

# Hartree-Fock

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## 1 Generalities

Given a set of orthonormal spin-orbitals  $\{\psi_\mu(\mathbf{x})\}_{\mu=1}^N$

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

a “Slater determinant” can be defined as

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

Alternatively, in abstract notation<sup>1</sup>, 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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<sup>1</sup>In the following we consider a set of states which we label with a set of integers  $|1\rangle, |2\rangle, \dots, |N\rangle$  rather than using the more cumbersome notation  $|\psi_1\rangle, |\psi_2\rangle, \dots, |\psi_N\rangle$ .

and the Slater determinant as

$$\begin{aligned} |\Psi\rangle &= \frac{1}{\sqrt{N!}} \sum_{P \in \mathcal{S}_{[N]}} \epsilon_P P \{|1\rangle |2\rangle \dots |N\rangle\} \\ &= \sqrt{N!} A_N \{|1\rangle |2\rangle \dots |N\rangle\} \end{aligned}$$

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

$$\begin{aligned} P &= \begin{pmatrix} 1 & 2 & \dots & N \\ p_1 & p_2 & \dots & p_N \end{pmatrix} \implies \\ P \{|1\rangle |2\rangle \dots |N\rangle\} &= \{|p_1\rangle |p_2\rangle \dots |p_N\rangle\} \end{aligned}$$

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

$$A_N = \frac{1}{N!} \sum_{P \in \mathcal{S}_N} \epsilon_P P$$

(i.e. as a linear combination of the  $P$  operators with coefficients given by the *parity*  $\epsilon_P$ ) and satisfies  $A_N^\dagger = A_N = A_N^2$ . This means that  $A_N$  is a *projector*.

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

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

and then

$$N! \langle 12\dots N | A_N | 12\dots N \rangle = N! \frac{1}{N!} \sum_{P \in \mathcal{S}_{[N]}} \epsilon_P \langle 12\dots N | p_1 p_2 \dots p_N \rangle \equiv 1$$

where in the last equality  $\langle 12\dots N | p_1 p_2 \dots p_N \rangle = \delta_{1p_1} \delta_{2p_2} \dots \delta_{Np_N}$  has been used. More generally, if

$$|\Psi\rangle = \sqrt{N!} A_N |\Phi\rangle$$

and

$$|\Psi'\rangle = \sqrt{N!} A_N |\Phi'\rangle$$

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<sup>2</sup>The notation for  $\mathcal{S}$  means that 1 must be replaced by  $p_1$ , 2 by  $p_2$  and so on. Thus  $p_1, p_2, \dots, p_N$  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  $\mathcal{S}_N$

we get

$$\langle \Psi | \Psi' \rangle = N! \langle \Phi | A_N | \Phi' \rangle = \sum_{P \in \mathcal{S}_{[N]}} \epsilon_P \langle \Phi | P | \Phi' \rangle$$

Furthermore, noticing that for any operator  $O$  which is *symmetric* under exchange of the electron labels we have  $[P, O] = [A_N, O] = 0$ , it also follows

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

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 over the 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 and thus

$$\begin{aligned} \langle \Psi | H^{(i)} | \Psi \rangle &= N! \langle A_N(12..N) | H^{(i)} | A_N(12..N) \rangle = \\ &= N! \langle 12..N | A_N H^{(i)} A_N | 12..N \rangle = \\ &= N! \langle 12..N | H^{(i)} A_N^2 | 12..N \rangle = \\ &= \sum_{P \in \mathcal{S}_{[N]}} \epsilon_P \langle 12..N | H^{(i)} | p_1 p_2 .. p_N \rangle \end{aligned}$$

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

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

In the last line the subscript 1 on  $h$  has been removed since it is dummy. With the same token

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

and 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

$$\begin{aligned} & \sum_{P \in \mathcal{S}_N} \epsilon_P \langle 12..N | g_{12} | p_1 p_2 .. p_N \rangle = \\ &= \sum_{P \in \mathcal{S}_N} \epsilon_P \langle 12 | g_{12} | p_1 p_2 \rangle \delta_{3p_3} \delta_{4p_4} .. \delta_{Np_N} = \\ &= \langle 12 | g | 12 \rangle - \langle 12 | g | 21 \rangle \end{aligned}$$

*i. e.* in general

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

This can be rewritten in a simpler form by introducing an *exchange operator*  $\pi$ <sup>3</sup>

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

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

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 contribute to the sum.

### 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

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

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<sup>3</sup>It can be readily shown that  $\pi = \pi^\dagger = \pi^{-1} = \pi^2$  and  $\pi g = g\pi$ .

or, equivalently, since  $|\delta\mu\rangle, |\delta\nu\rangle$  are arbitrary (try the  $|\delta\mu\rangle \rightarrow i|\delta\mu\rangle, |\delta\nu\rangle \rightarrow i|\delta\nu\rangle$  transformation!), the relation

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

must hold. From a geometrical point of view this means that  $|\delta\mu\rangle \in \{|\nu\rangle\}_{\nu=1..N}^\perp$ , i.e. the variation  $|\delta\mu\rangle$  is arbitrary in the orthogonal complement of the ‘‘occupied’’ orbital space<sup>4</sup>. Applying the variation of the orbital  $|\mu\rangle$  we get<sup>5</sup>

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

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

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

where the *Fock operator*

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

is here defined and turns out to be a mono-electronic, *self-adjoint* operator. **Now, an equation of the form**

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

<sup>4</sup>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,  $\{ |1\rangle, |2\rangle, \dots, |m\rangle \}^\perp = \{ |\psi\rangle \}$  such that  $\langle \mu | \psi \rangle = 0$  for  $\mu = 1, m$ .

<sup>5</sup>Note that it is *sufficient* to vary only the bra component. Why?

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

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

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

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 “diagonal” form

$$f|\mu\rangle = \epsilon_\mu |\mu\rangle \quad (3)$$

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  $|\mu\rangle$ 's are its eigenvectors. A closer look at  $f$  reveals that

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

or, in coordinate representation<sup>6</sup>,

$$k = -\frac{1}{2}\nabla^2$$

and

$$f = k + v_H(r) - v_{ex}(r, r')$$

where

$$v_H \equiv v(\mathbf{r}) + \sum_{\nu} \langle\nu|g|\nu\rangle = v(\mathbf{r}) + \int \frac{n(\mathbf{r}')}{\|\mathbf{r} - \mathbf{r}'\|} d\mathbf{r}'$$

and

$$v_{ex} = \sum_{\nu} \langle\nu|g\pi|\nu\rangle$$

Here

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

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<sup>6</sup>We use the following notation:  $\mathbf{x}$  is the full set of spin and spatial variables,  $\mathbf{r}$  is the set of spatial coordinates and  $\psi(\mathbf{x}) = \phi_{\psi}(\mathbf{r})\theta_{\psi}(\sigma)$  is a spin-orbital whose spatial component is  $\phi$  and spin component  $\theta$ .

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  $n(\mathbf{r})$ <sup>7</sup>. The term  $v_{ex}$  is a *non-local* “exchange” operator whose matrix elements in coordinate representation are of the form<sup>8</sup>

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

as can be seen by introducing the spectral representation of  $g$

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

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  $\bar{f}$  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

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

(with  $n$  in place of  $\mu$ ), *i.e.* **singly excited configurations do not mix with the HF one** (Brillouin’s theorem)<sup>9</sup>.

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

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

<sup>7</sup>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 above is considered.

<sup>8</sup>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  $\delta(\mathbf{x} - \mathbf{x}') = \delta(\mathbf{r} - \mathbf{r}') \delta_{\sigma\sigma'}$

<sup>9</sup>This is because we are imposing that the variation of the energy functional must be null at *first* order.

<sup>10</sup>This is a somewhat advanced topic, and can be skipped at a first reading.

be 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*  $\rho$  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 density 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  $p$

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

where

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

(e.g.  $\rho^{(2)} = \frac{1}{2!} \rho \otimes \rho (1 - \pi)$ ). 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  $\rho$  and varying it under the *normalization constraint*

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

and the projector properties

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