

Hartree-Fock Theory

I. *He* atom revisited

$$H = h(1) + h(2) + e^2/r_{12} \quad (1)$$

Consider a more general form for $\psi(1, 2)$, i.e.,

$$\psi(1, 2) = \frac{1}{\sqrt{2}} \psi_{1s}(1) \psi_{1s}(2) \quad (2)$$

Seek best form for ψ_{1s} . Hartree theory can be shown that optimum ψ_{1s} satisfies

$$h(1) + \left\langle \psi_{1s}(2) \left| \frac{e^2}{r_{12}} \right| \psi_{1s}(2) \right\rangle - \epsilon_1 \psi_{1s}(1) = 0 \quad (3a)$$

$$h(2) + \left\langle \psi_{1s}(1) \left| \frac{e^2}{r_{12}} \right| \psi_{1s}(1) \right\rangle - \epsilon_2 \psi_{1s}(2) = 0 \quad (3b)$$

These are coupled integro-differential equations. Difficult to solve directly. Instead, use an iterative method. Describe this later.

First, rewrite (3) as

$$\left[h_{eff}(1) - \epsilon_1 \right] \psi_{1s}(\mathbf{r}_1) = 0 \quad (4a)$$

$$\left[h_{eff}(2) - \epsilon_2 \right] \psi_{1s}(\mathbf{r}_2) = 0 \quad (4b)$$

where
$$h_{eff}(i) = \frac{-\hbar^2}{2m} \nabla_i^2 - \frac{Ze^2}{r_i} + \left\langle \psi_{1s}(j) \left| \frac{e^2}{r_{12}} \right| \psi_{1s}(j) \right\rangle. \quad (5)$$

The expectation value of H is, as usual,

$$E = \langle H \rangle = E_{1s}^{(0)} + E_{1s}^{(0)} + \left\langle 1s(1) 1s(2) \left| \frac{e^2}{r_{12}} \right| 1s(1) 1s(2) \right\rangle \quad (6)$$

$$= \frac{-Z^2}{2} - \frac{Z^2}{2} + J_{1s,1s} = -Z^2 + J_{1s,1s}, \quad (7)$$

$$\text{where } J_{1s,1s} = \left\langle 1s(1) 1s(2) \left| \frac{e^2}{r_{12}} \right| 1s(1) 1s(2) \right\rangle, \quad (8)$$

but where $1s$ here is determined from eq. (4), i.e., it is not the hydrogenic 1s wavefunction, nor even the one with the orbital exponent optimized.

More details

Define the effective potential $u_i^{eff}(r_i)$ by

$$u_i^{eff}(r_i) = \frac{-Ze^2}{r_i} + \left\langle (2) \left| \frac{e^2}{r_{12}} \right| (2) \right\rangle. \quad (9)$$

Make $u_i^{eff}(r_i)$ spherically symmetric by averaging over angles.

$$\text{So, if in general } \psi_i(r_i) = R_i(r_i) Y_{\ell_i m_i}(\theta_i, \phi_i) \quad (10)$$

we have

$$\frac{-\hbar^2}{2m} \frac{d^2}{dr_1^2} + \frac{2}{r_1} \frac{d}{dr_1} + \frac{\ell_1(\ell_1+1)\hbar^2}{2mr_1^2} + u_1^{eff} - \epsilon_1 R_1(r_1) = 0 \quad (11a)$$

$$\frac{-\hbar^2}{2m} \frac{d^2}{dr_2^2} + \frac{2}{r_2} \frac{d}{dr_2} + \frac{\ell_2(\ell_2+1)\hbar^2}{2mr_2^2} + u_2^{eff} - \epsilon_2 R_2(r_2) = 0 \quad (11b)$$

The solution to these equations is obtained by an iterative method, as follows.

Start with

$$\psi_{1s}^{(0)}(i) = \text{hydrogenic 1s orbital}$$

Calculate $u^{eff,0}(i)$, then solve as the uncoupled equations using a numerical method (see below for another approach). Call $\psi_i^{(0)}$ and $\psi_{1s}^{(1)}(i)$ the 1st iterate. Use these to obtain $u^{eff,1}(i)$ and re-solve the eigenvalue equations to get $\psi_i^{(2)}$ and $\psi_{1s}^{(2)}(i)$. Continue to iterate until the process converges, i.e.,

$$\psi_i^{(n)} = \psi_i^{(n-1)} \pm \epsilon_i$$

where ϵ_i is a small value, the convergence threshold.