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# Aromatic Units, Why We Need Them and How They Work

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# Atomic Units, Why We Need Them and How they Work

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## I. INTRODUCTION

We assume that the reader has gone through an initial discussion of the quantum mechanics of atoms and molecules, and seeks an alternative treatment which looks at the same material backwards, i.e., motivated by the question of why we have done what we've done? The *raison d'être* for changing units to "atomic units" is usually treated laconically as a side issue. Therefore, we here explore "atomic units" in a manner different from standard textbook treatments.

## II. EIGENFUNCTIONALITY

The world of atomic physics is "so small" that the unit systems we use in the macroscopic world you and I inhabit (by default) are inappropriate. To create a system of units which makes sense, one starts with the H-atom's associated Schrödinger Equation:

$$-\frac{\hbar^2}{2m}\nabla^2\psi - \frac{Ae^2}{R}\psi = E\psi \quad (1)$$

where we have used  $m_e$  for the mass of an electron, called the infinite nuclear mass approximation. If one carried out the more exact two body problem of the nucleus and extra nuclear electron moving about the common center of gravity, this would have become  $\mu$  i.e.,

$$\frac{1}{m_p} + \frac{1}{m_e} = \frac{1}{\mu}$$

and  $m_e \rightarrow \mu$ , the reduced mass of the entire H-atom. "A" is the atomic number of the nucleus (A=1 means H atom, A=2 means  $He^+$ , A=3 means  $Li^{2+}$ , where Ae is the charge on the nucleus and e is the charge on the electron). This is

We make only one notational change, defining the Cartesian and spherical polar forms of the Laplacian:

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$$\nabla_{(X,Y,Z)}^2 = \frac{\partial^2}{\partial X^2} + \frac{\partial^2}{\partial Y^2} + \frac{\partial^2}{\partial Z^2} = \nabla_{(R,\theta,\phi)}^2 = \frac{1}{R^2} \frac{\partial}{\partial R} \left( R^2 \frac{\partial}{\partial R} \right) + \frac{1}{R^2 \sin^2 \vartheta} \left( \sin \vartheta \frac{\partial}{\partial \vartheta} \left( \frac{\sin \vartheta}{\partial \vartheta} \right) + \frac{\partial^2}{\partial \phi^2} \right) \quad (2)$$

i.e., we use capital letters to indicate coordinates in centimeters (meters might be preferred, but since both are absurd from an atomic/molecular point of view, let's not go crazy), where  $R = \sqrt{X^2 + Y^2 + Z^2}$ . One has, for the ground (1s) state,

$$\psi_{1s}(R[cm], \vartheta[rad], \phi[rad]) = e^{-\alpha R[cm]}$$

where  $\alpha$  is a (to be determined) constant whose units must be  $cm^{-1}$  (This one time the units have been indicated in square brackets.). Substituting this 1s solution into the Schrödinger Equation one has

$$-\frac{\hbar^2}{2m} \nabla_{(R,\theta,\phi)}^2 e^{-\alpha R} - \frac{Ae^2}{R} e^{-\alpha R} = E e^{-\alpha R}$$

which is

$$-\frac{\hbar^2}{2m} \frac{1}{R^2} \frac{\partial}{\partial R} \left( R^2 \frac{\partial e^{-\alpha R}}{\partial R} \right) - \frac{Ae^2}{R} e^{-\alpha R} = E e^{-\alpha R}$$

where, of course, we only needed the radial part of the Laplacian. Carrying out the first (inner) partial derivative, we obtain

$$-\frac{\hbar^2}{2m} \frac{1}{R^2} \frac{\partial}{\partial R} \left( R^2 (-\alpha e^{-\alpha R}) \right) - \frac{Ae^2}{R} e^{-\alpha R} = E e^{-\alpha R}$$

and, after carrying out the second (outer) partial derivative, we have

$$-\frac{\hbar^2}{2m} \frac{1}{R^2} (\alpha^2 R^2 - 2\alpha R) e^{-\alpha R} - \frac{Ae^2}{R} e^{-\alpha R} = E e^{-\alpha R}$$

which simplifies to

$$-\frac{\hbar^2}{2m} \frac{1}{R^2} (\alpha^2 R^2 - 2\alpha R) - \frac{Ae^2}{R} = E$$

which becomes upon re-grouping

$$-\frac{\hbar^2}{2m} \alpha^2 + \left( \frac{\alpha \hbar^2}{m} - Ae^2 \right) \frac{1}{R} = E$$

Re-writing this in a suggestive form:

$$g(R) = -\frac{\hbar^2}{2m} \alpha^2 + \left( \frac{\alpha \hbar^2}{m} - Ae^2 \right) \frac{1}{R} - E = 0 \quad (3)$$

we see that if the left hand side, called temporarily  $g(R)$ , is to equal zero for arbitrary values of  $\alpha$ , then we have an equation here for a *special radius*,  $R^*$ , for which  $g(R^*) = 0$ . But we are charged with finding solutions to the original Schrödinger Equation for all  $R$ , not just some special one. *Therefore* we are forced to *choose* a value of  $\alpha$  which makes it possible for the equation  $g(R)$  to equal zero for all values of  $R$ .

If the coefficient of  $1/R$  were to vanish then  $E$  (a constant) would be identified, i.e., if

$$\left( \frac{\alpha \hbar^2}{m} - Ae^2 \right) = 0 \quad (4)$$

then Equation 3 would become

$$g(R) = -\frac{\hbar^2}{2m} \alpha^2 + (0) \frac{1}{R} - E = 0 \quad (5)$$

This is certainly possible (i.e., not a function of  $R$  anymore)! To achieve this, we need to choose  $\alpha$ :

$$\alpha = \frac{mAe^2}{\hbar^2}$$

and, squaring,

$$\alpha^2 = \frac{m^2 A^2 e^4}{\hbar^4}$$

so that, left multiplying both sides by  $-\frac{\hbar^2}{2m}$ , we then obtain

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

arriving finally at

$$E = -\frac{A^2 e^4 m}{2\hbar^2} \quad (6)$$

which is a well known result!

### III. WHAT WOULD CHANGE IF WE CHANGE THE SCALE OF X, Y AND Z

Knowing  $\alpha$ 's value, we return to the Schrödinger Equation:

$$-\frac{\hbar^2}{2m} \nabla_{(X,Y,Z)}^2 \psi(X, Y, Z) - \frac{Ae^2}{R} \psi(X, Y, Z) = E \psi(X, Y, Z)$$

or

$$-\frac{\hbar^2}{2m} \nabla_{(R,\theta,\phi)}^2 \psi(R, \theta, \phi) - \frac{Ae^2}{R} \psi(R, \theta, \phi) = E \psi(R, \theta, \phi)$$

(again, we use our non-standard notation to remind the reader that the Laplacian is still in terms of the original (cm) coordinate scheme) where we know that  $\hbar$  is in erg-seconds,  $m_e$  (the mass of the electron) is in grams,  $e$ , the charge on the electron ( $4.8 \times 10^{-10}$ ) is in statcoulomb, and  $E$ , the energy, is in ergs. This is the cgs system. Let us define a dimensionless radius,  $r$ , so that

$$r = \beta R ; R = r/\beta$$

which means

$$X = x/\beta ; Y = y/\beta ; Z = z/\beta$$

where  $\beta$  is a constant (to be determined) whose units are  $cm^{-1}$ , and  $x$ ,  $y$ , and  $z$  are to be **forced** dimensionless. Then

$$\frac{\partial}{\partial R} = \frac{\partial r}{\partial R} \frac{\partial}{\partial r} = \beta \frac{\partial}{\partial r}$$

using the chain rule. Then, we have

$$\frac{1}{R^2} \left( \frac{\partial R^2}{\partial R} \left( \frac{\partial e^{-\alpha R}}{\partial R} \right) \right) = \frac{1}{(r/\beta)^2} \beta \frac{\partial \left( (r/\beta)^2 \beta \frac{\partial e^{-\alpha r/\beta}}{\partial r} \right)}{\partial r}$$

so, we obtain

$$-\frac{\hbar^2}{2m} \frac{\beta}{\left(\frac{r}{\beta}\right)^2} \frac{\partial \left( (r/\beta)^2 \beta \frac{\partial e^{-\alpha r/\beta}}{\partial r} \right)}{\partial r} - \frac{Ae^2}{r/\beta} e^{-\alpha r/\beta} = E e^{-\alpha r/\beta}$$

or, taking the second partial derivative

$$-\frac{\hbar^2}{2m} \frac{\beta \alpha}{r^2} \frac{\partial \left( r^2 e^{-\alpha r/\beta} \right)}{\partial r} - \frac{Ae^2}{r/\beta} e^{-\alpha r/\beta} = E e^{-\alpha r/\beta}$$

so

$$-\frac{\hbar^2}{2m} \frac{\beta \alpha}{r^2} \left( 2r e^{-\alpha r/\beta} - r^2 \frac{\alpha}{\beta} e^{-\alpha r/\beta} \right) - \frac{Ae^2}{r/\beta} e^{-\alpha r/\beta} = E e^{-\alpha r/\beta}$$

$$+\frac{\hbar^2 \beta \alpha}{mr} - \frac{\hbar^2 \alpha^2}{2m} - \frac{Ae^2}{r/\beta} = E \quad (7)$$

and with  $A = 1$ ,

$$\left(\frac{\hbar^2\beta\alpha}{m} - e^2\beta\right)\frac{1}{r} - \frac{\hbar^2\alpha^2}{2m} - E = 0 = \beta\left(\frac{\hbar^2\alpha}{m} - e^2\right)\frac{1}{r} - \frac{\hbar^2\alpha^2}{2m} - E$$

(which shows that the argument concerning  $\alpha$  is independent of the value of  $\beta$ , since the coefficient of  $\frac{1}{r}$  is the same as in Equation 4) i.e.,  $\beta$  factors out.

We chose to set  $A=1$  momentarily, so that later we can handle the entire isoelectronic series of one electron atoms and ions in one fell swoop. The fact that  $\beta$  ultimately factors out of the first term (above)  $\frac{\hbar^2\alpha}{m} - e^2 \rightarrow 0$  indicates that the argument about choosing  $\beta$  will *not* influence the *form* of the Schrödinger Equation, i.e., we are free to choose it as we wish, and we choose to make it so that the exponential has no constants in it, i.e., we choose  $\frac{\alpha}{\beta} = 1$  as an appropriate form. This makes the exponential (since  $R = r/\beta$ )

$$e^{-\alpha R} \rightarrow e^{-\alpha r/\beta} \rightarrow e^{-r} = e^{-\sqrt{x^2+y^2+z^2}}$$

(said another way (substituting for  $\alpha$ ),  $e^{-\frac{me^2}{\hbar^2}R} \rightarrow e^{-\frac{me^2}{\hbar^2}r/\beta}$ ) where, or course,  $r = \sqrt{x^2 + y^2 + z^2}$ , and  $x$ ,  $y$ ,  $z$  and  $r$  all are now dimensionless.  $\psi(x, y, z)$  is a clean function if ever there was one.

With  $A = 1$  we have

$$\beta = \alpha = \frac{me^2}{\hbar^2} \quad (8)$$

i.e.,

$$\beta = \frac{\text{gram}(\text{dyne}^{1/2}\text{cm})^2}{(\text{erg} - \text{sec})^2} = \frac{\text{gram} - \text{dyne} - \text{cm}^2}{\text{erg}^2 - \text{sec}^2} = \frac{\text{gram} - \text{cm}}{\text{erg} - \text{sec}^2} = \text{cm}^{-1}$$

(which has the expected units reciprocal centimeters in cgs units). Further

$$\frac{1}{\beta} = \frac{\left(\frac{6.627 \times 10^{-27}}{(2 \times 3.14159)}\right)^2}{9.1 \times 10^{-28}(4.8 \times 10^{-10})^2} \sim 5.3 \times 10^{-9} \text{cm}$$

This happens to be approximately  $0.5\text{\AA}$ , the Bohr radius.

For the *isoelectronic one electron series* the 1s orbital would now be  $e^{-Ar}$ .

#### IV. FORMING THE DIMENSIONLESS SCHRÖDINGER EQUATION

Again, returning to the Schrödinger Equation, we had

$$-\frac{\hbar^2}{2m}\nabla_{(X,Y,Z)}^2\psi(X,Y,Z) - \frac{Ae^2}{R}\psi(X,Y,Z) = E\psi(X,Y,Z)$$

We re-write it as

$$-\frac{\hbar^2}{2m}\left\{\frac{\partial^2}{\partial X^2} + \frac{\partial^2}{\partial Y^2} + \frac{\partial^2}{\partial Z^2}\right\}\psi(X,Y,Z) - \frac{Ae^2}{R}\psi(X,Y,Z) = E\psi(X,Y,Z)$$

and since

$$R = \beta r ; r = R/\beta$$

we can write it in components using

$$X = x/\beta ; Y = y/\beta ; Z = z/\beta$$

where  $x, y, \& z$  are the new coordinates. the squared sum of which lead to  $r^2$ .

From the chain rule, we obtain

$$\frac{\partial}{\partial X} = \frac{\partial x}{\partial X} \frac{\partial}{\partial x} = \beta \frac{\partial}{\partial x}$$

$$\frac{\partial^2}{\partial X^2} = \beta^2 \frac{\partial^2}{\partial x^2}$$

so (with similar terms for  $y$  and  $z$ ) we transform the Laplacian from the set  $X, Y, Z$  to  $x, y, z$ .

$$-\frac{\beta^2 \hbar^2}{2m} \nabla_{(x,y,z)}^2 \psi(x,y,z) - \frac{Ae^2 \beta}{\sqrt{x^2 + y^2 + z^2}} \psi(x,y,z) = E \psi(x,y,z)$$

which becomes (using Equation 8)

$$-\frac{1}{2} \nabla_{(r,\theta,\phi)}^2 \psi - \frac{m A e^2}{\hbar^2 \beta r} \psi = \frac{m E}{\beta^2 \hbar^2} \psi$$

so, with A=1, choosing,

$$\frac{m e^2}{\hbar^2 \beta} = 1$$

one recovers Equation 8:

$$\beta = \frac{m e^2}{\hbar^2}$$

where we pull out the A so that later we can treat more than just H.

Continuing, we have

$$-\frac{1}{2} \nabla_{(r,\theta,\phi)}^2 \psi - \frac{1}{r} \psi = \frac{m E}{\hbar^2 \left(\frac{m e^2}{\hbar^2}\right)^2} \psi = \frac{E \hbar^2}{m e^4} \psi = \epsilon \psi \quad (9)$$

which makes

$$E = \epsilon \left( \frac{m e^4}{\hbar^2} \right) ; \quad \frac{\text{gram dyne}^2 \text{cm}^4}{\text{erg}^2 \text{sec}^2} = \text{erg} \quad (10)$$

( $\epsilon$  is unit-less, hereafter to be called a.u. for atomic unit) which resembles the Rydberg we've come to know and love (Equation 6):

$$Ry = \frac{m e^4}{2 \hbar^2}$$

With A=1 (Hydrogen) and n=1 (the ground state), one then has

$$E_H = -Ry = -\frac{m e^4}{2 \hbar^2} = -\frac{9.1 \times 10^{-28} (4.8 \times 10^{-10})^4}{2 \left( \frac{6.627 \times 10^{-27}}{2 * 3.14159} \right)^2}$$

which, since it comes out in ergs, can be converted to the easier to remember eV value using  $6.25 \times 10^{11} \frac{\text{eV}}{\text{erg}}$ . Thus

---

```
psi := exp(-alpha*r);
t1 := - ((1)/(2))*(1/r^2)*diff(r^2*diff(psi,r),r)-(1/r)*psi;
t1 := expand(t1/psi);#this line shows why the alpha=1 choice is needed
E_1s := subs(alpha=1,t1);
```

---

The resultant answer (-1/2) validates the assigning of the value of the a.u. carried out previously.

in this case, rearranging Equation 10 we have

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

and therefore

$$-Ry \frac{\hbar^2}{e^4 m} = \left( \frac{m e^4}{2 \hbar^2} \right) \left( -\frac{\hbar^2}{e^4 m} \right) = -\frac{1}{2} = \epsilon (\text{in au})$$

When E is (about) -13.6 eV for Z=1 we have  $\epsilon = \frac{1}{2} \text{au}$  so

$$\frac{1}{2} \text{au} = 13.6 \text{eV}$$

and

$$1 \text{au} = 2 * 13.6 \text{eV}$$

## V. VERIFYING EIGENFUNCTIONALITY

Once one has a dimensionless form for the Schrödinger Equation, 9, it becomes simple to “verify” whether or not a function is an eigenfunction of the Hamiltonian, i.e., solves the Schrödinger Equation. Consider, again, the 1s case,

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

We ask the question, what value of  $\alpha$  is required to solve the Schrödinger Equation? We had

$$-\frac{1}{2} \nabla_{(r,\theta,\phi)}^2 \psi - \frac{1}{r} \psi = \epsilon \psi$$

which is, for s-states

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial \psi}{\partial r} \right) - \frac{1}{r} \psi = \epsilon \psi$$

Here is a MAPLE example for showing the above:

## VI. RESTORING THE A VALUE

We had in Equation 7

$$+\frac{\hbar^2 \beta \alpha}{m r} - \frac{\hbar^2 \alpha^2}{2m} - \frac{A e^2}{r} = E$$

where we set A equal to 1 in order to proceed. Now, we allow A to continue having a value greater than or equal to 1, so

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

and now we set the coefficient of  $\frac{1}{r}$  equal to zero so that this equation can be true for all values of r, i.e.,

$$+ \beta \left( \frac{\hbar^2 \alpha}{m} - A e^2 \right) = 0$$

and since  $\beta$  isn't zero, the part in parenthesis must be, so

$$+ \frac{\hbar^2 \alpha}{m} = A e^2$$

which means that the A dependent value of  $\alpha$  should be

$$\alpha = \frac{A e^2 m}{\hbar^2}$$

and since  $\beta = \frac{m e^2}{\hbar^2}$

$$e^{-\alpha R} \rightarrow e^{-\alpha r / \beta} \rightarrow e^{-A r} = e^{-A \sqrt{x^2 + y^2 + z^2}}$$

## VII. THE 2S ORBITAL

We need the Laplacian in spherical polar coordinates rather than Cartesian coordinates (This is neither necessary nor sufficient, just expedient).

$$\nabla_{r,\vartheta,\phi}^2 = \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin^2 \vartheta} \left( \sin \vartheta \frac{\partial}{\partial \vartheta} \left( \frac{\sin \vartheta}{\sin \vartheta} \frac{\partial}{\partial \vartheta} \right) + \frac{\partial^2}{\partial \phi^2} \right)$$

We are interested in an s orbital, where the angular part of the wave function is a constant possessing no partial derivatives with respect to angles. Thus, we have

$$-\frac{1}{2} \nabla^2 \psi - \frac{A}{r} \psi = \epsilon \psi = -\frac{1}{2} \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) - \frac{A}{r} \psi$$

(Equation 9) as the equation for the dimensionless Schrödinger Equation. Now, we wish to attempt the discussion for the 2s orbital, to illustrate some aspects of the dimensionless form. We assume  $\psi_{test}$  (the analysis which leads to the following form will be pursued when the full H atom is discussed) exists and has the form

$$\psi_{test} = (1 + \gamma r) e^{-Ar/\delta}$$

so we have

$$-\frac{1}{2} \left( \frac{1}{r^2} \frac{\partial r^2 \frac{\partial \psi_{test}}{\partial r}}{\partial r} \right) - \frac{A}{r} (1 + \gamma r) e^{-Ar/\delta} = \epsilon (1 + \gamma r) e^{-Ar/\delta}$$

or

$$-\frac{1}{2} \left( \frac{1}{r^2} \frac{\partial \left( r^2 \left( \gamma e^{-Ar/\delta} - \frac{A}{\delta} (1 + \gamma r) e^{-Ar/\delta} \right) \right)}{\partial r} \right) - \frac{A}{r} (1 + \gamma r) e^{-Ar/\delta} = \epsilon (1 + \gamma r) e^{-Ar/\delta}$$

or

$$-\frac{1}{2} \left( \frac{1}{r^2} \frac{\partial \left( r^2 \left( \gamma - \frac{A}{\delta} (1 + \gamma r) \right) e^{-Ar/\delta} \right)}{\partial r} \right) - \frac{A}{r} (1 + \gamma r) e^{-Ar/\delta} = \epsilon (1 + \gamma r) e^{-Ar/\delta}$$

yielding

$$\begin{aligned} -\frac{1}{2} \left[ \frac{1}{r^2} \left( 2r \left( \gamma - \frac{A}{\delta} (1 + \gamma r) \right) + r^2 \left( -\frac{A}{\delta} (\gamma) \right) + r^2 \left( \gamma - \frac{A}{\delta} (1 + \gamma r) \right) \frac{-A}{\delta} \right) \right] e^{-Ar/\delta} \\ - \frac{A}{r} (1 + \gamma r) e^{-Ar/\delta} = \epsilon (1 + \gamma r) e^{-Ar/\delta} \end{aligned} \quad (11)$$

which becomes, assuming that the equal sign is ultimately going to hold, and that therefore the exponential will cancel from each term,

$$\begin{aligned} -\frac{1}{2} \left[ \left( \frac{2}{r} \left( \gamma - \frac{A}{\delta} (1 + \gamma r) \right) \right) - \frac{A\gamma}{\delta} - \left( \gamma - \frac{A}{\delta} (1 + \gamma r) \right) \frac{A}{\delta} \right] \\ - \frac{A}{r} (1 + \gamma r) = \epsilon (1 + \gamma r) \end{aligned} \quad (12)$$

or expanding selectively,

$$\begin{aligned} & \left( -\frac{1}{r} \left( \gamma - \frac{A}{\delta} (1 + \gamma r) \right) \right) + \frac{1}{2} \frac{A\gamma}{\delta} \\ & + \frac{1}{2} \left( \gamma - \frac{A}{\delta} (1 + \gamma r) \right) \frac{A}{\delta} - \frac{A}{r} (1 + \gamma r) = \epsilon (1 + \gamma r) \end{aligned} \quad (13)$$

which becomes

$$-\frac{\gamma}{r} + \frac{A}{\delta r} (1 + \gamma r) + \frac{1}{2} \frac{A\gamma}{\delta} + \frac{A\gamma}{2\delta} - \frac{A^2}{2\delta^2} (1 + \gamma r) - \frac{A}{r} (1 + \gamma r) = \epsilon (1 + \gamma r) \quad (14)$$

or

$$-\frac{\gamma}{r} + \frac{A}{\delta r} (1 + \gamma r) + \frac{A\gamma}{\delta} - \frac{A^2}{2\delta^2} (1 + \gamma r) - \frac{A}{r} (1 + \gamma r) = \epsilon (1 + \gamma r) \quad (15)$$

which becomes

$$-\frac{\gamma}{r} \left( 1 - \frac{Ar}{\delta} \right) + \frac{A}{\delta r} (1 + \gamma r) - \frac{A^2}{2\delta^2} (1 + \gamma r) - \frac{A}{r} (1 + \gamma r) = \epsilon (1 + \gamma r) \quad (16)$$

But, adding and subtracting  $\gamma r$

$$\left( 1 - \frac{Ar}{\delta} \right) = \left( 1 - \frac{Ar}{\delta} + \gamma r - \gamma r \right)$$

becomes

$$\left( 1 - \frac{Ar}{\delta} \right) = (1 + \gamma r)$$

and the part in square brackets can be forced to vanish if  $\frac{A}{\delta} + \gamma = 0$ . Then Equation 16 becomes

$$\gamma = -\frac{A}{\delta}$$

and therefore

$$+\frac{A}{\delta r} (1 + \gamma r) + \frac{A}{\delta r} (1 + \gamma r) - \frac{A^2}{2\delta^2} (1 + \gamma r) - \frac{A}{r} (1 + \gamma r) = \epsilon (1 + \gamma r) \quad (17)$$

or

$$+2\frac{A}{\delta r} (1 + \gamma r) - \frac{A}{r} (1 + \gamma r) - \frac{A^2}{2\delta^2} (1 + \gamma r) = \epsilon (1 + \gamma r) \quad (18)$$

so that the term

$$\left( \frac{2}{\delta} - 1 \right) \left( \frac{A}{r} \right) (1 + \gamma r)$$

can be forced to vanish if

$$\frac{2}{\delta} - 1 = 0$$

then  $\delta = 2$  is the required choice, and then

$$\epsilon = -\frac{A^2}{2 \times 2^2}$$

which is the “right” answer.

## VIII. MAPLE TREATMENT OF THE 2S ORBITAL

In MAPLE, we have (using a simpler scheme assuming  $\delta$  is 2 at the outset):

```
psi2 := (1+gamma*r)*exp(-(alpha/2)*r);# we've made some assumptions here
t2 := - ((1)/(2))*(1/r^2)*diff(r^2*diff(psi2,r),r)-(1/r)*psi2;
t2 := expand(t2/psi2);
t2a := coeff(t2,(1+gamma*r)^(-1));
t2b := coeff(t2a,1/r);
t2 := normal(subs(alpha=1,t2));
E_2s := normal(subs(gamma=-1/2,t2));
```

The answer here can be rewritten

$$-\frac{1}{2} \frac{1}{2^2} = -\frac{1}{8}$$

which is the correct value.