h}_{SO}|\psi_m^p\rangle\langle\psi_m^q|\hat{h}_{SO}|\psi_m^r\rangle\langle\psi_m^r|\hat{h}_{SO}|\psi\rangle}{(E-E_m^p)(E-E_m^q)(E-E_m^r)}\right] \\
+ {} & 2\sum_{m,n}^{\in occ}{}''\sum_{p,q}^{\in virt}{}''\mathcal{R}\left[\langle\psi_m^p|\hat{V}_{ee}-\left(\hat{C}-\hat{K}\right)|\psi_m^q\rangle\frac{\langle\psi|\hat{h}_{SO}|\psi_m^p\rangle\langle\psi_m^q|\hat{h}_{SO}|\psi_n^q\rangle\langle\psi_n^q|\hat{h}_{SO}|\psi\rangle}{(E-E_m^p)(E-E_m^q)(E-E_n^q)}\right] \\
+ {} & 2\sum_{m}^{\in occ}\sum_{p,q}^{\in virt}{}''\mathcal{R}\left[\langle\psi_m^p|\hat{V}_{ee}-\left(\hat{C}-\hat{K}\right)|\psi_m^q\rangle\frac{\langle\psi|\hat{h}_{SO}|\psi_m^p\rangle\langle\psi_m^q|\hat{h}_{SO}|\psi_m^p\rangle\langle\psi_m^p|\hat{h}_{SO}|\psi\rangle}{(E-E_m^p)(E-E_m^q)(E-E_m^p)}\right] \\
+ {} & 2\sum_{m}^{\in occ}\sum_{p,q}^{\in virt}{}''\mathcal{R}\left[\langle\psi_m^p|\hat{V}_{ee}-\left(\hat{C}-\hat{K}\right)|\psi_m^q\rangle\frac{\langle\psi|\hat{h}_{SO}|\psi_m^p\rangle\langle\psi_m^q|\hat{h}_{SO}|\psi_m^q\rangle\langle\psi_m^q|\hat{h}_{SO}|\psi\rangle}{(E-E_m^p)(E-E_m^q)(E-E_m^q)}\right] \\
+ {} & 2\sum_{m,n}^{\in occ}{}''\sum_{p,q}^{\in virt}{}''\mathcal{R}\left[\langle\psi_m^p|\hat{V}_{ee}-\left(\hat{C}-\hat{K}\right)|\psi_n^p\rangle\frac{\langle\psi|\hat{h}_{SO}|\psi_m^p\rangle\langle\psi_n^p|\hat{h}_{SO}|\psi_n^q\rangle\langle\psi_n^q|\hat{h}_{SO}|\psi\rangle}{(E-E_m^p)(E-E_n^p)(E-E_n^q)}\right] \\
+ {} & 2\sum_{m,n,o}^{\in occ}{}''\sum_{p}^{\in virt}\mathcal{R}\left[\langle\psi_m^p|\hat{V}_{ee}-\left(\hat{C}-\hat{K}\right)|\psi_n^p\rangle\frac{\langle\psi|\hat{h}_{SO}|\psi_m^p\rangle\langle\psi_n^p|\hat{h}_{SO}|\psi_o^p\rangle\langle\psi_o^p|\hat{h}_{SO}|\psi\rangle}{(E-E_m^p)(E-E_n^p)(E-E_o^p)}\right] \\
+ {} & 2\sum_{m,n}^{\in occ}{}''\sum_{p}^{\in virt}\mathcal{R}\left[\langle\psi_m^p|\hat{V}_{ee}-\left(\hat{C}-\hat{K}\right)|\psi_n^p\rangle\frac{\langle\psi|\hat{h}_{SO}|\psi_m^p\rangle\langle\psi_n^p|\hat{h}_{SO}|\psi_m^p\rangle\langle\psi_m^p|\hat{h}_{SO}|\psi\rangle}{(E-E_m^p)(E-E_n^p)(E-E_m^p)}\right] \\
+ {} & 2\sum_{m,n}^{\in occ}{}''\sum_{p}^{\in virt}\mathcal{R}\left[\langle\psi_m^p|\hat{V}_{ee}-\left(\hat{C}-\hat{K}\right)|\psi_n^p\rangle\frac{\langle\psi|\hat{h}_{SO}|\psi_m^p\rangle\langle\psi_n^p|\hat{h}_{SO}|\psi_n^p\rangle\langle\psi_n^p|\hat{h}_{SO}|\psi\rangle}{(E-E_m^p)(E-E_n^p)(E-E_n^p)}\right] \\
+ {} & 2\sum_{m}^{\in occ}\sum_{p,q}^{\in virt}{}''\mathcal{R}\left[\langle\psi_m^p|\hat{V}_{ee}-\left(\hat{C}-\hat{K}\right)-E^{(0,1)}|\psi_m^p\rangle\frac{\langle\psi|\hat{h}_{SO}|\psi_m^p\rangle\langle\psi_m^p|\hat{h}_{SO}|\psi_m^q\rangle\langle\psi_m^q|\hat{h}_{SO}|\psi\rangle}{(E-E_m^p)(E-E_m^p)(E-E_m^q)}\right] \\
+ {} & 2\sum_{m,n}^{\in occ}{}''\sum_{p}^{\in virt}\mathcal{R}\left[\langle\psi_m^p|\hat{V}_{ee}-\left(\hat{C}-\hat{K}\right)-E^{(0,1)}|\psi_m^p\rangle\frac{\langle\psi|\hat{h}_{SO}|\psi_m^p\rangle\langle\psi_m^p|\hat{h}_{SO}|\psi_n^p\rangle\langle\psi_n^p|\hat{h}_{SO}|\psi\rangle}{(E-E_m^p)(E-E_m^p)(E-E_n^p)}\right] \\
+ {} & 2\sum_{m}^{\in occ}\sum_{p}^{\in virt}\mathcal{R}\left[\langle\psi_m^p|\hat{V}_{ee}-\left(\hat{C}-\hat{K}\right)-E^{(0,1)}|\psi_m^p\rangle\frac{\langle\psi|\hat{h}_{SO}|\psi_m^p\rangle\langle\psi_m^p|\hat{h}_{SO}|\psi_m^p\rangle\langle\psi_m^p|\hat{h}_{SO}|\psi\rangle}{(E-E_m^p)(E-E_m^p)(E-E_m^p)}\right] \qquad \text{(H.262)}
\end{aligned}
$$

and $E_D^{(3,1)}$ is the contribution from doubly-excited determinants to $E^{(3,1)}$. This one contains non-vanishing contributions from both terms in Eq. (H.260), each of which is composed of a doubly-excited determinant $|\psi_{mn}^{pq}\rangle$ which interacts with sixteen different combinations of the singly-excited determinants $|\psi_m^p\rangle$, $|\psi_m^q\rangle$, $|\psi_n^p\rangle$

and $|\psi_n^q\rangle$. This results in a total of 16 + 16 = 32 possibly non-vanishing terms, as follows:

$$
\begin{aligned}
E_D^{(3,1)} &= 2\sum_{m,n}^{\in occ}{}^{>>}\sum_{p,q}^{\in virt}{}^{>>}\mathcal{R}\Bigg[\langle\psi_m^p|\hat{V}_{ee}-\left(\hat{C}-\hat{K}\right)|\psi_{mn}^{pq}\rangle\Bigg\{\frac{\langle\psi|\hat{h}_{SO}|\psi_m^p\rangle\langle\psi_{mn}^{pq}|\hat{h}_{SO}|\psi_m^p\rangle\langle\psi_m^p|\hat{h}_{SO}|\psi\rangle}{\left(E-E_m^p\right)\left(E-E_{mn}^{pq}\right)\left(E-E_m^p\right)} \\
&+ \frac{\langle\psi|\hat{h}_{SO}|\psi_m^p\rangle\langle\psi_{mn}^{pq}|\hat{h}_{SO}|\psi_n^p\rangle\langle\psi_n^p|\hat{h}_{SO}|\psi\rangle}{\left(E-E_m^p\right)\left(E-E_{mn}^{pq}\right)\left(E-E_n^p\right)}+\frac{\langle\psi|\hat{h}_{SO}|\psi_m^p\rangle\langle\psi_{mn}^{pq}|\hat{h}_{SO}|\psi_m^q\rangle\langle\psi_m^q|\hat{h}_{SO}|\psi\rangle}{\left(E-E_m^p\right)\left(E-E_{mn}^{pq}\right)\left(E-E_m^q\right)} \\
&+ \frac{\langle\psi|\hat{h}_{SO}|\psi_m^p\rangle\langle\psi_{mn}^{pq}|\hat{h}_{SO}|\psi_n^q\rangle\langle\psi_n^q|\hat{h}_{SO}|\psi\rangle}{\left(E-E_m^p\right)\left(E-E_{mn}^{pq}\right)\left(E-E_n^q\right)}\Bigg\}+\langle\psi_n^p|\hat{V}_{ee}-\left(\hat{C}-\hat{K}\right)|\psi_{mn}^{pq}\rangle \\
&\times \Bigg\{\frac{\langle\psi|\hat{h}_{SO}|\psi_n^p\rangle\langle\psi_{mn}^{pq}|\hat{h}_{SO}|\psi_m^p\rangle\langle\psi_m^p|\hat{h}_{SO}|\psi\rangle}{\left(E-E_n^p\right)\left(E-E_{mn}^{pq}\right)\left(E-E_m^p\right)}+\frac{\langle\psi|\hat{h}_{SO}|\psi_n^p\rangle\langle\psi_{mn}^{pq}|\hat{h}_{SO}|\psi_n^p\rangle\langle\psi_n^p|\hat{h}_{SO}|\psi\rangle}{\left(E-E_n^p\right)\left(E-E_{mn}^{pq}\right)\left(E-E_n^p\right)} \\
&+ \frac{\langle\psi|\hat{h}_{SO}|\psi_n^p\rangle\langle\psi_{mn}^{pq}|\hat{h}_{SO}|\psi_m^q\rangle\langle\psi_m^q|\hat{h}_{SO}|\psi\rangle}{\left(E-E_n^p\right)\left(E-E_{mn}^{pq}\right)\left(E-E_m^q\right)}+\frac{\langle\psi|\hat{h}_{SO}|\psi_n^p\rangle\langle\psi_{mn}^{pq}|\hat{h}_{SO}|\psi_n^q\rangle\langle\psi_n^q|\hat{h}_{SO}|\psi\rangle}{\left(E-E_n^p\right)\left(E-E_{mn}^{pq}\right)\left(E-E_n^q\right)}\Bigg\} \\
&+ \langle\psi_m^q|\hat{V}_{ee}-\left(\hat{C}-\hat{K}\right)|\psi_{mn}^{pq}\rangle\Bigg\{\frac{\langle\psi|\hat{h}_{SO}|\psi_m^q\rangle\langle\psi_{mn}^{pq}|\hat{h}_{SO}|\psi_m^p\rangle\langle\psi_m^p|\hat{h}_{SO}|\psi\rangle}{\left(E-E_m^q\right)\left(E-E_{mn}^{pq}\right)\left(E-E_m^p\right)} \\
&+ \frac{\langle\psi|\hat{h}_{SO}|\psi_m^q\rangle\langle\psi_{mn}^{pq}|\hat{h}_{SO}|\psi_n^p\rangle\langle\psi_n^p|\hat{h}_{SO}|\psi\rangle}{\left(E-E_m^q\right)\left(E-E_{mn}^{pq}\right)\left(E-E_n^p\right)}+\frac{\langle\psi|\hat{h}_{SO}|\psi_m^q\rangle\langle\psi_{mn}^{pq}|\hat{h}_{SO}|\psi_m^q\rangle\langle\psi_m^q|\hat{h}_{SO}|\psi\rangle}{\left(E-E_m^q\right)\left(E-E_{mn}^{pq}\right)\left(E-E_m^q\right)} \\
&+ \frac{\langle\psi|\hat{h}_{SO}|\psi_m^q\rangle\langle\psi_{mn}^{pq}|\hat{h}_{SO}|\psi_n^q\rangle\langle\psi_n^q|\hat{h}_{SO}|\psi\rangle}{\left(E-E_m^q\right)\left(E-E_{mn}^{pq}\right)\left(E-E_n^q\right)}\Bigg\}+\langle\psi_n^q|\hat{V}_{ee}-\left(\hat{C}-\hat{K}\right)|\psi_{mn}^{pq}\rangle \\
&\times \Bigg\{\frac{\langle\psi|\hat{h}_{SO}|\psi_n^q\rangle\langle\psi_{mn}^{pq}|\hat{h}_{SO}|\psi_m^p\rangle\langle\psi_m^p|\hat{h}_{SO}|\psi\rangle}{\left(E-E_n^q\right)\left(E-E_{mn}^{pq}\right)\left(E-E_m^p\right)}+\frac{\langle\psi|\hat{h}_{SO}|\psi_n^q\rangle\langle\psi_{mn}^{pq}|\hat{h}_{SO}|\psi_n^p\rangle\langle\psi_n^p|\hat{h}_{SO}|\psi\rangle}{\left(E-E_n^q\right)\left(E-E_{mn}^{pq}\right)\left(E-E_n^p\right)} \\
&+ \frac{\langle\psi|\hat{h}_{SO}|\psi_n^q\rangle\langle\psi_{mn}^{pq}|\hat{h}_{SO}|\psi_m^q\rangle\langle\psi_m^q|\hat{h}_{SO}|\psi\rangle}{\left(E-E_n^q\right)\left(E-E_{mn}^{pq}\right)\left(E-E_m^q\right)}+\frac{\langle\psi|\hat{h}_{SO}|\psi_n^q\rangle\langle\psi_{mn}^{pq}|\hat{h}_{SO}|\psi_n^q\rangle\langle\psi_n^q|\hat{h}_{SO}|\psi\rangle}{\left(E-E_n^q\right)\left(E-E_{mn}^{pq}\right)\left(E-E_n^q\right)}\Bigg\}\Bigg] \\
&+ 2\sum_{m,n}^{\in occ}{}^{>>}\sum_{p,q}^{\in virt}{}^{>>}\sum_{r}^{\in virt}{}^{\prime\prime}\mathcal{R}\Bigg[\langle\psi|\hat{V}_{ee}|\psi_{mn}^{pq}\rangle\Bigg\{\frac{\langle\psi_{mn}^{pq}|\hat{h}_{SO}|\psi_m^p\rangle\langle\psi_m^p|\hat{h}_{SO}|\psi_m^r\rangle\langle\psi_m^r|\hat{h}_{SO}|\psi\rangle}{\left(E-E_{mn}^{pq}\right)\left(E-E_m^p\right)(E-E_m^r)} \\
&+ \frac{\langle\psi_{mn}^{pq}|\hat{h}_{SO}|\psi_n^p\rangle\langle\psi_n^p|\hat{h}_{SO}|\psi_n^r\rangle\langle\psi_n^r|\hat{h}_{SO}|\psi\rangle}{\left(E-E_{mn}^{pq}\right)\left(E-E_n^p\right)(E-E_n^r)}+\frac{\langle\psi_{mn}^{pq}|\hat{h}_{SO}|\psi_m^q\rangle\langle\psi_m^q|\hat{h}_{SO}|\psi_m^r\rangle\langle\psi_m^r|\hat{h}_{SO}|\psi\rangle}{\left(E-E_{mn}^{pq}\right)\left(E-E_m^q\right)(E-E_m^r)} \\
&+ \frac{\langle\psi_{mn}^{pq}|\hat{h}_{SO}|\psi_n^q\rangle\langle\psi_n^q|\hat{h}_{SO}|\psi_n^r\rangle\langle\psi_n^r|\hat{h}_{SO}|\psi\rangle}{\left(E-E_{mn}^{pq}\right)\left(E-E_n^q\right)(E-E_n^r)}\Bigg\}\Bigg] \\
&+ 2\sum_{m,n}^{\in occ}{}^{>>}\sum_{p,q}^{\in virt}{}^{>>}\sum_{o}^{\in occ}{}^{\prime\prime}\mathcal{R}\Bigg[\langle\psi|\hat{V}_{ee}|\psi_{mn}^{pq}\rangle\Bigg\{\frac{\langle\psi_{mn}^{pq}|\hat{h}_{SO}|\psi_m^p\rangle\langle\psi_m^p|\hat{h}_{SO}|\psi_o^p\rangle\langle\psi_o^p|\hat{h}_{SO}|\psi\rangle}{\left(E-E_{mn}^{pq}\right)\left(E-E_m^p\right)\left(E-E_o^p\right)} \\
&+ \frac{\langle\psi_{mn}^{pq}|\hat{h}_{SO}|\psi_n^p\rangle\langle\psi_n^p|\hat{h}_{SO}|\psi_o^p\rangle\langle\psi_o^p|\hat{h}_{SO}|\psi\rangle}{\left(E-E_{mn}^{pq}\right)\left(E-E_n^p\right)\left(E-E_o^p\right)}+\frac{\langle\psi_{mn}^{pq}|\hat{h}_{SO}|\psi_m^q\rangle\langle\psi_m^q|\hat{h}_{SO}|\psi_o^q\rangle\langle\psi_o^q|\hat{h}_{SO}|\psi\rangle}{\left(E-E_{mn}^{pq}\right)\left(E-E_m^q\right)\left(E-E_o^q\right)} \\
&+ \frac{\langle\psi_{mn}^{pq}|\hat{h}_{SO}|\psi_n^q\rangle\langle\psi_n^q|\hat{h}_{SO}|\psi_o^q\rangle\langle\psi_o^q|\hat{h}_{SO}|\psi\rangle}{\left(E-E_{mn}^{pq}\right)\left(E-E_n^q\right)\left(E-E_o^q\right)}\Bigg\}\Bigg] \\
&+ 2\sum_{m,n}^{\in occ}{}^{>>}\sum_{p,q}^{\in virt}{}^{>>}\mathcal{R}\Bigg[\langle\psi|\hat{V}_{ee}|\psi_{mn}^{pq}\rangle\Bigg\{\frac{\langle\psi_{mn}^{pq}|\hat{h}_{SO}|\psi_m^p\rangle\langle\psi_m^p|\hat{h}_{SO}|\psi_m^q\rangle\langle\psi_m^q|\hat{h}_{SO}|\psi\rangle}{\left(E-E_{mn}^{pq}\right)\left(E-E_m^p\right)\left(E-E_m^q\right)} \\
&+ \frac{\langle\psi_{mn}^{pq}|\hat{h}_{SO}|\psi_m^p\rangle\langle\psi_m^p|\hat{h}_{SO}|\psi_n^p\rangle\langle\psi_n^p|\hat{h}_{SO}|\psi\rangle}{\left(E-E_{mn}^{pq}\right)\left(E-E_m^p\right)\left(E-E_n^p\right)}+\frac{\langle\psi_{mn}^{pq}|\hat{h}_{SO}|\psi_n^p\rangle\langle\psi_n^p|\hat{h}_{SO}|\psi_n^q\rangle\langle\psi_n^q|\hat{h}_{SO}|\psi\rangle}{\left(E-E_{mn}^{pq}\right)\left(E-E_n^p\right)\left(E-E_n^q\right)} \\
&+ \frac{\langle\psi_{mn}^{pq}|\hat{h}_{SO}|\psi_n^p\rangle\langle\psi_n^p|\hat{h}_{SO}|\psi_m^p\rangle\langle\psi_m^p|\hat{h}_{SO}|\psi\rangle}{\left(E-E_{mn}^{pq}\right)\left(E-E_n^p\right)\left(E-E_m^p\right)}+\frac{\langle\psi_{mn}^{pq}|\hat{h}_{SO}|\psi_m^q\rangle\langle\psi_m^q|\hat{h}_{SO}|\psi_m^p\rangle\langle\psi_m^p|\hat{h}_{SO}|\psi\rangle}{\left(E-E_{mn}^{pq}\right)\left(E-E_m^q\right)\left(E-E_m^p\right)} \\
&+ \frac{\langle\psi_{mn}^{pq}|\hat{h}_{SO}|\psi_m^q\rangle\langle\psi_m^q|\hat{h}_{SO}|\psi_n^q\rangle\langle\psi_n^q|\hat{h}_{SO}|\psi\rangle}{\left(E-E_{mn}^{pq}\right)\left(E-E_m^q\right)\left(E-E_n^q\right)}+\frac{\langle\psi_{mn}^{pq}|\hat{h}_{SO}|\psi_n^q\rangle\langle\psi_n^q|\hat{h}_{SO}|\psi_n^p\rangle\langle\psi_n^p|\hat{h}_{SO}|\psi\rangle}{\left(E-E_{mn}^{pq}\right)\left(E-E_n^q\right)\left(E-E_n^p\right)}\Bigg\} \\
&+ \frac{\langle\psi_{mn}^{pq}|\hat{h}_{SO}|\psi_n^q\rangle\langle\psi_n^q|\hat{h}_{SO}|\psi_m^q\rangle\langle\psi_m^q|\hat{h}_{SO}|\psi\rangle}{\left(E-E_{mn}^{pq}\right)\left(E-E_n^q\right)\left(E-E_m^q\right)}\Bigg]
\end{aligned}
\tag{H.263}
$$

For $E_S^{3,1}$, expanding the determinants in Eq. (H.262) in one-electron orbitals and making use of Eq. (H.229), we find:

$$
\begin{aligned}
E_S^{(3,1)} \;=\;& 2\sum_{m,n}^{\in occ}{}'' \sum_{p,q,r}^{\in virt}{}'' \mathcal{R}\Bigg[\{(pm|nq)-(pq|nm)\} \frac{\langle m|\hat{h}_{SO}|p\rangle\langle q|\hat{h}_{SO}|r\rangle\langle r|\hat{h}_{SO}|n\rangle}{\big(\epsilon_m-\epsilon_p\big)\big(\epsilon_n-\epsilon_q\big)(\epsilon_n-\epsilon_r)} \Bigg] \\
-\;& 2\sum_{m,n,o}^{\in occ}{}'' \sum_{p,q}^{\in virt}{}'' \mathcal{R}\Bigg[\{(pm|nq)-(pq|nm)\} \frac{\langle m|\hat{h}_{SO}|p\rangle\langle o|\hat{h}_{SO}|n\rangle\langle q|\hat{h}_{SO}|o\rangle}{\big(\epsilon_m-\epsilon_p\big)\big(\epsilon_n-\epsilon_q\big)\big(\epsilon_o-\epsilon_q\big)} \Bigg] \\
-\;& 2\sum_{m,n}^{\in occ}{}'' \sum_{p,q}^{\in virt}{}'' \mathcal{R}\Bigg[\{(pm|nq)-(pq|nm)\} \frac{\langle m|\hat{h}_{SO}|p\rangle\langle m|\hat{h}_{SO}|n\rangle\langle q|\hat{h}_{SO}|m\rangle}{\big(\epsilon_m-\epsilon_p\big)\big(\epsilon_n-\epsilon_q\big)\big(\epsilon_m-\epsilon_q\big)} \Bigg] \\
+\;& 2\sum_{m,n}^{\in occ}{}'' \sum_{p,q}^{\in virt}{}'' \mathcal{R}\Bigg[\{(pm|nq)-(pq|nm)\} \frac{\langle m|\hat{h}_{SO}|p\rangle\langle q|\hat{h}_{SO}|p\rangle\langle p|\hat{h}_{SO}|n\rangle}{\big(\epsilon_m-\epsilon_p\big)\big(\epsilon_n-\epsilon_q\big)\big(\epsilon_n-\epsilon_p\big)} \Bigg] \\
-\;& 2\sum_{m}^{\in occ} \sum_{p,q,r}^{\in virt}{}'' \mathcal{R}\Bigg[\{(pq|mm)-(pm|mq)\} \frac{\langle m|\hat{h}_{SO}|p\rangle\langle q|\hat{h}_{SO}|r\rangle\langle r|\hat{h}_{SO}|m\rangle}{\big(\epsilon_m-\epsilon_p\big)\big(\epsilon_m-\epsilon_q\big)(\epsilon_m-\epsilon_r)} \Bigg] \\
+\;& 2\sum_{m,n}^{\in occ}{}'' \sum_{p,q}^{\in virt}{}'' \mathcal{R}\Bigg[\{(pq|mm)-(pm|mq)\} \frac{\langle m|\hat{h}_{SO}|p\rangle\langle n|\hat{h}_{SO}|m\rangle\langle q|\hat{h}_{SO}|n\rangle}{\big(\epsilon_m-\epsilon_p\big)\big(\epsilon_m-\epsilon_q\big)\big(\epsilon_n-\epsilon_q\big)} \Bigg] \\
-\;& 2\sum_{m}^{\in occ} \sum_{p,q}^{\in virt}{}'' \mathcal{R}\Bigg[\{(pq|mm)-(pm|mq)\} \frac{\langle m|\hat{h}_{SO}|p\rangle\langle q|\hat{h}_{SO}|p\rangle\langle p|\hat{h}_{SO}|m\rangle}{\big(\epsilon_m-\epsilon_p\big)\big(\epsilon_m-\epsilon_q\big)\big(\epsilon_m-\epsilon_p\big)} \Bigg] \\
-\;& 2\sum_{m,n}^{\in occ}{}'' \sum_{p,q}^{\in virt}{}'' \mathcal{R}\Bigg[\{(nm|pp)-(np|pm)\} \frac{\langle m|\hat{h}_{SO}|p\rangle\langle p|\hat{h}_{SO}|q\rangle\langle q|\hat{h}_{SO}|n\rangle}{\big(\epsilon_m-\epsilon_p\big)\big(\epsilon_n-\epsilon_p\big)\big(\epsilon_n-\epsilon_q\big)} \Bigg] \\
+\;& 2\sum_{m,n,o}^{\in occ}{}'' \sum_{p}^{\in virt} \mathcal{R}\Bigg[\{(nm|pp)-(np|pm)\} \frac{\langle m|\hat{h}_{SO}|p\rangle\langle o|\hat{h}_{SO}|n\rangle\langle p|\hat{h}_{SO}|o\rangle}{\big(\epsilon_m-\epsilon_p\big)\big(\epsilon_n-\epsilon_p\big)\big(\epsilon_o-\epsilon_p\big)} \Bigg] \\
+\;& 2\sum_{m,n}^{\in occ}{}'' \sum_{p}^{\in virt} \mathcal{R}\Bigg[\{(nm|pp)-(np|pm)\} \frac{\langle m|\hat{h}_{SO}|p\rangle\langle m|\hat{h}_{SO}|n\rangle\langle p|\hat{h}_{SO}|m\rangle}{\big(\epsilon_m-\epsilon_p\big)\big(\epsilon_n-\epsilon_p\big)\big(\epsilon_m-\epsilon_p\big)} \Bigg] \\
-\;& 2\sum_{m}^{\in occ} \sum_{p,q}^{\in virt}{}'' \mathcal{R}\Bigg[\{(pp|mm)-(pm|mp)\} \frac{\langle m|\hat{h}_{SO}|p\rangle\langle p|\hat{h}_{SO}|q\rangle\langle q|\hat{h}_{SO}|m\rangle}{\big(\epsilon_m-\epsilon_p\big)\big(\epsilon_m-\epsilon_p\big)\big(\epsilon_m-\epsilon_q\big)} \Bigg] \\
+\;& 2\sum_{m,n}^{\in occ}{}'' \sum_{p}^{\in virt} \mathcal{R}\Bigg[\{(pp|mm)-(pm|mp)\} \frac{\langle m|\hat{h}_{SO}|p\rangle\langle n|\hat{h}_{SO}|m\rangle\langle p|\hat{h}_{SO}|n\rangle}{\big(\epsilon_m-\epsilon_p\big)\big(\epsilon_m-\epsilon_p\big)\big(\epsilon_n-\epsilon_p\big)} \Bigg] \qquad \text{(H.264)}
\end{aligned}
$$

where the four terms containing diagonal matrix elements of the SOC operator have been set to zero. Eq. (H.264) can be simplified, by combining terms 1,4,5,7,8,11 and 2,3,6,9,10,12, such that it is reduced to the following expression:

$$
\begin{aligned}
E_S^{(3,1)} \;=\;& 2\sum_{m,n}^{\in occ} \sum_{p,q}^{\in virt} \mathcal{R}\Bigg[\{(pm|nq)-(pq|nm)\} \Bigg\{ \sum_{r}^{\in virt} \frac{\langle m|\hat{h}_{SO}|p\rangle\langle q|\hat{h}_{SO}|r\rangle\langle r|\hat{h}_{SO}|n\rangle}{\big(\epsilon_m-\epsilon_p\big)\big(\epsilon_n-\epsilon_q\big)(\epsilon_n-\epsilon_r)} \\
-\;& \sum_{o}^{\in occ} \frac{\langle m|\hat{h}_{SO}|p\rangle\langle o|\hat{h}_{SO}|n\rangle\langle q|\hat{h}_{SO}|o\rangle}{\big(\epsilon_m-\epsilon_p\big)\big(\epsilon_n-\epsilon_q\big)\big(\epsilon_o-\epsilon_q\big)} \Bigg\} \Bigg] \qquad \text{(H.265)}
\end{aligned}
$$

Now moving on to $E_D^{(3,1)}$, from Eq. (H.263), we first need to find the expression of a few matrix-elements involving the correlation potential:

$$\langle\psi_m^p|\hat{V}_{ee} - \left(\hat{C} - \hat{K}\right)|\psi_{mn}^{pq}\rangle \quad = \quad -\left[(nq|mm) - (nm|mq)\right] + \left[(nq|pp) - (np|pq)\right] \tag{H.266a}$$

$$\langle\psi_n^p|\hat{V}_{ee} - \left(\hat{C} - \hat{K}\right)|\psi_{mn}^{pq}\rangle \quad = \quad \left[(mq|nn) - (mn|nq)\right] - \left[(mq|pp) - (mp|pq)\right] \tag{H.266b}$$

$$\langle\psi_m^q|\hat{V}_{ee} - \left(\hat{C} - \hat{K}\right)|\psi_{mn}^{pq}\rangle \quad = \quad \left[(np|mm) - (nm|mp)\right] - \left[(np|qq) - (nq|qp)\right] \tag{H.266c}$$

$$\langle\psi_n^q|\hat{V}_{ee} - \left(\hat{C} - \hat{K}\right)|\psi_{mn}^{pq}\rangle \quad = \quad -\left[(mp|nn) - (mn|np)\right] + \left[(mp|qq) - (mq|qp)\right] \tag{H.266d}$$

Substituting Eqs. (H.229) and (H.266) into Eq. (H.263) and expressing the determinants in terms of one-electron orbitals:

$$
\begin{aligned}
E_D^{(3,1)} &= 2\sum_{m,n}^{\in occ}{}^{>>}\sum_{p,q}^{\in virt}{}^{>>}\mathcal{R}\bigg[\{-[(nq|mm)-(nm|mq)]+[(nq|pp)-(np|pq)]\}\bigg\{\frac{\langle m|\hat{h}_{SO}|p\rangle\langle q|\hat{h}_{SO}|n\rangle\langle p|\hat{h}_{SO}|m\rangle}{\big(\epsilon_m-\epsilon_p\big)\big(\epsilon_m+\epsilon_n-\epsilon_p-\epsilon_q\big)\big(\epsilon_m-\epsilon_p\big)} \\
&- \frac{\langle m|\hat{h}_{SO}|p\rangle\langle q|\hat{h}_{SO}|m\rangle\langle p|\hat{h}_{SO}|n\rangle}{\big(\epsilon_m-\epsilon_p\big)\big(\epsilon_m+\epsilon_n-\epsilon_p-\epsilon_q\big)\big(\epsilon_n-\epsilon_p\big)} - \frac{\langle m|\hat{h}_{SO}|p\rangle\langle p|\hat{h}_{SO}|n\rangle\langle q|\hat{h}_{SO}|m\rangle}{\big(\epsilon_m-\epsilon_p\big)\big(\epsilon_m+\epsilon_n-\epsilon_p-\epsilon_q\big)\big(\epsilon_m-\epsilon_q\big)} \\
&+ \frac{\langle m|\hat{h}_{SO}|p\rangle\langle p|\hat{h}_{SO}|m\rangle\langle q|\hat{h}_{SO}|n\rangle}{\big(\epsilon_m-\epsilon_p\big)\big(\epsilon_m+\epsilon_n-\epsilon_p-\epsilon_q\big)\big(\epsilon_n-\epsilon_q\big)}\bigg\} + \{[(mq|nn)-(mn|nq)]-[(mq|pp)-(mp|pq)]\} \\
&\times \bigg\{\frac{\langle n|\hat{h}_{SO}|p\rangle\langle q|\hat{h}_{SO}|n\rangle\langle p|\hat{h}_{SO}|m\rangle}{\big(\epsilon_n-\epsilon_p\big)\big(\epsilon_m+\epsilon_n-\epsilon_p-\epsilon_q\big)\big(\epsilon_m-\epsilon_p\big)} - \frac{\langle n|\hat{h}_{SO}|p\rangle\langle q|\hat{h}_{SO}|m\rangle\langle p|\hat{h}_{SO}|n\rangle}{\big(\epsilon_n-\epsilon_p\big)\big(\epsilon_m+\epsilon_n-\epsilon_p-\epsilon_q\big)\big(\epsilon_n-\epsilon_p\big)} \\
&- \frac{\langle n|\hat{h}_{SO}|p\rangle\langle p|\hat{h}_{SO}|n\rangle\langle q|\hat{h}_{SO}|m\rangle}{\big(\epsilon_n-\epsilon_p\big)\big(\epsilon_m+\epsilon_n-\epsilon_p-\epsilon_q\big)\big(\epsilon_m-\epsilon_q\big)} + \frac{\langle n|\hat{h}_{SO}|p\rangle\langle p|\hat{h}_{SO}|m\rangle\langle q|\hat{h}_{SO}|n\rangle}{\big(\epsilon_n-\epsilon_p\big)\big(\epsilon_m+\epsilon_n-\epsilon_p-\epsilon_q\big)\big(\epsilon_n-\epsilon_q\big)}\bigg\} \\
&+ \{[(np|mm)-(nm|mp)]-[(np|qq)-(nq|qp)]\}\bigg\{\frac{\langle m|\hat{h}_{SO}|q\rangle\langle q|\hat{h}_{SO}|n\rangle\langle p|\hat{h}_{SO}|m\rangle}{\big(\epsilon_m-\epsilon_q\big)\big(\epsilon_m+\epsilon_n-\epsilon_p-\epsilon_q\big)\big(\epsilon_m-\epsilon_p\big)} \\
&- \frac{\langle m|\hat{h}_{SO}|q\rangle\langle q|\hat{h}_{SO}|m\rangle\langle p|\hat{h}_{SO}|n\rangle}{\big(\epsilon_m-\epsilon_q\big)\big(\epsilon_m+\epsilon_n-\epsilon_p-\epsilon_q\big)\big(\epsilon_n-\epsilon_p\big)} - \frac{\langle m|\hat{h}_{SO}|q\rangle\langle p|\hat{h}_{SO}|n\rangle\langle q|\hat{h}_{SO}|m\rangle}{\big(\epsilon_m-\epsilon_q\big)\big(\epsilon_m+\epsilon_n-\epsilon_p-\epsilon_q\big)\big(\epsilon_m-\epsilon_q\big)} \\
&+ \frac{\langle m|\hat{h}_{SO}|q\rangle\langle p|\hat{h}_{SO}|m\rangle\langle q|\hat{h}_{SO}|n\rangle}{\big(\epsilon_m-\epsilon_q\big)\big(\epsilon_m+\epsilon_n-\epsilon_p-\epsilon_q\big)\big(\epsilon_n-\epsilon_q\big)}\bigg\} + \{-[(mp|nn)-(mn|np)]+[(mp|qq)-(mq|qp)]\} \\
&\times \bigg\{\frac{\langle n|\hat{h}_{SO}|q\rangle\langle q|\hat{h}_{SO}|n\rangle\langle p|\hat{h}_{SO}|m\rangle}{\big(\epsilon_n-\epsilon_q\big)\big(\epsilon_m+\epsilon_n-\epsilon_p-\epsilon_q\big)\big(\epsilon_m-\epsilon_p\big)} - \frac{\langle n|\hat{h}_{SO}|q\rangle\langle q|\hat{h}_{SO}|m\rangle\langle p|\hat{h}_{SO}|n\rangle}{\big(\epsilon_n-\epsilon_q\big)\big(\epsilon_m+\epsilon_n-\epsilon_p-\epsilon_q\big)\big(\epsilon_n-\epsilon_p\big)} \\
&- \frac{\langle n|\hat{h}_{SO}|q\rangle\langle p|\hat{h}_{SO}|n\rangle\langle q|\hat{h}_{SO}|m\rangle}{\big(\epsilon_n-\epsilon_q\big)\big(\epsilon_m+\epsilon_n-\epsilon_p-\epsilon_q\big)\big(\epsilon_m-\epsilon_q\big)} + \frac{\langle n|\hat{h}_{SO}|q\rangle\langle p|\hat{h}_{SO}|m\rangle\langle q|\hat{h}_{SO}|n\rangle}{\big(\epsilon_n-\epsilon_q\big)\big(\epsilon_m+\epsilon_n-\epsilon_p-\epsilon_q\big)\big(\epsilon_n-\epsilon_q\big)}\bigg\}\bigg] \\
&+ 2\sum_{m,n}^{\in occ}{}^{>>}\sum_{p,q}^{\in virt}{}^{>>}\sum_{r}^{\in virt}{}''\mathcal{R}\bigg[\frac{\{(mp|nq)-(mq|np)\}}{\big(\epsilon_m+\epsilon_n-\epsilon_p-\epsilon_q\big)}\bigg\{\frac{\langle q|\hat{h}_{SO}|n\rangle\langle p|\hat{h}_{SO}|r\rangle\langle r|\hat{h}_{SO}|m\rangle}{\big(\epsilon_m-\epsilon_p\big)(\epsilon_m-\epsilon_r)} \\
&- \frac{\langle q|\hat{h}_{SO}|m\rangle\langle p|\hat{h}_{SO}|r\rangle\langle r|\hat{h}_{SO}|n\rangle}{\big(\epsilon_n-\epsilon_p\big)(\epsilon_n-\epsilon_r)} - \frac{\langle p|\hat{h}_{SO}|n\rangle\langle q|\hat{h}_{SO}|r\rangle\langle r|\hat{h}_{SO}|m\rangle}{\big(\epsilon_m-\epsilon_q\big)(\epsilon_m-\epsilon_r)} \\
&+ \frac{\langle p|\hat{h}_{SO}|m\rangle\langle q|\hat{h}_{SO}|r\rangle\langle r|\hat{h}_{SO}|n\rangle}{\big(\epsilon_n-\epsilon_q\big)(\epsilon_n-\epsilon_r)}\bigg\}\bigg] \\
&- 2\sum_{m,n}^{\in occ}{}^{>>}\sum_{p,q}^{\in virt}{}^{>>}\sum_{o}^{\in occ}{}''\mathcal{R}\bigg[\frac{\{(mp|nq)-(mq|np)\}}{\big(\epsilon_m+\epsilon_n-\epsilon_p-\epsilon_q\big)}\bigg\{\frac{\langle q|\hat{h}_{SO}|n\rangle\langle o|\hat{h}_{SO}|m\rangle\langle p|\hat{h}_{SO}|o\rangle}{\big(\epsilon_m-\epsilon_p\big)\big(\epsilon_o-\epsilon_p\big)} \\
&- \frac{\langle q|\hat{h}_{SO}|m\rangle\langle o|\hat{h}_{SO}|n\rangle\langle p|\hat{h}_{SO}|o\rangle}{\big(\epsilon_n-\epsilon_p\big)\big(\epsilon_o-\epsilon_p\big)} - \frac{\langle p|\hat{h}_{SO}|n\rangle\langle o|\hat{h}_{SO}|m\rangle\langle q|\hat{h}_{SO}|o\rangle}{\big(\epsilon_m-\epsilon_q\big)\big(\epsilon_o-\epsilon_q\big)} \\
&+ \frac{\langle p|\hat{h}_{SO}|m\rangle\langle o|\hat{h}_{SO}|n\rangle\langle q|\hat{h}_{SO}|o\rangle}{\big(\epsilon_n-\epsilon_q\big)\big(\epsilon_o-\epsilon_q\big)}\bigg\}\bigg] \\
&+ 2\sum_{m,n}^{\in occ}{}^{>>}\sum_{p,q}^{\in virt}{}^{>>}\mathcal{R}\bigg[\frac{\{(mp|nq)-(mq|np)\}}{\big(\epsilon_m+\epsilon_n-\epsilon_p-\epsilon_q\big)}\bigg\{\frac{\langle q|\hat{h}_{SO}|n\rangle\langle p|\hat{h}_{SO}|q\rangle\langle q|\hat{h}_{SO}|m\rangle}{\big(\epsilon_m-\epsilon_p\big)\big(\epsilon_m-\epsilon_q\big)} \\
&- \frac{\langle q|\hat{h}_{SO}|n\rangle\langle n|\hat{h}_{SO}|m\rangle\langle p|\hat{h}_{SO}|n\rangle}{\big(\epsilon_m-\epsilon_p\big)\big(\epsilon_n-\epsilon_p\big)} - \frac{\langle q|\hat{h}_{SO}|m\rangle\langle p|\hat{h}_{SO}|q\rangle\langle q|\hat{h}_{SO}|n\rangle}{\big(\epsilon_n-\epsilon_p\big)\big(\epsilon_n-\epsilon_q\big)} \\
&+ \frac{\langle q|\hat{h}_{SO}|m\rangle\langle m|\hat{h}_{SO}|n\rangle\langle p|\hat{h}_{SO}|m\rangle}{\big(\epsilon_n-\epsilon_p\big)\big(\epsilon_m-\epsilon_p\big)} - \frac{\langle p|\hat{h}_{SO}|n\rangle\langle q|\hat{h}_{SO}|p\rangle\langle p|\hat{h}_{SO}|m\rangle}{\big(\epsilon_m-\epsilon_q\big)\big(\epsilon_m-\epsilon_p\big)} \\
&+ \frac{\langle p|\hat{h}_{SO}|n\rangle\langle n|\hat{h}_{SO}|m\rangle\langle q|\hat{h}_{SO}|n\rangle}{\big(\epsilon_m-\epsilon_q\big)\big(\epsilon_n-\epsilon_q\big)} + \frac{\langle p|\hat{h}_{SO}|m\rangle\langle q|\hat{h}_{SO}|p\rangle\langle p|\hat{h}_{SO}|n\rangle}{\big(\epsilon_n-\epsilon_q\big)\big(\epsilon_n-\epsilon_p\big)} \\
&- \frac{\langle p|\hat{h}_{SO}|m\rangle\langle m|\hat{h}_{SO}|n\rangle\langle q|\hat{h}_{SO}|m\rangle}{\big(\epsilon_n-\epsilon_q\big)\big(\epsilon_m-\epsilon_q\big)}\bigg\}\bigg]
\end{aligned}
\tag{H.267}
$$

We now recognize that all terms go to zero for the cases $m = n$ or $p = q$, so that we may extend the sums over m, n and p, q over all values and write:

$$
\begin{aligned}
E_D^{(3,1)} &= \frac{1}{2}\sum_{m,n}^{\in occ}\sum_{p,q}^{\in virt}\mathcal{R}\Bigg[\{-[(nq|mm)-(nm|mq)]+[(nq|pp)-(np|pq)]\}\Bigg\{\frac{\langle m|\hat{h}_{SO}|p\rangle\langle q|\hat{h}_{SO}|n\rangle\langle p|\hat{h}_{SO}|m\rangle}{\left(\epsilon_m-\epsilon_p\right)\left(\epsilon_m+\epsilon_n-\epsilon_p-\epsilon_q\right)\left(\epsilon_m-\epsilon_p\right)} \\
&- \frac{\langle m|\hat{h}_{SO}|p\rangle\langle q|\hat{h}_{SO}|m\rangle\langle p|\hat{h}_{SO}|n\rangle}{\left(\epsilon_m-\epsilon_p\right)\left(\epsilon_m+\epsilon_n-\epsilon_p-\epsilon_q\right)\left(\epsilon_n-\epsilon_p\right)} - \frac{\langle m|\hat{h}_{SO}|p\rangle\langle p|\hat{h}_{SO}|n\rangle\langle q|\hat{h}_{SO}|m\rangle}{\left(\epsilon_m-\epsilon_p\right)\left(\epsilon_m+\epsilon_n-\epsilon_p-\epsilon_q\right)\left(\epsilon_m-\epsilon_q\right)} \\
&+ \frac{\langle m|\hat{h}_{SO}|p\rangle\langle p|\hat{h}_{SO}|m\rangle\langle q|\hat{h}_{SO}|n\rangle}{\left(\epsilon_m-\epsilon_p\right)\left(\epsilon_m+\epsilon_n-\epsilon_p-\epsilon_q\right)\left(\epsilon_n-\epsilon_q\right)}\Bigg\} + \{[(mq|nn)-(mn|nq)]-[(mq|pp)-(mp|pq)]\} \\
&\times \Bigg\{\frac{\langle n|\hat{h}_{SO}|p\rangle\langle q|\hat{h}_{SO}|n\rangle\langle p|\hat{h}_{SO}|m\rangle}{\left(\epsilon_n-\epsilon_p\right)\left(\epsilon_m+\epsilon_n-\epsilon_p-\epsilon_q\right)\left(\epsilon_m-\epsilon_p\right)} - \frac{\langle n|\hat{h}_{SO}|p\rangle\langle q|\hat{h}_{SO}|m\rangle\langle p|\hat{h}_{SO}|n\rangle}{\left(\epsilon_n-\epsilon_p\right)\left(\epsilon_m+\epsilon_n-\epsilon_p-\epsilon_q\right)\left(\epsilon_n-\epsilon_p\right)} \\
&- \frac{\langle n|\hat{h}_{SO}|p\rangle\langle p|\hat{h}_{SO}|n\rangle\langle q|\hat{h}_{SO}|m\rangle}{\left(\epsilon_n-\epsilon_p\right)\left(\epsilon_m+\epsilon_n-\epsilon_p-\epsilon_q\right)\left(\epsilon_m-\epsilon_q\right)} + \frac{\langle n|\hat{h}_{SO}|p\rangle\langle p|\hat{h}_{SO}|m\rangle\langle q|\hat{h}_{SO}|n\rangle}{\left(\epsilon_n-\epsilon_p\right)\left(\epsilon_m+\epsilon_n-\epsilon_p-\epsilon_q\right)\left(\epsilon_n-\epsilon_q\right)}\Bigg\} \\
&+ \{[(np|mm)-(nm|mp)]-[(np|qq)-(nq|qp)]\}\Bigg\{\frac{\langle m|\hat{h}_{SO}|q\rangle\langle q|\hat{h}_{SO}|n\rangle\langle p|\hat{h}_{SO}|m\rangle}{\left(\epsilon_m-\epsilon_q\right)\left(\epsilon_m+\epsilon_n-\epsilon_p-\epsilon_q\right)\left(\epsilon_m-\epsilon_p\right)} \\
&- \frac{\langle m|\hat{h}_{SO}|q\rangle\langle q|\hat{h}_{SO}|m\rangle\langle p|\hat{h}_{SO}|n\rangle}{\left(\epsilon_m-\epsilon_q\right)\left(\epsilon_m+\epsilon_n-\epsilon_p-\epsilon_q\right)\left(\epsilon_n-\epsilon_p\right)} - \frac{\langle m|\hat{h}_{SO}|q\rangle\langle p|\hat{h}_{SO}|n\rangle\langle q|\hat{h}_{SO}|m\rangle}{\left(\epsilon_m-\epsilon_q\right)\left(\epsilon_m+\epsilon_n-\epsilon_p-\epsilon_q\right)\left(\epsilon_m-\epsilon_q\right)} \\
&+ \frac{\langle m|\hat{h}_{SO}|q\rangle\langle p|\hat{h}_{SO}|m\rangle\langle q|\hat{h}_{SO}|n\rangle}{\left(\epsilon_m-\epsilon_q\right)\left(\epsilon_m+\epsilon_n-\epsilon_p-\epsilon_q\right)\left(\epsilon_n-\epsilon_q\right)}\Bigg\} + \{-[(mp|nn)-(mn|np)]+[(mp|qq)-(mq|qp)]\} \\
&\times \Bigg\{\frac{\langle n|\hat{h}_{SO}|q\rangle\langle q|\hat{h}_{SO}|n\rangle\langle p|\hat{h}_{SO}|m\rangle}{\left(\epsilon_n-\epsilon_q\right)\left(\epsilon_m+\epsilon_n-\epsilon_p-\epsilon_q\right)\left(\epsilon_m-\epsilon_p\right)} - \frac{\langle n|\hat{h}_{SO}|q\rangle\langle q|\hat{h}_{SO}|m\rangle\langle p|\hat{h}_{SO}|n\rangle}{\left(\epsilon_n-\epsilon_q\right)\left(\epsilon_m+\epsilon_n-\epsilon_p-\epsilon_q\right)\left(\epsilon_n-\epsilon_p\right)} \\
&- \frac{\langle n|\hat{h}_{SO}|q\rangle\langle p|\hat{h}_{SO}|n\rangle\langle q|\hat{h}_{SO}|m\rangle}{\left(\epsilon_n-\epsilon_q\right)\left(\epsilon_m+\epsilon_n-\epsilon_p-\epsilon_q\right)\left(\epsilon_m-\epsilon_q\right)} + \frac{\langle n|\hat{h}_{SO}|q\rangle\langle p|\hat{h}_{SO}|m\rangle\langle q|\hat{h}_{SO}|n\rangle}{\left(\epsilon_n-\epsilon_q\right)\left(\epsilon_m+\epsilon_n-\epsilon_p-\epsilon_q\right)\left(\epsilon_n-\epsilon_q\right)}\Bigg\}\Bigg] \\
&+ \frac{1}{2}\sum_{m,n}^{\in occ}\sum_{p,q}^{\in virt}\sum_{r}^{\in virt}{}''\mathcal{R}\Bigg[\frac{\{(mp|nq)-(mq|np)\}}{\left(\epsilon_m+\epsilon_n-\epsilon_p-\epsilon_q\right)}\Bigg\{\frac{\langle q|\hat{h}_{SO}|n\rangle\langle p|\hat{h}_{SO}|r\rangle\langle r|\hat{h}_{SO}|m\rangle}{\left(\epsilon_m-\epsilon_p\right)(\epsilon_m-\epsilon_r)} \\
&- \frac{\langle q|\hat{h}_{SO}|m\rangle\langle p|\hat{h}_{SO}|r\rangle\langle r|\hat{h}_{SO}|n\rangle}{\left(\epsilon_n-\epsilon_p\right)(\epsilon_n-\epsilon_r)} - \frac{\langle p|\hat{h}_{SO}|n\rangle\langle q|\hat{h}_{SO}|r\rangle\langle r|\hat{h}_{SO}|m\rangle}{\left(\epsilon_m-\epsilon_q\right)(\epsilon_m-\epsilon_r)} \\
&+ \frac{\langle p|\hat{h}_{SO}|m\rangle\langle q|\hat{h}_{SO}|r\rangle\langle r|\hat{h}_{SO}|n\rangle}{\left(\epsilon_n-\epsilon_q\right)(\epsilon_n-\epsilon_r)}\Bigg\}\Bigg] \\
&- \frac{1}{2}\sum_{m,n}^{\in occ}\sum_{p,q}^{\in virt}\sum_{o}^{\in occ}{}''\mathcal{R}\Bigg[\frac{\{(mp|nq)-(mq|np)\}}{\left(\epsilon_m+\epsilon_n-\epsilon_p-\epsilon_q\right)}\Bigg\{\frac{\langle q|\hat{h}_{SO}|n\rangle\langle o|\hat{h}_{SO}|m\rangle\langle p|\hat{h}_{SO}|o\rangle}{\left(\epsilon_m-\epsilon_p\right)\left(\epsilon_o-\epsilon_p\right)} \\
&- \frac{\langle q|\hat{h}_{SO}|m\rangle\langle o|\hat{h}_{SO}|n\rangle\langle p|\hat{h}_{SO}|o\rangle}{\left(\epsilon_n-\epsilon_p\right)\left(\epsilon_o-\epsilon_p\right)} - \frac{\langle p|\hat{h}_{SO}|n\rangle\langle o|\hat{h}_{SO}|m\rangle\langle q|\hat{h}_{SO}|o\rangle}{\left(\epsilon_m-\epsilon_q\right)\left(\epsilon_o-\epsilon_q\right)} \\
&+ \frac{\langle p|\hat{h}_{SO}|m\rangle\langle o|\hat{h}_{SO}|n\rangle\langle q|\hat{h}_{SO}|o\rangle}{\left(\epsilon_n-\epsilon_q\right)\left(\epsilon_o-\epsilon_q\right)}\Bigg\}\Bigg] \\
&+ \frac{1}{2}\sum_{m,n}^{\in occ}\sum_{p,q}^{\in virt}\mathcal{R}\Bigg[\frac{\{(mp|nq)-(mq|np)\}}{\left(\epsilon_m+\epsilon_n-\epsilon_p-\epsilon_q\right)}\Bigg\{\frac{\langle q|\hat{h}_{SO}|n\rangle\langle p|\hat{h}_{SO}|q\rangle\langle q|\hat{h}_{SO}|m\rangle}{\left(\epsilon_m-\epsilon_p\right)\left(\epsilon_m-\epsilon_q\right)} \\
&- \frac{\langle q|\hat{h}_{SO}|n\rangle\langle n|\hat{h}_{SO}|m\rangle\langle p|\hat{h}_{SO}|n\rangle}{\left(\epsilon_m-\epsilon_p\right)\left(\epsilon_n-\epsilon_p\right)} - \frac{\langle q|\hat{h}_{SO}|m\rangle\langle p|\hat{h}_{SO}|q\rangle\langle q|\hat{h}_{SO}|n\rangle}{\left(\epsilon_n-\epsilon_p\right)\left(\epsilon_n-\epsilon_q\right)} \\
&+ \frac{\langle q|\hat{h}_{SO}|m\rangle\langle m|\hat{h}_{SO}|n\rangle\langle p|\hat{h}_{SO}|m\rangle}{\left(\epsilon_n-\epsilon_p\right)\left(\epsilon_m-\epsilon_p\right)} - \frac{\langle p|\hat{h}_{SO}|n\rangle\langle q|\hat{h}_{SO}|p\rangle\langle p|\hat{h}_{SO}|m\rangle}{\left(\epsilon_m-\epsilon_q\right)\left(\epsilon_m-\epsilon_p\right)} \\
&+ \frac{\langle p|\hat{h}_{SO}|n\rangle\langle n|\hat{h}_{SO}|m\rangle\langle q|\hat{h}_{SO}|n\rangle}{\left(\epsilon_m-\epsilon_q\right)\left(\epsilon_n-\epsilon_q\right)} + \frac{\langle p|\hat{h}_{SO}|m\rangle\langle q|\hat{h}_{SO}|p\rangle\langle p|\hat{h}_{SO}|n\rangle}{\left(\epsilon_n-\epsilon_q\right)\left(\epsilon_n-\epsilon_p\right)} \\
&- \frac{\langle p|\hat{h}_{SO}|m\rangle\langle m|\hat{h}_{SO}|n\rangle\langle q|\hat{h}_{SO}|m\rangle}{\left(\epsilon_n-\epsilon_q\right)\left(\epsilon_m-\epsilon_q\right)}\Bigg\}\Bigg]
\end{aligned}
\tag{H.268}
$$

Now interchanging the names of the labels *m* and *n* in the fourth to eigth terms, as well as the thirteenth to sixteenth terms of Eq. (H.268):

$$
\begin{aligned}
E_D^{(3,1)} &= \frac{1}{2}\sum_{m,n}^{\in occ}\sum_{p,q}^{\in virt}\mathcal{R}\Bigg[\Bigg\{\frac{-[(nq|mm)-(nm|mq)]+[(nq|pp)-(np|pq)]}{\left(\epsilon_m+\epsilon_n-\epsilon_p-\epsilon_q\right)}\Bigg\}\Bigg\{\frac{2\langle m|\hat{h}_{SO}|p\rangle\langle q|\hat{h}_{SO}|n\rangle\langle p|\hat{h}_{SO}|m\rangle}{\left(\epsilon_m-\epsilon_p\right)\left(\epsilon_m-\epsilon_p\right)} \\
&- \frac{2\langle m|\hat{h}_{SO}|p\rangle\langle q|\hat{h}_{SO}|m\rangle\langle p|\hat{h}_{SO}|n\rangle}{\left(\epsilon_m-\epsilon_p\right)\left(\epsilon_n-\epsilon_p\right)} - \frac{2\langle m|\hat{h}_{SO}|p\rangle\langle p|\hat{h}_{SO}|n\rangle\langle q|\hat{h}_{SO}|m\rangle}{\left(\epsilon_m-\epsilon_p\right)\left(\epsilon_m-\epsilon_q\right)} + \frac{2\langle m|\hat{h}_{SO}|p\rangle\langle p|\hat{h}_{SO}|m\rangle\langle q|\hat{h}_{SO}|n\rangle}{\left(\epsilon_m-\epsilon_p\right)\left(\epsilon_n-\epsilon_q\right)}\Bigg\} \\
&+ \Bigg\{\frac{[(np|mm)-(nm|mp)]-[(np|qq)-(nq|qp)]}{\left(\epsilon_m+\epsilon_n-\epsilon_p-\epsilon_q\right)}\Bigg\}\Bigg\{\frac{2\langle m|\hat{h}_{SO}|q\rangle\langle q|\hat{h}_{SO}|n\rangle\langle p|\hat{h}_{SO}|m\rangle}{\left(\epsilon_m-\epsilon_q\right)\left(\epsilon_m-\epsilon_p\right)} \\
&- \frac{2\langle m|\hat{h}_{SO}|q\rangle\langle q|\hat{h}_{SO}|m\rangle\langle p|\hat{h}_{SO}|n\rangle}{\left(\epsilon_m-\epsilon_q\right)\left(\epsilon_n-\epsilon_p\right)} - \frac{2\langle m|\hat{h}_{SO}|q\rangle\langle p|\hat{h}_{SO}|n\rangle\langle q|\hat{h}_{SO}|m\rangle}{\left(\epsilon_m-\epsilon_q\right)\left(\epsilon_m-\epsilon_q\right)} + \frac{2\langle m|\hat{h}_{SO}|q\rangle\langle p|\hat{h}_{SO}|m\rangle\langle q|\hat{h}_{SO}|n\rangle}{\left(\epsilon_m-\epsilon_q\right)\left(\epsilon_n-\epsilon_q\right)}\Bigg\}\Bigg] \\
&+ \frac{1}{2}\sum_{m,n}^{\in occ}\sum_{p,q}^{\in virt}\sum_{r}^{\in virt}{}''\mathcal{R}\Bigg[\frac{\{(mp|nq)-(mq|np)\}}{\left(\epsilon_m+\epsilon_n-\epsilon_p-\epsilon_q\right)}\Bigg\{\frac{\langle q|\hat{h}_{SO}|n\rangle\langle p|\hat{h}_{SO}|r\rangle\langle r|\hat{h}_{SO}|m\rangle}{\left(\epsilon_m-\epsilon_p\right)(\epsilon_m-\epsilon_r)} \\
&- \frac{\langle q|\hat{h}_{SO}|m\rangle\langle p|\hat{h}_{SO}|r\rangle\langle r|\hat{h}_{SO}|n\rangle}{\left(\epsilon_n-\epsilon_p\right)(\epsilon_n-\epsilon_r)} - \frac{\langle p|\hat{h}_{SO}|n\rangle\langle q|\hat{h}_{SO}|r\rangle\langle r|\hat{h}_{SO}|m\rangle}{\left(\epsilon_m-\epsilon_q\right)(\epsilon_m-\epsilon_r)} \\
&+ \frac{\langle p|\hat{h}_{SO}|m\rangle\langle q|\hat{h}_{SO}|r\rangle\langle r|\hat{h}_{SO}|n\rangle}{\left(\epsilon_n-\epsilon_q\right)(\epsilon_n-\epsilon_r)}\Bigg\}\Bigg] \\
&- \frac{1}{2}\sum_{m,n}^{\in occ}\sum_{p,q}^{\in virt}\sum_{o}^{\in occ}{}''\mathcal{R}\Bigg[\frac{\{(mp|nq)-(mq|np)\}}{\left(\epsilon_m+\epsilon_n-\epsilon_p-\epsilon_q\right)}\Bigg\{\frac{\langle q|\hat{h}_{SO}|n\rangle\langle o|\hat{h}_{SO}|m\rangle\langle p|\hat{h}_{SO}|o\rangle}{\left(\epsilon_m-\epsilon_p\right)\left(\epsilon_o-\epsilon_p\right)} \\
&- \frac{\langle q|\hat{h}_{SO}|m\rangle\langle o|\hat{h}_{SO}|n\rangle\langle p|\hat{h}_{SO}|o\rangle}{\left(\epsilon_n-\epsilon_p\right)\left(\epsilon_o-\epsilon_p\right)} - \frac{\langle p|\hat{h}_{SO}|n\rangle\langle o|\hat{h}_{SO}|m\rangle\langle q|\hat{h}_{SO}|o\rangle}{\left(\epsilon_m-\epsilon_q\right)\left(\epsilon_o-\epsilon_q\right)} \\
&+ \frac{\langle p|\hat{h}_{SO}|m\rangle\langle o|\hat{h}_{SO}|n\rangle\langle q|\hat{h}_{SO}|o\rangle}{\left(\epsilon_n-\epsilon_q\right)\left(\epsilon_o-\epsilon_q\right)}\Bigg\}\Bigg] \\
&+ \frac{1}{2}\sum_{m,n}^{\in occ}\sum_{p,q}^{\in virt}\mathcal{R}\Bigg[\frac{\{(mp|nq)-(mq|np)\}}{\left(\epsilon_m+\epsilon_n-\epsilon_p-\epsilon_q\right)}\Bigg\{\frac{\langle q|\hat{h}_{SO}|n\rangle\langle p|\hat{h}_{SO}|q\rangle\langle q|\hat{h}_{SO}|m\rangle}{\left(\epsilon_m-\epsilon_p\right)\left(\epsilon_m-\epsilon_q\right)} \\
&- \frac{\langle q|\hat{h}_{SO}|n\rangle\langle n|\hat{h}_{SO}|m\rangle\langle p|\hat{h}_{SO}|n\rangle}{\left(\epsilon_m-\epsilon_p\right)\left(\epsilon_n-\epsilon_p\right)} - \frac{\langle q|\hat{h}_{SO}|m\rangle\langle p|\hat{h}_{SO}|q\rangle\langle q|\hat{h}_{SO}|n\rangle}{\left(\epsilon_n-\epsilon_p\right)\left(\epsilon_n-\epsilon_q\right)} \\
&+ \frac{\langle q|\hat{h}_{SO}|m\rangle\langle m|\hat{h}_{SO}|n\rangle\langle p|\hat{h}_{SO}|m\rangle}{\left(\epsilon_n-\epsilon_p\right)\left(\epsilon_m-\epsilon_p\right)} - \frac{\langle p|\hat{h}_{SO}|n\rangle\langle q|\hat{h}_{SO}|p\rangle\langle p|\hat{h}_{SO}|m\rangle}{\left(\epsilon_m-\epsilon_q\right)\left(\epsilon_m-\epsilon_p\right)} \\
&+ \frac{\langle p|\hat{h}_{SO}|n\rangle\langle n|\hat{h}_{SO}|m\rangle\langle q|\hat{h}_{SO}|n\rangle}{\left(\epsilon_m-\epsilon_q\right)\left(\epsilon_n-\epsilon_q\right)} + \frac{\langle p|\hat{h}_{SO}|m\rangle\langle q|\hat{h}_{SO}|p\rangle\langle p|\hat{h}_{SO}|n\rangle}{\left(\epsilon_n-\epsilon_q\right)\left(\epsilon_n-\epsilon_p\right)} \\
&- \frac{\langle p|\hat{h}_{SO}|m\rangle\langle m|\hat{h}_{SO}|n\rangle\langle q|\hat{h}_{SO}|m\rangle}{\left(\epsilon_n-\epsilon_q\right)\left(\epsilon_m-\epsilon_q\right)}\Bigg\}\Bigg]
\end{aligned}
\tag{H.269}
$$

Then, interchanging the names of the labels p and q in the fourth to eigth terms of Eq. (H.269):

$$
\begin{aligned}
E_D^{(3,1)} \;=\;& 2\sum_{m,n}^{\in occ}\sum_{p,q}^{\in virt}\mathcal{R}\Biggl[\Biggl\{\frac{-\left[(nq|mm)-(nm|mq)\right]+\left[(nq|pp)-(np|pq)\right]}{\left(\epsilon_m+\epsilon_n-\epsilon_p-\epsilon_q\right)}\Biggr\}\Biggl\{\frac{\langle m|\hat{h}_{SO}|p\rangle\langle q|\hat{h}_{SO}|n\rangle\langle p|\hat{h}_{SO}|m\rangle}{\left(\epsilon_m-\epsilon_p\right)\left(\epsilon_m-\epsilon_p\right)} \\
-\;& \frac{\langle m|\hat{h}_{SO}|p\rangle\langle q|\hat{h}_{SO}|m\rangle\langle p|\hat{h}_{SO}|n\rangle}{\left(\epsilon_m-\epsilon_p\right)\left(\epsilon_n-\epsilon_p\right)}-\frac{\langle m|\hat{h}_{SO}|p\rangle\langle p|\hat{h}_{SO}|n\rangle\langle q|\hat{h}_{SO}|m\rangle}{\left(\epsilon_m-\epsilon_p\right)\left(\epsilon_m-\epsilon_q\right)}+\frac{\langle m|\hat{h}_{SO}|p\rangle\langle p|\hat{h}_{SO}|m\rangle\langle q|\hat{h}_{SO}|n\rangle}{\left(\epsilon_m-\epsilon_p\right)\left(\epsilon_n-\epsilon_q\right)}\Biggr\} \\
+\;& \frac{1}{2}\sum_{m,n}^{\in occ}\sum_{p,q}^{\in virt}{\sum_{r}^{\in virt}}''\mathcal{R}\Biggl[\frac{\{(mp|nq)-(mq|np)\}}{\left(\epsilon_m+\epsilon_n-\epsilon_p-\epsilon_q\right)}\Biggl\{\frac{\langle q|\hat{h}_{SO}|n\rangle\langle p|\hat{h}_{SO}|r\rangle\langle r|\hat{h}_{SO}|m\rangle}{\left(\epsilon_m-\epsilon_p\right)(\epsilon_m-\epsilon_r)} \\
-\;& \frac{\langle q|\hat{h}_{SO}|m\rangle\langle p|\hat{h}_{SO}|r\rangle\langle r|\hat{h}_{SO}|n\rangle}{\left(\epsilon_n-\epsilon_p\right)(\epsilon_n-\epsilon_r)}-\frac{\langle p|\hat{h}_{SO}|n\rangle\langle q|\hat{h}_{SO}|r\rangle\langle r|\hat{h}_{SO}|m\rangle}{\left(\epsilon_m-\epsilon_q\right)(\epsilon_m-\epsilon_r)} \\
+\;& \frac{\langle p|\hat{h}_{SO}|m\rangle\langle q|\hat{h}_{SO}|r\rangle\langle r|\hat{h}_{SO}|n\rangle}{\left(\epsilon_n-\epsilon_q\right)(\epsilon_n-\epsilon_r)}\Biggr\}\Biggr] \\
-\;& \frac{1}{2}\sum_{m,n}^{\in occ}\sum_{p,q}^{\in virt}{\sum_{o}^{\in occ}}''\mathcal{R}\Biggl[\frac{\{(mp|nq)-(mq|np)\}}{\left(\epsilon_m+\epsilon_n-\epsilon_p-\epsilon_q\right)}\Biggl\{\frac{\langle q|\hat{h}_{SO}|n\rangle\langle o|\hat{h}_{SO}|m\rangle\langle p|\hat{h}_{SO}|o\rangle}{\left(\epsilon_m-\epsilon_p\right)\left(\epsilon_o-\epsilon_p\right)} \\
-\;& \frac{\langle q|\hat{h}_{SO}|m\rangle\langle o|\hat{h}_{SO}|n\rangle\langle p|\hat{h}_{SO}|o\rangle}{\left(\epsilon_n-\epsilon_p\right)\left(\epsilon_o-\epsilon_p\right)}-\frac{\langle p|\hat{h}_{SO}|n\rangle\langle o|\hat{h}_{SO}|m\rangle\langle q|\hat{h}_{SO}|o\rangle}{\left(\epsilon_m-\epsilon_q\right)\left(\epsilon_o-\epsilon_q\right)} \\
+\;& \frac{\langle p|\hat{h}_{SO}|m\rangle\langle o|\hat{h}_{SO}|n\rangle\langle q|\hat{h}_{SO}|o\rangle}{\left(\epsilon_n-\epsilon_q\right)\left(\epsilon_o-\epsilon_q\right)}\Biggr\}\Biggr] \\
+\;& \frac{1}{2}\sum_{m,n}^{\in occ}\sum_{p,q}^{\in virt}\mathcal{R}\Biggl[\frac{\{(mp|nq)-(mq|np)\}}{\left(\epsilon_m+\epsilon_n-\epsilon_p-\epsilon_q\right)}\Biggl\{\frac{\langle q|\hat{h}_{SO}|n\rangle\langle p|\hat{h}_{SO}|q\rangle\langle q|\hat{h}_{SO}|m\rangle}{\left(\epsilon_m-\epsilon_p\right)\left(\epsilon_m-\epsilon_q\right)} \\
-\;& \frac{\langle q|\hat{h}_{SO}|n\rangle\langle n|\hat{h}_{SO}|m\rangle\langle p|\hat{h}_{SO}|n\rangle}{\left(\epsilon_m-\epsilon_p\right)\left(\epsilon_n-\epsilon_p\right)}-\frac{\langle q|\hat{h}_{SO}|m\rangle\langle p|\hat{h}_{SO}|q\rangle\langle q|\hat{h}_{SO}|n\rangle}{\left(\epsilon_n-\epsilon_p\right)\left(\epsilon_n-\epsilon_q\right)} \\
+\;& \frac{\langle q|\hat{h}_{SO}|m\rangle\langle m|\hat{h}_{SO}|n\rangle\langle p|\hat{h}_{SO}|m\rangle}{\left(\epsilon_n-\epsilon_p\right)\left(\epsilon_m-\epsilon_p\right)}-\frac{\langle p|\hat{h}_{SO}|n\rangle\langle q|\hat{h}_{SO}|p\rangle\langle p|\hat{h}_{SO}|m\rangle}{\left(\epsilon_m-\epsilon_q\right)\left(\epsilon_m-\epsilon_p\right)} \\
+\;& \frac{\langle p|\hat{h}_{SO}|n\rangle\langle n|\hat{h}_{SO}|m\rangle\langle q|\hat{h}_{SO}|n\rangle}{\left(\epsilon_m-\epsilon_q\right)\left(\epsilon_n-\epsilon_q\right)}+\frac{\langle p|\hat{h}_{SO}|m\rangle\langle q|\hat{h}_{SO}|p\rangle\langle p|\hat{h}_{SO}|n\rangle}{\left(\epsilon_n-\epsilon_q\right)\left(\epsilon_n-\epsilon_p\right)} \\
-\;& \frac{\langle p|\hat{h}_{SO}|m\rangle\langle m|\hat{h}_{SO}|n\rangle\langle q|\hat{h}_{SO}|m\rangle}{\left(\epsilon_n-\epsilon_q\right)\left(\epsilon_m-\epsilon_q\right)}\Biggr\}\Biggr]
\end{aligned}
\tag{H.270}
$$

Now interchanging the names of the labels m and n in terms 6,7,10,11,15,16,19,20 of Eq. (H.270) and combining terms 5 and 6, 7 and 8, 9 and 10, 11 and 12, 13 and 15, 14 and 16, 17 and 19, 18 and 20, we find:

$$
\begin{aligned}
E_D^{(3,1)} \quad = \quad & 2\sum_{m,n}^{\in occ}\sum_{p,q}^{\in virt}\mathcal{R}\Bigg[\left\{\frac{-\left[(nq|mm)-(nm|mq)\right]+\left[(nq|pp)-(np|pq)\right]}{\left(\epsilon_m+\epsilon_n-\epsilon_p-\epsilon_q\right)}\right\}\Bigg\{\frac{\langle m|\hat{h}_{SO}|p\rangle\langle q|\hat{h}_{SO}|n\rangle\langle p|\hat{h}_{SO}|m\rangle}{\left(\epsilon_m-\epsilon_p\right)\left(\epsilon_m-\epsilon_p\right)} \\
- \quad & \frac{\langle m|\hat{h}_{SO}|p\rangle\langle q|\hat{h}_{SO}|m\rangle\langle p|\hat{h}_{SO}|n\rangle}{\left(\epsilon_m-\epsilon_p\right)\left(\epsilon_n-\epsilon_p\right)}-\frac{\langle m|\hat{h}_{SO}|p\rangle\langle p|\hat{h}_{SO}|n\rangle\langle q|\hat{h}_{SO}|m\rangle}{\left(\epsilon_m-\epsilon_p\right)\left(\epsilon_m-\epsilon_q\right)}+\frac{\langle m|\hat{h}_{SO}|p\rangle\langle p|\hat{h}_{SO}|m\rangle\langle q|\hat{h}_{SO}|n\rangle}{\left(\epsilon_m-\epsilon_p\right)\left(\epsilon_n-\epsilon_q\right)}\Bigg\} \\
+ \quad & \sum_{m,n}^{\in occ}\sum_{p,q}^{\in virt}\sum_{r}^{\in virt}{}''\mathcal{R}\Bigg[\frac{\{(mp|nq)-(mq|np)\}}{\left(\epsilon_m+\epsilon_n-\epsilon_p-\epsilon_q\right)}\Bigg\{\frac{\langle q|\hat{h}_{SO}|n\rangle\langle p|\hat{h}_{SO}|r\rangle\langle r|\hat{h}_{SO}|m\rangle}{\left(\epsilon_m-\epsilon_p\right)(\epsilon_m-\epsilon_r)}+\frac{\langle p|\hat{h}_{SO}|m\rangle\langle q|\hat{h}_{SO}|r\rangle\langle r|\hat{h}_{SO}|n\rangle}{\left(\epsilon_n-\epsilon_q\right)(\epsilon_n-\epsilon_r)}\Bigg\}\Bigg] \\
- \quad & \sum_{m,n}^{\in occ}\sum_{p,q}^{\in virt}\sum_{o}^{\in occ}{}''\mathcal{R}\Bigg[\frac{\{(mp|nq)-(mq|np)\}}{\left(\epsilon_m+\epsilon_n-\epsilon_p-\epsilon_q\right)}\Bigg\{\frac{\langle q|\hat{h}_{SO}|n\rangle\langle o|\hat{h}_{SO}|m\rangle\langle p|\hat{h}_{SO}|o\rangle}{\left(\epsilon_m-\epsilon_p\right)\left(\epsilon_o-\epsilon_p\right)}+\frac{\langle p|\hat{h}_{SO}|m\rangle\langle o|\hat{h}_{SO}|n\rangle\langle q|\hat{h}_{SO}|o\rangle}{\left(\epsilon_n-\epsilon_q\right)\left(\epsilon_o-\epsilon_q\right)}\Bigg\}\Bigg] \\
+ \quad & \sum_{m,n}^{\in occ}\sum_{p,q}^{\in virt}\mathcal{R}\Bigg[\frac{\{(mp|nq)-(mq|np)\}}{\left(\epsilon_m+\epsilon_n-\epsilon_p-\epsilon_q\right)}\Bigg\{\frac{\langle q|\hat{h}_{SO}|n\rangle\langle p|\hat{h}_{SO}|q\rangle\langle q|\hat{h}_{SO}|m\rangle}{\left(\epsilon_m-\epsilon_p\right)\left(\epsilon_m-\epsilon_q\right)}-\frac{\langle q|\hat{h}_{SO}|n\rangle\langle n|\hat{h}_{SO}|m\rangle\langle p|\hat{h}_{SO}|n\rangle}{\left(\epsilon_m-\epsilon_p\right)\left(\epsilon_n-\epsilon_p\right)} \\
- \quad & \frac{\langle p|\hat{h}_{SO}|n\rangle\langle q|\hat{h}_{SO}|p\rangle\langle p|\hat{h}_{SO}|m\rangle}{\left(\epsilon_m-\epsilon_q\right)\left(\epsilon_m-\epsilon_p\right)}+\frac{\langle p|\hat{h}_{SO}|n\rangle\langle n|\hat{h}_{SO}|m\rangle\langle q|\hat{h}_{SO}|n\rangle}{\left(\epsilon_m-\epsilon_q\right)\left(\epsilon_n-\epsilon_q\right)}\Bigg\}\Bigg]
\end{aligned}
\tag{H.271}
$$

Then, expression the first and fourth terms, as well as the second and third terms of Eq. (H.271) with a common denominator, interchanging the labels of n, q and m, p sixth and eighth terms, and interchanging the labels of p and q in the eleventh and twelfth terms:

$$
\begin{aligned}
E_D^{(3,1)} \quad = \quad & 4\sum_{m,n}^{\in occ}\sum_{p,q}^{\in virt}\mathcal{R}\Bigg[\left\{-\left[(nq|mm)-(nm|mq)\right]+\left[(nq|pp)-(np|pq)\right]\right\}\Bigg\{\frac{\langle m|\hat{h}_{SO}|p\rangle\langle q|\hat{h}_{SO}|n\rangle\langle p|\hat{h}_{SO}|m\rangle}{\left(\epsilon_n-\epsilon_q\right)\left(\epsilon_m-\epsilon_p\right)\left(\epsilon_m-\epsilon_p\right)} \\
- \quad & \frac{\langle m|\hat{h}_{SO}|p\rangle\langle q|\hat{h}_{SO}|m\rangle\langle p|\hat{h}_{SO}|n\rangle}{\left(\epsilon_m-\epsilon_p\right)\left(\epsilon_n-\epsilon_p\right)\left(\epsilon_m-\epsilon_q\right)}\Bigg\}+2\sum_{m,n}^{\in occ}\sum_{p,q}^{\in virt}\sum_{r}^{\in virt}{}''\mathcal{R}\Bigg[\frac{\{(mp|nq)-(mq|np)\}}{\left(\epsilon_m+\epsilon_n-\epsilon_p-\epsilon_q\right)}\Bigg\{\frac{\langle q|\hat{h}_{SO}|n\rangle\langle p|\hat{h}_{SO}|r\rangle\langle r|\hat{h}_{SO}|m\rangle}{\left(\epsilon_m-\epsilon_p\right)(\epsilon_m-\epsilon_r)}\Bigg\}\Bigg] \\
- \quad & 2\sum_{m,n}^{\in occ}\sum_{p,q}^{\in virt}\sum_{o}^{\in occ}{}''\mathcal{R}\Bigg[\frac{\{(mp|nq)-(mq|np)\}}{\left(\epsilon_m+\epsilon_n-\epsilon_p-\epsilon_q\right)}\Bigg\{\frac{\langle q|\hat{h}_{SO}|n\rangle\langle o|\hat{h}_{SO}|m\rangle\langle p|\hat{h}_{SO}|o\rangle}{\left(\epsilon_m-\epsilon_p\right)\left(\epsilon_o-\epsilon_p\right)}\Bigg\}\Bigg] \\
+ \quad & 2\sum_{m,n}^{\in occ}\sum_{p,q}^{\in virt}\mathcal{R}\Bigg[\frac{\{(mp|nq)-(mq|np)\}}{\left(\epsilon_m+\epsilon_n-\epsilon_p-\epsilon_q\right)}\Bigg\{\frac{\langle q|\hat{h}_{SO}|n\rangle\langle p|\hat{h}_{SO}|q\rangle\langle q|\hat{h}_{SO}|m\rangle}{\left(\epsilon_m-\epsilon_p\right)\left(\epsilon_m-\epsilon_q\right)}-\frac{\langle q|\hat{h}_{SO}|n\rangle\langle n|\hat{h}_{SO}|m\rangle\langle p|\hat{h}_{SO}|n\rangle}{\left(\epsilon_m-\epsilon_p\right)\left(\epsilon_n-\epsilon_p\right)}\Bigg\}\Bigg]
\end{aligned}
\tag{H.272}
$$

Finally, combining terms three to six of Eq. (H.272):

$$
\begin{aligned}
E_D^{(3,1)} = \quad & 4\sum_{m,n}^{\in occ}\sum_{p,q}^{\in virt}\mathcal{R}\Bigg[\left\{-\left[(nq|mm)-(nm|mq)\right]+\left[(nq|pp)-(np|pq)\right]\right\}\Bigg\{\frac{\langle m|\hat{h}_{SO}|p\rangle\langle q|\hat{h}_{SO}|n\rangle\langle p|\hat{h}_{SO}|m\rangle}{\left(\epsilon_n-\epsilon_q\right)\left(\epsilon_m-\epsilon_p\right)\left(\epsilon_m-\epsilon_p\right)} \\
- \quad & \frac{\langle m|\hat{h}_{SO}|p\rangle\langle q|\hat{h}_{SO}|m\rangle\langle p|\hat{h}_{SO}|n\rangle}{\left(\epsilon_m-\epsilon_p\right)\left(\epsilon_n-\epsilon_p\right)\left(\epsilon_m-\epsilon_q\right)}\Bigg\}+2\sum_{m,n}^{\in occ}\sum_{p,q}^{\in virt}\mathcal{R}\Bigg[\frac{\{(mp|nq)-(mq|np)\}\,\langle q|\hat{h}_{SO}|n\rangle}{\left(\epsilon_m-\epsilon_p\right)\left(\epsilon_m+\epsilon_n-\epsilon_p-\epsilon_q\right)} \\
\times \quad & \Bigg\{\sum_{r}^{\in virt}\frac{\langle p|\hat{h}_{SO}|r\rangle\langle r|\hat{h}_{SO}|m\rangle}{(\epsilon_m-\epsilon_r)}-\sum_{o}^{\in occ}\frac{\langle o|\hat{h}_{SO}|m\rangle\langle p|\hat{h}_{SO}|o\rangle}{\left(\epsilon_o-\epsilon_p\right)}\Bigg\}\Bigg]
\end{aligned}
\tag{H.273}
$$

H.6.5 Equations in a Finite Basis: The Singles Contribution

We start by finding the expression in the AO basis for the singles term $E_S^{(3,1)}$ of Eq. (H.265). Substituting Eqs. (H.149) and (H.154) in Eq. (H.265), we find:

$$E_S^{(3,1)} = E_{S,C}^{(3,1)} - E_{S,K}^{(3,1)} \tag{H.274}$$

The Coulomb-like contribution $E_{S,C}^{(3,1)}$ reads:

$$\begin{aligned} E_{S,C}^{(3,1)} &= 2\sum_{m,n}^{\in occ}\sum_{p,q}^{\in virt}(pm|nq)\mathcal{R}\Bigg[\sum_{r}^{\in virt}\frac{\langle m|\hat{h}_{SO}|p\rangle\langle q|\hat{h}_{SO}|r\rangle\langle r|\hat{h}_{SO}|n\rangle}{\left(\epsilon_m-\epsilon_p\right)\left(\epsilon_n-\epsilon_q\right)(\epsilon_n-\epsilon_r)} - \sum_{o}^{\in occ}\frac{\langle m|\hat{h}_{SO}|p\rangle\langle o|\hat{h}_{SO}|n\rangle\langle q|\hat{h}_{SO}|o\rangle}{\left(\epsilon_m-\epsilon_p\right)\left(\epsilon_n-\epsilon_q\right)\left(\epsilon_o-\epsilon_q\right)}\Bigg] \\ &= 2\sum_{\sigma,\sigma'}\mathcal{R}\left[\sum_{\mu\nu}\left[M_{\mu\nu}^{\sigma\sigma(1)}\right]^*\sum_{\tau\omega}M_{\omega\tau}^{\sigma'\sigma'(2)}(\mu\nu|\tau\omega)\right] \end{aligned} \tag{H.275}$$

and the exchange-like contribution $E_{S,K}^{(3,1)}$ reads:

$$\begin{aligned} E_{S,K}^{(3,1)} &= 2\sum_{m,n}^{\in occ}\sum_{p,q}^{\in virt}(pq|nm)\mathcal{R}\Bigg[\sum_{r}^{\in virt}\frac{\langle m|\hat{h}_{SO}|p\rangle\langle q|\hat{h}_{SO}|r\rangle\langle r|\hat{h}_{SO}|n\rangle}{\left(\epsilon_m-\epsilon_p\right)\left(\epsilon_n-\epsilon_q\right)(\epsilon_n-\epsilon_r)} - \sum_{o}^{\in occ}\frac{\langle m|\hat{h}_{SO}|p\rangle\langle o|\hat{h}_{SO}|n\rangle\langle q|\hat{h}_{SO}|o\rangle}{\left(\epsilon_m-\epsilon_p\right)\left(\epsilon_n-\epsilon_q\right)\left(\epsilon_o-\epsilon_q\right)}\Bigg] \\ &= 2\sum_{\sigma,\sigma'}\mathcal{R}\left[\sum_{\mu\nu}\left[M_{\mu\nu}^{\sigma\sigma'(1)}\right]^*\sum_{\tau\omega}M_{\omega\tau}^{\sigma\sigma'(2)}(\mu\omega|\tau\nu)\right] \end{aligned} \tag{H.276}$$

H.7 Extrapolation of Perturbative Series to Infinite Order

Following Weniger and Kirtman (Comput Math Appl, 45, 189-215, 2003) we assume that we have constructed a partial sequence s_n of terms:

$$s_n = a_1 + a_2 + \cdots + a_n \tag{H.277}$$

and we write the difference between s_n and s_∞ as:

$$r_n = s_n - s_\infty \tag{H.278}$$

provided that r_n can be written as a single exponential $r_n = c\lambda^n$, with $c \neq 0$ and $|\lambda| \neq 1$, then the infinite series s_∞ can be approximated as:

$$s_\infty \approx s_n - \frac{(s_{n+1} - s_n)^2}{(s_{n+2} - 2s_{n+1} + s_n)} \tag{H.279}$$

For application to the evaluation of the SOC contribution to the energy, let us first consider the series involving the terms $E^{(n,0)}$ that is of arbitrary order in SOC and of zeroth order in correlation. Since we know that $E^{(1,0)} = 0$, we can apply Eq. (H.279) to the terms of even order in SOC and approximate those of odd order in SOC by $E^{(3,0)}$, which gives us the formula:

$$E \approx E^{(0,0)} + E^{(3,0)} - \frac{(E^{(2,0)})^2}{E^{(4,0)} - E^{(2,0)}} + E^{(0,1)} + E^{(1,1)} + E^{(2,1)} + E^{(3,1)} + \ldots \tag{H.280}$$

For the series involving the terms $E^{(n,1)}$ of order one in correlation and arbitrary order in SOC, we know that $E^{(1,1)} = 0$ and we can approximate all other terms using the partial sums of order two and three in SOC, to find:

$$E \approx E^{(0,0)} + E^{(0,1)} + E^{(3,0)} - \frac{(E^{(2,0)})^2}{E^{(4,0)} - E^{(2,0)}} - \frac{(E^{(2,1)})^2}{E^{(3,1)} - E^{(2,1)}} \tag{H.281}$$

H.8 Numerical Results on the Biatomic Halogens

Table H.1: SOC contribution to the HF energy (in H a.u.) calculated for the biatomic molecules of the Halogen series. The energies are calculated from uncoupled non-degenerate Rayleigh-Schrodinger perturbation theory at second-order (RSPT2), third-order (RSPT3), fourth-order (RSPT4), and the extrapolation to infinite order RSPT∞, RSPT∞ with the first-order correlation contribution $E^{(2,1)}$ that couples with SOC, the second-variational method (SV) and the full two-component self-consistent field procedure (2c-SCF). The SCF procedure was converged to an energy criterion of 10^{-12} Ha. The table reports results obtained with the fully relativistic shape-consistent RECPs and associated basis sets of the Columbus group available at https://people.clarkson.edu/ pchristi/reps.html. 7 electrons are included in the valence space. The experimental bond lengths of 1.42 Å, 2.00 Å, 2.28 Å, 2.67 Å and 3.00 Å were used.

	F_2	Cl_2	Br_2	I_2
$E^{(0,0)}$	$-1.41\times10^{+01}$	$-9.89\times10^{+00}$	$-9.04\times10^{+00}$	$-7.87\times10^{+00}$
$E^{(0,1)}$	$-5.18\times10^{+02}$	$-3.24\times10^{+02}$	$-2.86\times10^{+02}$	$-2.42\times10^{+02}$
$E^{(2,0)}$	-4.41×10^{-05}	-1.60×10^{-04}	-3.60×10^{-03}	-2.07×10^{-02}
$E^{(3,0)}$	-6.98×10^{-08}	-2.16×10^{-07}	-2.08×10^{-05}	-7.19×10^{-04}
$E^{(4,0)}$	-4.87×10^{-10}	-6.63×10^{-09}	-4.41×10^{-06}	-2.49×10^{-04}
$E^{(2,1)}$	-1.57×10^{-05}	-7.56×10^{-05}	-2.11×10^{-03}	-9.05×10^{-03}
$E_S^{(3,1)}$	-1.99×10^{-08}	-6.53×10^{-08}	-1.80×10^{-06}	-1.39×10^{-04}
RSPT2	-4.09×10^{-05}	-1.60×10^{-04}	-3.60×10^{-03}	-2.07×10^{-02}
RSPT3	-4.10×10^{-05}	-1.61×10^{-04}	-3.62×10^{-03}	-2.14×10^{-02}
RSPT4	-4.10×10^{-05}	-1.61×10^{-04}	-3.63×10^{-03}	-2.17×10^{-02}
RSPT∞	-4.10×10^{-05}	-1.61×10^{-04}	-3.63×10^{-03}	-2.17×10^{-02}
RSPT∞ + $E^{(2,1)}$	-5.16×10^{-05}	-2.36×10^{-04}	-5.74×10^{-03}	-3.07×10^{-02}
SV	-5.30×10^{-05}	-2.21×10^{-04}	-5.18×10^{-03}	-2.95×10^{-02}
2c-SCF	-7.10×10^{-05}	-2.86×10^{-04}	-6.90×10^{-03}	-3.75×10^{-02}
2c-SCF($E^{(0,0)}$)	$+1.99\times10^{-06}$	-1.48×10^{-05}	-1.34×10^{-03}	-7.52×10^{-03}
2c-SCF ($E^{(0,1)}$)	-7.28×10^{-05}	-2.71×10^{-04}	-5.56×10^{-03}	-3.00×10^{-02}

Table H.2: Same as Table H.1, but using instead the energy-consistent RECPs and associated basis sets of the Stuttgart group available at http://www.tc.uni-koeln.de/PP/clickpse.en.html, with 7 electrons in the valence space. The asterisk denotes a calculation on the I_2 molecule using the larger valence basis set of Martin and Sundermann (JCP, 114, 3408, 2001)

	Br_2	I_2	I_2^*	At_2
$E^{(0,0)}$	$-9.01\times10^{+00}$	$-7.82\times10^{+00}$	$-7.74\times10^{+00}$	$-7.69\times10^{+00}$
$E^{(0,1)}$	$-2.86\times10^{+01}$	$-2.42\times10^{+01}$	$-2.44\times10^{+01}$	$-2.26\times10^{+01}$
$E^{(2,0)}$	-2.86×10^{-03}	-3.86×10^{-03}	-3.59×10^{-03}	-3.70×10^{-02}
$E^{(3,0)}$	-4.17×10^{-05}	-2.32×10^{-05}	-1.68×10^{-05}	-5.59×10^{-04}
$E^{(4,0)}$	-5.13×10^{-06}	-6.41×10^{-06}	-5.40×10^{-06}	-7.96×10^{-04}
$E^{(2,1)}$	-6.54×10^{-04}	-1.48×10^{-03}	-5.89×10^{-03}	-2.73×10^{-02}
$E_S^{(3,1)}$	$+5.41\times10^{-06}$	-6.65×10^{-07}	$+4.40\times10^{-07}$	-1.58×10^{-04}
RSPT2	-2.86×10^{-03}	-3.86×10^{-03}	-3.59×10^{-03}	-3.70×10^{-02}
RSPT3	-2.82×10^{-03}	-3.88×10^{-03}	-3.61×10^{-03}	-3.75×10^{-02}
RSPT4	-2.82×10^{-03}	-3.89×10^{-03}	-3.61×10^{-03}	-3.84×10^{-02}
RSPT∞	-2.82×10^{-03}	-3.89×10^{-03}	-3.61×10^{-03}	-3.84×10^{-02}
RSPT∞ + $E^{(2,1)}$	-3.47×10^{-03}	-5.37×10^{-03}	-9.51×10^{-03}	-6.57×10^{-02}
SV	-3.12×10^{-03}	-5.49×10^{-03}	-5.17×10^{-03}	-5.35×10^{-02}
2c-SCF	-3.43×10^{-03}	-7.37×10^{-03}	-6.94×10^{-03}	-7.15×10^{-02}
2c-SCF($E^{(0,0)}$)	-9.30×10^{-04}	-2.61×10^{-03}	-1.92×10^{-03}	-4.11×10^{-02}
2c-SCF ($E^{(0,1)}$)	-2.50×10^{-03}	-4.76×10^{-03}	-5.02×10^{-03}	-3.04×10^{-02}

Table H.3: Same as Tables H.1 and H.2 above, but this time using a smaller core shape-consistent RECP from the Columbus group, in which 17 electrons are treated explicitly in the valence space

	Br_2	I_2	At_2
$E^{(0,0)}$	$-7.22\times10^{+02}$	$-5.40\times10^{+02}$	$-4.46\times10^{+02}$
$E^{(0,1)}$	$-3.01\times10^{+03}$	$-2.22\times10^{+03}$	$-1.96\times10^{+03}$
$E^{(2,0)}$	-5.73×10^{-03}	-2.83×10^{-02}	$-2.40\times10^{+00}$
$E^{(3,0)}$	-2.78×10^{-05}	-9.04×10^{-04}	-1.69×10^{-02}
$E^{(4,0)}$	-4.74×10^{-06}	-2.91×10^{-04}	-2.09×10^{-02}
$E^{(2,1)}$	-2.50×10^{-03}	-1.07×10^{-02}	$+5.72\times10^{-02}$
$E_S^{(3,1)}$	-4.18×10^{-06}	-1.98×10^{-04}	$+1.18\times10^{-02}$
RSPT2	-5.73×10^{-03}	-2.83×10^{-02}	-2.40×10^{-01}
RSPT3	-5.76×10^{-03}	-2.92×10^{-02}	-2.56×10^{-01}
RSPT4	-5.76×10^{-03}	-2.95×10^{-02}	-2.77×10^{-01}
RSPT∞	-5.76×10^{-03}	-2.95×10^{-02}	-2.79×10^{-01}
RSPT∞ + $E^{(2,1)}$	-8.26×10^{-03}	-4.02×10^{-02}	-2.22×10^{-01}
SV	-7.57×10^{-03}	-3.82×10^{-02}	-3.32×10^{-01}
2c-SCF	-9.27×10^{-03}	-4.62×10^{-02}	-3.81×10^{-01}
2c-SCF($E^{(0,0)}$)	$+1.57\times10^{-02}$	$+1.04\times10^{-01}$	$+1.88\times10^{-01}$
2c-SCF ($E^{(0,1)}$)	-2.50×10^{-02}	-1.50×10^{-01}	-5.69×10^{-01}

I Input Decks for Benchmark Periodic Two-Component Calculations

```
IO 2c polymer PBE0
POLYMER
1
4.0
2
253  0. 0. 0.
8    0. 0. 2.0
END
253 4
INPUT
7. 0 2 4 4 4 0
3.380230 83.107547 0
1.973454 5.099343 0
2.925323 27.299020 0
3.073557 55.607847 0
1.903188 0.778322 0
1.119689 1.751128 0
1.999036 8.234552 0
1.967767 12.488097 0
0.998982 2.177334 0
0.972272 3.167401 0
2.928812 -11.777154 0
2.904069 -15.525522 0
0.287352 -0.148550 0
0.489380 -0.273682 0
0 0 6 2.0 1
5.31117 -0.098004949
3.762566 0.297109165
1.628957 -0.53392089
1.163541 -0.088148553
0.289886 0.82629557
0.114132 0.422835255
0 2 6 5.0 1
5.727873 -0.0180737446
4.068994 0.062840471
1.743004 -0.19562182
0.37818 0.434152
0.162712 0.52386141
0.066961 0.194462423
0 1 1 0.0 1
0.45 1. 1.
0 1 1 0.0 1
0.15 1. 1.
8 4
0 0 8 2.0 1.0
 8020.0 0.00108
 1338.0 0.00804
 255.4 0.05324
```

```
 69.22 0.1681
 23.90 0.3581
 9.264 0.3855
 3.851 0.1468
 1.212 0.0728
0 1 4 6.0 1.0
 49.43 -0.00883 0.00958
 10.47 -0.0915 0.0696
 3.235 -0.0402 0.2065
 1.217 0.379 0.347
0 1 1 0.0 1.0
 0.4764 1.0 1.0
0 1 1 0.0 1.0
 0.1802 1.0 1.0
99 0
END
TWOCOMPON
SOC
PRTENESOC
NONCOLSC
ENDTWO
DFT
PBE0
ENDDFT
FMIXING
70
SHRINK
20 20
TOLINTEG
20 20 20 20 60
TOLPSEUD
20
INTGPACK
3
POLEORDR
6
NOBIPOLA
TOLDEE
7
MAXCYCLE
10000
ATOMSPIN
1
2 +1
END
1
STUTTGART  3
  P   4 1.
```

```
0    -81.89706000      2.92532300
0     83.41177050      3.07355700
0     -2.33496450      1.90318800
0      2.62669200      1.11968900
D   4 1.
0    -20.58638000      1.99903600
0     20.81349500      1.96776700
0     -5.44333500      0.99898200
0      5.27900250      0.97227200
F   4 1.
0     27.48002600      2.92881200
0    -27.16966350      2.90406900
0      0.34661550      0.28735200
0     -0.47894350      0.48938000
```

```
TaAs 2c PBE0 (optimized 1c B3LYP geom)
CRYSTAL
0 0 0
1
6.45675706    6.45675706    6.45675706   148.587595 148.587595  45.018701
4
273  -9.653040401397E-04 -9.653040401397E-04  0.000000000000E+00
273  -2.509653040401E-01  2.490346959599E-01  5.000000000000E-01
233   4.169653040401E-01  4.169653040401E-01  1.110223024625E-16
233   1.669653040401E-01 -3.330346959599E-01  5.000000000000E-01
END
273 13
INPUT
13. 0 3 6 6 2 2
10.318069 454.600649 0
10.540267 2.837975 2
2.574726 -0.814736 0
8.743342 96.910783 0
7.916223 195.850432 0
9.275736 4.812524 2
8.101675 6.338512 2
2.077127 -0.459173 0
2.750372 -0.644586 0
5.447314 45.969976 0
5.212545 69.638972 0
5.884358 0.802933 2
5.649579 0.429595 2
1.388180 -0.307227 0
1.294398 -0.461560 0
2.161275 5.757773 0
2.125939 7.678167 0
3.145920 -5.684066 0
3.127942 -7.062313 0
0 0 5 2. 1.                          ecp-60-dhf-QZV
  24.473650944      0.48239461915E-01
  18.721372549     -0.11130803862
  11.500000000      -4.3871385439
  10.350000000       14.773276225
  9.7732783383      -10.295986879
0 0 1 0. 1.
  3.8125414615       1.0000000000
0 0 1 0. 1.
  1.0507430630       1.0000000000
0 0 1 0. 1.
 0.49732275755       1.0000000000
0 0 1 0. 1.
 0.15602650970       1.0000000000
0 2 4 6. 1.
```

```
  23.290413736      0.13565200450E-01
  17.000000000     -0.74349450243E-01
  12.008186536      0.14135027656
  5.0278760583     -0.29185231563
0 2 1 0. 1.
  1.1937124184      0.52092880326
0 2 1 0. 1.
 0.57889707053       1.0000000000
0 2 1 0. 1.
 0.27225198801       1.0000000000
0 2 1 0. 1.
 0.10000000000       1.0000000000
0 3 3 2. 1.
  6.4242952246      0.94769104117E-01
  5.1122245125     -0.18492990619
  1.2009867996      0.44048238003
0 3 1 0. 1.
 0.51923142085       1.0000000000
0 3 1 0. 1.
 0.21323328623       1.0000000000
233 5
INPUT
5. 0 1 2 2 2 0
3.625150 54.926164 0
3.406953 26.001212 0
3.260195 32.935199 0
1.355950 2.629742 0
1.341843 3.930051 0
5.303850 -2.568085 0
5.486171 -4.652918 0
0 0 3 2. 1           ecp28MDF
3.069423 0.332502
2.268204 -0.565786
0.858631 -0.168471
0 0 1 0. 1
0.415970 1.0
0 0 1 0. 1
0.180588 1.0
0 2 3 6. 1
1.275524 -0.321208
0.942483 0.300478
0.289765 0.466271
0 2 1 0. 1
0.125374 1.0
99 0
END
TWOCOMPON
SOC
```

```
PRTENESOC
ENDTWO
DFT
PBE0
ENDDFT
SHRINK
30 30
MAXCYCLE
200
NOSHIFT
FMIXING
70
TOLINTEG
8 8 8 8 20
SMEAR
0.001
TOLDEE
7
END
1 2
STUTTGART  4
  P   6 1
  0    -290.732349    8.743342
  0     293.775648    7.916223
  2     -14.4375705   9.275736
  2       9.507768    8.101675
  0       1.3775175   2.077127
  0      -0.966879    2.750372
  D   6 1
  0    -114.92494     5.447314
  0     116.0649525   5.212545
  2      -2.0073325    5.884358
  2       0.7159925    5.649579
  0       0.7680675    1.388180
  0      -0.7692675    1.294398
  F   2 1
  0     -13.4348025   2.161275
  0      13.4367905   2.125939
  G   2 1
  0      12.7891485   3.145920
  0     -12.7121625   3.127942
3 4
STUTTGART  3
  P   2 1
  0     -52.0024230   3.406953
  0      49.4027985   3.260195
  D   2 1
  0      -6.574355    1.355950
```

```
0       6.550085    1.341843
F   2 1
0       5.992196    5.303850
0      -8.1426065   5.486171
```

```
WS2 2c PBE0 (exp geom)
CRYSTAL
0 0 0
194
3.1532 12.323
2
274 0.333333333334 0.666666666667 0.250000000000
 16 0.333333333334 0.666666666667 0.62250
SLABCUT
0 0 1
1 3
END
274 14
INPUT
14. 0 2 6 6 2 2
11.063795 419.227599 0
8.217641 41.191307 0
9.338188 107.348110 0
8.430448 214.699568 0
9.490020 0.025442 2
9.489947 0.051895 2
1.882997 -0.117184 0
1.906972 0.296689 0
6.205433 58.881279 0
6.122157 98.683556 0
6.274556 0.019537 2
6.226375 0.021956 2
1.963875 -0.088577 0
1.888287 -0.209726 0
2.307953 6.232472 0
2.270609 8.311345 0
3.583491 -6.802944 0
3.562515 -8.443232 0
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  12.000000000      1.0228484726
0 0 1 2. 1.
  5.2610967725      1.0000000000
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0 2 4 6. 1.
  7.2496570000      0.46749049338
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0 3 1 4. 1.
  4.0131231332      1.0000000000
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0 4 1 0. 1.
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0 4 1 0. 1.
 0.3               1.0
16 6
0 0 8 2.0 1.0
 109211.0 0.0002520
 16235.206 0.0019934
 3573.0286 0.0111177
 943.23811 0.0498945
 287.26179 0.1661455
 99.914226 0.3627018
 38.602137 0.4108787
 15.531224 0.1457875
0 1 6 8.0 1.0
 281.22171 -0.0057780 0.0081427
 67.106575 -0.0665855 0.0565570
 21.794135 -0.1203552 0.2039582
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 1.5452225 0.2925792 0.1544345
0 1 3 6.0 1.0
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99 0
END
TWOCOMPON
SOC
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DFT
PBE0
ENDDFT
SHRINK
24 24
FMIXING
90
SMEAR
0.001
TOLINTEG
8 8 8 8 30
TOLDEE
8
MAXCYCLE
1000
END
2
STUTTGART  4
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 0     322.0493400     8.430448
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 2       0.0778425     9.489947
 0       0.3515535     1.882997
 0       0.4450335     1.906972
  D   6 1.
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 0     164.4725925     6.122157
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 2       0.0365950     6.226375
 0       0.2214425     1.963875
 0      -0.3495425     1.888287
  F   2 1.
 0     -14.5424370     2.307953
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  G   2 1.
 0      15.3066240     3.583491
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