

1. The Hartree-Fock method

1.1. The determinant wave function (Slater determinant)

$$\Psi(1, 2, \dots, n) = \frac{1}{\sqrt{n!}} \begin{vmatrix} \varphi_1(1) & \varphi_2(1) & \cdots & \varphi_n(1) \\ \varphi_1(2) & \varphi_2(2) & \cdots & \varphi_n(2) \\ \vdots & \vdots & \ddots & \vdots \\ \varphi_1(n) & \varphi_2(n) & \cdots & \varphi_n(n) \end{vmatrix}$$

with φ_i as one-electron functions (orbitals).

1.2. Expression of the energy with determinant wave function

Split up the Hamiltonian into zero-, one- and two-electron contributions:

$$\hat{H} = \underbrace{-\sum_i \frac{1}{2} \Delta_i - \sum_i \sum_A \frac{Z_A}{r_{iA}}}_{\hat{H}_1 =: \sum_i \hat{h}(i)} + \underbrace{\sum_{i < j} \frac{1}{r_{ij}}}_{\hat{H}_2} + \underbrace{\sum_{A < B} \frac{Z_A Z_B}{r_{AB}}}_{\hat{H}_0}$$

For simplicity, consider the two electron problem (2x2 determinant):

$$E = \langle \Psi(1, 2) | \hat{H} | \Psi(1, 2) \rangle$$

$$\Psi(1, 2) = \frac{1}{\sqrt{2}} \left(\varphi_1(1) \varphi_2(2) - \varphi_2(1) \varphi_1(2) \right) \quad \langle \varphi_i | \varphi_j \rangle = \delta_{ij}$$

Let start with \hat{H}_0 . Since it does not act on electron coordinates, gives a constant term:

$$\begin{aligned} \langle \Psi | \hat{H}_0 | \Psi \rangle &= \sum_{A < B} \left\langle \Psi \left| \frac{1}{r_{AB}} \right| \Psi \right\rangle = \sum_{A < B} \frac{1}{r_{AB}} \langle \Psi | \Psi \rangle \\ &= \sum_{A < B} \frac{1}{r_{AB}} \left\langle \frac{1}{\sqrt{2}} \left(\varphi_1(1) \varphi_2(2) - \varphi_2(1) \varphi_1(2) \right) \left| \frac{1}{\sqrt{2}} \left(\varphi_1(1) \varphi_2(2) - \varphi_2(1) \varphi_1(2) \right) \right\rangle \\ &= \sum_{A < B} \frac{1}{r_{AB}} \frac{1}{2} \left[\begin{aligned} &\langle \varphi_1(1) \varphi_2(2) | \varphi_1(1) \varphi_2(2) \rangle \\ &- \langle \varphi_1(1) \varphi_2(2) | \varphi_2(1) \varphi_1(2) \rangle \\ &- \langle \varphi_2(1) \varphi_1(2) | \varphi_1(1) \varphi_2(2) \rangle \\ &+ \langle \varphi_2(1) \varphi_1(2) | \varphi_2(1) \varphi_1(2) \rangle \end{aligned} \right] \\ &= \sum_{A < B} \frac{1}{r_{AB}} \frac{1}{2} [1 - 0 - 0 + 1] = \sum_{A < B} \frac{1}{r_{AB}} \end{aligned}$$

Note that by this calculation we essentially checked that the 2x2 Slater determinant is normalized.

Continue with the one-electron term:

$$\langle \Psi | \hat{H}_1 | \Psi \rangle = \left\langle \Psi \left| \sum_i \hat{h}(i) \right| \Psi \right\rangle$$

$$\begin{aligned}
&= \frac{1}{2} \left\langle \varphi_1(1)\varphi_2(2) - \varphi_2(1)\varphi_1(2) \left| \hat{h}(1) \right| \varphi_1(1)\varphi_2(2) - \varphi_2(1)\varphi_1(2) \right\rangle \\
&\quad + \frac{1}{2} \left\langle \varphi_1(1)\varphi_2(2) - \varphi_2(1)\varphi_1(2) \left| \hat{h}(2) \right| \varphi_1(1)\varphi_2(2) - \varphi_2(1)\varphi_1(2) \right\rangle \\
&= \frac{1}{2} \left[\left\langle \varphi_1(1)\varphi_2(2) \left| \hat{h}(1) \right| \varphi_1(1)\varphi_2(2) \right\rangle \rightarrow \langle \varphi_1 | \hat{h} | \varphi_1 \rangle \langle \varphi_2 | \varphi_2 \rangle = h_{11} \right. \\
&\quad - \left\langle \varphi_1(1)\varphi_2(2) \left| \hat{h}(1) \right| \varphi_2(1)\varphi_1(2) \right\rangle \rightarrow \langle \varphi_1 | \hat{h} | \varphi_2 \rangle \langle \varphi_2 | \varphi_1 \rangle = 0 \\
&\quad - \left\langle \varphi_2(1)\varphi_1(2) \left| \hat{h}(1) \right| \varphi_1(1)\varphi_2(2) \right\rangle \rightarrow \langle \varphi_2 | \hat{h} | \varphi_1 \rangle \langle \varphi_1 | \varphi_2 \rangle = 0 \\
&\quad \left. + \left\langle \varphi_2(1)\varphi_1(2) \left| \hat{h}(1) \right| \varphi_2(1)\varphi_1(2) \right\rangle \right] \rightarrow \langle \varphi_2 | \hat{h} | \varphi_2 \rangle \langle \varphi_1 | \varphi_1 \rangle = h_{22} \\
&\quad + \text{the same for } \hat{h}(2) \\
&= \frac{1}{2} (h_{11} + h_{22}) + \frac{1}{2} (h_{11} + h_{22}) = h_{11} + h_{22}
\end{aligned}$$

In the general case:

$$\left\langle \Psi \left| \hat{H}_1 \right| \Psi \right\rangle = \sum_i h_{ii}$$

Finally, the two-electron contribution:

$$\begin{aligned}
\left\langle \Psi \left| \hat{H}_2 \right| \Psi \right\rangle &= \left\langle \Psi \left| \frac{1}{r_{12}} \right| \Psi \right\rangle \\
&= \frac{1}{2} \left[\left\langle \varphi_1(1)\varphi_2(2) \left| \frac{1}{r_{12}} \right| \varphi_1(1)\varphi_2(2) \right\rangle \rightarrow J_{12} \right. \\
&\quad - \left\langle \varphi_2(1)\varphi_1(2) \left| \frac{1}{r_{12}} \right| \varphi_1(1)\varphi_2(2) \right\rangle \rightarrow K_{21} = K_{12} \\
&\quad - \left\langle \varphi_1(1)\varphi_2(2) \left| \frac{1}{r_{12}} \right| \varphi_2(1)\varphi_1(2) \right\rangle \rightarrow K_{12} \\
&\quad \left. - \left\langle \varphi_2(1)\varphi_1(2) \left| \frac{1}{r_{12}} \right| \varphi_2(1)\varphi_1(2) \right\rangle \right] \rightarrow J_{21} = J_{12} \\
&= J_{12} - K_{12}
\end{aligned}$$

In the general case, using the fact that $J_{ii} = K_{ii}$:

$$\left\langle \Psi \left| \hat{H}_2 \right| \Psi \right\rangle = \sum_{i < j} (J_{ij} - K_{ij}) = \frac{1}{2} \sum_{ij} (J_{ij} - K_{ij})$$

In the above expressions, J_{ij} and K_{ij} are called the Coulomb and exchange integrals, respectively. These are responsible for the electron-electron interaction. J_{ij} describes the Coulomb interaction of two charge densities $\rho_i(1) = \varphi_i(1)\varphi_i(1)$ and $\rho_j(2) = \varphi_j(2)\varphi_j(2)$:

$$J_{ij} = \int \int \varphi_i(1)\varphi_j(2) \frac{1}{r_{12}} \varphi_i(1)\varphi_j(2) dv_1 dv_2 = \int \int \rho_i(1) \frac{1}{r_{12}} \rho_j(2) dv_1 dv_2$$

K_{ij} exchange integral is the consequence of the determinant wave function, thus of the Pauli principle.

If also spin is considered ($\varphi_1 = u_1\alpha$, $\varphi_2 = u_1\beta$):

$$J_{12} = \left\langle u_1\alpha(1)u_1\beta(2) \left| \frac{1}{r_{12}} \right| u_1\alpha(1)u_1\beta(2) \right\rangle = \tilde{J}_{11} (\neq 0)$$

$$\begin{aligned}
K_{12} &= \left\langle u_1\alpha(1)u_1\beta(2) \left| \frac{1}{r_{12}} \right| u_1\beta(1)u_1\alpha(2) \right\rangle \\
&= \left\langle u_1(1)u_1(2) \left| \frac{1}{r_{12}} \right| u_1(1)u_1(2) \right\rangle \langle \alpha(1)\beta(2) | \beta(1)\alpha(2) \rangle = 0
\end{aligned}$$

This means that exchange integral is non-zero only in case of two electrons of the same spin. As example, consider the ground state of the H_2 molecule ($\varphi_1 = u_1\alpha$, $\varphi_2 = u_1\beta$):

$$E_0 = h_{11} + h_{22} + J_{12} = 2\tilde{h}_{11} + \tilde{J}_{11}$$

i.e. no exchange contribution is present.

In case of a triplet excited state ($\varphi_1 = u_1\alpha$, $\varphi_2 = u_2\alpha$) we have:

$$\begin{aligned}
K_{12} &= \left\langle u_1\alpha(1)u_2\alpha(2) \left| \frac{1}{r_{12}} \right| u_2\alpha(1)u_1\alpha(2) \right\rangle \\
&= \left\langle u_1(1)u_2(2) \left| \frac{1}{r_{12}} \right| u_2(1)u_1(2) \right\rangle \langle \alpha(1)\alpha(2) | \alpha(1)\alpha(2) \rangle = \tilde{K}_{12}
\end{aligned}$$

$$E_1 = h_{11} + h_{22} + J_{12} - K_{12} = \tilde{h}_{11} + \tilde{h}_{22} + \tilde{J}_{12} - \tilde{K}_{12}$$

i.e. exchange is present.

This is the theoretical explanation for the Hund's rule.

1.3. Obtaining the orbitals by variational method

In the HF theory the orbitals building the Slater determinant need to be obtained. One can use the *variational principle*, i.e. we look for those orbitals which result in a determinant giving the lowest energy. The functional of the energy in terms of the orbitals:

$$E = \langle \Psi | \hat{H} | \Psi \rangle = \sum_i h_{ii} + \frac{1}{2} \sum_{ij} (J_{ij} - K_{ij})$$

The extremum of this energy expression should be obtained with maintaining the orthonormality of the orbitals:

$$\langle \Psi | \Psi \rangle = 1 \quad \rightarrow \quad \langle \varphi_i | \varphi_j \rangle = S_{ij} = \delta_{ij} \quad \forall i, j$$

thus the functional to be varied:

$$G = E - \sum_i \sum_j \varepsilon_{ij} (S_{ij} - \delta_{ij})$$

$$\delta G = \sum_i \delta h_{ii} + \frac{1}{2} \sum_{ij} (\delta J_{ij} - \delta K_{ij}) - \sum_{ij} \varepsilon_{ij} \delta S_{ij} = 0$$

with ε_{ij} being the Langrange multiplier.

Consider the variation of the different terms one by one:

$$h_{ii} = \langle \varphi_i | \hat{h} | \varphi_i \rangle$$

$$\delta h_{ii} = \langle \delta \varphi_i | \hat{h} | \varphi_i \rangle + \underbrace{\langle \varphi_i | \hat{h} | \delta \varphi_i \rangle}_{c.c.}$$

$$J_{ij} = \left\langle \varphi_i(1) \varphi_j(2) \left| \frac{1}{r_{12}} \right| \varphi_i(1) \varphi_j(2) \right\rangle =: \langle \varphi_i(1) | \hat{J}_j(1) | \varphi_i(1) \rangle$$

$$\delta J_{ij} = \left\langle \delta \varphi_i(1) \varphi_j(2) \left| \frac{1}{r_{12}} \right| \varphi_i(1) \varphi_j(2) \right\rangle + \left\langle \varphi_i(1) \delta \varphi_j(2) \left| \frac{1}{r_{12}} \right| \varphi_i(1) \varphi_j(2) \right\rangle + c.c.$$

$$= \langle \delta \varphi_i(1) | \hat{J}_j(1) | \varphi_i(1) \rangle + \langle \delta \varphi_j(2) | \hat{J}_i(2) | \varphi_j(2) \rangle + c.c.$$

$$\frac{1}{2} \sum_{ij} \delta J_{ij} = \frac{1}{2} \sum_{ij} \langle \delta \varphi_i(1) | \hat{J}_j(1) | \varphi_i(1) \rangle + \frac{1}{2} \sum_{ij} \langle \delta \varphi_j(2) | \hat{J}_i(2) | \varphi_j(2) \rangle + c.c.$$

$$= \sum_{ij} \langle \delta \varphi_i(1) | \hat{J}_j(1) | \varphi_i(1) \rangle + c.c.$$

$$K_{ij} = \left\langle \varphi_i(1) \varphi_j(2) \left| \frac{1}{r_{12}} \right| \varphi_i(2) \varphi_j(1) \right\rangle =: \langle \varphi_i(1) | \hat{K}_j(1) | \varphi_i(1) \rangle$$

$$\left(\hat{K}_j \varphi_i := \int \varphi_j(2) \frac{1}{r_{12}} \varphi_i(2) \varphi_j(1) d\mathbf{r}_2 \right)$$

$$\delta K_{ij} = \langle \delta \varphi_i(1) | \hat{K}_j(1) | \varphi_i(1) \rangle + \langle \delta \varphi_j(2) | \hat{K}_i(2) | \varphi_j(2) \rangle + c.c.$$

$$\frac{1}{2} \sum_{ij} \delta K_{ij} = \sum_{ij} \langle \delta \varphi_i(1) | \hat{K}_j | \varphi_i(1) \rangle$$

$$\delta S_{ij} = \langle \delta \varphi_i | \varphi_j \rangle + c.c.$$

Thus, the variation of the functional reads:

$$\begin{aligned}
\delta G &= \sum_i \langle \delta \varphi_i | \hat{h} | \varphi_i \rangle + c.c. \\
&+ \sum_i \langle \delta \varphi_i | \sum_j \hat{J}_j | \varphi_i \rangle + c.c. \\
&- \sum_i \langle \delta \varphi_i | \sum_j \hat{K}_j | \varphi_i \rangle + c.c. \\
&- \sum_i \langle \delta \varphi_i | \sum_j \varepsilon_{ij} \varphi_j \rangle + c.c. \\
&= 0
\end{aligned}$$

This is fulfilled for any variation of $\delta \varphi_i$, if

$$\left[\hat{h} + \sum_j (\hat{J}_j - \hat{K}_j) \right] | \varphi_i \rangle = \sum_j \varepsilon_{ij} | \varphi_j \rangle \quad i = 1, \dots, n$$

1.4. The Fockian and its eigenvalue equation

One can define the so called *Fockian*, which is the one electron operator of the Hartree-Fock method:

$$\hat{f} := \hat{h} + \sum_j (\hat{J}_j - \hat{K}_j) = \hat{h} + \hat{U}^{HF}$$

With this the above equation reads as:

$$\hat{f} \varphi_i = \sum_j \varepsilon_{ij} \varphi_j \quad i = 1, \dots, n$$

These are the so called *Hartree-Fock equations*. These are not real eigenvalue equations since $\underline{\underline{\varepsilon}}$ couple them.

When using determinant wave function, *the energy is invariant under any unitary transformation of the occupied orbitals* forming the determinant. One of the possible transformation brings $\underline{\underline{\varepsilon}}$ into a diagonal form: ($\varepsilon_{ij} = \varepsilon_i \delta_{ij}$).

These new orbitals are called the *canonical orbitals*, which make the Hartree-Fock equation proper eigenvalue equations:

$$\hat{f} \varphi_i = \varepsilon_i \varphi_i \quad i = 1, \dots, n$$

These equations are called the *canonical Hartree-Fock equations*, which seems to be independent for the individual electrons. This is, however, not the case since \hat{f} is a one-electron operator, but both \hat{J}_j and \hat{K}_j depends on all orbitals:

$$\hat{f} = f(\{\varphi_i\})$$

For this reason, the equations need to be solved iteratively:

$$\{\varphi_i^{(0)}\} \rightarrow \hat{f}^{(0)} \rightarrow \{\varphi_i^{(1)}\} \rightarrow \hat{f}^{(1)} \rightarrow \dots$$

which is called the *SCF (Self-Consistent Field)* procedure.

(At convergence, the Fock operator build up from the orbitals will give the same orbitals as eigenfunctions, i.e. these are self-consistent.)

1.5. The Hartree-Fock-Roothaan method

Above we have derived the HF equations which, as solution to them, result in orbitals (one-electron wave functions):

$$\hat{f}\varphi_i = \varepsilon_i \varphi_i$$

These are still complicated differential equation without analytical solution. Therefore, further approximation is needed: look for the orbitals as the linear combination of atomic basis function. This is the so called (*LCAO-MO* approximation):

$$\varphi_i = \sum_a C_{ai} \chi_a$$

with χ_a standing for the atomic orbitals. Inserting this into the HF equations:

$$\begin{aligned} \hat{f} \sum_a C_{ai} \chi_a &= \varepsilon_i \sum_a C_{ai} \chi_a & / \langle \chi_b | \\ \sum_a C_{ai} \underbrace{\langle \chi_b | \hat{f} | \chi_a \rangle}_{F_{ba}} &= \varepsilon_i \sum_a C_{ai} \underbrace{\langle \chi_b | \chi_a \rangle}_{S_{ba}} \end{aligned}$$

$$\underline{\underline{F}} \underline{\underline{C}}_i = \varepsilon_i \underline{\underline{S}} \underline{\underline{C}}_i$$

and then by gathering all vectors $\underline{\underline{C}}_i$ into a matrix:

$$\underline{\underline{F}} \underline{\underline{C}} = \underline{\underline{\varepsilon}} \underline{\underline{S}} \underline{\underline{C}}$$

We are at a matrix eigenvalue equation. Furthermore, $\underline{\underline{F}}$ depends on the orbitals:

$$\underline{\underline{F}} = f(\hat{J}, \hat{K}) = f(\{\varphi_i\}) = f(\{\underline{\underline{C}}_i\})$$

therefore again an SCF iterative solution is need.

During this SCF procedure, the *Fock matrix* is constructed using the $\underline{\underline{C}}$ coefficients, solve the *H-F-R* equations (essentially diagonalize the Fock matrix) and then we use the new $\underline{\underline{C}}$ built by the eigenvectors to construct a new $\underline{\underline{F}}$ matrix and we repeat this until convergence.