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A Review of Helium Hamiltonians

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A Review of Helium Hamiltonians and Related Wave Function Expansions

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I. SYNOPSIS

When one thinks about why chemistry is unable to fulfill Dirac's prediction that (approximately [15]) "all of chemistry and a large part of physics is now known $\cdots$", it comes to mind that the many body problem lies at the core of our problems. The simplest many body problem, the one that killed Bohr theory, is Helium and its two electrons. Even in the non-relativistic, infinite nuclear mass approximation, the difficulties of dealing with two electrons in the field of a fixed +2 nucleus, has defeated all abilities of all analysts so far.** That the energy can be computed to 50+ significant figures is not the issue.

Here, we treat the kinetic energy part of the Hamiltonian of the problem, $-\frac{\hbar^2}{2m_e}\left(\nabla_2^2+\nabla_2^2\right)$ in accordance with elementary calculus, in the hopes of finding alternative coördinate systems which might better allow us to see an "analytical" solution to the Schrödinger Equation; or at least see a better form for the expansion of the "analytical" solution in terms which would be *a priori* convergent.

This also relates to two (or more) other readings in this little library. One concerns the Gronwall form of the Hamiltonian, where an attempt to find an orthogonal coördinate system applicable to the case is discussed, as well as one concerning the Eisenhart form of the same Hamiltonian. The Fock form is also included somewhere here. In all, lots of smart people have worked on this problem, some with ϵ's of success, others with such energy that the literature is indeed vast and unappetizing.

The quantum mechanical treatment of the Helium atom's 2 electrons is discussed with the idea that the details of "old-fashioned" coördinate transformations should exist somewhere in the literature, collected in a manner that will allow future investigators to bypass reinventing the proverbial wheel.

II. THE SCHRÖDINGER EQUATION

For this two electron problem, the Schrödinger Equation has the form

$$-\frac{\hbar^2}{2m}\left(\nabla_1^2+\nabla_2^2\right)\psi-\frac{Ze^2}{r_1}\psi-\frac{Ze^2}{r_2}\psi=E\psi \qquad (2.1)$$

where m is the mass of an electron, and the subscripts refer to electron 1 and 2 respectively.

It is traditional to set Z=2, since Z=1 is H^-, Z=3 would be Li^+, etc., i.e., to specialize to Helium itself. Then, cross multiplying one has

$$-\left(\nabla_1^2+\nabla_2^2\right)\psi-\frac{2m}{\hbar^2}\frac{Ze^2}{r_1}\psi-\frac{2m}{\hbar^2}\frac{Ze^2}{r_2}\psi=E\frac{2m}{\hbar^2}\psi \qquad (2.2)$$

which is the form most people start with.

III. THE HAMILTONIAN

Assuming infinite nuclear masses, (m = $m_{electron}$) one has

$$H_{op}=-\frac{\hbar^2}{2m}\left(\nabla_1^2+\nabla_2^2\right)-\frac{Ze^2}{r_1}-\frac{Ze^2}{r_2}+\frac{e^2}{r_{12}} \qquad (3.1)$$

We start with the idea of expressing the kinetic energy part of the Hamiltonian in a form appropriate for this problem. That operator surely has the form

$$-\frac{\hbar^2}{2m_e}\left(\nabla_1^2+\nabla_2^2\right)$$

where ∇ has its traditional functional meaning. That means that we need to obtain six terms, the first of which might be

$$\frac{\partial^2}{\partial x_1^2}$$

(remember, we are holding x_2 constant as well as y_1, z_1, y_2, z_2 for this first (example) term) for electron 1 and electron 2, as a function or r_1, r_2 and ϑ, the angle between the location vectors of the two electrons, $\vec{r_1}$ and $\vec{r_2}$.

IV. THE COORDINATE TRANSFORMATION

. Remember that

$$r_1=\sqrt{x_1^2+y_1^2+z_1^2}$$

and

$$r_2=\sqrt{x_2^2+y_2^2+z_2^2}$$

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while, of course,

$$r_{12} = \sqrt{(x_1 - x_2)^2 + (y_1 - y_2)^2 + (z_1 - z_2)^2} \qquad (4.1)$$

Actually, the notation r_{12} implies (in my mind) a vector stretching from 1 to 2, but the definition (above) again, in my mind, implies the reverse. Usually, this is of no consequence, but in this case there is a subtle effect, as we will see below.

A. Preliminary Partial Derivatives

First, some preliminaries:

$$\frac{\partial r_1}{\partial x_1} = \frac{\partial \sqrt{x_1^2 + y_1^2 + z_1^2}}{\partial x_1} = \frac{1}{2} r_1^{-1} \frac{\partial \left(x_1^2 + y_1^2 + z_1^2\right)}{\partial x_1} = \frac{x_1}{r_1}$$

and

$$\frac{\partial r_1^{-1}}{\partial x_1} = \frac{-1}{r_1^2} \frac{\partial r_1}{\partial x_1} = -\frac{x_1}{r_1^3}$$

Then, we have

$$\frac{\partial r_1^{-2}}{\partial x_1} = -2 r_1^{-3} \frac{\partial r_1}{\partial x_1}$$

or

$$= -\frac{2}{r_1^3} \frac{x_1}{r_1} = -\frac{2x_1}{r_1^4}$$

Clearly, the other five groups of terms are equivalent. We start with the equation for the angle between the two radii $\vec{r}_1$ and $\vec{r}_2$. From the law of cosines, we have

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

while from vector algebra we know

$$\cos\vartheta = \frac{\vec{r}_1 \cdot \vec{r}_2}{r_1 r_2}$$

An alternative formulation for this vector algebraic statement

$$\cos\vartheta = \frac{\vec{r}_1 \cdot \vec{r}_2}{r_1 r_2} = \frac{x_1 x_2 + y_1 y_2 + z_1 z_2}{r_1 r_2} \equiv y \qquad (4.2)$$

We have

$$\frac{\partial r_1}{\partial x_1} = \frac{\partial \sqrt{x_1^2 + y_1^2 + z_1^2}}{\partial x_1} = \frac{1}{2} r_1^{-1} \frac{\partial \left(x_1^2 + y_1^2 + z_1^2\right)}{\partial x_1} = \frac{x_1}{r_1}$$

and

$$\frac{\partial r_1^{-1}}{\partial x_1} = \frac{-1}{r_1^2} \frac{\partial r_1}{\partial x_1} = -\frac{x_1}{r_1^3}$$

(from above) so, we have

$$\frac{\partial y}{\partial x_1} = \frac{\partial \left(\frac{x_1 x_2 + y_1 y_2 + z_1 z_2}{r_1 r_2} \right)}{\partial x_1}$$

which gives us

$$= \frac{x_2}{r_1 r_2} + \frac{x_1 x_2 + y_1 y_2 + z_1 z_2}{r_2} \frac{\partial r_1^{-1}}{\partial x_1}$$

$$= \frac{x_2}{r_1 r_2} - \left(\frac{x_1 x_2 + y_1 y_2 + z_1 z_2}{r_2} \right) \frac{x_1}{r_1^3}$$

$$= \frac{x_2}{r_1 r_2} - \frac{\vec{r}_1 \cdot \vec{r}_2}{r_2} \frac{x_1}{r_1^3}$$

$$= \frac{x_2}{r_1 r_2} - \frac{r_1 r_2 y}{r_2} \frac{x_1}{r_1^3}$$

Clearly, the other five groups of terms are equivalent.

Now, using the chain rule, we have

$$\frac{\partial}{\partial x_1} = \frac{\partial r_1}{\partial x_1} \frac{\partial}{\partial r_1} + \frac{\partial y}{\partial x_1} \frac{\partial}{\partial y}$$

and the two multiplicative partial derivatives are known. Using Equation 4.2 we have

$$\frac{\partial}{\partial x_1} = \frac{x_1}{r_1} \frac{\partial}{\partial r_1} + \left(\frac{x_2}{r_1 r_2} - \frac{\vec{r}_1 \cdot \vec{r}_2 x_1}{r_1^3 r_2} \right) \frac{\partial}{\partial y}$$

which is

$$\frac{\partial}{\partial x_1} = \frac{x_1}{r_1} \frac{\partial}{\partial r_1} + \left(\frac{x_2}{r_1 r_2} - \frac{x_1 y}{r_1^2} \right) \frac{\partial}{\partial y}$$

Here (we will use y for $\cos\vartheta$, a very, very common abbreviation).

B. Second Partial Derivatives

The second derivative would be

$$\frac{\partial^2}{\partial x_1^2} = \frac{\partial \left(\frac{x_1}{r_1} \frac{\partial}{\partial r_1} + \left(\frac{x_2}{r_1 r_2} - \frac{x_1 y}{r_1^2} \right) \frac{\partial}{\partial y} \right)}{\partial x_1}$$

which would be

$$\frac{\partial^2}{\partial x_1^2} = \frac{\partial \left(\frac{x_1}{r_1} \frac{\partial}{\partial r_1} \right)}{\partial x_1} + \frac{\partial \left(\left(\frac{x_2}{r_1 r_2} - \frac{x_1 y}{r_1^2} \right) \frac{\partial}{\partial y} \right)}{\partial x_1}$$

We have achieved a mixed representation of the second partial derivative.

Now we take the derivative with respect to x_1 where appropriate, before converting $\frac{\partial}{\partial x_1}$ to $\frac{\partial}{\partial r_1}$ and $\frac{\partial}{\partial y}$. We obtain

$$\frac{\partial^2}{\partial x_1^2} = \frac{1}{r_1} \frac{\partial}{\partial r_1} + x_1 \frac{\partial \left(\frac{1}{r_1} \frac{\partial}{\partial r_1} \right)}{\partial x_1} \qquad (4.3)$$

$$+ \frac{\partial \left(\left(\frac{x_2}{r_1 r_2} \right) \frac{\partial}{\partial y} \right)}{\partial x_1} \qquad (4.4)$$

$$- \left(\frac{y}{r_1^2} \right) \frac{\partial}{\partial y} \qquad (4.5)$$

$$- x_1 \frac{\partial \left(\left(\frac{y}{r_1^2} \right) \frac{\partial}{\partial y} \right)}{\partial x_1} \qquad (4.6)$$

Now we expand the partial derivatives with respect to x_1 to their replacements. We are going to get a devil of a lot of terms. We obtain for the first term

$$\frac{\partial^2}{\partial x_1^2} =$$

$$Equation-4.3 \rightarrow \frac{1}{r_1}\frac{\partial}{\partial r_1} + x_1\frac{\partial r_1^{-1}}{\partial x_1}\frac{\partial}{\partial r_1} + \frac{x_1}{r_1}\frac{\partial^2}{\partial x_1 \partial r_1} \rightarrow \frac{1}{r_1}\frac{\partial}{\partial r_1} + x_1\left(\frac{-x_1}{r_1^3}\right)\frac{\partial}{\partial r_1} + \frac{x_1}{r_1}\frac{\partial^2}{\partial x_1 \partial r_1} \tag{4.7}$$

$$Equation-4.4 \rightarrow +\frac{\partial\left(\left(\frac{x_2}{r_1 r_2}\right)\frac{\partial}{\partial y}\right)}{\partial x_1} \rightarrow +\frac{x_2}{r_2}\frac{\partial r_1^{-1}}{\partial x_1}\frac{\partial}{\partial y} + \frac{x_2}{r_1 r_2}\frac{\partial^2}{\partial x_1 \partial y} \tag{4.8}$$

$$Equation-4.5 \ \rightarrow -\left(\frac{y}{r_1^2}\right)\frac{\partial}{\partial y} \tag{4.9}$$

$$Equation-4.6 \ -x_1\frac{\partial\left(\left(\frac{y}{r_1^2}\right)\frac{\partial}{\partial y}\right)}{\partial x_1} \rightarrow -x_1 y\left(\frac{\partial r_1^{-2}}{\partial x_1}\right)\frac{\partial}{\partial y} - \frac{x_1}{r_1^2}\left(\frac{\partial y}{\partial x_1}\right)\frac{\partial}{\partial y} - \left(\frac{x_1 y}{r_1^2}\right)\frac{\partial^2}{\partial x_1 \partial y} \tag{4.10}$$

which is

$$\frac{\partial^2}{\partial x_1^2} =$$

$$Equation-4.7 \rightarrow \frac{1}{r_1}\frac{\partial}{\partial r_1} + \left(\frac{-x_1^2}{r_1^3}\right)\frac{\partial}{\partial r_1} + \frac{x_1}{r_1}\left(\frac{x_1}{r_1}\frac{\partial}{\partial r_1} + \left(\frac{x_2}{r_1 r_2} - \frac{x_1 y}{r_1^2}\right)\frac{\partial}{\partial y}\right)\frac{\partial}{\partial r_1} \tag{4.11}$$

$$Equation-4.8 \rightarrow -\frac{x_2}{r_2}\frac{x_1}{r_1^3}\frac{\partial}{\partial y} + \frac{x_2}{r_1 r_2}\left(\frac{x_1}{r_1}\frac{\partial}{\partial r_1} + \left(\frac{x_2}{r_1 r_2} - \frac{x_1 y}{r_1^2}\right)\frac{\partial}{\partial y}\right)\frac{\partial}{\partial y} \tag{4.12}$$

$$Equation-4.9 \rightarrow -\frac{y}{r_1^2}\frac{\partial}{\partial y} \tag{4.13}$$

$$Equation-4.10 \rightarrow -x_1 y\frac{\partial r_1^{-2}}{\partial x_1}\frac{\partial}{\partial y} - \frac{x_1}{r_1^2}\left(\frac{x_2}{r_1 r_2} - \frac{x_1(\vec{r}_1\cdot\vec{r}_2)}{r_1^3 r_2}\right)\frac{\partial}{\partial y} \tag{4.14}$$

$$Equation-4.10 \rightarrow -\frac{x_1 y}{r_1^2}\left\{\frac{x_1}{r_1}\frac{\partial}{\partial r_1} + \left(\frac{x_2}{r_1 r_2} - \frac{x_1 y}{r_1^2}\right)\frac{\partial}{\partial y}\right\}\frac{\partial}{\partial y} \tag{4.15}$$

which is, upon cleaning up the expressions

$$\frac{\partial^2}{\partial x_1^2} =$$

$$Equation-4.11 \rightarrow \frac{1}{r_1}\frac{\partial}{\partial r_1} - \frac{x_1^2}{r_1^3}\frac{\partial}{\partial r_1} + \frac{x_1^2}{r_1^2}\frac{\partial^2}{\partial r_1^2} + \frac{x_1}{r_1}\left(\frac{x_2}{r_1 r_2} - \frac{x_1 y}{r_1^2}\right)\frac{\partial^2}{\partial r_1 \partial y} \tag{4.16}$$

$$Equation-4.12 \rightarrow \ -\frac{x_2}{r_2}\frac{x_1}{r_1^3}\frac{\partial}{\partial y} + \frac{x_2 x_1}{r_1^2 r_2}\frac{\partial^2}{\partial r_1 \partial y} + \left(\frac{x_2}{r_1 r_2}\left(\frac{x_2}{r_1 r_2} - \frac{x_1 y}{r_1^2}\right)\frac{\partial}{\partial y}\right)\frac{\partial}{\partial y} \tag{4.17}$$

$$Equation 4.13 \rightarrow \ -\frac{y}{r_1^2}\frac{\partial}{\partial y} \tag{4.18}$$

$$Equation - 4.14 \rightarrow \ -x_1 y\left(\frac{-2x_1}{r_1^4}\right)\frac{\partial}{\partial y} - \left(\frac{x_1 x_2}{r_1^3 r_2} - x_1^2\frac{\vec{r_1}\cdot\vec{r_2}}{r_1^5 r_2}\right)\frac{\partial}{\partial y} \tag{4.19}$$

$$Equation 4.15 \rightarrow -\frac{x_1 y}{r_1^2}\left(\frac{x_1}{r_1}\frac{\partial^2}{\partial r_1 \partial y}\right) - \frac{x_1 y}{r_1^2}\left(\frac{x_2}{r_1 r_2} - \frac{x_1 y}{r_1^2}\right)\frac{\partial^2}{\partial y^2} \tag{4.20}$$

and, cleaning up again, we have

$$\frac{\partial^2}{\partial x_1^2} =$$

$$Equation - 4.16 \rightarrow \frac{1}{r_1}\frac{\partial}{\partial r_1} - \frac{x_1^2}{r_1^3}\frac{\partial}{\partial r_1} + \frac{x_1^2}{r_1^2}\frac{\partial^2}{\partial r_1^2} + \frac{x_1}{r_1}\left(\frac{x_2}{r_1 r_2} - \frac{x_1 y}{r_1^2}\right)\frac{\partial^2}{\partial r_1 \partial y} \tag{4.21}$$

$$Equation - 4.17 \rightarrow \ -\frac{x_2}{r_2}\frac{x_1}{r_1^3}\frac{\partial}{\partial y} + \frac{x_2 x_1}{r_1^2 r_2}\frac{\partial^2}{\partial r_1 \partial y} + \left(\frac{x_2}{r_1 r_2}\left(\frac{x_2}{r_1 r_2} - \frac{x_1 y}{r_1^2}\right)\right)\frac{\partial^2}{\partial y^2} \tag{4.22}$$

$$Equation 4.18 \rightarrow \ -\frac{y}{r_1^2}\frac{\partial}{\partial y} \tag{4.23}$$

$$Equation - 4.19 \rightarrow \ +\left(\frac{2x_1^2 y}{r_1^4}\right)\frac{\partial}{\partial y} - \frac{x_1 x_2}{r_1^3 r_2}\frac{\partial}{\partial y} \tag{4.24}$$

$$Equation - 4.19 \rightarrow \ +x_1^2\frac{\vec{r_1}\cdot\vec{r_2}}{r_1^5 r_2}\frac{\partial}{\partial y} \tag{4.25}$$

$$Equation 4.20 \rightarrow -\left(\frac{x_1^2 y}{r_1^3}\frac{\partial^2}{\partial r_1 \partial y}\right) - \frac{x_1 y x_2}{r_1^3 r_2}\frac{\partial^2}{\partial y^2} + \frac{x_1^2 y^2}{r_1^4}\frac{\partial^2}{\partial y^2} \tag{4.26}$$

which is, penultimately, when all six term are added together,

$$\frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial y_1^2} + \frac{\partial^2}{\partial z_1^2} + \frac{\partial^2}{\partial x_2^2} + \frac{\partial^2}{\partial y_2^2} + \frac{\partial^2}{\partial z_2^2} =$$

$$Equation - 4.21 \rightarrow \frac{3}{r_1}\frac{\partial}{\partial r_1} - \frac{r_1^2}{r_1^3}\frac{\partial}{\partial r_1} + \frac{r_1^2}{r_1^2}\frac{\partial^2}{\partial r_1^2} +$$

$$\frac{x_1 x_2 + y_1 y_2 + z_1 z_2}{r_1^2 r_2}\frac{\partial^2}{\partial r_1 \partial y} - \frac{(x_1^2 + y_1^2 + z_1^2) y}{r_1^3}\frac{\partial^2}{\partial r_1 \partial y}$$

$$Equation - 4.21 \rightarrow \frac{3}{r_2}\frac{\partial}{\partial r_2} - \frac{r_2^2}{r_2^3}\frac{\partial}{\partial r_2} + \frac{r_2^2}{r_2^2}\frac{\partial^2}{\partial r_2^2} +$$

$$\frac{x_1 x_2 + y_1 y_2 + z_1 z_2}{r_2^2 r_1}\frac{\partial^2}{\partial r_2 \partial y} - \frac{(x_2^2 + y_2^2 + z_2^2) y}{r_2^2 r_1}\frac{\partial^2}{\partial r_2 \partial y}$$

$$Equation - 4.22 \rightarrow -\frac{x_1 x_2 + y_1 y_2 + z_1 z_2}{r_1^3 r_2}\frac{\partial}{\partial y} + \frac{r_2 r_1 y}{r_1^2 r_2}\frac{\partial^2}{\partial r_1 \partial y} +$$

$$\left(\frac{r_2^2}{r_1^2 r_2^2} - \frac{(x_1 x_2 + y_1 y_2 + z_1 z_2) y}{r_1^3 r_2}\right)\frac{\partial^2}{\partial y^2}$$

$$Equation - 4.22 \rightarrow -\frac{x_2 x_1 + y_1 y_2 + z_1 z_2}{r_2^3 r_1}\frac{\partial}{\partial y} + \frac{(x_2 x_1 + y_1 y_2 + z_1 z_2)}{r_2^2 r_1}\frac{\partial^2}{\partial r_2 \partial y} + \left(\frac{r_1^2}{r_2^2 r_1^2} - \frac{r_1 r_2 y^2}{r_2^3 r_1}\right)\frac{\partial^2}{\partial y^2}$$

$$Equation - 4.23 \rightarrow -\frac{3y}{r_2^2}\frac{\partial}{\partial y} - \frac{3y}{r_1^2}\frac{\partial}{\partial y} - \frac{3y}{r_2^2}\frac{\partial}{\partial y} - \frac{3y}{r_1^2}\frac{\partial}{\partial y}$$

$$Equation - 4.24 \rightarrow +\left(\frac{2r_1^2 y}{r_1^3}\right)\frac{\partial}{\partial y} + \left(\frac{2r_2^2 y}{r_2^3}\right)\frac{\partial}{\partial y}$$

$$Equation - 4.24 \rightarrow -\frac{\vec{r_1}\cdot\vec{r_2}}{r_1^3 r_2}\frac{\partial}{\partial y} + \frac{\vec{r_1}\cdot\vec{r_2}}{r_2^3 r_1}\frac{\partial}{\partial y}$$

$$Equation - 4.25 \rightarrow -\frac{\vec{r_2}\cdot\vec{r_1}}{r_2^3 r_1}\frac{\partial}{\partial y} + \frac{\vec{r_2}\cdot\vec{r_1}}{r_2^3 r_1}\frac{\partial}{\partial y}$$

$$Equation - 4.26 \to -\left(\frac{r_1^2 y}{r_1^3}\frac{\partial^2}{\partial r_1 \partial y}\right) - \frac{\vec{r_1}\cdot\vec{r_2} y}{r_1^3 r_2}\frac{\partial^2}{\partial y^2} + \frac{y^2}{r_1^2}\frac{\partial^2}{\partial y^2}$$
$$Equation - 4.26 \to -\left(\frac{r_2^2 y}{r_2^3}\frac{\partial^2}{\partial r_2 \partial y}\right) - \frac{\vec{r_1}\cdot\vec{r_2} y}{r_1 r_2^3}\frac{\partial^2}{\partial y^2} + \frac{y^2}{r_2^2}\frac{\partial^2}{\partial y^2}$$

The term $x_1x_2 + y_1y_2 + z_1z_2$ is just r_1r_2y, yields the gorgeous cancellations (see above) leading to which becomes

$$\frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial y_1^2} + \frac{\partial^2}{\partial z_1^2} + \frac{\partial^2}{\partial x_2^2} + \frac{\partial^2}{\partial y_2^2} + \frac{\partial^2}{\partial z_2^2} =$$
$$Equation - 4.27 \to \frac{2}{r_1}\frac{\partial}{\partial r_1} + \frac{\partial^2}{\partial r_1^2} \quad (4.27)$$
$$Equation - 4.27 \to +\frac{r_1 r_2 y}{r_1^2 r_2}\frac{\partial^2}{\partial r_1 \partial y} - \frac{y}{r_1}\frac{\partial^2}{\partial r_1 \partial y} = 0 \quad (4.28)$$
$$Equation - 4.27 \to \frac{2}{r_2}\frac{\partial}{\partial r_2} + \frac{\partial^2}{\partial r_2^2} \quad (4.29)$$
$$Equation - 4.27 \to +\frac{r_1 r_2 y}{r_2^2 r_1}\frac{\partial^2}{\partial r_2 \partial y} - \frac{y}{r_2}\frac{\partial^2}{\partial r_2 \partial y} = 0 \quad (4.30)$$
$$Equation - 4.27 \to -\frac{r_1 r_2 y}{r_1^3 r_2}\frac{\partial}{\partial y} + \frac{y}{r_1}\frac{\partial^2}{\partial r_1 \partial y} + \left(\frac{1}{r_1^2} - \frac{r_1 r_2 y^2}{r_1^3 r_2}\right)\frac{\partial^2}{\partial y^2} \quad (4.31)$$
$$Equation - 4.27 \to -\frac{r_2 r_1 y}{r_2^3 r_1}\frac{\partial}{\partial y} + \frac{r_2 r_1 y}{r_2^2 r_1}\frac{\partial^2}{\partial r_2 \partial y} + \left(\frac{1}{r_2^2} - \frac{r_1 r_2 y^2}{r_2^3 r_1}\right)\frac{\partial^2}{\partial y^2} \quad (4.32)$$
$$Equation - 4.27 \to -\frac{3y}{r_2^2}\frac{\partial}{\partial y} - \frac{3y}{r_1^2}\frac{\partial}{\partial y} \quad (4.33)$$
$$Equation - 4.27 \to +\left(\frac{2y}{r_1^2}\right)\frac{\partial}{\partial y} + \left(\frac{2y}{r_2^2}\right)\frac{\partial}{\partial y} \quad (4.34)$$
$$Equation - 4.27 \to -\frac{y}{r_1^2}\frac{\partial}{\partial y} + \frac{y}{r_1^2}\frac{\partial}{\partial y} - \frac{y}{r_2^2}\frac{\partial}{\partial y} + \frac{y}{r_2^2}\frac{\partial}{\partial y} = 0 \quad (4.35)$$
$$Equation - 4.27 \to -\left(\frac{y}{r_1}\frac{\partial^2}{\partial r_1 \partial y}\right) \quad (4.36)$$
$$Equation - 4.27 \to -\left(\frac{y}{r_2}\frac{\partial^2}{\partial r_1 \partial y}\right) \quad (4.37)$$

We obtain

$$\frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial y_1^2} + \frac{\partial^2}{\partial z_1^2} + \frac{\partial^2}{\partial x_2^2} + \frac{\partial^2}{\partial y_2^2} + \frac{\partial^2}{\partial z_2^2} =$$
$$Equation - 4.27 \to \frac{2}{r_1}\frac{\partial}{\partial r_1} + \frac{\partial^2}{\partial r_1^2} \quad (4.38)$$
$$Equation - 4.29 \to \frac{2}{r_2}\frac{\partial}{\partial r_2} + \frac{\partial^2}{\partial r_2^2} \quad (4.39)$$
$$Equation - 4.31 \to -\frac{y}{r_1^2}\frac{\partial}{\partial y} + \underbrace{\frac{y}{r_1}\frac{\partial^2}{\partial r_1 \partial y}} + \left(\frac{1}{r_1^2} - \frac{y^2}{r_1^2}\right)\frac{\partial^2}{\partial y^2} \quad (4.40)$$
$$Equation - 4.32 \to -\frac{y}{r_2^2}\frac{\partial}{\partial y} + \underbrace{\frac{y}{r_2}\frac{\partial^2}{\partial r_2 \partial y}} + \left(\frac{1}{r_2^2} - \frac{y^2}{r_2^2}\right)\frac{\partial^2}{\partial y^2} = 0 \quad (4.41)$$
$$Equation - 4.33 \to -\frac{3y}{r_2^2}\frac{\partial}{\partial y} - \frac{3y}{r_1^2}\frac{\partial}{\partial y} \quad (4.42)$$
$$Equation - 4.34 \to +\left(\frac{2y}{r_1^2}\right)\frac{\partial}{\partial y} + \left(\frac{2y}{r_2^2}\right)\frac{\partial}{\partial y} \quad (4.43)$$
$$Equation - 4.36 \to -\underbrace{\left(\frac{y}{r_1}\frac{\partial^2}{\partial r_1 \partial y}\right)} \quad (4.44)$$

$$Equation - 4.37 \rightarrow -\underbrace{\left(\frac{y}{r_2}\frac{\partial^2}{\partial r_1 \partial y}\right)} \quad (4.45)$$

(where we notice that the underbraced material (above) cancels) which (almost) finally becomes

C. Final Cancellations

$$\frac{\partial^2}{\partial x_1^2}+\frac{\partial^2}{\partial y_1^2}+\frac{\partial^2}{\partial z_1^2}+\frac{\partial^2}{\partial x_2^2}+\frac{\partial^2}{\partial y_2^2}+\frac{\partial^2}{\partial z_2^2}=$$

$$Equation - 4.38 \rightarrow \frac{2}{r_1}\frac{\partial}{\partial r_1}+\frac{\partial^2}{\partial r_1^2} \quad (4.46)$$

$$Equation - 4.39 \rightarrow \frac{2}{r_2}\frac{\partial}{\partial r_2}+\frac{\partial^2}{\partial r_2^2} \quad (4.47)$$

$$Equation - 4.40 \rightarrow -\frac{y}{r_1^2}\frac{\partial}{\partial y}+\left(\frac{1-y^2}{r_1^2}\right)\frac{\partial^2}{\partial y^2} \quad (4.48)$$

$$Equation - 4.41 \rightarrow -\frac{y}{r_2^2}\frac{\partial}{\partial y}+\left(\frac{1-y^2}{r_2^2}\right)\frac{\partial^2}{\partial y^2} \quad (4.49)$$

$$Equation - 4.42 \rightarrow -\frac{3y}{r_2^2}\frac{\partial}{\partial y}-\frac{3y}{r_1^2}\frac{\partial}{\partial y} \quad (4.50)$$

$$+\left(\frac{2y}{r_1^2}\right)\frac{\partial}{\partial y}+\left(\frac{2y}{r_2^2}\right)\frac{\partial}{\partial y} \quad (4.51)$$

which finally, and we mean that(!) is

$$\frac{\partial^2}{\partial x_1^2}+\frac{\partial^2}{\partial y_1^2}+\frac{\partial^2}{\partial z_1^2}+\frac{\partial^2}{\partial x_2^2}+\frac{\partial^2}{\partial y_2^2}+\frac{\partial^2}{\partial z_2^2}=$$

$$\frac{2}{r_1}\frac{\partial}{\partial r_1}+\frac{\partial^2}{\partial r_1^2}+\frac{2}{r_2}\frac{\partial}{\partial r_2}+\frac{\partial^2}{\partial r_2^2}-\left(\frac{1}{r_1^2}+\frac{1}{r_2^2}\right)2y\frac{\partial}{\partial y}+\left(\frac{1}{r_1^2}+\frac{1}{r_2^2}\right)(1-y^2)\frac{\partial^2}{\partial y^2} \quad (4.52)$$

OK, we lied. There is a traditional form which we have to include:

$$\frac{\partial^2}{\partial x_1^2}+\frac{\partial^2}{\partial y_1^2}+\frac{\partial^2}{\partial z_1^2}+\frac{\partial^2}{\partial x_2^2}+\frac{\partial^2}{\partial y_2^2}+\frac{\partial^2}{\partial z_2^2}=$$

$$\frac{1}{r_1^2}\frac{\partial\left(r_1^2\frac{\partial}{\partial r_1}\right)}{\partial r_1}+\frac{1}{r_2^2}\frac{\partial\left(r_2^2\frac{\partial}{\partial r_2}\right)}{\partial r_2}+\left(\frac{1}{r_1^2}+\frac{1}{r_2^2}\right)\frac{\partial\left((1-y^2)\frac{\partial}{\partial y}\right)}{\partial y} \quad (4.53)$$

which is, one must believe, the most compact form possible.

V. THE r_1, r_2, r_{12} FORM

We had the following expression for the Kinetic Energy Operator:

$$\frac{\partial^2}{\partial x_1^2}+\frac{\partial^2}{\partial y_1^2}+\frac{\partial^2}{\partial z_1^2}+\frac{\partial^2}{\partial x_2^2}+\frac{\partial^2}{\partial y_2^2}+\frac{\partial^2}{\partial z_2^2}=$$

$$\nabla_1^2+\nabla_2^2=$$

$$\frac{1}{r_1^2}\frac{\partial\frac{r_1^2\partial}{\partial r_1}}{\partial r_1}+\frac{1}{r_2^2}\frac{\partial\frac{r_2^2\partial}{\partial r_2}}{\partial r_2}-\left(\frac{1}{r_1^2}+\frac{1}{r_2^2}\right)\frac{\partial(1-y^2)\frac{\partial}{\partial y}}{\partial y} \quad (5.1)$$

which we derived in $r1, r2, \vartheta$ space. Now we turn to a different spatial representation, r_1, r_2, r_{12}. Again we seek the Kinetic Energy Operator $\left(-\frac{1}{2m_e}\left(\nabla_1^2+\nabla_2^2\right)\right)$.

We start with

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

and use the chain rule to obtain

$$\frac{\partial}{\partial x_1}=\frac{\partial r_1}{\partial x_1}\frac{\partial}{\partial r_1}+\frac{\partial r_{12}}{\partial x_1}\frac{\partial}{\partial r_{12}}$$

which is, by direct differentiation

$$\frac{\partial}{\partial x_1}=\frac{x_1}{r_1}\frac{\partial}{\partial r_1}+\frac{x_1-x_2}{r_{12}}\frac{\partial}{\partial r_{12}}$$

since $2r_1 dr_1 = 2x_1 dx_1$. We have

$$\frac{\partial^2}{\partial x_1^2}=\frac{\partial\frac{\partial}{\partial x_1}}{\partial x_1} \quad (5.2)$$

$$\frac{\partial^2}{\partial x_1^2}=\frac{\partial\left(\frac{x_1}{r_1}\frac{\partial}{\partial r_1}+\frac{x_1-x_2}{r_{12}}\frac{\partial}{\partial r_{12}}\right)}{\partial x_1} \quad (5.3)$$

which is

$$\frac{\partial^2}{\partial x_1^2} = \frac{\partial\left(\frac{x_1}{r_1}\frac{\partial}{\partial r_1}\right)}{\partial x_1} + \frac{\partial\left(\frac{x_1-x_2}{r_{12}}\frac{\partial}{\partial r_{12}}\right)}{\partial x_1} \quad (5.4)$$

which becomes

$$\frac{1}{r_1}\frac{\partial}{\partial r_1} + x_1\frac{\partial r_1^{-1}}{\partial x_1}\frac{\partial}{\partial r_1} + \frac{x_1}{r_1}\frac{\partial^2}{\partial x_1 \partial r_1} + \quad (5.5)$$

$$\frac{1}{r_{12}}\frac{\partial}{\partial r_{12}} + (x_1 - x_2)\frac{\partial r_{12}^{-1}}{\partial x_1}\frac{\partial}{\partial r_{12}} + \frac{x_1 - x_2}{r_{12}}\frac{\partial^2}{\partial x_1 \partial r_{12}} \quad (5.6)$$

which is seen to be

$$Equation\ 5.5 \rightarrow \frac{1}{r_1}\frac{\partial}{\partial r_1} - x_1\frac{x_1}{r_1^3}\frac{\partial}{\partial r_1} + \frac{x_1}{r_1}\left(\frac{x_1}{r_1}\frac{\partial\frac{\partial}{\partial r_1}}{\partial r_1} + \frac{x_1 - x_2}{r_{12}}\frac{\partial\frac{\partial}{\partial r_1}}{\partial r_{12}}\right) \quad (5.7)$$

$$Equation\ 5.6 \rightarrow +\frac{1}{r_{12}}\frac{\partial}{\partial r_{12}} - (x_1 - x_2)\frac{(x_1 - x_2)}{r_{12}^3}\frac{\partial}{\partial r_{12}} + \frac{x_1 - x_2}{r_{12}}\left(\frac{x_1}{r_1}\frac{\partial\frac{\partial}{\partial r_{12}}}{\partial r_1} + \frac{x_1 - x_2}{r_{12}}\frac{\partial\frac{\partial}{\partial r_{12}}}{\partial r_{12}}\right) \quad (5.8)$$

and this becomes when repeated for y_1 and z_1:

$$Equation\ 5.7 \rightarrow \frac{1}{r_1}\frac{\partial}{\partial r_1} - \frac{x_1^2}{r_1^3}\frac{\partial}{\partial r_1} \rightarrow \frac{3}{r_1}\frac{\partial}{\partial r_1} - \frac{1}{r_1}\frac{\partial}{\partial r_1} \rightarrow \frac{2}{r_1}\frac{\partial}{\partial r_1} \quad (5.9)$$

$$+Equation\ 5.7 \rightarrow \frac{x_1^2}{r_1^2}\frac{\partial^2}{\partial r_1^2} \rightarrow \frac{\partial^2}{\partial r_1^2} \quad (5.10)$$

$$Equation\ 5.7 \rightarrow +\frac{x_1(x_1 - x_2)}{r_1 r_{12}}\frac{\partial\frac{\partial}{\partial r_1}}{\partial r_{12}} \rightarrow \frac{\vec{r}_1 \cdot \vec{r}_{12}}{r_1 r_{12}}\frac{\partial^2}{\partial r_1^2 \partial r_{12}} \quad (5.11)$$

$$Equation\ 5.8 \rightarrow +\frac{1}{r_{12}}\frac{\partial}{\partial r_{12}} - \frac{(x_1 - x_2)^2}{r_{12}^3}\frac{\partial}{\partial r_{12}} \rightarrow \left(\frac{3}{r_{12}} - \frac{1}{r_{12}}\right)\frac{\partial}{\partial r_{12}} \rightarrow +\frac{2}{r_{12}}\frac{\partial}{\partial r_{12}} \quad (5.12)$$

$$Equation\ 5.8 \rightarrow +\frac{x_1(x_1 - x_2)}{r_1 r_{12}}\frac{\partial^2}{\partial r_{12}\partial r_1} \rightarrow \frac{\vec{r}_1 \cdot \vec{r}_{12}}{r_1 r_{12}}\frac{\partial^2}{\partial r_1 \partial r_{12}} \quad (5.13)$$

$$+Equation\ 5.8 \rightarrow \frac{r_{12}^2}{r_{12}^2}\frac{\partial^2}{\partial r_{12}^2} \rightarrow \frac{\partial^2}{\partial r_{12}^2} \quad (5.14)$$

which becomes

$$\frac{\partial^2}{\partial r_1^2} + \frac{2}{r_1}\frac{\partial}{\partial r_1} + 2\frac{\vec{r}_1 \cdot \vec{r}_{12}}{r_1 r_{12}}\frac{\partial^2}{\partial r_1 \partial r_{12}} + \frac{2}{r_{12}}\frac{\partial}{\partial r_{12}} + \frac{\partial^2}{\partial r_{12}^2}$$

which is for the 3 r_1 terms, i.e., we get a second set from the r_2 terms, leading to

$$\begin{aligned} \nabla_1^2 + \nabla_2^2 = \\ \frac{\partial^2}{\partial r_1^2} + \frac{2}{r_1}\frac{\partial}{\partial r_1} + 2\hat{r}_1 \cdot \hat{r}_{12}\frac{\partial^2}{\partial r_1 \partial r_{12}} \\ +\frac{\partial^2}{\partial r_2^2} + \frac{2}{r_2}\frac{\partial}{\partial r_2} - 2\hat{r}_2 \cdot \hat{r}_{12}\frac{\partial^2}{\partial r_2 \partial r_{12}} \\ +\frac{4}{r_{12}}\frac{\partial}{\partial r_{12}} + 2\frac{\partial^2}{\partial r_{12}^2} \end{aligned} \quad (5.15)$$

These dot products are not the standard form due to Hylleraas, so we write

$$2\vec{r}_1 \cdot \vec{r}_{12} = 2\left[x_1(x_1 - x_2) + y_1(y_1 - y_2) + z_1(z_1 - z_2)\right]$$

(employing Equation 4.1 explicitly) which is

$$2\vec{r}_1 \cdot \vec{r}_{12} = 2\left(x_1^2 - x_1x_2 + y_1^2 - y_1y_2 + z_1^2 - z_1z_2\right)$$

$$2\vec{r}_1 \cdot \vec{r}_{12} = 2\left(-(x_1x_2 + y_1y_2 + z_1z_2) + r_1^2\right)$$

or

$$2\vec{r}_1 \cdot \vec{r}_{12} = 2\left(-\vec{r}_1 \cdot \vec{r}_2 + r_1^2\right)$$

but since

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

(the law of cosines) and

$$\vec{r}_1 \cdot \vec{r}_2 = r_1r_2\cos\vartheta_{12}$$

we have

$$2\vec{r}_1 \cdot \vec{r}_{12} = 2\left(r_1 r_2 \cos\vartheta_{12} - r_1^2\right)$$

which becomes

$$2\vec{r}_1 \cdot \vec{r}_{12} = 2\left(r_1^2 - \left(\frac{r_1^2 + r_2^2 - r_{12}^2}{2}\right)\right)$$

or

$$2\vec{r}_1 \cdot \vec{r}_{12} = 2\left(\frac{2r_1^2 - r_1^2 - r_2^2 + r_{12}^2}{2}\right)$$

or

$$2\vec{r}_1 \cdot \vec{r}_{12} = 2\left(\frac{r_1^2 - r_2^2 + r_{12}^2}{2}\right)$$

(with an inverted ($1 \rightleftharpoons 2$) accompanying result for the $\vec{r_2}$, $\vec{r_{12}}$ combination) so we finally obtain

$$\begin{aligned} \nabla_1^2 + \nabla_2^2 = \\ \frac{\partial^2}{\partial r_1^2} + \frac{2}{r_1}\frac{\partial}{\partial r_1} + \left(\frac{r_1^2 - r_2^2 + r_{12}^2}{r_1 r_{12}}\right)\frac{\partial^2}{\partial r_1 \partial r_{12}} \\ + \frac{\partial^2}{\partial r_2^2} + \frac{2}{r_2}\frac{\partial}{\partial r_2} - \left(\frac{r_2^2 - r_1^2 + r_{12}^2}{r_1 r_{12}}\right)\frac{\partial^2}{\partial r_2 \partial r_{12}} \\ + \frac{4}{r_{12}}\frac{\partial}{\partial r_{12}} + 2\frac{\partial^2}{\partial r_{12}^2} \end{aligned} \quad (5.16)$$

VI. DOUBLE SPHERICAL POLAR COÖRDINATES

$$\begin{aligned} = -\frac{\hbar^2}{2m}\Bigg(\frac{1}{r_1^2}\frac{\partial r_1^2 \frac{\partial}{\partial r_1}}{\partial r_1} + \frac{1}{\sin^2\vartheta_1}\left(\sin\vartheta_1 \frac{\partial \sin\vartheta_1 \frac{\partial}{\partial \vartheta_1}}{\partial \vartheta_1} + \frac{\partial^2}{\partial \varphi_1^2}\right) \\ + \frac{1}{r_2^2}\frac{\partial r_2^2 \frac{\partial}{\partial r_2}}{\partial r_2} + \frac{1}{\sin^2\vartheta_2}\left(\sin\vartheta_2 \frac{\partial \sin\vartheta_2 \frac{\partial}{\partial \vartheta_2}}{\partial \vartheta_2} + \frac{\partial^2}{\partial \varphi_2^2}\right)\Bigg) \\ - \frac{Ze^2}{r_1} - \frac{Ze^2}{r_2} + \frac{e^2}{r_{12}} \end{aligned} \quad (6.1)$$

and again, in another set of mixed coördinates,

$$\begin{aligned} = -\frac{\hbar^2}{2m}\Bigg(\frac{1}{r_1^2}\frac{\partial r_1^2 \frac{\partial}{\partial r_1}}{\partial r_1} + \frac{1}{\sin^2\vartheta_1}\left(\sin\vartheta_1 \frac{\partial \sin\vartheta_1 \frac{\partial}{\partial \vartheta_1}}{\partial \vartheta_1} + \frac{\partial^2}{\partial \varphi_1^2}\right) \\ + \frac{1}{r_2^2}\frac{\partial r_2^2 \frac{\partial}{\partial r_2}}{\partial r_2} + \frac{1}{\sin^2\vartheta_2}\left(\sin\vartheta_2 \frac{\partial \sin\vartheta_2 \frac{\partial}{\partial \vartheta_2}}{\partial \vartheta_2} + \frac{\partial^2}{\partial \varphi_2^2}\right)\Bigg) \\ - \frac{Ze^2}{r_1} - \frac{Ze^2}{r_2} + \frac{e^2}{\sqrt{r_1^2 + r_2^2 - 2r_1 r_2 \cos\vartheta_{12}}} \end{aligned} \quad (6.2)$$

which can be transformed into an equation without "12" subscripts, since

$$\vec{r}_1 \cdot \vec{r}_2 = r_1 r_2 \cos\vartheta_{12}$$

so, we have

$$\begin{aligned} r_1 \sin\vartheta_1 \cos\varphi_1 r_2 \sin\vartheta_2 \cos\varphi_2 &+ \\ r_1 \sin\vartheta_1 \sin\varphi_1 r_2 \sin\vartheta_2 \sin\varphi_2 &+ \\ r_1 r_2 \cos\vartheta_1 \cos\vartheta_2 &= r_1 r_2 \cos\vartheta_{12} \end{aligned}$$

which can be be solved for $\cos\vartheta_{12}$. We obtain, now in a single consistent coordinate system,

$$\begin{aligned} = -\frac{\hbar^2}{2m_e}\Bigg(\frac{1}{r_1^2}\frac{\partial r_1^2 \frac{\partial}{\partial r_1}}{\partial r_1} + \frac{1}{\sin^2\vartheta_1}\left(\sin\vartheta_1 \frac{\partial \sin\vartheta_1 \frac{\partial}{\partial \vartheta_1}}{\partial \vartheta_1} + \frac{\partial^2}{\partial \varphi_1^2}\right) \\ + \frac{1}{r_2^2}\frac{\partial r_2^2 \frac{\partial}{\partial r_2}}{\partial r_2} + \frac{1}{\sin^2\vartheta_2}\left(\sin\vartheta_2 \frac{\partial \sin\vartheta_2 \frac{\partial}{\partial \vartheta_2}}{\partial \vartheta_2} + \frac{\partial^2}{\partial \varphi_2^2}\right)\Bigg) \\ - \frac{Ze^2}{r_1} - \frac{Ze^2}{r_2} + \frac{e^2}{\sqrt{r_1^2 + r_2^2 - 2r_1 r_2\left(\cos\vartheta_1 \cos\vartheta_2 + \sin\vartheta_1 \sin\vartheta_2 \cos(\varphi_1 - \varphi_2)\right)}} \end{aligned} \quad (6.3)$$

This last form shows explicitly not only the non-separability of the Schrödinger Equation for Helium's electrons, but how horribly intertwined the coördinates actually are due to the r_{12} term.

VII. DISCUSSION

We have seen that the Schrödinger Equation for the 2-electron atom/ion has a 6-dimensional representation in double-3-space $\{x_1, y_1, z_1, x_2, y_2, z_2\}$. We assert elsewhere that this is reducible to a $\{r_1,\ r_2,\ r_{12}\}$ set for ^{1}S states.

The first major attack on the solution to this problem was due to Hylleraas, vide infra, who obtained spectacular (for the time) energies for the Helium atom's electrons.

Bartlett [3] vide supra showed that the series solution to the Schrödinger equation using the Hylleraas' expansion gave rise to equations which yielded different values for the **same** coëfficients depending on which equations were used to determine them. Further, Withers [14] showed that there is no Frobenius solution to the Schrödinger equation (see also Coolidge and James [4]).

The analytical situation was clarified by Fock [5] (for the English translation, see Fock [6]) who found that introducing hyperspherical coördinates required that logarithmic terms exist in the expansion of the wave function. This result overshadowed Bartlett's similar [2] independent discovery. A review of the current situation in this field may be found in the work of Abbot and Maslen [1] as well as in the recent work of Myers et al [12]. The convergence of the Fock expansion has been investigated by [11].

VIII. DISCUSSION

If one substitutes a series (Ansatz) into the appropriate Schrödinger equation, one expects that one can sequentially obtain recurrence relations between linked coëfficients with only boundary conditions effecting the resolution of these linked recurrence relations. Then, using these recurrence relations to determine as many coëfficients as possible relative to arbitrary ones, one expects that this truncated and partially evaluated Ansatz, when used in a variational calculation, will lead to the fastest possible convergence to the exact answers (and coëfficients) as the truncation of the series is altered. One expects the variationally determined coëfficients to monatonically approach their limiting "exact" values as the series is extended.

An alternative approach might be to ask, what is the potential energy function which gives rise to the simplest correlated wave function? Consider the function

$$\psi = e^{-\alpha(r_1+r_2)+\beta r_{12}} \tag{8.1}$$

What, we ask, is the potential energy function which has this function as an eigenfunction?

We will work in the full six dimensional coördinate system. Then, we have

$$\nabla_6^2\psi = \frac{\partial^2\psi}{\partial x_1^2} + \frac{\partial^2\psi}{\partial y_1^2} + \frac{\partial^2\psi}{\partial z_1^2} + \frac{\partial^2\psi}{\partial x_2^2} + \frac{\partial^2\psi}{\partial y_2^2} + \frac{\partial^2\psi}{\partial z_2^2} \tag{8.2}$$

and we will evaluate one term of this set to see what is going on. We have

$$\frac{\partial^2\psi}{\partial x_1^2} = \frac{\partial^2 e^{-\alpha(r_1+r_2)+\beta r_{12}}}{\partial x_1^2} \tag{8.3}$$

substituting Equation (8.1) into Equation (8.2).

First, one has

$$\frac{\partial \frac{\partial e^{-\alpha(r_1+r_2)+\beta r_{12}}}{\partial x_1}}{\partial x_1} = \frac{\partial\left(-\alpha\frac{x_1}{r_1} + \beta\frac{x_1-x_2}{r_{12}}\right)e^{-\alpha(r_1+r_2)+\beta r_{12}}}{\partial x_1} \tag{8.4}$$

$$\frac{\partial \frac{\partial e^{-\alpha(r_1+r_2)+\beta r_{12}}}{\partial x_2}}{\partial x_2} = \frac{\partial\left(-\alpha\frac{x_2}{r_2} - \beta\frac{x_1-x_2}{r_{12}}\right)e^{-\alpha(r_1+r_2)+\beta r_{12}}}{\partial x_2} \tag{8.5}$$

We obtain

$$\frac{\partial^2\psi}{\partial x_1^2} = \left(-\frac{\alpha}{r_1} + \frac{\alpha x_1^2}{r_1^3} + \frac{\beta}{r_{12}} - \frac{\beta(x_1-x_2)^2}{r_{12}^3} + \frac{\alpha^2 x_1^2}{r_1^2} + \frac{\beta^2(x_1-x_2)^2}{r_{12}^3} - 2\alpha\beta\frac{x_1(x_1-x_2)}{r_1 r_{12}}\right)e^{-\alpha(r_1+r_2)+\beta r_{12}}$$

$$\frac{\partial^2\psi}{\partial x_2^2} = \left(-\frac{\alpha}{r_2} + \frac{\alpha x_2^2}{r_2^3} + \frac{\beta}{r_{12}} - \frac{\beta(x_1-x_2)^2}{r_{12}^3} + \frac{\alpha^2 x_2^2}{r_2^2} + \frac{\beta^2(x_1-x_2)^2}{r_{12}^3} - 2\alpha\beta\frac{x_2(x_1-x_2)}{r_2 r_{12}}\right)e^{-\alpha(r_1+r_2)+\beta r_{12}}$$

When we add the five other sets of terms similar to these, we obtain

$$\nabla_6^2\psi = \left(-\frac{3\alpha}{r_1} + \frac{\alpha}{r_1} - \frac{3\alpha}{r_2} + \frac{\alpha}{r_2} + \frac{3\beta}{r_{12}} - \frac{\beta}{r_{12}} + \alpha^2 + \beta^2 - 2\alpha\beta\left(\frac{\vec{r_1}\cdot\vec{r_{12}}}{r_1 r_{12}} - \frac{\vec{r_2}\cdot\vec{r_{12}}}{r_2 r_{12}}\right)\right)\psi \tag{8.6}$$

which is

$$\nabla_6^2\psi = \left(-\frac{2\alpha}{r_1} - \frac{2\alpha}{r_2} + \frac{2\beta}{r_{12}} + \alpha^2 + \beta^2 - 2\alpha\beta\left(\frac{\vec{r_1}\cdot\vec{r_{12}}}{r_1 r_{12}} - \frac{\vec{r_2}\cdot\vec{r_{12}}}{r_2 r_{12}}\right)\right)\psi \tag{8.7}$$

What this is saying is that ψ is **not** an eigenfunction, since the term proportional to $\alpha\beta$ shouldn't be there if it were.

$$-\frac{1}{2}\nabla_6^2\psi - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}} = \left(-\frac{Z-\alpha}{r_1} - \frac{Z-\alpha}{r_2} + \frac{1-\beta}{r_{12}} - \frac{1}{2}\left(\alpha^2+\beta^2\right) + \alpha\beta\left(\frac{\vec{r_1}\cdot\vec{r_{12}}}{r_1 r_{12}} - \frac{\vec{r_2}\cdot\vec{r_{12}}}{r_2 r_{12}}\right)\right)\psi \tag{8.8}$$

IX. A VARIABLE SEPARABLE COORDINATE SCHEME OF SORTS

Another, alternate coördinate scheme, defines

$$\vec{u} = \vec{r_1} + \vec{r_2}$$

i.e.,

$$u_1 = x_1 + x_2$$
$$u_2 = y_1 + y_2$$
$$u_3 = z_1 + z_2$$

and

$$\vec{v} = \vec{r_1} - \vec{r_2}$$

$$v_1 = x_1 - x_2$$
$$v_2 = y_1 - y_2$$
$$v_3 = z_1 - z_2$$

so that, in forming the Laplacian one has

$$\frac{\partial}{\partial x_1} = \frac{\partial u_1}{\partial x_1}\frac{\partial}{\partial u_1} + \frac{\partial v_1}{\partial x_1}\frac{\partial}{\partial v_1} = \frac{\partial}{\partial u_1} + \frac{\partial}{\partial v_1}$$

Interestingly enough, in this new coördinate system the Laplacian becomes variable separable and the potential energy becomes unseparable, i.e.,

$$= -\frac{\hbar^2}{2m}\left(\nabla_u^2 + \nabla_v^2\right)\psi - \frac{2Ze^2}{|\vec{u}+\vec{v}|}\psi - \frac{2Ze^2}{|\vec{u}-\vec{v}|}\psi + \frac{e^2}{v}\psi = E\psi \tag{9.1}$$

If one expands the Coulomb attraction terms and drops terms of order v and higher, then standard $e^{-\frac{Z(u+v)}{2}}$ as a solution!

The transformation equations

$$v_y = v\sin\vartheta_v\sin\varphi_v$$
$$v_x = v\sin\vartheta_v\cos\varphi_v$$
$$v_z = v\cos\vartheta_v$$

and

$$u_y = u\sin\vartheta_u\sin\varphi_u$$
$$u_x = u\sin\vartheta_u\cos\varphi_u$$
$$u_z = u\cos\vartheta_u$$

allow us to write

$$|\vec{u}-\vec{v}| = \sqrt{(u\sin\vartheta_u\cos\varphi_u - v\sin\vartheta_v\cos\varphi_v)^2 + (u\sin\vartheta_u\sin\varphi_u - v\sin\vartheta_v\sin\varphi_v)^2 + (u\cos\vartheta_u - v\cos\vartheta_v)^2}$$

$$|\vec{u}+\vec{v}| = \sqrt{(u\sin\vartheta_u\cos\varphi_u + v\sin\vartheta_v\cos\varphi_v)^2 + (u\sin\vartheta_u\sin\varphi_u + v\sin\vartheta_v\sin\varphi_v)^2 + (u\cos\vartheta_u + v\cos\vartheta_v)^2}$$

i.e.,

$$|\vec{u}-\vec{v}| = \sqrt{(u^2+v^2-2uv\sin\vartheta_u\sin\varphi_u\sin\vartheta_v\sin\varphi_v - 2uv\cos\vartheta_u\cos\vartheta_v)}$$

$$|\vec{u}+\vec{v}| = \sqrt{(u^2+v^2+2uv\sin\vartheta_u\sin\varphi_u\sin\vartheta_v\sin\varphi_v + 2uv\cos\vartheta_u\cos\vartheta_v)}$$

but no obvious simplification occurs at this point.

X. THE BARTLETT ARGUMENT

In Bartlett's variables the Schrödinger Equation for the non-relativistic 2-electron Helium problem has the form:

$$\frac{\partial^2\psi}{\partial x^2} + \frac{2}{x}\frac{\partial\psi}{\partial x} + \frac{\partial^2\psi}{\partial y^2} + \frac{2}{y}\frac{\partial\psi}{\partial y} + 2\frac{\partial^2\psi}{\partial z^2} + \frac{4}{z}\frac{\partial\psi}{\partial z}$$

$$+\frac{(x^2-y^2+z^2)}{xz}\frac{\partial^2\psi}{\partial x\partial z} + \frac{(y^2-x^2+z^2)}{yz}\frac{\partial^2\psi}{\partial y\partial z}$$

$$+\left(\frac{\lambda}{4} + \frac{1}{x} + \frac{1}{y} - \frac{1}{2z}\right)\psi = 0 \tag{10.1}$$

where $r_1 \equiv x$, $r_2 \equiv y$ and $r_{12} \equiv z$. In substituting the power series form of the Hylleraas [7–9] Ansatz, Equation (10.1),

$$\psi = \sum_{i,j,k} C_{i,j,k} {r_1}^i {r_2}^j {r_{12}}^k = \sum_{i,j,k} C_{i,j,k} x^i y^j z^k$$

into the appropriately formulated Schrödinger Equation 8.2, the coëfficients $C_{1,0,1}$ and $C_{0,1,1}$ become undeterminable, i.e., two different values for these coëfficients can be found depending on which equations in the recurrence set one chooses to apply.

Alternatively stated, the problem emerges from the existence of the xz (and yz) terms in the expansion, and the operation of the operator

$$\frac{(x^2 - y^2 + z^2)}{xz} \frac{\partial^2}{\partial x \partial z}$$

(and $\frac{(y^2-x^2+z^2)}{yz}\frac{\partial^2}{\partial y \partial z}$). The resultant term when operating on the $C_{1,0,1}xz$ term, i.e.,

$$C_{1,0,1}\frac{(x^2 - y^2 + z^2)}{xz} \frac{\partial^2 xz}{\partial x \partial z}$$

yields a term of the form $-C_{1,0,1}y^2/xz$ which can not be generated by any higher term in the expansion, and languishes uncanceled, destroying the purported solution to the differential equation. Only choosing $C_{1,0,1} = 0$ saves the expansion, but this leads to no solution at all. (A similar argument for the yz (and $C_{0,1,1}$) term follows.)

Thus, the Hylleraas Ansatz fails.

XI. THE KINOSHITA-SCHERR EXPANSION

Kinoshita [10] introduced a wave function Ansatz which extended and enlarged upon the Hylleraas scheme. Kinoshita assumed a wave function form

$$e^{-s/2} \sum_{\ell=0,m=0,n=0}^{\infty} C_{\ell,m,n} s^\ell p^m q^n$$

where $s = r_1 + r_2$, $p = r_{12}/(r_1 + r_2)$ and $q = (-r_1 + r_2)/r_{12}$. This power series purports to include the Hylleraas form. However, Scherr [13] has shown that negative powers of (r_{12}) "are not needed, and in fact, that they violate the boundary conditions". If one now, following Scherr's discussion of the Kinoshita wave function Ansatz, substitutes the Kinoshita-Scherr Ansatz.

$$e^{-As} \sum_{\ell=0}^{\infty} \sum_{m=0}^{\infty} \sum_{n=0}^{m/2} C_{\ell,m,n} s^\ell p^m q^{2n}$$

into the Bartlett form of the Schrödinger equation 8.2, sets $C_{0,0,0} = 1$, and collects terms in relevant powers of x, y, and z, one obtains a curious situation:

$$\begin{aligned}
&\frac{1}{xz}\left(\left(-AC_{1,1,0} + C_{2,1,0}\right)x^2 + \left(AC_{1,1,0} - C_{2,1,0}\right)y^2 + \cdots\right)\\
&+\frac{1}{yz}\left(\left(-AC_{1,1,0} + C_{2,1,0}\right)x^2 + \left(AC_{1,1,0} - C_{2,1,0}\right)y^2 + \cdots\right)\\
&+\frac{1}{x}\left(C_{0,0,0} - 2AC_{0,0,0} + 2C_{1,0,0} - \left(2AC_{1,0,0} - 4C_{2,0,0} + 4C_{2,2,2}\right)y + \cdots\right)\\
&+\frac{1}{y}\left(C_{0,0,0} - 2AC_{0,0,0} + 2C_{1,0,0} - \left(2AC_{1,0,0} - 4C_{2,0,0} + 4C_{2,2,2}\right)x + \cdots\right)\\
&+\frac{1}{z}\left(\frac{-C_{0,0,0}}{2} + 4C_{1,1,0} - \left(\frac{C_{1,0,0}}{2} - 4C_{2,1,0}\right)x - \left(\frac{C_{1,0,0}}{2} - 4C_{2,1,0}\right)y + \cdots\right)\\
&+\cdots = 0
\end{aligned}$$

It is traditional to choose $C_{0,0,0} = 1$ for simplicity.

The first terms (order=0) which are to be forced to zero yield

$$\left(AC_{1,1,0} - C_{2,1,0}\right)\left(y^2 - x^2\right) = 0 \qquad (11.1)$$

i.e., $C_{2,1,0} = AC_{1,1,0}$, (with a similar term for 1/yz).

Then, deferring consideration of all other higher terms with denominator $1/xz$ and $1/yz$, one finds that the leading $1/x$ (and $1/y$) residuum term is

$$\left(1 - 2A + 2C_{1,0,0}\right)\frac{1}{x} = 0$$

i.e., $C_{1,0,0} = -(1 - 2A)/2$, (which implies that the best choice for A is 1/2, (forcing $C_{1,0,0} = 0$) reducing the $1/x$ and $1/y$ terms to zero and reducing this Ansatz to the original Kinoshita-Scherr form) and finds that the leading

$1/z$ residuum term is

$$\left(-\frac{1}{2}+4C_{1,1,0}\right)\frac{1}{z}=0$$

i.e., $C_{1,1,0}=1/8$. We would then have

$$C_{2,1,0}=\frac{1}{16}$$

from Equation (11.1).

When one looks at the very next term in $1/z$, one has

$$\frac{x}{z}\left(-\frac{C_{1,0,0}}{2}+4C_{2,1,0}\right)=0 \qquad (11.2)$$

$$C_{2,1,0}=0$$

which is impossible given the above (always assuming $A=1/2$).

We have obtained

$$C_{2,1,0}=0=\frac{1}{16}$$

a clear contradiction.

XII. DISCUSSION

This argument parallels the original Bartlett [3] and therefore appears as valid as his original argument. This argument has nothing to do with boundary conditions, but relies solely on the cascading determination of determinable coëfficients.

One expects two sets of coëfficients emerging during the standard series method of solution for this differential equation. One set should be completely determinable algorithmically from recurrence relations, the other determinable after application of boundary conditions. Given that we have shown that the first set is self-contradictory, it is clear that there is something terribly wrong with the initial Ansatz.

Kinoshita was aware of the need for a logarithmic term in the wave function, which he dismissed (see footnote 14 in Reference 1). He was further aware of the fact that improper ordering of solving for coëfficients in the wave function expansion could lead to ambiguities (see Appendix B, reference 1, last paragraph). Kinoshita declared that he had obtained formal solutions to the Schrödinger Equation. We here show that the modified Kinoshita-Scherr Ansatz is not a formal solution of the Bartlett form of the Schrödinger Equation for this problem. Therefore, there is no reason to believe that the variationally determined coëfficients of Kinoshita-like expansions will converge onto the "true" coëfficients (which should have been obtainable through the recurrence relations).

It appears that the Fock form of the Helium wave function remains the only known form which unambiguously allows coëfficient determination.

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