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**To cite this version :**

Francisco CHINESTA, Emmanuelle ABISSET-CHAVANNE - Ab-Initio Calculations - 2018

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Arts Institute of Technology et Métiers

# Chapter 2
# Ab-initio calculations

Due to the difficulties found in the direct solution of the Schrödinger equation different simplified approaches were proposed and are nowadays widely used. Among them, the most usually employed are the Hartree-Fock and the Density Functional Theory, that we revisit in the present chapter. The former makes use of nonstandard numerical approximations in order to calculate the wavefunction while circumventing the curse of dimensionality whereas the latter involves the electronic density that is now defined in three dimensions but that requires deeper analyses to retain in a 'coarse" 3D model the most relevant features present in the wavefunction description.

## 2.1 The Hartree-Fock description

### 2.1.1 The orbital model

The set of all the solutions to the one-electron Schrödinger equation reads

$$\hat{\mathscr{H}} \; \phi_i = \hat{E}_i \; \phi_i, \tag{2.1}$$

where $\hat{\mathscr{H}}$ represents the one-electron Hamiltonian hermitian operator. The eigenfuctions $\phi_i$, known as spatial orbitals, related to the eigenvalues $\hat{E}_i$ (energies), define a complete basis of the 3D space, such that any 3D function can be written as

$$f(\mathbf{r}) = \sum_{j=1}^{\infty} c_j \; \phi_j(\mathbf{r}), \tag{2.2}$$

where $\mathbf{r}$ denotes the space coordinates, after eliminating the spin coordinate in expression (1.129), i.e. $\mathbf{r} = (x, y, z)$.

If we define the spin-orbitals $\varphi_j(\mathbf{x})$ as

$$\varphi_j(\mathbf{x}) = \phi_j(\mathbf{r}) \cdot \alpha(s), \tag{2.3}$$

or

$$\varphi_j(\mathbf{x}) = \phi_j(\mathbf{r}) \cdot \beta(s), \tag{2.4}$$

then the solution $\Psi(\mathbf{x}_1, \mathbf{x}_2)$ of the two-electrons Schrödinger equation could be approximated as follows: fixing the value of one of the coordinates, e.g. $\mathbf{x}_2$, and using the rationale just described, it results

$$\Psi(\mathbf{x}_1; \mathbf{x}_2) = \sum_{j=1}^{\infty} c_j(\mathbf{x}_2)\, \varphi_j(\mathbf{x}_1), \tag{2.5}$$

and considering

$$c_j(\mathbf{x}_2) = \sum_{k=1}^{\infty} d_k^j\, \varphi_k(\mathbf{x}_2), \tag{2.6}$$

it finally results

$$\Psi(\mathbf{x}_1, \mathbf{x}_2) = \sum_{j=1}^{\infty}\sum_{k=1}^{\infty} c_{jk}\, \varphi_j(\mathbf{x}_1) \cdot \varphi_k(\mathbf{x}_2), \tag{2.7}$$

where $c_{jk} = d_k^j$.

This expression can be generalized to the many-electrons distribution function.


### 2.1.2 Accounting for the Pauli exclusion principle

In order to ensure the verification of the Pauli exclusion principle, we define the determinants

$$\Phi_k(\mathbf{x}_1, \cdots, \mathbf{x}_{N_e}) = \begin{vmatrix} \varphi_{m_1^k}(\mathbf{x}_1) & \cdots & \varphi_{m_1^k}(\mathbf{x}_{N_e}) \\ \vdots & \ddots & \vdots \\ \varphi_{m_{N_e}^k}(\mathbf{x}_1) & \cdots & \varphi_{m_{N_e}^k}(\mathbf{x}_{N_e}) \end{vmatrix}, \tag{2.8}$$

where $k$ refers to a particular choice of the $N_e$ indexes $m_1^k, \cdots, m_{N_e}^k$.

Thus, the multi-electronic wavefunction can be approximated as

$$\Psi(\mathbf{x}_1, \cdots, \mathbf{x}_{N_e}) = \sum_{k=1}^{\infty} D_k\, \Phi_k(\mathbf{x}_1, \cdots, \mathbf{x}_{N_e}). \tag{2.9}$$

A permutation in the label of two electrons implies the exchange of two columns of the different determinants involved in Eq. (2.9) and then a change of the sign in agreement with Pauli exclusion principle.

### 2.1.3 The variational principle

In order to compute the vawefunction approximate given by Eq. (2.9), we are proving the existence of a variational principle whose minimization will result in the searched wavefunction.

The eigenproblem related to the multi-electronic system reads

$$\mathcal{H}\,\Psi = E\,\Psi, \tag{2.10}$$

which results in the eigenfunctions $\Psi_i$ verifying the orthonormality condition

$$\int \overline{\Psi_i}\,\Psi_j\,d\mathbf{r} = \delta_{ij}, \tag{2.11}$$

where $d\mathbf{r} = d\mathbf{r}_1 \cdot d\mathbf{r}_2 \cdots d\mathbf{r}_{N_e}$. It is important to note that since the hamiltonian is independent of the spin, the resulting eigenfunctions only depend on the space coordinates.

Although $\Psi_i$ are and remain unknown, their formal properties ensure that they form a complete basis for the expression of any function. Thus, if we write

$$\Psi' = \sum_{j=1}^{\infty} B_j\,\Psi_j, \tag{2.12}$$

where $B_j$ are arbitrary coefficients, then the associated energy (according to (1.83)), results

$$E' = \frac{\int \overline{\Psi'}\mathcal{H}\Psi'd\mathbf{r}}{\int \overline{\Psi'}\Psi'd\mathbf{r}}, \tag{2.13}$$

where the denominator accounts for the non-normality of $\Psi'$.

Introducing the approximation (2.12) into the expression (2.13) and taking into account Eq. (2.11) it results

$$E' = \frac{\sum_{j=1}^{\infty} |B_j|^2 E_j}{\sum_{j=1}^{\infty} |B_j|^2}, \tag{2.14}$$

that subtracting the lowest energy $E_1$ (ground state) yields

$$(E' - E_1) = \frac{1}{\sum_{j=1}^{\infty} |B_j|^2} \sum_{j=1}^{\infty} |B_j|^2\,(E_j - E_1) \geq 0, \tag{2.15}$$

that implies

$$E' \geq E_1, \tag{2.16}$$

that means that whatever function of $N_e$ electronic coordinates one chooses, the mean value of the Hamiltonian operator is always greater than the lowest true en-

ergy of the associated Schrödinger equation, giving the procedure for finding numerical solutions. It suffices to minimize the Hamiltonian operator applied on the test wavefunction approximate as described in the next section.

### 2.1.4 A direct solution procedure

If the expression of $\Psi'$ is written as a linear combination of a finite number $M$ of determinants, i.e.

$$\Psi'(\mathbf{x}_1, \ldots, \mathbf{x}_{N_e}) = \sum_{j=1}^{M} D_j \, \Phi_j(\mathbf{x}_1, \ldots, \mathbf{x}_{N_e}), \tag{2.17}$$

then, the associated energy results

$$E' = \frac{\sum_{j=1}^{M} \sum_{k=1}^{M} \overline{D_j} D_k \int \overline{\Phi_j} \mathscr{H} \Phi_k d\mathbf{r}}{\sum_{j=1}^{M} \sum_{k=1}^{M} \overline{D_j} D_k \int \overline{\Phi_j} \Phi_k d\mathbf{r}}. \tag{2.18}$$

Introducing the notation

$$\begin{cases} H_{jk} = \int \overline{\Phi_j} \mathscr{H} \Phi_k \, d\mathbf{r} \\ S_{jk} = \int \overline{\Phi_j} \Phi_k \, d\mathbf{r} \end{cases}, \tag{2.19}$$

Eq. (2.18) reads

$$\left( \sum_{j=1}^{M} \sum_{k=1}^{M} \overline{D_j} D_k S_{jk} \right) E' = \sum_{j=1}^{M} \sum_{k=1}^{M} \overline{D_j} D_k H_{jk}, \tag{2.20}$$

whose minimization leads to

$$\left( \sum_{k=1}^{M} D_k S_{jk} \right) E = \sum_{k=1}^{M} D_k H_{jk}, \quad \forall j \tag{2.21}$$

that can be written in the matrix form

$$\begin{pmatrix} H_{11} & \ldots & H_{1M} \\ \vdots & \ddots & \vdots \\ H_{M1} & \ldots & H_{MM} \end{pmatrix} \begin{pmatrix} D_1 \\ \vdots \\ D_M \end{pmatrix} = E \begin{pmatrix} S_{11} & \ldots & S_{1M} \\ \vdots & \ddots & \vdots \\ S_{M} & \ldots & S_{MM} \end{pmatrix} \begin{pmatrix} D_1 \\ \vdots \\ D_M \end{pmatrix}, \tag{2.22}$$

or

$$\mathbf{H}\,\mathbf{D} = E\,\mathbf{S}\,\mathbf{D}. \tag{2.23}$$

The main difficulties in this numerical approach are the following:

- How many determinants $M$ should be considered in the expansion (2.12)?
- How to quantify the solution quality?
- What are the most appropriate spin-orbitals $\varphi_i(\mathbf{x})$ to perform the development?
- What are the best determinants to consider, that is, the best choices of indices $m_i^k$, $\forall k$?
- Despite the fact that coefficients $H_{jk}$ and $S_{jk}$ are known in principle because everything is known about the integrals, they still remain formidable technical problems because they are integrals of $3N_e$ spatial variables. The integrals can be separated as a sum of products of integrals defined in the 3D spaces. However, the separated form of integrals $H_{jk}$ requires the integration in 6D spaces because of the electron-electron potential that appears in the Hamiltonian.

### 2.1.5 The Hartree-Fock approach

As the general expansion (2.17) is computationally too expensive, one could try to capture the main features of the solution by assuming that this sum reduces to a single term. Of course if one try to use

$$\Psi'(\mathbf{x}_1,\ldots,\mathbf{x}_{N_e}) = D \; \Phi(\mathbf{x}_1,\ldots,\mathbf{x}_{N_e}), \tag{2.24}$$

there is no chance to define an acceptable solution, except if we consider that now the determinant $\Phi(\mathbf{x}_1,\ldots,\mathbf{x}_{N_e})$ is defined from a set of separate unknown orbitals that should be computed from the minimization that the variational principle imposes. Thus, the Hartree-Fock approach considers the Hartree-Fock wavefunction $\Phi^{HF}(\mathbf{x}_1,\ldots,\mathbf{x}_{N_e})$ defined from

$$\Phi^{HF}(\mathbf{x}_1,\ldots,\mathbf{x}_{N_e}) = \begin{vmatrix} \chi_{m_1}(\mathbf{x}_1) & \cdots & \chi_{m_1}(\mathbf{x}_{N_e}) \\ \vdots & \ddots & \vdots \\ \chi_{m_{N_e}}(\mathbf{x}_1) & \cdots & \chi_{m_{N_e}}(\mathbf{x}_{Ne}) \end{vmatrix}, \tag{2.25}$$

that, as just indicated, orbitals $\chi_i$ are approximated from $m$ spin-orbitals (previously introduced) according to

$$\chi_i(\mathbf{x}) = \sum_{r=1}^{m} C_{ri} \; \varphi_r(\mathbf{x}). \tag{2.26}$$

Coefficients $C_{ri}$ are computed by using the variational formulation associated with the energy

$$E\left[\Phi^{HF}\right] = \frac{\int \overline{\Phi}^{HF} \mathscr{H} \Phi^{HF} d\mathbf{r}}{\int \overline{\Phi}^{HF} \Phi^{HF} d\mathbf{r}}, \tag{2.27}$$

where $E\left[\Phi^{HF}\right]$ indicates that the energy is a functional of the Hartree-Fock wavefunction, that could be also written as $E[\chi_i]$. The interested reader can refer to [22] for additional details on the calculation procedure.

### 2.1.6 Post-Hartree-Fock methods

Note that Eq. (2.26) involves $N_e \cdot m$ unknown complex coefficients. Thus, the computational complexity scales in $N_e \cdot m$ , that is, linearly with the dimension of the space (number of electrons $N_e$) or with the number $m$ of functions used in the approximation of the orbitals $\chi_i$. This scalability is characteristic of separated representations [6].

The main limitation of the Hartree-Fock method lies in the single-determinant expansion used in the approximation of the wavefunction solution of the multi-electronic Schrödinger equation. If the main features present in this solution cannot be expressed from a single-determinant expansion, the Hartree-Fock solution could be inaccurate.

To circumvent this crude approximation different multi-determinant approaches have been proposed. Interested readers can refer to [14] as well as to the different chapters of the handbook on computational chemistry [31]. The simplest alternative consists in writing the solution as a linear combination of some Slater determinants built by combining $m$ orbitals, with $m > N_e$. These orbitals are assumed known (e.g. the orbitals related to the hydrogen atom) and the weights are searched to minimize the electronic energy. When the molecular orbitals are built from the Hartree-Fock solution (by employing the ground state and some excited eigenfunctions) the technique is known as Configuration Interaction method (CI).

A more sophisticated technique consists in writing this many-determinants approximation of the solution by using a number of molecular orbitals $m$ (with $m > N_e$) assumed unknown. Thus, the minimization of the electronic energy leads to compute simultaneously the molecular orbitals as well as the associated coefficients of this many-determinants expansion. Obviously, each one of these unknown molecular orbitals are expressed in an appropriate functional basis (e.g. gaussian functions, ...). This strategy is known as Multi-Configuration Self-Consistent Field (MCSCF).

All the just mentioned strategies (and others like the coupled cluster or the Moller-Plesset perturbation methods) belong to the family of the wavefunction based methods. They can be only used to solve quantum systems composed of a moderate number of electrons, because the number of terms involved in the determinants scales with the factorial of the number of electrons, i.e. with $N_e!$.

## 2.2 Density Functional Theory

Solid physics deals with many-electrons systems implying billions of particles, not just dozens as in molecular theories. This means that methods based on the electron density are much more widely used. The constant efforts to develop such methods have been rewarded by a series of amazing theorems showing that it is possible to obtain the exact electron density without using the wavefunction.

Density functional theory – DFT – is based on two major results, the so-called Hohenberg and Kohn theorems.

### 2.2.1 The first Hohenberg and Kohn theorem

The first Hohenberg and Kohn theorem states that the electronic density determines uniquely the external potential, the one created by the nuclei.

We start by defining the electronic density in the context of the single-determinant approach (that implies operating with space-spin coordinates)

$$\rho(\mathbf{r}) = N_e \int \overline{\Phi}(\mathbf{x}, \mathbf{x}_2, \dots, \mathbf{x}_{N_e}) \Phi(\mathbf{x}, \mathbf{x}_2, \dots, \mathbf{x}_{N_e}) \, d\mathbf{r}_2 \dots d\mathbf{r}_{N_e}, \tag{2.28}$$

or

$$\rho(\mathbf{r}) = N_e \int |\Psi(\mathbf{x}, \mathbf{x}_2, \dots, \mathbf{x}_{N_e})|^2 \, d\mathbf{r}_2 \dots d\mathbf{r}_{N_e}. \tag{2.29}$$

We assume the following Hamiltonian partition

$$\mathcal{H} = \mathcal{T} + \mathcal{V} + \mathcal{G}, \tag{2.30}$$

where $\mathcal{T}$ represents the kinetic energy operator, $\mathcal{V}$ the external potential operator (the one created by the nuclei) and $\mathcal{G}$ the inter-electron repulsions potential.

In order to prove that the electronic density determines uniquely the external potential, we assume that two different external potentials correspond to the same electronic density. This fact implies different Hamiltonians that only differ due to the difference in the external potentials because the kinetic energy part and the one corresponding to the inter-electron interactions are the same as soon as the number of electrons is the same. We denote the two different external potentials by $\mathcal{V}$ and $\mathcal{V}'$, and their corresponding Hamiltonians $\mathcal{H}$ and $\mathcal{H}'$ respectively. As the Hamiltonian determines the wavefunction, these will be denoted by $\Psi$ and $\Psi'$.

Now, the variational principle introduced in Section 2.1.3 states

$$\begin{cases} \int \overline{\Psi'} \mathcal{H} \Psi' \, d\mathbf{r}_1 \cdots d\mathbf{r}_{N_e} > E \\ \int \overline{\Psi} \mathcal{H}' \Psi \, d\mathbf{r}_1 \cdots d\mathbf{r}_{N_e} > E' \end{cases}, \tag{2.31}$$

with

$$\begin{cases} E = \int \overline{\Psi} \mathcal{H} \Psi \, d\mathbf{r}_1 \cdots d\mathbf{r}_{N_e} \\ E' = \int \overline{\Psi'} \mathcal{H}' \Psi' \, d\mathbf{r}_1 \cdots d\mathbf{r}_{N_e} \end{cases}. \tag{2.32}$$

Thus, considering the first expression in Eq. (2.31), it results

$$E < \int \overline{\Psi'} \mathcal{H} \Psi' \, d\mathbf{r}_1 \cdots d\mathbf{r}_{N_e} =$$

$$\int \overline{\Psi'} \mathcal{H}' \Psi' \, d\mathbf{r}_1 \cdots d\mathbf{r}_{N_e} + \int \overline{\Psi'} (\mathcal{H} - \mathcal{H}') \Psi' \, d\mathbf{r}_1 \cdots d\mathbf{r}_{N_e} =$$

$$E' + \int \overline{\Psi'} (\mathcal{V} - \mathcal{V}') \Psi' \, d\mathbf{r}_1 \cdots d\mathbf{r}_{N_e} = E' + \int (v(\mathbf{r}) - v'(\mathbf{r})) \rho(\mathbf{r}) \, d\mathbf{r}, \qquad (2.33)$$

where $v(\mathbf{x})$ refers to the one-electron potential (see section 1.9).

Now, applying the same rationale to the second expression in Eq. (2.31) we obtain

$$E' < \int \overline{\Psi} \mathcal{H}' \Psi \, d\mathbf{r}_1 \cdots d\mathbf{r}_{N_e} =$$

$$\int \overline{\Psi} \mathcal{H} \Psi \, d\mathbf{r}_1 \cdots d\mathbf{r}_{N_e} + \int \overline{\Psi} (\mathcal{H}' - \mathcal{H}) \Psi \, d\mathbf{r}_1 \cdots d\mathbf{r}_{N_e} =$$

$$E + \int \overline{\Psi} (\mathcal{V}' - \mathcal{V}) \Psi \, d\mathbf{r}_1 \cdots d\mathbf{r}_{N_e} =$$

$$E + \int (v'(\mathbf{x}) - v(\mathbf{x})) \rho(\mathbf{x}) \, d\mathbf{r} = E - \int (v(\mathbf{r}) - v'(\mathbf{r})) \rho(\mathbf{r}) \, d\mathbf{r}. \qquad (2.34)$$

By adding Eqs. (2.33) and (2.34) it results

$$E' + E < E' + E, \qquad (2.35)$$

from which we conclude that $\mathcal{V}' = \mathcal{V}$ and $\mathcal{H}' = \mathcal{H}$. Since the wavefunction depends on the Hamiltonian, we can affirm that the wevefunction is uniquely determined by the electron density and consequently $\Psi' = \Psi$.

### 2.2.2 The second Hohenberg and Kohn theorem

Now, in order to determine the electronic density, the second Hohenberg and Kohn theorem estabishes a variational principle whose minimization results in the searched electronic distribution.

From a given electronic density $\rho'(\mathbf{r})$ we can write

$$E' = \int \overline{\Psi'} \mathcal{H} \Psi' d\mathbf{r}_1 \cdots d\mathbf{r}_{N_e} = W[\rho'(\mathbf{r})]. \qquad (2.36)$$

The variational principle introduced in Section 2.1.3 implies

$$E' = W[\rho'(\mathbf{r})] \geq E = \int \overline{\Psi} \mathcal{H} \Psi d\mathbf{r}_1 \cdots d\mathbf{r}_{N_e} = W[\rho(\mathbf{r})], \qquad (2.37)$$

with $\mathcal{H} \Psi = E \Psi$, that establishes the searched result

$$\begin{cases} W[\rho'(\mathbf{r})] \geq W[\rho(\mathbf{r})] \\ \int \rho'(\mathbf{r})d\mathbf{r} = N_e \end{cases}.$$  (2.38)

### *2.2.3 The Hohn-Sham equations*

In the density functional theory two conceptual difficulties remain:

- How to quantify the electrons kinetic energy from the only knowledge of their distributions in space?
- What is the role of antisymmetry (Pauli exclusion principle) requirements in the electron density function?

We start by approximating the unknown function, the trial density, within a single-determinant approach

$$\rho(\mathbf{r}) = N_e \int \overline{\Phi}(\mathbf{x}, \mathbf{x}_2, \dots, \mathbf{x}_{N_e}) \Phi(\mathbf{x}, \mathbf{x}_2, \dots, \mathbf{x}_{N_e}) \, d\mathbf{r}_2 \dots d\mathbf{r}_{N_e},$$  (2.39)

where the determinant $\Phi$ involves the unknown orthonormal spin-orbitals $\chi_i(\mathbf{x}_i)$, approximation that is in agreement with the Pauli exclusion principle and that verifies the $N_e$-representability

$$\int \rho(\mathbf{r})d\mathbf{r} = N_e.$$  (2.40)

The total energy $W[\rho(\mathbf{r})]$ can be decomposed in three contributions, one related to the kinetic energy $T[\rho(\mathbf{r})]$, one that consider the external potential (electron-nuclei interactions) $V[\rho(\mathbf{r})]$ and finally one representing the electron-electron interactions $J[\rho(\mathbf{r})]$, the last two contributions read

$$V[\rho(\mathbf{r})] = \int v(\mathbf{r})\rho(\mathbf{r})d\mathbf{r},$$  (2.41)

and

$$J[\rho(\mathbf{r})] = \int \rho(\mathbf{r}_1) \frac{1}{||\mathbf{r}_1 - \mathbf{r}_2||} \rho(\mathbf{r}_2)d\mathbf{r}_1 d\mathbf{r}_2.$$  (2.42)

For the kinetic energy we assume a first contribution $\hat{T}$ by assuming non-interacting electrons

$$\hat{T}[\rho(\mathbf{r})] = \sum_{i=1}^{N_e} \int \overline{\chi_i} \left( \frac{1}{2}\nabla^2 \right) \chi_i \, d\mathbf{r}_i,$$  (2.43)

where $\chi_i$ are the orbitals considered in the expression of the determinant $\Phi$.

The remaining contribution to the kinetic energy and the non-Coulomb effects are grouped in the exchange-correlation-residual-kinetic energy $E_{XCKE}[\rho(\mathbf{r})]$. The main difficulty concerns the expression of the exchange-correlation-kinetic-residual

energy that is not known. In general this term is obtained by a combination of heuristic arguments, a model based on simple systems and calibrates using known results, because more accurate techniques exploiting the self-consistency are too expensive to be used.

Now, the solution procedure consists of:

- A variation in the density is associated to linearly independent variations in $\chi_i$ and $\overline{\chi}_i$;
- Generate the form of the variations of each functional involving $\chi_i$ and $\overline{\chi}_i$: $\hat{T}$, $V$, $J$ and $E_{XCKE}$;
- Add a Lagrange multiplier to enforce the $N_e$-representability;
- Enforce optimality conditions of the variational principle.

The interested reader can refer to [22] for additional details on the calculation procedure.

## 2.3 Concluding remarks on the quantum scale

After this brief analysis of the quantum scale we conclude:

- The Schrödinger formalism represents the nowadays finest level of description. In the formalism introduced here, there is no mention in the Hamiltonian of spin-dependent magnetic interactions. These effects as well as the relativistic ones, taken into account in the Dirac's equation, are neglected. The consideration of very heavy nuclei needs the introduction of such relativistic effects.
- The wavefunction involved in the Schrödinger equation is spatially continuous and its evolution is governed by a PDE.
- The Schrödinger equation is defined in a multidimensional space leading to curse of dimensionality issues. It has been solved exactly for systems containing a reduced number of electrons.
- Ab-initio approximations, density functional or Hartree-Fock theories just summarized seem sometimes to be crude approximations but the only valuable route for addressing multi-electronic systems.
- The solution of the Schrödinger equation could provide an excellent description of the world at the nanometric scale as well as accurate interatomic potentials to be used in molecular dynamics simulations.
- There are some quantum systems in which the solution explores the whole multidimensional configuration space and thus remain almost intractable despite all the possible advances in the computational performances.