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LCAO-MO's are not Eigenfunctions of the H_2^+ Hamiltonian

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I. SYNOPSIS

A simple LCAO-MO for H_2^+ is tested for eigenfunctionality against the correct Hamiltonian for the problem, and found to be wanting. This is done in Cartesian coördinates and in Elliptical coördinates. This is a reworking of an earlier article, C. W. David, *J. Chem. Ed.*, **59**, 288 *(1982)*

II. INTRODUCTION

The standard coördinate system for diatomic molecules has the two nucleii on the z axis, one (say A) at +R/2 and the other (say B) at -R/2 (so that the internuclear distance is R) (see Figure 1). Although this system is used in studying H_2, we here start with H_2^+, the one electron problem, which is, of course, significantly simpler than H_2 [1]. Even here, in this simplest of all diatomic "molecules", the simplest LCAO-MO fails as an exact wave function for this system!

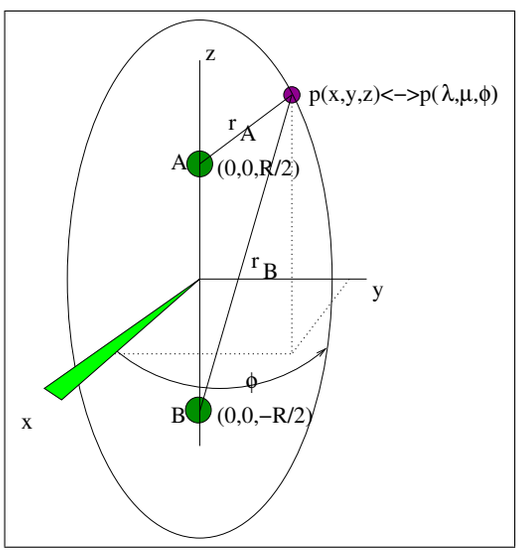

FIG. 1: The Standard Elliptical Coördinate System for Diatomic Molecules

Remember that

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

and

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

so, for a trial LCAO-MO (an approximate wave function, not an eigenfunction of the H_2^+ system)

$$\psi_{trial} = \left(c_A e^{-\alpha r_A} + c_B e^{-\alpha r_B}\right) = c_A 1s_A + c_B 1s_B = \psi_{LCAO} = \psi_{1\sigma}$$

(which is intentionally left in un-normalized form). Notice that we have approximated a 1σ (and, inadvertantly, a $1\sigma^*$ orbital in our example), although any combinatation of two atomic orbitals, one centered on nucleus A and the other centered on nucleus B, would be appropriate. Of course, using orbitals higher than 1s would mean considering excited electronic molecular states!

The Hamiltonian is (as shown operating on a wave function *Ansatz*):

$$H_{op}\psi(x,y,z) = -\frac{\hbar^2}{2m_e}\nabla^2\psi(x,y,z) - \frac{Z_A e^2\psi(x,y,z)}{r_A} - \frac{Z_B e^2\psi(x,y,z)}{r_B} \tag{2.1}$$

where we will stipulate that $Z_A = Z_B = 1$ so that we are truly dealing with the hydrogen molecular ion.

It is important to emphasize that the Schrödinger Equation, when applied to an LCAO, does not yield a proper '=' sign, i.e., the LCAO is *not* an eigenfunction of the Hamiltonian, and does *not* provide a true solution to the Schrödinger Equation.

III. DOING OUR THING IN CARTESIAN COÖRDINATES

To see this, one needs only substitute an LCAO into the appropriate Schrödinger equation, i.e., the appropriate Hamiltonian, and conclude that the equal sign does not hold!

Since

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

and

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

and given an LCAO, *say* a π approximation, specifically, a π_x^* LCAO, one would have

$$\psi = xe^{-\alpha r_A} - xe^{-\alpha r_B}$$

i.e.,

$$\psi = p_x^A - p_x^B$$

(had we used an intervening plus sign above we would have been treating a π_x rather than an anti-bonding π_x^* orbital).

Rathen than proceed with a computation using the π^* orbital, which is quite messy we here change back to a simple σ orbital. We assume that

$$\psi_{trial} = e^{-\alpha r_A} + e^{-\alpha r_B} \tag{3.1}$$

Using brute force we can obtain the effect of the Hamiltonian on this trial wave function.

We need to first obtain some useful partial derivatives, i.e.

$$\frac{\partial(r_A)}{\partial x} = \frac{\partial(\sqrt{x^2 + y^2 + (z - R/2)^2})}{\partial x} = \frac{\partial((x^2 + y^2 + (z - R/2)^2)^{1/2})}{\partial x} = \left(\frac{1}{2}\right)\left(\frac{2x}{(x^2 + y^2 + (z - R/2)^2)^{1/2}}\right)$$

so

$$\frac{\partial(r_A)}{\partial x} = \frac{x}{(x^2 + y^2 + (z - R/2)^2)^{1/2}} = \frac{x}{r_A} = \left(\frac{\partial r_A}{\partial x}\right)_{y,z}$$

and

$$\frac{\partial({r_A}^{-1})}{\partial x} = \frac{\partial((x^2 + y^2 + (z - R/2)^2)^{-1/2})}{\partial x} = -\frac{1}{2}\frac{2x}{(x^2 + y^2 + (z - R/2)^2)^{3/2}}$$

i.e.,

$$\frac{\partial({r_A}^{-1})}{\partial x} = -\frac{x}{(x^2 + y^2 + (z - R/2)^2)^{3/2}} = -\frac{x}{{r_A}^3} = \left(\frac{\partial\left(\frac{1}{r_A}\right)}{\partial x}\right)_{y,z}$$

Next, we obtain

$$\frac{\partial({r_A}^{-2})}{\partial x} = \frac{\partial((x^2 + y^2 + (z - R/2)^2)^{-1})}{\partial x} = -1\frac{2x}{(x^2 + y^2 + (z - R/2)^2)^2}$$

i.e.,

$$\frac{\partial({r_A}^{-2})}{\partial x} = -\frac{2x}{(x^2 + y^2 + (z - R/2)^2)^2} = -\frac{2x}{{r_A}^4} = \left(\frac{\partial\left(\frac{1}{{r_A}^2}\right)}{\partial x}\right)_{y,z}$$

and, finally,

$$\frac{\partial({r_A}^{-3})}{\partial x} = \frac{\partial((x^2 + y^2 + (z - R/2)^2)^{-3/2})}{\partial x} = -3/2\frac{2x}{(x^2 + y^2 + (z - R/2)^2)^{5/2}}$$

i.e.,

$$\frac{\partial({r_A}^{-3})}{\partial x} = -\frac{\frac{3}{2}(2x)}{(x^2+y^2+(z-R/2)^2)^{5/2}} = -\frac{3x}{{r_A}^5} = \left(\frac{\partial\left(\frac{1}{{r_A}^3}\right)}{\partial x}\right)_{y,z}$$

Derivative of	Result is
$\frac{\partial r_A}{\partial x}$	$\frac{x}{r_A}$
$\left(\frac{\partial\left(\frac{1}{r_A}\right)}{\partial x}\right)_{y,z}$	$-\frac{x}{{r_A}^3}$
$\left(\frac{\partial\left(\frac{1}{{r_A}^2}\right)}{\partial x}\right)_{y,z}$	$-\frac{2x}{{r_A}^4}$
$\left(\frac{\partial\left(\frac{1}{{r_A}^3}\right)}{\partial x}\right)_{y,z}$	$-\frac{3x}{{r_A}^5}$

Now, we have enough information to begin.

IV. ENDING PRELIMINARIES, THE ACTUAL DERIVATION PROCEEDS NOW

We need to form the partial derivative of the LCAO with respect to x (then y, and then z). We write out, in excrutiating detail (so you can verify the steps one by one without resorting to pencil and paper), the following:

$$\frac{\partial\psi_{trial}}{\partial x} = \left(\frac{\partial e^{-\alpha r_A}}{\partial x}\right) + \left(\frac{\partial e^{-\alpha r_B}}{\partial x}\right)$$

which is

$$\frac{\partial\psi_{trial}}{\partial x} = \left(-\alpha\frac{x}{r_A}\right)e^{-\alpha r_A} + \left(-\alpha\frac{x}{r_B}\right)e^{-\alpha r_B}$$

and then

$$\frac{\partial^2\psi}{\partial x^2} = \left(-\alpha\frac{1}{r_A} + \alpha\frac{x^2}{{r_A}^3} + \left(-\alpha\frac{x}{r_A}\right)^2\right)e^{-\alpha r_A} + \left(-\alpha\frac{1}{r_B} + \alpha\frac{x^2}{{r_B}^3} + \left(-\alpha\frac{x}{r_B}\right)^2\right)e^{-\alpha r_B} \tag{4.1}$$

Then, continuing, we have

$$\frac{\partial^2\psi}{\partial y^2} = \left(-\alpha\frac{1}{r_A} + \alpha\frac{y^2}{{r_A}^3} + \left(-\alpha\frac{y}{r_A}\right)^2\right)e^{-\alpha r_A} + \left(-\alpha\frac{1}{r_B} + \alpha\frac{y^2}{{r_B}^3} + \left(-\alpha\frac{y}{r_B}\right)^2\right)e^{-\alpha r_B} \tag{4.2}$$

with a similar term for the partial with respect to z:

$$\begin{aligned}\frac{\partial^2\psi}{\partial z^2} = &\left(-\alpha\frac{1}{r_A} + \alpha\frac{(z-R/2)^2}{{r_A}^3} + \left(-\alpha\frac{(z-R/2)}{r_A}\right)^2\right)e^{-\alpha r_A} \\ &+ \left(-\alpha\frac{1}{r_B} + \alpha\frac{(z+R/2)^2}{{r_B}^3} + \left(-\alpha\frac{(z+R/2)}{r_B}\right)^2\right)e^{-\alpha r_B}\end{aligned} \tag{4.3}$$

We can now add these three (Equations 4.1, 4.2 and 4.3) together:

$$\nabla^2\psi = \left(-\alpha\frac{3}{r_A} + \alpha\frac{1}{r_A} + \alpha^2\right)e^{-\alpha r_A}\left(-\alpha\frac{3}{r_B} + \alpha\frac{1}{r_B} + \alpha^2\right)e^{-\alpha r_B} \tag{4.4}$$

i.e.,

$$\nabla^2\psi = \left(-\alpha\frac{2}{r_A} + \alpha^2\right)e^{-\alpha r_A}\left(-\alpha\frac{2}{r_B} + \alpha^2\right)e^{-\alpha r_B} \tag{4.5}$$

so, in atomic units, we have

$$H_{op}\psi_{trial}(x,y,z) = -\frac{1}{2}\left\{\left(-\alpha\frac{2}{r_A}+\alpha^2\right)c_A e^{-\alpha r_A}\left(-\alpha\frac{2}{r_B}+\alpha^2\right)c_B e^{-\alpha r_B}\right\} - \frac{Z_A e^2\left(c_A e^{-\alpha r_A}+c_B e^{-\alpha r_B}\right)}{r_A} - \frac{Z_B e^2\left(c_A e^{-\alpha r_A}+c_B e^{-\alpha r_B}\right)}{r_B} \tag{4.6}$$

It is apparent that this wave function ψ_{trial}, is not an eigenfunction. Notice there is no way of "getting rid" of the terms

$$-\frac{Z_A e^2\left(e^{-\alpha r_B}\right)}{r_A} - \frac{Z_B e^2\left(c_A e^{-\alpha r_A}\right)}{r_B}$$

i.e., there is no choice of α or any other adjustable constant which can obliterate these terms. Since they do not appear elsewhere, they languish, uncancelled, destroying the "eigenfunctionality" of ψ_{trial}. As a general statement, LCAO's are not eigenfunctions, even of one electron Hamiltonians. That means that invoking LCAO's is *a priori* approximating!

V. THE LCAO-MO IN ELLIPTICAL COÖRDINATES

We start with a quick review.

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 coördinate 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

$$r_A^2 = \left(\frac{R}{2}\right)^2(\lambda+\mu)^2 = x^2+y^2+(z-R/2)^2 = x^2+y^2+z^2-2zR/2+\left(\frac{R}{2}\right)^2 \tag{5.1}$$

i.e.,

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

and

$$r_B^2 = \left(\frac{R}{2}\right)^2(\lambda-\mu)^2 = x^2+y^2+(z+R/2)^2 = x^2+y^2+z^2+2zR/2+\left(\frac{R}{2}\right)^2 \tag{5.2}$$

i.e.,

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

so that (adding Equations 5.1 and 5.2)

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

so

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

and

$$r^2 = \left(\frac{R}{2}\right)^2\left(\lambda^2 + \mu^2 - 1\right) \tag{5.3}$$

A. the z-coördinate

We need the z-coördinate first, so, subtracting Equation 5.2 from Equation 5.1 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

$$z = -\frac{R\lambda\mu}{2} \tag{5.4}$$

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 Figure 2 (r.h.s).

From Equation 5.4 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

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

which, being a tautology, means that we were correct.

B. x and y coördinates

We return now to obtaining x and y in this new coördinate system. Since, in spherical polar coördinates 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 5.4, we have

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

and (using Equation 5.3)

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

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

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

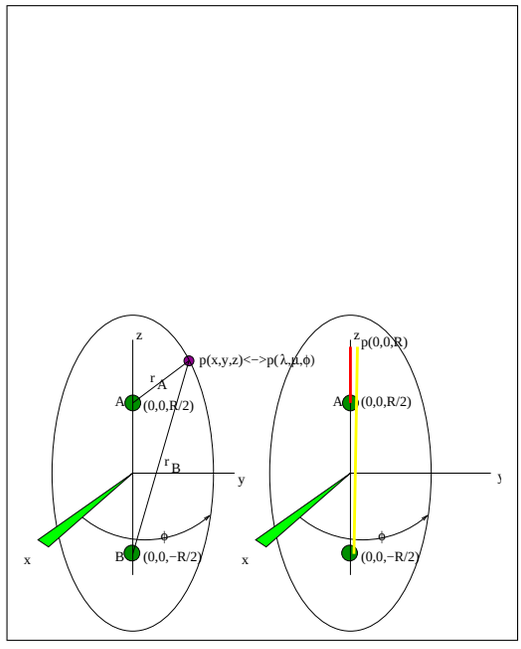

FIG. 2: The Elliptical Coordinate System for Diatomic Molecules. The μ coördinate is not depicted. On the right hand side, one sees the depiction of the point (0,0,R) which would make r_A=R/2 and r_B=3R/2

VI. RE-CAPITULATION

For future reference, we collect the transformation equations here:

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

VII. KINETIC ENERGY OPERATOR IN ELLIPTICAL COÖRDINATES

Here we introduce the Laplacian in elliptical coördinates [2]. (See http://digitalcommons.uconn.edu/chem_educ/5)

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

Equation 2.1 becomes,

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

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

$$\psi_{LCAO-MO} = e^{-\alpha r_A} + e^{-\alpha r_B}$$

We put the protons arbitrarily at point A (0,0,R/2) and B (0,0,-R/2). Since

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

and

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

we know then that

$$\psi_{LCAO-MO} = e^{-\alpha\frac{R}{2}(\lambda+\mu)} + e^{-\alpha\frac{R}{2}(\lambda-\mu)}$$

Alternatively, we can write this as

$$\psi_{LCAO-MO} = e^{-\alpha\frac{R}{2}\lambda}\left(e^{-\alpha\frac{R}{2}(\mu)} + e^{+\alpha\frac{R}{2}(\mu)}\right) = 2e^{-\alpha\frac{R}{2}\lambda}\cosh\left(\frac{R}{2}\mu\right)$$

Therefore we have

$$-\frac{\hbar^2}{2m}\left(\frac{4}{R^2\left(\lambda^2-\mu^2\right)}\left[\left(e^{-\alpha\frac{R}{2}(+\mu)}+e^{-\alpha\frac{R}{2}(-\mu)}\right)\left(\frac{\partial\left(\left(\lambda^2-1\right)\frac{\partial e^{-\alpha\frac{R}{2}\lambda}}{\partial\lambda}\right)}{\partial\lambda}\right)+\right.\right.$$
$$\left.\left.e^{-\alpha\frac{R}{2}\lambda}\left(\frac{\partial\left(\left(1-\mu^2\right)\frac{\partial\left(e^{-\alpha\frac{R}{2}(+\mu)}e^{-\alpha\frac{R}{2}(-\mu)}\right)}{\partial\mu}\right)}{\partial\mu}\right)\right]\right)$$
$$-\left(\frac{Z_Ae^2}{\frac{R}{2}(\lambda+\mu)}+\frac{Z_Be^2}{\frac{R}{2}(\lambda-\mu)}\right)\left(e^{-\alpha\frac{R}{2}(\lambda+\mu)}+e^{-\alpha\frac{R}{2}(\lambda-\mu)}\right)=E\left(e^{-\alpha\frac{R}{2}(\lambda+\mu)}+e^{-\alpha\frac{R}{2}(\lambda-\mu)}\right) \tag{7.1}$$

or, taking the first derivatives

$$-\frac{4\hbar^2}{2mR^2\left(\lambda^2-\mu^2\right)}\left(\left(e^{-\alpha\frac{R}{2}(+\mu)}+e^{-\alpha\frac{R}{2}(-\mu)}\right)\frac{\partial\left(\left(\lambda^2-1\right)\left(-\alpha\frac{R}{2}\right)e^{-\alpha\frac{R}{2}(\lambda)}\right)}{\partial\lambda}+\right.$$
$$\left.\left(e^{-\alpha\frac{R}{2}(-\lambda)}\right)\frac{\partial\left(\left(1-\mu^2\right)\left[\left(-\alpha\frac{R}{2}\right)e^{-\alpha\frac{R}{2}(\mu)}+\left(\alpha\frac{R}{2}\right)e^{\alpha\frac{R}{2}(\mu)}\right]\right)}{\partial\mu}\right)+$$
$$-\left(\frac{Z_Ae^2}{\frac{R}{2}(\lambda+\mu)}+\frac{Z_Be^2}{\frac{R}{2}(\lambda-\mu)}\right)\left(e^{-\alpha\frac{R}{2}(\lambda+\mu)}+e^{-\alpha\frac{R}{2}(\lambda-\mu)}\right)=E\left(e^{-\alpha\frac{R}{2}(\lambda+\mu)}+e^{-\alpha\frac{R}{2}(\lambda-\mu)}\right)$$

which we re-write prior to the next step as

$$-\frac{4\hbar^2}{2mR^2\left(\lambda^2-\mu^2\right)}\left(\left(e^{-\alpha\frac{R}{2}(+\mu)}+e^{-\alpha\frac{R}{2}(-\mu)}\right)\left(-\alpha\frac{R}{2}\right)\frac{\partial\left(\left(\lambda^2-1\right)e^{-\alpha\frac{R}{2}(\lambda)}\right)}{\partial\lambda}+\right.$$
$$\left.\left(e^{-\alpha\frac{R}{2}(\lambda)}\right)\left(\alpha\frac{R}{2}\right)\frac{\partial\left(\left(1-\mu^2\right)\left[-e^{-\alpha\frac{R}{2}(\mu)}+e^{\alpha\frac{R}{2}(\mu)}\right]\right)}{\partial\mu}\right)+$$
$$-\left(\frac{Z_Ae^2}{\frac{R}{2}(\lambda+\mu)}+\frac{Z_Be^2}{\frac{R}{2}(\lambda-\mu)}\right)\left(e^{-\alpha\frac{R}{2}(\lambda+\mu)}+e^{-\alpha\frac{R}{2}(\lambda-\mu)}\right)=E\left(e^{-\alpha\frac{R}{2}(\lambda+\mu)}+e^{-\alpha\frac{R}{2}(\lambda-\mu)}\right)$$

and, taking the second derivative:

$$-\frac{4\hbar^2}{2mR^2\left(\lambda^2-\mu^2\right)}\left(\left(e^{-\alpha\frac{R}{2}(+\mu)}+e^{-\alpha\frac{R}{2}(-\mu)}\right)\left\{\left(-\alpha\frac{R}{2}\right)\left(2\lambda+\left(\lambda^2-1\right)\left(-\alpha\frac{R}{2}\right)\right\}e^{-\alpha\frac{R}{2}(\lambda)}\right)+\right.$$
$$\left.\left(e^{-\alpha\frac{R}{2}(\lambda)}\right)\left(\alpha\frac{R}{2}\right)\left(-2\mu+\left(1-\mu^2\right)\left[-\left(-\alpha\frac{R}{2}\right)e^{-\alpha\frac{R}{2}(\mu)}+\left(\alpha\frac{R}{2}\right)e^{\alpha\frac{R}{2}(\mu)}\right]\right)\right)+$$
$$-\left(\frac{Z_Ae^2}{\frac{R}{2}(\lambda+\mu)}+\frac{Z_Be^2}{\frac{R}{2}(\lambda-\mu)}\right)\left(e^{-\alpha\frac{R}{2}(\lambda+\mu)}+e^{-\alpha\frac{R}{2}(\lambda-\mu)}\right)=E\left(e^{-\alpha\frac{R}{2}(\lambda+\mu)}+e^{-\alpha\frac{R}{2}(\lambda-\mu)}\right)$$

and re-arranging

$$-\frac{4\hbar^2}{2mR^2\left(\lambda^2-\mu^2\right)}\left\{\left(-\alpha\frac{R}{2}\right)\left(2\lambda+\left(\lambda^2-1\right)\left(-\alpha\frac{R}{2}\right)\right)+\right.$$
$$\left.\left(\alpha\frac{R}{2}\right)\left(-2\mu+\left(1-\mu^2\right)\left(\alpha\frac{R}{2}\right)\right)\right\}+$$
$$-\left(\frac{Z_Ae^2}{\frac{R}{2}(\lambda+\mu)}+\frac{Z_Be^2}{\frac{R}{2}(\lambda-\mu)}\right)=E$$

which becomes, upon artful simplification:

$$-\frac{4\hbar^2}{2mR^2\left(\lambda^2-\mu^2\right)}\left(-\alpha\frac{R}{2}\right)\left(2(\lambda-\mu)+\left(\lambda^2-\mu^2\right)\left(-\alpha\frac{R}{2}\right)\right) - \left(\frac{Z_Ae^2}{\frac{R}{2}(\lambda+\mu)}+\frac{Z_Be^2}{\frac{R}{2}(\lambda-\mu)}\right)=E$$

Unless I've made a calculus mistake, something completely inside the realm of reason, there is no complete cancellation here, and the wave function does not solve the differential equation.

VIII. DO THE H ATOM ALONE STARTING HERE

It is fun to check that the 1s orbital does work properly in the single nucleus case.

$$-\frac{\hbar^2}{2m}\left(\frac{4}{R^2\left(\lambda^2-\mu^2\right)}\left[\left(e^{-\alpha\frac{R}{2}(+\mu)}\right)\left(\frac{\partial\left(\left(\lambda^2-1\right)\frac{\partial e^{-\alpha\frac{R}{2}\lambda}}{\partial\lambda}\right)}{\partial\lambda}\right)+ e^{-\alpha\frac{R}{2}\lambda}\left(\frac{\partial\left(\left(1-\mu^2\right)\frac{\partial\left(e^{-\alpha\frac{R}{2}(+\mu)}\right)}{\partial\mu}\right)}{\partial\mu}\right)\right]\right) - \left(\frac{Z_Ae^2}{\frac{R}{2}(\lambda+\mu)}+\frac{Z_Be^2}{\frac{R}{2}(\lambda-\mu)}\right)\left(e^{-\alpha\frac{R}{2}(\lambda+\mu)}\right)=E\left(e^{-\alpha\frac{R}{2}(\lambda+\mu)}\right) \tag{8.1}$$

which is, taking the first derivative

$$-\frac{\hbar^2}{2m}\left(\frac{4}{R^2\left(\lambda^2-\mu^2\right)}\left[\left(e^{-\alpha\frac{R}{2}(+\mu)}\right)\left(\frac{\partial\left(\left(\lambda^2-1\right)\left(-\alpha\frac{R}{2}\right)e^{-\alpha\frac{R}{2}\lambda}\right)}{\partial\lambda}\right)+ e^{-\alpha\frac{R}{2}\lambda}\frac{\partial\left(\left(1-\mu^2\right)\left(-\alpha\frac{R}{2}\right)\left(e^{-\alpha\frac{R}{2}(+\mu)}\right)\right)}{\partial\mu}\right]\right) - \left(\frac{Z_Ae^2}{\frac{R}{2}(\lambda+\mu)}+\frac{Z_Be^2}{\frac{R}{2}(\lambda-\mu)}\right)\left(e^{-\alpha\frac{R}{2}(\lambda+\mu)}\right)=E\left(e^{-\alpha\frac{R}{2}(\lambda+\mu)}\right) \tag{8.2}$$

or, taking the partial derivative again

$$-\frac{\hbar^2}{2m}\frac{4}{R^2\left(\lambda^2-\mu^2\right)}\left[\left(2\lambda+\left(\lambda^2-1\right)\left(-\alpha\frac{R}{2}\right)\right)\left(-\alpha\frac{R}{2}\right) + \left(-2\mu+\left(1-\mu^2\right)\left(-\alpha\frac{R}{2}\right)\right)\left(-\alpha\frac{R}{2}\right)\right] - \frac{Ze^2}{\frac{R}{2}(\lambda+\mu)}=E$$

which becomes

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

and rearranging terms once again

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

$$-\frac{Ze^2}{\frac{R}{2}(\lambda+\mu)} = E$$

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.,

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

makes the first term vanish, and

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

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

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

which cleans up to

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

a most famous, at this point, result.

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[1] C. W. David, J. Chem. Ed., 59,288 (1982).

[2] 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.