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The Hamiltonian and Schrodinger Equation for Helium's Electrons (Hylleraas)

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I. INTRODUCTION

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

$$-\frac{\hbar^2}{2m}\left(\nabla_1^2+\nabla_2^2\right)\psi-\frac{Ze^2}{r_1}\psi-\frac{Ze^2}{r_2}\psi=E\psi \qquad (1.1)$$

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

$$\nabla_1=\frac{\partial^2}{\partial x_1^2}+\frac{\partial^2}{\partial y_1^2}+\frac{\partial^2}{\partial z_1^2}$$

where the subscript "1" means we are refering to electron 1 (we have a similar expression for electron 2).

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

$$-\left(\nabla_1^2+\nabla_2^2\right)\psi-\frac{2m}{\hbar^2}\frac{Ze^2}{r_1}\psi-\frac{2m}{\hbar^2}\frac{Ze^2}{r_2}\psi=E\frac{2m}{\hbar^2}\psi \qquad (1.2)$$

which is the form most people start with.

II. THE HAMILTONIAN

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

$$H_{op}=-\frac{\hbar^2}{2m}\left(\nabla_1^2+\nabla_2^2\right)-\frac{Ze^2}{r_1}-\frac{Ze^2}{r_2}+\frac{e^2}{r_{12}} \qquad (2.1)$$

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:

$$\nabla_1=\frac{\partial^2}{\partial x_1^2}+\frac{\partial^2}{\partial y_1^2}+\frac{\partial^2}{\partial z_1^2}$$

with a second almost identical term for electron 2's kinetic energy operator.

That means that we need to obtain

$$\left(\frac{\partial}{\partial x_1}\right)_{y_1,z_1,x_2,y_2,z_2}$$

Typeset by REVTEX

(remember, we are holding all the other $\{x_i\}$ constant) for electron 1 and electron 2, with equivalent terms for y and z (two each) as a function or r_1, r_2 and ϑ, the angle between the location vectors of the two electrons, $\vec{r_1}$ and $\vec{r_2}$.

III. THE COORDINATE TRANSFORMATION

. Remember that

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

and

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

while, of course,

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

A. Preliminary Partial Derivatives

We need, according to the chain rule, the following terms:

$$\frac{\partial}{\partial x_1}=\frac{\partial r_1}{\partial x_1}\frac{\partial}{\partial r_1}+\frac{\partial y}{\partial x_1}\frac{\partial}{\partial \mu} \qquad (3.1)$$

so, focussing on the first of these, we ask, what is $\frac{\partial r_1}{\partial x_1}$?

We have

$$\frac{\partial r_1}{\partial x_1}=\frac{\partial\sqrt{x_1^2+y_1^2+z_1^2}}{\partial x_1}=\frac{1}{2}r_1^{-1}\frac{\partial\left(x_1^2+y_1^2+z_1^2\right)}{\partial x_1}=\frac{x_1}{r_1} \qquad (3.2)$$

Parenthetically,

$$\frac{\partial r_1^{-1}}{\partial x_1}=\frac{-1}{r_1^2}\frac{\partial r_1}{\partial x_1}=-\frac{x_1}{r_1^3} \qquad (3.3)$$

Then, we have

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

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

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

For the second term in Equation 3.1 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

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

while from vector algebra we know

$$\cos\vartheta = \frac{\vec{r}_1 \cdot \vec{r}_2}{r_1r_2}$$

(An alternative formulation for this vector algebraic statement is:

$$\cos\vartheta = \frac{\vec{r}_1 \cdot \vec{r}_2}{r_1r_2} = \frac{x_1x_2 + y_1y_2 + z_1z_2}{r_1r_2} \equiv \mu \tag{3.4}$$

which defines $\mu = cos\vartheta$.

Since

$$\frac{\partial\mu}{\partial x_1} = \frac{\partial\left(\frac{x_1x_2+y_1y_2+z_1z_2}{r_1r_2}\right)}{\partial x_1}$$

gives us (using Equations 3.2 and 3.3)

$$= \frac{x_2}{r_1r_2} + \frac{x_1x_2 + y_1y_2 + z_1z_2}{r_2}\frac{\partial r_1^{-1}}{\partial x_1}$$

$$= \frac{x_2}{r_1r_2} - \left(\frac{x_1x_2 + y_1y_2 + z_1z_2}{r_2}\right)\frac{x_1}{r_1^3}$$

$$= \frac{x_2}{r_1r_2} - \frac{\vec{r_1} \cdot \vec{r_2}}{r_2}\frac{x_1}{r_1^3}$$

$$\frac{\partial\mu}{\partial x_1} = \frac{x_2}{r_1r_2} - \frac{r_1r_2\mu}{r_2}\frac{x_1}{r_1^3} \tag{3.5}$$

Clearly, the other five groups of terms are equivalent.

$$\frac{\partial\mu}{\partial y_1} = \frac{y_2}{r_1r_2} - \frac{r_1r_2\mu}{r_2}\frac{y_1}{r_1^3} \tag{3.6}$$

$$\frac{\partial\mu}{\partial z_1} = \frac{z_2}{r_1r_2} - \frac{r_1r_2\mu}{r_2}\frac{z_1}{r_1^3} \tag{3.7}$$

$$\frac{\partial\mu}{\partial x_2} = \frac{x_1}{r_1r_2} - \frac{r_1r_2\mu}{r_1}\frac{x_2}{r_2^3} \tag{3.8}$$

$$\frac{\partial\mu}{\partial y_2} = \frac{y_1}{r_1r_2} - \frac{r_1r_2\mu}{r_1}\frac{y_2}{r_2^3} \tag{3.9}$$

$$\frac{\partial\mu}{\partial z_2} = \frac{z_1}{r_1r_2} - \frac{r_1r_2\mu}{r_1}\frac{z_2}{r_2^3} \tag{3.10}$$

Now, using the chain rule, we have

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

and the two multiplicative partial derivatives are known. Using Equation 3.5and Equation 3.4 we have

$$\frac{\partial}{\partial x_1} = \frac{x_1}{r_1}\frac{\partial}{\partial r_1} + \left(\frac{x_2}{r_1r_2} - \frac{\vec{r}_1 \cdot \vec{r}_2x_1}{r_1^3r_2}\right)\frac{\partial}{\partial y}$$

which is

$$\frac{\partial}{\partial x_1} = \frac{x_1}{r_1}\frac{\partial}{\partial r_1} + \left(\frac{x_2}{r_1r_2} - \frac{x_1\mu}{r_1^2}\right)\frac{\partial}{\partial y}$$

B. Second Partial Derivatives

The second derivative would be

$$\frac{\partial^2}{\partial x_1^2} = \frac{\partial\left(\frac{x_1}{r_1}\frac{\partial}{\partial r_1} + \left(\frac{x_2}{r_1r_2} - \frac{x_1\mu}{r_1^2}\right)\frac{\partial}{\partial\mu}\right)}{\partial x_1}$$

which would be

$$\frac{\partial^2}{\partial x_1^2} = \frac{\partial\left(\frac{x_1}{r_1}\frac{\partial}{\partial r_1}\right)}{\partial x_1} + \frac{\partial\left(\left(\frac{x_2}{r_1r_2} - \frac{x_1\mu}{r_1^2}\right)\frac{\partial}{\partial\mu}\right)}{\partial x_1}$$

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 $\frac{\partial}{\partial\mu}$. We obtain

$$\frac{\partial^2}{\partial x_1^2} = \frac{1}{r_1}\frac{\partial}{\partial r_1} + x_1\frac{\partial\left(\frac{1}{r_1}\frac{\partial}{\partial r_1}\right)}{\partial x_1} \tag{3.11}$$

$$+\frac{\partial\left(\left(\frac{x_2}{r_1r_2}\right)\frac{\partial}{\partial\mu}\right)}{\partial x_1} \tag{3.12}$$

$$-\left(\frac{\mu}{r_1^2}\right)\frac{\partial}{\partial\mu} \tag{3.13}$$

$$-x_1\frac{\partial\left(\left(\frac{\mu}{r_1^2}\right)\frac{\partial}{\partial\mu}\right)}{\partial x_1} \tag{3.14}$$

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

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

$$Equation-3.11 \rightarrow \frac{1}{r_1}\frac{\partial}{\partial r_1} + x_1\frac{\partial r_1^{-1}}{\partial x_1}\frac{\partial}{\partial r_1} + \frac{x_1}{r_1}\frac{\partial^2}{\partial x_1 \partial r_1} \rightarrow \frac{1}{r_1}\frac{\partial}{\partial r_1} + x_1\left(\frac{-x_1}{r_1^3}\right)\frac{\partial}{\partial r_1} + \frac{x_1}{r_1}\frac{\partial^2}{\partial x_1 \partial r_1} \tag{3.15}$$

$$Equation-3.12 \rightarrow +\frac{\partial\left(\left(\frac{x_2}{r_1 r_2}\right)\frac{\partial}{\partial \mu}\right)}{\partial x_1} \rightarrow +\frac{x_2}{r_2}\frac{\partial r_1^{-1}}{\partial x_1}\frac{\partial}{\partial \mu} + \frac{x_2}{r_1 r_2}\frac{\partial^2}{\partial x_1 \partial \mu} \tag{3.16}$$

$$Equation-3.13 \ \rightarrow -\left(\frac{\mu}{r_1^2}\right)\frac{\partial}{\partial \mu} \tag{3.17}$$

$$Equation-3.14 \ -x_1\frac{\partial\left(\left(\frac{\mu}{r_1^2}\right)\frac{\partial}{\partial \mu}\right)}{\partial x_1} \rightarrow -x_1\mu\left(\frac{\partial r_1^{-2}}{\partial x_1}\right)\frac{\partial}{\partial \mu} - \frac{x_1}{r_1^2}\left(\frac{\partial \mu}{\partial x_1}\right)\frac{\partial}{\partial \mu} - \left(\frac{x_1\mu}{r_1^2}\right)\frac{\partial^2}{\partial x_1 \partial \mu} \tag{3.18}$$

which is

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

$$Equation-3.15 \rightarrow \frac{1}{r_1}\frac{\partial}{\partial r_1} + \left(\frac{-x_1^2}{r_1^3}\right)\frac{\partial}{\partial r_1} + \frac{x_1}{r_1}\left(\frac{x_1}{r_1}\frac{\partial}{\partial r_1} + \left(\frac{x_2}{r_1 r_2} - \frac{x_1\mu}{r_1^2}\right)\frac{\partial}{\partial \mu}\right)\frac{\partial}{\partial r_1} \tag{3.19}$$

$$Equation-3.16 \rightarrow -\frac{x_2}{r_2}\frac{x_1}{r_1^3}\frac{\partial}{\partial \mu} + \frac{x_2}{r_1 r_2}\left(\frac{x_1}{r_1}\frac{\partial}{\partial r_1} + \left(\frac{x_2}{r_1 r_2} - \frac{x_1\mu}{r_1^2}\right)\frac{\partial}{\partial \mu}\right)\frac{\partial}{\partial \mu} \tag{3.20}$$

$$Equation-3.17 \rightarrow -\frac{\mu}{r_1^2}\frac{\partial}{\partial \mu} \tag{3.21}$$

$$Equation-3.18 \rightarrow -x_1\mu\frac{\partial r_1^{-2}}{\partial x_1}\frac{\partial}{\partial \mu} - \frac{x_1}{r_1^2}\left(\frac{x_2}{r_1 r_2} - \frac{x_1(\vec{r}_1\cdot\vec{r}_2)}{r_1^3 r_2}\right)\frac{\partial}{\partial \mu} \tag{3.22}$$

$$Equation-3.18 \rightarrow -\frac{x_1\mu}{r_1^2}\left\{\frac{x_1}{r_1}\frac{\partial}{\partial r_1} + \left(\frac{x_2}{r_1 r_2} - \frac{x_1\mu}{r_1^2}\right)\frac{\partial}{\partial \mu}\right\}\frac{\partial}{\partial \mu} \tag{3.23}$$

which is, upon cleaning up the expressions

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

$$Equation-3.19 \rightarrow \frac{1}{r_1}\frac{\partial}{\partial r_1} - \frac{x_1^2}{r_1^3}\frac{\partial}{\partial r_1} + \frac{x_1^2}{r_1^2}\frac{\partial^2}{\partial r_1^2} + \frac{x_1}{r_1}\left(\frac{x_2}{r_1 r_2} - \frac{x_1\mu}{r_1^2}\right)\frac{\partial^2}{\partial r_1 \partial \mu} \tag{3.24}$$

$$Equation-3.20 \rightarrow \ -\frac{x_2}{r_2}\frac{x_1}{r_1^3}\frac{\partial}{\partial \mu} + \frac{x_2 x_1}{r_1^2 r_2}\frac{\partial^2}{\partial r_1 \partial \mu} + \left(\frac{x_2}{r_1 r_2}\left(\frac{x_2}{r_1 r_2} - \frac{x_1\mu}{r_1^2}\right)\frac{\partial}{\partial \mu}\right)\frac{\partial}{\partial \mu} \tag{3.25}$$

$$Equation 3.21 \rightarrow \ -\frac{\mu}{r_1^2}\frac{\partial}{\partial \mu} \tag{3.26}$$

$$Equation-3.22 \rightarrow \ -x_1\mu\left(\frac{-2x_1}{r_1^4}\right)\frac{\partial}{\partial \mu} - \left(\frac{x_1 x_2}{r_1^3 r_2} - x_1^2\frac{\vec{r}_1\cdot\vec{r}_2}{r_1^5 r_2}\right)\frac{\partial}{\partial \mu} \tag{3.27}$$

$$Equation 3.23 \rightarrow -\frac{x_1\mu}{r_1^2}\left(\frac{x_1}{r_1}\frac{\partial^2}{\partial r_1 \partial \mu}\right) - \frac{x_1\mu}{r_1^2}\left(\frac{x_2}{r_1 r_2} - \frac{x_1\mu}{r_1^2}\right)\frac{\partial^2}{\partial \mu^2} \tag{3.28}$$

and, cleaning up again, we have

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

$$Equation-3.24 \rightarrow \frac{1}{r_1}\frac{\partial}{\partial r_1} - \frac{x_1^2}{r_1^3}\frac{\partial}{\partial r_1} + \frac{x_1^2}{r_1^2}\frac{\partial^2}{\partial r_1^2} + \frac{x_1}{r_1}\left(\frac{x_2}{r_1 r_2} - \frac{x_1\mu}{r_1^2}\right)\frac{\partial^2}{\partial r_1 \partial\mu} \tag{3.29}$$

$$Equation-3.25 \rightarrow \; -\frac{x_2}{r_2}\frac{x_1}{r_1^3}\frac{\partial}{\partial\mu} + \frac{x_2 x_1}{r_1^2 r_2}\frac{\partial^2}{\partial r_1\partial\mu} + \left(\frac{x_2}{r_1 r_2}\left(\frac{x_2}{r_1 r_2} - \frac{x_1\mu}{r_1^2}\right)\right)\frac{\partial^2}{\partial\mu^2} \tag{3.30}$$

$$Equation 3.26 \rightarrow \; -\frac{\mu}{r_1^2}\frac{\partial}{\partial\mu} \tag{3.31}$$

$$Equation-3.27 \rightarrow \; +\left(\frac{2x_1^2\mu}{r_1^4}\right)\frac{\partial}{\partial\mu} - \frac{x_1 x_2}{r_1^3 r_2}\frac{\partial}{\partial\mu} \tag{3.32}$$

$$Equation-3.27 \rightarrow \; +x_1^2\frac{\vec{r_1}\cdot\vec{r_2}}{r_1^5 r_2}\frac{\partial}{\partial\mu} \tag{3.33}$$

$$Equation 3.28 \rightarrow -\left(\frac{x_1^2\mu}{r_1^3}\frac{\partial^2}{\partial r_1\partial\mu}\right) - \frac{x_1\mu x_2}{r_1^3 r_2}\frac{\partial^2}{\partial\mu^2} + \frac{x_1^2\mu^2}{r_1^4}\frac{\partial^2}{\partial\mu^2} \tag{3.34}$$

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

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

$$Equation-3.29 \rightarrow \frac{3}{r_1}\frac{\partial}{\partial r_1} - \frac{r_1^2}{r_1^3}\frac{\partial}{\partial r_1} + \frac{r_1^2}{r_1^2}\frac{\partial^2}{\partial r_1^2} +$$

$$\frac{x_1x_2 + y_1y_2 + z_1z_2}{r_1^2 r_2}\frac{\partial^2}{\partial r_1\partial\mu} - \frac{(x_1^2 + y_1^2 + z_1^2)\mu}{r_1^3}\frac{\partial^2}{\partial r_1\partial\mu}$$

$$Equation-3.29 \rightarrow \frac{3}{r_2}\frac{\partial}{\partial r_2} - \frac{r_2^2}{r_2^3}\frac{\partial}{\partial r_2} + \frac{r_2^2}{r_2^2}\frac{\partial^2}{\partial r_2^2} +$$

$$\frac{x_1x_2 + y_1y_2 + z_1z_2}{r_2^2 r_1}\frac{\partial^2}{\partial r_2\partial\mu} - \frac{(x_2^2 + y_2^2 + z_2^2)\mu}{r_2^2 r_1}\frac{\partial^2}{\partial r_2\partial\mu}$$

$$Equation-3.30 \rightarrow -\frac{x_1x_2 + y_1y_2 + z_1z_2}{r_1^3 r_2}\frac{\partial}{\partial\mu} + \frac{r_2 r_1\mu}{r_1^2 r_2}\frac{\partial^2}{\partial r_1\partial\mu} +$$

$$\left(\frac{r_2^2}{r_1^2 r_2^2} - \frac{(x_1x_2 + y_1y_2 + z_1z_2)\mu}{r_1^3 r_2}\right)\frac{\partial^2}{\partial\mu^2}$$

$$Equation-3.30 \rightarrow -\frac{x_2x_1 + y_1y_2 + z_1z_2}{r_2^3 r_1}\frac{\partial}{\partial\mu} + \frac{(x_2x_1 + y_1y_2 + z_1z_2)}{r_2^2 r_1}\frac{\partial^2}{\partial r_2\partial\mu} + \left(\frac{r_1^2}{r_2^2 r_1^2} - \frac{r_1 r_2 y^2}{r_2^3 r_1}\right)\frac{\partial^2}{\partial\mu^2}$$

$$Equation-3.31 \rightarrow -\frac{3\mu}{r_2^2}\frac{\partial}{\partial\mu} - \frac{3\mu}{r_1^2}\frac{\partial}{\partial\mu} - \frac{3\mu}{r_2^2}\frac{\partial}{\partial\mu} - \frac{3\mu}{r_1^2}\frac{\partial}{\partial\mu}$$

$$Equation-3.32 \rightarrow +\left(\frac{2r_1^2\mu}{r_1^3}\right)\frac{\partial}{\partial\mu} + \left(\frac{2r_2^2\mu}{r_2^3}\right)\frac{\partial}{\partial\mu}$$

$$Equation-3.32 \rightarrow -\frac{\vec{r_1}\cdot\vec{r_2}}{r_1^3 r_2}\frac{\partial}{\partial\mu} + \frac{\vec{r_1}\cdot\vec{r_2}}{r_2^3 r_1}\frac{\partial}{\partial\mu}$$

$$Equation-3.33 \rightarrow -\frac{\vec{r_2}\cdot\vec{r_1}}{r_2^3 r_1}\frac{\partial}{\partial\mu} + \frac{\vec{r_2}\cdot\vec{r_1}}{r_2^3 r_1}\frac{\partial}{\partial\mu}$$

$$Equation-3.34 \rightarrow -\left(\frac{r_1^2\mu}{r_1^3}\frac{\partial^2}{\partial r_1\partial\mu}\right) - \frac{\vec{r_1}\cdot\vec{r_2}\mu}{r_1^3 r_2}\frac{\partial^2}{\partial\mu^2} + \frac{\mu^2}{r_1^2}\frac{\partial^2}{\partial\mu^2}$$

$$Equation-3.34 \rightarrow -\left(\frac{r_2^2\mu}{r_2^3}\frac{\partial^2}{\partial r_2\partial\mu}\right) - \frac{\vec{r_1}\cdot\vec{r_2}\mu}{r_1 r_2^3}\frac{\partial^2}{\partial\mu^2} + \frac{\mu^2}{r_2^2}\frac{\partial^2}{\partial\mu^2}$$

The term $x_1x_2 + y_1y_2 + z_1z_2$ is just $r_1r_2\mu$, yields the gorgeous cancellations (see above) leading to which becomes

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

$$Equation-3.35 \rightarrow \frac{2}{r_1}\frac{\partial}{\partial r_1}+\frac{\partial^2}{\partial r_1^2} \tag{3.35}$$

$$Equation-3.35 \rightarrow +\frac{r_1 r_2 \mu}{r_1^2 r_2}\frac{\partial^2}{\partial r_1 \partial \mu}-\frac{\mu}{r_1}\frac{\partial^2}{\partial r_1 \partial \mu}=0 \tag{3.36}$$

$$Equation-3.35 \rightarrow \frac{2}{r_2}\frac{\partial}{\partial r_2}+\frac{\partial^2}{\partial r_2^2} \tag{3.37}$$

$$Equation-3.35 \rightarrow +\frac{r_1 r_2 \mu}{r_2^2 r_1}\frac{\partial^2}{\partial r_2 \partial \mu}-\frac{\mu}{r_2}\frac{\partial^2}{\partial r_2 \partial \mu}=0 \tag{3.38}$$

$$Equation-3.35 \rightarrow -\frac{r_1 r_2 \mu}{r_1^3 r_2}\frac{\partial}{\partial \mu}+\frac{\mu}{r_1}\frac{\partial^2}{\partial r_1 \partial \mu}+\left(\frac{1}{r_1^2}-\frac{r_1 r_2 \mu^2}{r_1^3 r_2}\right)\frac{\partial^2}{\partial \mu^2} \tag{3.39}$$

$$Equation-3.35 \rightarrow -\frac{r_2 r_1 \mu}{r_2^3 r_1}\frac{\partial}{\partial \mu}+\frac{r_2 r_1 \mu}{r_2^2 r_1}\frac{\partial^2}{\partial r_2 \partial \mu}+\left(\frac{1}{r_2^2}-\frac{r_1 r_2 \mu^2}{r_2^3 r_1}\right)\frac{\partial^2}{\partial \mu^2} \tag{3.40}$$

$$Equation-3.35 \rightarrow -\frac{3\mu}{r_2^2}\frac{\partial}{\partial \mu}-\frac{3\mu}{r_1^2}\frac{\partial}{\partial \mu} \tag{3.41}$$

$$Equation-3.35 \rightarrow +\left(\frac{2\mu}{r_1^2}\right)\frac{\partial}{\partial \mu}+\left(\frac{2\mu}{r_2^2}\right)\frac{\partial}{\partial \mu} \tag{3.42}$$

$$Equation-3.35 \rightarrow -\frac{\mu}{r_1^2}\frac{\partial}{\partial \mu}+\frac{\mu}{r_1^2}\frac{\partial}{\partial \mu}-\frac{\mu}{r_2^2}\frac{\partial}{\partial \mu}+\frac{\mu}{r_2^2}\frac{\partial}{\partial \mu}=0 \tag{3.43}$$

$$Equation-3.35 \rightarrow -\left(\frac{\mu}{r_1}\frac{\partial^2}{\partial r_1 \partial \mu}\right) \tag{3.44}$$

$$Equation-3.35 \rightarrow -\left(\frac{\mu}{r_2}\frac{\partial^2}{\partial r_1 \partial \mu}\right) \tag{3.45}$$

We obtain

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

$$Equation-3.35 \rightarrow \frac{2}{r_1}\frac{\partial}{\partial r_1}+\frac{\partial^2}{\partial r_1^2} \tag{3.46}$$

$$Equation-3.37 \rightarrow \frac{2}{r_2}\frac{\partial}{\partial r_2}+\frac{\partial^2}{\partial r_2^2} \tag{3.47}$$

$$Equation-3.39 \rightarrow -\frac{\mu}{r_1^2}\frac{\partial}{\partial \mu}+\underbrace{\frac{\mu}{r_1}\frac{\partial^2}{\partial r_1 \partial \mu}}+\left(\frac{1}{r_1^2}-\frac{\mu^2}{r_1^2}\right)\frac{\partial^2}{\partial \mu^2} \tag{3.48}$$

$$Equation-3.40 \rightarrow -\frac{\mu}{r_2^2}\frac{\partial}{\partial \mu}+\underbrace{\frac{\mu}{r_2}\frac{\partial^2}{\partial r_2 \partial \mu}}+\left(\frac{1}{r_2^2}-\frac{\mu^2}{r_2^2}\right)\frac{\partial^2}{\partial \mu^2}=0 \tag{3.49}$$

$$Equation-3.41 \rightarrow -\frac{3\mu}{r_2^2}\frac{\partial}{\partial \mu}-\frac{3\mu}{r_1^2}\frac{\partial}{\partial \mu} \tag{3.50}$$

$$Equation-3.42 \rightarrow \ +\left(\frac{2\mu}{r_1^2}\right)\frac{\partial}{\partial \mu}+\left(\frac{2\mu}{r_2^2}\right)\frac{\partial}{\partial \mu} \tag{3.51}$$

$$Equation-3.44 \rightarrow -\underbrace{\left(\frac{\mu}{r_1}\frac{\partial^2}{\partial r_1 \partial \mu}\right)} \tag{3.52}$$

$$Equation-3.45 \rightarrow -\underbrace{\left(\frac{\mu}{r_2}\frac{\partial^2}{\partial r_1 \partial \mu}\right)} \tag{3.53}$$

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

C. Final Cancellations

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

$$Equation-3.46 \rightarrow \frac{2}{r_1}\frac{\partial}{\partial r_1}+\frac{\partial^2}{\partial r_1^2} \tag{3.54}$$

$$Equation-3.47 \rightarrow \frac{2}{r_2}\frac{\partial}{\partial r_2} + \frac{\partial^2}{\partial r_2^2} \quad (3.55)$$

$$Equation-3.48 \rightarrow -\frac{\mu}{r_1^2}\frac{\partial}{\partial\mu} + \left(\frac{1-\mu^2}{r_1^2}\right)\frac{\partial^2}{\partial\mu^2} \quad (3.56)$$

$$Equation-3.49 \rightarrow -\frac{\mu}{r_2^2}\frac{\partial}{\partial\mu} + \left(\frac{1-\mu^2}{r_2^2}\right)\frac{\partial^2}{\partial\mu^2} \quad (3.57)$$

$$Equation-3.50 \rightarrow -\frac{3\mu}{r_2^2}\frac{\partial}{\partial\mu} - \frac{3\mu}{r_1^2}\frac{\partial}{\partial\mu} \quad (3.58)$$

$$+\left(\frac{2\mu}{r_1^2}\right)\frac{\partial}{\partial\mu} + \left(\frac{2\mu}{r_2^2}\right)\frac{\partial}{\partial\mu} \quad (3.59)$$

which finally, and we mean that(!) is

$$\frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial y_1^2} + \frac{\partial^2}{\partial z_1^2} + \frac{\partial^2}{\partial x_2^2} + \frac{\partial^2}{\partial y_2^2} + \frac{\partial^2}{\partial z_2^2} =$$
$$\frac{2}{r_1}\frac{\partial}{\partial r_1} + \frac{\partial^2}{\partial r_1^2} + \frac{2}{r_2}\frac{\partial}{\partial r_2} + \frac{\partial^2}{\partial r_2^2} - \left(\frac{1}{r_1^2}+\frac{1}{r_2^2}\right)2\mu\frac{\partial}{\partial\mu} + \left(\frac{1}{r_1^2}+\frac{1}{r_2^2}\right)(1-\mu^2)\frac{\partial^2}{\partial\mu^2} \quad (3.60)$$

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

$$\frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial y_1^2} + \frac{\partial^2}{\partial z_1^2} + \frac{\partial^2}{\partial x_2^2} + \frac{\partial^2}{\partial y_2^2} + \frac{\partial^2}{\partial z_2^2} =$$
$$\frac{1}{r_1^2}\frac{\partial\left(r_1^2\frac{\partial}{\partial r_1}\right)}{\partial r_1} + \frac{1}{r_2^2}\frac{\partial\left(r_2^2\frac{\partial}{\partial r_2}\right)}{\partial r_2} + \left(\frac{1}{r_1^2}+\frac{1}{r_2^2}\right)\frac{\partial\left((1-\mu^2)\frac{\partial}{\partial\mu}\right)}{\partial\mu} \quad (3.61)$$

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

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

We had the following expression for the Kinetic Energy Operator:

$$\frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial y_1^2} + \frac{\partial^2}{\partial z_1^2} + \frac{\partial^2}{\partial x_2^2} + \frac{\partial^2}{\partial y_2^2} + \frac{\partial^2}{\partial z_2^2} =$$
$$\nabla_1^2 + \nabla_2^2 =$$
$$\frac{1}{r_1^2}\frac{\partial\frac{r_1^2\partial}{\partial r_1}}{\partial r_1} + \frac{1}{r_2^2}\frac{\partial\frac{r_2^2\partial}{\partial r_2}}{\partial r_2} - \left(\frac{1}{r_1^2}+\frac{1}{r_2^2}\right)\frac{\partial(1-\mu^2)\frac{\partial}{\partial\mu}}{\partial\mu} \quad (4.1)$$

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. $\frac{1}{2\mu}(\nabla_1^2+\nabla_2^2)$

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 $2r_1dr_1 = 2x_1dx_1$. We have

$$\frac{\partial^2}{\partial x_1^2} = \frac{\partial\frac{\partial}{\partial x_1}}{\partial x_1} \quad (4.2)$$

$$\frac{\partial^2}{\partial x_1^2} = \frac{\partial\left(\frac{x_1}{r_1}\frac{\partial}{\partial r_1} + \frac{x_1-x_2}{r_{12}}\frac{\partial}{\partial r_{12}}\right)}{\partial x_1} \quad (4.3)$$

which is

$$\frac{\partial^2}{\partial x_1^2} = \frac{\partial\frac{x_1}{r_1}\frac{\partial}{\partial r_1}}{\partial x_1} + \frac{\partial\frac{x_1-x_2}{r_{12}}\frac{\partial}{\partial r_{12}}}{\partial x_1} \quad (4.4)$$

which becomes

$$\frac{1}{r_1}\frac{\partial}{\partial r_1} + x_1\frac{\partial r_1^{-1}}{\partial x_1}\frac{\partial}{\partial r_1} + \frac{x_1}{r_1}\frac{\partial^2}{\partial x_1\partial r_1} \quad (4.5)$$

$$+\frac{1}{r_{12}}\frac{\partial}{\partial r_{12}} + (x_1-x_2)\frac{\partial r_{12}^{-1}}{\partial x_1}\frac{\partial}{\partial r_{12}} + \frac{x_1-x_2}{r_{12}}\frac{\partial^2}{\partial x_1\partial r_{12}} \quad (4.6)$$

which is seen to be

$$\textit{Equation 4.5} \to \frac{1}{r_1}\frac{\partial}{\partial r_1} - x_1\frac{x_1}{r_1^3}\frac{\partial}{\partial r_1} + \frac{x_1}{r_1}\left(\frac{x_1}{r_1}\frac{\partial\frac{\partial}{\partial r_1}}{\partial r_1} + \frac{x_1-x_2}{r_{12}}\frac{\partial\frac{\partial}{\partial r_1}}{\partial r_{12}}\right) \tag{4.7}$$

$$\textit{Equation 4.6} \to +\frac{1}{r_{12}}\frac{\partial}{\partial r_{12}} - (x_1-x_2)\frac{(x_1-x_2)}{r_{12}^3}\frac{\partial}{\partial r_{12}} + \frac{x_1-x_2}{r_{12}}\left(\frac{x_1}{r_1}\frac{\partial\frac{\partial}{\partial r_{12}}}{\partial r_1} + \frac{x_1-x_2}{r_{12}}\frac{\partial\frac{\partial}{\partial r_{12}}}{\partial r_{12}}\right) \tag{4.8}$$

and this becomes

$$\textit{Equation IV} \to \frac{1}{r_1}\frac{\partial}{\partial r_1} - \frac{x_1^2}{r_1^3}\frac{\partial}{\partial r_1} \to \frac{3}{r_1}\frac{\partial}{\partial r_1} - \frac{1}{r_1}\frac{\partial}{\partial r_1} \to \frac{2}{r_1}\frac{\partial}{\partial r_1} \tag{4.9}$$

$$+\textit{Equation IV} \to \frac{x_1^2}{r_1^2}\frac{\partial^2}{\partial r_1^2} \to \frac{\partial^2}{\partial r_1^2} \tag{4.10}$$

$$\textit{Equation IV} \to +\frac{x_1(x_1-x_2)}{r_1 r_{12}}\frac{\partial\frac{\partial}{\partial r_1}}{\partial r_{12}} \to \frac{\vec{r_1}\cdot\vec{r_{12}}}{r_1 r_{12}}\frac{\partial^2}{\partial r_1^2 \partial r_{12}} \tag{4.11}$$

$$\textit{Equation 4.8} \to +\frac{1}{r_{12}}\frac{\partial}{\partial r_{12}} - \frac{(x_1-x_2)^2}{r_{12}^3}\frac{\partial}{\partial r_{12}} \to \left(\frac{3}{r_{12}} - \frac{1}{r_{12}}\right)\frac{\partial}{\partial r_{12}} \to +\frac{2}{r_{12}}\frac{\partial}{\partial r_{12}} \tag{4.12}$$

$$\textit{Equation 4.8} \to +\frac{x_1(x_1-x_2)}{r_1 r_{12}}\frac{\partial^2}{\partial r_{12}\partial r_1} \to \frac{\vec{r_1}\cdot\vec{r_{12}}}{r_1 r_{12}}\frac{\partial^2}{\partial r_1 \partial r_{12}} \tag{4.13}$$

$$+\textit{Equation 4.8} \to \frac{r_{12}^2}{r_{12}^2}\frac{\partial^2}{\partial r_{12}^2} \to \frac{\partial^2}{\partial r_{12}^2} \tag{4.14}$$

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

$$\begin{aligned} \nabla_1^2 + \nabla_2^2 = \\ \frac{\partial^2}{\partial r_1^2} + \frac{2}{r_1}\frac{\partial}{\partial r_1} + 2\hat{r_1}\cdot\hat{r_{12}}\frac{\partial^2}{\partial r_1 \partial r_{12}} \\ +\frac{\partial^2}{\partial r_2^2} + \frac{2}{r_2}\frac{\partial}{\partial r_2} + 2\hat{r_2}\cdot\hat{r_{12}}\frac{\partial^2}{\partial r_2 \partial r_{12}} \\ +\frac{4}{r_{12}}\frac{\partial}{\partial r_{12}} + 2\frac{\partial^2}{\partial r_{12}^2} \end{aligned} \tag{4.15}$$

This is our result! When combined with the potential energy operator, one can easily form the Hamiltonian of this system in this representation.

V. YET ANOTHER FORMULATION

In yet another coordinate scheme (double spherical polar coordinates) we have:

$$\begin{aligned} = -\frac{\hbar^2}{2m}\left(\frac{1}{r_1^2}\frac{\partial r_1^2\frac{\partial}{\partial r_1}}{\partial r_1} + \frac{1}{\sin^2\vartheta_1}\left(\sin\vartheta_1\frac{\partial\sin\vartheta_1\frac{\partial}{\partial\vartheta_1}}{\partial\vartheta_1} + \frac{\partial^2}{\partial\phi_1^2}\right)\right. \\ \left. + \frac{1}{r_2^2}\frac{\partial r_2^2\frac{\partial}{\partial r_2}}{\partial r_2} + \frac{1}{\sin^2\vartheta_2}\left(\sin\vartheta_2\frac{\partial\sin\vartheta_2\frac{\partial}{\partial\vartheta_2}}{\partial\vartheta_2} + \frac{\partial^2}{\partial\phi_2^2}\right)\right) \\ -\frac{Ze^2}{r_1} - \frac{Ze^2}{r_2} + \frac{e^2}{r_{12}} \end{aligned} \tag{5.1}$$

and again, in another set of mixed coordinates,

$$= -\frac{\hbar^2}{2m}\left(\frac{1}{r_1^2}\frac{\partial r_1^2\frac{\partial}{\partial r_1}}{\partial r_1} + \frac{1}{\sin^2\vartheta_1}\left(\sin\vartheta_1\frac{\partial\sin\vartheta_1\frac{\partial}{\partial\vartheta_1}}{\partial\vartheta_1} + \frac{\partial^2}{\partial\phi_1^2}\right)\right.$$
$$\left.+\frac{1}{r_2^2}\frac{\partial r_2^2\frac{\partial}{\partial r_2}}{\partial r_2} + \frac{1}{\sin^2\vartheta_2}\left(\sin\vartheta_2\frac{\partial\sin\vartheta_2\frac{\partial}{\partial\vartheta_2}}{\partial\vartheta_2} + \frac{\partial^2}{\partial\phi_2^2}\right)\right)$$
$$-\frac{Ze^2}{r_1} - \frac{Ze^2}{r_2} + \frac{e^2}{\sqrt{r_1^2 + r_2^2 - 2r_1r_2\cos\vartheta_{12}}} \tag{5.2}$$

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

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

so, we have

$$r_1\sin\vartheta_1\cos\phi_1 r_2\sin\vartheta_2\cos\phi_2 + r_1\sin\vartheta_1\sin\phi_1 r_2\sin\vartheta_2\sin\phi_2 + r_1r_2\cos\vartheta_1\cos\vartheta_2 = r_1r_2\cos\vartheta_{12}$$

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

$$= -\frac{\hbar^2}{2m}\left(\frac{1}{r_1^2}\frac{\partial r_1^2\frac{\partial}{\partial r_1}}{\partial r_1} + \frac{1}{\sin^2\vartheta_1}\left(\sin\vartheta_1\frac{\partial\sin\vartheta_1\frac{\partial}{\partial\vartheta_1}}{\partial\vartheta_1} + \frac{\partial^2}{\partial\phi_1^2}\right)\right.$$
$$\left.+\frac{1}{r_2^2}\frac{\partial r_2^2\frac{\partial}{\partial r_2}}{\partial r_2} + \frac{1}{\sin^2\vartheta_2}\left(\sin\vartheta_2\frac{\partial\sin\vartheta_2\frac{\partial}{\partial\vartheta_2}}{\partial\vartheta_2} + \frac{\partial^2}{\partial\phi_2^2}\right)\right)$$
$$-\frac{Ze^2}{r_1} - \frac{Ze^2}{r_2} + \frac{e^2}{\sqrt{r_1^2 + r_2^2 - 2r_1r_2\left(\cos\vartheta_1\cos\vartheta_2 + \sin\vartheta_1\sin\vartheta_2\cos(\phi_1-\phi_2)\right)}} \tag{5.3}$$

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.

VI. DISCUSSION (I)

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*[1, 2], 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 [4] showed that there is no Frobenius solution to the Schrödinger equation (see also Coolidge and James [5]).

The analytical situation was clarified by Fock [6] (for the English translation, see Fock [7]) who found that introducing hyperspherical coördinates required that logarithmic terms exist in the expansion of the wave function. This result overshadowed Bartlett's similar [8] independent discovery. A review of the current situation in this field may be found in the work of Abbot and Maslen [9] as well as in the recent work of Myers et al [10]. The convergence of the Fock expansion has been investigated by [11].

As of the date of writing, the best computation of the energy of the ground electronic state of Helium is due to Schwartz [12, 13].

VII. DISCUSSION (II)

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

$$\psi = e^{-\alpha(r_1+r_2)+\beta r_{12}} \tag{7.1}$$

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

$$\nabla_6^2\psi = \frac{\partial^2\psi}{\partial x_1^2} + \frac{\partial^2\psi}{\partial y_1^2} + \frac{\partial^2\psi}{\partial z_1^2} + \frac{\partial^2\psi}{\partial x_2^2} + \frac{\partial^2\psi}{\partial y_2^2} + \frac{\partial^2\psi}{\partial z_2^2} \tag{7.2}$$

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

$$\frac{\partial^2\psi}{\partial x_1^2} = \frac{\partial^2 e^{-\alpha(r_1+r_2)+\beta r_{12}}}{\partial x_1^2} \tag{7.3}$$

substituting Equation (7.1) into Equation (7.2).

First, one has

$$\frac{\partial \frac{\partial e^{-\alpha(r_1+r_2)+\beta r_{12}}}{\partial x_1}}{\partial x_1} = \frac{\partial \left(-\alpha\frac{x_1}{r_1} + \beta\frac{x_1-x_2}{r_{12}}\right) e^{-\alpha(r_1+r_2)+\beta r_{12}}}{\partial x_1} \tag{7.4}$$

$$\frac{\partial \frac{\partial e^{-\alpha(r_1+r_2)+\beta r_{12}}}{\partial x_2}}{\partial x_2} = \frac{\partial \left(-\alpha\frac{x_2}{r_2} - \beta\frac{x_1-x_2}{r_{12}}\right) e^{-\alpha(r_1+r_2)+\beta r_{12}}}{\partial x_2} \tag{7.5}$$

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

$$\nabla_6^2\psi = \left(-\frac{3\alpha}{r_1} + \frac{\alpha}{r_1} - \frac{3\alpha}{r_2} + \frac{\alpha}{r_2} + \frac{3\beta}{r_{12}} - \frac{\beta}{r_{12}} + \alpha^2 + \beta^2 - 2\alpha\beta\left(\frac{\vec{r_1}\cdot\vec{r_{12}}}{r_1 r_{12}} - \frac{\vec{r_2}\cdot\vec{r_{12}}}{r_2 r_{12}}\right)\right)\psi \tag{7.6}$$

which is

$$\nabla_6^2\psi = \left(-\frac{2\alpha}{r_1} - \frac{2\alpha}{r_2} + \frac{2\beta}{r_{12}} + \alpha^2 + \beta^2 - 2\alpha\beta\left(\frac{\vec{r_1}\cdot\vec{r_{12}}}{r_1 r_{12}} - \frac{\vec{r_2}\cdot\vec{r_{12}}}{r_2 r_{12}}\right)\right)\psi \tag{7.7}$$

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.

$$-\frac{1}{2}\nabla_6^2\psi - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}} = \left(-\frac{Z-\alpha}{r_1} - \frac{Z-\alpha}{r_2} + \frac{1-\beta}{r_{12}} - \frac{1}{2}\left(\alpha^2+\beta^2\right) + \alpha\beta\left(\frac{\vec{r_1}\cdot\vec{r_{12}}}{r_1 r_{12}} - \frac{\vec{r_2}\cdot\vec{r_{12}}}{r_2 r_{12}}\right)\right)\psi \tag{7.8}$$

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