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# The Hartree Fock Method Applied to Helium's Electrons

C. W. David  
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## I. SYNOPSIS

The difficulties of applying the Hartree-Fock method to many body problems is illustrated by treating Helium's electrons up to the point where tractability vanishes.

Second, the problem of applying Hartree-Fock methods to the helium atom's electrons, when they are constrained to remain on a sphere, is revisited. The 6-dimensional total energy operator is reduced to a 2-dimensional one, and the application of that 2-dimensional operator in the Hartree-Fock mode is discussed.

## II. HELIUM HAMILTONIAN AND STARTING WAVE FUNCTION APPROXIMATIONS

We start with the Hamiltonian (in symbolic form):

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

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

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

where  $Z = 2$  for Helium.

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

$$\psi = \phi_1(r_1)\phi_1(r_2)$$

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

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

which becomes

$$\left(\hat{H}_1 + \hat{H}_2 + \frac{1}{r_{12}}\right)\phi_1(r_1)\phi_1(r_2) = E\phi_1(r_1)\phi_1(r_2)$$

Left multiplying by  $\phi_1(r_1)$  and integrating over  $dx_1dy_1dz_1$  we have

$$\int_{space\ 1} dx_1dy_1dz_1 \left(\phi_1^*(r_1) \left(\hat{H}_1 + \hat{H}_2 + \frac{1}{r_{12}}\right)\phi_1(r_1)\phi_1(r_2)\right) = E \int_{space\ 1} dx_1dy_1dz_1 \phi_1^*(r_1)\phi_1(r_1)\phi_1(r_2) \quad (2.1)$$

with a similar term when using  $\phi_1(r_2)$ , and integrating over space 2, i.e.,

$$\int_{space\ 2} dx_2dy_2dz_2 \left(\phi_1^*(r_2) \left(\hat{H}_1 + \hat{H}_2 + \frac{1}{r_{12}}\right)\phi_1(r_1)\phi_1(r_2)\right) = E \int_{space\ 2} dx_2dy_2dz_2 \phi_1^*(r_2)\phi_1(r_1)\phi_1(r_2)$$

We then obtain, for the first of these (Equation 5.6), assuming pre-normalized orbitals:

$$\int_{space\ 1} dx_1dy_1dz_1 \phi_1^*(r_1)\hat{H}_1\phi_1(r_1)\phi_1(r_2) + \int_{space\ 1} dx_1dy_1dz_1 \phi_1^*(r_1)\hat{H}_2\phi_1(r_1)\phi_1(r_2)$$

$$+ \int_{space\ 1} dx_1dy_1dz_1 \phi_1^*(r_1) \left(\frac{1}{r_{12}}\right)\phi_1(r_1)\phi_1(r_2) = E\phi_1(r_2) \quad (2.2)$$

or

$$\langle 1|\hat{H}_1|1\rangle\phi_1(r_2) + \hat{H}_2\phi_1(r_2) + \phi_1(r_2) \int_{space\ 1} dx_1dy_1dz_1 \phi_1^*(r_1) \left(\frac{1}{r_{12}}\right)\phi_1(r_1) = E\phi_1(r_2) \quad (2.3)$$

where  $H_{1,1} = \int \phi_1^*(r_1) (H_1) \phi_1(r_1)$  over it's own space.  
The term

$$\langle 1|V|1 \rangle \equiv \int_{space\ 1} dx_1 dy_1 dz_1 \phi_1^*(r_1) \left( \frac{1}{r_{12}} \right) \phi_1(r_1)$$

is the key to this (and virtually all other “self-consistent field” methods) scheme, and we define it as  $\langle 1|V|1 \rangle$  for future reference. Symmetrically, we have

$$\langle 2|V|2 \rangle \equiv \int_{space\ 2} dx_2 dy_2 dz_2 \phi_1^*(r_2) \left( \frac{1}{r_{12}} \right) \phi_1(r_2)$$

is the key to this (and virtually all other “self-consistent field” methods) Then our SCF equation becomes

$$\left[ \langle 1|\hat{H}_1|1 \rangle + \hat{H}_2 + \langle 1|V|1 \rangle \right] \phi_1(r_2) = E\phi_1(r_2) \quad (2.4)$$

which is an equation for  $\phi_1(r_2)$  based on one “number” and two operators ( $H_2$  and  $\langle 1|V|1 \rangle$ ), i.e., re-ordering terms,

$$\begin{aligned} \left[ \hat{H}_2 + \left\{ \langle 1|\hat{H}_1|1 \rangle + \langle 1|V|1 \rangle \right\} \right] \phi_1(r_2) &= E\phi_1(r_2) \\ \left[ \hat{H}_1 + \left\{ \langle 1|\hat{H}_2|1 \rangle + \langle 2|V|2 \rangle \right\} \right] \phi_1(r_1) &= E\phi_1(r_1) \end{aligned} \quad (2.5)$$

The “trick” now is to solve each of these equations for starting assumptions concerning the other function, i.e., assume a form for  $\phi_1(r_1)$  and solve for  $\phi_1(r_2)$ , then use this new form for  $\phi_1(r_2)$  to solve for  $\phi_1(r_1)$ , which you then cycle around again.

$\langle 1|V|1 \rangle$  (and its equivalent,  $\langle 2|V|2 \rangle$ ) are functions of coördinates, i.e.,

$$\langle 1|V|1 \rangle = f(\vec{r}_2)$$

and

$$\langle 2|V|2 \rangle = f(\vec{r}_1)$$

is the key to this (and virtually all other “self-consistent field” methods)

To see what these integrals entail (in terms of actually carrying them out), we have (from above)

$$\langle 1|V|1 \rangle \equiv \int_{space\ 1} dx_1 dy_1 dz_1 \phi_1^*(r_1) \left( \frac{1}{r_{12}} \right) \phi_1(r_1)$$

which, assuming we are looking solely for the ground state of the Helium atom's electrons, based on the ground states  $1s^2$ , we would have, as an example,

$$\langle 1|V|1 \rangle (r_2, \vartheta_2, \varphi_2) \equiv \int_{space\ 1} r_1^2 dr_1 \sin \vartheta_1 d\vartheta_1 d\varphi_1 e^{-2\alpha r_1} \left( \frac{1}{\sqrt{r_1^2 + r_2^2 - 2r_1 r_2 \cos \gamma}} \right)$$

with

$$\cos \gamma = \cos \vartheta_2 \cos \vartheta_1 + \sin \vartheta_1 \sin \vartheta_2 \cos(\varphi_2 - \varphi_1)$$

Clearly, this is a non-trivial integral, and is not susceptible to the treatments used when the integral is done over both  $r_1$  and  $r_2$ . which, assuming we are looking solely for the ground state of the Helium atom's electrons, based on the ground states  $1s^2$ , we would have, as an example,

Solving the equation set Equation 2.5 is non-trivial, to say the least.

### III. AN EXAMPLE ILLUSTRATING HOW EASY MISTAKES CAN BE MADE; ELECTRONS ON A SPHERE USING HF METHODOLOGY

A simplified model for helium's electrons, useful in studying the Hartree-Fock method, was introduced [1] in which helium's electrons moved on the surface of a sphere centered on the nucleus. Since the distance from the

electrons to the nucleus was constant in this model, the Hamiltonian simplified to such an extent as to make the problem tractable from the Hartree-Fock point of view.

The authors introduce the kinetic energy operator without derivation as

$$\hat{H}_{op} = -\frac{1}{2\mu R^2} \frac{d^2}{d\vartheta^2} \rightarrow -\frac{1}{2\mu R^2} \frac{d^2}{d\zeta^2} \quad (3.1)$$

We here derive a variant of Equation 3.1 and explain and explore how the Hartree Fock method works in this simple case.

### IV. 6-DIMENSIONAL HELIUM HAMILTONIAN

The “true” kinetic energy operator portion of the Hamiltonian operating on a wave function  $\psi$  (for “real” helium's electrons) is

$$-\frac{\hbar^2}{2m_e} \left\{ \frac{1}{r_1^2} \left[ \frac{\partial \left( r_1^2 \frac{\partial \psi}{\partial r_1} \right)}{\partial r_1} + \frac{1}{\sin \vartheta_1} \frac{\partial \left( \sin \vartheta_1 \frac{\partial \psi}{\partial \vartheta_1} \right)}{\partial \vartheta_1} + \frac{1}{\sin^2 \vartheta_1} \frac{\partial^2 \psi}{\partial \varphi_1^2} \right] + \frac{1}{r_2^2} \left[ \frac{\partial \left( r_2^2 \frac{\partial \psi}{\partial r_2} \right)}{\partial r_2} + \frac{1}{\sin \vartheta_2} \frac{\partial \left( \sin \vartheta_2 \frac{\partial \psi}{\partial \vartheta_2} \right)}{\partial \vartheta_2} + \frac{1}{\sin^2 \vartheta_2} \frac{\partial^2 \psi}{\partial \varphi_2^2} \right] \right\} \quad (4.1)$$

which is six-dimensional (see Appendix III). It is written in the infinite nuclear mass approximation using double

spherical polar coordinates. This is comparable to the algorithmic (from  $p_x = -i\hbar \frac{\partial}{\partial x}$ , etc.) induced form

$$-\frac{\hbar^2}{2m_e} [\nabla_1^2 + \nabla_2^2] = -\frac{\hbar^2}{2m_e} \left[ \frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial y_1^2} + \frac{\partial^2}{\partial z_1^2} + \frac{\partial^2}{\partial x_2^2} + \frac{\partial^2}{\partial y_2^2} + \frac{\partial^2}{\partial z_2^2} \right]$$

The 1-subscript refers to electron one, and the 2-subscript refers to the other electron.

We endeavor to obtain Equation 3.1 from Equation 4.1. First, we note that the radius for both electrons in this model is fixed at  $r_1 = r_2 = R$ , so the radial kinetic energy contributors vanish (there is no radial kinetic energy),

$$\frac{1}{r_1^2} \left[ 0 \frac{\partial \left( r_1^2 \frac{\partial \psi}{\partial r_1} \right)}{\partial r_1} \right]$$

(with a similar expression for  $r_2$ ) i.e.,  $\psi \neq f(r_1, r_2)$  where  $r_1$  is the magnitude of  $\vec{r}_1$  and  $r_2$  is the magnitude of  $\vec{r}_2$ . We assume then that  $\vec{r}_1 = \vec{r}_2 = R$ , and then are left with

$$-\frac{\hbar^2}{2m_e R^2} \left\{ \left[ \frac{1}{\sin \vartheta_1} \frac{\partial \left( \sin \vartheta_1 \frac{\partial \psi}{\partial \vartheta_1} \right)}{\partial \vartheta_1} + \frac{1}{\sin^2 \vartheta_1} \frac{\partial^2 \psi}{\partial \varphi_1^2} \right] + \left[ \frac{1}{\sin \vartheta_2} \frac{\partial \left( \sin \vartheta_2 \frac{\partial \psi}{\partial \vartheta_2} \right)}{\partial \vartheta_2} + \frac{1}{\sin^2 \vartheta_2} \frac{\partial^2 \psi}{\partial \varphi_2^2} \right] \right\}$$

We have achieved a reduction in dimensionality from 6 to 4.

Next, we note that the angle between the two radius vectors, denoted as  $\vartheta$  in the original paper, is given (here denoted by  $\eta$ ) as

$$\cos \eta = \cos \vartheta_1 \cos \vartheta_2 + \sin \vartheta_1 \sin \vartheta_2 \cos(\varphi_2 - \varphi_1)$$

(see Appendix I).

In order to continue along the path of deriving Equation 3.1 from Equation 4.1 we note that the terms involving  $\vartheta$  differentiation do not appear in the final result, so it behooves us to fix  $\vartheta_1 = \vartheta_2 = \frac{\pi}{2}$  for both electrons, which is a value that make  $\sin \vartheta_1$  and  $\sin \vartheta_2$  equal to one,

and eliminates taking partial derivatives with respect to these angles. This means that we are working in the x-y plane of each electron, i.e., *the electrons are not on a sphere, they are on a circle in the x-y plane!*

We now have

$$-\frac{\hbar^2}{2m_e R^2} \left\{ \frac{1}{(\sin^2 \vartheta_1)} \frac{\partial^2}{\partial \varphi_1^2} + \frac{1}{(\sin^2 \vartheta_2)} \frac{\partial^2}{\partial \varphi_2^2} \right\} \quad (4.2)$$

with  $\sin \vartheta_i = 1$  for  $i=1$  and  $2$ .

Lastly, defining  $\eta = \varphi_2 - \varphi_1$ , and using the chain rule, we have

$$-\frac{\hbar^2}{2m_e R^2} \left\{ \frac{\partial^2}{\partial \eta^2} + \frac{\partial^2}{\partial \eta^2} \right\} = -\frac{\hbar^2}{m_e R^2} \left\{ \frac{\partial^2}{\partial \eta^2} \right\} \quad (4.3)$$

which completes this derivation of part of Equation 3.1. We differ by a factor of two from Equation 3.1 and have retained  $m_e$  rather than using  $\mu$  (which is inappropriate here).

## V. THE HARTREE-FOCK EQUATIONS

The reduction of the Hartree-Fock treatment of helium's electrons from a six-dimensional to a "one-dimensional" (in  $\eta$ ) problem is wonderful, in making it tractable, but misses the sense of how the Hartree-Fock method is supposed to work, and might be better left in a two-dimensional form, using  $\varphi_1$  and  $\varphi_2$  as variables, so that students could see what is going on.

Therefore, we continue the derivation using the two dimensional form:

$$-\frac{\hbar^2}{2m_e R^2} \left\{ \frac{\partial^2 \psi}{\partial \varphi_1^2} + \frac{\partial^2 \psi}{\partial \varphi_2^2} \right\} + \left( -\frac{Z}{R} - \frac{Z}{R} + \frac{1}{r_{12}} \right) \psi = E\psi \quad (5.1)$$

(where  $Z=2$  for helium) for the total energy operator, as suggested by Equation 4.2.

The repulsive part of the potential energy is

$$\frac{1}{r_{12}} = \frac{1}{\sqrt{r_1^2 + r_2^2 - 2r_1r_2 \cos \eta}}$$

(law of cosines) which in this specialized case is

$$\frac{1}{\sqrt{R^2 + R^2 - 2R^2 \cos \eta}} = \frac{1}{\sqrt{2R}\sqrt{1 - \cos \eta}} \quad (5.2)$$

which is the simplification which makes the original paper “work”. In our notation this becomes

$$\frac{1}{\sqrt{2R}\sqrt{1 - \cos(\varphi_2 - \varphi_1)}}$$

which is again two-dimensional in the same sense as Equation 5.1.

We thus have

$$\hat{H}_{op} = -\frac{\hbar^2}{2m_e R^2} \left\{ \frac{\partial^2}{\partial \varphi_1^2} + \frac{\partial^2}{\partial \varphi_2^2} \right\} - \frac{2Z}{R} + \frac{1}{\sqrt{2R}\sqrt{1 - \cos(\varphi_2 - \varphi_1)}} \quad (5.3)$$

(where  $Z/R$  is the potential energy of attraction of an electron to the nucleus) as the Hamiltonian operator, complete with (constant) nuclear-electron attraction and electron-electron repulsion.

We write this Hamiltonian in “standard” form

$$\hat{H}_{op} = \hat{H}_1 + \hat{H}_2 + \frac{1}{\sqrt{2R}\sqrt{1 - \cos(\varphi_2 - \varphi_1)}} \quad (5.4)$$

where  $\hat{H}_1$  is the hydrogenic Hamiltonian for electron one, and  $\hat{H}_2$  is obviously, the same for electron 2, i.e.,

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

For the ground state, we write the spatial part of the

wave function as

$$\psi = \chi[\vec{r}_1]\chi[\vec{r}_2] = \chi[\varphi_1]\chi[\varphi_2] \quad (5.5)$$

(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 anti-symmetric.

We seek a “solution” of the equation

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

and using Equation 5.3 as decomposed using Equation 5.4, which becomes (using the Ansatz Equation 5.5)

$$\left( \hat{H}_1 + \hat{H}_2 + \frac{1}{\sqrt{2R}\sqrt{1 - \cos(\varphi_2 - \varphi_1)}} \right) \chi[\varphi_1]\chi[\varphi_2] = E\chi[\varphi_1]\chi[\varphi_2]$$

Left multiplying by  $\chi^*[\varphi_1]$  and integrating over  $d\varphi_1$  we have

$$\int_{space\ 1} d\varphi_1 \left( \chi^*[\varphi_1] \left( \hat{H}_1 + \hat{H}_2 + \frac{1}{\sqrt{2R}\sqrt{1 - \cos(\varphi_2 - \varphi_1)}} \right) \chi[\varphi_1]\chi[\varphi_2] \right) = E \int_{space\ 1} d\varphi_1 (\chi^*[\varphi_1]\chi[\varphi_1]\chi[\varphi_2]) \quad (5.6)$$

with a similar term when using  $\chi^*[\varphi_2]$ , and integrating over space 2, i.e.,

$$\int_{space\ 2} d\varphi_2 \left( \chi^*[\varphi_2] \left( \hat{H}_1 + \hat{H}_2 + \frac{1}{\sqrt{2R}\sqrt{1 - \cos(\varphi_2 - \varphi_1)}} \right) \chi[\varphi_1]\chi[\varphi_2] \right) = E \int_{space\ 2} d\varphi_2 (\chi^*[\varphi_2]\chi[\varphi_1]\chi[\varphi_2])$$

For the first of these (Equation 5.6), assuming *pre-normalized orbitals* we have:

$$\begin{aligned}
& \int_{space\ 1} d\varphi_1 \left\{ \chi^*[\varphi_1] \left( \hat{H}_1 \chi[\varphi_1] \chi[\varphi_2] \right) \right\} \\
& + \int_{space\ 1} d\varphi_1 \left\{ \chi^*[\varphi_1] \left( \hat{H}_2 \chi[\varphi_1] \chi[\varphi_2] \right) \right\} \\
& + \int_{space\ 1} d\varphi_1 \left\{ \chi^*[\varphi_1] \left( \frac{1}{\sqrt{2R}\sqrt{1-\cos(\varphi_2-\varphi_1)}} \right) \chi[\varphi_1] \chi[\varphi_2] \right\} \\
& = E\chi[\varphi_2]
\end{aligned} \tag{5.7}$$

or

$$\int_{space\ 1} d\varphi_1 \left\{ \chi^*[\varphi_1] \left( \frac{1}{\sqrt{2R}\sqrt{1-\cos(\varphi_2-\varphi_1)}} \right) \chi[\varphi_1] \right\} \chi[\varphi_2] = E\chi[\varphi_2] \tag{5.8}$$

where  $\langle 1|\hat{H}_1|1 \rangle = \int d\varphi_1 \chi^*[\varphi_1] \hat{H}_1 \chi[\varphi_1]$  over its own space (and a similar term for electron 2).

The last term on the l.h.s. of Equation 5.8 allows us to define

$$\langle 1|V|1 \rangle \equiv \int_{space\ 1} d\varphi_1 \left\{ \chi^*[\varphi_1] \left( \frac{1}{\sqrt{2R}\sqrt{1-\cos(\varphi_2-\varphi_1)}} \right) \chi[\varphi_1] \right\}$$

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

$$\langle 2|V|2 \rangle \equiv \int_{space\ 2} d\varphi_2 \left\{ \chi^*[\varphi_2] \left( \frac{1}{\sqrt{2R}\sqrt{1-\cos(\varphi_2-\varphi_1)}} \right) \chi[\varphi_2] \right\}$$

Then our SCF equation becomes

$$\left[ \langle 1|\hat{H}_1|1 \rangle + \hat{H}_2 + \langle 1|V|1 \rangle \right] \chi[\varphi_2] = E\chi[\varphi_2] \tag{5.9}$$

which is an equation for  $\chi[\varphi_2]$  based on one “number” ( $\langle 1|\hat{H}_1|1 \rangle$ ) and two operators ( $\hat{H}_2$  and  $\langle 1|V|1 \rangle$ ), i.e., re-ordering terms,

$$\begin{aligned}
& \left[ \hat{H}_2 + \left\{ \langle 1|\hat{H}_1|1 \rangle + \langle 1|V|1 \rangle \right\} \right] \chi[\varphi_2] = E\chi[\varphi_2] \\
& \left[ \hat{H}_1 + \left\{ \langle 2|\hat{H}_2|2 \rangle + \langle 2|V|2 \rangle \right\} \right] \chi[\varphi_1] = E\chi[\varphi_1]
\end{aligned} \tag{5.10}$$

or, re-arranging,

$$\begin{aligned}
& \left[ \hat{H}_2 + \left\{ \langle 1|V|1 \rangle \right\} \right] \chi[\varphi_2] = (E - \langle 1|\hat{H}_1|1 \rangle) \chi[\varphi_2] \\
& \left[ \hat{H}_1 + \left\{ \langle 2|V|2 \rangle \right\} \right] \chi[\varphi_1] = (E - \langle 2|\hat{H}_2|2 \rangle) \chi[\varphi_1]
\end{aligned} \tag{5.11}$$

The “trick” now is to solve each of these equations for starting assumptions concerning the other function,

i.e., assume a form for  $\chi[\varphi_1]$  and solve for  $\chi[\varphi_2]$ , then use this new form for  $\chi[\varphi_2]$  to solve for  $\chi[\varphi_1]$ , which one then cycles around again and again, until convergence of some kind is achieved.

$\langle 1|V|1 \rangle$  (and its equivalent,  $\langle 2|V|2 \rangle$ ) are functions of coördinates, i.e.,

$$\langle 1|V|1 \rangle = f[\varphi_2]$$

and

$$\langle 2|V|2 \rangle = f[\varphi_1]$$

To see what these integrals entail (in terms of actually carrying them out), we have for a real electron-electron interaction term

$$\langle 1|V|1 \rangle [\varphi_2] \equiv \int_{space\ 1} d\varphi_1 \left\{ \chi^*[\varphi_1] \left( \frac{1}{r_{12}} \right) \chi[\varphi_1] \right\}$$

which would become

$$\langle 1|V|1 \rangle [\varphi_2] \equiv \int_0^{2\pi} d\varphi_1 \left\{ \chi^2[\varphi_1] \left( \frac{1}{\sqrt{2R}\sqrt{1-\cos(\phi_2-\phi_1)}} \right) \right\}$$

This integral evaluates to a function of  $\varphi_2$  (see Appendix II)!

The opposite obtains for  $\langle 2|V|2 \rangle$ , i.e., it evaluates to a function of  $\varphi_1$ .

It is this double interdependence which makes the Hartree-Fock scheme “entangled” in the sense that the equation for  $\chi[\varphi_2]$  depends on  $\varphi_1$  and *vice versa* and the coupled Equations 5.10 commingle the two variables again.

### Appendix I, The angle between two radius vectors

Let

$$\vec{r}_1 = x_1\hat{i} + y_1\hat{j} + z_1\hat{k}$$

and

$$\vec{r}_2 = x_2\hat{i} + y_2\hat{j} + z_2\hat{k}$$

which are, in spherical polar coördinates:

$$\vec{r}_1 = r_1 \sin \vartheta_1 \cos \varphi_1 \hat{i} + r_1 \sin \vartheta_1 \sin \varphi_1 \hat{j} + r_1 \cos \vartheta_1 \hat{k}$$

and

$$\vec{r}_2 = r_2 \sin \vartheta_2 \cos \varphi_2 \hat{i} + r_2 \sin \vartheta_2 \sin \varphi_2 \hat{j} + r_2 \cos \vartheta_2 \hat{k}$$

Now

$$r_{12}^2 = r_1^2 + r_2^2 - 2r_1r_2 \cos \eta$$

and

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

which, in double spherical polar coordinates becomes

$$r_{12}^2 = (r_1 \sin \vartheta_1 \cos \varphi_1 - r_2 \sin \vartheta_2 \cos \varphi_2)^2 + (r_1 \sin \vartheta_1 \sin \varphi_1 - r_2 \sin \vartheta_2 \sin \varphi_2)^2 + (r_1 \cos \vartheta_1 - r_2 \cos \vartheta_2)^2$$

which is

$$r_{12}^2 = r_1^2 + r_2^2 - 2r_1r_2 (\sin \vartheta_2 \sin \vartheta_1 (\cos \varphi_2 \cos \varphi_1 + \sin \varphi_2 \sin \varphi_1) + \cos \vartheta_1 \cos \vartheta_2)$$

which means that

$$r_1^2 + r_2^2 - 2r_1r_2 \cos \eta = r_1^2 + r_2^2 - 2r_1r_2 (\sin \vartheta_2 \sin \vartheta_1 (\cos \varphi_2 \cos \varphi_1 + \sin \varphi_2 \sin \varphi_1) + \cos \vartheta_1 \cos \vartheta_2)$$

so that

$$\cos \eta = (\sin \vartheta_2 \sin \vartheta_1 (\cos \varphi_2 \cos \varphi_1 + \sin \varphi_2 \sin \varphi_1) + \cos \vartheta_1 \cos \vartheta_2)$$

or,

$$\cos \eta = \cos \vartheta_2 \cos \vartheta_1 + \sin \vartheta_2 \sin \vartheta_1 \cos(\varphi_2 - \varphi_1)$$

### Appendix II, Evaluating the Hartree-Fock Equations

The functions

$$\chi_n[\varphi_1] = A_n \sin n\varphi_1 + B_n \cos n\varphi_1 \quad (5.12)$$

$$\chi_n[\varphi_2] = C_n \sin n\varphi_2 + D_n \cos n\varphi_2 \quad (5.13)$$

which are designed to give proper behavior at  $\varphi + 2\pi$  in standard manner are appropriate as eigenfunctions of the unperturbed Hamiltonians.

Arbitrarily choosing  $B_1 = 0$  and  $n=1$  we have

$$\langle 1|V|1 \rangle [\varphi_2] = \int_0^{2\pi} d\varphi_1 \left( \frac{A_1^2 \sin^2 \varphi_1}{\sqrt{2}R\sqrt{1 - \cos(\varphi_2 - \varphi_1)}} \right)$$

Since

$$\sin \frac{\alpha}{2} = \pm \sqrt{\frac{1 - \cos \alpha}{2}}$$

we have

$$\langle 1|V|1 \rangle [\varphi_2] = \int_0^{2\pi} d\varphi_1 \left( \frac{A_1^2 \sin^2 \varphi_1}{2\sqrt{2}R \sin(\frac{\varphi_2 - \varphi_1}{2})} \right)$$

Although tractable, we see that we do not achieve the simplicity of the original Summerfield et al. paper. Notice the explicit  $\varphi_2$  dependence!

### Appendix III-Hyperspherical Polar Coördinates

Consider transforming from the traditional  $x_1, y_1, z_1, x_2, y_2, z_2$  not into double spherical coördinates, but instead into a single 6-dimensional coördinate

scheme analogous to normal 3-dimensional spherical polar coordinates.

We would have

$$\begin{aligned}
 x_1 &= r \cos \vartheta \\
 y_1 &= r \sin \vartheta \cos \varphi_1 \\
 z_1 &= r \sin \vartheta \sin \varphi_1 \cos \varphi_2 \\
 x_2 &= r \sin \vartheta \sin \varphi_1 \sin \varphi_2 \cos \varphi_3 \\
 y_2 &= r \sin \vartheta \sin \varphi_1 \sin \varphi_2 \sin \varphi_3 \cos \varphi_4 \\
 z_2 &= r \sin \vartheta \sin \varphi_1 \sin \varphi_2 \sin \varphi_3 \sin \varphi_4
 \end{aligned} \tag{5.14}$$

following Sommerfeld [2] where his  $p = 4$ . In this case, we have  $r^2 = r_1^2 + r_2^2$ , when we sum the squares of the coordinates. The ties between fully polar and double spherical polar coordinates might lead to some simplification, but to see if that is true one needs to slog through

the rest of the transformation of the kinetic energy operator. Parenthetically, we note that the volume element in this 6-dimensional space is

$$dV = r^5 \sin^4 \vartheta \sin^3 \varphi_1 \sin^2 \varphi_2 \sin \varphi_3 \sin \varphi_4 dr d\vartheta d\varphi_1 d\varphi_2 d\varphi_3 d\varphi_4$$

and

$$\nabla^2 \chi = \frac{1}{r^5} \frac{\partial \left( r^2 \frac{\partial \chi}{\partial r} \right)}{\partial r} + \frac{1}{r^2} \Lambda_{op} \chi$$

where  $\Lambda_{op}$  is the 5-dimensional angular part of the kinetic energy operator [3]. Since  $r_1$  and  $r_2$  do not separate cleanly in this hyperspherical coordinate system, it is far from clear whether or not this latter system is superior to the double spherical polar system used above for our purposes.

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- [1] J. H. Summerfield, G. S. Beltrame, and J. G. Loeser, *J. Chem. Ed.*, 76, 1430 (1999)  
 [2] A. Sommerfeld, "Partial Differential Equations in Physics", Academic Press, 1949, page 227

- [3] R. J. White and F. H. Stillinger Jr., *J. Chem. Phys.*, 52, 5800 (1970).