Contents

Notations . . . 5

1 Laying the foundations **7**
1.1 The Born-Oppenheimer Approximation . . . 8
1.2 Hartree Product *vs* Slater Determinants . . . 9
1.3 The "single-determinant" approximation . . . 12
1.4 Linear Combination of Atomic Orbitals . . . 13
1.5 The variational principle . . . 13
1.6 Lagrange Multipliers . . . 16
1.6.1 A first example : finding the orbitals of a mono-electronic operator . . . 16
1.6.2 Lagrange multiplier and energy . . . 18
1.7 Summary . . . 19

2 The Hartree-Fock method **21**
2.1 Mono and Bi-Electronic Operators : the Slater-Condon Rules . . . 21
2.1.1 Mono-electronic operator terms . . . 22
2.1.2 Bi-electronic terms . . . 24
2.2 The Fock Operator . . . 26
2.2.1 Derivation of the mono-electronic part . . . 27
2.2.2 Derivation of the bi-electronic part . . . 27
2.2.3 Derivation of the constraint of orthogonality . . . 29
2.2.4 Full Derivation . . . 29
2.2.5 Fock, Coulombian and Exchange operators . . . 29
2.3 Roothan equations . . . 31
2.3.1 Orthogonalization of the basis set . . . 32
2.3.2 The same problem expressed in different basis sets . . . 34
2.4 SCF Method . . . 35

3 Applications **37**
3.1 Orbital energies and total energy . . . 37
3.2 One-particle reduced density matrix and electronic densities . . . 38

4 A new beginning **41**
4.1 First Hohenberg and Kohn Theorem . . . 41
4.2 Second Hohenberg and Kohn Theorem . . . 42

Appendices **43**

A Mathematical developments **45**
A.1 Expanding a Slater determinant . . . 45
A.2 Computation of a mono-electronic operator . . . 45

A.2.1 Computation of a diagonal element 45
A.2.2 Off Diagonal Element 46
A.3 Bi-electronic operators 47

Foreword

In terms of bibliography, despite being no longer "modern" the quantum mechanics presented here comes mainly from the excellent **Modern Quantum Chemistry** by Szabo and Ostlund [1]. Although dating from the 1980s, this book remains a reference book with a broad scope for usual methods (excluding DFT). To go much further, particularly for wavefunction-based methods, one can use the book written by Helgaker, **Molecular Electronic-Structure Theory** [2], which goes way beyond "Modern Quantum Chemistry" and makes extensive use of second quantization – neither used nor presented here. The goal here is to build the foundations of several major families of methods. The emphasis is therefore placed on several aspects:

- The Hartree-Fock method, which constructs the "best" atomic orbitals. It depicts the classical vision of the electronic structure of molecules by chemists.
- Demonstrating a method for partitioning the multi-electron Hamiltonian into a sum of single-electron Hamiltonians, all while explicitly accounting for the electron repulsion term as much as possible.
- Explaining the SCF (*Self-Consistent Field*) procedure, which is the foundation of many methods in theoretical chemistry.

I would like to warmly thank the people who have contributed directly or indirectly to the creation of this handout: Vincent Robert, Paul Fleury-Lessard, Jean-Baptiste Rota, Mikaël Képénékian, Hélène Bolvin, Vincent Krakoviak, Élise Dumont, Tommaso Roscilde, and Tangui Le Bahers. It is through long discussions with them that I have been able to clear my ideas on various technical aspects and points. I hope that this handout can serve as a modest gateway for the new generation of theoretical chemists. I would like to thank the echem organizing committee for their kind invitation.

If you notice any errors, mistakes, or inaccuracies, please report them to me at the address « martin.verot # ens-lyon.fr » with an @ in place of the #.

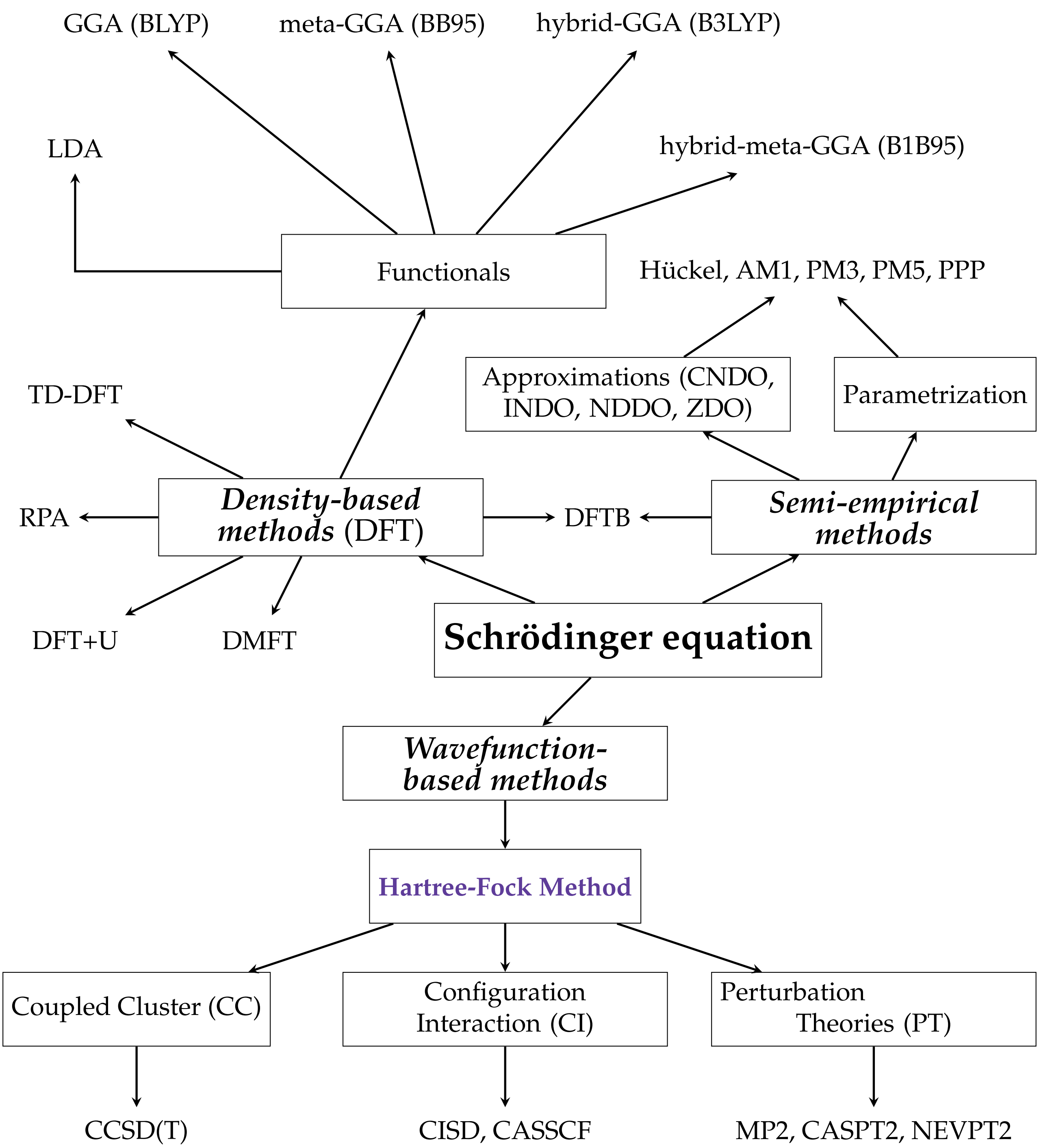


Figure 1: Mind map to show common methods used to solve the Schrödinger equation.

Notations

I will use atomic units, which hides the following constants :

- the electron mass m_e;
- the elementary charge e;
- the reduced Planck constant $\hbar$;
- the vacuum permittivity $4\pi\epsilon_0$;
- the Bohr radius $a_0 = \frac{4\pi\epsilon_0\hbar^2}{m_e e^2}$;
- the Hartree $1\ \text{Ha} = \frac{e^2}{4\pi\epsilon_0 a_0} = m_\text{e}\left(\frac{e^2}{4\pi\varepsilon_0\hbar}\right)^2$.

Notation	Meaning
δ_{ij}	Kronecker delta: $\delta_{ij} = 1$ if $i = j$, 0 otherwise
$\alpha(\omega)$	Spin function associated with $m_s = 1/2$
$\beta(\omega)$	Spin function associated with $m_s = -1/2$
$\mathbf{R}_A$	Nuclear coordinates
$\mathbf{r}_i$	Electronic coordinates
N	Total number of electrons
Q	Total number of nuclei
M	Total number of basis function orbitals
Indices	
A, B	Nuclei
i, j	Electrons
μ, ν, τ, κ	Atomic orbitals
k, m	Molecular orbitals
a, b	Occupied molecular orbitals
r, s	Unoccupied molecular orbitals
$\alpha, \cdots, \zeta$	Occupied molecular orbitals
Operators	
$A^* = \overline{A}$	Complex conjugate
$A^\dagger = \overline{A^t}$	Hermitian conjugate (adjoint) of operator $\hat{A}$
Ω_1	A generic one-electron operator
Ω_2	A generic two-electron operator
$\hat{h}^i$	A one-electron Hamiltonian operator acting on electron i
$\hat{H}$	A multi-electron Hamiltonian operator
$\hat{J}_{ab}$	Coulomb operator acting on orbitals ϕ_a and ϕ_b
$\hat{K}_{ab}$	Exchange operator acting on orbitals ϕ_a and ϕ_b
$\hat{E}\left[\Psi\right]$	Energy operator associated with the eigenvector Ψ: $\hat{E}\left[\Psi\right] = \frac{\langle\Psi\vert\hat{H}\vert\Psi\rangle}{\langle\Psi\vert\Psi\rangle}$

Notation	Meaning
One-electron quantities	
χ_μ	Atomic orbital (or spin orbital)
ϕ_k	Molecular orbital (or spin orbital)
$\hat{h}_1^i$	A one-electron Hamiltonian operator acting on electron i
ϵ_k	Energy associated with an orbital (atomic or molecular): $\hat{h}\|\phi_k\rangle = \epsilon_k\|\phi_k\rangle$
Many-electron quantities	
Ψ_i	Many-electron wavefunction
$\hat{H}$	Multi-electronic Hamiltonian operator
E_i	Energy associated with a complete wavefunction: $\hat{H}\|\Psi_i\rangle = E_i\|\Psi_i\rangle$
Integrals	
h_{km}	Matrix element of operator $\hat{h}$, $$h_{km} = \left\langle \phi_k \middle\| \hat{h} \middle\| \phi_m \right\rangle = \left\langle \phi_k(\mathbf{r}_i) \middle\| \hat{h}_i \middle\| \phi_m(\mathbf{r}_j) \right\rangle = \iiint \phi_k^*(\mathbf{r}_i)\hat{h}_i\phi_m(\mathbf{r}_i)\,\mathrm{d}\mathbf{r_i}$$
$S_{\mu\nu}$	Overlap between atomic orbitals χ_μ and χ_ν, $$S_{\mu\nu} = \langle \chi_\mu \,\|\, \chi_\nu \rangle = \iiint \chi_\mu^*(\mathbf{r})\chi_\nu(\mathbf{r})\,\mathrm{d}\mathbf{r}$$
$\langle ij\|kl\rangle$	Two-electron integral, "physicist's" notation $$\langle ij\|kl\rangle = \left\langle \phi_i\phi_j \middle\| \frac{1}{\mathbf{r}_{12}} \middle\| \phi_k\phi_l \right\rangle = \iiint\iiint \phi_i^*(\mathbf{r}_1)\phi_j^*(\mathbf{r}_2)\frac{1}{r_{12}}\phi_k(\mathbf{r}_1)\phi_l(\mathbf{r}_2)\,\mathrm{d}\mathbf{r}_1\,\mathrm{d}\mathbf{r}_2$$
J_{ab}	Coulomb integral $$J_{ab} = \langle ij\|ij\rangle = [ii\|jj] = \iiint\iiint \|\phi_i(\mathbf{r}_1)\|^2 \frac{1}{r_{12}} \|\phi_j(\mathbf{r}_2)\|^2\,\mathrm{d}\mathbf{r}_1\,\mathrm{d}\mathbf{r}_2$$
K_{ab}	Exchange integral $$K_{ab} = \langle ij\|ji\rangle = [ij\|ji] = \iiint\iiint \phi_i^*(\mathbf{r}_1)\phi_j^*(\mathbf{r}_2)\frac{1}{r_{12}}\phi_j(\mathbf{r}_1)\phi_i(\mathbf{r}_2)\,\mathrm{d}\mathbf{r}_1\,\mathrm{d}\mathbf{r}_2$$

Tableau 1: Some notations and their meanings.

Chapter 1

Laying the foundations

We will try to ... solve the Schrödinger equation for a molecular system with Q atoms and N electrons. We will use the Schrödinger equation in its usual form:[a]

$$\hat{H}^{\text{tot}}\Psi_i = E_i^{\text{tot}}\Psi_i \tag{1.1}$$

$$\hat{H}^{\text{tot}} = \underbrace{-\sum_{A}^{Q}\frac{1}{2m_A}\Delta_A}_{\hat{T}_N} + \underbrace{\frac{1}{2}\sum_{A}^{Q}\sum_{B}^{Q}\frac{Z_A Z_B}{R_{AB}}}_{\hat{V}_{NN}} \underbrace{-\sum_{i}^{N}\frac{1}{2}\Delta_i}_{\hat{T}_e} \underbrace{-\sum_{A}^{Q}\sum_{i}^{N}\frac{Z_A}{r_{Ai}}}_{\hat{V}_{Ne}} + \underbrace{\sum_{i>j}\frac{1}{r_{ij}}}_{\hat{V}_{ee}} \tag{1.2}$$

where :

- $\hat{T}_{\text{N}}$ is the kinetic energy of the nuclei ;
- $\hat{V}_{\text{NN}}$ is the nuclei-nuclei repulsion ;
- $\hat{T}_{\text{e}}$ is the kinetic energy of the electrons ;
- $\hat{V}_{\text{Ne}}$ is the nuclei-electron attraction;
- $\hat{V}_{\text{ee}}$ is the electron-electron repulsion.

and Ψ_i is the solution, called the wavefunction. It's a mathematical object function of all the electronic and nuclei coordinates $\Psi_i = \Psi\left(\mathbf{r}_1, \ldots, \mathbf{r}_N, \mathbf{R}_1, \ldots, \mathbf{R}_Q\right)$.

Among those terms :

- $\hat{T}_{\text{N}}$ and $\hat{V}_{\text{NN}}$ depend only on nuclei coordinates $\{\mathbf{R}_A\}$
- $\hat{T}_{\text{e}}$ and $\hat{V}_{\text{ee}}$ depend only on electronic coordinates $\{\mathbf{r}_i\}$
- $\hat{V}_{\text{Ne}}$ couples nuclei and electronic coordinates

[a] Or more modestly/pragmatically: do the best we can to obtain an approximate solution of the problem.

1.1 The Born-Oppenheimer Approximation

This approximation simplifies the expression of the wavefunction by decoupling the nuclei and electronic parts :

$$\Psi\left(\mathbf{r}_1,\ldots,\mathbf{r}_N,\mathbf{R}_1,\ldots,\mathbf{R}_Q\right) = \Psi_e\left(\mathbf{r}_1,\ldots,\mathbf{r}_N;\mathbf{R}_1,\ldots,\mathbf{R}_Q\right)\times\Psi_{\mathrm{N}}\left(\mathbf{R}_1,\ldots,\mathbf{R}_Q\right) \tag{1.3}$$

where :

- Ψ_{N} is the nuclei wavefunction, which depends only on the nuclei coordinates $\{\mathbf{R}_A\}$;
- Ψ_{e} is the electronic wavefunction which depends only on the electronic coordinates $\{\mathbf{r}_i\}$ but where *the nuclei positions are parameters*. This is shown by the semicolon ";" between the two sets of coordinates. It shows that the nuclei are still taken into account to solve the electronic part of the problem !

The validity of this hypothesis comes from the huge difference of mass between electrons and nuclei. In the worst case scenario, for an hydrogen atom, the mass ratio is equal to $\dfrac{m_p}{m_e} = \dfrac{1,673\cdot10^{-27}}{9,109\cdot10^{-31}} \approx 1836.$

The full Hamiltonian can be decoupled into two parts thanks to this approximation : a nuclear Hamiltonian $\hat{H}_{\mathrm{N}}$ and an electronic one $\hat{H}_{\mathrm{e}}$.

$$\hat{H}^{\mathrm{tot}} = \underbrace{\hat{T}_{\mathrm{N}} + \hat{V}_{\mathrm{NN}}}_{\hat{H}_{\mathrm{N}}} + \underbrace{\hat{T}_{\mathrm{e}} + \hat{V}_{\mathrm{Ne}} + \hat{V}_{\mathrm{ee}}}_{\hat{H}_{\mathrm{e}}} \tag{1.4}$$

$$\hat{H}_{\mathrm{N}} = \hat{T}_{\mathrm{N}} + \hat{V}_{\mathrm{NN}} \tag{1.5}$$

$$\hat{H}_{\mathrm{e}} = \hat{T}_{\mathrm{e}} + \hat{V}_{\mathrm{Ne}} + \hat{V}_{\mathrm{ee}} \tag{1.6}$$

$$\hat{H}_{\mathrm{N}}\Psi_{\mathrm{N}} = E_{\mathrm{N}}\Psi_{\mathrm{N}} \tag{1.7}$$

$$\hat{H}_{\mathrm{e}}\Psi_{\mathrm{e}} = E_{\mathrm{e}}\Psi_{\mathrm{e}} \tag{1.8}$$

$$\hat{H}^{\mathrm{tot}}\Psi_{\mathrm{e}}\Psi_{\mathrm{N}} = \underbrace{\left(E_{\mathrm{e}} + E_{\mathrm{N}}\right)}_{=E^{\mathrm{tot}}}\Psi_{\mathrm{e}}\Psi_{\mathrm{N}} \tag{1.9}$$

By decoupling the coordinates, we can set aside the nuclear part – which is much simpler to solve than the electronic one. For purely static nuclei, $\hat{T}_{\mathrm{N}}$ is void and E_N reduces to :

$$E_N = \frac{1}{2}\sum_{A}^{Q}\sum_{B\neq A}^{Q}\frac{Z_A Z_B}{R_{AB}} \tag{1.10}$$

The other way around :

- the full energy E^{tot} is easily obtained from the electronic energy E_{e} by adding E_N to it.
- for a given and static geometry : the energy difference of the full problem is already given by the electronic energy difference ΔE_{e} and it's even not necessary to compute E_N.

To sum it up : the Born-Oppenheimer approximation is a convenient way to focus on the electronic part of the Hamiltonian (equation (1.8)) which holds the main hurdle to solve the Schrödinger equation : the electron-electron repulsion. From now on, we will limit our focus on the electronic Hamiltonian $\hat{H}_{\mathrm{e}}$ and omit the "e" indix.

$$\hat{H} = \hat{H}_{\mathrm{e}} = -\sum_{i}^{N} \frac{1}{2}\Delta_i - \sum_{A}^{Q}\sum_{i}^{N} \frac{Z_A}{r_{Ai}} + \sum_{i>j} \frac{1}{r_{ij}} \tag{1.11}$$

Warning : The Born-Oppenheimer holds for most cases. However, it's known to fail for conical intersections when there is a strong coupling between between potential energy surfaces of different states. The approximation corresponds to assuming that electrons can react almost instantly to the change of nuclear coordinates. But sometimes, a small change of nuclear coordinates has a huge impact on the electronic structure. Som common cases are :

- at the transition state for chemical reactions;
- when studying the dynamics of excited states (photochemical reactions);
- when the Jahn -Teller effect occurs (asymmetric occupation of degenerate orbitals).

1.2 Hartree Product, Pauli Exclusion Principle and Slater Determinants

If we ever end up with a problem that can be reduced to a mono-electronic operator $\hat{h}_1^i$ for which we have the eigenstates (ϕ_k), called spin-orbitals, and eigenvalues (ϵ_k),

$$\hat{h}\phi_k = \phi_k \tag{1.12}$$

And if the full Hamiltonian can be derived as nearly the sum of the mono-electronic ones ($\hat{H} \approx \sum_i \hat{h}_1^i$). Then, the wavefunction constructed by placing an electron in spin-orbitals is called a Hartree product :

$$\Psi^{\mathrm{Hartree}}\left(\mathbf{r}_1, \ldots, \mathbf{r}_N\right) = \phi_a\left(\mathbf{r}_1\right)\phi_b\left(\mathbf{r}_2\right)\cdots\phi_k\left(\mathbf{r}_N\right) \tag{1.13}$$

By construction, it's an eigenvector of $\hat{H}' = \sum_i \hat{h}_1^i$:

$$\hat{H}'\Psi^{\mathrm{Hartree}} = E\Psi^{\mathrm{Hartree}} \tag{1.14}$$

with :

$$E = \epsilon_a + \epsilon_b + \cdots + \epsilon_k \tag{1.15}$$

In the Hartree product, we have a 1 to 1 correspondence between a given electron and the orbital it's placed into : $a, b, .., k$ are occupied by electrons $1, 2, ..., N$ respectively. But electrons are undistinguishable particles, so the Hartree product does not hold a correct physical meaning and is not a proper solution.

Permutation Operators To write down the Schrödinger equation, we had to give indices to electrons in its mathematical expression. But as electrons are indistinguishable, we can do a permutation of all the indices without changing the operator. We can write down a permutation operator which exchanges two electrons "i" and "j" :

$$\hat{P}_{ij} f\left(\mathbf{r}_i, \mathbf{r}_j\right) = f\left(\mathbf{r}_j, \mathbf{r}_i\right) \tag{1.16}$$

One can note that :

- the hamiltonian commute with all $\hat{P}_{ij}$ operators as we have dummy indices for electrons :

$$\hat{P}_{ij}\hat{H} = \hat{H}\hat{P}_{ij} = \hat{H} \tag{1.17}$$

  As both operators commute, they have a common set of eigenvectors (the $\{\Psi\}$).

- As $\hat{P}_{ij}^2$ is the identity operator, all its eigenvalues η are equal to ± 1. ($\hat{P}_{ij}^2\Psi = \Psi = \eta^2\Psi$)

- As the Ψ_i are also eigenstates of all the permutation operators :

$$\hat{P}_{ij}\Psi = \eta\Psi \qquad \text{avec } \eta = \pm 1 \tag{1.18}$$

  By definition (or postulate) :

  – all the particles for which $\eta = -1$ for permutations on two indices are called fermions (those particles have a half-integer spin). Electrons are fermions (with a spin of 1/2). It means that they must verify the antisymmetry principle : the wavefunction must be antisymmetric with respect to the exchange of two electrons : $\Psi(\ldots, \mathbf{r}_i, \ldots, \mathbf{r}_j, \ldots) = -\Psi(\ldots, \mathbf{r}_j, \ldots, \mathbf{r}_i, \ldots)$.

  – all the particles for which $\eta = 1$ for permutations on two indices are called bosons (they have an integer spin).

To help us build a wavefunction which fulfills this principle, we can use mathematical objects built to obey the antisymmetry principle which are called determinants. We will also try to build normalized wavefunctions. The physical objects respecting both conditions are called *Slater determinants*. They correspond to the antisymmetrized product corresponding to the Hartree product :

$$\Psi(\mathbf{r}_1, \ldots, \mathbf{r}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_a(\mathbf{r}_1) & \phi_b(\mathbf{r}_1) & \ldots & \phi_k(\mathbf{r}_1) \\ \phi_a(\mathbf{r}_2) & \phi_b(\mathbf{r}_2) & \ldots & \phi_k(\mathbf{r}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_a(\mathbf{r}_N) & \phi_b(\mathbf{r}_N) & & \phi_k(\mathbf{r}_N) \end{vmatrix} \tag{1.19}$$

where all the spin-orbitals $\phi_{a,b,..k}$ are occupied by a single electron.[bc] We can use a much lighter notation than the one used equation (**??**). It consists in writing only the diagonal which contains all the meaningful information:

$$\Psi(\mathbf{r}_1, \ldots, \mathbf{r}_N) = \left|\phi_a\left(\mathbf{r}_1\right)\phi_b\left(\mathbf{r}_2\right)\cdots\phi_k\left(\mathbf{r}_N\right)\right\rangle \tag{1.20}$$

$$= \left|\phi_a\phi_b\cdots\phi_k\right\rangle \tag{1.21}$$

[b]Here, to write the determinant we placed each orbital in a single column and each electronic coordinate in a row. But we could have done the opposite without changing the final object as both a matrix and its transpose share the same determinant.

[c]The Pauli exclusion principle appears here as a consequence of the antisymmetry of the wavefunction. If two identical orbitals (sharing the same quantum numbers for atoms), two columns would be identical. And by construction, the determinant would vanish.

We can see a Slater determinant as an equivalent for an electronic diagram indicating only the occupied orbitals (figure 1.1).

vision spin-orbitales

$$\Psi = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_a(\mathbf{r}_1,\omega_1) & \phi_b(\mathbf{r}_1,\omega_1) & \dots & \phi_k(\mathbf{r}_1,\omega_1) \\ \phi_a(\mathbf{r}_2,\omega_2) & \phi_b(\mathbf{r}_2,\omega_2) & \dots & \phi_k(\mathbf{r}_2,\omega_2) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_a(\mathbf{r}_N,\omega_N) & \phi_b(\mathbf{r}_N,\omega_N) & & \phi_k(\mathbf{r}_N,\omega_N) \end{vmatrix}$$

vision orbitales

$$\Psi = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi'_a(\mathbf{r}_1) & \overline{\phi}'_a(\mathbf{r}_1) & \dots & \overline{\phi}_f(\mathbf{r}_1) \\ \phi'_a(\mathbf{r}_2) & \overline{\phi}'_a(\mathbf{r}_2) & \dots & \overline{\phi}_f(\mathbf{r}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \phi'_a(\mathbf{r}_N) & \overline{\phi}'_a(\mathbf{r}_N) & & \overline{\phi}_f(\mathbf{r}_N) \end{vmatrix}$$

$\equiv$

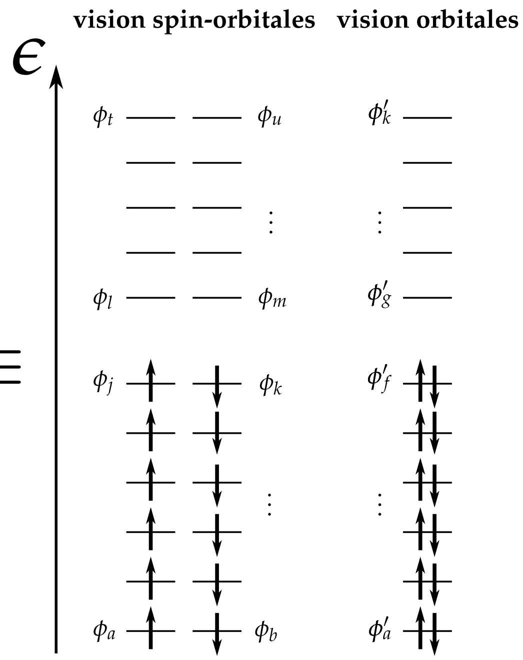


Figure 1.1: Equivalence between Slater determinants and the corresponding electronic diagrams. We can either use spin-orbitals, where a spin-orbital can contain only a single electron of given spin or use orbitals where we can put two electrons of opposite spin.

Spin-orbitals or orbitals ? Even if the spin does not appear explicitly in the Schrödinger equation, it is something to consider to describe properly the electronic structure. For molecules having an even number of electrons, we have two spin-orbitals with the same energy, one can hold an electron with a $m_s = 1/2$ spin and the other with a $-1/2$ spin. In this case, it means that we can decouple spin (ω_i) and space variables ($\mathbf{r}_i$) and we can re-index orbitals to keep only the spatial part.

We will still keep some information about the spin of the electron by writing a bar on top of the orbital if it's occupied by an electron of $m_s = 1/2$ projection and nothing otherwise :

$$\phi_a(\mathbf{r}_1,\omega_1) = \phi'_a(\mathbf{r}_1)\alpha(\omega_1) = \phi'_a(\mathbf{r}_1) \tag{1.22}$$
$$\phi_b(\mathbf{r}_2,\omega_2) = \phi'_a(\mathbf{r}_2)\beta(\omega_2) = \overline{\phi'_a(\mathbf{r}_2)} \tag{1.23}$$
$$\tag{1.24}$$

For the Slater determinant given figure 1.1, we have a full correspondance :

$$\Psi(\mathbf{r}_1,\ldots,\mathbf{r}_N,\omega_1,\ldots,\omega_N) = \frac{1}{\sqrt{N!}}\begin{vmatrix} \phi_a(\mathbf{r}_1,\omega_1) & \phi_b(\mathbf{r}_1,\omega_1) & \ldots & \phi_k(\mathbf{r}_1,\omega_1) \\ \phi_a(\mathbf{r}_2,\omega_2) & \phi_b(\mathbf{r}_2,\omega_2) & \ldots & \phi_k(\mathbf{r}_2,\omega_2) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_a(\mathbf{r}_N,\omega_N) & \phi_b(\mathbf{r}_N,\omega_N) & & \phi_k(\mathbf{r}_N,\omega_N) \end{vmatrix} \tag{1.25}$$

$$= \frac{1}{\sqrt{N!}}\begin{vmatrix} \phi'_a(\mathbf{r}_1) & \overline{\phi}'_a(\mathbf{r}_1) & \ldots & \overline{\phi}_f(\mathbf{r}_1) \\ \phi'_a(\mathbf{r}_2) & \overline{\phi}'_a(\mathbf{r}_2) & \ldots & \overline{\phi}_f(\mathbf{r}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \phi'_a(\mathbf{r}_N) & \overline{\phi}'_a(\mathbf{r}_N) & & \overline{\phi}_f(\mathbf{r}_N) \end{vmatrix} \tag{1.26}$$

$$= |\phi_a\phi_b\cdots\phi_j\phi_k\rangle = |\phi'_a\overline{\phi}'_a\cdots\phi'_f\overline{\phi}'_f\rangle \tag{1.27}$$

The two notations for the Slater determinant (equations (1.26) and (1.27)) are nice but not really useful to perform calculations. For that, we need to be able to expand the Slater determinants. We can use several rules such as expanding recursively with respect to each row or column. But in the end, we will always end up with $N!$ terms where :

- all the occupied spin-orbitals (ϕ_a to ϕ_k) appear exactly once,
- all the electronic coordinates appear exactly once ($\mathbf{r}_1$ to $\mathbf{r}_N$),
- a $+$ or $-$ sign in front of them, we will write.

It's the way to pair electrons with orbitals that will change in each term. We will re-organize each term to put the first-electron first and the N^{th} electron last. In this way all the orbitals will appear, but not in the same order as on the diagonal of the Slater determinant. The set of required permutations of two indices to go from the "diagonal" order to the other is called a permutation and is noted σ_μ and there are $N!$ of them. In the end, the expanded determinant can always be written :

$$\Psi(\mathbf{r}_1,\ldots,\mathbf{r}_N) = \frac{1}{\sqrt{N!}}\begin{vmatrix} \phi_a(\mathbf{r}_1) & \phi_b(\mathbf{r}_1) & \ldots & \phi_k(\mathbf{r}_1) \\ \phi_a(\mathbf{r}_2) & \phi_b(\mathbf{r}_2) & \ldots & \phi_k(\mathbf{r}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_a(\mathbf{r}_N) & \phi_b(\mathbf{r}_N) & & \phi_k(\mathbf{r}_N) \end{vmatrix} \tag{1.28}$$

$$= \frac{1}{\sqrt{N!}}\sum_{\mu}^{N!} \underbrace{\mathrm{Sgn}(\sigma_\mu)}_{=\pm 1}\, \phi_{\sigma_\mu^1}(\mathbf{r}_1)\times\cdots\times\phi_{\sigma_\mu^N}(\mathbf{r}_N) \tag{1.29}$$

with the $\{\sigma_\mu^1,\cdots,\sigma_\mu^N\}$ corresponding to the indices $\{a,\cdots,k\}$ given in a fixed order. An example for a system with three electrons split into three spin-orbitals is given in appendix A.1, page 45.

1.3 Which Slater Determinants ? The "Single-Determinant" Approximation

From a set of M spin-orbitals, it's possible to build $\binom{M}{N}$ Slater determinants: one for each way to place the N electrons into the M spin-orbitals. For the Hartree-Fock method, we will use what I will call the "single-determinant" approximation :

- we will use only **one** Slater determinant for the wavefunction;
- this unique determinant will be the one where all the orbitals with the lowest energies are occupied.

Warning : A single determinant cannot be a true eigenvector of the full Hamiltonian. Otherwise we would have solved the N-electron problem thanks to N coupled equations, each one dealing with only one electron.

1.4 Linear Combination of Atomic Orbitals

As molecular orbitals are functions of $\mathbb{R}^3$, if we have a full basis set $\{\chi_\mu\}$ for $\mathbb{R}^3$, then we can write them as:

$$\phi_k = \sum_{\mu}^{\infty} c_{\mu k}\chi_\mu \tag{1.30}$$

If the basis set is full, there is no approximation, but, it requires an infinite number of coefficients as this vector space is not finite. As a consequence it's quite common to truncate over a given set of functions that will be used as basis set of order M. It's this truncation that transforms the Linear Combination of Atomic Orbitals into an approximation :

$$\phi_k \approx \sum_{\mu}^{M} c_{\mu k}\chi_\mu \tag{1.31}$$

As all future calculations will have a cost that raises really fast with the size of the basis set (as $M^4/8$ for integrals for the Hartree Fock method, even higher for post-Hartree-Fock methods). It is important to have a basis set as small as possible. For real calculations, we will always end up with a compromise between the cost of the computation linked to the size of the basis, the accuracy needed and how simple it is to compute integrals with the chosen basis. There is no such thing as the "best" basis set. For example, if we use plane waves, the integrals are super easy to compute, but it requires an enormous basis set to be accurate. On the other hand, with Slater functions, the size of the basis can be much smaller, but the cost to compute integrals will be really high. Gaussian functions take a bit from both ends : it requires a basis set of moderate size and the integrals are rather simple to compute.

1.5 The variational principle

The variational principle is a really potent tool to find the ground state. The main idea is to minimize the following quantity :

$$\hat{E}\left[\Psi\right] = \frac{\langle \Psi_\zeta \mid \hat{H} \mid \Psi_\zeta \rangle}{\langle \Psi | \Psi \rangle} \tag{1.32}$$

by playing with all the variables contained in Ψ. For the Hartree-Fock method, it means finding all the coefficients $c_{\mu k}$ appearing equation 1.31 to minimize the energy. Usually, we operate in a way such that Ψ is normalized, but it's not necessary in principle. This principle holds only for the ground state, but searching a minimum brings *a lot* of extra information on what we are trying to find : all the derivatives with respect to all the parameters will have to be zero. We will also be able to use a lot of mathematical tools developed to find minima and zeros of functions. [d]

For a wavefunction depending on a single parameter ζ, it would mean that we are searching a value ζ_0 such that :

$$\left.\frac{\partial \hat{E}\left[\psi_\zeta\right]}{\partial \quad \zeta}\right|_{\zeta_0} = \frac{\partial}{\partial \zeta}\left.\left(\frac{\langle \psi_\zeta \mid \hat{H} \mid \psi_\zeta \rangle}{\langle \psi_\zeta \mid \psi_\zeta \rangle}\right)\right|_{\zeta_0} = 0 \tag{1.33}$$

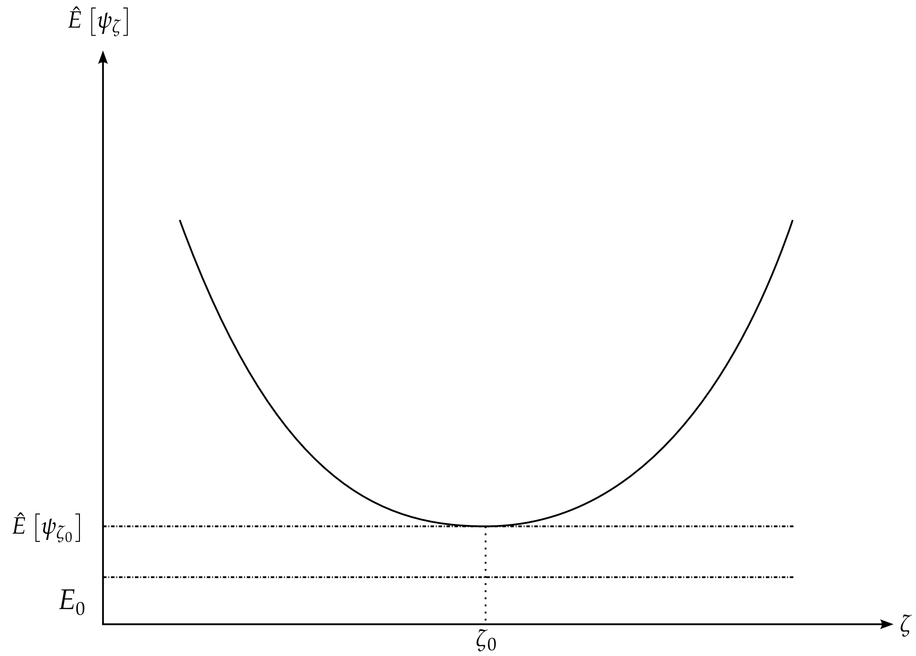


Figure 1.2: Illustration of the variational principle : we are trying to minimize the energy, for a single parameter ζ here, we hope to find an energy as close as possible to the ground state.

The variational principle gives a really important property of the energy of our trial wavefunction.

$$\hat{E}\left[\Psi\right] = \min \hat{E}\left[\Psi\right] \geqslant E_0 \tag{1.34}$$

where E_0 is the exact ground state energy. Or said in another way : the minimum energy for a given set of trial wavefunctions gives an upper bound of the energy of the ground state.

Proof If we write the "true" eigenvectors of $\hat{H}$ as Υ_i. They form a complete basis set for the vector space. We order them by their energy : $E_1 \leqslant E_2 \leqslant \cdots$ and orthonormalize them : $\langle \Upsilon_i \,|\, \Upsilon_j \rangle = \delta_{ij}$.

And if we decompose our trial wavefunction on this basis set:

$$\Psi = \sum_j c_j \Upsilon_j = \sum_j \underbrace{\left\langle \Psi \middle| \Upsilon_j \right\rangle}_{=c_j} \Upsilon_j \tag{1.35}$$

[d] In principle we could also find maxima of the energy. To check if it's minimum or not, we can either compute the second derivative with respect to the parameters or compute $\hat{E}\left[\Psi\right]$ close to the extrema and see if it's above or below the value found for the extremum.

If the trial wavefunction is normalized, as $\{\Upsilon_j\}$ are eigenstates of $\hat{H}$, $\hat{E}(\Psi)$ is easy to compute:

$$\hat{E}\left[\Psi\right] = \langle \Psi \mid \hat{H} \mid \Psi \rangle = \left\langle \sum_j c_j \Upsilon_j \middle| \hat{H} \middle| \sum_i c_i \Upsilon_i \right\rangle = \sum_{i;j} c_j^* c_i \langle \Upsilon_j \mid \hat{H} \mid \Upsilon_i \rangle \tag{1.36}$$

$$= \sum_j c_j^2 \underbrace{\langle \Upsilon_j \mid \hat{H} \mid \Upsilon_j \rangle}_{=E_j} \tag{1.37}$$

As $E_0 \leqslant E_j \quad \forall j$, we have the following inequality :

$$\hat{E}\left[\Psi\right] = \sum_j c_j^2 \underbrace{\langle \Upsilon_j \mid \hat{H} \mid \Upsilon_j \rangle}_{=E_j} \geqslant \left(\sum_j c_j^2\right) E_0 \tag{1.38}$$

As our trial wavefunction is normalized $\left(\sum_j c_j^2\right) = \langle \Psi | \Psi \rangle = 1$. We showed the inequality and that the equality holds only for the true ground state Υ_0. By minimizing the energy we are getting as close as possible to the ground state energy.

Note 1: The variational principle holds for the ground state of a given spin multiplicity for a given symmetry and not only for the true ground state. As the Hamiltonian is block diagonal, the variational principle holds for each block.

Note 2: The quantity $\min \hat{E}\left[\Psi\right]$ found with the variational principle is an upper bound of E_0. There is no reason to attain the true ground state energy. The variational principle gives only an inequality. In a finite basis set, the truncation done with the LCAO gives us many reasons to have difficulties to reach the true ground state. To be more optimistic : we also know that by expanding the basis set, we will be able to get closer to the ground state. But we should also remember that with the Hartree-Fock method, we will be in the vector space of wavefunctions described by a single determinant which is not the full vector space.

Note 3: In our case, the wavefunction will be an indirect function of all the coefficients decomposing the occupied molecular orbitals over the basis set functions used for the LCAO : $\Psi = f(\{c_{\mu k}\}; \{\chi_\mu\})$ (the k index runs over the N occupied molecular orbitals from ϕ_α to ϕ_ζ and the μ index runs over the M basis set functions χ_μ chosen for the LCAO). It means that we are finding the minimum of a function having $N \times M$ parameters.

Note 5: It is quite common to perform the same calculation of $\hat{E}[\Psi]$ for growing basis sets: once the energy converges to a given value, it usually means that we took a vector space big enough to obtain the best minimum to describe the ground state as well as we could within our set of hypothesis and approximations. If the cost of the computation to attain the convergence, we have to make a compromise.

1.6 Lagrange Multipliers

The presentation of Lagrange multipliers given here focuses on quantum theory, for a introduction from a mathematical standpoint, you can watch these videos https://www.youtube.com/watch?v=8mjcnxGMwFo, https://www.youtube.com/watch?v=5A39Ht9Wcu0 or go to https://tutorial.math.lamar.edu/Classes/CalcIII/LagrangeMultipliers.aspx for simple examples.

Lagrange multipliers are a convenient way to apply the variational principle while adding some extra additional constraints linked to the physical meaning of the objects that we are trying to find. We will build an operator called a Lagrangian by putting together the quantity we want to minimize and the constraints (stated as "something is equal to zero") multiplied by an unknown quantity called a Lagrange multiplier :

$$\hat{\mathcal{L}}[\phi] = \underbrace{\hat{f}[\phi]}_{\text{quantity to minimize}} - \underbrace{\lambda}_{\text{Lagrange multiplier}} \times \underbrace{\hat{g}[\phi]}_{\text{constraint written as } \hat{g}[\phi]=0} \tag{1.39}$$

where $\hat{f}$ and $\hat{g}$ are operators acting on the object ϕ. This object combines in a single quantity both the physical problem and its constraints. It's a way to gather several equations together.

In quantum chemistry, the constraints are generally linked to the normalization or the orthonormality of the orbitals or the wavefunction.

After building the Lagrangian, we will derive it with respect to all its variable and require all derivatives to be equal to zero. This derivation can be either a functional derivative (where we change continuously the function ϕ) or a "common" derivative with respect to some given variables. In the second case, it means that we require :

$$\frac{\partial \, \hat{\mathcal{L}}[\phi]}{\partial \quad c_i} = 0 \qquad \qquad \forall c_i \tag{1.40}$$

where c_i is a variable appearing in ϕ, such as the coefficient for the decomposition of the molecular orbital ϕ on the atomic orbitals χ_μ.

1.6.1 A first example : finding the orbitals of a mono-electronic operator

Before using Lagrange multipliers for the full wavefunction, we will show how this mathematical tool can be used to find the orbitals ϕ_k for a mono-electronic operator $\hat{h}_1$. As stated in section 1.5 we will use simultaneously :

- the variational principle : we want too minimize the orbital energies

$$\hat{\epsilon}[\phi_k] = \frac{\left\langle \phi_k \middle| \hat{h} \middle| \phi_k \right\rangle}{\langle \phi_k | \phi_k \rangle} \tag{1.41}$$

- but we also want the orbitals to be normalized which will add a new constraint : $\langle \phi_k | \phi_k \rangle - 1$

We will thus create the Lagrangian as :

$$\begin{aligned} \hat{\mathcal{L}}[\phi_k] &= \underbrace{\left\langle \phi_k \middle| \hat{h} \middle| \phi_k \right\rangle}_{\text{« principe variationnel »}} && -\lambda \underbrace{\left[\langle \phi_k | \phi_k \rangle - 1\right]}_{\text{normalisation}} && (1.42) \\ &= \hat{f}[\phi_k] && -\lambda \hat{g}[\phi_k] && (1.43) \end{aligned}$$

as the constraint is to have normalized orbital, it is possible to replace $\langle\phi_k|\phi_k\rangle$ by 1 in the first part of the Lagrangian.

We can now derive $\hat{\mathcal{L}}[\phi_k]$ with respect to all its variables which are the $\{c_{\mu k}\}$. We will consider both real orbitals χ_μ and real coefficients $c_{\mu k}$ to make the calculations easier.

$$\frac{\partial\,\hat{\mathcal{L}}[\phi_k]}{\partial\ \ c_{\tau k}} = \frac{\partial\,\left\langle \phi_k \,\middle|\, \hat{h} \,\middle|\, \phi_k \right\rangle}{\partial\ \ \ \ c_{\tau k}} - \lambda \frac{\partial\ [\langle\phi_k|\phi_k\rangle - 1]}{\partial\ \ \ \ c_{\tau k}} \tag{1.44}$$

For the first term, we have to expand it:

$$\frac{\partial\,\left\langle \phi_k \,\middle|\, \hat{h} \,\middle|\, \phi_k \right\rangle}{\partial\ \ \ \ c_{\tau k}} = \left\langle \frac{\partial\ \phi_k}{\partial\, c_{\tau k}} \,\middle|\, \hat{h} \,\middle|\, \phi_k \right\rangle + \left\langle \phi_k \,\middle|\, \hat{h} \,\middle|\, \frac{\partial\ \phi_k}{\partial\, c_{\tau k}} \right\rangle = \left\langle \chi_\tau \,\middle|\, \hat{h} \,\middle|\, \phi_k \right\rangle + \left\langle \phi_k \,\middle|\, \hat{h} \,\middle|\, \chi_\tau \right\rangle \tag{1.45}$$

As :

$$\left\langle \phi_k \,\middle|\, \hat{h} \,\middle|\, \phi_k \right\rangle = \left\langle \sum_{\mu}^{M} c_{\mu k}\chi_\mu \,\middle|\, \hat{h} \,\middle|\, \sum_{\nu}^{M} c_{\nu k}\chi_\nu \right\rangle \tag{1.46}$$

$$= \sum_{\mu}^{M} c_{\mu k}^2 \underbrace{\langle \chi_\mu \mid h \mid \chi_\mu \rangle}_{h_{\mu\mu}} + 2 \sum_{\nu>\mu}^{M;M} c_{\mu k} c_{\nu k} \langle \chi_\mu \mid h \mid \chi_\nu \rangle \tag{1.47}$$

We can use it to express the derivative :

$$\frac{\partial\,\left\langle \phi_k \,\middle|\, \hat{h} \,\middle|\, \phi_k \right\rangle}{\partial\ \ \ \ c_{\tau k}} = 2c_{\tau k}h_{\tau\tau} + 2\sum_{\nu\neq\tau} c_{\nu k}h_{\tau\nu} = 2\sum_{\mu} c_{\mu k}h_{\tau\nu} \tag{1.48}$$

For the second term, we can use the expression of the overlap :

$$\langle\phi_k|\phi_k\rangle = \sum_{\mu}^{M} c_{\mu k}^2 + 2\sum_{\nu>\mu}^{M;M} c_{\mu k}c_{\nu k}S_{\mu\nu} \tag{1.49}$$

$$= \sum_{\mu}^{M} c_{\mu k}^2 + \sum_{\mu}^{M}\sum_{\nu\neq\mu}^{M} c_{\mu k}c_{\nu k}S_{\mu\nu} \tag{1.50}$$

to compute the other derivative:

$$\frac{\partial\ [\langle\phi_k|\phi_k\rangle - 1]}{\partial\ \ \ \ c_{\tau k}} = \frac{\partial\ \langle\phi_k|\phi_k\rangle}{\partial\ \ \ c_{\tau k}} = \left\langle \frac{\partial\ \phi_k}{\partial\, c_{\tau k}} \,\middle|\, \phi_k \right\rangle + \left\langle \phi_k \,\middle|\, \frac{\partial\ \phi_k}{\partial\, c_{\tau k}} \right\rangle = 2\,\langle\chi_\tau|\phi_k\rangle = 2\sum_{\mu} c_{\mu k}S_{\tau\mu} \tag{1.51}$$

As we are looking for a minimum of $\hat{\mathcal{L}}[\phi_k]$, we have :

$$\frac{\partial\,\hat{\mathcal{L}}[\phi_k]}{\partial\ \ c_{\tau k}} = 2\sum_{\mu}\left(h_{\tau\mu} - \lambda S_{\tau\mu}\right)c_{\mu k} = 0 \qquad \tau = 1,\cdots,M \tag{1.52}$$

$$\Leftrightarrow \sum_{\mu}\left(h_{\tau\mu} - \lambda S_{\tau\mu}\right)c_{\mu k} = 0 \qquad \tau = 1,\cdots,M \tag{1.53}$$

The equation (1.53) is a generalized eigenstate problem. In the basis of the χ_μ, ϕ_i can be written as a vector (equation (1.54). And we can write the matrices of $\hat{h}$ (equation (1.55) and S in the same basis set :

$$\phi_k = \begin{pmatrix} c_{1k} \\ \vdots \\ c_{\mu k} \\ \vdots \\ c_{Mk} \end{pmatrix} \tag{1.54}$$

$$\hat{h} = \begin{pmatrix} h_{11} & \cdots & h_{1\tau} & h_{1\mu} & \cdots & h_{1M} \\ \vdots & \ddots & \vdots & \vdots & & \vdots \\ h_{\tau 1} & \cdots & h_{\tau\tau} & h_{\tau\mu} & \cdots & \vdots \\ h_{\mu 1} & \cdots & h_{\mu\tau} & h_{\mu\mu} & \cdots & \vdots \\ \vdots & & \vdots & \vdots & \ddots & \vdots \\ h_{M1} & \cdots & \cdots & \cdots & & h_{MM} \end{pmatrix} \tag{1.55}$$

$$\hat{S} = \begin{pmatrix} S_{11} & \cdots & \cdots & S_{1\mu} & S_{1M} \\ \vdots & \ddots & & \vdots & \\ S_{\tau 1} & & S_{\tau\tau} & S_{\tau\mu} & \vdots \\ \vdots & & & \ddots & \vdots \\ S_{M1} & \cdots & \cdots & \cdots & S_{MM} \end{pmatrix} \tag{1.56}$$

Equations (1.53) are equivalent to :

$$\left(\hat{h} - \lambda\hat{S}\right)\phi_k = 0 \tag{1.57}$$

As $\hat{h} - \lambda\hat{S}$ is an hermitian matrix, the eigenvalues are real. If we find an eigenvector ϕ_k (not null), it can be easily normalized to normalize it.

Note : We can see that using the variational principle on the Lagrangian is equivalent to solving the secular equation :

$$|H - \epsilon S| = 0 \tag{1.58}$$

1.6.2 Lagrange multiplier and energy

First Method: doing a othonormalization of the basis set We can orthonormalize the basis set, (with the Gram-Schmidt method or with any other method). In this basis set, the problem is a simple eigenvalue problem (as the overlap matrix is the identity matrix). The expression of $\hat{h}$ written in this basis set will be written h' and equation (1.57) becomes :

$$\left(\hat{h}' - \lambda I\right)\phi_k = 0 \tag{1.59}$$
$$\hat{h}'\phi_k = \lambda\phi_k \tag{1.60}$$

The Lagrange multiplier which was introduced rather artificially equation (1.42) has a profound physical meaning : it is the energy/eigenvalue ϵ_k for the eigenvector ϕ_k! Solving the set of equations found with the variational principle is strictly equivalent to finding all the eigenvalues and eigenvectors of equation (1.57) (or equation (1.60)). In practice, only the lower end of the spectra is of interest. We usually order the eigenvectors ϕ_k in raising order of energy. This way it's easier to build the proper Slater determinant where only the first spin-orbitals are filled (up to the number N of electrons).

Second method n°2 : Computing explicitly the energy We can also start from (1.57) and then compute the energy thanks to equation (1.32) :

$$\hat{\epsilon}\left[\phi_k\right] = \frac{\left\langle \phi_k \middle| \hat{h} \middle| \phi_k \right\rangle}{\left\langle \phi_k \middle| \phi_k \right\rangle} = \frac{\left\langle \sum_\mu^M c_{\mu k}\chi_\mu \middle| \hat{h} \middle| \sum_\nu^M c_{\nu k}\chi_\nu \right\rangle}{\left\langle \sum_\mu^M c_{\mu k}\chi_\mu \middle| \sum_\nu^M c_{\nu k}\chi_\nu \right\rangle} = \frac{\sum_\mu^M \sum_\nu^M c^*_{\mu k} c_{\nu k} \left\langle \chi_\mu \middle| \hat{h} \middle| \chi_\nu \right\rangle}{\sum_\mu^M \sum_\nu^M c^*_{\mu k} c_{\nu k} \left\langle \chi_\mu \middle| \chi_\nu \right\rangle} \tag{1.61}$$

We can then multiply equation (1.53) by $c^*_{\tau k}$ and sum over a dummy index τ :

$$\Leftrightarrow \sum_\mu \left(h_{\tau\mu} - \lambda S_{\tau\mu}\right) c_{\mu k} = 0 \qquad \tau = 1, \cdots, M \tag{1.62}$$

$$\Leftrightarrow \sum_\mu h_{\tau\mu} c_{\mu k} = \lambda \sum_\mu S_{\tau\mu} c_{\mu k} \tag{1.63}$$

$$\Leftrightarrow \sum_\mu \sum_\tau c^*_{\tau k} c_{\mu k} \underbrace{h_{\tau\mu}}_{\langle \chi_\tau | \hat{h} | \chi_\mu \rangle} = \lambda \sum_\mu \sum_\tau c^*_{\tau k} c_{\mu k} \underbrace{S_{\tau\mu}}_{\langle \chi_\tau | \chi_\mu \rangle} \tag{1.64}$$

As the we have dummy indices, we can the that the left-hand side corresponds to $\left\langle \phi_k \middle| \hat{h} \middle| \phi_k \right\rangle$ (equation (1.47)) and the right-hand side corresponds to $\left\langle \phi_k \middle| \phi_k \right\rangle$ (equation (1.50)). We can again see that λ is in fact $\hat{\epsilon}\left[\phi_k\right]$.

1.7 Summary

Up to now we :

1. simplified the Schrödinger equation into two parts : a nuclear one $\hat{H}_N$ (equation (1.5)) and an electronic one $\hat{H}_e$ (equation (1.6)).

2. saw that finding a mono-electronic operator linked to the full Hamiltonian will make the problem of solving the Schrödinger equation easier

3. saw that spin-orbitals ϕ_k are eigenvectors of mono-electronic operators and they have an eigenvalue which is their energy ϵ_k.

4. saw how to build Slater determinants from those orbitals $\Psi = f(\{\phi_k\})$. We will take the wavefunction as a single determinant and we will have to build its poly-electronic energy $E = g(\{\epsilon_k\})$.

These steps are schematically given on figure 1.3. At step 1, 2, 3 and 4, various approximations are involved:

- the Born-Oppenheimer approximation at step 1 ;
- the mono-electronic approximation at step 2 ;
- the LCAO approximation at step 3 ;
- the single-determinant approximation at step 4 ;

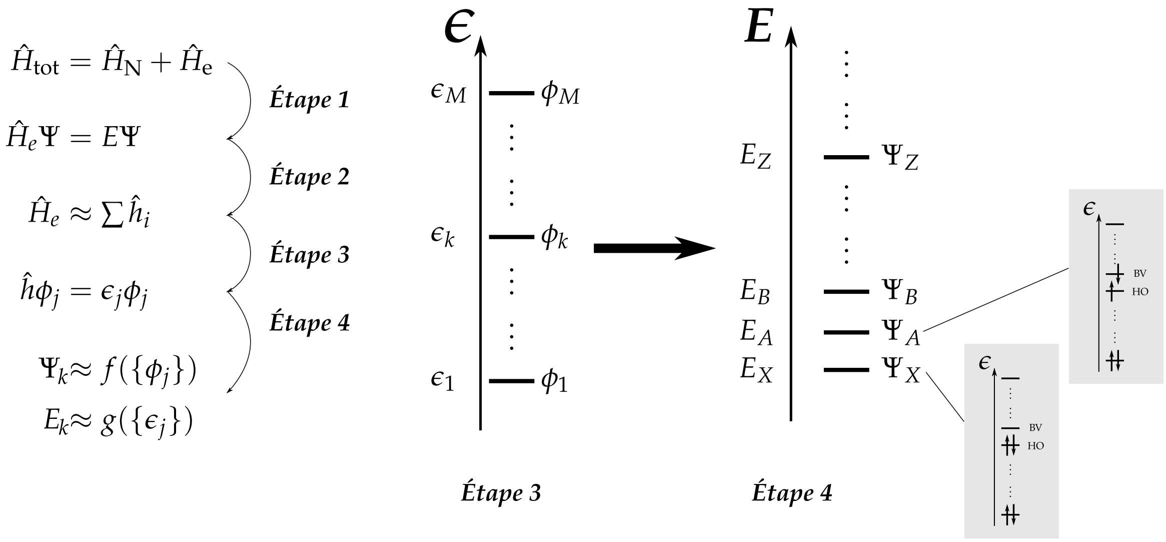


Figure 1.3: Common steps to solve the Schrödinger equation through mono-electronic operators.

Chapter 2

The Hartree-Fock method

2.1 Mono and Bi-Electronic Operators : the Slater-Condon Rules

To solve the Schrödinger equation, we will need to compute some terms like $\langle \Psi \mid \hat{H} \mid \Psi \rangle$ to find the energy associated to Ψ.

$$\hat{H} = -\sum_{i}^{N} \underbrace{\left(\frac{1}{2}\Delta_i + \sum_{A}^{Q} \frac{Z_A}{r_{Ai}} \right)}_{\hat{\Omega}_1^i} + \sum_{i>j} \underbrace{\frac{1}{r_{ij}}}_{\hat{\Omega}_2^{ij}} \tag{2.1}$$

The Hamiltonian has only two types of terms :

- mono-electronic operators acting on a single electron (for the kinetic and potential energy)
- bi-electronic operators acting on two electrons (for the electron-electron repulsion)

We saw the computation of some term in section 1.4. But here, we will have some differences :

- instead of working with orbitals, we now have a wavefunction which is a Slater determinant;
- we have bi-electronic terms in $\hat{H}$ that were not present in $\hat{h}$.

2.1.1 Mono-electronic operator terms

We take $\hat{\Omega}_1^i$ as a mono-electronic operator acting only on electron i.

Afterwards, all the orbitals will appear in "electron order" : the first orbital will hold the first electron and so-on (as in equation (1.29)). This way, we will be able to omit the $\mathbf{r}_i$ notations for the moment.

Diagonal elements

For the following Slater determinant:

$$|\Psi\rangle = |\phi_\alpha(\mathbf{r}_1)\cdots\phi_\tau(\mathbf{r}_i)\cdots\phi_\zeta(\mathbf{r}_N)\rangle = |\phi_\alpha\cdots\phi_\tau\cdots\phi_\zeta\rangle \tag{2.2}$$

$$\left\langle \Psi \middle| \hat{\Omega}_1^i \middle| \Psi \right\rangle = \frac{1}{N!}\left\langle \sum_\mu^{N!}\text{Sgn}(\sigma_\mu)\phi_{\sigma_\mu^1}\cdots\phi_{\sigma_\mu^i}\cdots\times\phi_{\sigma_\mu^N} \middle| \hat{\Omega}_1^i \middle| \sum_\nu^{N!}\text{Sgn}(\sigma_\nu)\phi_{\sigma_\nu^1}\cdots\phi_{\sigma_\nu^i}\cdots\phi_{\sigma_\nu^N} \right\rangle \tag{2.3}$$

$$= \frac{1}{N!}\sum_\mu^{N!}\sum_\nu^{N!}\text{Sgn}(\sigma_\mu)\,\text{Sgn}(\sigma_\nu)\left\langle \phi_{\sigma_\mu^1}\cdots\phi_{\sigma_\mu^i}\cdots\phi_{\sigma_\mu^N} \middle| \hat{\Omega}_1^i \middle| \phi_{\sigma_\nu^1}\cdots\phi_{\sigma_\nu^i}\cdots\phi_{\sigma_\nu^N} \right\rangle \tag{2.4}$$

$$= \frac{1}{N!}\sum_\mu^{N!}\sum_\nu^{N!}\text{Sgn}(\sigma_\mu)\,\text{Sgn}(\sigma_\nu)\underbrace{\left\langle \phi_{\sigma_\mu^1} \middle| \phi_{\sigma_\nu^1} \right\rangle}_{=\delta_{\sigma_\mu^1\sigma_\nu^1}}\cdots\left\langle \phi_{\sigma_\mu^i} \middle| \hat{\Omega}_1^i \middle| \phi_{\sigma_\nu^i} \right\rangle\cdots\underbrace{\left\langle \phi_{\sigma_\mu^N} \middle| \phi_{\sigma_\nu^N} \right\rangle}_{=\delta_{\sigma_\mu^N\sigma_\nu^N}} \tag{2.5}$$

As long as any term $\left\langle \phi_{\sigma_\mu^j} \middle| \phi_{\sigma_\nu^j} \right\rangle$ for any $j \neq i$ does not have the same indices on the left and right part of the braket, the full term vanishes because of the orthogonality of the orbitals ϕ_k. As a consequence, among the $N!$ terms, only the ones where $\sigma_\mu^j = \sigma_\nu^j$ pour $\forall j \neq i$ remain. And in this case, it also means that $\sigma_\mu^i = \sigma_\nu^i$, that is to say $\sigma_\mu = \sigma_\nu$.

$$\left\langle \Psi \middle| \hat{\Omega}_1^i \middle| \Psi \right\rangle = \frac{1}{N!}\sum_\mu^{N!}\underbrace{\text{Sgn}(\sigma_\mu)^2}_{=1}\underbrace{\prod_{j\neq i}\left\langle \phi_{\sigma_\mu^j} \middle| \phi_{\sigma_\nu^j} \right\rangle}_{=1}\times\left\langle \phi_{\sigma_\mu^i} \middle| \hat{\Omega}_1^i \middle| \phi_{\sigma_\nu^i} \right\rangle \tag{2.6}$$

In this sum, σ_μ^i can take the value $\alpha, \cdots, \tau, \cdots, \zeta$. So we must see how many terms of this kind exist. If we set $\sigma_\mu^i = \alpha$, then all the other $N-1$ indices in the permutation are free. We have $(N-1)!$ possibilities. It means that we can sum $(N-1)!$ identical terms for the N possibilities of σ_μ^i

$$\left\langle \Psi \middle| \hat{\Omega}_1^i \middle| \Psi \right\rangle = \left\langle \phi_\alpha(\mathbf{r}_1)\cdots\phi_\tau(\mathbf{r}_i)\cdots\phi_\zeta(\mathbf{r}_N) \middle| \hat{\Omega}_1^i \middle| \phi_\alpha(\mathbf{r}_1)\cdots\phi_\tau(\mathbf{r}_i)\cdots\phi_\zeta(\mathbf{r}_N) \right\rangle \tag{2.7}$$

$$= \frac{1}{N!}(N-1)!\sum_{k=\alpha,\cdots,\zeta}\left\langle \phi_k(\mathbf{r}_i) \middle| \hat{\Omega}_1^i \middle| \phi_k(\mathbf{r}_i) \right\rangle = \frac{1}{N}\sum_{k=\alpha,\cdots,\zeta}\left\langle \phi_k \middle| \hat{\Omega}_1^i \middle| \phi_k \right\rangle \tag{2.8}$$

If we now sum over the N identical Ω_1^i operators and not only the i-th one, and if the ϕ_k are eigenvalues of Ω_1:

$$\hat{\Omega}_1^{\text{tot}} = \sum_{i=1}^{N} \hat{\Omega}_1^i \tag{2.9}$$

$$\left\langle \Psi \mid \hat{\Omega}_1^{\text{tot}} \mid \Psi \right\rangle = N \left\langle \Psi \middle| \hat{\Omega}_1^i \middle| \Psi \right\rangle = \sum_{k=\alpha,\cdots,\zeta} \left\langle \phi_k \middle| \hat{\Omega}_1^i \middle| \phi_k \right\rangle = \sum_{k=\alpha,\cdots,\zeta} \epsilon_k \tag{2.10}$$

We find that the full term corresponds to the sum of the expectation values for all the orbitals as for a simple Hartree product.

If the ϕ_k are not eigenvectors:

$$\left\langle \Psi \mid \hat{\Omega}_1^{\text{tot}} \mid \Psi \right\rangle = \sum_{k=\alpha,\cdots,\zeta} h_{kk} = \sum_{k=\alpha,\cdots,\zeta} \langle \phi_k | \, \Omega_1 \, | \phi_k \rangle \tag{2.11}$$

An example is given in the appendices (section A.2.1).

Off diagonal elements

We will now compute terms involving different Slater determinants.[a]

$$|\Psi\rangle = |\phi_\alpha(\mathbf{r}_1)\cdots\phi_\tau(\mathbf{r}_i)\cdots\phi_\zeta(\mathbf{r}_N)\rangle = |\phi_\alpha\cdots\phi_\tau\cdots\phi_\zeta\rangle \tag{2.12}$$

$$|\Psi'\rangle = |\phi_{\alpha'}(\mathbf{r}_1)\cdots\phi_{\tau'}(\mathbf{r}_i)\cdots\phi_{\zeta'}(\mathbf{r}_N)\rangle = |\phi_{\alpha'}\cdots\phi_{\tau'}\cdots\phi_{\zeta'}\rangle \tag{2.13}$$

The calculation is done in a similar manner as previously. From equation (2.5), we can see that now there is only a single possibility to have a non vanishing term : σ_μ^i must now be equal to τ or τ', otherwise, we will have a $\langle\phi_\tau|\phi_{\tau'}\rangle$ which will cancel the whole term. Thus we have

$$\left\langle \Psi' \middle| \hat{\Omega}_1^i \middle| \Psi \right\rangle = \left\langle \phi_{\alpha'}\cdots\phi_{\tau'}\cdots\phi_{\zeta'} \middle| \hat{\Omega}_1^i \middle| \phi_\alpha\cdots\phi_\tau\cdots\phi_\zeta \right\rangle \tag{2.14}$$

$$= \frac{1}{N} \left\langle \phi_{\tau'} \middle| \hat{\Omega}_1^i \middle| \phi_\tau \right\rangle \tag{2.15}$$

Then we can deduce that:

- if the determinants do differ by more than a single orbital (there would always be a term $\langle\phi_\tau|\phi_{\tau'}\rangle$ equal to zero):

$$\left\langle \Psi' \middle| \sum_i^N \hat{\Omega}_1^i \middle| \Psi \right\rangle = 0 \tag{2.16}$$

- if the determinants differ by only one spin-orbital (which has the index τ or τ').

$$\left\langle \Psi' \middle| \sum_i^N \hat{\Omega}_1^i \middle| \Psi \right\rangle = 0 \tag{2.17}$$

An example is given in the appendices (section A.2.2).

[a] It's not useful for the Hartree-Fock method but it might be of interest in other cases.

2.1.2 Bi-electronic terms

The principle is similar. We will first start for two Slater determinants not necessarily equal for an operator acting on the first and second electron :

$$|\Psi\rangle = \phi_\alpha(\mathbf{r}_1)\phi_\beta(\mathbf{r}_2)\cdots\phi_\tau(\mathbf{r}_i)\cdots\phi_\zeta(\mathbf{r}_N) \tag{2.18}$$

$$|\Psi'\rangle = \phi_{\alpha'}(\mathbf{r}_1)\phi_{\beta'}(\mathbf{r}_2)\cdots\phi_{\tau'}(\mathbf{r}_i)\cdots\phi_{\zeta'}(\mathbf{r}_N) \tag{2.19}$$

$$\left\langle \Psi' \,\middle|\, \Omega_2^{12} \,\middle|\, \Psi \right\rangle = \frac{1}{N!}\sum_\mu^{N!}\sum_\nu^{N!} \mathrm{Sgn}(\sigma_\mu)\,\mathrm{Sgn}(\sigma_\nu)\left\langle \phi_{\alpha'}(\mathbf{r}_1)\phi_{\beta'}(\mathbf{r}_2) \,\middle|\, \Omega_2^{12} \,\middle|\, \phi_\alpha(\mathbf{r}_1)\phi_\beta(\mathbf{r}_2) \right\rangle \times \prod_{i=3}^{N}\delta_{\tau\tau'} \tag{2.20}$$

The matrix element does not vanish if and only if $\tau = \tau', \forall i > 2$. Otherwise, at least one term on the last part is zero becasue of the orthogonality of the basis set. It means that : *the integral is zero for a bi-electronic operator as soon as more than two spin orbitals differ in the two determinants considered.*

Before going further, we will consider what happens for two Hartree products.

Same determinant : $\psi' = \psi$ **or** $\{\phi_{\alpha'}, \cdots, \phi_{\zeta'}\} = \{\phi_\alpha, \cdots, \phi_\zeta\}$

As all orbitals must be identical except the one for electron 1 and 2, we can have only two cases: :

- $\alpha' = \alpha$ and $\beta' = \beta$, then :

$$\left\langle \phi_{\alpha'}(\mathbf{r}_1)\phi_{\beta'}(\mathbf{r}_2) \,\middle|\, \Omega_2^{12} \,\middle|\, \phi_\alpha(\mathbf{r}_1)\phi_\beta(\mathbf{r}_2) \right\rangle = \left\langle \phi_\alpha(\mathbf{r}_1)\phi_\beta(\mathbf{r}_2) \,\middle|\, \Omega_2^{12} \,\middle|\, \phi_\alpha(\mathbf{r}_1)\phi_\beta(\mathbf{r}_2) \right\rangle \tag{2.21}$$

- $\alpha' = \beta$ and $\beta' = \alpha$, then :

$$\left\langle \phi_{\alpha'}(\mathbf{r}_1)\phi_{\beta'}(\mathbf{r}_2) \,\middle|\, \Omega_2^{12} \,\middle|\, \phi_\alpha(\mathbf{r}_1)\phi_\beta(\mathbf{r}_2) \right\rangle = \left\langle \phi_\beta(\mathbf{r}_1)\phi_\alpha(\mathbf{r}_2) \,\middle|\, \Omega_2^{12} \,\middle|\, \phi_\alpha(\mathbf{r}_1)\phi_\beta(\mathbf{r}_2) \right\rangle \tag{2.22}$$

Off diagonal elements

It's not needed in the Hartree-Fock method, but may be of use in a near future. In this case, there is no restriction on the indices and we have:

- If there is a single difference of occupation between the two Slater determinants ($\alpha \neq \alpha'; \beta' = \beta$):

$$\left\langle \psi' \,\middle|\, \Omega_2^{12} \,\middle|\, \psi \right\rangle = \sum_\beta \left(\left\langle \phi_{\alpha'}\phi_\beta \,\middle|\, \Omega_2^{12} \,\middle|\, \phi_\alpha\phi_\beta \right\rangle - \left\langle \phi_{\alpha'}\phi_\beta \,\middle|\, \Omega_2^{12} \,\middle|\, \phi_\beta\phi_\alpha \right\rangle \right) \tag{2.23}$$

- if there are two differences($\alpha \neq \alpha'; \beta' \neq \beta$):

$$\left\langle \psi' \,\middle|\, \Omega_2^{12} \,\middle|\, \psi \right\rangle = \left(\left\langle \phi_{\alpha'}\phi_\beta \,\middle|\, \Omega_2^{12} \,\middle|\, \phi_\alpha\phi_\beta \right\rangle - \left\langle \phi_{\alpha'}\phi_\beta \,\middle|\, \Omega_2^{12} \,\middle|\, \phi_\beta\phi_\alpha \right\rangle \right) \tag{2.24}$$

- otherwise :

$$\left\langle \psi' \,\middle|\, \Omega_2^{12} \,\middle|\, \psi \right\rangle = 0 \tag{2.25}$$

For a Slater Determinant For the Slater determinant corresponding to the Hartree product seen equation (2.18) :

$$\left\langle \Psi \middle| \Omega_2^{12} \middle| \Psi \right\rangle = \frac{1}{N!} \sum_{\mu}^{N!} \sum_{\nu}^{N!} \mathrm{Sgn}(\sigma_\mu)\, \mathrm{Sgn}(\sigma_\nu) \left\langle \phi_{\sigma_\mu^1} \phi_{\sigma_\mu^2} \middle| \Omega_2^{12} \middle| \phi_{\sigma_\nu^1} \phi_{\sigma_\nu^2} \right\rangle \times \delta_{\sigma_\mu^3 \cdots \sigma_\mu^N ; \sigma_\nu^3 \cdots \sigma_\nu^N} \tag{2.26}$$

Among the $N!$ terms, all those where the permutations differ by more than two indices are zero. For the remaining terms, there are all possible pairs of spin-orbitals for σ_μ^1 and σ_μ^2, and once these two indices are fixed, there are $(N-2)!$ corresponding permutations, all of which will yield identical terms. Furthermore, for each pair of indices σ_μ^1 and σ_μ^2, we have seen that there are two corresponding terms (equation (2.21) and equation (2.22)). If $\sigma_\mu^1 = \sigma_\nu^1$ and $\sigma_\mu^2 = \sigma_\nu^2$, the two permutations have the same signature. If $\sigma_\mu^1 = \sigma_\nu^2$ and $\sigma_\mu^2 = \sigma_\nu^1$, then in this case, the signatures of the two permutations are opposite.[b]

$$\begin{aligned}\left\langle \Psi \middle| \Omega_2^{12} \middle| \Psi \right\rangle = \frac{1}{N!}(N-2)! \sum_{k=\alpha,\cdots,\zeta}^{N} \sum_{\substack{m=\alpha,\cdots,\zeta;\\ m\neq k}}^{N} \Big[&\left\langle \phi_k(\mathbf{r}_1)\phi_m(\mathbf{r}_2) \middle| \Omega_2^{12} \middle| \phi_k(\mathbf{r}_1)\phi_m(\mathbf{r}_2) \right\rangle \\ &- \left\langle \phi_m(\mathbf{r}_1)\phi_k(\mathbf{r}_2) \middle| \Omega_2^{12} \middle| \phi_k(\mathbf{r}_1)\phi_m(\mathbf{r}_2) \right\rangle \Big]\end{aligned} \tag{2.27}$$

$$= \frac{1}{N(N-1)} \sum_{k=\alpha,\cdots,\zeta}^{N} \sum_{\substack{m=\alpha,\cdots,\zeta;\\ m\neq k}}^{N} \left[\left\langle \phi_k\phi_m \middle| \Omega_2^{12} \middle| \phi_k\phi_m \right\rangle - \left\langle \phi_m\phi_k \middle| \Omega_2^{12} \middle| \phi_k\phi_m \right\rangle \right] \tag{2.28}$$

If we now sum over all possible pairs of two-electron operators:

$$\Omega_2^{\mathrm{tot}} = \frac{1}{2} \sum_{i,j}^{N} \Omega_2^{ij} \tag{2.29}$$

$$\left\langle \Psi \middle| \Omega_2^{\mathrm{tot}} \middle| \Psi \right\rangle = \frac{1}{N(N-1)} \frac{1}{2} \sum_{i,j}^{N} \sum_{k=\alpha,\cdots,\zeta}^{N} \sum_{\substack{m=\alpha,\cdots,\zeta;\\ m\neq k}}^{N} \left[\left\langle \phi_k\phi_m \middle| \Omega_2^{ij} \middle| \phi_k\phi_m \right\rangle - \left\langle \phi_m\phi_k \middle| \Omega_2^{ij} \middle| \phi_k\phi_m \right\rangle \right] \tag{2.30}$$

The summation over all the i, j indices give $N(N-1)$ identical terms, so :

$$\left\langle \Psi \middle| \Omega_2^{\mathrm{tot}} \middle| \Psi \right\rangle = \frac{1}{2} \sum_{k=\alpha,\cdots,\zeta}^{N} \sum_{\substack{m=\alpha,\cdots,\zeta;\\ m\neq k}}^{N} \left[\left\langle \phi_k\phi_m \middle| \Omega_2^{12} \middle| \phi_k\phi_m \right\rangle - \left\langle \phi_m\phi_k \middle| \Omega_2^{12} \middle| \phi_k\phi_m \right\rangle \right] \tag{2.31}$$

$$= \frac{1}{2} \sum_{k=\alpha,\cdots,\zeta}^{N} \sum_{m=\alpha,\cdots,\zeta}^{N} \left[\underbrace{\left\langle \phi_k\phi_m \middle| \Omega_2^{12} \middle| \phi_k\phi_m \right\rangle}_{=J_{km}} - \underbrace{\left\langle \phi_m\phi_k \middle| \Omega_2^{12} \middle| \phi_k\phi_m \right\rangle}_{=K_{km}} \right] \tag{2.32}$$

because $\left\langle \phi_k\phi_m \middle| \Omega_2^{12} \middle| \phi_k\phi_m \right\rangle = \left\langle \phi_k\phi_m \middle| \Omega_2^{12} \middle| \phi_m\phi_k \right\rangle$ if $k = m$, so we can add the missing term without changing the result.

[b] Because an additional exchange is needed to go back to the same permutation.

This sum contains the sum over all the possible pairs of orbitals of two types of integrals (which will be discussed in more detail in section 2.2.5):

- The first, J_{km}, with a "+" sign, where electron 1 occupies the same spin-orbital ϕ_k and electron 2 occupies the spin-orbital ϕ_m on both the left and right sides of the operator.
- The second, K_{km}, with a "$-$" sign, where electron 1 and electron 2 alternately occupy the orbitals ϕ_k and ϕ_m.

An example is provided in the appendices, section A.3, to illustrate the principle of the calculation.

An example is given in the appendices (section A.3).

2.2 The Fock Operator

Using the hamiltonian for the Schrödinger equation given equation (2.1) we will use the method of Lagrange multipliers seen section 1.6.

$$\hat{H} = -\sum_i^N \underbrace{\left(\frac{1}{2}\Delta_i + \sum_A^Q \frac{Z_A}{r_{Ai}}\right)}_{\hat{h}_1^i} + \sum_{i>j} \underbrace{\frac{1}{r_{ij}}}_{\hat{\Omega}_2^{ij}} = \hat{\Omega}_1^{\text{tot}} + \hat{\Omega}_2^{\text{tot}} \tag{2.33}$$

$$\hat{\mathcal{L}}[\Psi] = \left\langle \Psi \mid \hat{H} \mid \Psi \right\rangle - \sum_{k,m}^N \lambda_{km} \left(\langle \phi_k | \phi_m \rangle - \delta_{k,m} \right) \tag{2.34}$$

where $\hat{h}_1^{\text{tot}} = \sum_i^N \hat{h}_1^i$ et $\hat{\Omega}_2^{\text{tot}} = \frac{1}{2}\sum_{i\neq j}^N \frac{1}{r_{ij}}$.

Then we apply the variational principle seen at section 1.5 doing an infinitesimal variation $\delta\Psi$ of Ψ, which is done thanks to a variation of $\delta\phi_m$ on the spin orbitals ϕ_m.

$$\Psi \rightarrow \Psi + \delta\Psi \tag{2.35}$$

$$\phi_m \rightarrow \phi_m + \delta\phi_m \tag{2.36}$$

with

$$\delta\phi_m = \begin{pmatrix} \frac{\partial \phi_m}{\partial c_{1k}} \\ \vdots \\ \frac{\partial \phi_m}{\partial c_{\mu k}} \\ \vdots \\ \frac{\partial \phi_m}{\partial c_{Mk}} \end{pmatrix} \tag{2.37}$$

We want :

$$\frac{\delta\hat{\mathcal{L}}[\Psi]}{\delta\Psi} = 0 \tag{2.38}$$

$$\Leftrightarrow \frac{\delta\hat{\mathcal{L}}[\Psi]}{\delta\phi_m} = 0 \qquad \forall\delta\phi_m \qquad m = 1, \cdots, N \tag{2.39}$$

$$\Leftrightarrow \frac{\partial\, \hat{\mathcal{L}}[\Psi]}{\partial\ c_{\mu m}} = 0 \qquad \forall m, \mu \qquad m = 1, \cdots, N \qquad \mu = 1, \cdots, M \tag{2.40}$$

We will compute each term individually :

- the mono electronic part $\hat{h}_1^{\text{tot}}$;
- the bi-electronic part $\hat{\Omega}_2^{\text{tot}}$;
- the part linked to the constraint which is to have orthonormalized orbitals.

We will then write :

$$\delta\hat{\mathcal{L}}[\Psi] = \sum_{m}^{N} \delta_m \hat{\mathcal{L}}[\Psi] \tag{2.41}$$

2.2.1 Derivation of the mono-electronic part

We will compute the functional derivative :

$$\delta\hat{h}_1^{\text{tot}} = \left\langle \Psi + \delta\Psi \,\middle|\, \hat{h}_1^{\text{tot}} \,\middle|\, \Psi + \delta\Psi \right\rangle - \left\langle \Psi \,\middle|\, \hat{h}_1^{\text{tot}} \,\middle|\, \Psi \right\rangle \tag{2.42}$$

To this end, we will consider a variation of Ψ linked to a variation done on a given orbital ϕ_m. the "m" index after the δ in δ_m indicating the kind of derivation we are doing.

$$\delta_m\hat{h}_1^{\text{tot}} = \sum_{k=1,k\neq m}^{N} \left\langle \phi_k \,\middle|\, \hat{h}_1 \,\middle|\, \phi_k \right\rangle + \left\langle \phi_m + \delta\phi_m \,\middle|\, \hat{h}_1^m \,\middle|\, \phi_m + \delta\phi_m \right\rangle - \sum_{k=1}^{N} \left\langle \phi_k \,\middle|\, \hat{h}_1^k \,\middle|\, \phi_k \right\rangle \tag{2.43}$$

$$= \left\langle \phi_m + \delta\phi_m \,\middle|\, \hat{h}_1 \,\middle|\, \phi_m + \delta\phi_m \right\rangle - \left\langle \phi_m \,\middle|\, \hat{h}_1 \,\middle|\, \phi_m \right\rangle \tag{2.44}$$

$$= \iiint_{\mathbf{r}} (\phi_m + \delta\phi_m)^* \hat{h}_1 (\phi_m + \delta\phi_m)\, d\mathbf{r} - \iiint_{\mathbf{r}} \phi_m^* \hat{h}_1 \phi_m\, d\mathbf{r} \tag{2.45}$$

by linearity of $\hat{h}_1$ and of th integration operator:

$$= \iiint_{\mathbf{r}} \delta\phi_m^* \hat{h}_1 \delta\phi_m\, d\mathbf{r} + \iiint_{\mathbf{r}} \phi_m^* \hat{h}_1 \delta\phi_m\, d\mathbf{r} + \iiint_{\mathbf{r}} \delta\phi_m^* \hat{h}_1 \phi_m\, d\mathbf{r} \tag{2.46}$$

We neglect the first term as it is quadratic in $\delta\phi_m$ and we consider a small variation :

$$\delta_m\hat{h}_1^{\text{tot}} \approx \left\langle \delta\phi_m \,\middle|\, \hat{h}_1 \,\middle|\, \phi_m \right\rangle + \left\langle \phi_m \,\middle|\, \hat{h}_1 \,\middle|\, \delta\phi_m \right\rangle \tag{2.47}$$

As it has to b true for all $\delta\phi_m$:

$$\delta\hat{h}_1^{\text{tot}} \approx \sum_m \delta_m \hat{h}_1^{\text{tot}} = \left\langle \delta\Psi \,\middle|\, \hat{h}_1^{\text{tot}} \,\middle|\, \Psi \right\rangle + \left\langle \Psi \,\middle|\, \hat{h}_1^{\text{tot}} \,\middle|\, \delta\Psi \right\rangle \tag{2.48}$$

2.2.2 Derivation of the bi-electronic part

We can do the same kind of calculation for the bi-electronic part starting from equation (2.32).

$$\left\langle \Psi \,\middle|\, \Omega_2^{\text{tot}} \,\middle|\, \Psi \right\rangle = \frac{1}{2} \sum_{k=\alpha,\cdots,\zeta}^{N} \sum_{l=\alpha,\cdots,\zeta}^{N} \left[\left\langle \phi_k\phi_l \,\middle|\, \Omega_2^{12} \,\middle|\, \phi_k\phi_l \right\rangle - \left\langle \phi_k\phi_l \,\middle|\, \Omega_2^{12} \,\middle|\, \phi_l\phi_k \right\rangle \right] \tag{2.49}$$

For a small variation of ϕ_m, and as if it changes, it's changing in both the summation over l and k as we have dummy indices :

$$\begin{aligned}\delta_m\Omega_2^{\mathrm{tot}} = \frac{1}{2}\Bigg[& \sum_{\substack{k=\alpha,\cdots,\zeta;\\k\neq m}}^{N}\sum_{\substack{l=\alpha,\cdots,\zeta;\\l\neq m}}^{N}\cancel{(J_{kl}-K_{kl})}\\ & + \sum_{\substack{k=\alpha,\cdots,\zeta;\\k\neq m}}^{N}\left(\left\langle \phi_k(\phi_m+\delta\phi_m)\middle|\,\Omega_2^{12}\,\middle|\phi_k(\phi_m+\delta\phi_m)\right\rangle - \left\langle \phi_k(\phi_m+\delta\phi_m)\middle|\,\Omega_2^{12}\,\middle|(\phi_m+\delta\phi_m)\phi_k\right\rangle\right)\\ & + \sum_{\substack{l=\alpha,\cdots,\zeta;\\l\neq m}}^{N}\left(\left\langle (\phi_m+\delta\phi_m)\phi_l\middle|\,\Omega_2^{12}\,\middle|(\phi_m+\delta\phi_m)\phi_l\right\rangle - \left\langle (\phi_m+\delta\phi_m)\phi_l\middle|\,\Omega_2^{12}\,\middle|\phi_l(\phi_m+\delta\phi_m)\right\rangle\right)\\ & - \sum_{k=\alpha,\cdots,\zeta}^{N}\sum_{l=\alpha,\cdots,\zeta}^{N}\cancel{(J_{kl}-K_{kl})}\Bigg]\end{aligned} \tag{2.50}$$

Ω_2^{12} being linear, we can expand each term :

$$\begin{aligned}\left\langle \phi_k(\phi_m+\delta\phi_m)\middle|\,\Omega_2^{12}\,\middle|\phi_k(\phi_m+\delta\phi_m)\right\rangle = \Big[& \cancel{\left\langle \phi_k\phi_m\middle|\,\Omega_2^{12}\,\middle|\phi_k\phi_m\right\rangle} + \left\langle \phi_k\delta\phi_m)\middle|\,\Omega_2^{12}\,\middle|\phi_k\phi_m\right\rangle\\ & + \left\langle \phi_k\phi_m)\middle|\,\Omega_2^{12}\,\middle|\phi_k\delta\phi_m\right\rangle + \cancel{\left\langle \phi_k\delta\phi_m)\middle|\,\Omega_2^{12}\,\middle|\phi_k\delta\phi_m)\right\rangle}\Big]\end{aligned} \tag{2.51}$$

$$\left\langle (\phi_m+\delta\phi_m)\phi_k\middle|\,\Omega_2^{12}\,\middle|\phi_k(\phi_m+\delta\phi_m)\right\rangle = \cancel{\left\langle \phi_m\phi_k\middle|\,\Omega_2^{12}\,\middle|\phi_k\phi_m\right\rangle} + \left\langle \phi_m\phi_k\middle|\,\Omega_2^{12}\,\middle|\phi_k\delta\phi_m\right\rangle \tag{2.52}$$

$$\left\langle \delta\phi_m\phi_k\middle|\,\Omega_2^{12}\,\middle|\phi_k\phi_m\right\rangle + \cancel{\left\langle \delta\phi_m\phi_k\middle|\,\Omega_2^{12}\,\middle|\phi_k\delta\phi_m\right\rangle} \tag{2.53}$$

The last term can be neglected ($\nearrow$) as it is again quadratic in $\delta\phi_m$ and the sum of the first and last terms in (2.50) cancel out with the last term of (2.50) ($\searrow$).

As the two terms in the middle of equation (2.50) are equal (which deletes the factor $\frac{1}{2}$) :

$$\begin{aligned}\delta_m\Omega_2^{\mathrm{tot}} = \sum_{k;k\neq m}\Big[& \left\langle \phi_k\delta\phi_m\middle|\,\Omega_2^{12}\,\middle|\phi_k\phi_m\right\rangle + \left\langle \phi_k\phi_m\middle|\,\Omega_2^{12}\,\middle|\phi_k\delta\phi_m\right\rangle\\ & - \left\langle \phi_m\phi_k\middle|\,\Omega_2^{12}\,\middle|\phi_k\delta\phi_m\right\rangle - \left\langle \delta\phi_m\phi_k\middle|\,\Omega_2^{12}\,\middle|\phi_k\phi_m\right\rangle\Big]\end{aligned} \tag{2.54}$$

The summation over the indices is broken but as for $m=k$ the terms cancel each other :

$$\left\langle \phi_m\delta\phi_m\middle|\,\Omega_2^{12}\,\middle|\phi_m\phi_m\right\rangle = \left\langle \phi_m\delta\phi_m\middle|\,\Omega_2^{12}\,\middle|\phi_m\phi_m\right\rangle \tag{2.55}$$

We can add the term $k=m$ to the sum to restore the symmetry :

$$\begin{aligned}\delta_m\Omega_2^{\mathrm{tot}} = \sum_{k}\Big[& \left\langle \phi_k\delta\phi_m\middle|\,\Omega_2^{12}\,\middle|\phi_k\phi_m\right\rangle + \left\langle \phi_k\phi_m\middle|\,\Omega_2^{12}\,\middle|\phi_k\delta\phi_m\right\rangle\\ & - \left\langle \phi_k\phi_m\middle|\,\Omega_2^{12}\,\middle|\delta\phi_m\phi_k\right\rangle - \left\langle \phi_k\delta\phi_m\middle|\,\Omega_2^{12}\,\middle|\phi_k\phi_m\right\rangle\Big]\end{aligned} \tag{2.56}$$

2.2.3 Derivation of the constraint of orthogonality

Again, we can do the calculation by doing a variation $\delta\phi_m$ (the indices m and k are dummy indices) :

$$\delta_m \left(\sum_{k,m}^{N} \lambda_{km} \left(\langle \phi_k | \phi_m \rangle - \delta_{k,m} \right) \right) = \sum_{k}^{N} \lambda_{km} \left(\langle \delta\phi_m | \phi_k \rangle + \langle \phi_k | \delta\phi_m \rangle \right) \tag{2.57}$$

2.2.4 Full Derivation

We can now sum up the three terms and see that w always have a sum of one term and it's complex conjugate for all variations $\delta\phi_m$ of ϕ_m :

$$\begin{aligned} \delta_m \hat{\mathcal{L}}[\Psi] = & \left\langle \delta\phi_m \middle| \hat{h}_1 \middle| \phi_m \right\rangle + \sum_k \left(\left\langle \delta\phi_m \phi_k \middle| \Omega_2^{12} \middle| \phi_m \phi_k \right\rangle - \left\langle \delta\phi_m \phi_k \middle| \Omega_2^{12} \middle| \phi_k \phi_m \right\rangle \right) \\ & - \sum_k^N \lambda_{km} \langle \delta\phi_m | \phi_k \rangle + \text{c.c.} = 0 \end{aligned} \tag{2.58}$$

$$\begin{aligned} = & \iiint_{\mathbf{r}_1} \delta\phi_m^* (\mathbf{r}_1) \Bigg(\hat{h}_1 \phi_m (\mathbf{r}_1) \\ & + \sum_k^N \left(\iiint_{\mathbf{r}_2} \phi_k^* (\mathbf{r}_2) \frac{1}{r_{12}} \phi_k (\mathbf{r}_2) \phi_m (\mathbf{r}_1) \, \mathrm{d}\mathbf{r}_2 - \iiint_{\mathbf{r}_2} \phi_k^* (\mathbf{r}_2) \frac{1}{r_{12}} \phi_m (\mathbf{r}_2) \phi_k (\mathbf{r}_1) \, \mathrm{d}\mathbf{r}_2 \right. \\ & \left. - \lambda_{km} \phi_k (\mathbf{r}_1) \right) \Bigg) \mathrm{d}\mathbf{r}_1 + \text{c.c.} = 0 \end{aligned} \tag{2.59}$$

2.2.5 Fock, Coulombian and Exchange operators

As this relation must be true for any variation $\delta\phi_m$, it means that each term must be equal to zero. It may look intimidating but it can be written in a much simpler way :

$$\left\langle \delta\phi_m \middle| \hat{f} \middle| \phi_m \right\rangle = \left\langle \delta\phi_m \middle| \sum_k^N \lambda_{km} \phi_k \right\rangle \tag{2.60}$$

$$\Leftrightarrow \hat{f} \phi_m = \sum_k^N \lambda_{km} \phi_k \tag{2.61}$$

where we introduced the Fock operator:

$$\hat{f} = \hat{h}_1 + \sum_k^N \left(\hat{J}_k - \hat{K}_k \right) \tag{2.62}$$

with :

$$\hat{J}_k \phi_m (\mathbf{r}_1) = \left(\iiint_{\mathbf{r}_2, \omega_2} \phi_k^* (\mathbf{r}_2) \frac{1}{r_{12}} \phi_k (\mathbf{r}_2) \, \mathrm{d}\mathbf{r}_2 \right) \phi_m (\mathbf{r}_1) \tag{2.63}$$

$$\hat{K}_k \phi_m (\mathbf{r}_1) = \left(\iiint_{\mathbf{r}_2, \omega_2} \phi_k^* (\mathbf{r}_2) \frac{1}{r_{12}} \phi_m (\mathbf{r}_2) \, \mathrm{d}\mathbf{r}_2 \right) \phi_k (\mathbf{r}_1) \tag{2.64}$$

where $\hat{J}_k$ is called the Coulomb operator and $\hat{K}_k$ is the exchange operator (see below). Again the $k = m$ term ar added thanks to equations (2.55) and (2.56) as $\hat{J}_m\phi_m = \hat{K}_m\phi_m$.

The Fock operator is ... a mono-electronic operator! We will thus be able to fall down on the road paved in chapter 1 (see section 1.7).

But we must not be fooled : doing the variational minimization, we found a lower bound of the energy for the variational space that we chose, which is the one where we have a single determinant with "free" molecular orbitals. We should still be aware that :

- The variational principle decoupled the N-body problem in N problems of 1 variable. But doing so, we averaged the electronic repulsion as we integrated over the whole space. The Fock operator gives the best **single**-determinant wavefunction and the "best" orbitals.
- We can wonder on the importance of the basis set. Expanding it adds a lot of unoccupied orbitals that do not seem to play any role at the moment.

The Coulomb operator Equation (2.63) defining this operator shows that the Fock operator lowers the *averages* electronic repulsion.

$$\hat{J}_k\phi_m(\mathbf{r}_1) = \left(\iiint_{\mathbf{r}_2,\omega_2} |\phi_k(\mathbf{r}_2)|^2 \frac{1}{r_{12}}(\mathbf{r}_2)\, d\mathbf{r}_2 \right) \phi_m(\mathbf{r}_1) \tag{2.65}$$

The electron in r_1 in ϕ_m "feels" the *average* repulsion from electron 2 placed in ϕ_k. This operator is said to be local. As it depends only on $\mathbf{r}_1$.

The projection of equation (2.63) over ϕ_m gives:

$$\langle \phi_m |\, \hat{J}_k \,| \phi_m \rangle = \iiint_{\mathbf{r}_1} \iiint_{\mathbf{r}_2} |\phi_k(\mathbf{r}_2)|^2 \frac{1}{r_{12}} |\phi_m(\mathbf{r}_1)|^2\, d\mathbf{r}_2\, d\mathbf{r}_1 \tag{2.66}$$

We can see that it is the quantic equivalent of the electrostatic potential : instead of having two point charges in the classical approach, we now have the probability of having electron 1 in $\mathbf{r}_1$ and electron 2 en $\mathbf{r}_2$ if they lie in ϕ_m et ϕ_k respectively.

Exchange operator We can rewrite the operator defined equation (2.64) :

$$\hat{K}_k\phi_m(\mathbf{r}_1) = \left(\iiint_{\mathbf{r}_2,\omega_2} \phi_k^*(\mathbf{r}_2) \frac{1}{r_{12}} \phi_m(\mathbf{r}_2)\, d\mathbf{r}_2 \right) \phi_k(\mathbf{r}_1) \tag{2.67}$$

$$= \iiint_{\mathbf{r}_2,\omega_2} \phi_k^*(\mathbf{r}_2) \frac{1}{r_{12}} \hat{P}_{12} \left[\phi_k(\mathbf{r}_2)\, \phi_m(\mathbf{r}_1)\right] d\mathbf{r}_2 \tag{2.68}$$

where $\hat{P}_{12}$ is the permutation operator for electrons 1 and 2, it *exchanges* both electrons. This term really come from the antisymmetric structure of Slater determinants (equation (2.26)). Unlike the Coulomb operator, it is *non local* as it's value in $\mathbf{r}_1$ depends on the value of ϕ_k in $\mathbf{r}_2$.

Mean-field potential The Fock operator replaced the electron-electron repulsion by an *averaged* potential v^{HF} :

$$\hat{f} = \hat{h}_1^1 + \underbrace{\sum_k^N \iiint_{\mathbf{r}_2,\omega_2} \phi_k^*(\mathbf{r}_2) \frac{1}{r_{12}} \left(1 - \hat{P}_{12}\right) \phi_k(\mathbf{r}_2)\, d\mathbf{r}_2}_{v^{HF}} \tag{2.69}$$

Canonical form Equation (2.61) is not a standard eigenvector problem as there is the overlap matrix on the right-hand side of the equation, however, the λ_{km} are matrix elements of an hermitian matrix ($\lambda_{km} = \lambda^*_{mk}$). As the Fock operator does not depend on the electron considered, we can change the basis set to diagonalize the Fock operator in this basis, written $\{\phi'_k\}$. In this basis set, we fall down to a proper eigenstate problem where the Lagrange multiplier are the eigenstates of the Fock operator (see section 1.6.2) :

$$\hat{f}\phi'_m = \epsilon_m^{\mathrm{HF}}\phi'_m \tag{2.70}$$

From now on, we will use a basis set where equation (2.70) is valid.

Equation 2.70 looks like a simple eigenstate problem where the problem is just the diagonalization of a given matrix for a mono-electronic operator. But in fact it's much more complex : the Fock operator itself depends on the spin-orbitals that we are looking for! The ϕ_k do appear in equation 2.69. Thus, it would be more correct to write the equation as :

$$\hat{f}(\phi'_\alpha, \cdots, \phi'_\zeta) \times \phi'_m = \epsilon_m^{\mathrm{HF}} \times \phi'_m \tag{2.71}$$

To underline the non-linearity of the problem at hand. we will see how to solve it in section 2.4.

2.3 Roothan equations

As the problem is non linear and depends on unknown orbitals, it may seem untractable. But Roothan proposed a method to do the numerical resolution. The main idea is to use the LCAO approximation and express everything in the starting basis set of the atomic orbitals. Once it's done, we can do something similar to what was done at section 1.6 with the problem written as equation (2.70).

$$\phi_m = \sum_\mu^M c_{\mu m}\chi_k \qquad \forall m = 1, \cdots, M \tag{2.72}$$

$$\hat{f}\phi_m = \hat{f}\sum_\mu^M c_{\mu m}\chi_k = \epsilon_m \sum_\mu^M c_{\mu m}\chi_k \tag{2.73}$$

by projecting on χ_ν :

$$\Leftrightarrow \left\langle \chi_\nu \middle| \hat{f} \middle| \phi_m \right\rangle = \sum_\mu^M c_{\mu m} \left\langle \chi_\nu \middle| \hat{f} \middle| \chi_\mu \right\rangle = \epsilon_m \sum_\mu^M c_{\mu m} \left\langle \chi_\nu \middle| \chi_\mu \right\rangle \tag{2.74}$$

$$\sum_\mu^M f_{\nu\mu} c_{\mu m} = \epsilon_m \sum_\mu^M S_{\nu\mu} c_{\mu m} \tag{2.75}$$

Which is fully analogous to equation (1.53) :

$$\hat{f}C = \hat{S}C\hat{\varepsilon} \tag{2.76}$$

where :

$$\hat{f} = (f_{\nu\mu}) \qquad \hat{S} = (S_{\nu\mu}) \qquad \hat{\varepsilon} = \begin{pmatrix} \epsilon_1 & 0 & 0 & 0 \\ 0 & \epsilon_2 & 0 & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & 0 & \epsilon_M \end{pmatrix} \qquad C = \begin{pmatrix} c_{11} & \cdots & c_{1m} & \cdots & c_{1M} \\ c_{21} & \cdots & c_{2m} & \cdots & c_{2M} \\ \vdots & & \vdots & \ddots & \vdots \\ c_{M1} & \cdots & c_{mm} & \cdots & c_{MM} \end{pmatrix} \tag{2.77}$$

These are *the Roothan equations*.

From now on, we will have to compute the matrix elements $f_{\nu\mu}$:

$$f_{\nu\mu} = \left\langle \chi_\nu \middle| \hat{h}_1 \middle| \chi_\mu \right\rangle + \sum_k^N \left\langle \chi_\nu \times \sum_\tau^M c_{\tau k} \chi_\tau \middle| \frac{1}{r_{12}} (1 - \hat{P}_{12}) \middle| \chi_\mu \times \sum_\kappa^M c_{\kappa k} \chi_\kappa \right\rangle \tag{2.78}$$

$$= \left\langle \chi_\nu \middle| \hat{h}_1 \middle| \chi_\mu \right\rangle + \sum_k^N \sum_\tau^M \sum_\kappa^M c^*_{\tau k} c_{\kappa k} \left\langle \chi_\nu \chi_\tau \middle| \frac{1}{r_{12}} (1 - \hat{P}_{12}) \middle| \chi_\mu \chi_\kappa \right\rangle \tag{2.79}$$

$$= \left\langle \chi_\nu \middle| \hat{h}_1 \middle| \chi_\mu \right\rangle + \sum_k^N \sum_\tau^M \sum_\kappa^M c^*_{\tau k} c_{\kappa k} \left(\left\langle \chi_\nu \chi_\tau \middle| \frac{1}{r_{12}} \middle| \chi_\mu \chi_\kappa \right\rangle - \left\langle \chi_\nu \chi_\tau \middle| \frac{1}{r_{12}} \middle| \chi_\kappa \chi_\mu \right\rangle \right) \tag{2.80}$$

This shows that to compute the full matrix of the Fock operator we will have to compute three kinds of integrals :

- mono-electronic integrals for the kinetic energy of $\hat{h}_1$:

$$\iiint_{\mathbf{r}_1} \chi^*_\nu(\mathbf{r}_1) \left(-\frac{1}{2} \Delta \right) \chi^*_\mu(\mathbf{r}_1) \, d\mathbf{r}_1 \tag{2.81}$$

- mono-electronic integrals for the potential energy of $\hat{h}_1$:

$$\iiint_{\mathbf{r}_1} \chi^*_\nu(\mathbf{r}_1) \left(-\sum_A^Q \frac{Z_A}{\mathbf{r}_{A1}} \right) \chi^*_\mu(\mathbf{r}_1) \, d\mathbf{r}_1 \tag{2.82}$$

- bi-electronic integrals of the form :

$$\iiint_{\mathbf{r}_1} \iiint_{\mathbf{r}_2} \chi^*_\nu(\mathbf{r}_1) \chi^*_\tau(\mathbf{r}_2) \frac{1}{r_{12}} \chi_\mu(\mathbf{r}_1) \chi_\kappa(\mathbf{r}_2) \, d\mathbf{r}_1 \, d\mathbf{r}_2 \tag{2.83}$$

  As we have four indices, we have of the order $M^4/8$ of integrals to compute[c] with M being the size of the basis set. This huge amount of integrals to compute can be a limiting factor to perform a calculation (see table 2.1).

2.3.1 Orthogonalization of the basis set

If the starting basis set is orthonormal the Roothan equations (2.76) are directly an eigenstate problem as the overlap matrix is the identity.

---

[c] $\frac{1}{8} M (M+1) \left(M^2 + M + 2\right)$ exactly.

M	number of integrals to compute
4	55
10	1 540
100	12 753 775
1000	125 250 375 250
10000	1 250 250 037 502 500

Tableau 2.1: Number of bi-electronic integrals to compute with respect to the size of the basis set M.

But there is no reason to have an orthonormal basis set as they are not centered on the same atoms. Instead of keeping this non-orthonormal basis set which add a lot mathematical difficulties, it's much simpler to perform an orthonormalization first to make all further calculations much easier. The new orthonormal basis set will be noted $\{\chi_i^{\perp}\}$.

Any algorithm to do the orthogonalization of a basis set can work but there are two main ways used (the Gram-Schmidt algorithm is usually not used but it could).

Starting back from equation (1.50) we want a basis set where:

$$\chi_i^{\perp} = \sum_{\mu}^{M} z_{\mu i}\chi_{\mu} \tag{2.84}$$

$$\left\langle \chi_i^{\perp} \middle| \chi_j^{\perp} \right\rangle = \left\langle \sum_{\mu}^{M} z_{\mu i}\chi_{\mu} \middle| \sum_{\nu}^{M} z_{\nu j}\chi_{\nu} \right\rangle = \sum_{\mu}^{M}\sum_{\nu}^{M} z_{\mu i}^{*} z_{\nu j} \left\langle \chi_{\mu} \middle| \chi_{\nu} \right\rangle = \sum_{\mu}^{M}\sum_{\nu}^{M} z_{\mu i}^{*} z_{\nu j} S_{\mu\nu} \tag{2.85}$$

$$\Leftrightarrow Z^{\dagger}\hat{S}Z = I_M \tag{2.86}$$

where Z is the matrix of the coefficients $z_{\mu i}$, $\hat{S}$ is the overlap matrix and I_M is the identity matrix of size M. This equation gives a constraint that must be verified by Z to fulfill the orthonormalization.

As $\hat{S}$ is hermitian, w can diagonalize it thanks to a unitary transformation $\hat{U}$ (for which $\hat{U}^{\dagger}\hat{U} = I_M$):

$$\hat{S} = \hat{U}\hat{s}\hat{U}^{\dagger} \tag{2.87}$$

where $\hat{s}$ is diagonal matrix made from the eigenvalues of $\hat{S}$. We can show that all these eigenvalues are positive ($s_{ii} \geqslant 0$). We can then compute any power of the overlap matrix $\hat{S}^{\alpha}$:

$$\hat{S}^{\alpha} = \hat{U}\hat{s}^{\alpha}\hat{U}^{\dagger} \tag{2.88}$$

Löwdin orthogonalization The principle is to perform a symmetrical orthogonalization, to do so we use :

$$Z = \hat{S}^{-1/2} = \hat{U}\hat{s}^{-1/2}\hat{U}^{\dagger} \tag{2.89}$$

this choice respect the orthonormalization of the basis set :

$$Z^{\dagger}\hat{S}Z = \hat{U}\cancel{\hat{s}^{-1/2}}\underbrace{\hat{U}^{\dagger}\hat{U}}_{=I_M}\cancel{\hat{s}}\underbrace{\hat{U}^{\dagger}\hat{U}}_{=I_M}\cancel{\hat{s}^{-1/2}}\hat{U}^{\dagger} = I_M \tag{2.90}$$

Canonical orthogonalization We can also choose another choice Z' :

$$Z' = Us^{-1/2} \qquad\qquad Z'^{\dagger} = s^{-1/2}U^{\dagger} \tag{2.91}$$

qui vérifie également :

$$Z'^{\dagger}\hat{S}Z' = s^{-1/2}U^{\dagger}\hat{U}\hat{s}\hat{U}^{\dagger}Us^{-1/2} = I_M \tag{2.92}$$

Note: it may happen that an eigenvalue s_{ii} is really small, then we would have to divide by a quantity close to zero that may cause numerical problems. It happens with huge basis sets where a given orbital is nearly a linear combination of some others centered on other atoms. If it happens, we can solve the problem by getting rid of those useless vectors. To do so, we can order the s_{ii} in descending order and remove the base vectors for which s_{ii} is below a given threshold $s_{ii} < \varepsilon$. Doing so means that we eliminate redundant vectors in the basis set.

2.3.2 The same problem expressed in different basis sets

Solving the Roothan equation in this new orthonormal basis set $\{\chi_i^{\perp}\}$ brings it to a standard eigenvalue problem instead of remaining with a generalized eigenstate problem.

Instead of having to recompute all the integrals in the new $\{\chi_i^{\perp}\}$ basis set, we prefer to :

1. compute $\hat{F}$ in the starting basis set $\{\chi_\mu\}$;
2. compute Z which diagonalize $\hat{S}$;
3. perform the change of basis set $\hat{F}' = Z^{\dagger}FZ$;
4. solve the eignstate problem in the orthonormalized basis set $\hat{F}'$: $\hat{F}'C' = C'\epsilon$
5. compute back the coefficient in the starting basis set $C = ZC'$

By doing so, we can solve the Roothan equations (equation (2.76)) :

$$\hat{F}C = \hat{S}C\epsilon \tag{2.93}$$

$$\hat{F}ZC' = \hat{S}ZC'\epsilon \tag{2.94}$$

$$\Leftrightarrow \underbrace{Z^{\dagger}FZ}_{=\hat{F}'}C' = \epsilon \underbrace{Z^{\dagger}\hat{S}Z}_{\text{éq. (2.86)} \atop = \; I_M} C' \tag{2.95}$$

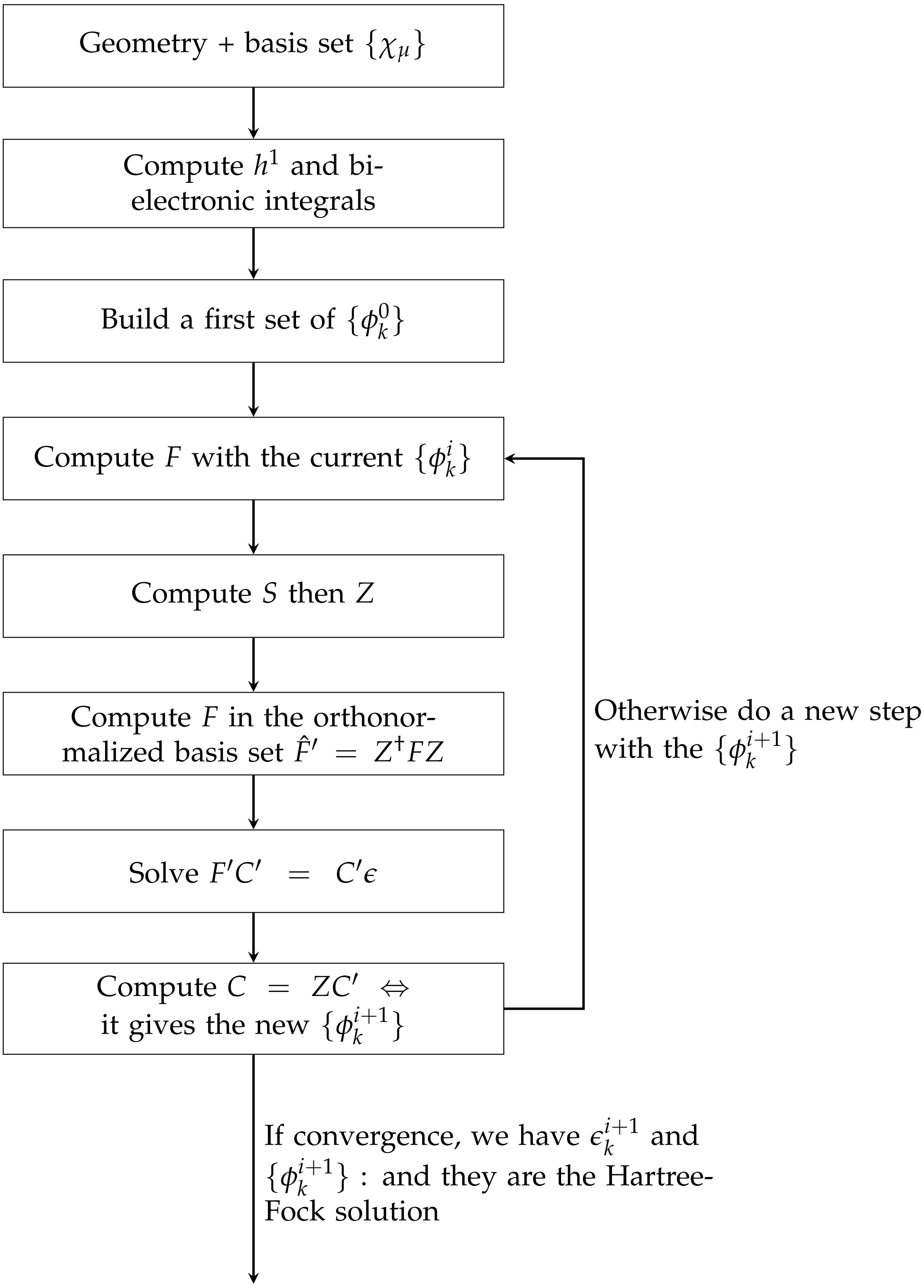
$$\Leftrightarrow \hat{F}'C' = C'\epsilon \tag{2.96}$$

In this way, we only need to compute $\hat{F}' = Z^{\dagger}FZ$ instead of computing again all the integrals.

2.4 SCF Method

Now we have a full plan to do a Hartree-Fock calculation :

1. Choose a basis set of atomic orbitals and define the geometry of the molcule and its charge to define N.
2. Compute all the mono electronic integrals to obtain $\hat{h}_1^i$ (defined equation (2.1) or (2.33) and written equation (2.81) and (2.82)).
3. Compute the $\frac{M(M+1)}{8}\left(M^2+M+2\right)$ bi-electronic integrals.
4. Build a starting set of molecular orbitals ϕ_i.
5. Build the Fock operator (équation (2.80)) for the current set of molecular orbitals.
6. Build the overlap matrix $\hat{S}$ then diagonalize it thanks to the proper change of basis set through Z (see section 2.3.1).
7. Compute the matrix $\hat{F}' = Z^\dagger F Z$. (see section 2.3.2)
8. Solve the eigenvalue problem $\hat{F}'$: $\hat{F}'C' = C'\epsilon$. (see section 2.3.2)
9. Compute the molecular orbitals in the starting basis set $C = ZC'$. (see section 2.3.2)
10. If the calculation did converge (measured with a given convergence criterion on the energy or on the change of molecular orbitals). It's done, otherwise go back to step 5 with the new set of molecular orbitals.


Geometry + basis set $\{\chi_\mu\}$
Compute h^1 and bi-electronic integrals
Build a first set of $\{\phi_k^0\}$
Compute F with the current $\{\phi_k^i\}$
Compute S then Z
Compute F in the orthonormalized basis set $\hat{F}' = Z^\dagger F Z$
Solve $F'C' = C'\epsilon$
Compute $C = ZC' \Leftrightarrow$ it gives the new $\{\phi_k^{i+1}\}$
Otherwise do a new step with the $\{\phi_k^{i+1}\}$
If convergence, we have ϵ_k^{i+1} and $\{\phi_k^{i+1}\}$: and they are the Hartree-Fock solution

Chapter 3

Applications

3.1 Orbital energies and total energy

Now that we have the molecular orbitals out of the diagonalization of mono-electronic operator, it's time to make a link between the orbitals energies $\{\epsilon_j\}$ and the energy of the full state E_Ψ associated to the corresponding SLater determinant (stp 4, section 1.7, figure 1.3).

We can start by computing the energy of a single orbital ϕ_k :

$$\epsilon_k = \frac{\left\langle \phi_k \middle| \hat{f} \middle| \phi_k \right\rangle}{\langle \phi_k | \phi_k \rangle} = \left\langle \phi_k \middle| \hat{h}_1 + \sum_m^N (\hat{J}_m - \hat{K}_m) \middle| \phi_k \right\rangle \tag{3.1}$$

$$= \left\langle \phi_k \middle| \hat{h}_1 \middle| \phi_k \right\rangle + \sum_m^N (J_{km} - K_{km}) \tag{3.2}$$

where J_{km} et K_{km} are the Coulomb and exchange integrals (defined in table 1). The energy is the sum of the mono-electronic term plus all the bi-electronic integrals which minimize the average electron-electron repulsion.

For the full energy, we have to compute it for the full Slater determinant corresponding to the ground state :

$$E = \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle} = \left\langle \Psi \middle| \sum_i^N \hat{h}_1^i \middle| \Psi \right\rangle + \left\langle \Psi \middle| \sum_{i>j}^N \frac{1}{r_{ij}} \middle| \Psi \right\rangle \tag{3.3}$$

We computed each term at equations (2.10) and (2.32), wo we have :

$$E = \sum_{k=\alpha,\cdots,\zeta}^N \left\langle \phi_k \middle| \hat{h}_1^i \middle| \phi_k \right\rangle + \frac{1}{2} \sum_{k=\alpha,\cdots,\zeta}^N \sum_{m=\alpha,\cdots,\zeta}^N (J_{km} - K_{km}) \tag{3.4}$$

Thanks to the Roothan equations, in the atomic orbitals basis, we have:

$$E = \sum_k^N \sum_\mu^M \sum_\nu^M c_{\mu k}^* c_{\nu k} \left\langle \chi_\mu \middle| \hat{h}_1^i \middle| \chi_\nu \right\rangle + \frac{1}{2} \sum_{k,m}^N \sum_{\mu\nu\tau\kappa}^M c_{\nu m}^* c_{\tau k}^* c_{\mu m} c_{\kappa k} \left(\left\langle \chi_\nu \chi_\tau \middle| \frac{1}{r_{12}} \middle| \chi_\mu \chi_\kappa \right\rangle - \left\langle \chi_\nu \chi_\tau \middle| \frac{1}{r_{12}} \middle| \chi_\kappa \chi_\mu \right\rangle \right) \tag{3.5}$$

where the indices $k = \alpha, \cdots, \zeta$ indicate the occupied orbitals in the Slater determinant. The energy is th sum od the mono-lectronic terms $\hat{h_1}$ and the bi-electronic terms summed over all pairs. The factor $1/2$ being here to avoid double counting for the pair i/j of electrons placed in ϕ_k and ϕ_m respectively.

For a closed shell molecule, equation (3.4) simplifies to:

$$E = \sum_{\Bbbk}^{N/2} \left\langle \phi_{\Bbbk} \middle| \hat{h}_1^i \middle| \phi_{\Bbbk} \right\rangle + \frac{1}{2} \sum_{\Bbbk}^{N/2} \sum_{m}^{N/2} \left(2J_{\Bbbk m} - K_{\Bbbk m}\right) \tag{3.6}$$

On important thing to note is that the total energy E **IS NOT** the sum of the orbital energies:

$$E = \sum_{k=\alpha,\cdots,\zeta}^{N} \left\langle \phi_k \middle| \hat{h}_1^i \middle| \phi_k \right\rangle + \frac{1}{2} \sum_{k=\alpha,\cdots,\zeta}^{N} \sum_{m=\alpha,\cdots,\zeta}^{N} \left(J_{km} - K_{km}\right) \tag{3.7}$$

$$\neq \sum_{k=\alpha,\cdots,\zeta} \epsilon_k = \sum_{k=\alpha,\cdots,\zeta}^{N} \left\langle \phi_k \middle| \hat{h}_1 \middle| \phi_k \right\rangle + \sum_{k=\alpha,\cdots,\zeta}^{N} \sum_{m=\alpha,\cdots,\zeta}^{N} \left(J_{km} - K_{km}\right) \tag{3.8}$$

The difference between the two being the double counting of electron pairs in the sum of the Hartree-Fock energies of the orbitals. This sum overestimates the energy of the ground states.

If we take into account the double counting of the electron-electron repulsion, we can still get the energy E by double counting the mono-electronic part and dividing by two:

$$E = \frac{1}{2} \sum_{k=\alpha,\cdots,\zeta}^{N} \left(\left\langle \phi_k \middle| \hat{h}_1^i \middle| \phi_k \right\rangle + \epsilon_k \right) \tag{3.9}$$

3.2 One-particle reduced density matrix and electronic densities

Once the orbitals are found, the wavefunction corresponding to the ground state can be found. But the orbitals are not observables. The electronic density on the other hand is an observable and it's interesting to compute it.

It is customary to link the square of the wavefunction of a single electron system to the probability of having the electron in the corresponding portion of space:

$$\rho_1^1(\mathbf{r}) = |\chi_k(\mathbf{r}_1)|^2 = \iiint_{\mathbf{r}_1} \chi^*(\mathbf{r}_1)\delta(\mathbf{r}_1 - \mathbf{r})\,\chi^*(\mathbf{r}_1)\,\mathrm{d}\mathbf{r}_1 \iiint_{\omega_1} s^*(\omega_1)\,s(\omega_1)\,\mathrm{d}\omega_1 \tag{3.10}$$

where $s(\omega_1)$ is the spin function of the spin-orbital. By construction, if χ is normed, ρ also is.

We can do the same for a molecular orbital decomposed on a set of atomic orbitals to find $\rho_1^1(\mathbf{r}_1)$:

$$|\phi_k|^2(\mathbf{r}) = \phi_k^*(\mathbf{r}) = \left(\sum_{\mu}^{M} c_{\mu k}^* \chi_\mu^*(\mathbf{r})\right)\left(\sum_{\nu}^{M} c_{\nu k}\chi_\nu(\mathbf{r})\right) \tag{3.11}$$

$$= \sum_{\mu}^{M}\sum_{\nu}^{M} c_{\mu k}^* c_{\nu k} \chi_\mu^*(\mathbf{r})\,\chi_\nu(\mathbf{r}) \tag{3.12}$$

We can extend this to a multi-electronic wavefunction by building the equivalent operator :

$$\hat{\rho}_1^{\text{tot}}(\mathbf{r}) = \sum_{i=1}^{N} \hat{\rho}_1^i(\mathbf{r}) = \sum_{i=1}^{N} \delta\left(\mathbf{r}_i - \mathbf{r}\right) \tag{3.13}$$

$$\rho_1^{\text{tot}}\left(\mathbf{r}\right) = \left\langle \Psi \,\middle|\, \hat{\rho}_1^{\text{tot}} \,\middle|\, \Psi \right\rangle = \sum_{k=\alpha,\cdots,\zeta}^{N} \left|\phi_k\left(\mathbf{r}\right)\right|^2 \tag{3.14}$$

as $\hat{\rho}_1^{\text{tot}}(\mathbf{r})$ is a mono-electronic operator, we can use the results of équation (2.10).

We can expand it over any chosen basis set :

$$\hat{\rho}_1^{\text{tot}}(\mathbf{r}) = \sum_{k=\alpha,\cdots,\zeta}^{N} \sum_{\mu}^{M} \sum_{\nu}^{M} c_{\mu k}^{*} c_{\nu k} \chi_{\mu}^{*}\left(\mathbf{r}\right) \chi_{\nu}\left(\mathbf{r}\right) = \sum_{\mu}^{M} \sum_{\nu}^{M} \underbrace{\left(\sum_{k=\alpha,\cdots,\zeta}^{N} c_{\mu k}^{*} c_{\nu k} \right)}_{=P_{\mu\nu}} \chi_{\mu}^{*}\left(\mathbf{r}\right) \chi_{\nu}\left(\mathbf{r}\right) \tag{3.15}$$

We can introduc the matrix $\mathbf{P} = P_{\mu\nu}$, called the *one-particle reduced density matrix* defined from the matrix of coefficients C defined equation (2.77) : $\mathbf{P} = (C^t)^* \times C$. By knowing $\mathbf{P}$ we know directly $\hat{\rho}_1^{\text{tot}}(\mathbf{r})$: we have to sum over the corresponding orbitals. We can also use it to write the Roothan equations to use only the density matrix. Equation (2.80) can be written as :

$$f_{\nu\mu} = \left\langle \chi_{\nu} \,\middle|\, \hat{h}_1 \,\middle|\, \chi_{\mu} \right\rangle + \sum_{\tau}^{M} \sum_{\kappa}^{M} \underbrace{\left(\sum_{k}^{N} c_{\tau k}^{*} c_{\kappa k} \right)}_{P_{\tau\kappa}} \left(\left\langle \chi_{\nu}\chi_{\tau} \,\middle|\, \frac{1}{r_{12}} \,\middle|\, \chi_{\mu}\chi_{\kappa} \right\rangle - \left\langle \chi_{\nu}\chi_{\tau} \,\middle|\, \frac{1}{r_{12}} \,\middle|\, \chi_{\kappa}\chi_{\mu} \right\rangle \right) \tag{3.16}$$

$$= \left\langle \chi_{\nu} \,\middle|\, \hat{h}_1 \,\middle|\, \chi_{\mu} \right\rangle + \sum_{\tau}^{M} \sum_{\kappa}^{M} P_{\tau\kappa} \left(\left\langle \chi_{\nu}\chi_{\tau} \,\middle|\, \frac{1}{r_{12}} \,\middle|\, \chi_{\mu}\chi_{\kappa} \right\rangle - \left\langle \chi_{\nu}\chi_{\tau} \,\middle|\, \frac{1}{r_{12}} \,\middle|\, \chi_{\kappa}\chi_{\mu} \right\rangle \right) \tag{3.17}$$

Solving the Roothan equations can be seen as finding a matrix density stable by the iterative SCF procedure. It also diagonalizes F in the basis of the orbitals that can be built out of the density matrix.

As the Fock operator, the full energy can be computed from equation (3.5) by using the one-particle reduced density matrix:

$$E = \sum_{\mu}^{M} \sum_{\nu}^{M} \underbrace{\sum_{k}^{N} c_{\mu k}^{*} c_{\nu k}}_{P_{\mu\nu}} \left\langle \chi_{\mu} \,\middle|\, \hat{h}_1^i \,\middle|\, \chi_{\nu} \right\rangle + \frac{1}{2} \sum_{\mu\nu\tau\kappa}^{M} \underbrace{\sum_{m}^{N} c_{\nu m}^{*} c_{\mu m}}_{P_{\nu\mu}} \underbrace{\sum_{k}^{N} c_{\tau k}^{*} c_{\kappa k}}_{P_{\tau\kappa}} \left(\left\langle \chi_{\nu}\chi_{\tau} \,\middle|\, \frac{1}{r_{12}} \,\middle|\, \chi_{\mu}\chi_{\kappa} \right\rangle - \left\langle \chi_{\nu}\chi_{\tau} \,\middle|\, \frac{1}{r_{12}} \,\middle|\, \chi_{\kappa}\chi_{\mu} \right\rangle \right) \tag{3.18}$$

$$= \sum_{\mu\nu}^{M} P_{\mu\nu} \left\langle \chi_{\mu} \,\middle|\, \hat{h}_1^i \,\middle|\, \chi_{\nu} \right\rangle + \frac{1}{2} \sum_{\mu\nu\tau\kappa}^{M} P_{\nu\mu} P_{\tau\kappa} \left(\left\langle \chi_{\nu}\chi_{\tau} \,\middle|\, \frac{1}{r_{12}} \,\middle|\, \chi_{\mu}\chi_{\kappa} \right\rangle - \left\langle \chi_{\nu}\chi_{\tau} \,\middle|\, \frac{1}{r_{12}} \,\middle|\, \chi_{\kappa}\chi_{\mu} \right\rangle \right) \tag{3.19}$$

$$= \frac{1}{2} \sum_{\mu} \sum_{\nu} P_{\mu\nu} \left(\hat{h}_{1,\mu\nu} + f_{\mu\nu} \right) \tag{3.20}$$

Chapter 4

A new beginning

With the Hartee-Fock method, we saw that we used orbitals as intermediate objects to build a wavefunction based on a single determinant. But in the end, all the information is contained within the electron density and the reduced particle density matrices. Thus we can try to take a different approach and use only the density as the object used to solve the Schrödinger equation, and skip everything related to molecular orbitals. That's the main idea behind DFT (Density Functional Theory). This method corresponds to another starting point to solve the Schrödinger equation as pointed in figure 1. We won't go into the details yet but we will only show that this new stance is also valid.

This approach was taken by Thomas and Fermi at the beginning of quantum mechanics, but fell in disgrace because of the poor results found at that time compared to wavefunction based approaches. This idea was also based on a naive idea without any solid foundation proving that it could give the proper solution to the Schrodinger equation. It took another 40 years to start afresh with a landmark paper from Hohenberg and Kohn to revive this field and obtain much more accurate results.

4.1 First Hohenberg and Kohn Theorem

The aim of this theorem is to prove that there is a 1 to 1 correspondence between the potential appearing in the full Hamiltonian and the electron density.

> The external potential $V_{\text{ext}}(\mathbf{r})$ is (to within a constant) a unique functional of $\rho(\mathbf{r})$; since, in turn $V_{\text{ext}}(\mathbf{r})$ fixes $\hat{H}$ we see that the full many particle ground state is a unique functional of $\rho(\mathbf{r})$.

This theorem tells us that instead of having to find a function of $3 \times N$ coordinates (3 coordinate per electron) as in the Hartree-Fock wavefunction, a function of only 3 coordinates, the density, is enough.

Proof If we have two external potentials $V_{\text{ext}}(\mathbf{r})$ and $V'_{\text{ext}}(\mathbf{r})$ that do differ by more than a constant but give the same electron density $\rho(\mathbf{r})$. Then we can build two Hamiltonians and two exact wavefunctions (true solutions of the Schrödinger equation) that give rise to the same electron density :

$$\hat{H} = \hat{T} + \hat{V}_{\text{ext}} + \hat{V}_{ee} \quad (4.1)$$

$$\hat{H}\Psi = E_0\Psi' \quad (4.2)$$

$$\rho(\mathbf{r}) = N \int \cdots \int |\Psi|^2 \, \mathrm{d}\mathbf{r}_2 \cdots \mathrm{d}\mathbf{r}_N \quad (4.3)$$

$$\hat{H}' = \hat{T} + \hat{V}'_{\text{ext}} + \hat{V}_{ee} \quad (4.4)$$

$$\hat{H}'\Psi' = E'_0\Psi' \quad (4.5)$$

$$\rho(\mathbf{r}) = N \int \cdots \int |\Psi'|^2 \, \mathrm{d}\mathbf{r}_2 \cdots \mathrm{d}\mathbf{r}_N \quad (4.6)$$

We can apply the variational principle for Ψ and Ψ' to $\hat{H}$ and $\hat{H}'$ and use $\hat{H} - \hat{H}' = \hat{V}_{\text{ext}} - \hat{V}'_{\text{ext}}$:

$$\begin{aligned}\left\langle \Psi' \right| \hat{H} \left| \Psi' \right\rangle &= \left\langle \Psi' \right| \hat{H}' \left| \Psi' \right\rangle + \left\langle \Psi' \right| \hat{H} - \hat{H}' \left| \Psi' \right\rangle && (4.7)\\ &= E'_0 + \iiint \rho(\mathbf{r}) \left(\hat{V}_{\text{ext}} - \hat{V}'_{\text{ext}}\right) \mathrm{d}\mathbf{r} && (4.8)\end{aligned}$$

$$\begin{aligned}\left\langle \Psi \right| \hat{H}' \left| \Psi \right\rangle &= \left\langle \Psi \right| \hat{H} \left| \Psi \right\rangle + \left\langle \Psi \right| \hat{H}' - \hat{H} \left| \Psi \right\rangle && (4.9)\\ &= E_0 + \iiint \rho(\mathbf{r}) \left(\hat{V}'_{\text{ext}} - \hat{V}_{\text{ext}}\right) \mathrm{d}\mathbf{r} && (4.10)\end{aligned}$$

As given by the variational principle, as Ψ and Ψ' differ as they are solution of equations that differ by more than a constant:

$$\begin{aligned}\left\langle \Psi \right| \hat{H} \left| \Psi \right\rangle = E_0 &< \left\langle \Psi' \right| \hat{H} \left| \Psi' \right\rangle && (4.11)\\ \left\langle \Psi' \right| \hat{H}' \left| \Psi' \right\rangle = E'_0 &< \left\langle \Psi \right| \hat{H} \left| \Psi \right\rangle && (4.12)\end{aligned}$$

Summing both equations and replacing by the results of equations (4.8) and (4.10) gives:

$$E_0 + E'_0 < E_0 + E'_0 \tag{4.13}$$

which is not true, thus we proved that our hypothesis was wrong: $V_{\text{ext}}(\mathbf{r})$ and $V'_{\text{ext}}(\mathbf{r})$ cannot differ by more than a constant.

As the energy of the ground state is a functional of the corresponding density for all possible external potentials, it can be written as the sum of a functional depending on the external potential and a universal functional taking into account the electronic energy and the electron-electron repulsion:

$$\hat{E}\left[\rho\right] = \iiint V_{\text{ext}}(\mathbf{r})\rho(\mathbf{r})\,\mathrm{d}\mathbf{r} + \hat{T}\left[\rho\right] + \hat{V}_{ee}\left[\rho\right] \tag{4.14}$$

It defines the Hohenberg and Kohn functional : $\hat{F}_{HK}\left[\rho\right] = \hat{T}\left[\rho\right] + \hat{V}_{ee}\left[\rho\right]$ which is independent of the problem. As the quantity $\iiint V_{\text{ext}}(\mathbf{r})\rho(\mathbf{r})\,\mathrm{d}\mathbf{r}$ is a simple one variable integral, it is "easy" to compute if we have access to $\rho(\mathbf{r})$. And as a consequence, it means that if we ever know $\hat{F}_{HK}$ and have access to the ground state density of the corresponding Schrödinger equation, the problem is fully solved.

As we used the variational principle, everything holds as long as we use the ground state properties (i.e. the ground state density). But it is no longer true for excited states.

4.2 Second Hohenberg and Kohn Theorem

We saw that if we have access to the ground state density, we can make a 1 to 1 correspondence between the external potential and the density. But we do not have yet a way to check that the density found/used is the true ground state density. But we have an ally that we already met : the variational principle. As $\hat{E}\left[\rho\right] = \iiint V_{\text{ext}}(\mathbf{r})\rho(\mathbf{r})\,\mathrm{d}\mathbf{r} + \hat{F}_{HK}\left[\rho\right]$. It means that:

$$E_0 = \hat{E}\left[\rho_0\right] \leqslant \hat{E}\left[\rho\right] \tag{4.15}$$

Thus to find the ground state density:

- with the variational principle, we have to find the minimum of $\hat{E}[\rho]$ out of all possible $\rho(\mathbf{r})$.

  A common problem is that all densities $\rho(\mathbf{r})$ are not necessarily linked to a Schrödinger equation. It means that we should be sure that a given antisymmetric wavefunction solution of the given Hamiltonian can give rise to the found density. That is called the V-representability problem. This is a simple problem to state but a hard mathematical problem to solve. It can be shown that taking only an antisymmetric wavefunction (not necessarily solution of a Schrödinger equation) is sufficient to obtain a proper density. Those densities are called N-representable. The Levy scheme (not presented here) ensures that N-representability of a density (it is a weaker constraint than V-representability) is enough to have a proper ground state density.

- As we will use the variational principle, it means that we will be able to use tools really similar to the ones that we used for the Hartree-Fock method.

  But as $\hat{F}_{HK}$ in not known, we will have to approximate it by another function $\hat{F}_{HK}^{\approx}$ and the quality of the ground state density found will be directly linked to the quality of $\hat{F}_{HK}^{\approx}$.

Appendix A

Mathematical developments

A.1 Expanding a Slater determinant

For a wavefunction of a system with 3 electrons placed in orbitals ϕ_a, ϕ_b, ϕ_c :

$$\Psi = |\phi_a\phi_b\phi_c\rangle = \frac{1}{\sqrt{3!}}\begin{vmatrix} \phi_a(\mathbf{r_1}) & \phi_b(\mathbf{r_1}) & \phi_c(\mathbf{r_1}) \\ \phi_a(\mathbf{r_2}) & \phi_b(\mathbf{r_2}) & \phi_c(\mathbf{r_2}) \\ \phi_a(\mathbf{r_3}) & \phi_b(\mathbf{r_3}) & \phi_c(\mathbf{r_3}) \end{vmatrix} \tag{A.1}$$

que l'on peut développer sous la forme suivante :

$$\begin{aligned} = \frac{1}{\sqrt{6}}[&-\phi_a(\mathbf{r_3})\phi_b(\mathbf{r_2})\phi_c(\mathbf{r_1}) + \phi_a(\mathbf{r_2})\phi_b(\mathbf{r_3})\phi_c(\mathbf{r_1}) + \phi_a(\mathbf{r_3})\phi_b(\mathbf{r_1})\phi_c(\mathbf{r_2}) \\ &-\phi_a(\mathbf{r_1})\phi_b(\mathbf{r_3})\phi_c(\mathbf{r_2}) - \phi_a(\mathbf{r_2})\phi_b(\mathbf{r_1})\phi_c(\mathbf{r_3}) + \phi_a(\mathbf{r_1})\phi_b(\mathbf{r_2})\phi_c(\mathbf{r_3})] \end{aligned} \tag{A.2}$$

En réorganisant pour conserver l'ordre des électrons :

$$\begin{aligned} = \frac{1}{\sqrt{6}}[&-\phi_c(\mathbf{r_1})\phi_b(\mathbf{r_2})\phi_a(\mathbf{r_3}) + \phi_c(\mathbf{r_1})\phi_a(\mathbf{r_2})\phi_b(\mathbf{r_3}) + \phi_b(\mathbf{r_1})\phi_c(\mathbf{r_2})\phi_a(\mathbf{r_3}) \\ &-\phi_a(\mathbf{r_1})\phi_c(\mathbf{r_2})\phi_b(\mathbf{r_3}) - \phi_b(\mathbf{r_1})\phi_a(\mathbf{r_2})\phi_c(\mathbf{r_3}) + \phi_a(\mathbf{r_1})\phi_b(\mathbf{r_2})\phi_c(\mathbf{r_3})] \end{aligned} \tag{A.3}$$

There are six permutations σ_μ in equation (A.3) :

$$\sigma_1 = cba \qquad \mathrm{Sgn}(\sigma_1) = -1 \tag{A.4}$$
$$\sigma_2 = cab \qquad \mathrm{Sgn}(\sigma_2) = +1 \tag{A.5}$$
$$\sigma_3 = bca \qquad \mathrm{Sgn}(\sigma_3) = +1 \tag{A.6}$$
$$\sigma_4 = acb \qquad \mathrm{Sgn}(\sigma_4) = -1 \tag{A.7}$$
$$\sigma_5 = bac \qquad \mathrm{Sgn}(\sigma_5) = -1 \tag{A.8}$$
$$\sigma_6 = abc \qquad \mathrm{Sgn}(\sigma_6) = +1 \tag{A.9}$$

We can see that $\mathrm{Sgn}(\sigma_\mu)$ equals $+1$ if the number of permutations needed to go back to the order *abc* (on the diagonal) is even and -1 if it's odd.

A.2 Computation of a mono-electronic operator

A.2.1 Computation of a diagonal element

This example illustrates section 2.1.1 for the Slater determinant expanded in the previous section. We suppose that the orbitals ϕ_i are eigenvectors associated to ϵ_i. The full calculation of $\left\langle \Psi \middle| \hat{h}_1 \middle| \Psi \right\rangle$ should have 36 terms. Among those terms, 30 are equal to zero : those were the permutation is not the same on the left and right hand side. For example if we have the permutation σ_3 on the left and σ_6 on the right:

$$\left\langle \phi_b(\mathbf{r_1})\phi_c(\mathbf{r_2})\phi_a(\mathbf{r_3}) \middle| \hat{h}_1 \middle| \phi_a(\mathbf{r_1})\phi_b(\mathbf{r_2})\phi_c(\mathbf{r_3}) \right\rangle = \left\langle \phi_b(\mathbf{r_1}) \middle| \hat{h}_1 \middle| \phi_a(\mathbf{r_1}) \right\rangle \times \underbrace{\langle \phi_c(\mathbf{r_2})|\phi_b(\mathbf{r_2})\rangle}_{=0} \times \underbrace{\langle \phi_a(\mathbf{r_3})|\phi_c(\mathbf{r_3})\rangle}_{=0} \tag{A.10}$$

$$= 0 \tag{A.11}$$

For the 6 remaining terms (identical permutations on the left and the right) the value of the term is equal to the energy of the orbital occupied by electron 1 in the permutation :

$$\left\langle \phi_a(\mathbf{r_1})\phi_b(\mathbf{r_2})\phi_c(\mathbf{r_3}) \middle| \hat{h}_1 \middle| \phi_a(\mathbf{r_1})\phi_b(\mathbf{r_2})\phi_c(\mathbf{r_3}) \right\rangle = \left\langle \phi_a(\mathbf{r_1}) \middle| \hat{h}_1 \middle| \phi_a(\mathbf{r_1}) \right\rangle \times 1 \times 1 = \epsilon_a \tag{A.12}$$

And among those 6 permutations there are always $(N-1)! = 2$ permutations where electron 1 occupies ϕ_a, ϕ_b and ϕ_c respctively (for example, electron 1 is in orbital ϕ_a for permutations σ_4 and σ_6), so :

$$\left\langle \Psi \middle| \hat{h}_1 \middle| \Psi \right\rangle = \frac{1}{6}\left(2 \times \epsilon_a + 2 \times \epsilon_b + 2 \times \epsilon_c\right) = \frac{1}{3}\left(\epsilon_a + \epsilon_b + \epsilon_c\right) \tag{A.13}$$

$$\left\langle \Psi \middle| \hat{h}_1 + \hat{h}_2 + \hat{h}_3 \middle| \Psi \right\rangle = 3 \times \frac{1}{3}\left(\epsilon_a + \epsilon_b + \epsilon_c\right) = \epsilon_a + \epsilon_b + \epsilon_c \tag{A.14}$$

A.2.2 Off Diagonal Element

We will take another Slater determinant differing by exactly one spin-orbital:

$$\Psi' = |\phi_a\phi_b\phi_d\rangle = \frac{1}{\sqrt{3!}}\begin{vmatrix} \phi_a(\mathbf{r_1}) & \phi_b(\mathbf{r_1}) & \phi_d(\mathbf{r_1}) \\ \phi_a(\mathbf{r_2}) & \phi_b(\mathbf{r_2}) & \phi_d(\mathbf{r_2}) \\ \phi_a(\mathbf{r_3}) & \phi_b(\mathbf{r_3}) & \phi_d(\mathbf{r_3}) \end{vmatrix} \tag{A.15}$$

There are 6 permutations σ'_μ :

$$\sigma'_1 = dba \qquad \mathrm{Sgn}(\sigma'_1) = -1 \tag{A.16}$$
$$\sigma'_2 = dab \qquad \mathrm{Sgn}(\sigma'_2) = +1 \tag{A.17}$$
$$\sigma'_3 = bda \qquad \mathrm{Sgn}(\sigma'_3) = +1 \tag{A.18}$$
$$\sigma'_4 = adb \qquad \mathrm{Sgn}(\sigma'_4) = -1 \tag{A.19}$$
$$\sigma'_5 = bad \qquad \mathrm{Sgn}(\sigma'_5) = -1 \tag{A.20}$$
$$\sigma'_6 = abd \qquad \mathrm{Sgn}(\sigma'_6) = +1 \tag{A.21}$$

Now, for the 36 terms, all cross terms are again null (with different permutations). For example, for σ'_1 et σ_2 :

$$\left\langle \phi_d\phi_b\phi_a \middle| \hat{h}_1 \middle| \phi_c\phi_a\phi_b \right\rangle = \left\langle \phi_d \middle| \hat{h}_1 \middle| \phi_c \right\rangle \underbrace{\langle \phi_b|\phi_a\rangle}_{=0} \underbrace{\langle \phi_a|\phi_b\rangle}_{=0} \tag{A.22}$$

And now for the 6 remaining terms, only those where σ_l differ only by the first index 1 are not null ($l = 1, 2$), the others ($l = 3, 4, 5, 6$) vanish bcause of the orthogonality of the ϕ_k :

For σ_1' and σ_1 (difference for électron 1) :

$$\left\langle \phi_d\phi_b\phi_a \middle| \hat{h}_1 \middle| \phi_c\phi_b\phi_a \right\rangle = \left\langle \phi_d \middle| \hat{h}_1 \middle| \phi_c \right\rangle \underbrace{\langle \phi_b|\phi_b \rangle}_{=1} \underbrace{\langle \phi_a|\phi_a \rangle}_{=1} \tag{A.23}$$

For σ_6' and σ_6 (no difference for electron 1) :

$$\left\langle \phi_a\phi_b\phi_d \middle| \hat{h}_1 \middle| \phi_a\phi_b\phi_c \right\rangle = \left\langle \phi_a \middle| \hat{h}_1 \middle| \phi_a \right\rangle \underbrace{\langle \phi_b|\phi_b \rangle}_{=1} \underbrace{\langle \phi_d|\phi_c \rangle}_{=0} \tag{A.24}$$

Thus we have :

$$\left\langle \Psi' \middle| \hat{h}_1 \middle| \Psi \right\rangle = \frac{2}{6} \left\langle \phi_d \middle| \hat{h}_1 \middle| \phi_c \right\rangle = \frac{1}{3} \left\langle \phi_d \middle| \hat{h}_1 \middle| \phi_c \right\rangle \tag{A.25}$$

$$\left\langle \Psi' \middle| \hat{h}_1 + \hat{h}_2 + \hat{h}_3 \middle| \Psi \right\rangle = \left\langle \phi_d \middle| \hat{h}_1 \middle| \phi_c \right\rangle \tag{A.26}$$

A.3 Bi-electronic operators

This example corresponds to section 2.1.2 for the Slater determinant expanded section A.1. We now want to compute : $\langle \Psi \mid \Omega_2^{12} \mid \Psi \rangle$.

Now, among the 36 terms, we need to keep all the ones where the index for electron 3 is unchanged. We can form three groups of this kind (equations (A.4) to (A.9)):

- σ_1 and σ_3 ;
- σ_2 and σ_4 ;
- σ_5 and σ_6 ;

Each time, we have four terms, for example for σ_5/σ_6 :

$$\left\langle \phi_b\phi_a\phi_c \middle| \Omega_2^{12} \middle| \phi_b\phi_a\phi_c \right\rangle = \left\langle \phi_b\phi_a \middle| \Omega_2^{12} \middle| \phi_b\phi_a \right\rangle \tag{A.27}$$

$$\left\langle \phi_a\phi_b\phi_c \middle| \Omega_2^{12} \middle| \phi_a\phi_b\phi_c \right\rangle = \left\langle \phi_a\phi_b \middle| \Omega_2^{12} \middle| \phi_a\phi_b \right\rangle \tag{A.28}$$

$$\left\langle \phi_b\phi_a\phi_c \middle| \Omega_2^{12} \middle| \phi_a\phi_b\phi_c \right\rangle = \left\langle \phi_b\phi_a \middle| \Omega_2^{12} \middle| \phi_a\phi_b \right\rangle \tag{A.29}$$

$$\left\langle \phi_a\phi_b\phi_c \middle| \Omega_2^{12} \middle| \phi_b\phi_a\phi_c \right\rangle = \left\langle \phi_a\phi_b \middle| \Omega_2^{12} \middle| \phi_b\phi_a \right\rangle \tag{A.30}$$

For real orbitals, the elements of equation (A.27) and (A.28) are equal. And the signature/sign of the permutation is the same and we will thus have a + sign. Similarly, the elements of equation (A.29) and (A.30) are equal but the signature/sign of the permutations differ, thus we will have a $-$ sign overall.

We deduce that :

$$\left\langle \Psi \middle| \; \Omega_2^{12} \; \middle| \Psi \right\rangle = \frac{2}{6} \left[\left\langle \phi_b \phi_a \middle| \; \Omega_2^{12} \; \middle| \phi_b \phi_a \right\rangle - \left\langle \phi_b \phi_a \middle| \; \Omega_2^{12} \; \middle| \phi_a \phi_b \right\rangle \right.$$
$$+ \left\langle \phi_c \phi_a \middle| \; \Omega_2^{12} \; \middle| \phi_c \phi_a \right\rangle - \left\langle \phi_c \phi_a \middle| \; \Omega_2^{12} \; \middle| \phi_a \phi_c \right\rangle$$
$$\left. + \left\langle \phi_b \phi_c \middle| \; \Omega_2^{12} \; \middle| \phi_b \phi_c \right\rangle - \left\langle \phi_b \phi_c \middle| \; \Omega_2^{12} \; \middle| \phi_c \phi_b \right\rangle \right] \quad \text{(A.31)}$$

$$\left\langle \Psi \middle| \; \Omega_2^{\mathrm{tot}} \; \middle| \Psi \right\rangle = \left\langle \Psi \middle| \; \Omega_2^{12} + \Omega_2^{13} + \Omega_2^{23} \; \middle| \Psi \right\rangle \quad \text{(A.32)}$$
$$= \left[\left\langle \phi_b \phi_a \middle| \; \Omega_2^{12} \; \middle| \phi_b \phi_a \right\rangle - \left\langle \phi_b \phi_a \middle| \; \Omega_2^{12} \; \middle| \phi_a \phi_b \right\rangle \right.$$
$$+ \left\langle \phi_c \phi_a \middle| \; \Omega_2^{12} \; \middle| \phi_c \phi_a \right\rangle - \left\langle \phi_c \phi_a \middle| \; \Omega_2^{12} \; \middle| \phi_a \phi_c \right\rangle$$
$$\left. + \left\langle \phi_b \phi_c \middle| \; \Omega_2^{12} \; \middle| \phi_b \phi_c \right\rangle - \left\langle \phi_b \phi_c \middle| \; \Omega_2^{12} \; \middle| \phi_c \phi_b \right\rangle \right] \quad \text{(A.33)}$$

We can see that we have a sum of two kinds of terms over all the existing pairs of electron.

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