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LIMITS OF VARIATIONALITY IN FULL CONFIGURATION INTERACTION FOR THE H_2 MODEL SYSTEM

A Thesis

by

OSCAR OBED RODRIGUEZ VARGAS

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The University of Texas Rio Grande Valley
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LIMITS OF VARIATIONALITY IN FULL CONFIGURATION INTERACTION FOR THE H_2 MODEL SYSTEM

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May 2021

ABSTRACT

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We proposed a framework for exploring the limits of variationality in full configuration interaction (FCI) calculation of molecular electronic structure. We performed FCI calculations on the minimal basis (STO-3G) H_2 model for the energy, gradient, and derivative coupling. These calculations were validated by finite difference. These quantities were recalculated with controlled injection of error in the FCI coefficient. The gradient was observed to be highly sensitive to error, while the energy and derivative coupling were robust to errors in the coefficients of nearly 10%. This study lays the groundwork for calculation of other derived quantities, such as the Hessian, adiabatic correction, and spin-orbit couplings.

DEDICATION

Con amor para la única familia que tengo, mi madre y padre.,
que janas que se cansaron de ayudarme.

ACKNOWLEDGMENTS

I am very fortunate to have a great committee chair, Dr. Shervin Fatehi. His mentoring, patience and advice made this project possible. I am also grateful for the committee members and the UTRGV Department of Chemistry for assisting me throughout my graduate career. I would like to acknowledge the UTRGV Presidential Graduate Research Assistantship program for making it possible to complete my Master's degree, the Welch Foundation under Research Grant No. BX-1921-20170325 for supporting this research project, and the Welch Foundation Grant No. BX-0048 for supporting us at the UTRGV Department of Chemistry.

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INTRODUCTION

I.1 Schrödinger equation

The Schrödinger equation is the commanding equation of chemistry and an essential ingredient for many-electron systems in quantum field theory [1]. In its time-dependent form it states that

$$H\psi(t,x) = i\hbar \frac{d}{dt}\psi(t,x) \tag{1.0}$$

The Hamiltonian operator **H** includes the information of the motion of the system**.** Since the Hamiltonian is not a function of time, we can separate the wavefunction into a spatial and time-related part:

$$\psi(t,x) \;= \psi(x)\,\tau(t) \tag{1.1}$$

Where the time dependent factor $\tau(t)$ does not change. Meaning we can always solve this for time-independent problems with the spatial part and the $i\hbar\frac{d}{dt}$ term can always be replaced by the eigenvalue E. Resulting in a eigenvalue equation for the Hamiltonian: the time-independent Schrödinger equation.

$$H\psi = E\psi \tag{1.2}$$

This can be calculated for any number of particles in a time-independent potential. Solving this equation is paramount for this investigation. Generally, the Hamiltonian can be calculated with the following formula (in atomic units):

$$H = -\sum_i \frac{1}{2}\nabla_i^2 + \sum_{r>j}\frac{1}{r_{ij}} - \sum_A \frac{1}{2M_A}\nabla_A^2 - \sum_{i,A}\frac{Z_A}{r_{iA}} + \sum_{A>B}\frac{Z_A Z_B}{R_{AB}} \qquad (1.3)$$

If we want to obtain a specific depiction of any chemical system, we must specify a state $|\psi_0\rangle$, build a Hamiltonian that describes the system in question and then solve Equation 1.0. However, if we increase the number of nuclei and electrons that we must account for the complexity of the solution increases significantly to the point of intractability.

I.2 Born-Oppenheimer approximation

A central and pertinent topic in quantum chemistry is the approximation from M. Born and R. Oppenheimer [2]. The Hamiltonian contains all potential and kinetic energies of the system, but if the distance between nuclei-nuclei or nuclei-electron changes with the natural momentum of the nucleus, so does its relative projected energies. Hence a desirable approximation to achieve simplicity is to consider the electrons of a molecule to be moving around fixed points or nuclei. With this approach, the third term in the Hamiltonian in Equation 1.3 involving the kinetic energy of the nucleus (∇_A^2) could and will be ignored. Also, the internuclear repulsion term in Equation 1.3 will remain a constant. If we ignore these two terms and collect the remaining three, the Hamiltonian represents purely electronic quantities that depend parametrically on the nuclear positions. You can compute the entire potential energy surface by computing the electronic energy for different nuclear geometries.

$$H_{\text{electronic}}\phi_{\text{electronic}} = E_{\text{electronic}}\phi_{\text{electronic}} \quad (1.4)$$

The focus of this study revolves around the electronic problem, and we will use electronic Hamiltonians and wavefunctions while only adding the nuclear-nuclear repulsion term to achieve the total energy of the system in question.

I.3 Variational method

Here we discuss a method for approximating solutions to eigenvalue equations. This mathematical procedure can be used to calculate the energy levels of different quantum systems. More importantly, this can also allow the user to obtain the accuracy of the method by comparing the obtained approximations to known values. This method is most useful in systems with more than one electron as the Schrödinger equation cannot be solved exactly in such scenarios, and this will be most useful in our future discussion of the Hartree-Fock method.

The variational theorem states that: Given a normalized wave function, we can predict its expectation value of the Hamiltonian to be an upper bound to the exact ground state energy. If:

$$|\tilde{\psi}\rangle = \sum_\alpha c_\alpha |\psi_\alpha\rangle = \sum_\alpha |\psi_\alpha\rangle\langle\psi_\alpha|\tilde{\psi}\rangle \quad (1.5)$$

and

$$\langle\tilde{\psi}|\tilde{\psi}\rangle = 1 \quad (1.6)$$

Then

$$\langle\tilde{\psi}|H|\tilde{\psi}\rangle \geq \varepsilon_0 \quad (1.7)$$

For proof we can take the definition:

$$\langle\tilde{\psi}|\tilde{\psi}\rangle = 1 = \sum_{\alpha\beta} \langle\tilde{\psi}|\psi_\alpha\rangle\langle\psi_\alpha|\psi_\beta\rangle\langle\psi_\beta|\tilde{\psi}\rangle = \sum_{\alpha\beta} \langle\tilde{\psi}|\psi_\alpha\rangle\langle\psi_\alpha|\tilde{\psi}\rangle = \sum_{\alpha\beta} \langle\tilde{\psi}|\psi_\alpha\rangle^2 \quad (1.8)$$

Then

$$\langle\tilde{\psi}|H|\tilde{\psi}\rangle = \sum_{\alpha\beta} \langle\tilde{\psi}|\psi_\alpha\rangle\langle\psi_\alpha|H|\psi_\beta\rangle\langle\psi_\beta|\tilde{\psi}\rangle = \sum_{\alpha\beta} \langle\tilde{\psi}|\psi_\alpha\rangle^2 \varepsilon_0 = \varepsilon_0 \quad (1.9)$$

And since $\varepsilon_\alpha \geq \varepsilon_0 \; for \; all \; \alpha$ then we get Equation 1.7 back:

$$\langle\tilde{\psi}|H|\tilde{\psi}\rangle \geq \sum_{\alpha\beta} \langle\tilde{\psi}|\psi_\alpha\rangle^2 \varepsilon_0 = \varepsilon_0 \quad (1.10)$$

This demonstrates that an energy approximation from a wavefunction will always be bigger or equal to the ground state energy of the system. The lower a resulting energy is, the "better" we regard the wavefunction.

In short, we take a normalized wavefunction contraction $\tilde{\psi}$ and alter or vary its parameters until the expectation value $\langle\tilde{\psi}|H|\tilde{\psi}\rangle$ reaches a minimum. This minimum is the approximated variational ground state energy.

I.4 Basis sets

A single multielectron atom with its nucleus centered at the origin, as instructed by the Born-Oppenheimer approximation, has electrons orbiting at coordinates r, θ, ϕ. To describe this system, we would need multielectron wavefunctions, but we approximate that with single electron orbitals that are hydrogenic in character and approximate those orbitals as a linear combination of Gaussian functions.

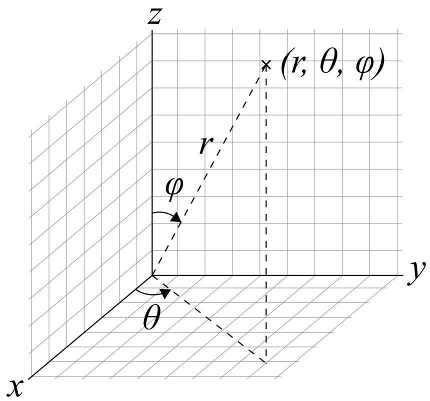

Figure 1: Spherical coordinate system; source image is in the public domain [3].

Calculations in computational chemistry are performed using these basis functions [4], which represent the wavefunction as a vector and its components are included in the coefficients of the contraction of the basis set. Out of the many different basis sets available, we will focus on two of the most common ones.

The normalized 1s Slater type function:

$$\boldsymbol{\phi}_{1s}^{SF}(\boldsymbol{\zeta},\ \boldsymbol{r}-\boldsymbol{R_A}) = \left(\frac{\zeta^3}{\pi}\right)^{\frac{1}{2}} \boldsymbol{e}^{-\zeta\,|r-R_A|} \tag{1.11}$$

Centered nuclear position $\boldsymbol{R_A}$, where $\boldsymbol{\zeta}$ is the slater orbital exponent. And the normalized 1s Gaussian-type function:

$$\boldsymbol{\phi}_{1s}^{GF}(\boldsymbol{\alpha},\boldsymbol{r}-\boldsymbol{R_A}) = \left(\frac{2\alpha}{\pi}\right)^{\frac{3}{4}} \boldsymbol{e}^{-\alpha\,|r-R_A|^2} \tag{1.12}$$

where $\boldsymbol{\alpha}$ is the orbital Gaussian exponent. The main difference between these two are shown at large values of $\mathbf{r}$, where the Gaussian function $\boldsymbol{e}^{-\alpha r^2}$ decays much more rapidly than the Slater function $\boldsymbol{e}^{-\zeta r}$, however, this does not mean that Slater functions are our best choice.

In an ideal world we would prefer to use the Slater functions, nevertheless, if we would use them, we would come across huge complex calculations of two-electron integrals involving computations over four nuclear coordinates ($\mathbf{R_A}, \mathbf{R_B}, \mathbf{R_C}, \mathbf{R_D}$). This makes Slater functions much more difficult and time consuming to compute. We mainly consider the Gaussian function because these types of complicated integrals are much easier to solve. The reason being that the product of two 1s Gaussian functions (on two different centers $\mathbf{R_A}, \mathbf{R_B}$) is a third Gaussian function (at a new center $\mathbf{R_p}$**).** This effectively reduces a four-center integral into a two-center integral. Now to *"fix"* the problem of the inaccuracy of Gaussian functions at large values of **r**, we use parameterized linear combinations of primitive Gaussians $\boldsymbol{\phi_{1s}^{GF}}$**.** Also known as contracted Gaussian functions (CGF).

$$\boldsymbol{\phi_u^{CGF}(r - R_A) = \sum_{p=1}^{L} d_{pu}\phi_p^{GF}} \tag{1.13}$$

where $\boldsymbol{d_{pu}}$ is the contraction coefficient. By proper choice of contraction parameters (**L**, $\boldsymbol{d_{pu}}$, and $\boldsymbol{\alpha}$**)** one can approximate Slater-type orbital (STO) functions, while still evaluating integrals only with primitive Gaussians. For our research we are using Slater-type orbitals with a contraction of **L**=3, hence the name STO-3G. It has been reported by Szabo and Ostlund [5] how the STO-LG approximates the Slater functions, as the contraction L increases in the following figure:

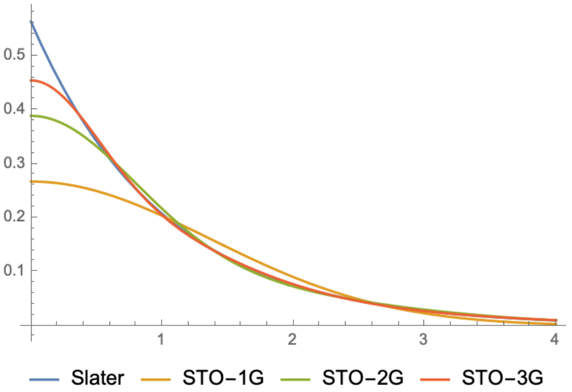

Figure 2: Comparison of quality between a Slater 1s function ($\boldsymbol{\zeta = 1}$) generated with STO-1G, 2G and 3G. Figure adapted from [5].

I.5 Hartree-Fock method

Here we will discuss a very important topic to solving the many electron problem in quantum chemistry, the Hartree-Fock method. This approximation method can also be used as a steppingstone for more accurate calculations. It was first proposed by D. R. Hartree in the early 20th century [6] and he called this method the *"self-consistent field"* which approximates wave functions and energies of atoms. Shortly after, the method was reaffirmed by J. C. Slater and J. A. Gaunt by using the variational principle to a trial wave function.

In broad terms, this theory is computed using single determinant theory where the wavefunction is given by a single Slater determinant of N-spin orbitals.

$$\psi = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(x_1) & \cdots & \psi_1(x_N) \\ \vdots & \ddots & \vdots \\ \psi_N(x_1) & \cdots & \psi_N(x_N) \end{vmatrix} \tag{1.14}$$

It is important to note, that this wavefunction is antisymmetric and will change with the exchange of any two electrons as required by the Pauli exclusion principle [7].

$$\psi(x_1, x_2) = -\,\psi(x_2, x_1) \tag{1.15}$$

We postulate a set of spin orbitals so that our ground state determinant will look like:

$$|\psi_0\rangle \quad = \quad |\mathrm{X}_1\mathrm{X}_2 \ldots \mathrm{X}_a\mathrm{X}_b \ldots \mathrm{X}_N\rangle \tag{1.16}$$

which is the most accurate approximation this method offers to the ground state of N-electrons described by the electronic Hamiltonian:

$$\langle\psi_0|\boldsymbol{H_{elec}}|\psi_0\rangle \quad = \quad E_0 \tag{1.17}$$

then by minimizing E_0 with respect to the orbitals, we get a new eigenequation called the Hartree-Fock Equation:

$$f(i)\chi(xi) = \epsilon\,\chi(xi) \tag{1.18}$$

where $f(i)$ is called the Fock operator and is defined as:

$$f(i) = -\tfrac{1}{2}\nabla_i^2 - \textstyle\sum_{A=1}^{N} \tfrac{Z_A}{r_{iA}} + \upsilon^{HF}(i) \tag{1.19}$$

where the Hartree-Fock potential $\upsilon^{HF}(i)$ term represents the average potential experienced by the i-th electron against all of the other electrons. This means that to solve the Hartree-Fock potential (and therefore the Hartree-Fock approximation) one must take an iterative approach. The method by which we solve this equation is called the self-consistent field and will be discussed momentarily.

I.6 Roothaan equations

Now we will look at how to calculate the restricted Hartree-Fock wavefunctions. All calculations in this procedure will be represented in a restricted (both spin up and spin down functions occupying the same spatial state) Hartree-Fock wave function. This is significant since doing so will limit our calculation to closed-shell systems with every electron paired with an opposite spin. To get an accurate result of the ground state for open-shell systems one could perform the calculation with the unrestricted formalism of the Hartree-Fock, and although we will talk about both, for now, we will start with the restricted version. If we take the standard Fock operator single electron semi-eigenfunction equation:

$$f\varphi_i = \varepsilon_i \varphi_i \tag{1.20}$$

One of the main contributions of Roothaan [8] was to introduce a set of basis functions and expand the molecular orbitals:

$$\varphi_i = \sum_{u=1}^{K} C_{ui}\phi_u \qquad \text{i = 1, 2, 3… K} \tag{1.21}$$

From this point forward the problem of solving the Hartree-Fock equation revolves around calculating the coefficients C_{ui}. This arithmetic is started by inserting the linear expansion.

$$f\sum_v C_{vi}\phi_v = \varepsilon_i \sum_v C_{vi}\phi_v \tag{1.22}$$

We multiply by ϕ_u^* and integrate

$$\sum_v C_{vi} \int dr\, \phi_u^*\, f\, \phi_v = \varepsilon_i \sum_v C_{vi} \int dr\, \phi_u^*\, \phi_v \tag{1.23}$$

In this representation of the equation, we define two matrices: the overlap matrix S and the Fock Matrix F.

$$S_{uv} = \int dr\, \phi_u^*\, \phi_v \tag{1.24}$$

$$F_{uv} = \int dr\, \phi_u^*\, f\, \phi_v \tag{1.25}$$

turning our Hartree-Fock equation into

$$\sum_v C_{vi}\, F_{uv} = \varepsilon_i \sum_v C_{vi}\, S_{uv} \qquad \text{i = 1, 2, … ,K} \tag{1.26}$$

These are called the Roothaan equations which in its compact form looks like:

$$\boldsymbol{FC} = \boldsymbol{SC\varepsilon} \tag{1.27}$$

where C is a square matrix with all the C_{vi} values in the expansion, and ε is a diagonal matrix or vector including the orbital energies. At this point we have everything we need to start solving the Hartree-Fock orbital energies and molecular orbitals.

I.7 Brillouin's theorem

Since now we know how the Fock operator looks like along with the Hartree-Fock ground state ($|\psi_0\rangle$), we can prove an important theorem that describes the interaction between said ground state with its singly exited state $|\psi_a^r\rangle$, the Brillouin's theorem [9].

The theorem states: In case of the Hartree-Fock ground-state determinant $|\psi_0\rangle$, the Hamiltonian matrix element between it and any singly excited determinant $|\psi_a^r\rangle$ reduces to zero.

$$\langle\psi_0|\boldsymbol{H_{elec}}|\psi_a^r\rangle \quad = 0 \tag{1.28}$$

To justify this, we can simply take the definition of the eigenvalue equation in the Fock operator for state ***i*** and multiply in the left side by a generic ground state **j**.

$$\int dr\, \varphi_j \ \ (f_i\varphi_i = \varepsilon_i\varphi_i) \tag{1.29}$$

$$\langle\varphi_j|f_i|\varphi_i\rangle \ = \varepsilon_i\langle\varphi_i|\varphi_j\rangle \tag{1.30}$$

$$\langle\varphi_j|f_i|\varphi_i\rangle = \varepsilon_i\delta_{ij} \tag{1.31}$$

$$= 0 \text{ because } i \neq j$$

Equation 1.31 signals that in any post Hartree-Fock method, the singly excited state will mix only indirectly with the ground state as we will see it is clearly the case in the Full Configuration Interaction method solution.

I.8 Self-consistent field procedure

To illustrate the intermediate steps of an iterative calculation of the ground state of any system we have detailed the general self-consistent field procedure [5] below. There are a total of 10 steps involved in this process:

1. Choose a molecule and basis set (In our case the molecule of interest is Hydrogen and basis set is STO-3G, however we won't specify this system and keep our terms general in the introduction)
2. Calculate the overlap matrix, H_{uv}^{core}, and two-electron integrals.
3. Use the following equations to diagonalize the overlap and obtain the transformation matrix **X**.

$$U^{\dagger}SU = s \tag{1.32}$$

$$X = U\, s^{\frac{1}{2}}\, U^{\dagger} \tag{1.33}$$

   where U is a unitary matrix and we have chosen to show the symmetric orthogonalization.

4. Guess the Density matrix **P (**usually a null matrix, zeros).
5. Form the two-electron integrals and the density matrix, obtain the **G** matrix.

$$G_{uv} = \sum_{\lambda\sigma} P_{\lambda\sigma} \left[(uv|\lambda\sigma) - \frac{1}{2} (u\lambda|\sigma v) \right] \tag{1.34}$$

6. Obtain the Fock matrix by adding **G** to the core-Hamiltonian

$$F = H_{core} + G \tag{1.35}$$

7. Calculate the transformed Fock matrix.

$$F' = X^{\dagger}FX \tag{1.36}$$

8. Diagonalize *F'* to obtain the respective coefficients and energies.

$$F'C' = \varepsilon C' \tag{1.37}$$

9. Calculate the C coefficients by transforming C'

$$C = XC' \tag{1.38}$$

10. From this C, calculate a new density matrix P

$$P_{\lambda\sigma} = 2\sum_{\lambda\sigma} C_{\lambda\sigma} C^{*}_{\sigma\lambda} \tag{1.39}$$

At this step we should be able to check for convergence of the SCF procedure. A common way of doing this is to see if the density matrix is different from the one calculated before within a certain tolerance. If the calculation has not converged yet, use the produced density matrix in step 10 and repeat the steps from number 5 to 10 until converged.

If the procedure has converged, the produced **F, C, P,** matrices can be used to compute post Hartree-Fock calculations or other quantities of interest.

I.9 Pople-Nesbet equations

The unrestricted Hartree-Fock equations need to be approached slightly differently when applying the SCF procedure. We must introduce a basis set linear expansion into the Fock operator for electrons of β spin:

$$f^{\beta}(1) = h(1) + \sum_{a}^{N\beta}[J_a{}^{\beta}(1) - K_a{}^{\beta}(1)] + \sum_{a}^{N\alpha} J_a{}^{\alpha}(1) \tag{1.40}$$

and the α spin counterpart:

$$f^{\alpha}(1) = h(1) + \sum_{a}^{N\alpha}[J_a{}^{\alpha}(1) - K_a{}^{\alpha}(1)] + \sum_{a}^{N\beta} J_a{}^{\beta}(1) \tag{1.41}$$

Both of these equations must be solved simultaneously, since the f^{α} operator depends on the occupied β orbitals, φ_a^{β}, through J^{β} and f^{β} operator depends on the occupied α orbitals, φ_a^{α}, through J^{α}. The equations are coupled and cannot be solved independently of eachother.

Now, like in the restricted version (Equation1.21), we can introduce our unrestricted basis set linear expansions:

$$\psi_i^{\alpha} = \sum_{u=1}^{K} C_{ui}^{\alpha}\phi_u \qquad i = 1, 2, \ldots K \tag{1.42}$$

$$\psi_i^\beta = \sum_{u=1}^{K} C_{ui}^\beta \phi_u \qquad i = 1, 2, \ldots K \tag{1.43}$$

and insert them in the Hartree-Fock equations while following the procedure detailed in the *"Roothaan equations"* section of the introduction and produce the unrestricted generalization of the restricted Roothaan equations first given by Poble and Nesbet [11].

$$\boldsymbol{F^\alpha C^\alpha} = \boldsymbol{S C^\alpha \varepsilon^\alpha} \tag{1.44}$$

$$\boldsymbol{F^\beta C^\beta} = \boldsymbol{S C^\beta \varepsilon^\beta} \tag{1.45}$$

These two equations can be solved in a very similar fashion to the restricted version of the SCF procedure and will follow the 10 steps stated above.

I.10 Configuration interaction

We have discussed a method for creating the potential energy of a molecule using either Restricted Hartree-Fock or Unrestricted Hartree-Fock, however, these procedures have their own limitations. For the Restricted HF, it cannot be used to explain the dissociation of a molecule into open-shell fragments. For the Unrestricted HF, although it can represent such a dissociation, the results still differ from the exact known result. A common goal of many post-Hartree-Fock methods is to correct the error in the potential energy results. Specifically, for the Configuration Interaction it solves for the difference between the exact known energy of a system ($\mathcal{E}_0$) and the Hartree-Fock energy (E_o). This value is called the correlation energy.

$$E_{corr} = \mathcal{E}_0 - E_0 \tag{1.46}$$

To perform the procedure, we must of course construct the molecular orbitals from the Hartree-Fock procedure as in any post-HF methodology. We then consider the structure of the full CI matrix, which is an expanded version of the Hamiltonian matrix with all possible excitations to the Hartree-Fock ground state. Usually this would mean having a potentially humongous amount of data as the excitations can grow exponentially with the number of electrons. This increases the complexity of the calculation and forces many to use truncating methods to control the computational cost of running such an algorithm. Nevertheless, our system of choice for this study is very tractable and does not require a complicated number of excitations.

In general, the exact ground state wave function of our system $|\phi_0\rangle$ in its intermediate normalized form:

$$|\phi_0\rangle = |\psi_0\rangle + \sum_{ct} c_c^t|\psi_c^t\rangle + \sum_{\substack{c<d\\t<u}} c_{cd}^{tu}|\psi_{cd}^{tu}\rangle + \sum_{\substack{c<d<e\\t<u<v}} c_{cde}^{tuv}|\psi_{cde}^{tuv}\rangle + \cdots \quad (1.47)$$

which is not a normalized wavefunction since:

$$\langle\phi_0|\phi_0\rangle = 1 + \sum_{ct}(c_c^t)^2 + \sum_{\substack{c<d\\t<u}}(c_{cd}^{tu})^2 + \cdots \quad (1.48)$$

However, this can be fixed by multiplying each term in the expansion by a coefficient:

$$|\phi_0{}'\rangle = c'|\phi_0\rangle \quad (1.49)$$

so that:

$$\langle\phi'{}_0|\phi_0\rangle = 1 \quad (1.50)$$

As we had stated before, the variational principle allows us to calculate the ground state of such a wave function by:

$$\mathrm{H}|\phi_0\rangle = \mathcal{E}_0\,|\phi_0\rangle \tag{1.51}$$

Substracting $E_0|\phi_0\rangle$ on both sides

$$\mathrm{H} - E_0|\phi_0\rangle = \mathcal{E}_0 - E_0|\phi_0\rangle \tag{1.52}$$

Multiplying $\langle\psi_0|$ on both sides

$$\langle\psi_0|\mathrm{H} - E_0|\phi_0\rangle = \langle\psi_0|\mathcal{E}_0 - E_0|\phi_0\rangle = E_{corr}\langle\psi_0|\phi_0\rangle \tag{1.53}$$

It is very convenient that our state wavefunction has the property that

$$\langle\psi_0|\phi_0\rangle = 1 \tag{1.54}$$

so

$$\langle\psi_0|\mathrm{H} - E_0|\phi_0\rangle = E_{corr} \tag{1.55}$$

Expanding wave function

$$\langle\psi_0|\mathrm{H} - E_0\left(|\psi_0\rangle + \sum_{ct} c_c^t|\psi_c^t\rangle + \sum_{\substack{c<d\\t<u}} c_{cd}^{tu}|\psi_{cd}^{tu}\rangle + \cdots\right) = E_{corr} \tag{1.56}$$

At this point we have many combinations of different states. However, many terms in this summation will be neglected as stated by the Brillouin's theorem and the fact that any state that differs by more than two spin orbitals cannot mix with ψ_0. This ultimately narrows the expression into:

$$\sum_{\substack{a<b\\i<j}} c_{ij}^{ab}\langle\psi_0|\mathrm{H}|\phi_{ij}^{ab}\rangle = E_{corr} \tag{1.57}$$

I.11 Energy gradient derivation

Calculations of derivatives of molecular energies are a fundamental step toward the exploration of computational efficiency [12], which facilitates transition state searches, geometry optimizations and molecular dynamics simulations. Here we will present our own derivation of the full configuration interaction energy gradient for Hydrogen. The total energy calculated from the FCI state is:

$$E_{FCI} = \langle \psi_{H_2} | \hat{\mathrm{H}} | \psi_{H_2} \rangle \tag{1.58}$$

$$= {c_{HF}}^2 \langle \phi_{HF} | \hat{\mathrm{H}} | \phi_{HF} \rangle + 2\, c_{HF} c_D \langle \phi_{HF} | \hat{\mathrm{H}} | \phi_D \rangle + {c_D}^2 \langle \phi_D | \hat{\mathrm{H}} | \phi_D \rangle \tag{1.59}$$

Taking the derivative would yield

$$\frac{\partial}{\partial \mathrm{x}} E_{FCI} = {c_{HF}}^2 \frac{\partial}{\partial \mathrm{x}} \langle \phi_{HF} | \hat{\mathrm{H}} | \phi_{HF} \rangle + 2\, c_{HF} c_D \frac{\partial}{\partial \mathrm{x}} \langle \phi_{HF} | \hat{\mathrm{H}} | \phi_D \rangle + {c_D}^2 \frac{\partial}{\partial \mathrm{x}} \langle \phi_D | \hat{\mathrm{H}} | \phi_D \rangle \tag{1.60}$$

where the Hamiltonian $\hat{\mathrm{H}}$ has been defined as:

$$\hat{\mathrm{H}} = \sum_{pq} h_{pq} a_p^\dagger a_q + \frac{1}{4} \sum_{pqrs} \Pi_{pqrs} a_p^\dagger a_q^\dagger a_r a_s \tag{1.61}$$

where

$$\Pi_{pqrs} = \langle pq|rs \rangle - \langle pq|sr \rangle = [pr|qs] - [ps|qr] \tag{1.62}$$

It is necessary now to rearrange each term and solve the derivatives one by one. We start with the Hartree-Fock ground state:

$$\langle \phi_{HF} | \hat{\mathrm{H}} | \phi_{HF} \rangle = \sum_{pq} h_{pq} \langle \phi_{HF} | a_p^\dagger a_q | \phi_{HF} \rangle + \frac{1}{4} \sum_{pqrs} \Pi_{pqrs} \langle \phi_{HF} | a_p^\dagger a_q^\dagger a_r a_s | \phi_{HF} \rangle \tag{1.63}$$

Taking the liberty to use the fact that $a_c a_d^\dagger = \delta_{cd} - a_d^\dagger a_c$ and $a_c a_d^\dagger = -a_c^\dagger a_d$ we can rearrange so that:

$$\langle \phi_{HF} | \widehat{\mathrm{H}} | \phi_{HF} \rangle = \sum_{pq} h_{pq} \langle \, | a_j a_i a_p^\dagger a_q a_i^\dagger a_j^\dagger | \, \rangle + \frac{1}{4} \sum_{pqrs} \Pi_{pqrs} \langle \, | a_j a_i a_p^\dagger a_q^\dagger a_r a_s a_i^\dagger a_j^\dagger | \, \rangle \tag{1.64}$$

$$= \sum_{pq} h_{pq} \left(\delta_{ip} \delta_{jj} \delta_{iq} + \delta_{ii} \delta_{jp} \delta_{jq} \right) + \frac{1}{4} \sum_{pqrs} \Pi_{pqrs} \left(\delta_{ip} \delta_{jq} - \delta_{iq} \delta_{jp} \right) \left(\delta_{is} \delta_{jr} - \delta_{ir} \delta_{js} \right) \tag{1.65}$$

$$= \sum_{pq} h_{pq} \left(\delta_{ip} \delta_{iq} + \delta_{jp} \delta_{jq} \right) + \frac{1}{4} \sum_{pqrs} \Pi_{pqrs} \left(\delta_{ip} \delta_{jq} - \delta_{iq} \delta_{jp} \right) \left(\delta_{is} \delta_{jr} - \delta_{ir} \delta_{js} \right) \tag{1.66}$$

Similar treatment of the doubles-doubles term yields:

$$\langle \phi_D | \widehat{\mathrm{H}} | \phi_D \rangle = \sum_{pq} h_{pq} \langle \, | a_b a_a a_p^\dagger a_q a_a^\dagger a_b^\dagger | \, \rangle + \frac{1}{4} \sum_{pqrs} \Pi_{pqrs} \langle \, | a_b a_a a_p^\dagger a_q^\dagger a_r a_s a_a^\dagger a_b^\dagger | \, \rangle \tag{1.67}$$

$$= \sum_{pq} h_{pq} \left(\delta_{ap} \delta_{aq} + \delta_{bp} \delta_{bq} \right) + \frac{1}{4} \sum_{pqrs} \Pi_{pqrs} \left(\delta_{ap} \delta_{bq} - \delta_{aq} \delta_{bp} \right) \left(\delta_{as} \delta_{br} - \delta_{ar} \delta_{bs} \right) \tag{1.68}$$

and then the final off-diagonal terms:

$$\langle \phi_{HF} | \widehat{\mathrm{H}} | \phi_D \rangle = 0 + \frac{1}{4} \sum_{pqrs} \Pi_{pqrs} \langle \, | a_j a_i a_p^\dagger a_q^\dagger a_r a_s a_a^\dagger a_b^\dagger | \, \rangle \tag{1.69}$$

$$= \frac{1}{4} \sum_{pqrs} \Pi_{pqrs} \left(\delta_{ip} \delta_{jq} - \delta_{iq} \delta_{jp} \right) \left(\delta_{as} \delta_{br} - \delta_{ar} \delta_{bs} \right) \tag{1.70}$$

$$\langle \phi_D | \widehat{\mathrm{H}} | \phi_{HF} \rangle = 0 + \frac{1}{4} \sum_{pqrs} \Pi_{pqrs} \langle \, | a_b a_a a_p^\dagger a_q^\dagger a_r a_s a_i^\dagger a_j^\dagger | \, \rangle \tag{1.71}$$

$$= \frac{1}{4} \sum_{pqrs} \Pi_{pqrs} \left(\delta_{ap} \delta_{bq} - \delta_{aq} \delta_{bp} \right) \left(\delta_{is} \delta_{jr} - \delta_{ir} \delta_{js} \right) \tag{1.72}$$

where the one electron term is neglected since they differ by more than two electrons. When we combine the results for the

$$\langle\phi_D|\hat{\mathrm{H}}|\phi_D\rangle = \sum_{pq} h_{pq}\left(\delta_{ap}\delta_{aq} + \delta_{bp}\delta_{bq}\right)$$

$$+\frac{1}{4}\sum_{pqrs}\Pi_{pqrs}\left(\delta_{ap}\delta_{bq} - \delta_{aq}\delta_{bp}\right)\left(\delta_{as}\delta_{br} - \delta_{ar}\delta_{bs}\right) \quad (1.73)$$

$$= h_{aa} + h_{bb} + \frac{1}{4}(\Pi_{abab} + \Pi_{baba} - \Pi_{abba} - \Pi_{baab}) \quad (1.74)$$

$$= h_{aa} + h_{bb} + \Pi_{abab} \quad (1.75)$$

$$\langle\phi_{HF}|\hat{\mathrm{H}}|\phi_{HF}\rangle = \sum_{pq} h_{pq}\left(\delta_{ip}\delta_{iq} + \delta_{jp}\delta_{jq}\right)$$

$$+\frac{1}{4}\sum_{pqrs}\Pi_{pqrs}\left(\delta_{ip}\delta_{jq} - \delta_{iq}\delta_{jp}\right)\left(\delta_{is}\delta_{jr} - \delta_{ir}\delta_{js}\right) \quad (1.76)$$

$$= h_{ii} + h_{jj} + \frac{1}{4}(\Pi_{ijij} + \Pi_{jiji} - \Pi_{ijji} - \Pi_{jiij}) \quad (1.77)$$

$$= h_{ii} + h_{jj} + \Pi_{ijij} \quad (1.78)$$

$$\langle\phi_{HF}|\hat{\mathrm{H}}|\phi_D\rangle = \frac{1}{4}\sum_{pqrs}\Pi_{pqrs}\left(\delta_{ip}\delta_{jq} - \delta_{iq}\delta_{jp}\right)\left(\delta_{as}\delta_{br} - \delta_{ar}\delta_{bs}\right) \quad (1.79)$$

$$= \Pi_{ijab} = \langle\phi_D|\hat{\mathrm{H}}|\phi_{HF}\rangle \quad (1.80)$$

So out total energy gradient can be re-written as:

$$E_{FCI} = c_{HF}{}^2(h_{ii} + h_{jj} + \Pi_{ijij}) + 2\, c_{HF}c_D\Pi_{ijab} + c_D{}^2(h_{aa} + h_{bb} + \Pi_{abab}) \quad (1.81)$$

To solve this, we must take the derivative of Equation 1.81, however, to finish the derivative terms we must perform a coupled-perturbed Hartree-Fock (CPHF) procedure [13].

$$\frac{\partial}{\partial \mathrm{x}}E_{FCI} = c_{HF}{}^2\frac{\partial}{\partial \mathrm{x}}(h_{ii} + h_{jj} + \Pi_{ijij}) + 2\, c_{HF}c_D\frac{\partial}{\partial \mathrm{x}}\Pi_{ijab} + c_D{}^2\frac{\partial}{\partial \mathrm{x}}(h_{aa} + h_{bb} + \Pi_{abab}) \quad (1.82)$$

First let's start with the doubles term $\mathrm{E_D}$

$$\frac{\partial}{\partial \mathrm{x}} \mathrm{E}_D = \frac{\partial}{\partial \mathrm{x}} (h_{aa} + h_{bb} + \Pi_{abab}) \tag{1.83}$$

$$= h^{\bar{x}}{}_{aa} + h^{\bar{x}}{}_{bb} + \Pi^{\bar{x}}{}_{abab} \;\; + \sum_{\mu\nu} \mathrm{h}_{\mu\nu} \sum_{c} \frac{\partial}{\partial \mathrm{x}} \mathrm{C}_{\mu c} \mathrm{C}_{\nu c}$$

$$+ \tfrac{1}{2} \textstyle\sum_{\mu\nu\lambda\sigma} \Pi_{\mu\lambda\nu\sigma} \sum_{cd} (\tfrac{\partial \mathrm{C}_{\mu c} \mathrm{C}_{\nu c}}{\partial \mathrm{x}} \, \mathrm{C}_{\mu d} \mathrm{C}_{\nu d} + \, \tfrac{\partial \mathrm{C}_{\mu d} \mathrm{C}_{\nu d}}{\partial \mathrm{x}} \, \mathrm{C}_{\mu c} \mathrm{C}_{\nu c})$$

Here we take advantage of the fact that the system that we chose (Hydrogen) is symmetric just like the last term in the expression. We rearrange terms and labels to yield:

$$h^{\bar{x}}{}_{aa} + h^{\bar{x}}{}_{bb} + \Pi^{\bar{x}}{}_{abab} + \textstyle\sum_{\mu\nu} \mathrm{h}_{\mu\nu} \sum_{c} \tfrac{\partial}{\partial \mathrm{x}} \mathrm{C}_{\mu c} \mathrm{C}_{\nu c} + \sum_{\mu\nu\lambda\sigma} \Pi_{\mu\lambda\nu\sigma} \sum_{cd} \tfrac{\partial \mathrm{C}_{\mu c} \mathrm{C}_{\nu c}}{\partial \mathrm{x}} \, \mathrm{C}_{\mu d} \mathrm{C}_{\nu d} \tag{1.84}$$

$$= h^{\bar{x}}{}_{aa} + h^{\bar{x}}{}_{bb} + \Pi^{\bar{x}}{}_{abab} + \textstyle\sum_{\mu\nu c} \tfrac{\partial \mathrm{C}_{\mu c} \mathrm{C}_{\nu c}}{\partial \mathrm{x}} [\mathrm{h}_{\mu\nu} + \sum_{d} \Pi_{\mu d\nu d}] \tag{1.85}$$

Then we can use the following equations from [14] to facilitate the derivation procedure of the coefficients

$$\frac{\partial \mathrm{C}_{\mu c} \mathrm{C}_{\nu c}}{\partial \mathrm{S}_{\alpha\beta}} = -\tfrac{1}{2} \big(\widetilde{\mathrm{P}_{\mu\alpha}} \mathrm{C}_{\beta c} \mathrm{C}_{\nu c} + \widetilde{\mathrm{P}_{\nu\alpha}} \mathrm{C}_{\beta c} \mathrm{C}_{\mu c} \big) = -\textstyle\sum_{p} \mathrm{C}_{\mu p} \mathrm{C}_{\alpha p} \mathrm{C}_{\beta c} \mathrm{C}_{\mu c} \tag{1.86}$$

$$\frac{\partial \mathrm{C}_{\mu c} \mathrm{C}_{\nu c}}{\partial \theta_{fk}} = \delta_{fc} (\mathrm{C}_{\mu k} \mathrm{C}_{\nu c} + \mathrm{C}_{\mu c} \mathrm{C}_{\nu k}) = 2 \, \delta_{fc} \, \mathrm{C}_{\mu k} \mathrm{C}_{\nu c} \tag{1.87}$$

Inserting the definitions into our expression

$$\frac{\partial \mathrm{E}_D}{\partial \mathrm{x}} = h^{\bar{x}}{}_{aa} + h^{\bar{x}}{}_{bb} + \Pi^{\bar{x}}{}_{abab}$$

$$- \sum_{\mu\nu\alpha\beta} \mathrm{S}_{\alpha\beta}{}^{\bar{x}} \mathrm{C}_{\mu p} \mathrm{C}_{\alpha p} \mathrm{C}_{\beta c} \mathrm{C}_{\mu c} \left[\mathrm{h}_{\mu\nu} + \sum_{d} \Pi_{\mu d\nu d} \right]$$

$$+\sum_{\substack{\mu\nu \\ cfk}} \theta_{fk}{}^{\bar{x}}\, \delta_{fc} \mathrm{C}_{\mu c} \mathrm{C}_{\nu k}\left[\mathrm{h}_{\mu\nu} + \sum_d \Pi_{\mu d \nu d}\right] \tag{1.88}$$

$$= h^{\bar{x}}{}_{aa} + h^{\bar{x}}{}_{bb} + \Pi^{\bar{x}}{}_{abab} - \sum_{cp} \mathrm{S}^{\bar{x}}_{pc}\left[\mathrm{h}_{pc} + \sum_d \Pi_{pdcd}\right] + \sum_{ck} \theta^{\bar{x}}_{ck}\left[\mathrm{h}_{ck} + \sum_d \Pi_{cdkd}\right] \tag{1.89}$$

The orbital response term vanishes because the $\theta^{\bar{x}}_{ck}$ term is antisymmetric while $\left[\mathrm{h}_{pq} + \sum_d \Pi_{pdqd}\right]$ is symmetric in c and k. With this result we can specify the sum of terms by applying this equation to our modeled Hydrogen system to this equation and produce the specialized result below:

$$\frac{\partial \mathrm{E}_D}{\partial \mathrm{x}} = h^{\bar{x}}{}_{aa} + h^{\bar{x}}{}_{bb} + \Pi^{\bar{x}}{}_{abab} - \mathrm{S}^{\bar{x}}_{ia}\left[\mathrm{h}_{ia} + \Pi_{ibab}\right]$$

$$-\mathrm{S}^{\bar{x}}_{jb}\left[\mathrm{h}_{jb} + \Pi_{jaba}\right] - \mathrm{S}^{\bar{x}}_{aa}\left[\mathrm{h}_{aa} + \Pi_{abab}\right] - \mathrm{S}^{\bar{x}}_{bb}\left[\mathrm{h}_{bb} + \Pi_{baba}\right] \tag{1.90}$$

Here we can neglect terms that vanish because of spin and (since our calculation is restricted) we combined terms with the same spatial orbitals. The final term for the derivative of the doubles term is:

$$\boldsymbol{\frac{\partial \mathrm{E}_D}{\partial \mathrm{x}} = 2\, h^{\bar{x}}{}_{aa} + (\mathrm{aa}|\mathrm{aa})^{\bar{x}} - 2\, \mathrm{S}^{\bar{x}}_{ia}[\mathrm{h}_{ia} + (ai|aa)] - 2\, \mathrm{S}^{\bar{x}}_{aa}[\mathrm{h}_{aa} + (aa|aa)]} \tag{1.91}$$

by a similar methodology we can conclude that the Hartree-Fock derivative is:

$$\boldsymbol{\frac{\partial \mathrm{E}_{HF}}{\partial \mathrm{x}} = 2\, h^{\bar{x}}{}_{ii} + (\mathrm{ii}|\mathrm{ii})^{\bar{x}} - 2\, \mathrm{S}^{\bar{x}}_{ii}(\mathrm{h}_{ii} + (ii|ii))} \tag{1.92}$$

then we can solve the remaining derivative term:

$$\Pi_{ijab} = ([ia|jb] - [ib|ja]) = [ia|jb] = [ai|ai] \tag{1.93}$$

$$\frac{\partial}{\partial \mathrm{x}} \Pi_{ijab} = [ai|ai]^{\bar{x}} + \sum_{\mu\nu\lambda\sigma}[\mu\nu|\lambda\sigma]\ \left(\frac{\partial \mathrm{C}_{\mu a} \mathrm{C}_{\nu i}}{\partial \mathrm{x}}\, \mathrm{C}_{\lambda a} \mathrm{C}_{\sigma i} + \mathrm{C}_{\mu a} \mathrm{C}_{\nu i} \frac{\partial \mathrm{C}_{\lambda a} \mathrm{C}_{\sigma i}}{\partial \mathrm{x}}\right) \tag{1.94}$$

$$= [ai|ai]^{\bar{x}} + 2 \sum_{\mu\nu}[\mu\nu|ai]\ \frac{\partial \mathrm{C}_{\mu a} \mathrm{C}_{\nu i}}{\partial \mathrm{x}} \tag{1.95}$$

Applying Equation 1.86 and 1.87 we get

$$\frac{\partial}{\partial \mathrm{x}}\Pi_{ijab} = [ai|ai]^{\bar{x}} - \sum_{\nu\beta p} \mathrm{S}^{\bar{x}}_{p\beta}\ [p\nu|ai]\ (\mathrm{C}_{\beta a}\mathrm{C}_{\nu i} + \mathrm{C}_{\beta i}\mathrm{C}_{\nu a}) + 2\sum_{\substack{\mu\nu \\ ck}} [\mu\nu|ai]\theta_{ck}{}^{\bar{x}}\ \delta_{ca}\mathrm{C}_{\mu k}\mathrm{C}_{\nu i} -$$

$$2\sum_{\substack{\mu\nu \\ ck}}[\mu\nu|ai]\theta_{ck}{}^{\bar{x}}\ \delta_{ki}\mathrm{C}_{\mu a}\mathrm{C}_{\nu c} \tag{1.96}$$

$$\frac{\partial}{\partial \mathrm{x}}\Pi_{ijab} = [ai|ai]^{\bar{x}} - \mathrm{S}^{\bar{x}}_{aa}\ [ai|ai] - \mathrm{S}^{\bar{x}}_{ia}\ [ii|ai] - \mathrm{S}^{\bar{x}}_{ai}\ [aa|ai]$$

$$-\mathrm{S}^{\bar{x}}_{ii}\ [ia|ai] + 2[ii|ai]\theta_{ai}{}^{\bar{x}} - 2[aa|ai]\theta_{ai}{}^{\bar{x}} \tag{1.97}$$

$$\frac{\partial}{\partial \mathrm{x}}\Pi_{ijab} = [ai|ai]^{\bar{x}} - (\mathrm{S}^{\bar{x}}_{aa} + \mathrm{S}^{\bar{x}}_{ii})\ [ai|ai] - \mathrm{S}^{\bar{x}}_{ai}\ ([ii|ai] + [aa|ai]) + 2\theta_{ai}{}^{\bar{x}}([ii|ai] + [aa|ai]) \tag{1.98}$$

Finally, we plug in the three derived quantities from Equation 1.98, 1.92 and 1.91 into Equation 1.82 to get the case specific energy gradient derivative that we will use in the calculation of our energy gradient:

$$\frac{\partial}{\partial \mathrm{x}}E_{FCI} = c_{HF}{}^2\left[2\ h^{\bar{x}}{}_{ii} + (\mathrm{ii|ii})^{\bar{x}} - 2\ \mathrm{S}^{\bar{x}}_{ii}\big(\mathrm{h}_{ii} + (ii|ii)\big)\right]$$

$$+2\ c_{HF}c_D\left[[ai|ai]^{\bar{x}} - (\mathrm{S}^{\bar{x}}_{aa} + \mathrm{S}^{\bar{x}}_{ii})\ [ai|ai] - \mathrm{S}^{\bar{x}}_{ai}\ ([ii|ai] + [aa|ai]) + 2\theta_{ai}{}^{\bar{x}}([ii|ai] + [aa|ai])\right]$$

$$+c_D{}^2\left[2\ h^{\bar{x}}{}_{aa} + (\mathrm{aa|aa})^{\bar{x}} - 2\ \mathrm{S}^{\bar{x}}_{ia}[\mathrm{h}_{ia} + (ai|aa)] - 2\ \mathrm{S}^{\bar{x}}_{aa}[\mathrm{h}_{aa} + (aa|aa)]\right] \tag{1.99}$$

CHAPTER II

RESULTS AND DISCUSSION

II.1 Data collection

We now present a framework for investigating the degree to which error can be injected into the results of the full-configuration interaction calculation before the wavefunction and quantities derived from it no longer the match their variational values. To assess that, we chose a computationally tractable system (the hydrogen molecule) as a test bed for the implementation and testing of the full gradient and injections of arbitrary errors. Then, we will examine it to see how these anomalies affect the exact known answer.

We tested and compared several different ways of obtaining derived quantities: First, a full traditional calculation of the system; and second, a finite-difference calculation that does not rely on any prior wavefunction information. If the errors we injected are negligible, these obtained quantities should be in reliable range of each other; the only error present should be the ones expected from the finite-difference method. If the errors we injected are not negligible, the full calculation and the finite-difference should match.

II.2 Choosing a molecule and basis set

To begin the computation of the traditional calculation we decided to implement all the previously explained methodologies in a C++ code. All calculations discussed have been performed using this code. We can start the foundations of our test bed experiment by selecting a basis set. All calculations were performed using a STO-3G basis set containing three Gaussian functions approximating Hartree-Fock atomic Hydrogen functions. We used Equation 1.13 to construct the specific function below

$$|\phi_0\rangle = 0.444635\boldsymbol{\phi}_{\boldsymbol{1s}}^{\boldsymbol{GF}}(0.168856) + 0.535328\boldsymbol{\phi}_{\boldsymbol{1s}}^{\boldsymbol{GF}}(0.623913) + 0.154329\boldsymbol{\phi}_{\boldsymbol{1s}}^{\boldsymbol{GF}}(3.42525)$$

II.3 Hydrogen STO-3G SCF

From here it is straightforward to continue to perform the self-consistent field procedure to calculate our Hartree-Fock ground state energy. We begin by calculating all the necessary overlap **(S)**, kinetic energy **(K)**, potential energy **(V1 & V2)** and two-electron integrals. With them it's simple to calculate the core-Hamiltonian,

$$H_{core} = K + V1 + V2 \tag{2.0}$$

take an initial guess at the density matrix

$$P = \begin{bmatrix} 0 & 0 \\ 0 & 0 \end{bmatrix}$$

To form the **G** matrix with the two-electron integral

$$G_{\upsilon\nu} = \sum_{\lambda\upsilon} P_{\lambda\sigma}[(\upsilon\nu|\sigma\lambda) - \tfrac{1}{2}(\upsilon\lambda|\sigma\upsilon)] \tag{2.1}$$

Now we can add the core-Hamiltonian and the G matrix to form the Fock matrix. Using the calculated transformation matrix **X** from the SCF procedure**,** calculate the transformed Fock matrix and diagonalize to get the corresponding coefficients.

$$F = H + G \tag{2.2}$$

$$F' = X^{\dagger} F X \tag{2.3}$$

$$F'C' = \varepsilon C' \tag{2.4}$$

Use the transformation matrix **X** again to calculate C and the new density matrix with Equation 1.38 and 1.39

$$C = XC'$$

$$P_{\lambda\sigma} = 2 \sum_{\lambda\sigma} C_{\lambda a} C_{\sigma a}$$

All of this will repeat until the last calculated density matrix differs by a factor less than $1\text{x}10^{-8}$ from its last iteration. Once the SCF procedure converges, the energy is calculated using the formula

$$E = \frac{1}{2} \sum\nolimits_{\lambda\sigma} P_{\lambda\sigma}(H_{\lambda\sigma} + F_{\lambda\sigma}) \tag{2.5}$$

It is important to note that by using a general formula for the density matrix we have neglected any interaction between states with different spins, hence the factor of two outside the sum of the density matrix in Equation 1.39. This effectively obligates the calculation to be a restricted Hartree-Fock. For completion, we also performed the Unrestricted Hartree-Fock calculation following the procedure detailed by Poble-Nesbet [11]. Instead we use the nest equations to calculate the density matrix.

$$P^{\alpha}{}_{\lambda\sigma} = \sum_{\lambda\sigma} C^{\alpha}{}_{\lambda a} C^{\alpha}{}_{\sigma a} \tag{2.6}$$

$$P^{\beta}{}_{\lambda\sigma} = \sum_{\lambda\sigma} C^{\beta}{}_{\lambda a} C^{\beta}{}_{\sigma a} \tag{2.7}$$

For the Fock matrix me must also distinguish for spin, creating two eigenvalue equations of the form

$$\boldsymbol{F^{\alpha} C^{\alpha}} = \boldsymbol{S C^{\alpha} \varepsilon^{\alpha}} \tag{2.8}$$

$$\boldsymbol{F^{\beta} C^{\beta}} = \boldsymbol{S C^{\beta} \varepsilon^{\beta}} \tag{2.9}$$

This, in short, forces us to compute the self-consistent field procedure twice, once for alpha spin states and twice for beta spin states, however, the procedure is self-convergent, meaning both alpha and beta spin values must be calculated simultaneously before jumping into the new iteration. Nevertheless, besides some additional terms and redefining some factors, the Unrestricted Hartree-Fock (URHF) does not raise the complexity of our calculation in comparison to Restricted Hartree-Fock (RHF). We performed a SCF procedure for both RHF and URHF in Hydrogen STO-3G. Repeating the calculation at each interatomic distance from 0.1 a.u. increasing the distance stepwise by +0.01 a.u. until 5.0 a.u. The obtained potential energy graphs are reported in **Figure 3.**

At this point, we have successfully calculated the ground state energy (E_0) through two different SCF procedures. We continue by applying the Full Configuration Interaction methodology to correct this energy using the correlation energy in Equation 1.57. The Hartree-Fock ground state wave function for Hydrogen which includes four spin orbitals $(1,\ \bar{1}, 2, \bar{2})$ we can form, in addition to the ground state, five other and build the full CI wavefunction.

$$|\phi_0\rangle = c_{1\bar{1}}|1\bar{1}\rangle + c_{2\bar{1}}|2\bar{1}\rangle + c_{1\bar{2}}|1\bar{2}\rangle + c_{12}|12\rangle + c_{\overline{21}}|\overline{21}\rangle + c_{2\bar{2}}|2\bar{2}\rangle \tag{2.10}$$

Using this wave function, we can construct the CI matrix and use the variational method to determine the lowest eigenvalue—which would be the corresponding correlation energy. The resulting matrix is:

$$\mathbf{H} = \begin{bmatrix} \langle 1\bar{1}|H|1\bar{1}\rangle & \langle 1\bar{1}|H|2\bar{1}\rangle & \langle 1\bar{1}|H|1\bar{2}\rangle & \langle 1\bar{1}|H|12\rangle & \langle 1\bar{1}|H|\overline{21}\rangle & \langle 1\bar{1}|H|2\bar{2}\rangle \\ & \langle 2\bar{1}|H|2\bar{1}\rangle & \langle 2\bar{1}|H|1\bar{2}\rangle & \langle 2\bar{1}|H|12\rangle & \langle 2\bar{1}|H|\overline{21}\rangle & \langle 2\bar{1}|H|2\bar{2}\rangle \\ & & \langle 1\bar{2}|H|1\bar{2}\rangle & \langle 1\bar{2}|H|12\rangle & \langle 1\bar{2}|H|\overline{21}\rangle & \langle 1\bar{2}|H|2\bar{2}\rangle \\ & & & \langle 12|H|12\rangle & \langle 12|H|\overline{21}\rangle & \langle 12|H|2\bar{2}\rangle \\ & & & & \langle \overline{21}|H|\overline{21}\rangle & \langle \overline{21}|H|2\bar{2}\rangle \\ & & & & & \langle 2\bar{2}|H|2\bar{2}\rangle \end{bmatrix} \tag{2.11}$$

where we have omitted the lower triangle of the matrix because of its symmetry.

Although a 6x6 matrix is not the most complicated when speaking in terms of full CI, this matrix has been simplified further before [5] by realizing the symmetry of our system. In short, because the ground state from Hartree-Fock is a singlet, only configurations of singlet symmetry need to be included, namely the ground state and the doubly excited state. Both are closed shells and therefore singlets.

As a result, Equation 2.10 reduces to:

$$|\phi_0\rangle = |1\bar{1}\rangle + c|2\bar{2}\rangle \tag{2.12}$$

and our corresponding full CI matrix is:

$$\mathbf{H} = \begin{bmatrix} \langle 1\bar{1}|H|1\bar{1}\rangle & \langle 1\bar{1}|H|2\bar{2}\rangle \\ \langle 2\bar{2}|H|1\bar{1}\rangle & \langle 2\bar{2}|H|2\bar{2}\rangle \end{bmatrix} = \begin{bmatrix} \langle \phi_{HF}|H|\phi_{HF}\rangle & \langle \phi_{HF}|H|\phi_D\rangle \\ \langle \phi_D|H|\phi_{HF}\rangle & \langle \phi_D|H|\phi_D\rangle \end{bmatrix} \tag{2.13}$$

The logical next step would be to evaluate the matrix elements in Equation 2.11. Having evaluated all the matrix elements, we can determine the lowest eigenvalue of the matrix using secular determinant or unitary transformation. We performed several calculations, the 2.11 matrix including all possible spin combinations, the symmetry simplified spin excluding 2x2 matrix and a calculation including the singlet state:

$$|{}^1\psi_{\bar{1}}^{2}\rangle = \sqrt{2}\ \left(|1\bar{2}\rangle + |2\bar{1}\rangle\right) \tag{2.14}$$

Yielding the Hamiltonian:

$$\mathbf{H} = \begin{bmatrix} \langle 1\bar{1}|H|1\bar{1}\rangle & \langle 1\bar{1}|H|{}^1\psi_{\bar{1}}^{2}\rangle & \langle 1\bar{1}|H|2\bar{2}\rangle \\ \langle {}^1\psi_{\bar{1}}^{2}|H|1\bar{1}\rangle & \langle {}^1\psi_{\bar{1}}^{2}|H|{}^1\psi_{\bar{1}}^{2}\rangle & \langle {}^1\psi_{\bar{1}}^{2}|H|2\bar{2}\rangle \\ \langle 2\bar{2}|H|1\bar{1}\rangle & \langle 2\bar{2}|H|{}^1\psi_{\bar{1}}^{2}\rangle & \langle 2\bar{2}|H|2\bar{2}\rangle \end{bmatrix} \tag{2.15}$$

After performing the calculations, we found that all three FCI procedures using Equation 2.15, 2.13 or 2.11 agreed with the potential energy graph reported in **Figure 4.** And although in **Figure 3** we can see the difference in accuracy between the RHF and URHF, the FCI potential energy is independent of which version of Hartree-Fock we use as a reference. In other words, in a RHF-FCI calculation Equation 1.46 perfectly corrects the ground state energy to match that of an URHF-FCI. When performing a FCI calculation, a restricted representation of the wavefunction (Equation 2.12) is sufficient.

From here we have completed the traditional calculation of the system that will be our point of reference. Now we must inject some error into the important coefficients **c** in the FCI methodology (Equation 2.12).

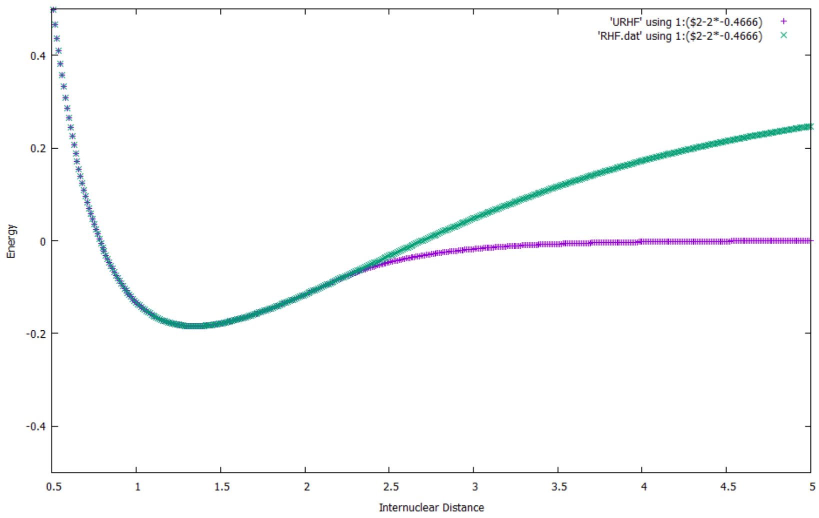

Figure 3: The potential energy from the Restricted Hartree-Fock (green) and Unrestricted Hartree-Fock (purple) using the self-consistent field procedure from 0.1 a.u.-5.0 a.u. increasing by +0.01 at every step.

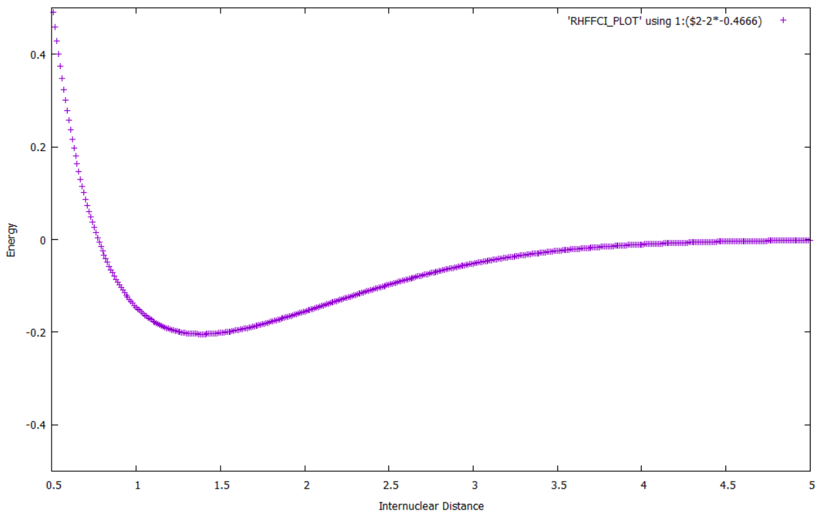

Figure 4: Full configuration interaction potential energy. The energies recorded here are an addition of the SCF ground state energy and the correlation energy from 0.1 a.u.-5.0 a.u. increasing by +0.01 at every step.

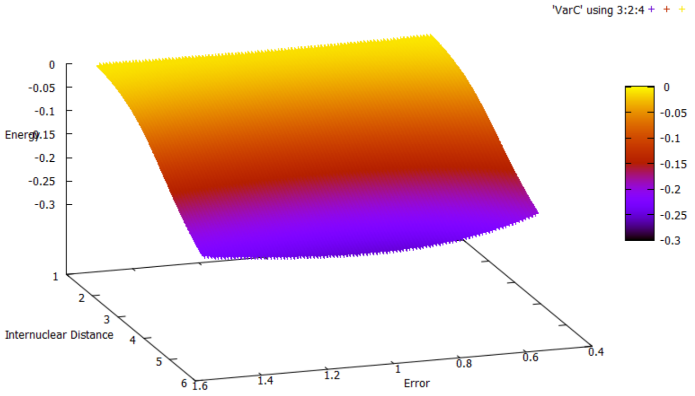

Figure 5: Potential energy graph of the total energy obtained with the RHF-FCI procedure with an extra dimension in the x-axis measuring the perturbation of the FCI coefficient (0.5-1.5).

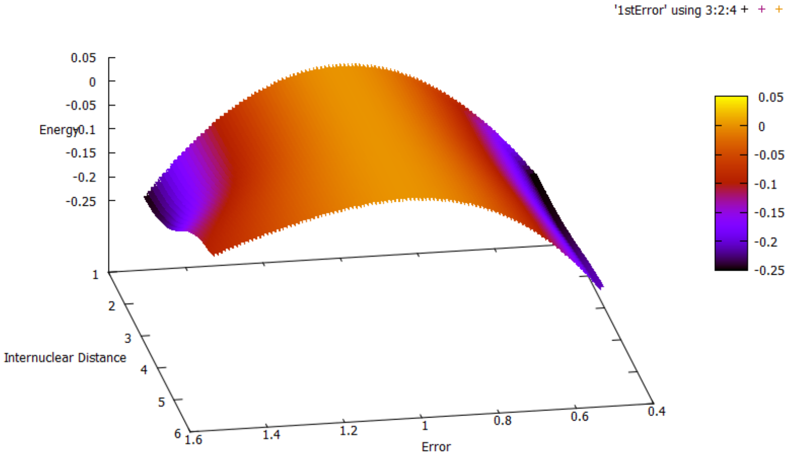

Figure 6: Fractional Error graph of the potential energy graph in Figure 3. Internuclear distance in x-axis (0 to 6 a.u.), perturbation to the coefficient in y-axis (0.5-1.5) and percent error in the z-axis.

In the FCI procedure, we scaled the exact known coefficient of the doubles term which includes information about the HF and Doubles state simultaneously. The errors injected in this coefficient took the form of a scale factor on the coefficients such that normalization is maintained. This experiment should reveal places in our potential energy surface that are more sensitive to error, giving us better understanding of the global behavior of our system.

In **Figure 5** is the potential energy graph presented in **Figure 4** without the repulsion energy (since the correlation energy is solely electronic), but with an extra dimension that measures the perturbance applied into the coefficient of the FCI procedure from -50% to +50%.

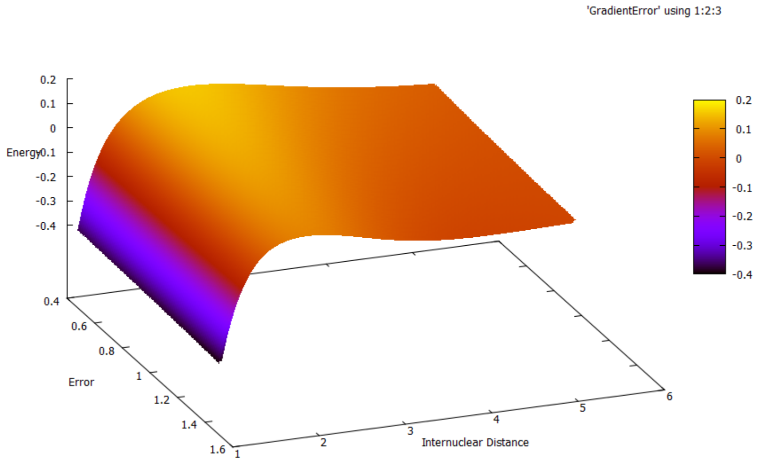

Figure 7: Energy gradient results with changing internuclear distance and perturbation of the FCI coefficients the reported perturbations and the known accurate value.

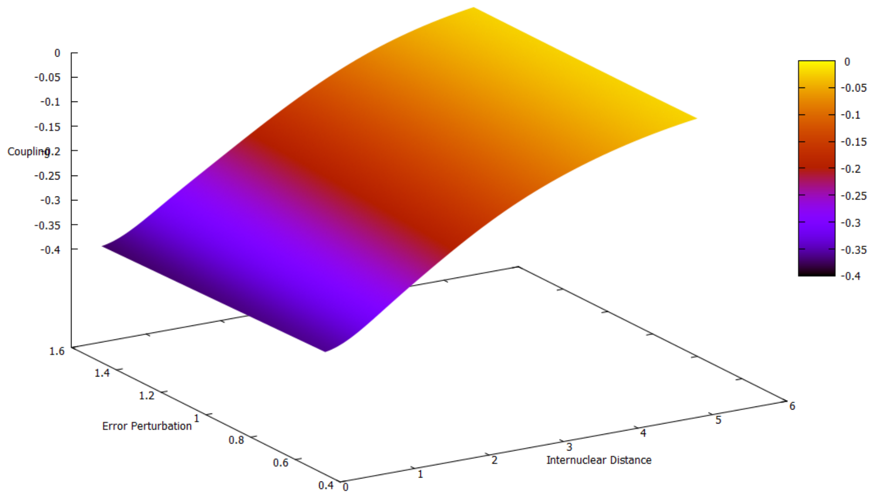

Figure 8: Derivative coupling results with changing internuclear distance and perturbation of the FCI coefficients

Target Error (%)	Energy	Gradient	Derivative
0.001	6.858	0.000	0.154
0.00316	12.299	0.000	0.773
0.01	21.954	0.038	2.618
0.0316	39.098	0.368	8.515
0.1	69.609	1.430	27.209
0.316	123.866	4.749	86.622
0.562	165.103	8.529	134.777

Table 1: Sensitivity of the energy, gradient, and derivative coupling terms in ppt in targeted percent error.

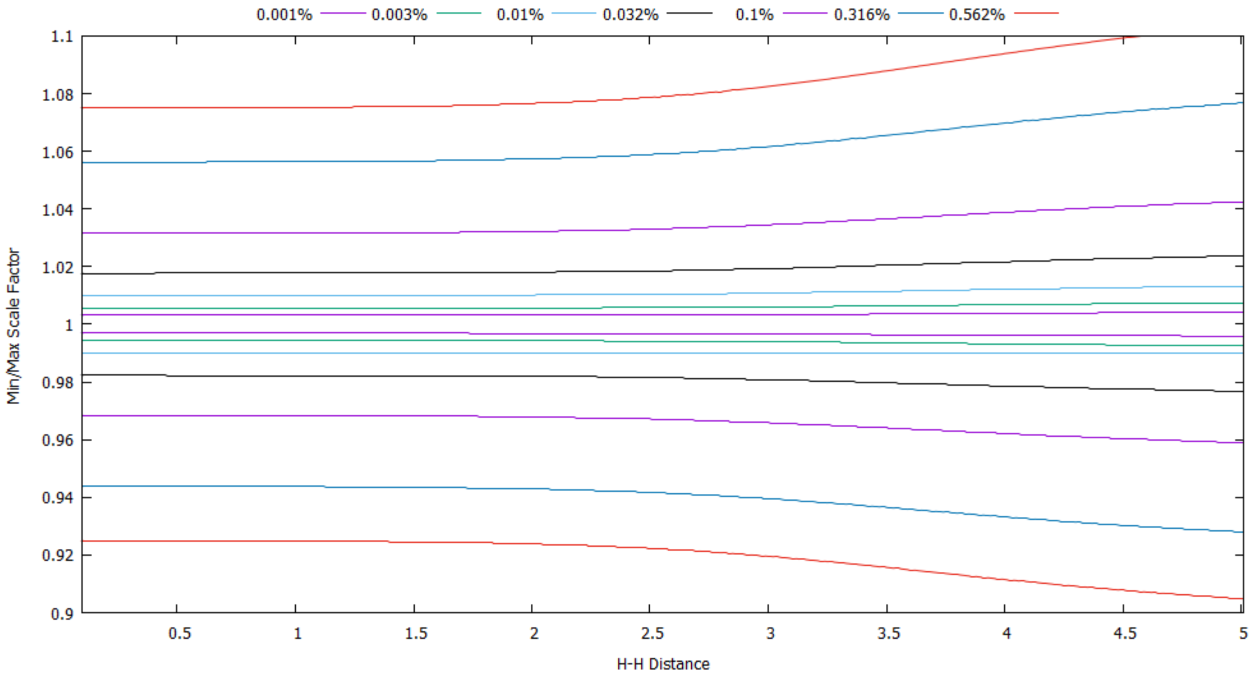

Figure 9: Minimum vs Maximum scale of the perturbation of the correlation energy results

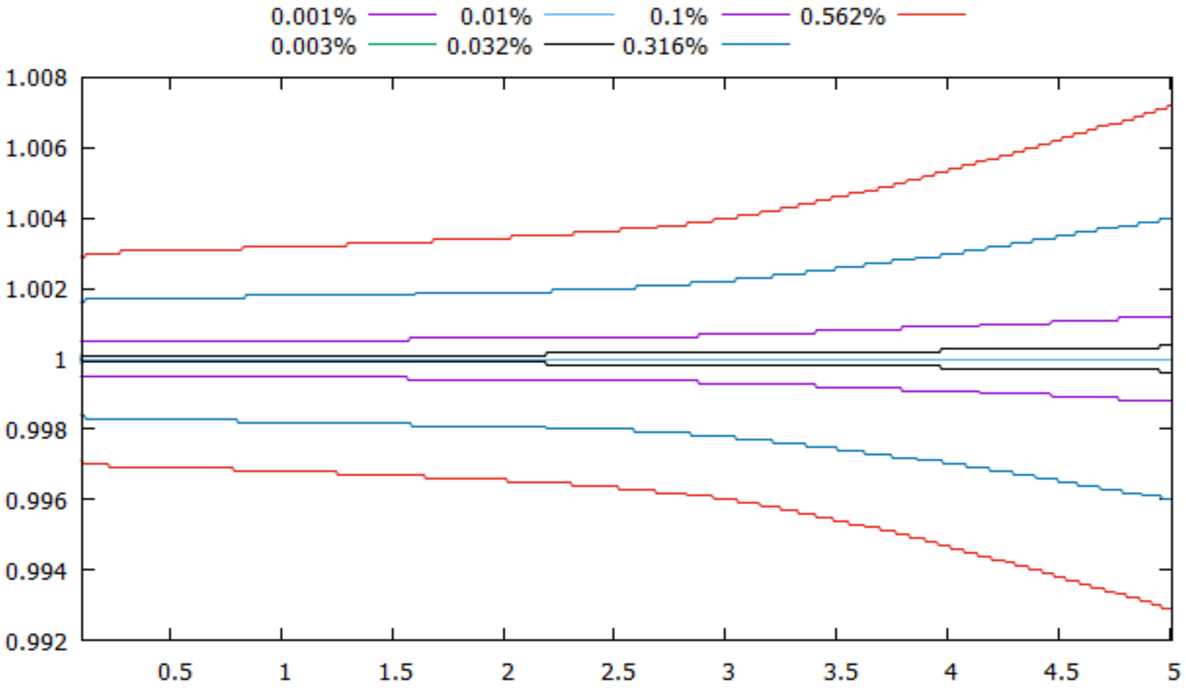

Figure 10: Minimum vs Maximum scale of the perturbation of the energy gradient results.

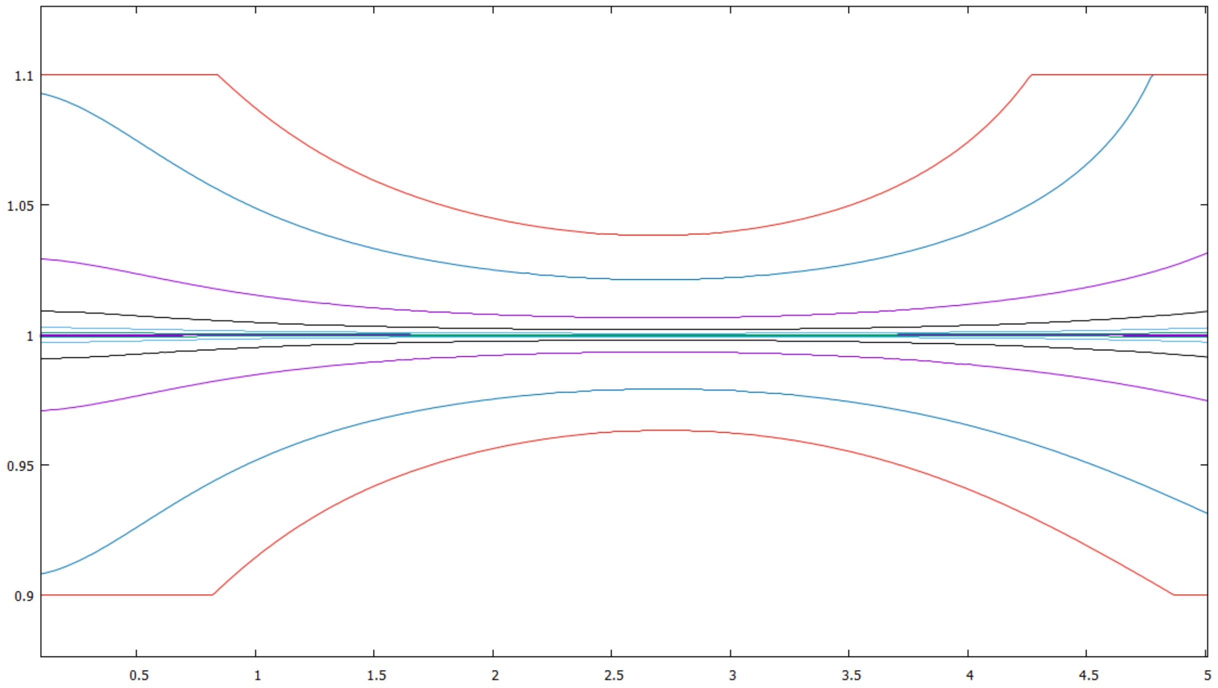

Figure 11: Minimum vs Maximum scale of the perturbation of the derivative coupling results.

II.4 Conclusion

We performed and compared three different calculations, a classical computation, a finite difference calculation, and a calculation with perturbation against different terms. With this we were able to find the total energy of the system as the least sensitive to the perturbation of the FCI coefficient as reported in **Table 1**. While the gradient and derivative coupling are more sensitive to error than the energy, it still displayed a relative sensitivity in the point of unrestriction in the potential energy curve. Its also important to notice the behavior of the quantities when questioning the relative maximum or minimum perturbation allowed. Both the gradient and correlation energy showed a decrease in sensitivity to error as the internuclear distance goes beyond the Coulson-Fischer point.

II.5 Future work

Several derived quantities remain to be examined for their sensitivity to our error-injecting scale factor, including the Hessian matrix (and thus the vibrational frequencies of the molecule), the adiabatic correction (aka the diagonal portion for the second-order derivative couplings), and the spin-orbit coupling between the singlet and the triplet states. In addition to implementing and computing the error sensitivities of these quantities, we will also examine the effect of having omitted the analytic response terms that describe the loss of variationality in the Hartree–Fock coefficients. To the extent that the response calculations can be avoided, then the derived quantities can still be at least partially variational.

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BIOGRAPHICAL SKETCH

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