

Hartree-Fock method:

$$\Psi = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(\vec{r}_1) & \psi_1(\vec{r}_2) & \dots & \psi_1(\vec{r}_N) \\ \psi_2(\vec{r}_1) & \psi_2(\vec{r}_2) & & \vdots \\ \vdots & & \ddots & \vdots \\ \psi_N(\vec{r}_1) & \dots & \dots & \psi_N(\vec{r}_N) \end{vmatrix} \leftarrow \begin{matrix} \text{Slater} \\ \text{determinant} \\ \text{state assumed.} \end{matrix}$$

also $\mathcal{H} = \sum_i \left(\frac{-\nabla_i^2}{2m} + U_{\text{ion}}(r_i) \right) + \sum_{j \neq i} \frac{e^2}{2|r_i - r_j|}$

now, assume $\psi_i \rightarrow \phi_i(r) |s_i\rangle$.

We want to minimize $\langle \Psi | \mathcal{H} | \Psi \rangle$ which contains N integrals $\int d^3 r_i$. First 2 terms of \mathcal{H} contain only r_i ; the $(N-1)$ other integrals are trivial. That removes $(N-1)!$ terms. Also since r_i is a dummy index, we can reduce by N terms, keeping only r_1 as a variable. This leaves,

$$\sum_j \int d^3 r_1 \phi_j^*(r_1) \left[\frac{-\nabla_1^2}{2m} + U_{\text{ion}}(r_1) \right] \phi_j(r_1) \langle s_j | s_j \rangle$$

For the last term of \mathcal{H} , for each (r_i, r_j) pair, $(N-2)$ other integrals in $\langle \Psi | \mathcal{H} | \Psi \rangle$ are trivial. Also we can limit notation to $r_1 \& r_2$ since electron indices are arbitrary. This removes $N!$ factors.

There are two possibilities that contribute:

- (1) Terms in which $\langle \Psi | \hat{\epsilon} | \Psi \rangle$ contribute the same functions $\phi_i(r_1) \& \phi_j(r_2)$ on both sides.

(2) terms where $\varphi_i(r_1)$ & $\varphi_j(r_2)$ are interchanged on the two sides.

Case (2) has an overall negative sign since there will be one more (or less) permutation from the determinant on one side vs. the other.

Case (1) will have $\langle s_i | s_i \rangle \langle s_j | s_j \rangle = 1$ automatically.

Case (2) will have $\langle s_i | s_j \rangle \langle s_j | s_i \rangle = \delta_{s_i s_j}$. The Kronecker delta enforces the requirement that the two interchanged spin functions have the same sign.

$$\begin{aligned} \text{So, } \langle \Psi | \mathcal{H} | \Psi \rangle &= \sum_j \int d^3 r_1 \varphi_j^*(r_1) \left[\frac{-\nabla_1^2}{2m} + U_{\text{ion}}(r_1) \right] \varphi_j(r_1) \\ &+ \frac{1}{2} \sum_j \sum_{i \neq j} \iint d^3 r_1 d^3 r_2 \varphi_j^*(r_1) \varphi_i^*(r_2) \frac{e^2}{|r_1 - r_2|} \varphi_j(r_1) \varphi_i(r_2) \\ &- \frac{1}{2} \sum_j \sum_{i \neq j} \iint d^3 r_1 d^3 r_2 \varphi_j^*(r_1) \varphi_i^*(r_2) \frac{e^2}{|r_1 - r_2|} \varphi_j(r_2) \varphi_i(r_1) \delta_{s_i s_j} \end{aligned}$$

Note that the " $\neq j$ " can be omitted since the extra terms cancel. That is important when sum is turned into an integral (for plane-wave states).

$\langle \Psi | \mathcal{H} | \Psi \rangle$ is an energy functional (of functions φ_i) and it can be minimized using variational calculus methods.