The Hartree-Fock method

The trial function should be totally antisymmetric

    IEA − Slater-determinant

q_i − spatial and spin coordinates $(q_i \equiv (\mathbf{r_i}, \sigma_i), \, i = \overline{1, N})$,

    λ − the states $(\lambda = \alpha, \beta, \dots, \nu)$.

N no. of electrons and of occupied states (Pauli principle)

$$\phi(q_1, q_2, \dots, q_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} u_\alpha(q_1) & u_\beta(q_1) & \cdots & u_\nu(q_1) \\ u_\alpha(q_2) & u_\beta(q_2) & \cdots & u_\nu(q_2) \\ \vdots & \vdots & & \vdots \\ u_\alpha(q_N) & u_\beta(q_N) & \cdots & u_\nu(q_N) \end{vmatrix}. \tag{1}$$

In the ground state of the atoms (S and L has maximum value) the wavefunction of the system can be expressed by a single Slater-determinant.

    This determinant is taken to be the trial function for the variational method.

    We have to minimize the $E[\phi] = \langle \phi | H | \phi \rangle$ functional with the orthonormality conditions of the ~~pi~~-orbitals
            spin

$$\langle u_\mu | u_\lambda \rangle = \delta_{\mu\lambda}, \qquad \mu, \lambda = \overline{\alpha, \nu}. \tag{2}$$

We split he Hamiltonian into two parts

$$H_1 = \sum_{i=1}^{N} h_i; \quad h_i = -\frac{1}{2}\nabla_i^2 - \frac{Z}{r_i} \tag{3}$$

$$H_2 = \sum_{i<j} \frac{1}{r_{ij}}, \tag{4}$$

leading to

$$E[\phi] = \langle\phi|H_1|\phi\rangle + \langle\phi|H_2|\phi\rangle. \tag{5}$$

We write the Slater-determinants into more compact form

$$\phi(q_1, q_2, \ldots, q_N) = \frac{1}{\sqrt{N!}}\sum_P (-1)^P P u_\alpha(q_1)u_\beta(q_2)\cdots u_\nu(q_N)$$

$$= \sqrt{N!}A\phi_H, \tag{6}$$

P – the permutations of coordinates q_i
ϕ_H – the non-symmetrized wavefunction

$$\phi_H = u_\alpha(q_1)u_\beta(q_2)\cdots u_\nu(q_N), \tag{7}$$

while A is the anti-symmetrization operator

$$A = \frac{1}{N!}\sum_P (-1)^P P. \tag{8}$$

It has no effect on a totally antisymmetric wavefunction. This operator projects a wavefunction on the subfield of totally antisymmetric wavefunctions.

$$A^2 = A. \tag{9}$$

H_1 and H_2 are invariant under permutations of the electron coordinates, hence commute with A

$$[H_1, A] \quad = \quad 0 \tag{10}$$
$$[H_2, A] \quad = \quad 0. \tag{11}$$

Let's calculate the matrix element

$$\langle \phi | H_1 | \phi \rangle \quad = \quad N! \langle \phi_H | A H_1 A | \phi_H \rangle = N! \langle \phi_H | H_1 A^2 | \phi_H \rangle$$
$$= \quad N! \langle \phi_H | H_1 A | \phi_H \rangle, \tag{12}$$

where we ave used (10) and (9). Introducing (8) and (3) we obtain

$$\langle \phi | H_1 | \phi \rangle \quad = \quad \sum_{i=1}^{N} \sum_{P} (-1)^P \langle \phi_H | h_i P | \phi_H \rangle = \sum_{i=1}^{N} \langle u_\lambda(q_i) | h_i | u_\lambda(q_i) \rangle$$
$$= \quad \sum_{\lambda=\alpha}^{\nu} \langle u_\lambda(q_i) | h_i | u_\lambda(q_i) \rangle. \tag{13}$$

We have taken into account the (2) orthogonality conditions. Finally we have replaced the sum over the electrons with the sum over the occupied states.

We introduce the notation

$$I_\lambda = \langle u_\lambda(q_i) | h_i | u_\lambda(q_i) \rangle, \tag{14}$$

obtaining

$$\langle \phi | H_1 | \phi \rangle = \sum_\lambda I_\lambda. \tag{15}$$

Similarly we can write for the matrix elements of the two-electron operators

$$
\begin{aligned}
\langle \phi | H_2 | \phi \rangle &= N! \langle \phi_H | A H_2 A | \phi_H \rangle = N! \langle \phi_H | H_2 A | \phi_H \rangle \\
&= \sum_{i<j} \sum_P (-1)^P \langle \phi_H | \frac{1}{r_{ij}} P | \phi_H \rangle \\
&= \sum_{i<j} \langle \phi_H | \frac{1}{r_{ij}} (1 - P_{ij}) | \phi_H \rangle.
\end{aligned}
\tag{16}
$$

We have taken into account that because the orthogonality of u_λ for a given i, j pair from the sum of permutations remain only u_λ and u_μ depending on q_i and q_j coordinates. P_{ij} is the exchange operator for the coordinates of electrons i and j.

Switching to the sum over the states

$$\langle\phi|H_2|\phi\rangle \quad = \quad \sum_{\lambda<\mu}\left[\langle u_\lambda(q_i)u_\mu(q_j)|\frac{1}{r_{ij}}|u_\lambda(q_i)u_\mu(q_j)\rangle\right.$$

$$\left.-\langle u_\lambda(q_i)u_\mu(q_j)|\frac{1}{r_{ij}}|u_\mu(q_i)u_\lambda(q_j)\rangle\right]. \qquad (17)$$

The sum is over $N(N-1)/2$ orbital pairs. We introduce the notation for the matrix elements

$$J_{\lambda\mu} \quad = \quad \langle u_\lambda(q_i)u_\mu(q_j)|\frac{1}{r_{ij}}|u_\lambda(q_i)u_\mu(q_j)\rangle \qquad (18)$$

$$K_{\lambda\mu} \quad = \quad \langle u_\lambda(q_i)u_\mu(q_j)|\frac{1}{r_{ij}}|u_\mu(q_i)u_\lambda(q_j)\rangle, \qquad (19)$$

$J_{\lambda\mu}$ – Coulomb (direct) integral
$K_{\lambda\mu}$ – exchange integral
   We can extend the sum over all λ, μ, because the terms with $\lambda = \mu$ will be zero ($J_{\lambda\lambda} = K_{\lambda\lambda}$), and all other terms will appear twice. Finally

$$\langle\phi|H_2|\phi\rangle = \frac{1}{2}\sum_{\lambda,\mu}[J_{\lambda\mu} - K_{\lambda\mu}]. \qquad (20)$$

The functional

$$E[\phi] = \sum_\lambda I_\lambda + \frac{1}{2} \sum_{\lambda,\mu} [J_{\lambda\mu} - K_{\lambda\mu}]. \tag{21}$$

We have to take into account the (2) additional conditions in the minimization.

Lagrange-multiplier method

$$\delta \left(E[\phi] - \sum_{\lambda,\mu} \epsilon_{\lambda\mu} \langle u_\lambda | u_\mu \rangle \right) = 0. \tag{22}$$

It can be proved, that the $\epsilon_{\lambda\mu}$ matrix can be diagonalized. We assume, it is done, so $\epsilon_{\lambda\mu} = E_\lambda \delta_{\lambda\mu}$. In these conditions

$$\delta E[\phi] - \sum_\lambda E_\lambda \delta \langle u_\lambda | u_\lambda \rangle = 0. \tag{23}$$

We perform the variation as for the Hartree-method

$$\left[-\frac{1}{2} \nabla_i^2 - \frac{Z}{r_i} + \sum_\mu \langle u_\mu | \frac{1}{r_{ij}} | u_\mu \rangle \right] u_\lambda(q_i) - \sum_\mu \langle u_\mu | \frac{1}{r_{ij}} | u_\lambda \rangle u_\mu(q_i) = E_\lambda u_\lambda(q_i), \tag{24}$$

where λ takes all the values for the N occupied states between α and ν. The equation above are the Hartree–Fock equations.

– exchange integrals

The Hartree–Fock-potential is the same for each electron, and the u_λ solutions (Hartree–Fock orbitals) are orthogonal to each other.

Introducing the direct and exchange operators

$$V_\mu^{\mathrm{d}}(q_i) = \langle u_\mu | \frac{1}{r_{ij}} | u_\mu \rangle \equiv V_\mu^{\mathrm{d}}(\mathbf{r_i}) \tag{25}$$

$$V_\mu^{\mathrm{ex}}(q_i) f(q_i) = \langle u_\mu | \frac{1}{r_{ij}} | f \rangle u_\mu(q_i), \tag{26}$$

and the potentials

$$\mathcal{V}^{\mathrm{d}}(\mathbf{r_i}) = \sum_\mu V_\mu^{\mathrm{d}}(\mathbf{r_i}) \tag{27}$$

$$\mathcal{V}^{\mathrm{ex}}(q_i) = \sum_\mu V_\mu^{\mathrm{ex}}(q_i). \tag{28}$$

we can write

$$\left[-\frac{1}{2} \nabla_i^2 - \frac{Z}{r_i} + \mathcal{V}^{\mathrm{d}}(\mathbf{r_i}) + \mathcal{V}^{\mathrm{ex}}(q_i) \right] u_\lambda(q_i) = E_\lambda u_\lambda(q_i). \tag{29}$$

This system can be solved by the self-consistent field method.

Usually we separate the spatial and spin-dependent part of the wavefunctions

$$u_\lambda(q_i) = u_\lambda(\mathbf{r_i})\chi_{m_s^\lambda}(\sigma_i), \tag{30}$$

where

$$\langle\chi_{m_s^\lambda}|\chi_{m_s^\mu}\rangle = \delta_{m_s^\lambda m_s^\mu}, \tag{31}$$

and m_s^λ is the magnetic spin quantum number for the electron in state λ. Introducing (30) into (24) the Hartree–Fock equations may be written for the wavefunctions depending only on spatial coordinates

$$\left[-\frac{1}{2}\nabla_i^2 - \frac{Z}{r_i} + \sum_\mu \langle u_\mu|\frac{1}{r_{ij}}|u_\mu\rangle\right] u_\lambda(\mathbf{r_i})$$

$$-\sum_\mu \delta_{m_s^\lambda m_s^\mu}\langle u_\mu|\frac{1}{r_{ij}}|u_\lambda\rangle u_\mu(\mathbf{r_i}) = E_\lambda u_\lambda(\mathbf{r_i}), \tag{32}$$

$$\lambda = \overline{\alpha,\nu}.$$

Generally these partial differential equations should be solved in 3 dimensions. If the potentials are not spherically symmetric, solving these equations is very complicated.

If we have closed shells – the Hartree-Fock potentials are spherically symmetric.

In other cases usually the potentials are approximated by a spherically symmetric potential – spherically averaged.

In these cases the orbital parts of the wavefunctions are described by the spherical harmonics, and we can write the following radial equations

$$\left[-\frac{1}{2}\frac{d^2}{dr_i^2} + \frac{l(l+1)}{2r_i^2} - \frac{Z}{r_i} + \mathcal{V}^{\mathrm{d}}(r_i) - \mathcal{V}^{\mathrm{ex}}(r_i) \right] P_{nl}(r_i) = E_{nl} P_{nl}(r_i), \qquad (33)$$

where

$$\mathcal{V}^{\mathrm{d}}(r_i) \;=\; \sum_{n'l'} \mathcal{V}_{n'l'}^{\mathrm{d}}(r_i) \qquad (34)$$

$$\mathcal{V}^{\mathrm{ex}}(r_i) \;=\; \sum_{n'l'} \mathcal{V}_{n'l'}^{\mathrm{ex}}(r_i) \qquad (35)$$

are the potentials created by all closed subshells.

The summary of the Hartree–Fock method:

1. the calculation of potentials (34)–(35) using Slater-determinants

2. the solution of (33) differential equations

3. the two item above are repeated it until the system becomes self-consistent

We obtain the Hartree-Fock wavefunctions in numeric form. Often is useful to express these functions in analytical form using a few parameters – they are fitted to the numerical solution.

Example – the ground state of beryllium

Closed shells – two electrons on $1s$ and two on $2s$ spatial orbitals.

The Slater-determinant

$$\phi(q_1, q_2, q_3, q_4) = \frac{1}{\sqrt{4!}} \begin{vmatrix} u_{1s\uparrow}(q_1) & u_{1s\downarrow}(q_1) & u_{2s\uparrow}(q_1) & u_{2s\downarrow}(q_1) \\ u_{1s\uparrow}(q_2) & u_{1s\downarrow}(q_2) & u_{2s\uparrow}(q_2) & u_{2s\downarrow}(q_2) \\ u_{1s\uparrow}(q_3) & u_{1s\downarrow}(q_3) & u_{2s\uparrow}(q_3) & u_{2s\downarrow}(q_3) \\ u_{1s\uparrow}(q_4) & u_{1s\downarrow}(q_4) & u_{2s\uparrow}(q_4) & u_{2s\downarrow}(q_4) \end{vmatrix}, \tag{36}$$

The $\mathcal{V} = \mathcal{V}^{\mathrm{d}} + \mathcal{V}^{\mathrm{ex}}$ Hartree–Fock potentials from (29)

$$\mathcal{V} = V^d_{1s\uparrow} + V^d_{1s\downarrow} + V^d_{2s\uparrow} + V^d_{2s\downarrow} - (V^{ex}_{1s\uparrow} + V^{ex}_{1s\downarrow} + V^{ex}_{2s\uparrow} + V^{ex}_{2s\downarrow}). \tag{37}$$

The direct and exchange potentials are given by (25) and (26).

We separate for each spin-orbital the dependence on the spatial and spin coordinates

$$u_{1s\uparrow}(q) = u_{1s}(r)\alpha \tag{38}$$

$$u_{1s\downarrow}(q) = u_{1s}(r)\beta \tag{39}$$

$$u_{2s\uparrow}(q) = u_{2s}(r)\alpha \tag{40}$$

$$u_{2s\downarrow}(q) = u_{2s}(r)\beta. \tag{41}$$

We apply the (32) Hartree–Fock equations. The effect of $V_{1s\uparrow}^d$ and $V_{1s\uparrow}^{ex}$ on $u_{1s}(r)\alpha$ orbital will be the same (and the two terms are reduced), while $V_{1s\downarrow}^{ex}$ leads to zero. Similarly, analyzing the effect of the direct and exchange operators on orbitals $u_{1s}(r)\beta$, $u_{2s}(r)\alpha$ and $u_{2s}(r)\beta$, and simplifying by the functions depending only on spin coordinates, we obtain

$$\left[-\frac{1}{2}\nabla^2 - \frac{Z}{r} + V_{1s}^d(r) + 2V_{2s}^d(r) - V_{2s}^{ex}(r)\right] u_{1s}(r) \;=\; E_{1s} u_{1s}(r) \tag{42}$$

$$\left[-\frac{1}{2}\nabla^2 - \frac{Z}{r} + V_{2s}^d(r) + 2V_{1s}^d(r) - V_{1s}^{ex}(r)\right] u_{2s}(r) \;=\; E_{2s} u_{2s}(r), \tag{43}$$

where the

$$V_{1,2s}^d(r) \;=\; \langle u_{1,2s}(r')| \frac{1}{|\mathbf{r}-\mathbf{r'}|} |u_{1,2s}(r')\rangle \tag{44}$$

$$V_{1,2s}^{ex}(r)f(r) \;=\; \langle u_{1,2s}(r')| \frac{1}{|\mathbf{r}-\mathbf{r'}|} |f(r')\rangle u_{1,2s}(r) \tag{45}$$

operators act only on the spatial coordinates.

The equations above are three-dimensional partial differential equations. However, the potentials are spherically symmetric, and the orbital part of the solutions will be given by the spherical harmonics. For s orbitals $Y_{00}(\hat{\mathbf{r}}) = 1/\sqrt{4\pi}$ is constant and $u_{1,2s}(r) = r^{-1}P_{1,2s}(r)Y_{00}$. We may write the radial equations for the radial functions $P_{1,2s}$, for the special case of $l = 0$

$$\left[-\frac{1}{2}\frac{d^2}{dr^2} - \frac{Z}{r} + V_{1s}^d(r) + 2V_{2s}^d(r) - V_{2s}^{ex}(r) \right] P_{1s}(r) = E_{1s}P_{1s}(r) \tag{46}$$

$$\left[-\frac{1}{2}\frac{d^2}{dr^2} - \frac{Z}{r} + V_{2s}^d(r) + 2V_{1s}^d(r) - V_{1s}^{ex}(r) \right] P_{2s}(r) = E_{2s}P_{2s}(r). \tag{47}$$

This system can be solved by the self-consistent field method.