1.5. 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 ($\lambda = \alpha, \beta, \ldots, \nu$).

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

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

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

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

We split he Hamiltonian into two parts

$$\begin{aligned} H_1 &= \sum_{i=1}^{N} h_i; \qquad h_i = -\frac{1}{2}\nabla_i^2 - \frac{Z}{r_i} & (3) \\ H_2 &= \sum_{i<j} \frac{1}{r_{ij}}, & (4) \end{aligned}$$

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

$$\begin{aligned} \phi(q_1, q_2, \ldots, q_N) &= \frac{1}{\sqrt{N!}} \sum_P (-1)^P P u_\alpha(q_1) u_\beta(q_2) \cdots u_\nu(q_N) \\ &= \sqrt{N!} A \phi_H, & (6) \end{aligned}$$

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

$$\begin{aligned} [H_1, A] &= 0 \qquad (10)\\ [H_2, A] &= 0. \qquad (11)\end{aligned}$$

Let's calculate the matrix element

$$\begin{aligned} \langle\phi|H_1|\phi\rangle &= N!\langle\phi_H|AH_1A|\phi_H\rangle = N!\langle\phi_H|H_1A^2|\phi_H\rangle \\ &= N!\langle\phi_H|H_1A|\phi_H\rangle, \end{aligned} \tag{12}$$

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

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

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

$$\begin{aligned} \langle\phi|H_2|\phi\rangle &= N!\langle\phi_H|AH_2A|\phi_H\rangle = N!\langle\phi_H|H_2A|\phi_H\rangle \\ &= \sum_{i<j}\sum_{P}(-1)^P\langle\phi_H|\frac{1}{r_{ij}}P|\phi_H\rangle \\ &= \sum_{i<j}\langle\phi_H|\frac{1}{r_{ij}}(1-P_{ij})|\phi_H\rangle. \end{aligned} \tag{16}$$

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

$$\begin{aligned}\langle\phi|H_2|\phi\rangle &= \sum_{\lambda<\mu}\left[\langle u_\lambda(q_i)u_\mu(q_j)|\frac{1}{r_{ij}}|u_\lambda(q_i)u_\mu(q_j)\rangle\right.\\ &\left.\quad -\langle u_\lambda(q_i)u_\mu(q_j)|\frac{1}{r_{ij}}|u_\mu(q_i)u_\lambda(q_j)\rangle\right].\end{aligned} \tag{17}$$

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

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

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

$J_{\lambda\mu}$ – 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

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

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

$$\begin{aligned} V_\mu^{\mathrm{d}}(q_i) &= \langle u_\mu|\frac{1}{r_{ij}}|u_\mu\rangle \equiv V_\mu^{\mathrm{d}}(\mathbf{r_i}) \qquad (25)\\ V_\mu^{\mathrm{ex}}(q_i)f(q_i) &= \langle u_\mu|\frac{1}{r_{ij}}|f\rangle u_\mu(q_i), \qquad (26)\end{aligned}$$

and the potentials

$$\begin{aligned} \mathcal{V}^{\mathrm{d}}(\mathbf{r_i}) &= \sum_\mu V_\mu^{\mathrm{d}}(\mathbf{r_i}) \qquad (27)\\ \mathcal{V}^{\mathrm{ex}}(q_i) &= \sum_\mu V_\mu^{\mathrm{ex}}(q_i). \qquad (28)\end{aligned}$$

we can write

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

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

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

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

where

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

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

$$\begin{aligned} &\left[-\frac{1}{2}\nabla_i^2 - \frac{Z}{r_i} + \sum_\mu \langle u_\mu|\frac{1}{r_{ij}}|u_\mu\rangle\right] u_\lambda(\mathbf{r_i}) \\ &\qquad -\sum_\mu \delta_{m_s^\lambda m_s^\mu}\langle u_\mu|\frac{1}{r_{ij}}|u_\lambda\rangle u_\mu(\mathbf{r_i}) = E_\lambda u_\lambda(\mathbf{r_i}), \qquad (32)\\ &\qquad \lambda = \overline{\alpha,\nu}.\end{aligned}$$

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

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

where

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

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

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.