

A Hartree-Fock Example Using Helium*

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The Hartree-Fock Equations

We write this Hamiltonian in “standard” form

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

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

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

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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.,

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

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

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

or

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

where

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

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

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

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

5 and 3:

$$\begin{aligned} \left[\hat{H}_2 + \left\{ \langle 1|\hat{H}_1|1 \rangle + \langle 1|V|1 \rangle \right\} \right] \chi[\vec{r}_2] &= E\chi[\vec{r}_2] \\ \left[\hat{H}_1 + \left\{ \langle 2|\hat{H}_2|2 \rangle + \langle 2|V|2 \rangle \right\} \right] \chi[\vec{r}_1] &= E\chi[\vec{r}_1] \end{aligned} \quad (7)$$

or, re-arranging,

$$\begin{aligned} \left[\hat{H}_2 + \left\{ \langle 1|V|1 \rangle \right\} \right] \chi[\vec{r}_2] &= (E - \langle 1|\hat{H}_1|1 \rangle) \chi[\vec{r}_2] \\ \left[\hat{H}_1 + \left\{ \langle 2|V|2 \rangle \right\} \right] \chi[\vec{r}_1] &= (E - \langle 2|\hat{H}_2|2 \rangle) \chi[\vec{r}_1] \end{aligned} \quad (8)$$

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

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

where θ is the angle between \vec{r}_1 and \vec{r}_2 (there is an equivalent term for $\langle 2|V|2 \rangle$). We see that $\langle 1|V|1 \rangle$ is a function of the coördinates of electron 2 and $\langle 2|V|2 \rangle$ 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.