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I. SYNOPSIS

This material sets up a Hartree Fock computation for the two electrons of Helium so that the formalism can be understood in a simple context.

II. INTRODUCTION

The equations used in treating the Hartree-Fock methodology are abstract enough that it is not at all clear whether one understands what they mean when applied to a real world case. Since the method is incorporated into a multitude of *ab initio* computer programs, students have little opportunity to actually work with an example and see what is going on, why assumptions need to be made, and where in the procedure these assumptions are used.

This tract attempts to give students an example which can be used to help in the understanding of this important methodology.

III. THE MODEL

Consider Helium's electrons. They are governed by a Schrödinger Equation of the form

$$H\psi = E\psi$$

where H us the Hamiltonian for these electrons. We write this Hamiltonian in "standard" form

$$\hat{H}_{op} = \hat{H}_1 + \hat{H}_2 + \frac{1}{r_{12}} \tag{3.1}$$

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

$$\hat{H}_i = -\frac{1}{2}\nabla_i^2 - \frac{Z}{r_i}$$

(in atomic units) where Z=2 for helium.

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

$$\psi = \chi[\vec{r}_1]\chi[\vec{r}_2] \tag{3.2}$$

(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. Notice that the product nature of our "Ansatz" influences everything else which follows. This remains an assumption, one which is not absolutely necessary!

IV. THE HARTREE-FOCK SCHEME APPLIED TO HELIUM

We seek a "solution" of the equation

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

using Equation 3.1 and Equation 3.2 (our "Ansatz"), 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

$$\int_{space\ 1} dx_1dy_1dz_1 \left(\chi^*[\vec{r}_1]\left(\hat{H}_1 + \hat{H}_2 + \frac{1}{r_{12}}\right)\chi[\vec{r}_1]\chi[\vec{r}_2]\right) = E\int_{space\ 1} dx_1dy_1dz_1\left(\chi^*[\vec{r}_1]\chi[\vec{r}_1]\chi[\vec{r}_2]\right) \tag{4.1}$$

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.,

$$\int_{space\ 2} dx_2 dy_2 dz_2 \left(\chi^*[\vec{r}_2]\left(\hat{H}_1 + \hat{H}_2 + \frac{1}{r_{12}}\right)\chi[\vec{r}_1]\chi[\vec{r}_2]\right) = E\int_{space\ 2} dx_2 dy_2 dz_2 \left(\chi^*[\vec{r}_2]\chi[\vec{r}_1]\chi[\vec{r}_2]\right) \quad (4.2)$$

which is a function of $\vec{r}_1$. For the first of these (Equation 4.1), assuming *pre-normalized orbitals,* χ we have:

$$\begin{aligned}
&\int_{space\ 1} dx_1 dy_1 dz_1 \left\{\chi^*[\vec{r}_1]\left(\hat{H}_1\chi[\vec{r}_1]\chi[\vec{r}_2]\right)\right\} \\
&+\int_{space\ 1} dx_1 dy_1 dz_1 \left\{\chi^*[\vec{r}_1]\left(\hat{H}_2\chi[\vec{r}_1]\chi[\vec{r}_2]\right)\right\} \\
&+\int_{space\ 1} dx_1 dy_1 dz_1 \left\{\chi^*[\vec{r}_1]\left(\frac{1}{r_{12}}\right)\chi[\vec{r}_1]\chi[\vec{r}_2]\right\} \\
&= E\chi[\vec{r}_2]
\end{aligned} \quad (4.3)$$

or

$$\begin{aligned}
&< 1|\hat{H}_1|1 > \chi[\vec{r}_2] \\
&+\hat{H}_2\chi[\vec{r}_2] \\
&+\left(\int_{space\ 1} dx_1 dy_1 dz_1 \left\{\chi^*[\vec{r}_1]\left(\frac{1}{r_{12}}\right)\chi[\vec{r}_1]\right\}\right)\chi[\vec{r}_2] \\
&= E\chi[\vec{r}_2]
\end{aligned} \quad (4.4)$$

where

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

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

V. GENERATING THE SIMULTANEOUS EQUATIONS

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. Then our first SCF equation (Equation 4.1) becomes

$$\left[< 1|\hat{H}_1|1 > +\hat{H}_2 + < 1|V|1 >\right]\chi[\vec{r}_2] = E\chi[\vec{r}_2] \quad (5.1)$$

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 4.4 and 4.2:

$$\begin{aligned}
\left[\hat{H}_2 + \left\{< 1|\hat{H}_1|1 > + < 1|V|1 >\right\}\right]\chi[\vec{r}_2] &= E\chi[\vec{r}_2] \\
\left[\hat{H}_1 + \left\{< 2|\hat{H}_2|2 > + < 2|V|2 >\right\}\right]\chi[\vec{r}_1] &= E\chi[\vec{r}_1]
\end{aligned} \quad (5.2)$$

(symmetrically, we have

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

) or, re-arranging,

$$\begin{aligned}
\left[\hat{H}_2 + \{< 1|V|1 >\}\right]\chi[\vec{r}_2] &= (E - < 1|\hat{H}_1|1 >)\chi[\vec{r}_2] \\
\left[\hat{H}_1 + \{< 2|V|2 >\}\right]\chi[\vec{r}_1] &= (E - < 2|\hat{H}_2|2 >)\chi[\vec{r}_1]
\end{aligned} \quad (5.3)$$

What we have here is the essence of the method, i.e., two coupled equations one for each electron, which explicitly includes the other electron!

VI. SIMULTANEOUS SOLVING OF THE TWO EQUATIONS

The "trick" now is to solve each of these equations (using 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 (using the law of cosines to replace r_{12})

$$< 1|V|1 >= \int_{space\ 1} dx_1 dy_1 dz_1 \left\{ \chi^*[\vec{r}_1] \left(\frac{1}{\sqrt{r_1^2 + r_2^2 - 2r_1 r_2 \cos\gamma}} \right) \chi[\vec{r}_1] \right\} \tag{6.1}$$

where γ 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 i.e., $< 1|V|1 > [\vec{r}_2]$, and $< 2|V|2 >$ is a function of the coördinates of electron 1 i.e., $< 2|V|2 > [\vec{r}_1]$! 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 might therefore ossify.

VII. EVALUATING THE REQUISITE INTEGRAL

$$< 1|V|1 >= \int_{space\ 1} dx_1 dy_1 dz_1 \left\{ \chi^*[\vec{r}_1] \left(\frac{1}{\sqrt{(x_1 - x_2)^2 + (y_1 - y_2)^2 + (x_1 - z_2)^2}} \right) \chi[\vec{r}_1] \right\} \tag{7.1}$$

Even if one were to assume that the ground state here has the form of 1s orbitals, i.e.,

$$\chi[\vec{r}_1] = e^{-\alpha r_1}$$

either integral form Equation 6.1 or 7.1 remains an intractable integral!

We would have, from Equation 6.1

$$< 1|V|1 >= \int_0^\infty r_1^2 dr_1 \int_0^\pi \sin\vartheta_1 d\vartheta_1 \int_0^{2\pi} d\varphi_1 \left\{ e^{-\alpha r_1} \left(\frac{1}{\sqrt{r_1^2 + r_2^2 - 2r_1 r_2 \cos\gamma}} \right) e^{-\alpha r_1} \right\} \tag{7.2}$$

which clearly remains a function of r_2 after integration. γ (as above) refers to the angle between r_1 and r_2 while the latter refers to the spherical polar angle from the z_1 axis.

This is a none trivial integral.

$$r_{12} = \sqrt{r_1^2 + r_2^2 - 2r_1 r_2 \cos\gamma}$$

where γ is the angle between $\vec{r}_1$ and $\vec{r}_2$, it seem reasonable to convert to double spherical polar coördinates in order to isolate maximally the radial parts, i.e.,

Consider

$$r_{12}^2 = (x_1 - x_2)^2 + (y_1 - y_2)^2 + (z_1 - z_2)^2$$

which equals, in double spherical polar coördinates

$$r_{12}^2 = (r_1 \sin\vartheta_1 \cos\phi_1 - r_2 \sin\vartheta_2 \cos\phi_2)^2 + (r_1 \sin\vartheta_1 \sin\phi_1 - r_2 \sin\vartheta_2 \sin\phi_2)^2 + (r_1 \cos\vartheta_1 - r_2 \cos\vartheta_2)^2$$

which is

$$r_{12}^2 = r_1^2 - r_2^2 - 2r_1 r_2 \left(\sin\vartheta_2 \sin\vartheta_1 \left(\cos\phi_2 \cos\phi_1 + \sin\phi_2 \sin\phi_1\right) + \cos\vartheta_1 \cos\vartheta_2\right)$$

which means that

$$r_1^2 + r_2^2 - 2r_1 r_2 \cos\gamma = r_1^2 + r_2^2 - 2r_1 r_2 \left(\sin\vartheta_2 \sin\vartheta_1 \left(\cos\phi_2 \cos\phi_1 + \sin\phi_2 \sin\phi_1\right) + \cos\vartheta_1 \cos\vartheta_2\right)$$

so that

$$\cos\gamma = \left(\sin\vartheta_2 \sin\vartheta_1 \left(\cos\phi_2 \cos\phi_1 + \sin\phi_2 \sin\phi_1\right) + \cos\vartheta_1 \cos\vartheta_2\right)$$

or,

$$\cos\vartheta_2 \cos\vartheta_1 + \sin\vartheta_2 \sin\vartheta_1 \cos(\phi_2 - \phi_1)$$

which would, on the surface, make the desired integral simpler. But it doesn't.

$$< 1|V|1 >= \int_0^\infty r_1^2 dr_1 \int_0^\pi \sin\vartheta_1 d\vartheta_1 \int_0^{2\pi} d\varphi_1 \left\{ e^{-\alpha r_1} \left(\frac{1}{\sqrt{r_1^2 + r_2^2 - 2r_1 r_2 \cos\vartheta_2 \cos\vartheta_1 + \sin\vartheta_2 \sin\vartheta_1 \cos(\phi_2 - \phi_1)}} \right) e^{-\alpha r_1} \right\} \tag{7.3}$$

VIII. AN ASIDE

If

$$\frac{1}{r_{12}} = \frac{1}{\sqrt{r_1^2 + r_2^2 - 2r_1 r_2 \cos\gamma}}$$

then choosing $r_1 \geq r_2$ (temporarily) we have

$$\frac{1}{r_{12}} = \frac{1}{r_1 \sqrt{1 + \left(\frac{r_2}{r_1}\right)^2 - 2\frac{r_2}{r_1}\cos\gamma}}$$

and allowing $x = \frac{r_2}{r_1}$ we have

$$\frac{1}{r_{12}} = \frac{1}{r_1 \sqrt{1 + x^2 - 2x\cos\gamma}}$$

which we re-write one more time

$$\frac{1}{r_{12}} = \frac{1}{r_1 \sqrt{1 + x^2 - 2x\mu}}$$

where $\mu = \cos\gamma$. Then, generating the Taylor expansion as a function of μ we have

$$\frac{r_1}{r_{12}} = \frac{1}{\sqrt{1+x^2}} + \left.\frac{\partial\left(\frac{1}{\sqrt{1+x^2-2x\mu}}\right)}{\partial\mu}\right|_{\mu=0} \mu + \frac{1}{2!}\left.\frac{\partial^2\left(\frac{1}{\sqrt{1+x^2-2x\mu}}\right)}{\partial\mu^2}\right|_{\mu=0} \mu^2 \cdots$$

But

$$\frac{\partial \frac{1}{\sqrt{1+x^2-2x\mu}}}{\partial\mu} = -2x\left(-\frac{1}{2}\right)\frac{1}{\sqrt{1+x^2-2x\mu}^3}$$

which, at $\mu = 0$ is

$$\frac{\partial \frac{1}{\sqrt{1+x^2-2x\mu}}}{\partial\mu} = \frac{x}{(1+x^2)^{3/2}}$$

$$\frac{\partial^2 \frac{1}{\sqrt{1+x^2-2x\mu}}}{\partial\mu^2} = \frac{\partial\left(\frac{x}{\sqrt{1+x^2-2x\mu}^3}\right)}{\partial\mu} = \frac{3x}{(1+x^2)^{5/2}}$$

and

$$\frac{\partial^3 \frac{1}{\sqrt{1+x^2-2x\mu}}}{\partial\mu^3} = \frac{\partial^2 \left(\frac{x}{\sqrt{1+x^2-2x\mu}^3}\right)}{\partial\mu^2} = \frac{\partial \frac{3x}{(1+x^2-2x\mu)^{5/2}}}{\partial\mu} = \frac{(3)(5)x^2}{(1+x^2)^{7/2}}$$

etc., so

$$\frac{1}{r_{12}} \equiv \frac{1}{\sqrt{1+x^2}} + \frac{x}{(1+x^2)^{3/2}}\mu \cdots$$

which we re-write as

$$\frac{1}{r_{12}} \equiv \frac{1}{r_1}\left(\frac{1}{(1+x^2)^{1/2}} + \frac{x}{(1+x^2)^{3/2}}\mu + \right.$$
$$\left.\frac{(3)(1)x^2}{2!\,(1+x^2)^{5/2}}\mu^2 + \frac{(5)(3)(1)x^3}{3!\,(1+x^2)^{7/2}}\mu^3 + \frac{(7)(5)(3)(1)x^4}{4!\,(1+x^2)^{9/2}}\mu^4 + \frac{(9)(7)(5)(3)(1)x^5}{5!\,(1+x^2)^{11/2}}\mu^5 \cdots\right) \tag{8.1}$$

$$\frac{1}{r_{12}} \equiv \frac{1}{r_1}\left(\sum_{n=0}^{\infty} \frac{\prod_{i=0}^{n-1}(2i+1)}{n!} \frac{x^n\mu^n}{(1+x^2)^{\frac{2n+1}{2}}}\right)$$

which, we remember, means

$$\frac{1}{r_{12}} \equiv \frac{1}{r_1}\left(\sum_{n=0}^{\infty} \frac{\prod_{i=0}^{n-1}(2i+1)}{n!} \frac{x^n\left(\cos\vartheta_1\cos\vartheta_2 + \sin\vartheta_2\sin\vartheta_1\cos(\phi_2-\phi_1)\right)^n}{(1+x^2)^{\frac{2n+1}{2}}}\right)$$

where we have chosen to slightly simplify the term

$$\cos\phi_2\cos\phi_1 + \sin\phi_2\sin\phi_1\cos(\phi_2-\phi_1)$$

IX. RETURNING TO THE MAIN PROBLEM

We need to substitute the expansion into the integral, and then integrate term by term. We obtain

$$< 1|V|1 >= \int_0^\infty r_1^2 dr_1 \int_0^\pi \sin\vartheta_1 d\vartheta_1 \int_0^{2\pi} d\varphi_1$$
$$\left\{e^{-\alpha r_1}\frac{1}{r_1}\left(\sum_{n=0}^{\infty} \frac{\prod_{i=0}^{n-1}(2i+1)}{n!} \frac{\left(\frac{r_2}{r_1}\right)^n\left(\cos\vartheta_1\cos\vartheta_2 + \sin\vartheta_2\sin\vartheta_1\cos(\phi_2-\phi_1)\right)^n}{(1+\left(\frac{r_2}{r_1}\right)^2)^{\frac{2n+1}{2}}}\right)e^{-\alpha r_1}\right\}$$

It is obvious that there are no further simplifications, and we are doomed to evaluate an infinite number of terms, doing non-trivial integrals adding insult to injury.

One sees where semi-empirical methods come from now, since declaring the entire integral to have a "value" sidesteps actually finding that "value". How shrewd.