Hartree-Fock

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1 Generalities

Given a set of orthonormal spin-orbitals $\{\psi_\mu(\mathbf{x})\}_{\mu=1}^N$ (where $\mathbf{x} = (\mathbf{r}, \sigma)$ represents the spatial-spin coordinate of an electron)

$$\int \psi_\mu^*(\mathbf{x})\psi_\nu(\mathbf{x})d^4\mathbf{x} = \delta_{\mu\nu}$$

a **Slater determinant** can be defined as

$$\Psi(\mathbf{x}_1, ..\mathbf{x}_N) = \begin{vmatrix} \psi_1(\mathbf{x}_1) & \psi_1(\mathbf{x}_2) & ... & \psi_1(\mathbf{x}_N) \\ \psi_2(\mathbf{x}_1) & \psi_2(\mathbf{x}_2) & & \psi_2(\mathbf{x}_N) \\ ... & ... & & \\ \psi_N(\mathbf{x}_1) & \psi_N(\mathbf{x}_2) & ... & \psi_N(\mathbf{x}_N) \end{vmatrix}$$

Alternatively, in abstract notation[1], if $\{|\mu\rangle\}_{\mu=1}^N$ denotes the set of spin-orbitals we write the orthonormalization condition as

$$\langle \mu | \nu \rangle = \delta_{\mu\nu}$$

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[1] In the following we consider a set of states which we label with a set of integers $|1\rangle, |2\rangle, .. |N\rangle$ rather than using the more cumbersome notation $|\psi_1\rangle, |\psi_2\rangle, .. |\psi_N\rangle$.

and the Slater determinant as

$$
\begin{aligned}
|\Psi\rangle &= \frac{1}{\sqrt{N!}} \sum_{P \epsilon S_N} \epsilon_P P \left\{ |1\rangle \, |2\rangle \, .. \, |N\rangle \right\} \\
&= \sqrt{N!} A_N \left\{ |1\rangle \, |2\rangle \, .. \, |N\rangle \right\}
\end{aligned}
$$

Here P is a **permutation operator** $(P^\dagger = P^{-1})$ and runs over the group S_N of permutations of the first N integers[2]

$$
\begin{aligned}
P &= \begin{pmatrix} 1 & 2 & .. & N \\ p_1 & p_2 & .. & p_N \end{pmatrix} \Longrightarrow \\
P &\left\{ |1\rangle \, |2\rangle \, .. \, |N\rangle \right\} = \left\{ |p_1\rangle \, |p_2\rangle \, .. \, |p_N\rangle \right\}
\end{aligned}
$$

The **antisymmetrizer** A_N introduced above has been defined according to

$$
A_N = \frac{1}{N!} \sum_{P \epsilon S_N} \epsilon_P P
$$

(i.e. as a linear combination of the P operators with coefficients given by the *parity* ϵ_P) and satisfies $A_N^\dagger = A_N = A_N^2$. Hence, A_N defined in this way is a *projector*.

The wavefunction is correctly normalized. Indeed, using the projection properties of A_N we obtain

$$
\begin{aligned}
\langle \Psi \, | \, \Psi \rangle &= N! \, \langle A_N(12..N) \, | \, A_N(12..N) \rangle = \\
&= N! \, \langle 12..N \, | \, A_N^2 | 12..N \rangle \\
&= N! \, \langle 12..N \, | \, A_N | 12..N \rangle
\end{aligned}
$$

and

$$
N! \, \langle 12..N \, | \, A_N | 12..N \rangle = N! \frac{1}{N!} \sum_{P \epsilon S_N} \epsilon_P \, \langle 12..N | p_1 p_2 .. p_N \rangle \equiv 1
$$

where in the last equality $\langle 12..N \, | \, p_1 p_2 .. p_N \rangle = \delta_{1p_1} \delta_{2p_2} .. \delta_{Np_N}$ has been used. More generally, for $|\Psi\rangle$ and $|\Psi'\rangle$ defined as

$$
|\Psi\rangle = \sqrt{N!} A_N \, |\Phi\rangle \quad \text{and} \quad |\Psi'\rangle = \sqrt{N!} A_N \, |\Phi'\rangle
$$

---

[2]The notation for P means that 1 must be replaced by p_1, 2 by p_2 and so on. Thus $p_1, p_2..p_N$ is the same set of integers on the first line, but possibly with a different order. The whole set of P makes up a group, called the **symmetric group** - of order N- and usually denoted as S_N.

we have

$$\langle\Psi|\Psi'\rangle = N!\,\langle\Phi|A_N|\Phi'\rangle = \sum_{P\epsilon S_N} \epsilon_P\,\langle\Phi|P|\Phi'\rangle$$

This is actually a special case of a general result: for any operator O which is *symmetric* under exchange of the electron labels it holds

$$[P,O] = [A_N,O] = 0$$

hence

$$\langle\Psi|O|\Psi'\rangle = \sum_{P\epsilon\mathcal{S}_{[N]}} \epsilon_P\,\langle\Phi|OP|\Phi'\rangle$$

These formula replace the $N!^2$ sum appearing in the scalar product between two antisymmetrized vectors with a simpler $N!$ sum.

2 Expectation values

Let us now write down the expectation value of the Hamiltonian operator on a Slater determinant

$$\langle\Psi\,|\,H|\Psi\rangle = E_{HF} \quad H = \sum_{i=1}^{N} h_i + \frac{1}{2}\sum_{j,i\neq j}^{N} g_{ij} = H^{(1)} + H^{(2)}$$

Here h_i's are monoelectronic operators, $h_i = k_i + v_i$, and g_{ij} is the interelectronic repulsion potential. Correspondingly, $H^{(1)}$ and $H^{(2)}$ are the one- and two- electron terms of the Hamiltonian, respectively. Both $H^{(1)}$and $H^{(2)}$ are symmetric operators, hence

$$
\begin{aligned}
\left\langle\Psi\,\middle|\,H^{(i)}|\Psi\right\rangle = &\ N!\left\langle A_N(12..N)\,\middle|\,H^{(i)}|A_N(12..N)\right\rangle = \\
= &\ N!\left\langle 12..N\,\middle|\,A_N H^{(i)} A_N|12..N\right\rangle = \\
= &\ N!\left\langle 12..N\,\middle|\,H^{(i)} A_N^2|12..N\right\rangle = \\
= &\ \sum_{P\epsilon S_N}\epsilon_P\left\langle 12..N\,\middle|\,H^{(i)}|p_1 p_2..p_N\right\rangle
\end{aligned}
$$

Let us first consider the monoelectronic term and focus attention on the first electron

$$
\begin{aligned}
&\sum_{P\in S_N}\epsilon_P\,\langle 12..N\,|\,h_1|p_1 p_2..p_N\rangle = \\
= &\sum_{P\in S_N}\epsilon_P\,\langle 1\,|\,h_1|p_1\rangle\,\langle 2\,|\,p_2\rangle..\langle N\,|\,p_N\rangle = \\
= &\sum_{P\in S_N}\epsilon_P\,\langle 1\,|\,h_1|p_1\rangle\,\delta_{2p_2}..\delta_{Np_N} = \langle 1|h|1\rangle
\end{aligned}
$$

In the last line the subscript 1 on h has been removed since it is dummy. By the same token we have

$$\sum_{P \in S_N} \epsilon_P \langle 12..N|h_\mu|p_1 p_2..p_N \rangle = \langle \mu|h|\mu \rangle$$

Thus, we can write the one-electron Hamiltonian as

$$\langle \Psi|H^{(1)}\Psi \rangle = \sum_{\mu=1}^{N} \langle \mu|h|\mu \rangle$$

Analogously

$$\sum_{P \in S_N} \epsilon_P \langle 12..N|g_{12}|p_1 p_2..p_N \rangle =$$
$$= \sum_{P \in S_N} \epsilon_P \langle 12|g_{12}|p_1 p_2 \rangle \, \delta_{3 p_3} \delta_{4 p_4}..\delta_{N p_N} =$$
$$= \langle 12|g|12 \rangle - \langle 12|g|21 \rangle$$

i.e. in general

$$\langle \Psi|H^{(2)}\Psi \rangle = \frac{1}{2} \sum_{\mu,\nu(\neq\mu)=1}^{N} \left(\langle \mu\nu|g|\mu\nu \rangle - \langle \mu\nu|g|\nu\mu \rangle \right)$$

This can be rewritten in a simpler form by introducing an **exchange operator** π[3]

$$\pi \, |\mu\nu \rangle = |\nu\mu \rangle$$

$$\left\langle \Psi \, \middle| \, H^{(2)}\Psi \right\rangle = \frac{1}{2} \sum_{\mu,\nu(\neq\mu)=1}^{N} \langle \mu\nu \, | \, g(1-\pi)|\mu\nu \rangle$$

In conclusion, the expectation value of H (the **Hartree-Fock energy**) reads as

$$\langle \Psi \, | \, H\Psi \rangle = \sum_{\mu=1}^{N} \langle \mu \, | \, h|\mu \rangle + \frac{1}{2} \sum_{\mu,\nu(\neq\mu)=1}^{N} \langle \mu\nu \, | \, g(1-\pi)|\mu\nu \rangle$$

Note that in the last term on the r.h.s. we can remove the restriction $\nu \neq \mu$ since the term $\nu = \mu$ does not contribuite to the sum.

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[3]It can be readily shown that $\pi = \pi^\dagger = \pi^{-1} = \pi^2$ and $\pi g = g\pi$.

3 Variation of the orbitals

Let us now apply the variational principle. In doing this, we take care of the orthogonalization condition

$$\langle \mu \,|\, \nu \rangle = 1$$

which implies

$$\langle \delta\mu \,|\, \nu \rangle + \langle \mu \,|\, \delta\nu \rangle = 0$$

or, equivalently,

$$\langle \delta\mu \,|\, \nu \rangle = 0 \qquad \mu \neq \nu$$
$$\Re \langle \delta\mu | \mu \rangle = 0 \qquad \mu = \nu$$

and focus on the (special class of) variations that satisfy[4]

$$\langle \delta\mu | \nu \rangle = 0 \ \text{ for any } \ \nu = 1, 2..N$$

From a geometrical point of view they satisfy $|\delta\mu\rangle \in \{|\nu\rangle\}_{\nu=1..N}^{\perp}$, i.e. they are such that the $|\delta\mu\rangle$ is (arbitrarly) confined in the orthogonal complement of the "occupied" orbital space[5]. Applying the variation of the orbital $|\mu\rangle$ we obtain

$$
\begin{aligned}
0 = \langle \delta\Psi | H\Psi \rangle \ &= \ \langle \delta\mu | h | \mu \rangle + \\
&+ \frac{1}{2} \sum_{\nu(\neq\mu)=1}^{N} \langle \delta\mu\nu | g(1-\pi) | \mu\nu \rangle + \\
&+ \frac{1}{2} \sum_{\nu(\neq\mu)=1}^{N} \langle \nu\delta\mu | g(1-\pi) | \nu\mu \rangle = \\
&= \ \langle \delta\mu | h | \mu \rangle + \sum_{\nu(\neq\mu)=1}^{N} \langle \delta\mu\nu | g(1-\pi) | \mu\nu \rangle = \\
&\equiv \ \langle \delta\mu | h | \mu \rangle + \sum_{\nu=1}^{N} \langle \delta\mu\nu | g(1-\pi) | \mu\nu \rangle
\end{aligned}
$$

---

[4]Variations of this kind are complex-linear, meaning they form a *complex* linear space, something that is not possible under the more general condition $\Re \langle \delta\mu | \mu \rangle = 0$). The remaining variations add nothing, and complicate the analysis because they would require application of the stationay condition in "full form", in contrast to the "Dirac-Frenkel" form $\langle \delta\Psi | H | \Psi \rangle = 0$.

[5]The symbol $\perp$ denotes the **orthogonal complement**. Remember that the orthogonal complement of a set of vector - *however chosen* - is the *linear space* spanned by the vectors that are orthogonal to each vector of the given set. That is, $\{|1\rangle, |2\rangle, .. |m\rangle\}^{\perp} = \{|\psi\rangle$ such that $\langle \mu | \psi \rangle = 0$ for $\mu = 1, m\}$.

where $\pi \, |\mu\mu\rangle = |\mu\mu\rangle$ has been used in the last line. Thus,

$$\langle \delta\Psi | H\Psi\rangle = \langle\delta\mu|h + \sum_{\nu=1}^{N} \langle\nu|g(1-\pi)|\mu\rangle \, |\nu\rangle = \langle\delta\mu|f|\mu\rangle = 0 \qquad (1)$$

where f is a mono-electronic, *self-adjoint* operator known as **Fock operator**

$$f = h + \sum_{\nu=1}^{N} \langle\nu \,|\, g(1-\pi)|\nu\rangle \qquad (2)$$

Now, an equation of the form

$$\langle\delta\mu \,|\, \phi\rangle = 0$$

with $|\delta\mu\rangle$ *arbitrary* in $\{|\mu\rangle\}_{\mu=1,..N}^{\perp}$ implies $|\phi\rangle \in \{|\mu\rangle\}_{\mu=1,..N}^{\perp\perp}$, i.e., in other words,

$$f \, |\mu\rangle = \sum_{\nu=1}^{N} |\nu\rangle \, \epsilon_{\nu\mu}$$

where $\epsilon_{\nu\mu} = \langle\nu|f|\mu\rangle$ is a hermitean matrix since f is self-adjoint.

The Fock operator depends on the kets $|\mu\rangle$ entering the Slater determinant but, on inspecting of Eq.(2), it is clear that it is manifestly invariant under unitary transformations of the orbitals. Thus, a unitary transformation in the occupied space can be performed to put the variational equations above in "canonical" form

$$f \, |\mu\rangle = \epsilon_{\mu} \, |\mu\rangle \qquad (3)$$

Here, the solution orbitals and eigenvalues are known as **canonical** orbitals and orbital energies.

Note 1 As noticed above, the f operator depends on $\{|\mu\rangle\}$, i.e. the HF equations are *not* simple linear equations. However, at convergence, f is a well defined operator and the $|\mu\rangle$'s are its eigenvectors. A closer look at f reveals that

$$f = k + v + \sum_{\nu} \left(\langle\nu \,|\, g|\nu\rangle - \langle\nu \,|\, g\pi|\nu\rangle \right)$$

or, in coordinate representation[6],

$$\hat{f} = \hat{k} + v(\mathbf{r}) + v_H(\mathbf{r}) - \hat{v}_{\text{ex}}$$

---

[6]In the following the spin-orbtials are taken of the "spin-collinear" form, $\psi_\nu(\mathbf{x}) = \phi_\nu(\mathbf{r})\theta_\nu(\sigma)$, where ϕ is the spatial component and θ its spin component. Hence, ϕ_ν stands for the spatial orbital of the ν-th one-electron state employed.

where $\hat{k} = -\frac{1}{2}\nabla^2$ is the kinetic energy, $v(\mathbf{r})$ is the "external" potential (e.g. the electrostatic potential nuclear generated by the nuclei), and the remaining terms take the form

$$v_H(\mathbf{r}) = \sum_\nu \langle \nu \mid g|\nu\rangle = \int \frac{n(\mathbf{r}')}{\|\mathbf{r} - \mathbf{r}'\|}d^3\mathbf{r}' \quad \hat{v}_{\text{ex}} = \sum_\nu \langle \nu \mid g\pi|\nu\rangle$$

Here

$$n(\mathbf{r}) = \sum_\nu |\phi_\nu(\mathbf{r})|^2$$

is the **electron density** of the N electrons in the N HF orbitals, and v_H is the so-called **Hartree potential**, *i.e.* the potential felt by an electron in the field of the nuclei *and* of an $N-$electron distribution described by[7] $n(\boldsymbol{r})$. The term v_{ex} is a *non-local* **exchange operator** whose matrix elementes in coordinate representation are of the form[8]

$$\langle \mathbf{x}|v_{ex}|\mathbf{x}'\rangle = \sum_\nu \frac{\psi_\nu(\mathbf{x})\psi_\nu^*(\mathbf{x}')}{\|\boldsymbol{r} - \boldsymbol{r}'\|}$$

as can be seen by introducing the spectral representation of g

$$g = \int d\mathbf{x}_2 d\mathbf{x}_3 \frac{|\mathbf{x}_2\mathbf{x}_3\rangle \langle \mathbf{x}_2\mathbf{x}_3|}{\|\boldsymbol{r}_2 - \boldsymbol{r}_3\|}$$

and noticing that

$$\langle \mathbf{x}\nu|\mathbf{x}_2\mathbf{x}_3\rangle \langle \mathbf{x}_2\mathbf{x}_3|\nu\mathbf{x}'\rangle = \langle \mathbf{x}|\mathbf{x}_2\rangle \phi_\nu^*(\mathbf{x}_3)\phi_\nu(\mathbf{x}_2) \langle \mathbf{x}_3|\mathbf{x}'\rangle$$

Note 2 Let $\overline{f}$ be the *self-consistent field* Fock operator and

$$\{|\mu\rangle\}_{\mu=1}^N \rightarrow \text{ occupied orbitals}$$

$$\{|n\rangle\}_{n>N} \rightarrow \text{ virtual orbitals}$$

Clearly $|n\rangle \in \{|\mu\rangle\}_{\mu=1,N}^\perp$. Let us put $|n\rangle = |\delta\mu\rangle$ in eq.(1). It follows

$$\langle \delta\Psi \mid H|\Psi\rangle = 0, \text{ with } |\delta\Psi\rangle = \sqrt{N!}A\,|1, 2, ..n..N\rangle$$

---

[7]Note that each electron feels *all* the N electrons, i.e. this Hartree potential contains the so-called *self -interaction*. The latter cancels when the exchange term is taken into account.

[8]Note, in contrast, that for a local operator v we have $\langle \mathbf{x}|v|\mathbf{x}'\rangle = v(\mathbf{x})\delta(\mathbf{x} - \mathbf{x}')$, where for $\mathbf{x} = (\mathbf{r}, \sigma)$ we have $\delta(\mathbf{x} - \mathbf{x}') = \delta(\mathbf{r} - \mathbf{r}')\delta_{\sigma\sigma'}$

(with n in place of μ), i.e. *singly excited configurations do not mix with the HF one* (**Brillouin's theorem**)[9].

Note 3[10] A Slater determinant is *invariant* under non-singular (but otherwise arbitrary) linear transformation of vectors. That is, let

$$|\mu'\rangle = \sum_\mu T_{\mu'\mu} |\mu\rangle , \ \det T \neq 0$$

define a non-singular transformation and apply the multiplication rule of determinants. It follows

$$|\Psi'\rangle = |1'2'..N'\rangle = \det T |12..N\rangle$$

where the normalization factor $\det T$ (which is non null since T is non-singular) is immaterial for physical purposes. From a geometrical point of view, $\{|\mu\rangle\}_{\mu=1,N}$ span an N-dimensional linear space and T is a change of basis in this space. The (N-particle) HF vector depends *on the N-dimensional linear space **only***, i.e. it depends on the *projector* ρ in this space. For orthogonal orbitals it reads as

$$\rho = \sum_{\mu=1}^N |\mu\rangle \langle\mu|$$

and satisfies of course

$$\rho^2 = \rho = \rho^\dagger$$

This projector is the one-particle (HF) *density operator*. The above comment suggests that densisty operators of whatever order, *in the HF approximation*, depend on the 1-particle one **only**. This is indeed the case, in that it can be shown that for any order p

$$\rho^{(p)} = \underbrace{\rho \otimes \rho \otimes \rho.. \otimes \rho}_{p \, \text{times}} A_p$$

where

$$A_p = \frac{1}{p!} \sum_{P \in S_p} \epsilon_P P$$

---

[9]This is because we are imposing that the variation of the energy functional must be null at *first* order.

[10]This is a somewhat advanced topic, and can be skipped at a first reading.

For instance, for the second order (2-particle) density operator we have

$$\rho^{(2)} = \frac{1}{2!}\rho \otimes \rho\,(1 - \pi)$$

It follows that the HF equations can also be obtained by writing the expectation value of H in terms of the *one*-particle density matrix ρ and varying it under the *normalization constraint*

$$\mathrm{Tr}\rho = N$$

and the projector properties

$$\rho^2 = \rho = \rho^\dagger$$

This results in the equation

$$[f[\rho], \rho] = 0$$

which is equivalent to the HF equations given above. Here, we emphasized the functional dependence of f on ρ which makes the problem self-consistent.