A Hartree-Fock Example Using Helium*

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The Hartree-Fock Equations

We write this Hamiltonian in "standard" form

$$\hat{H}_{op} = \hat{H}_1 + \hat{H}_2 + \frac{1}{r_{12}} \tag{1}$$

where H_1 is the hydrogenic Hamiltonian for electron one, and H_2 is obviously, the same for electron 2, i.e.,

$$\hat{H}_i = -\frac{\hbar^2}{2m_e}\nabla_i^2 - \frac{Z}{r_i}$$

where Z=2 for helium.

For the ground state, we write the spatial part of the wave function as

$$\psi = \chi[\vec{r}_1]\chi[\vec{r}_2]$$

(where we indicate the functional dependence using square brackets) i.e., spatially symmetric, since we know that the spin part $(\alpha(1)\beta(2) - \alpha(2)\beta(1))$ is going to be antisymmetric.

We seek a "solution" of the equation

$$\hat{H}_{op}\psi = E\psi$$

using Equation 1, which becomes

$$\left(\hat{H}_1 + \hat{H}_2 + \frac{1}{r_{12}}\right)\chi[\vec{r}_1]\chi[\vec{r}_2] = E\chi[\vec{r}_1]\chi[\vec{r}_2]$$

Left multiplying by $\chi^*[\vec{r}_1]$ and integrating over $dx_1dy_1dz_1$ we have

$$\int_{space\ 1} dx_1dy_1dz_1 \left(\chi^*[\vec{r}_1]\left(\hat{H}_1 + \hat{H}_2 + \frac{1}{r_{12}}\right)\chi[\vec{r}_1]\chi[\vec{r}_2]\right) = E\int_{space\ 1} dx_1dy_1dz_1 \left(\chi^*[\vec{r}_1]\chi[\vec{r}_1]\chi[\vec{r}_2]\right) \tag{2}$$

*l2h2:HF2.tex

which is a function of $\vec{r}_2$, with a similar term when using $\chi^*[\vec{r}_2]$, and integrating over space 2, i.e.,

$$\int_{space\ 2} dx_2 dy_2 dz_2 \left(\chi^*[\vec{r}_2]\left(\hat{H}_1+\hat{H}_2+\frac{1}{r_{12}}\right)\chi[\vec{r}_1]\chi[\vec{r}_2]\right) = E\int_{space\ 2} dx_2 dy_2 dz_2 \left(\chi^*[\vec{r}_2]\chi[\vec{r}_1]\chi[\vec{r}_2]\right) \tag{3}$$

which is a function of $\vec{r}_1$. For the first of these (Equation 2), assuming *pre-normalized orbitals* we have:

$$\begin{aligned} &\int_{space\ 1} dx_1 dy_1 dz_1 \left\{\chi^*[\vec{r}_1]\left(\hat{H}_1\chi[\vec{r}_1]\chi[\vec{r}_2]\right)\right\} \\ &+\int_{space\ 1} dx_1 dy_1 dz_1 \left\{\chi^*[\vec{r}_1]\left(\hat{H}_2\chi[\vec{r}_1]\chi[\vec{r}_2]\right)\right\} \\ &+\int_{space\ 1} dx_1 dy_1 dz_1 \left\{\chi^*[\vec{r}_1]\left(\frac{1}{r_{12}}\right)\chi[\vec{r}_1]\chi[\vec{r}_2]\right\} \\ &= E\chi[\vec{r}_2] \end{aligned} \tag{4}$$

or

$$\begin{aligned} &<1|\hat{H}_1|1>\chi[\vec{r}_2] \\ &+\hat{H}_2\chi[\vec{r}_2] \\ &+\left(\int_{space\ 1} dx_1 dy_1 dz_1 \left\{\chi^*[\vec{r}_1]\left(\frac{1}{r_{12}}\right)\chi[\vec{r}_1]\right\}\right)\chi[\vec{r}_2] = E\chi[\vec{r}_2] \end{aligned} \tag{5}$$

where

$$<1|\hat{H}_1|1> = \int dx_1 dy_1 dz_1 \left\{\chi^*[\vec{r}_1] H_1 \chi[\vec{r}_1]\right\}$$

over it's own space (with a similar term for electron 2).

The term

$$<1|V|1> \equiv \int_{space\ 1} dx_1 dy_1 dz_1 \left\{\chi^*[\vec{r}_1]\left(\frac{1}{r_{12}}\right)\chi[\vec{r}_1]\right\}$$

is the key to this (and virtually all other "self-consistent field" methods) scheme. Symmetrically, we have

$$<2|V|2> \equiv \int_{space\ 2} dx_2 dy_2 dz_2 \left\{\chi^*[\vec{r}_2]\left(\frac{1}{r_{12}}\right)\chi[\vec{r}_2]\right\}$$

Then our first SCF equation (Equation 2) becomes

$$\left[<1|\hat{H}_1|1>+\hat{H}_2+<1|V|1>\right]\chi[\vec{r}_2] = E\chi[\vec{r}_2] \tag{6}$$

which is an equation for $\chi[\vec{r}_2]$ based on one "number" ($<1|\hat{H}_1|1>$) and two operators (H_2 and $<1|V|1>$), i.e., re-ordering terms and listing both equations 2 and 3:

$$\begin{aligned} \left[\hat{H}_2+\left\{<1|\hat{H}_1|1>+<1|V|1>\right\}\right]\chi[\vec{r}_2] &= E\chi[\vec{r}_2] \\ \left[\hat{H}_1+\left\{<2|\hat{H}_2|2>+<2|V|2>\right\}\right]\chi[\vec{r}_1] &= E\chi[\vec{r}_1] \end{aligned} \tag{7}$$

or, re-arranging,

$$\left[\hat{H}_2 + \{< 1|V|1 >\}\right]\chi[\vec{r}_2] = (E- < 1|\hat{H}_1|1 >)\chi[\vec{r}_2]$$
$$\left[\hat{H}_1 + \{< 2|V|2 >\}\right]\chi[\vec{r}_1] = (E- < 2|\hat{H}_2|2 >)\chi[\vec{r}_1] \tag{8}$$

The "trick" now is to solve each of these equations for starting assumptions concerning the other function, i.e., assume a form for $\chi[\vec{r}_1]$ and solve for $\chi[\vec{r}_2]$, then use this new form for $\chi[\vec{r}_2]$ to solve for $\chi[\vec{r}_1]$, which you then cycle around again.

Ah, but life is not so kind. There are major problems left which make the above prescription fraught with peril. Consider the integral

$$< 1|V|1 >= \int_{space\ 1} dx_1 dy_1 dz_1 \left\{\chi^*[\vec{r}_1]\left(\frac{1}{\sqrt{r_1^2 + r_2^2 - 2r_1 r_2 \cos\theta}}\right)\chi[\vec{r}_1]\right\}$$

where θ is the angle between $\vec{r}_1$ and $\vec{r}_2$ (there is an equivalent term for $< 2|V|2 >$). We see that $< 1|V|1 >$ is a function of the coördinates of electron 2 and $< 2|V|2 >$ is a function of the coördinates of electron 1! This intermingling is the cause of our grief! Parenthetically, we note that if there was a simplification here, quantum chemistry would be tractable, and chemistry would therefore ossify.