Hartree - Fock method

Variational approach in which anti-symmetrized products of single-electrons wave functions are used. Notation

$$\Psi(x_1, x_2, \dots, x_N) = \frac{1}{\sqrt{N!}} \det |\phi_1(x_1)\, \phi_2(x_2) \dots \phi_N(x_N)|$$

$\uparrow$ normalization

$x_i \equiv (r_i, \sigma_i)$

$\hookrightarrow \begin{cases} \alpha & \text{spin up} \\ \beta & \text{spin down} \end{cases}$

Slater determinant

$$\det |\phi_1(x_1)\, \phi_2(x_2) \dots \phi_N(x_N)| =$$

$$\det \begin{vmatrix} \phi_1(x_1) & \phi_2(x_1) & \dots & \phi_N(x_1) \\ \phi_1(x_2) & \phi_2(x_2) & \dots & \phi_N(x_2) \\ \vdots & & & \\ \phi_1(x_N) & \phi_2(x_N) & \dots & \phi_N(x_N) \end{vmatrix}$$

$$\hat{H} = \sum_{i=1}^{N} \hat{h}_i + \frac{1}{2} \sum_{i \neq j} \hat{g}_{ij}$$

$$\hat{h}_i = -\frac{\hbar^2}{2m_i} \nabla_i^2 - \frac{Z e^2}{4\pi\varepsilon_0 \hat{r}_i} \qquad \text{(in coord rep.)}$$

$$\hat{g}_{ij} = + \frac{e^2}{4\pi\varepsilon_0} \frac{1}{\hat{r}_{ij}}$$

$\hookrightarrow |\hat{r}_i - \hat{r}_j|$

Atomic units will be used from now on $\hbar = m_i = e = 1$ ($4\pi\varepsilon_0$ also 1)

Note that $\langle \Psi | \Psi \rangle = 1$

$$E[\Psi] = \langle \Psi | \hat{H} | \Psi \rangle$$

$$= \langle \Psi | \sum_i \hat{h}_i | \Psi \rangle + \langle \Psi | \frac{1}{2} \sum_{i \neq j} \hat{g}_{ij} | \Psi \rangle$$

$\hat{h}_i$: depends only on $\hat{r}_i$ — $\hat{g}_{ij}$: depends only on $\hat{r}_{ij}$

To understand the structure of these terms consider the case

$$\Psi(x_1, x_2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_1(x_1) & \phi_2(x_1) \\ \phi_1(x_2) & \phi_2(x_2) \end{vmatrix}$$

$$= \frac{1}{\sqrt{2}} \left[\phi_1(x_1)\phi_2(x_2) - \phi_2(x_1)\phi_2(x_2) \right]$$

$$\hat{H} = \sum_{i=1}^{2} \underbrace{\left[-\frac{1}{2}\nabla_i^2 - \frac{Z}{r_i} \right]}_{h_i} + \frac{1}{r_{12}}$$

Then

$$\langle \Psi | \hat{H} | \Psi \rangle = \int dx_1\, dx_2\, \frac{1}{\sqrt{2}} \left[\phi_1^*(x_1)\phi_2^*(x_2) - \phi_2^*(x_1)\phi_1^*(x_2) \right] \sum_{i=1}^{2} \left[-\frac{1}{2}\nabla_i^2 - \frac{Z}{r_i} \right] \frac{1}{\sqrt{2}} \left[\phi_1(x_1)\phi_2(x_2) - \phi_2(x_1)\phi_1(x_2) \right]$$

$$+ \int dx_1\, dx_2\, \frac{1}{\sqrt{2}} \left[\phi_1^*(x_1)\phi_2^*(x_2) - \phi_2^*(x_1)\phi_1^*(x_2) \right] \frac{1}{r_{12}} \frac{1}{\sqrt{2}} \left[\phi_1(x_1)\phi_2(x_2) - \phi_2(x_1)\phi_1(x_2) \right]$$

⊕ Note that

1/ The operators are the identity in the spin space

⇒ the spin part of orbitals assigned to the same electron must be the same

$$\Rightarrow \langle \Psi | \hat{H} | \Psi \rangle = \int d\tau_1 d\tau_2 \frac{1}{\sqrt{2}} \left[\phi_1^*(r_1)\phi_2^*(r_2) - \phi_2^*(r_1)\phi_1^*(r_2) \right]$$

$$\left[\sum_{i=1}^{2} -\frac{1}{2}\nabla_i^2 - \frac{Z}{r_i} \right] \frac{1}{\sqrt{2}} \left[\phi_1(r_1)\phi_2(r_2) - \phi_2(r_1)\phi_1(r_2) \right]$$

$$+ \int d\tau_1 d\tau_2 \frac{1}{\sqrt{2}} \left[\phi_1^*(r_1)\phi_2^*(r_2) - \phi_2^*(r_1)\phi_1^*(r_2) \right] \frac{1}{r_{12}}$$

$$\frac{1}{\sqrt{2}} \left[\phi_1(r_1)\phi_2(r_2) - \phi_2(r_1)\phi_1(r_2) \right]$$

Let's focus on the first integral. This integral is the sum of two terms, identical except for the value of the label i. For example

$$\int d\tau_1 d\tau_2 \frac{1}{\sqrt{2}} \left[\phi_1^*(r_1)\phi_2^*(r_2) - \phi_2^*(r_1)\phi_1^*(r_2) \right]$$

$$\underbrace{\left[-\frac{1}{2}\nabla_1^2 - \frac{1}{r_1} \right]}_{h(1)} \frac{1}{\sqrt{2}} \left[\phi_1(r_1)\phi_2(r_2) - \phi_2(r_1)\phi_1(r_2) \right]$$

This is the product of four terms, always "factored" in the variables r_1 and r_2. i.e.

$$\frac{1}{2} \Big\{ \int d\tau_1 \, \phi_1^*(r_1) \, h(1) \, \phi_1(r_1) \overbrace{\int d\tau_2 \, \phi_2^*(r_2)\phi_2(r_2)}^{1}$$

$$- \int d\tau_1 \, \phi_1^*(r_1) \, h(1) \, \phi_2(r_1) \int d\tau_2 \, \phi_2^*(r_2)\phi_1(r_2) \overbrace{\quad}^{\times 0}$$

$$- \int d\tau_1 \, \phi_2^*(r_1) \, h(1) \, \phi_1(r_1) \int d\tau_2 \, \phi_1^*(r_2)\phi_2(r_2) \overbrace{\quad}^{0}$$

$$+ \int d\tau_1 \, \phi_2^*(r_1) \, h(1) \, \phi_2(r_1) \underbrace{\int d\tau_2 \, \phi_1^*(r_2)\phi_1(r_2)}_{1} \Big\}$$

$$= \frac{1}{2} \sum_k \langle \phi_k | h | \phi_k \rangle$$

The other term in the first integral gives an identical contribution (show it), so in the end the "diagonal" part of the Hamiltonian gives

$$\langle \Psi | \sum_i \hat{h}_i | \Psi \rangle = \sum_k \langle \phi_k | \hat{h} | \phi_k \rangle$$

$$\hat{h} \uparrow \; -\frac{1}{2}\nabla_k^2 - \frac{Z}{r_k}$$

Let us now consider

$$\int dr_1\, dr_2\, \frac{1}{\sqrt{2}} \left[\phi_1^*(r_1)\, \phi_2^*(r_2) - \phi_1^*(r_2)\, \phi_2^*(r_1) \right] \frac{1}{r_{12}}$$
$$\frac{1}{\sqrt{2}} \left[\phi_1(r_1)\, \phi_2(r_2) - \phi_1(r_2)\, \phi_2(r_1) \right]$$

$$= \frac{1}{2} \Big\{ \int dr_1\, \phi_1^*(r_1) \int dr_2\, \frac{|\phi_2^*(r_2)|^2}{r_{12}}\, \phi_1(r_1)$$

$$- \int dr_1\, \phi_1^*(r_1) \int dr_2\, \frac{\phi_2^*(r_2)\, \phi_1(r_2)}{r_{12}}\, \phi_2(r_1)$$

$$- \int dr_1\, \phi_2^*(r_1) \int dr_2\, \frac{\phi_1^*(r_2)\, \phi_2(r_2)}{r_{12}}\, \phi_1(r_1)$$

$$+ \int dr_2\, \phi_2^*(r_1) \int dr_2\, \frac{|\phi_1^*(r_2)|^2}{r_{12}}\, \phi_2(r_1) \Big\}$$

(*) Two types of terms: electron i assigned to the same orbital (Coulomb term) or to two different orbitals (exchange term). Define

$$\hat{J}_i\, \phi_k(r_1) = \int dr_2\, \frac{|\phi_i(r_2)|^2}{r_{12}}\, \phi_k(r_1)$$

and

$$\hat{K}_i \phi_k(r_1) = \int dr_2 \, \frac{\phi_i^*(r_2)\,\phi_k(r_2)}{r_{12}} \, \phi_i(r_1)$$

Then the second the "two body" integral can be formally written as

$$\langle \Psi | \frac{1}{r_{12}} | \Psi \rangle = \frac{1}{2} \sum_k \langle \phi_k | \sum_i \left(\hat{J}_i - \hat{K}_i \right) | \phi_k \rangle$$

The structure of the terms does not change in the case of N spin-orbitals so, in general,

$$\langle \Psi | \hat{H} | \Psi \rangle = \sum_k \langle \phi_k | \hat{h}_k | \phi_k \rangle + \frac{1}{2} \sum_k \langle \phi_k | \sum_i \left(\hat{J}_i - \hat{K}_i \right) | \phi_k \rangle$$

$$= \sum_k \langle \phi_k | \hat{h}_k + \frac{1}{2} \sum_i \left(\hat{J}_i - \hat{K}_i \right) | \phi_k \rangle$$

This is the functional that must be minimized to obtain the best (variational) orbitals. Taking the functional derivative with respect to $\phi_k^*(r_1)$ one obtains a set of N equations for the spin-orbitals that can be written as (show this for the two orbital case)

$$\hat{f}_k \phi_k(x) = \varepsilon_k \phi_k(x)$$

where

$$\hat{f}_k = \hat{h}_k + \sum_{i=1}^{N} \left(\hat{J}_i - \hat{K}_i \right)$$

is known as the Fock operator. The equation above looks like a time-independent Schrödinger equation BUT IT IS NOT. To see why, a few observations are in order:

1// This is a highly non linear set of coupled equations for the $\phi_k(x)$. The operator $\hat{F}_k$ is the sum of three types of terms, and both $\hat{J}_i$ and $\hat{K}_i$ "hide" all orbitals, in deed

$$\hat{J}_i \phi_k(x) = \int dx_2 \frac{|\phi_i(x_2)|^2}{r_{12}} \phi_k(x)$$

and

$$\hat{K}_i \phi_k(x) = \int dx_2 \frac{\phi_i^*(x_2)\phi_k(x_2)}{r_{12}} \phi_k(x)$$

2// The physical interpretation of the Coulomb and exchange terms is interesting

⊛ $\hat{J}_i$, also known as the Hartree potential, describes the (classical-like) interaction between two charge distributions described by $|\phi_i(x)|^2$ and $|\phi_k(x)|^2$ (see also structure on pag. ④). Due to the integral over x_2 this is a mean field like term.

∘ It has an unphysical aspect in that the sum over i includes k. This then represents the interaction of charge density k with itself: unphysical since an electron does not interact with itself (problem of the self-interaction, to be solved shortly)

* $\hat{K}_i$ has no classical analog. Formally, it originates from the antysimmetry of the electronic wave function. Note also that this term is non-local in space: The operator acts on $\phi_k(x)$ ↑ i.e. at x but the

value at x depends, via the integral, on the values of ϕ_k at all points x_2 (spin here is irrelevant, so $x \leftrightarrow r$).

- Finally this term automatically eliminates the self-interaction in the Fock equation. To see it, consider the term with $i = k$ in the sum

$$\hat{J}_k \phi_k(x) - \hat{K}_k \phi_k(x)$$

$$\equiv \int dx_2 \frac{|\phi_k(x_2)|^2}{r_{12}} \phi_k(x) - \int dx_2 \frac{\phi_k^*(x_2)\phi_k(x_2)}{r_{12}} \phi_k(x) = 0.$$

3// The single electron orbitals DO NOT HAVE a physical meaning. They represent the solutions of a non-interacting problem

4// The "eigenvalues" ε_k of the Fock equation do not have an immediate physical meaning

5// The solution of the equation must be "self-consisten

Let's go back to the Two orbital case. The Fock system is

$$\hat{h}_1 \phi_1(r_1) + \int dr_2 \frac{|\phi_2(r_2)|^2}{r_{12}} \phi_1(r_1) - \int dr_2 \frac{\phi_2^*(r_2)\phi_1(r_2)}{r_{12}} \phi_2(r_1) = \varepsilon_1 \phi_1(r_1)$$

$$\hat{h}_2 \phi_2(r_1) + \int dr_2 \frac{|\phi_1(r_2)|^2}{r_{12}} \phi_2(r_1) - \int dr_2 \frac{\phi_1^*(r_2)\phi_2(r_2)}{r_{12}} \phi_1(r_1) = \varepsilon_2 \phi_2(r_2)$$

(Rocco Meli's project for details).

6// With this scheme, the ground state is described as a function of the $3N$ electronic coordinates (plus spin). This is a huge space.