In application of the variational principle, we are looking for the density ρ minimizing $E[\rho]$ under the normalization constraint. In order to find it, we introduce the Lagrangian $\mathcal{L}[\rho]$ and the Lagrange multiplier $\varepsilon/2$ (because of the normalization) such that

$$\mathcal{L}[\rho] = \int_{\mathbf{R}} \frac{1}{16} \frac{\rho'(x)^2}{\rho(x)} + \frac{1}{2} V_{\text{eff}}(x)\rho(x) - \frac{\varepsilon}{2}\rho(x)\mathrm{d}x.$$

The minimizing density is a solution of the equation $\delta \mathcal{L}/\delta \rho = 0$. We thus need to compute this functional derivative. Let $f(x, \rho, \rho')$ represent the integrand of $\mathcal{L}[\rho]$. We have

$$\frac{\delta f}{\delta \rho} = -\frac{1}{16} \left(\frac{\rho'(x)}{\rho(x)} \right)^2 + \frac{1}{2} V_{\text{eff}}(x) - \frac{\varepsilon}{2}, \quad \frac{\delta f}{\delta \rho'} = \frac{1}{8} \frac{\rho'(x)}{\rho(x)}.$$

The Euler-Lagrange equation gives us

$$0 = \frac{\delta L}{\delta \rho} = \frac{\delta f}{\delta \rho} - \frac{\mathrm{d}}{\mathrm{d}x} \left\{ \frac{\delta f}{\delta \rho'} \right\} = -\frac{1}{16} \left(\frac{\rho'(x)}{\rho(x)} \right)^2 + \frac{1}{2} V_{\text{eff}}(x) - \frac{\varepsilon}{2} - \frac{1}{8} \left[\frac{\rho''(x)\rho(x) - \rho'(x)^2}{\rho(x)^2} \right].$$

Thus, after direct simplifications, we find (2) again

$$V_{\text{eff}}(x) = \varepsilon + \frac{1}{4} \left[\frac{\rho''(x)}{\rho(x)} - \frac{1}{2} \left(\frac{\rho'(x)}{\rho(x)} \right)^2 \right].$$

The use of the variational principle seems to be the strategy to follow for more general systems. Before doing that, we recall basic facts from quantum chemistry.

2 Basic facts from quantum chemistry

The fundamental quantity we will track down (in the first place) is the wave function Ψ. It is postulated it encodes all the physical and chemical properties of interest. The wave function is the solution to the Schrödinger equation. Various settings exist. We will mostly consider the time-dependent case and the main approximation we are making is the Born-Oppenheimer one in a non-relativistic setting. The dynamics of a quantum system of N electrons is thus described by the following time-dependent Schrödinger equation (abbreviated TDSE) using the atomic units

$$\partial_t \Psi(\mathbf{x}, t) = H(\mathbf{x}, t)\Psi(\mathbf{x}, t), \quad \Psi(\mathbf{x}, 0) = \Psi_0(\mathbf{x}). \tag{3}$$

The operator H is the Hamiltonian of the system and is composed of a kinetic part and a potential part

$$H = T + (V_{\text{ee}} + V_{\text{ext}}) = -\frac{1}{2} \sum_{i=1}^{N} \Delta_i + \left(\frac{1}{2} \sum_{i \neq j}^{N} \frac{1}{|\mathbf{x}_i - \mathbf{x}_j|} + \sum_{i=1}^{N} v_{\text{ext}}(\mathbf{x}_i, t) \right) \tag{4}$$

the constant nuclear part is neglected for the presentation. One can be even more general and consider potentials other than the Coulomb electric potential and add interaction terms between the particles. The TDSE (3) admits an analytic solution only for a very limited number of systems (essentially hydrogen-like atom; see for instance Rivail, *Éléments de chimie quantique à l'usage des chimistes*, Chapter 2). This is why we will have to solve it numerically, i.e. find a numerical approximation of the wave function $\Psi(\mathbf{x}, t)$.

We can use plethora of methods specifically designed for the Schrödinger equation but it worth noting that other methods could also be used. For instance, if under a transformation the Schrödinger equation transforms to an other class of well-known equation, it would then be interesting to investigate solving the transformed Schrödinger equation using another set of numerical methods. For instance, the Schrödinger equation can be transformed into a Hamilton-Jacobi type equation. We show how. This part can be skipped during a first reading.

From Schrödinger to Hamilton-Jacobi. We briefly recall the context. We consider the one-dimensional time-dependent Schrödinger equation:

$$i\partial_t\varphi(x,t) = -\frac{1}{2}\partial_x^2\varphi(x,t) + V(x,t)\varphi(x,t). \tag{5}$$

The potential is subject to various hypotheses not specified here (subsequently, we will formally perform the calculations without worrying about differentiability conditions, division by zero problems (...)). By rewriting $\varphi(x,t)$ in an adequate manner, we obtain a system of coupled partial differential equations: a conservation equation and a Hamilton-Jacobi equation. To do so, apply the Madelung transformation to φ, i.e., $\varphi(x,t) = \sqrt{\rho(x,t)}\exp(i\alpha(x,t))$ where ρ is the density and α is a phase term. It then suffices to apply the operator

$$i\partial_t + 1/2\partial_x^2 - V(x,t)$$

to the transformed φ in order to obtain the new equations. To do this, we first determine the action of each term on φ. We will omit some variables for clarity and readability. We have:

$$i\partial_t\varphi = \frac{i}{2}\rho^{-1/2}e^{i\alpha}\partial_t\rho - \rho^{1/2}e^{i\alpha}\partial_t\alpha, \tag{6}$$

$$\partial_x\varphi = \frac{1}{2}\rho^{-1/2}e^{i\alpha}\partial_x\rho + i\rho^{1/2}e^{i\alpha}\partial_x\alpha,$$

$$\partial_x^2\varphi = \frac{1}{2}\rho^{-1/2}e^{i\alpha}\partial_x^2\rho - \frac{1}{4}\rho^{-3/2}e^{i\alpha}\left(\partial_x\rho\right)^2 + i\rho^{-1/2}e^{i\alpha}\partial_x\rho\partial_x\alpha + i\rho^{1/2}e^{i\alpha}\partial_x^2\alpha - \rho^{1/2}e^{i\alpha}\left(\partial_x\alpha\right)^2. \tag{7}$$

Using (6) and (7), the equation (5) is then equivalent to the following equation:

$$\begin{aligned}
\frac{i}{2}\rho^{-1/2}e^{i\alpha}\partial_t\rho - \rho^{1/2}e^{i\alpha}\partial_t\alpha = &-\frac{1}{4}\rho^{-1/2}e^{i\alpha}\partial_x^2\rho + \frac{1}{8}\rho^{-3/2}e^{i\alpha}\left(\partial_x\rho\right)^2 \\
&-\frac{i}{2}\rho^{-1/2}e^{i\alpha}\partial_x\rho\partial_x\alpha - \frac{i}{2}\rho^{1/2}e^{i\alpha}\partial_x^2\alpha \\
&+\frac{1}{2}\rho^{1/2}e^{i\alpha}\left(\partial_x\alpha\right)^2 + V(x,t)\rho^{1/2}e^{i\alpha}.
\end{aligned} \tag{8}$$

We thus obtain a system of coupled equations by considering the real and imaginary parts (after simplifying the $e^{i\alpha}$ terms). First, for the imaginary part, we obtain a continuity equation. Indeed, we have:

$$\frac{1}{2}\rho^{-1/2}\partial_t\rho = -\frac{1}{2}\rho^{-1/2}\partial_x\rho\partial_x\alpha - \frac{1}{2}\rho^{1/2}\partial_x^2\alpha. \tag{9}$$

After algebraic clean-up, noting that $\partial_x(\rho\partial_x\alpha) = \partial_x\rho\partial_x\alpha + \rho\partial_x^2\alpha$, we finally obtain the equation:

$$\partial_t\rho + \partial_x\left(\rho\partial_x\alpha\right) = 0. \tag{10}$$

Now, we consider the real part, we similarly obtain:

$$-\rho^{1/2}\partial_t\alpha = -\frac{1}{4}\rho^{-1/2}\partial_x^2\rho + \frac{1}{8}\rho^{-3/2}\left(\partial_x\rho\right)^2 + \frac{1}{2}\rho^{1/2}\left(\partial_x\alpha\right)^2 + V(x,t)\rho^{1/2}. \tag{11}$$

By dividing by $-\rho^{1/2}$, we deduce a Hamilton-Jacobi type equation:

$$\partial_t\alpha + \frac{1}{2}\left(\partial_x\alpha\right)^2 + V(x,t) = \frac{1}{4}\rho^{-1}\partial_x^2\rho - \frac{1}{8}\rho^{-2}\left(\partial_x\rho\right)^2. \tag{12}$$

By algebraic identity, we rewrite (12) in the form:

$$\partial_t\alpha + \frac{1}{2}\left(\partial_x\alpha\right)^2 + V(x,t) = \frac{1}{2}\rho^{-1/2}\partial_x^2\rho^{1/2}.$$

More generally (in N dimensions), proceeding identically, we find the following system:

$$\begin{cases} \partial_t \rho + \rho \Delta \alpha + \langle (\nabla \rho)^\intercal, \nabla \alpha \rangle & = 0 \\ \partial_t \alpha + \frac{1}{2} |\nabla \alpha|^2 + V(x,t) & = \frac{1}{4} \rho^{-1} \Delta \rho - \frac{1}{8} \rho^{-2} |\nabla \rho|^2 \end{cases} \tag{13}$$

where the gradients are to be calculated only on the spatial derivatives and where

$$\langle (\nabla \rho)^\intercal, \nabla \alpha \rangle = \sum_{j=1}^{N} \partial_j \rho \partial_j \alpha.$$

This concludes the derivation of a Hamilton-Jacobi equation from the TDSE.

The following two sections (2.1 – *One and two electrons* and 2.2 – *Many electrons*) follows and condenses the *Introduction to Quantum Chemistry* of Julien Toulouse. Let $\mathcal{H}_{\text{spatial}}$ be an infinite-dimensional complex Hilbert space with $d = 1, 2, 3$. We will fix $\mathcal{H}_{\text{spatial}}$ to be $L^2(\mathbf{R}^{Nd}, \mathbf{C})$ (there is better to do but we won't). In the two first sections N will be supposed to be equal to 1 or 2, in the second subsection we will have $N \geq 1$. To be fully rigorous, we will make an other assumption (anti-symmetry, see later). This space contains all the possible spatial (bound) states. According to the Dirac bra-ket notation, a ket is simply an element of $\mathcal{H}_{\text{spatial}}$ and a bra an element of the dual space. We've already seen an example of such notation, see the projection operator P_N from the last section.

2.1 One and two electrons

The situation for a single electron is quite straightforward. A (bound) state φ is an element of $\mathcal{H}_{\text{spatial}}$ and can thus be represented (at least) formally using an infinite-dimensional vector representation. In such case, given a discrete orthonormal basis $\{|f_i\rangle\}_{i \in \mathbf{N}}$, we can describe φ as

$$|\varphi\rangle = \sum_{i=1}^{\infty} c_i |f_i\rangle.$$

This allows us to define a functional calculus (for self-adjoint operators) and operator algebra on $\mathcal{H}_{\text{spatial}}$. The discrete decomposition previously defined can be generalized through continuous (position orthonormal) basis $\{|\vec{r}\rangle\}$ as

$$|\varphi\rangle = \int_{\mathbf{R}^d} \varphi(\vec{r}) |\vec{r}\rangle \mathrm{d}\vec{r}.$$

One of the main use of the Dirac bra-ket notation is its robustness, expressivity and elegance. For instance, we have $\varphi(\vec{r}) = \langle \vec{r} | \varphi \rangle$. An operator then decomposes as

$$\widehat{A} = \int_{\mathbf{R}^d} \int_{\mathbf{R}^d} A(\vec{r}, \vec{r'}) |\vec{r}\rangle \langle \vec{r'}| \mathrm{d}\vec{r} \mathrm{d}\vec{r'}.$$

The phase space can be enriched by considering spin states of electrons. We first restrict to the case of one single electron. The space of all spin states $\mathcal{H}_{\text{spin}}$ is a 2-dimensional complex Hilbert space spanned by two orthonormal basis states $|\alpha\rangle = \left(\begin{smallmatrix} 1 \\ 0 \end{smallmatrix}\right)$ and $|\beta\rangle = \left(\begin{smallmatrix} 0 \\ 1 \end{smallmatrix}\right)$. A physical spin state $|\chi\rangle \in \mathcal{H}_{\text{spin}}$ is given by

$$|\chi\rangle = c_1 |\alpha\rangle + c_2 |\beta\rangle = \begin{pmatrix} c_1 \\ c_2 \end{pmatrix}, \quad c_1^2 + c_2^2 = 1.$$

For future applications, it will be more convenient to view the vector spin as functions. Let σ be a spin coordinate, we then define

$$\chi : \{\downarrow, \uparrow\} \to \mathbf{C}$$
$$\sigma \mapsto \chi(\sigma) = c_1 \alpha(\sigma) + c_2 \beta(\sigma)$$

where α and β are elementary spin basis functions defined by

$$\alpha(\downarrow) = 0, \ \alpha(\uparrow) = 1, \quad \beta(\downarrow) = 1, \ \beta(\uparrow) = 0.$$

To be completed with one electron spin considerations, we ultimately need to define a dot product respecting the hermitian structure. Let χ_1 and χ_2 be two spin states of $\mathcal{H}_{\text{spin}}$, we then define

$$\langle \chi_1 | \chi_2 \rangle = \sum_{\sigma \in \{\downarrow, \uparrow\}} \chi_1^*(\sigma) \chi_2(\sigma) = \int_{\{\downarrow, \uparrow\}} \chi_1^*(\sigma) \chi_2(\sigma) \mathrm{d}\sigma.$$

for the discrete and continuous bases. Naturally, we find that $\chi(\sigma) = \langle \sigma | \chi \rangle$.

The total state space of an electron is thus given by $\mathcal{H}_1 = \mathcal{H}_{\text{spatial}} \otimes \mathcal{H}_{\text{spin}}$. It is still an infinite-dimensional space whose basis is given by $\{|f_i\rangle \otimes |\alpha\rangle, |f_i\rangle \otimes |\beta\rangle\}_{i \in \mathbf{N}}$ where we used back the basis elements from $\mathcal{H}_{\text{spatial}}$ and $\mathcal{H}_{\text{spin}}$. Formally, an element ψ of $\mathcal{H}_1$ is given by

$$|\psi\rangle = \sum_{i=1}^{\infty} c_i \left(|f_i\rangle \otimes |\alpha\rangle \right) + d_i \left(|f_i\rangle \otimes |\beta\rangle \right)$$

with c_i and d_i complex coefficients. Again to be fully complete, one needs to define how the tensor operator relates to the dot product. Let φ_1, φ_2 be bound states and χ_1, χ_2 be spin states. Then

$$\left(\langle \varphi_1 | \otimes \langle \chi_1 | \right) \left(|\varphi_2\rangle \otimes |\chi_2\rangle \right) = \langle \varphi_1 | \varphi_2 \rangle \langle \chi_1 | \chi_2 \rangle.$$

Using the function representation of the spin states, a state $\psi \in \mathcal{H}_1$ is represented as

$$\psi : \mathbf{R}^d \times \{\downarrow, \uparrow\} \to \mathbf{C}$$
$$\vec{x} \mapsto \psi(\vec{x}) = \left(\sum_{i=1}^{\infty} c_i |f_i\rangle(\vec{r}) \right) \alpha(\sigma) + \left(\sum_{i=1}^{\infty} d_i |f_i\rangle(\vec{r}) \right) \beta(\sigma)$$

with $\vec{x} = (\vec{r}, \sigma)$. Thus, for χ_1 and χ_2 two elements of $\mathcal{H}_1$, we find that

$$\langle \psi_1 | \psi_2 \rangle = \int_{\mathbf{R}^d \times \{\downarrow, \uparrow\}} \psi_1^*(\vec{x}) \psi_2(\vec{x}) \mathrm{d}\vec{x} = \sum_{\sigma \in \{\downarrow, \uparrow\}} \int_{\mathbf{R}^d} \psi_1^*(\vec{r}, \sigma) \psi_2(\vec{r}, \sigma) \mathrm{d}\vec{r}.$$

As before, we have that $\psi(\vec{x}) = \langle \vec{x} | \psi \rangle$.

If a solution ψ of the Schrödinger equation can be decomposed such that $\psi(\vec{x}) = \varphi(\vec{r}) \chi(\sigma)$, it will be called a spin-orbital. More generally, any element of $\mathcal{H}_1$ will be called a spin-orbital.

The many-electrons spin-orbitals are modeled after the case of one single electron. Because electrons are fermionic indistinguishable particles, one forms the two-electron state space $\mathcal{H}_2$ by taking the antisymmetric tensor product of two one-electron Hilbert spaces

$$\mathcal{H}_2 = \mathcal{H}_1 \wedge \mathcal{H}_1 = \left\{ \psi \in \mathrm{L}^2(\mathbf{R}^{2d} \times \{\downarrow, \uparrow\}^2, \mathbf{C}) \ : \ \psi(\vec{x_1}, \vec{x_2}) = -\psi(\vec{x_2}, \vec{x_1}) \right\}. \tag{14}$$

Given a spin-orbital basis $\{|\psi_i\rangle\}_{i\in\mathbf{N}}$ of $\mathcal{H}_1$, one can construct an orthonormal basis of $\mathcal{H}_2$ given by $\{|\psi_i\rangle \wedge |\psi_j\rangle\}_{i,j\in\mathbf{N} \text{ such that } i<j}$. Then, any state $|\Psi\rangle \in \mathcal{H}_2$ can be formally written down as

$$|\Psi\rangle = \sum_{\substack{i,j=1 \\ i<j}}^{\infty} c_{ij}|\psi_i\rangle \wedge |\psi_j\rangle = \sum_{\substack{i,j=1 \\ i<j}}^{\infty} \frac{c_{ij}}{\sqrt{2}} \left(|\psi_i\rangle \otimes |\psi_j\rangle - |\psi_j\rangle \otimes |\psi_i\rangle\right)$$

with c_{ij} complex coefficients and $\wedge$ the normalized antisymmetric tensor product of two states of $\mathcal{H}_1$. As usual, we have $\Psi(\vec{x_1}, \vec{x_2}) = \langle \vec{x_1}, \vec{x_2}|\Psi\rangle$ where $\langle \vec{x_1}, \vec{x_2}| = \langle \vec{x_1}|\otimes\langle \vec{x_2}|$ is just the two-variable evaluation linear form.

For future applications, it will be convenient to let $|\Phi_{ij}\rangle = |\psi_i\rangle \wedge |\psi_j\rangle$. As a direct consequence, we have

$$\Phi_{ij}(\vec{x_1}, \vec{x_2}) = \langle \vec{x_1}, \vec{x_2}|\Phi_{ij}\rangle = \frac{1}{\sqrt{2}}\langle \vec{x_1}, \vec{x_2}|\left(|\psi_i\rangle \otimes |\psi_j\rangle - |\psi_j\rangle \otimes |\psi_i\rangle\right)$$

$$= \frac{1}{\sqrt{2}}\left(\psi_i(\vec{x_1})\psi_j(\vec{x_2}) - \psi_j(\vec{x_1})\psi_i(\vec{x_2})\right) = \frac{1}{\sqrt{2}}\begin{vmatrix} \psi_i(\vec{x_1}) & \psi_j(\vec{x_1}) \\ \psi_i(\vec{x_2}) & \psi_j(\vec{x_2}) \end{vmatrix}.$$

With no further computations, the antisymmetric property of the determinant tells us that the wave function of two electrons is antisymmetric with respect to switching $\vec{x_1}$ and $\vec{x_2}$. Moreover, we naturally constructed our very first Slater determinant. By construction of $\mathcal{H}_2$, the set of all Slater determinants $\{\Phi_{ij}\}_{i,j\in\mathbf{N} \text{ such that } i<j}$ forms an orthonormal basis for two-electron wave functions.

For completeness, recall that the density of probability $|\Psi(\vec{x_1}, \vec{x_2})|^2 = \Psi(\vec{r_1}, \sigma_1, \vec{r_2}, \sigma_2)|^2$ is interpreted as the probability density of finding one electron at position $\vec{r_1}$ with spin σ_1 and the other electron at position $\vec{r_2}$ with spin σ_2 after a measurement.

Under the typical approximations, the electronic Hamiltonian $\widehat{H}$ acting on $\mathcal{H}_2$ takes the following form

$$\langle \vec{x_1}, \vec{x_2}|\widehat{H}|\vec{x_1}, \vec{x_2}\rangle = H(\vec{r_1}, \vec{r_2}) = -\frac{1}{2}\Delta_1 - \frac{1}{2}\Delta_2 + \frac{1}{|\vec{x_1} - \vec{x_2}|} + v_{\text{ne}}(\vec{r_1}) + v_{\text{ne}}(\vec{r_2})$$

where v_{ne} is the nuclei-electron potential depending on the system. The Hamiltonian is thus spin-independent. In this case, the (time-independent) Schrödinger equation reads as

$$H(\vec{r_1}, \vec{r_2})\Psi(\vec{x_1}, \vec{x_2}) = E\Psi(\vec{x_1}, \vec{x_2}). \tag{15}$$

Due to the electron-electron interaction, it is not possible to solve analytically this equation. In a subsequent section, we will explain how to solve it numerically. For now on, we will make a further assumption (non-interacting electrons).

Non-interacting electrons. The Schrödinger equation (15) simplifies to

$$\left(-\frac{1}{2}\Delta_1 - \frac{1}{2}\Delta_2 + v_{\text{ne}}(\vec{r_1}) + v_{\text{ne}}(\vec{r_2})\right)\Psi(\vec{x_1}, \vec{x_2}) = E\Psi(\vec{x_1}, \vec{x_2}).$$

Given two spin-orbitals ψ_1, ψ_2 each satisfying a one-electron problem

$$\left(-\frac{1}{2}\Delta_1 + v_{\text{ne}}(\vec{r_1})\right)\psi_1(\vec{x}) = \varepsilon_1\psi_1(\vec{x}),$$

$$\left(-\frac{1}{2}\Delta_2 + v_{\text{ne}}(\vec{r_2})\right)\psi_2(\vec{x}) = \varepsilon_2\psi_2(\vec{x}),$$

their Slater determinant is an eigenstate of energy $E = \varepsilon_1 + \varepsilon_2$. This is shown by direct computations

$$\left(-\frac{1}{2}\Delta_1 - \frac{1}{2}\Delta_2 + v_{\text{ne}}(\vec{r_1}) + v_{\text{ne}}(\vec{r_2})\right)\Psi(\vec{x_1}, \vec{x_2}) = \frac{1}{\sqrt{2}}\left(-\frac{1}{2}\Delta_1 - \frac{1}{2}\Delta_2 + v_{\text{ne}}(\vec{r_1}) + v_{\text{ne}}(\vec{r_2})\right)\psi_1(\vec{x_1})\psi_2(\vec{x_2})$$

$$- \frac{1}{\sqrt{2}}\left(-\frac{1}{2}\Delta_1 - \frac{1}{2}\Delta_2 + v_{\text{ne}}(\vec{r_1}) + v_{\text{ne}}(\vec{r_2})\right)\psi_2(\vec{x_1})\psi_1(\vec{x_2})$$

$$= \frac{1}{\sqrt{2}}\left(\varepsilon_1\psi_1(\vec{x_1})\psi_2(\vec{x_2}) + \psi_1(\vec{x_1})\varepsilon_2\psi_2(\vec{x_2})\right)$$

$$- \frac{1}{\sqrt{2}}\left(\varepsilon_1\psi_2(\vec{x_1})\psi_1(\vec{x_2}) + \psi_2(\vec{x_1})\varepsilon_2\psi_1(\vec{x_2})\right)$$

$$= \frac{\varepsilon_1 + \varepsilon_2}{\sqrt{2}}\left(\psi_1(\vec{x_1})\psi_2(\vec{x_2}) - \psi_2(\vec{x_1})\psi_1(\vec{x_2})\right)$$

$$= (\varepsilon_1 + \varepsilon_2)\Psi(\vec{x_1}, \vec{x_2}).$$

Two situations are possible: either the two electrons are in a single orbital or they are in two different spatial orbitals. Decompose ψ_1 and ψ_2 in a spatial and a spin part $\psi_i(\vec{x}) = \varphi(\vec{r})\chi(\sigma)$ for $i = 1, 2$.

Two electrons in a single spatial orbital φ. By the Pauli exclusion principle, the spin of the two electrons can't be identical. Assume the spin of the first electron is down $\downarrow$ and the second is up $\uparrow$, i.e. $\psi_1(\vec{x}) = \varphi(\vec{r})\alpha(\sigma)$ and $\psi_2(\vec{x}) = \varphi(\vec{r})\beta(\sigma)$. Moreover, we have $\varepsilon = \varepsilon_1 = \varepsilon_2$. The corresponding Slater determinant is a spin-singlet state

$$\Phi_{\text{S}_0}(\vec{x_1}, \vec{x_2}) = \frac{1}{\sqrt{2}}\begin{vmatrix}\varphi(\vec{r_1})\alpha(\sigma_1) & \varphi(\vec{r_1})\beta(\sigma_1) \\ \varphi(\vec{r_2})\alpha(\sigma_2) & \varphi(\vec{r_2})\beta(\sigma_2)\end{vmatrix} = \varphi(\vec{r_1})\varphi(\vec{r_2})\frac{\alpha(\sigma_1)\beta(\sigma_2) - \beta(\sigma_1)\alpha(\sigma_2)}{\sqrt{2}}.$$

The energy of this Slater determinant can be computed as follows

$$E_{\text{S}_0} = \langle\Phi_{\text{S}_0}|\widehat{H}|\Phi_{\text{S}_0}\rangle$$

$$= \int_{\mathbf{R}^d\times\{\downarrow,\uparrow\}}\int_{\mathbf{R}^d\times\{\downarrow,\uparrow\}}\Phi_{\text{S}_0}^*(\vec{x_1}, \vec{x_2})\left[-\frac{1}{2}\Delta_1 - \frac{1}{2}\Delta_2 + \frac{1}{|\vec{x_1} - \vec{x_2}|} + v_{\text{ne}}(\vec{r_1}) + v_{\text{ne}}(\vec{r_2})\right]\Phi_{\text{S}_0}(\vec{x_1}, \vec{x_2})\mathrm{d}\vec{x_1}\mathrm{d}\vec{x_2}.$$

By normalization, the integral over spin coordinates give 1. Moreover, for convenience, define the one-electron Hamiltonian

$$h(\vec{r_i}) = -\frac{1}{2}\Delta_i + v_{\text{ne}}(\vec{r_i}).$$

We then have

$$E_{\text{S}_0} = \int_{\mathbf{R}^d}\int_{\mathbf{R}^d}\varphi^*(\vec{r_1})\varphi^*(\vec{r_2})\left[h(\vec{r_1}) + h(\vec{r_2}) + \frac{1}{|\vec{x_1} - \vec{x_2}|}\right]\varphi(\vec{r_1})\varphi(\vec{r_2})\mathrm{d}\vec{r_1}\mathrm{d}\vec{r_2}$$

$$= 2\langle\varphi|\hat{h}|\varphi\rangle + \langle\varphi\varphi|\varphi\varphi\rangle$$

where $\langle\varphi|\hat{h}|\varphi\rangle$ is the one-electron integral

$$\langle\varphi|\hat{h}|\varphi\rangle = \int_{\mathbf{R}^d}\varphi^*(\vec{r})h(\vec{r})\varphi(\vec{r})\mathrm{d}\vec{r}$$

and $\langle\varphi\varphi|\varphi\varphi\rangle$ is the two-electrons integral

$$\langle\varphi\varphi|\varphi\varphi\rangle = \int_{\mathbf{R}^d}\int_{\mathbf{R}^d}\varphi^*(\vec{r_1})\varphi^*(\vec{r_2})\frac{1}{|\vec{x_1} - \vec{x_2}|}\varphi(\vec{r_1})\varphi(\vec{r_2})\mathrm{d}\vec{r_1}\mathrm{d}\vec{r_2}.$$

11

Two electrons in two different spatial orbitals φ_1, φ_2. The energies ε_1 and ε_2 can now be different. Again, due to the Pauli exclusion principle, there are four possible configurations: $\downarrow\downarrow, \downarrow\uparrow, \uparrow\downarrow, \uparrow\uparrow$. But, we suspect that $\downarrow\uparrow$ and $\uparrow\downarrow$ might be similar. Indeed, one can form three different Slater determinant, i.e. a spin-triplet state. They are $\downarrow\downarrow$, $\uparrow\uparrow$ and $1/\sqrt{2}(\downarrow\uparrow + \uparrow\downarrow)$ whereas $1/\sqrt{2}(\downarrow\uparrow - \uparrow\downarrow)$ generate the same spin function as the spin-singlet state. Formally, the spin-triplet state are

$$\Phi_{\mathrm{T},1}(\vec{x_1}, \vec{x_2}) = \frac{1}{\sqrt{2}} \begin{vmatrix} \varphi_1(\vec{r_1})\alpha(\sigma_1) & \varphi_2(\vec{r_1})\alpha(\sigma_1) \\ \varphi_1(\vec{r_2})\alpha(\sigma_2) & \varphi_2(\vec{r_1})\alpha(\sigma_2) \end{vmatrix} = \frac{\varphi(\vec{r_1})\varphi_2(\vec{r_2}) - \varphi_2(\vec{r_1})\varphi_1(\vec{r_2})}{\sqrt{2}} \alpha(\sigma_1)\alpha(\sigma_2),$$

$$\Phi_{\mathrm{T},-1}(\vec{x_1}, \vec{x_2}) = \frac{1}{\sqrt{2}} \begin{vmatrix} \varphi_1(\vec{r_1})\beta(\sigma_1) & \varphi_2(\vec{r_1})\beta(\sigma_1) \\ \varphi_1(\vec{r_2})\beta(\sigma_2) & \varphi_2(\vec{r_1})\beta(\sigma_2) \end{vmatrix} = \frac{\varphi(\vec{r_1})\varphi_2(\vec{r_2}) - \varphi_2(\vec{r_1})\varphi_1(\vec{r_2})}{\sqrt{2}} \beta(\sigma_1)\beta(\sigma_2),$$

$$\Phi_{\mathrm{T},0}(\vec{x_1}, \vec{x_2}) = \frac{1}{\sqrt{2}} \left(\frac{1}{\sqrt{2}} \begin{vmatrix} \varphi_1(\vec{r_1})\alpha(\sigma_1) & \varphi_2(\vec{r_1})\beta(\sigma_1) \\ \varphi_1(\vec{r_2})\alpha(\sigma_2) & \varphi_2(\vec{r_1})\beta(\sigma_2) \end{vmatrix} + \frac{1}{\sqrt{2}} \begin{vmatrix} \varphi_1(\vec{r_1})\beta(\sigma_1) & \varphi_2(\vec{r_1})\alpha(\sigma_1) \\ \varphi_1(\vec{r_2})\beta(\sigma_2) & \varphi_2(\vec{r_1})\alpha(\sigma_2) \end{vmatrix} \right)$$
$$= \frac{\varphi(\vec{r_1})\varphi_2(\vec{r_2}) - \varphi_2(\vec{r_1})\varphi_1(\vec{r_2})}{\sqrt{2}} \frac{\alpha(\sigma_1)\beta(\sigma_2) + \beta(\sigma_1)\alpha(\sigma_2)}{\sqrt{2}}.$$

Since these Slater determinants are degenerate, there is no difference in computing the energy of $\Phi_{\mathrm{T},0}$, $\Phi_{\mathrm{T},-1}$ or $\Phi_{\mathrm{T},1}$. We then have

$$E_{\mathrm{T}} = \frac{1}{2} \int_{\mathbf{R}^{2d}} (\varphi^*(\vec{r_1})\varphi^*(\vec{r_2}) - \varphi_2^*(\vec{r_1})\varphi_1^*(\vec{r_2})) \left[h(\vec{r_1}) + h(\vec{r_2}) + \frac{1}{|\vec{x_1} - \vec{x_2}|} \right] (\varphi(\vec{r_1})\varphi(\vec{r_2}) - \varphi_2(\vec{r_1})\varphi_1(\vec{r_2})) \, \mathrm{d}\vec{r_1}\mathrm{d}\vec{r_2}$$
$$= \langle\varphi_1|\hat{h}|\varphi_1\rangle + \langle\varphi_2|\hat{h}|\varphi_2\rangle - \langle\varphi_1\varphi_2|\varphi_1\varphi_2\rangle - \langle\varphi_1\varphi_2|\varphi_2\varphi_1\rangle.$$

For the sake of clarity, we give the formal expression of the Coulomb repulsion energy given by the two-electrons integral

$$\langle\varphi_1\varphi_2|\varphi_1\varphi_2\rangle = \int_{\mathbf{R}^d} \int_{\mathbf{R}^d} \varphi_1^*(\vec{r_1})\varphi_2^*(\vec{r_2}) \frac{1}{|\vec{x_1} - \vec{x_2}|} \varphi_1(\vec{r_1})\varphi_2(\vec{r_2})\mathrm{d}\vec{r_1}\mathrm{d}\vec{r_2}$$

and the exchange integral / exchange interaction

$$\langle\varphi_1\varphi_2|\varphi_2\varphi_1\rangle = \int_{\mathbf{R}^d} \int_{\mathbf{R}^d} \varphi_1^*(\vec{r_1})\varphi_2^*(\vec{r_2}) \frac{1}{|\vec{x_1} - \vec{x_2}|} \varphi_2(\vec{r_1})\varphi_1(\vec{r_2})\mathrm{d}\vec{r_1}\mathrm{d}\vec{r_2}.$$

2.2 Many electrons

Following (14), it is natural to define the N-electron state space as

$$\mathcal{H}_N = \underbrace{\mathcal{H}_1 \wedge \cdots \wedge \mathcal{H}_1}_{N \text{ terms}}$$
$$= \left\{ \psi \in \mathrm{L}^2(\mathbf{R}^{Nd} \times \{\downarrow,\uparrow\}^N, \mathbf{C}) \ : \ \psi(\vec{x_1}, \ldots, \vec{x_i}, \ldots, \vec{x_j}, \ldots, \vec{x_N}) = -\psi(\vec{x_1}, \ldots, \vec{x_j}, \ldots, \vec{x_i}, \ldots, \vec{x_N}) \right\}.$$

Nearly every last point generalizes easily in the many electrons configuration except that, unlike to the two-electrons case, the eigenstates of the N-electrons Hamiltonian do not generally factorize into a spatial part and a spin part.

Given a spin-orbital basis $\{|\psi_i\rangle\}_{i\in\mathbf{N}}$ of $\mathcal{H}_1$, one can construct an orthonormal basis of $\mathcal{H}_N$ given by $\{|\psi_{i_1}\rangle \wedge |\psi_{i_2}\rangle \wedge \cdots \wedge |\psi_{i_N}\rangle\}_{i_k\in\mathbf{N} \text{ such that } i_1<i_2<\cdots<i_N}$. Then, any state $|\Psi\rangle \in \mathcal{H}_N$ can be formally written down as

$$|\Psi\rangle = \sum_{\substack{i_1,i_2,\ldots,i_N=1 \\ i_1<i_2<\cdots<i_N}}^{\infty} c_{i_1 i_2 \ldots i_N} |\psi_{i_1}\rangle \wedge |\psi_{i_2}\rangle \wedge \cdots \wedge |\psi_{i_N}\rangle$$

with $c_{i_1 i_2 \ldots i_N}$ complex coefficients and $\wedge$ defined by induction from the two-electron case. As we did before, let $|\Phi_{i_1 i_2 \ldots i_N}\rangle = |\psi_{i_1}\rangle \wedge |\psi_{i_2}\rangle \wedge \cdots \wedge |\psi_{i_N}\rangle$. We naturally find that

$$\Psi(\vec{x_1}, \vec{x_2}, \ldots, \vec{x_N}) = \langle \vec{x_1}, \vec{x_2}, \ldots, \vec{x_N}|\Psi\rangle = \sum_{\substack{i_1, i_2, \ldots, i_N = 1 \\ i_1 < i_2 < \cdots < i_N}}^{\infty} c_{i_1 i_2 \ldots i_N} \Phi_{i_1 i_2 \ldots i_N}(\vec{x_1}, \vec{x_2}, \ldots, \vec{x_N})$$

where $\Phi_{i_1 i_2 \ldots i_N}(\vec{x_1}, \vec{x_2}, \ldots, \vec{x_N})$ is the N-electrons Slater determinant

$$\Phi_{i_1 i_2 \ldots i_N}(\vec{x_1}, \vec{x_2}, \ldots, \vec{x_N}) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_{i_1}(\vec{x_1}) & \psi_{i_2}(\vec{x_1}) & \ldots & \psi_{i_N}(\vec{x_1}) \\ \psi_{i_1}(\vec{x_2}) & \psi_{i_2}(\vec{x_2}) & \ldots & \psi_{i_N}(\vec{x_2}) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_{i_1}(\vec{x_N}) & \psi_{i_2}(\vec{x_N}) & \ldots & \psi_{i_N}(\vec{x_N}) \end{vmatrix}.$$

2.3 Variational principle

We already used it in Section 1, we now present it formally. This theorem states that the ground state energy E_0 and its associated ground state wave function Ψ_0 of a system can be obtained by minimizing the expectation value of the Hamiltonian over all possible wave functions Ψ satisfying the normalization constraint $\langle \Psi | \Psi \rangle = 1$, i.e.

$$E_0 = \min_{\substack{\Psi \in \mathcal{H}_N \\ \langle \Psi | \Psi \rangle = 1}} \langle \Psi | \widehat{H} | \Psi \rangle.$$

The minimum is reached by the ground state wave function Ψ_0 (or one of the ground state wave functions if it is degenerate). The proof is straightforward and left to the reader (hint: expand $|\Psi\rangle$ in an orthonormal basis and do not forget to number in increasing order the energy levels).

The variational principle gives a minimization procedure to find the ground state wave function and energy level.

We conclude this section by some considerations on the time-dependent case (needed in the TDDFT setting, see Section 3.2). Let Ω_{time} be the time period under consideration (typically a compact interval of $\mathbf{R}$). It would then be natural to introduce

$$\mathcal{A}[\rho] = \int_{\Omega_{\text{time}}} \langle \Psi[\rho](t)|i\partial_t - H(t)|\Psi[\rho](t)\rangle \mathrm{d}t.$$

The exact density would be given by the solution of $\delta\mathcal{A}[\rho] = 0$. Due to its nature, the principle will be more likely called a stationary action principle instead of a variational principle. Unfortunately, this definition makes paradoxes rise (see Section 4.1 from Leeuwen, *Key concepts in time-dependent density-functional theory*). To solve this problem, the Keldysh action was introduced (*k.o. technique déclaré, hors d'atteinte pour l'instant*).

2.4 Hartree-Fock method

We want to approximate the ground state wave function by a single Slater determinant of N orthonormal spin-orbitals $\{\psi_1, \ldots, \psi_N\}$

$$\Phi(\vec{x_1}, \vec{x_2}, \ldots, \vec{x_N}) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_{i_1}(\vec{x_1}) & \psi_{i_2}(\vec{x_1}) & \ldots & \psi_{i_N}(\vec{x_1}) \\ \psi_{i_1}(\vec{x_2}) & \psi_{i_2}(\vec{x_2}) & \ldots & \psi_{i_N}(\vec{x_2}) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_{i_1}(\vec{x_N}) & \psi_{i_2}(\vec{x_N}) & \ldots & \psi_{i_N}(\vec{x_N}) \end{vmatrix}.$$

(We could consider linear combinations of Slater determinants, see the configuration-interaction method (CI method)). Then, by the variational principle, the total Hartree-Fock energy is given by

$$E_{\text{HF}} = \min_{\substack{\{\psi_1,\ldots,\psi_N\} \\ \langle\psi_i|\psi_j\rangle=\delta_{ij}}} \langle\Phi|\widehat{H}|\Phi\rangle$$

The quantity to be minimized is then

$$E[\{\psi_1,\ldots,\psi_N\}] = \int_{\mathbf{R}^{Nd}\times\{\downarrow,\uparrow\}^N} \Phi^*(\vec{x_1},\vec{x_2},\ldots,\vec{x_N}) \left[\sum_{i=1}^N h(\vec{r_i}) + \sum_{\substack{i,j=1 \\ i<j}}^N \frac{1}{|\vec{x_i}-\vec{x_j}|}\right] \Phi(\vec{x_1},\vec{x_2},\ldots,\vec{x_N})\mathrm{d}\vec{x_1}\mathrm{d}\vec{x_2}\ldots\mathrm{d}\vec{x_N}$$

$$= \sum_{i=1}^N \langle\psi_i|\hat{h}|\psi_i\rangle + \sum_{\substack{i,j=1 \\ i<j}}^N \langle\psi_i\psi_j|\psi_i\psi_j\rangle - \langle\psi_i\psi_j|\psi_j\psi_i\rangle$$

$$= \sum_{i=1}^N \langle\psi_i|\hat{h}|\psi_i\rangle + \frac{1}{2}\sum_i^N\sum_j^N \langle\psi_i\psi_j|\psi_i\psi_j\rangle - \langle\psi_i\psi_j|\psi_j\psi_i\rangle.$$

We use the technique of Lagrange multipliers to find E_{HF}. To do so, introduce the Lagrangian

$$\mathcal{L}[\{\psi_1,\ldots,\psi_N\}] = E[\{\psi_1,\ldots,\psi_N\}] - \sum_{i=1}^N \varepsilon_i\left(\langle\psi_i|\psi_i\rangle - 1\right).$$

Minimizers are solution of

$$\frac{\delta\mathcal{L}}{\delta\psi_i^*} = 0$$

for each $i = 1,\ldots,N$. By computing this functional derivative, one finds the Hartree-Fock equations

$$h(\vec{r})\psi_i(\vec{x}) + v_{\text{H}}(\vec{r})\psi_i(\vec{x}) + \int_{\mathbf{R}^d\times\{\downarrow,\uparrow\}} v_{\text{x}}(\vec{x},\vec{x'})\psi_i(\vec{x'})\mathrm{d}\vec{x'} = \varepsilon_i\psi_i(\vec{x})$$

with $v_{\text{H}}(\vec{r})$ the Hartree potential

$$v_{\text{H}}(\vec{r}) = \sum_{i=1}^N \int_{\mathbf{R}^d\times\{\downarrow,\uparrow\}} \psi_i^*(\vec{x'})\frac{1}{|\vec{r}-\vec{r'}|}\psi_i(\vec{x'})\mathrm{d}\vec{x'}$$

and $v_{\text{x}}(\vec{x},\vec{x'})$ is the exchange / Fock potential

$$v_{\text{x}}(\vec{x},\vec{x'}) = -\sum_{i=1}^N \psi_i^*(\vec{x'})\frac{1}{|\vec{r}-\vec{r'}|}\psi_i(\vec{x'}).$$

In a condensed form, solving the Hartree-Fock is thus equivalent to finding the energy levels ε_i and the spin-orbitals ψ_i for the Hamiltonian given by $\hat{h} + v_{\text{HF}}$ where $v_{\text{HF}} = v_{\text{H}} + v_{\text{x}}$.

This equation will be solved iteratively by a self-consistent method. We will say that the N lowest energy eigenstates $\{\psi_1,\ldots,\psi_N\}$ are the occupied canonical Hartree-Fock spin-orbitals and the remaining eigenstates $\{\psi_{N+1},\psi_{N+2},\ldots\}$ are the virtual / unoccupied canonical Hartree-Fock spin-orbitals.