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Guessing Solutions to the H-atom Schrodinger Equation

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I. SYNOPSIS

Introducing Quantum Chemical methods requires an understanding of what it means to be an eigenfunction of the Hamiltonian. This reading addresses the question for the ground state (among others) of the H-atom's electron, in three coördinate systems, Cartesian, Spherical Polar, and Elliptical.

II. THE SCHRÖDINGER EQUATION

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

$$-\frac{\hbar^2}{2m}\nabla^2\psi - \frac{Ze^2}{r}\psi = E\psi \tag{2.1}$$

where m is the mass of an electron. We are going to guess solutions to this equation and develop some understanding of how it works.

III. A 1S ORBITAL

We start with

$$\psi_{guess\ 1} = e^{-\alpha r} = e^{-\alpha\sqrt{x^2+y^2+z^2}}$$

where α is a "to be determined" constant.

IV. CARTESIAN COÖRDINATE APPROACH

We re-write Equation 2.1 in its Cartesian manifestation:

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2}\right) - \frac{Ze^2}{\sqrt{x^2+y^2+z^2}}\psi = E\psi \tag{4.1}$$

so that we can "plug" $\psi_{guess\ 1}$ into Equation 4.1 and see what happens. We obtain:

$$\frac{\partial\psi_{guess\ 1}}{\partial x} = \frac{\partial e^{-\alpha\sqrt{x^2+y^2+z^2}}}{\partial x} = -\frac{\alpha(2)x\left(\frac{1}{2}\right)}{\sqrt{x^2+y^2+z^2}}e^{-\alpha\sqrt{x^2+y^2+z^2}}$$

for the first derivative and taking another partial derivative of this result we obtain

$$\begin{aligned}\frac{\partial^2\psi_{guess\ 1}}{\partial x^2} = \frac{-\alpha\frac{x}{\sqrt{x^2+y^2+z^2}}e^{-\alpha\sqrt{x^2+y^2+z^2}}}{\partial x} &= -\frac{\alpha}{\sqrt{x^2+y^2+z^2}}e^{-\alpha\sqrt{x^2+y^2+z^2}} \\ &+\frac{\alpha^2x^2}{\left(\sqrt{x^2+y^2+z^2}\right)^2}e^{-\alpha\sqrt{x^2+y^2+z^2}} \\ &+\alpha\frac{x^2}{(x^2+y^2+z^2)^{3/2}}e^{-\alpha\sqrt{x^2+y^2+z^2}}\end{aligned} \tag{4.2}$$

Now there will be two identical terms as this when we do the y- and z- second partials, with the exception that the second term will have a y^2 and a z^2 term instead of a x^2 term, so that adding them together we have:

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$$\frac{\partial^2\psi_{guess\ 1}}{\partial x^2}+\frac{\partial^2\psi_{guess\ 1}}{\partial y^2}+\frac{\partial^2\psi_{guess\ 1}}{\partial z^2}= \left(-3\frac{\alpha}{r}+\alpha^2\frac{\left(x^2+y^2+z^2\right)}{r}+\alpha\frac{\left(x^2+y^2+z^2\right)}{r^3}\right)e^{-\alpha\sqrt{x^2+y^2+z^2}} \tag{4.3}$$

That was easy, wasn't it?

We re-write this as

$$\frac{\partial^2\psi_{guess\ 1}}{\partial x^2}+\frac{\partial^2\psi_{guess\ 1}}{\partial y^2}+\frac{\partial^2\psi_{guess\ 1}}{\partial z^2}=\left(-3\frac{\alpha}{r}+\frac{\alpha}{r}+\alpha^2\right)e^{-\alpha r}$$

which is

$$\frac{\partial^2\psi_{guess\ 1}}{\partial x^2}+\frac{\partial^2\psi_{guess\ 1}}{\partial y^2}+\frac{\partial^2\psi_{guess\ 1}}{\partial z^2}=\left(-2\frac{\alpha}{r}+\alpha^2\right)e^{-\alpha r}$$

so, returning to our starting Equation 2.1:

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2\psi_{guess\ 1}}{\partial x^2}+\frac{\partial^2\psi_{guess\ 1}}{\partial y^2}+\frac{\partial^2\psi_{guess\ 1}}{\partial z^2}\right) -\frac{Ze^2}{r}\psi_{guess\ 1} =-\frac{\hbar^2}{2m}\left(-2\frac{\alpha}{r}+\alpha^2\right)e^{-\alpha r}-\frac{Ze^2}{r}e^{-\alpha r} \tag{4.4}$$

which becomes

$$\left(-\frac{\hbar^2}{2m}\left(-2\frac{\alpha}{r}+\alpha^2\right)-\frac{Ze^2}{r}\right)e^{-\alpha r}$$

which allows a choice of α which, serendipitously, offers great clarity of understanding! We have

$$\left(\frac{\hbar^2}{2m}2\frac{\alpha}{r}-\frac{\hbar^2}{2m}\alpha^2-\frac{Ze^2}{r}\right)e^{-\alpha r} \tag{4.5}$$

The choice (the right one) is

$$\frac{\hbar^2\alpha}{m}-Ze^2=0$$

which cleans up Equation 4.5 if we choose α to be

$$\alpha=\frac{Ze^2m}{\hbar^2}$$

Then the surviving term, α^2, must be related to E!

$$-\frac{\hbar^2}{2m}\alpha^2=E$$

or

$$-\frac{\hbar^2}{2m}\left(\frac{Ze^2m}{\hbar^2}\right)^2=E$$

i.e.,

$$E=-\frac{Z^2e^4m}{2\hbar^2}$$

which is the correct Bohr value for n=1! Further,

$$\psi_{1s}=e^{-\frac{Ze^2}{\hbar^2}r}$$

V. SPHERICAL POLAR COÖRDINATE APPROACH

The Schrödinger Equation in spherical polar coördinates is

$$-\frac{\hbar^2}{2m}\left(\frac{1}{r^2}\frac{\partial r^2\frac{\partial\psi}{\partial r}}{\partial r}+\frac{1}{r^2\sin^2\vartheta}\left[\sin\vartheta\frac{\partial\sin\vartheta\frac{\partial\psi}{\partial\vartheta}}{\partial\vartheta}+\frac{\partial^2\psi}{\partial\phi^2}\right]\right)-\frac{Ze^2}{r}\psi=E\psi \tag{5.1}$$

which means that substituting ψ_{guess1} into it is no more than an exercise in partial differentiation.

We see immediately that ψ_{guess1} does not depend on ϑ or ϕ, so the Schrödinger Equation simplifies to

$$-\frac{\hbar^2}{2m}\left(\frac{1}{r^2}\frac{\partial r^2\frac{\partial\psi_{guess1}}{\partial r}}{\partial r}\right)+\frac{Ze^2}{r}\psi_{guess1}=E\psi_{guess1} \tag{5.2}$$

which is, after one partial differentiation

$$-\frac{\hbar^2}{2m}\left(\frac{1}{r^2}\frac{\partial(-\alpha\psi_{guess1})}{\partial r}\right)+\frac{Ze^2}{r}\psi_{guess1}=E\psi_{guess1} \tag{5.3}$$

After the second differentiation, one has

$$-\frac{\hbar^2}{2m}\left(\frac{1}{r^2}(r^2\alpha^2\psi_{guess1}-r\alpha\psi_{guess1})\right)+\frac{Ze^2}{r}\psi_{guess1}=E\psi_{guess1} \tag{5.4}$$

so that, expanding, we have

$$-\frac{\hbar^2}{2m}\left(\alpha^2\psi_{guess1}\frac{-\alpha}{r}\psi_{guess1})\right)+\frac{Ze^2}{r}\psi_{guess1}=E\psi_{guess1} \tag{5.5}$$

Clearly, the 1/r terms can be forced to cancel by appropriate choice of α.

We have

$$\frac{\hbar\alpha}{m}+Ze^2=0$$

which is an equation for α. Solving it yields

$$\alpha=-\frac{Ze^2m}{\hbar}$$

which means that the energy now becomes

$$E=-\frac{\hbar^2}{2}\frac{Z^2e^4m}{\hbar^2}$$

which is, of course, the infamous correct answer and the one we got before).

VI. A P-ORBITAL

The $2p_x$ orbital is so called because of its special form which is

$$\psi_{2p_x}=xe^{-\beta r}$$

where the initial x can be changed to "y" to form a $2p_y$ orbital, and of course the z-change is obvious!

We choose a $2p_x$ orbital as a next example as it illustrates all aspects which will be encountered by other, more complicated orbitals. We have

$$\psi_{guess2}=re^{-\beta r}\sin\vartheta\cos\phi$$

where the β will not be the same as α.

Substituting into Equation 5.1 we have

$$-\frac{\hbar^2}{2m}\left(\frac{1}{r^2}\frac{\partial r^2\frac{\partial re^{-\beta r}\sin\vartheta\cos\phi}{\partial r}}{\partial r}\right.$$
$$\left.+\frac{1}{r^2\sin^2\vartheta}\left[\sin\vartheta\frac{\partial\sin\vartheta\frac{\partial re^{-\beta r}\sin\vartheta\cos\phi}{\partial\vartheta}}{\partial\vartheta}+\frac{\partial^2 re^{-\beta r}\sin\vartheta\cos\phi}{\partial\phi^2}\right]\right)-\frac{Ze^2}{r}\psi=E\psi \tag{6.1}$$

Recognizing that differential with respect to 'r' ignores ϑ and ϕ, and vice versa we have

$$-\frac{\hbar^2}{2m}\left(\sin\vartheta\cos\phi\frac{1}{r^2}\frac{\partial r^2\frac{\partial}{\partial r}}{\partial r}\right.$$
$$\left.-e^{-\beta r}\frac{1}{r^2\sin^2\vartheta}\left[\sin\vartheta\frac{\partial\sin\vartheta\frac{\partial\sin\vartheta\cos\phi}{\partial\vartheta}}{\partial\vartheta}+\frac{\partial^2\sin\vartheta\cos\phi}{\partial\phi^2}\right]\right)-\frac{Ze^2}{r}\psi=E\psi \tag{6.2}$$

Since the same thing applies when one differentiates with respect to either ϑ or ϕ, we "finally" have

$$-\frac{\hbar^2}{2m}\left(\frac{\sin\vartheta\cos\phi}{r^2}\frac{\partial r^2\frac{\partial e^{-\beta r}}{\partial r}}{\partial r}\right.$$

$$+\frac{re^{-\beta r}}{r^2\sin^2\vartheta}\cos\phi\left[\sin\vartheta\frac{\partial\sin\vartheta\frac{\partial\sin\vartheta}{\partial\vartheta}}{\partial\vartheta}+\sin\vartheta\frac{\partial^2\cos\phi}{\partial\phi^2}\right]\Bigg)-\frac{Ze^2}{r}\psi=E\psi \tag{6.3}$$

which becomes

$$-\frac{\hbar^2}{2m}\Bigg(\frac{\sin\vartheta\cos\phi}{r^2}\frac{\partial r^2\left(e^{-\beta r}-\beta re^{-\beta r}\right)}{\partial r}$$
$$+\frac{re^{-\beta r}}{r\sin\vartheta}\cos\phi\left[\sin\vartheta\frac{\partial\sin\vartheta\cos\vartheta}{\partial\vartheta}-\sin\vartheta\cos\phi\right]\Bigg)-\frac{Ze^2}{r}\psi=E\psi \tag{6.4}$$

and then becomes

$$-\frac{\hbar^2}{2m}\Bigg(\frac{\sin\vartheta\cos\phi}{r^2}\frac{\partial\left(r^2e^{-\beta r}-\beta r^3e^{-\beta r}\right)}{\partial r}$$
$$+\frac{re^{-\beta r}}{r^2\sin^2\vartheta}\cos\phi\left[\sin\vartheta\left(\cos^2\vartheta-\sin^2\vartheta\right)-\sin\vartheta\cos\phi\right]\Bigg)+\frac{Ze^2}{r}\psi=E\psi \tag{6.5}$$

which becomes

$$-\frac{\hbar^2}{2m}\Bigg(\frac{\sin\vartheta\cos\phi}{r^2}\left(2re^{-\beta r}-\beta r^2e^{-\beta r}-2\beta r^2e^{-\beta r}+\beta^2r^3e^{-\beta r}\right)$$
$$+\frac{re^{-\beta r}}{r^2\sin^2\vartheta}\cos\phi\left[\sin\vartheta\left(\cos^2\vartheta-\sin^2\vartheta\right)-\cos\vartheta\cos\phi\right]\Bigg)-\frac{Ze^2}{r}\psi=E\psi \tag{6.6}$$

which becomes

$$-\frac{\hbar^2}{2m}\Bigg(\frac{1}{r^2}\left(2-\beta r-2\beta r+\beta^2r^2\right)$$
$$+\frac{}{r^2\sin^2\vartheta}\left[\left(\cos^2\vartheta-\sin^2\vartheta\right)-\sin\vartheta\cos\vartheta\cos\phi\right]\Bigg)-\frac{Ze^2}{r}=E \tag{6.7}$$

$$-\frac{\hbar^2}{2m}\Bigg(\frac{\sin\vartheta\cos\phi}{r^2}\left(2re^{-\beta r}-3\beta r^2e^{-\beta r}+\beta^2r^3e^{-\beta r}\right)$$
$$+\frac{re^{-\beta r}}{r^2\sin^2\vartheta}\cos\phi\left[\sin\vartheta\left(\cos^2\vartheta-\sin^2\vartheta\right)-\cos\vartheta\cos\phi\right]\Bigg)-\frac{Ze^2}{r}\psi=E\psi \tag{6.8}$$

VII. 2S ORBITAL

We start with the assumption that the wave function for the 2s state has the form

$$\psi_{trial}=(1+\alpha r)e^{-\beta r}$$

where α and β are to be determined.

The Schrödinger Equation for the s-states of Hydrogen is

$$-\frac{\hbar^2}{2m_e}\left(\frac{1}{r^2}\frac{\partial\left(\frac{r^2\partial\psi_{trial}}{\partial r}\right)}{\partial r}\right)-\frac{Ze^2\psi_{trial}}{r}=E\psi_{trial}$$

and then it is

$$-\frac{\hbar^2}{2m_e}\left(\frac{2(\alpha-\beta(1+\alpha r))}{r}-\beta\alpha+\beta(\alpha-\beta(1+\alpha))\right)e^{-\beta r}-\frac{Ze^2(1+\alpha r)e^{-\beta r}}{r}=E(1+\alpha r)e^{-\beta r}$$

Assuming that the exponential is eventually going to cancel, provided all goes well, cross multiplying by $-\frac{2m_e}{\hbar^2}$, and collecting the terms multiplying 1/r, we have

$$\frac{2\alpha}{r} - \frac{2\beta(1+\alpha r)}{r} + \frac{2r}{r} + \frac{2m_eZe^2}{\hbar^2}\left(\frac{1+\alpha r}{r}\right) = 0$$

which we re-write as

$$\frac{2\alpha(1-\beta r)}{r} - \frac{2\beta(1+\alpha r)}{r} - \frac{2m_eZe^2}{\hbar^4}\left(\frac{1+\alpha}{r}\right) = 0$$

which works if $\alpha = -\beta$, so that

$$\frac{4\alpha(1+\alpha r)}{r} + \frac{2m_eZe^2}{\hbar^2}\left(\frac{1+\alpha r}{r}\right) = 0$$

which implies that

$$\alpha = -\frac{m_eZe^2}{2\hbar^2}$$

so that

$$\beta = \frac{m_eZe^2}{2\hbar^2}$$

so that finally,

$$\frac{2m_eE}{\hbar^2} = -\beta^2 = \frac{m_e^2Z^2e^4}{2^2\hbar^4}$$

so that, solving for E we obtain (the hoped for)

$$E = -\frac{m_eZ^2e^4}{2\hbar^2 2^2} = E_{n=2}$$

isn't that something?

VIII. ELLIPTICAL COÖRDINATE EXAMPLE FOR H_2^+ PRECURSOR

If r_A is the distance from nucleus A to a point P(x,y,z) (where the electron is located, in H_2^+, presumably), and r_B is the distance from nucleus B to the same point(!), then Elliptical Coordinates are defined as:

$$\lambda = \frac{r_A + r_B}{R}$$

and

$$\mu = \frac{r_A - r_B}{R}$$

(where ϕ is the same as the coordinate used in Spherical Polar Coordinates), which means that

$$r_A = \frac{R}{2}(\lambda + \mu)$$

and

$$r_B = \frac{R}{2}(\lambda - \mu)$$

This also means that

$$r_A = \sqrt{x^2 + y^2 + (z - R/2)^2}$$

and

$$r_B = \sqrt{x^2 + y^2 + (z + R/2)^2}$$

We seek the transformation equations between (x,y, and z) on the one hand and (λ, μ, ϕ) on the other. To start, we write

$$r_A^2 = \left(\frac{R}{2}\right)^2(\lambda+\mu)^2 = x^2 + y^2 + (z - R/2)^2 = x^2 + y^2 + z^2 - 2zR/2 + \left(\frac{R}{2}\right)^2 \tag{8.1}$$

i.e.,

$$r_A^2 = r^2 - 2zR/2 + \left(\frac{R}{2}\right)^2$$

and

$$r_B^2 = \left(\frac{R}{2}\right)^2(\lambda-\mu)^2 = x^2+y^2+(z+R/2)^2 = x^2+y^2+z^2+2zR/2+\left(\frac{R}{2}\right)^2 \tag{8.2}$$

i.e.,

$$r_B^2 = r^2 + 2zR/2 + \left(\frac{R}{2}\right)^2$$

so that (adding Equations 8.1 and 8.2)

$$r_A^2 + r_B^2 = 2\left(x^2 + y^2 + z^2 + \left(\frac{R}{2}\right)^2\right) = 2\left(\lambda^2 + \mu^2\right)\left(\frac{R}{2}\right)^2 = 2r^2 + 2\left(\frac{R}{2}\right)^2$$

so

$$r^2 = \left(\lambda^2 + \mu^2\right)\left(\frac{R}{2}\right)^2 - \left(\frac{R}{2}\right)^2$$

and

$$r^2 = \left(\frac{R}{2}\right)^2\left(\lambda^2 + \mu^2 - 1\right) \quad (8.3)$$

We need the z-coordinate first, so, subtracting Equation 8.2 from Equation 8.1 instead of adding, we obtain

$$(z - R/2)^2 - (z + R/2)^2 = \frac{R^2}{4}\left((\lambda+\mu)^2 - (\lambda-\mu)^2\right) = \left(\frac{R}{2}\right)^2\left(\lambda^2 + 2\lambda\mu + \mu^2 - (\lambda^2 - 2\lambda\mu + \mu^2)\right)$$

i.e.,

$$-4z\frac{R}{2} = \left(\frac{R}{2}\right)^2(4\lambda\mu)$$

or

$$z = -\frac{R\lambda\mu}{2} \quad (8.4)$$

This is our first transformation equation. To check that this is correct, we examine the point (0,0,R) which would have r_A=R/2 and r_B=3R/2 as shown in the diagram. From Equation 8.4 we have

$$R = -\frac{R}{2}\lambda\mu = -\frac{R}{2}\frac{1}{R}(R/2 + 3R/2)\frac{1}{R}(R/2 - 3R/2)$$

which is

$$R = -\frac{1}{2R}(2R)(-R)$$

We return now to obtaining x and y in this new coordinate system. Since, in spherical polar coordinates one has

$$\cos\theta = \frac{z}{r}$$

it follows that

$$\sin^2\theta = 1 - \cos^2\theta = 1 - \left(\frac{z}{r}\right)^2$$

i.e,

$$r\sin\theta = r\sqrt{1 - \left(\frac{z}{r}\right)^2} = \sqrt{r^2 - z^2}$$

Using Equation 8.4, we have

$$r\sin\theta = \sqrt{r^2 - \left(\frac{R\lambda\mu}{2}\right)^2}$$

and (using Equation 8.3)

$$r\sin\theta = \sqrt{\left(\frac{R}{2}\right)^2\left(\lambda^2 + \mu^2 - 1\right) - \left(\frac{R\lambda\mu}{2}\right)^2}$$

i.e.,

$$r\sin\theta = \frac{R}{2}\sqrt{(\lambda^2 + \mu^2 - 1 - \lambda^2\mu^2)}$$

then

$$x = r\sin\theta\cos\phi$$

i.e.,

$$x = \frac{R}{2}\cos\phi\sqrt{(\lambda^2 - 1)(1 - \mu^2)}$$

and

$$y = \frac{R}{2}\sin\phi\sqrt{(\lambda^2 - 1)(1 - \mu^2)}$$

IX. RE-CAPITULATION

For future reference, we collect the transformation equations here:

$\lambda = \frac{r_A + r_B}{R}$	$x = \frac{R}{2}\cos\phi\sqrt{(\lambda^2 - 1)(1 - \mu^2)}$
$\mu = \frac{r_A - r_B}{R}$	$y = \frac{R}{2}\sin\phi\sqrt{(\lambda^2 - 1)(1 - \mu^2)}$
$\phi = \phi$	$z = -\frac{R\lambda\mu}{2}$

X. KINETIC ENERGY OPERATOR IN ELLIPTICAL COÖRDINATES

Here we introduce the Laplacian in elliptical coordinates [1]. (See http://digitalcommons.uconn.edu/chem_educ/5)

$$\nabla^2 = \frac{4}{R^2\left(\lambda^2-\mu^2\right)}\left\{\left(\frac{\partial\left((\lambda^2-1)\frac{\partial}{\partial\lambda}\right)}{\partial\lambda}\right)+\left(\frac{\partial\left((1-\mu^2)\frac{\partial}{\partial\mu}\right)}{\partial\mu}\right)+\left(\frac{\partial\left(\frac{\lambda^2-\mu^2}{(\lambda^2-1)(1-\mu^2)}\frac{\partial}{\partial\phi}\right)}{\partial\phi}\right)\right\}$$

Equation 2.1 becomes,

$$-\frac{\hbar^2}{2m}\left(\frac{4}{R^2\left(\lambda^2-\mu^2\right)}\left(\left(\frac{\partial\left((\lambda^2-1)\frac{\partial}{\partial\lambda}\right)}{\partial\lambda}\right)+\left(\frac{\partial\left((1-\mu^2)\frac{\partial}{\partial\mu}\right)}{\partial\mu}\right)\right)\right)\psi-\frac{Ze^2}{r}\psi=E\psi$$

since there is not going to be any ϕ dependence in our wave function, where

$$\psi_{guess\ 1}=e^{-\alpha r}$$

We put the proton arbitrarily at point A (0,0,R/2), leaving point B empty until we consider H_2^+. Since

$$r_A=\frac{R}{2}(\lambda+\mu)$$

we know then that

$$\psi_{guess\ 1}=e^{-\alpha r}=e^{-\alpha\frac{R}{2}(\lambda+\mu)}$$

Therefore we have

$$-\frac{\hbar^2}{2m}\left(\frac{4}{R^2\left(\lambda^2-\mu^2\right)}\left(\left(\frac{\partial\left((\lambda^2-1)\frac{\partial e^{-\alpha\frac{R}{2}(\lambda+\mu)}}{\partial\lambda}\right)}{\partial\lambda}\right)+\left(\frac{\partial\left((1-\mu^2)\frac{\partial e^{-\alpha\frac{R}{2}(\lambda+\mu)}}{\partial\mu}\right)}{\partial\mu}\right)\right)\right)-\frac{Ze^2}{r}\psi=Ee^{-\alpha\frac{R}{2}(\lambda+\mu)}$$

or, taking the first derivatives

$$-\frac{4\hbar^2}{2mR^2\left(\lambda^2-\mu^2\right)}\left(\frac{\partial\left((\lambda^2-1)\left(-\alpha\frac{R}{2}\right)\right)e^{-\alpha\frac{R}{2}(\lambda+\mu)}}{\partial\lambda}+\frac{\partial\left((1-\mu^2)\left(-\alpha\frac{R}{2}\right)\right)e^{-\alpha\frac{R}{2}(\lambda+\mu)}}{\partial\mu}\right)$$
$$-\frac{Ze^2}{r}\psi=Ee^{-\alpha\frac{R}{2}(\lambda+\mu)}$$

and, taking the second derivative:

$$-\frac{4\hbar^2}{2mR^2\left(\lambda^2-\mu^2\right)}\left[\left(2\lambda+(\lambda^2-1)\left(-\alpha\frac{R}{2}\right)\right)\left(-\alpha\frac{R}{2}\right)+\left(-2\mu+(1-\mu^2)\left(-\alpha\frac{R}{2}\right)\right)\left(-\alpha\frac{R}{2}\right)\right]e^{-\alpha\frac{R}{2}(\lambda+\mu)}$$
$$-\frac{Ze^2}{r}\psi=Ee^{-\alpha\frac{R}{2}(\lambda+\mu)}$$

and re-arranging

$$\left(\alpha\frac{R}{2}\right)\frac{4\hbar^2}{2mR^2\left(\lambda^2-\mu^2\right)}\left[\left(2\lambda+(\lambda^2-1)\left(-\alpha\frac{R}{2}\right)\right)+\left(-2\mu+(1-\mu^2)\left(-\alpha\frac{R}{2}\right)\right)\right]e^{-\alpha\frac{R}{2}(\lambda+\mu)}$$
$$-\frac{Ze^2}{r}\psi=Ee^{-\alpha\frac{R}{2}(\lambda+\mu)}$$

or

$$\frac{\alpha\hbar^2}{mR\left(\lambda^2-\mu^2\right)}\left[\left(2\lambda+(\lambda^2-1)\left(-\alpha\frac{R}{2}\right)\right)\right.$$

$$+\left(-2\mu+(1-\mu^2)\left(-\alpha\frac{R}{2}\right)\right)\Bigg]$$
$$-\frac{Ze^2}{\frac{R}{2}(\lambda+\mu)}=E$$

which becomes

$$\frac{\alpha\hbar^2}{mR\left((\lambda-\mu)(\lambda+\mu)\right)}\left[2\lambda+(\lambda^2-1)\left(-\alpha\frac{R}{2}\right)-2\mu+(1-\mu^2)\left(-\alpha\frac{R}{2}\right)\right]$$
$$-\frac{Ze^2}{\frac{R}{2}(\lambda+\mu)}=E$$

or, rearranging

$$\frac{\alpha\hbar^2}{mR\left((\lambda-\mu)(\lambda+\mu)\right)}\left[2(\lambda-\mu)+\left\{(\lambda^2-1)+(1-\mu^2)\right\}\left(-\alpha\frac{R}{2}\right)\right]$$
$$-\frac{Ze^2}{\frac{R}{2}(\lambda+\mu)}=E$$

and rearranging terms once again

$$2\frac{\alpha\hbar^2}{mR\left(\cancel{(\lambda-\mu)}(\lambda+\mu)\right)}\cancel{(\lambda-\mu)}+$$
$$\frac{\alpha\hbar^2}{mR\left((\lambda-\mu)(\lambda+\mu)\right)}\left\{(\lambda^2-1)+(1-\mu^2)\right\}\left(-\alpha\frac{R}{2}\right)$$
$$-\frac{Ze^2}{\frac{R}{2}(\lambda+\mu)}=E$$

One sees that the term $\lambda-\mu$ cancels on the first term, leaving something which can "cancel" the potential energy term if α is appropriately chosen, i.e.,

$$2\frac{\alpha\hbar^2}{mR(\lambda+\mu)}-\frac{2Ze^2}{R(\lambda+\mu)}+$$
$$\frac{\alpha\hbar^2}{mR\left((\lambda-\mu)(\lambda+\mu)\right)}\left\{(\lambda^2-1)+(1-\mu^2)\right\}\left(-\alpha\frac{R}{2}\right)$$
$$=E$$

so that, combining terms, we have

$$2\left(\frac{\alpha\hbar^2}{mR}-\frac{Ze^2}{R}\right)\left(\frac{1}{\lambda+\mu}\right)$$
$$\frac{\alpha\hbar^2}{mR\left((\lambda-\mu)(\lambda+\mu)\right)}\left\{(\lambda^2-1)+(1-\mu^2)\right\}\left(-\alpha\frac{R}{2}\right)$$
$$=E$$

i.e., choosing $\frac{\alpha\hbar^2}{m}=Ze^2$ i.e.,

$$\alpha=\frac{Ze^2m}{\hbar^2}$$

makes the first term vanish, and

$$\frac{\alpha\hbar^2}{mR\,\cancel{\left((\lambda-\mu)(\lambda+\mu)\right)}}\left\{\cancel{(\lambda^2-1)+(1-\mu^2)}\right\}\left(-\alpha\frac{R}{2}\right)=E$$

Recognizing the appropriate cancellation, we have

$$-\frac{\alpha\hbar^2}{mR}\alpha\frac{R}{2}=E$$

i.e.,

$$-\frac{\alpha^2\hbar^2}{2m}=E$$

and interpreting α from above, we obtain

$$-\frac{\left(\frac{Ze^2m}{\hbar^2}\right)^2\hbar^2}{2m}=E$$

which cleans up to

$$-\frac{Z^2e^4m}{2\hbar^2}=E$$

a most famous, at this point, result.

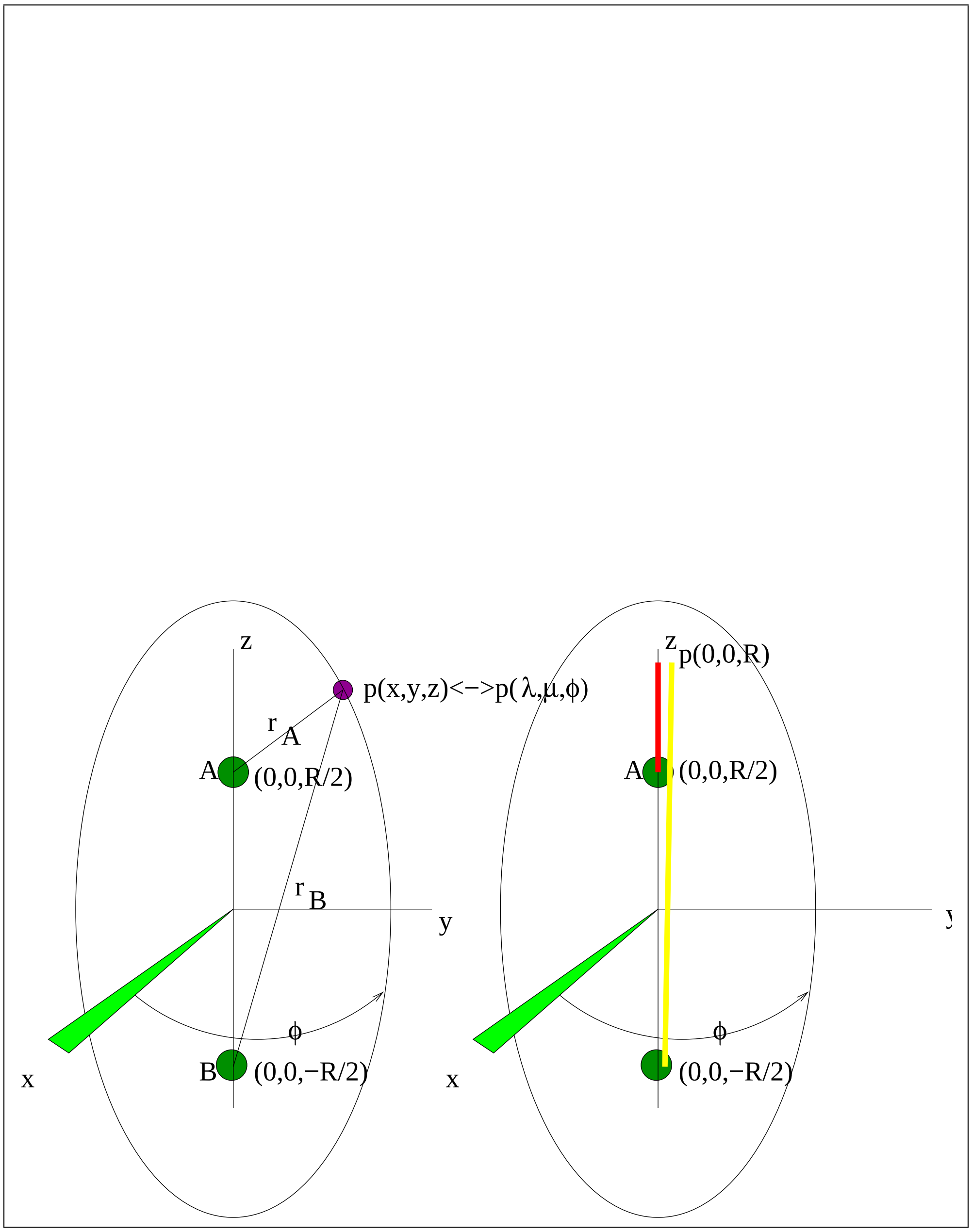

FIG. 1: The Elliptical Coordinate System for Diatomic Molecules. The μ coordinate is not depicted. On the right hand side, one sees the depiction of the point (0,0,R) which would make r_A=R/2 and r_B=3R/2

[1] Pauling and Wilson, "Introduction to Quantum Mechanics", McGraw Hill Book Co., page 444 calls them "Confocal Elliptic Coordinates (Prolate Spheroid)".
Margenau and Murphy, "The Mathematics of Physics and Chemistry", D. Van Nostrand Co., page 181 calls them "Prolate Spheroidal Coordinates". Take your pick.