2.18: 110. Critique of the Centrifugal Effect in the Hydrogen Atom

Some quantum textbooks invoke the concept of effective potential energy when introducing the quantum mechanical treatment of the hydrogen atom to undergraduate audiences. I will show that this concept is deeply flawed and leads to an incorrect analysis of the energy contributions to the various electronic states of the hydrogen atom. We begin with the one-dimensional Schrödinger radial equation (French and Taylor, An Introduction to Quantum Physics, pages 519-523) expressed in atomic units (e = m_e = h/2π = 4πε$_o$ = 1).

$$H\Psi(r) = (T+V)\Psi(r) = E\Psi(r) \quad \text{where} \quad H = -\frac{1}{2}\frac{d^2}{dr^2}\blacksquare + \frac{L(L+1)}{2r^2}\blacksquare - \frac{1}{r}\blacksquare$$

Solving Schrödinger′s equation yields the eigenstates and their eigenvalues, along with the ability to calculate the expectation value for any observable for which the appropriate operator is known. The allowed energy values are $E(n) = -0.5n^{-2}$, where the quantum number, n, can take integer values beginning with unity. The quantized electronic energies for the one-electron hydrogen atom do not depend on the angular momentum quantum number, L.

The problem I wish to deal with involves the middle term in the Hamiltonian given above. Some authors call it the centrifugal potential, combine it with the third term which is the coulombic potential energy, and call the combination the effective potential energy. In support of this maneuver they invoke the idea of centrifugal force, which unfortunately for them is only an apparent force (actually it′s just plain fictitious). Centrifugal means moving away from the center and so one might assume (and some authors claim) that the greater the centrifugal effect (″force″), i.e. the larger the L quantum number, the farther from the nucleus the electron should be for any given value of the principal quantum number n.

This, unfortunately, simply isn′t the case. The radial expectation values for the hydrogen atom are given below, along with a table that shows that the larger the angular momentum quantum number, the closer on average the electron is to the nucleus for any given n quantum number. This effect is also shown graphically in the Appendix.

$$r(n,\ L) = \frac{3n^2 - L(L+1)}{2} \quad \begin{pmatrix} L & 0 & 1 & 2 & 3 \\ n=1 & 1.5 & ' & ' & ' \\ n=2 & 6 & 5 & ' & ' \\ n=3 & 13.5 & 12.5 & 10.5 & ' \\ n=4 & 24 & 23 & 21 & 18 \end{pmatrix}$$

This is not the only difficulty with the effective potential energy approach. It also violates the virial theorem, which we all know is sacrosanct when it comes to quantum mechanical analyses. In other words, if your analysis or calculation violates the virial theorem discard it, because it′s wrong! The virial theorem for the hydrogen atom is <E>= -<T> = <V>/2. The expectation values for the centrifugal and coulombic contributions to the total energy are provided below. Note that I have used ″V″ for the centrifugal term, assuming that it really is a potential energy term. If this assignment is valid the virial theorem will be satisfied.

$$V_{centrifugal}(n,\ L) = \frac{L(L+1)}{2n^3\left(L+\frac{1}{2}\right)} \quad V_{coulomb}(n) = -\frac{1}{n^2}$$

Next the virial theorem is used as a check on this assignment using the version / = 0.5. What we see below is that the virial theorem is violated for all states for which L > 0. This strongly suggests that the centrifugal term is not a potential energy contribution, but a kinetic energy term.

$$1s \quad n=1 \quad L=0 \quad \frac{E(n)}{V_{centrifugal}(n,\ L)+V_{coulomb}(n)} = 0.5$$

$$2s \quad n=2 \quad L=0 \quad \frac{E(n)}{V_{centrifugal}(n,\ L)+V_{coulomb}(n)} = 0.5$$

$$2p \quad n=2 \quad L=1 \quad \frac{E(n)}{V_{centrifugal}(n,\ L)+V_{coulomb}(n)} = 0.75$$

$$3s \quad n=3 \quad L=0 \quad \frac{E(n)}{V_{centrifugal}(n,\ L)+V_{coulomb}(n)} = 0.5$$

$$3p \quad n=3 \quad L=1 \quad \frac{E(n)}{V_{centrifugal}(n,\ L)+V_{coulomb}(n)} = 0.833$$

$$1s \quad n=3 \quad L=2 \quad \frac{E(n)}{V_{centrifugal}(n,\ L)+V_{coulomb}(n)} = 0.833$$

This suspicion is confirmed by recalculating the above results after taking out the centrifugal ″potential energy″ term.

$$1s \quad n=1 \quad L=0 \quad \frac{E(n)}{V_{coulomb}(n)} = 0.5$$

$$2s \quad n=2 \quad L=0 \quad \frac{E(n)}{V_{coulomb}(n)} = 0.5 \quad 2p \quad n=2 \quad L=1 \quad \frac{E(n)}{V_{coulomb}(n)} = 0.5$$

$$3s \quad n=3 \quad L=0 \quad \frac{E(n)}{V_{coulomb}(n)} = 0.5 \quad 3p \quad n=3 \quad L=1 \quad \frac{E(n)}{V_{coulomb}(n)} = 0.5$$

$$3d \quad n=3 \quad L=2 \quad \frac{E(n)}{V_{coulomb}(n)} = 0.5$$

While this is decisive, we will also show that the virial theorem (in the form <T>/<V> = -1/2) is satisfied with expectation value calculations using the correct kinetic energy operator.

$$T = -\frac{1}{2}\frac{d^2}{dr^2}\blacksquare + \frac{L(L+1)}{2r^2}\blacksquare$$

This will be demonstrated using the 3s, 3p and 3d eigenfunctions. The n = 1, 2 and 4 eigenfunctions are provided in the Appendix.

$$\Psi_{3s}(r) = \frac{2}{\sqrt{27}}\left(1 - \frac{2}{3}r + \frac{2}{27}r^2\right)r\exp\left(-\frac{2}{3}\right) \qquad \Psi_{3p}(r) = \frac{8}{27\sqrt{6}}\left(1 - \frac{r}{6}\right)r^2\exp\left(\frac{-r}{3}\right) \qquad \Psi_{3d}(r) = \frac{4}{81\sqrt{30}}r^2\exp\left(\frac{-r}{3}\right)$$

$$3s \quad L=0 \quad \frac{\int_0^\infty \Psi_{3s}(r)\frac{-1}{2}\frac{d^2}{dr^2}\Psi_{3s}(r)dr + \int_0^\infty \frac{L(L+1)}{2r^2}\Psi_{3s}(r)^2 dr}{\int_0^\infty \frac{-1}{r}\Psi_{3s}(r)^2 dr} = -0.5$$

$$3p \quad L=1 \quad \frac{\int_0^\infty \Psi_{3p}(r)\frac{-1}{2}\frac{d^2}{dr^2}\Psi_{3p}(r)dr + \int_0^\infty \frac{L(L+1)}{2r^2}\Psi_{3p}(r)^2 dr}{\int_0^\infty \frac{-1}{r}\Psi_{3p}(r)^2 dr} = -0.5$$

$$3d \quad L=2 \quad \frac{\int_0^\infty \Psi_{3s}(r)\frac{-1}{2}\frac{d^2}{dr^2}\Psi_{3d}(r)dr + \int_0^\infty \frac{L(L+1)}{2r^2}\Psi_{3d}(r)^2 dr}{\int_0^\infty \frac{-1}{r}\Psi_{3d}(r)^2 dr} = -0.5$$

In summary, the "centrifugal effect" and the concept of "effective potential energy" are good examples of the danger in thinking classically about a quantum mechanical system. Furthermore, it's bad pedagogy to create fictitious forces and to mislabel energy contributions in a misguided effort to provide conceptual simplicity. Other concepts in this category, in my opinion, are screening and effective nuclear charge.

Appendix

The following calculations demonstrate that wave functions used are eigenfunctions of the energy operator.

$$1s \quad L=0 \quad \frac{-1}{2}\frac{d^2}{dr^2}\Psi_{1s}(r) + \frac{L(L+1)}{2r^2}\Psi_{1s}(r) - \frac{1}{r}\Psi_{1s}(r) = E_{1s}\Psi_{1s}(r)\text{solve}, E_{1s} \to -\frac{1}{2}$$

$$2s \quad L=0 \quad \frac{-1}{2}\frac{d^2}{dr^2}\Psi_{2s}(r) + \frac{L(L+1)}{2r^2}\Psi_{2s}(r) - \frac{1}{r}\Psi_{2s}(r) = E_{2s}\Psi_{2s}(r)\text{solve}, E_{2s} \to -\frac{1}{8}$$

$$2p \quad L=1 \quad \frac{-1}{2}\frac{d^2}{dr^2}\Psi_{2p}(r) + \frac{L(L+1)}{2r^2}\Psi_{2p}(r) - \frac{1}{r}\Psi_{2p}(r) = E_{2p}\Psi_{2p}(r)\text{solve}, E_{2p} \to -\frac{1}{8}$$

$$3s \quad L=0 \quad \frac{-1}{2}\frac{d^2}{dr^2}\Psi_{3s}(r) + \frac{L(L+1)}{2r^2}\Psi_{3s}(r) - \frac{1}{r}\Psi_{3s}(r) = E_{3s}\Psi_{3s}(r)\text{solve}, E_{3s} \to -\frac{1}{18}$$

$$3p \quad L=1 \quad \frac{-1}{2}\frac{d^2}{dr^2}\Psi_{3p}(r) + \frac{L(L+1)}{2r^2}\Psi_{3p}(r) - \frac{1}{r}\Psi_{3p}(r) = E_{3p}\Psi_{3p}(r)\text{solve}, E_{3p} \to -\frac{1}{18}$$

$$3d \quad L=2 \quad \frac{-1}{2}\frac{d^2}{dr^2}\Psi_{3d}(r) + \frac{L(L+1)}{2r^2}\Psi_{3d}(r) - \frac{1}{r}\Psi_{3d}(r) = E_{3d}\Psi_{3d}(r)\text{solve}, E_{3d} \to -\frac{1}{32}$$

$$4s \quad L=0 \quad \frac{-1}{2}\frac{d^2}{dr^2}\Psi_{4s}(r) + \frac{L(L+1)}{2r^2}\Psi_{4s}(r) - \frac{1}{r}\Psi_{4s}(r) = E_{4s}\Psi_{4s}(r)\text{solve}, E_{4s} \to -\frac{1}{32}$$

$$4p \quad L=1 \quad \frac{-1}{2}\frac{d^2}{dr^2}\Psi_{4p}(r) + \frac{L(L+1)}{2r^2}\Psi_{4p}(r) - \frac{1}{r}\Psi_{4p}(r) = E_{4p}\Psi_{4p}(r)\text{solve}, E_{4p} \to -\frac{1}{32}$$

$$4d \quad L=2 \quad \frac{-1}{2}\frac{d^2}{dr^2}\Psi_{4d}(r) + \frac{L(L+1)}{2r^2}\Psi_{4d}(r) - \frac{1}{r}\Psi_{4d}(r) = E_{4d}\Psi_{4d}(r)\text{solve}, E_{4d} \to -\frac{1}{32}$$

$$4f \quad L=3 \quad \frac{-1}{2}\frac{d^2}{dr^2}\Psi_{4f}(r) + \frac{L(L+1)}{2r^2}\Psi_{4f}(r) - \frac{1}{r}\Psi_{4f}(r) = E_{4f}\Psi_{4f}(r)\text{solve}, E_{4f} \to -\frac{1}{32}$$
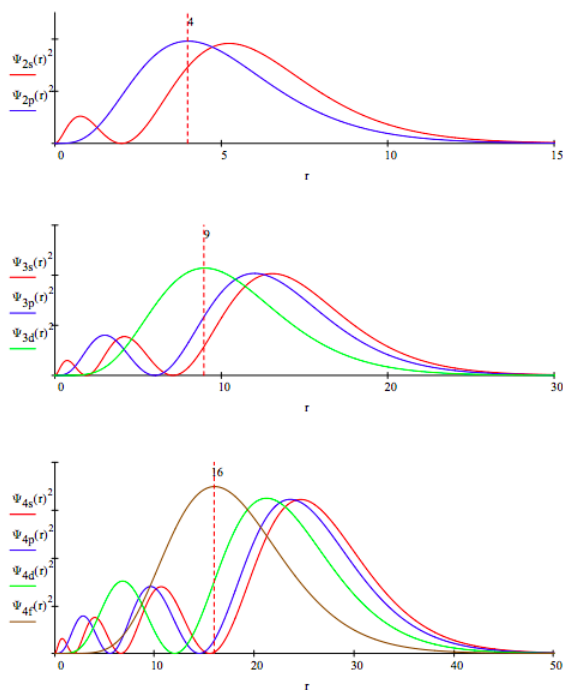
The computational results obtained using the three-dimensional Schrödinger equation,

$$\frac{-1}{2}\frac{d^2}{dr^2}(r,\ \Psi(\theta,\ \phi)) - \frac{1}{2r^2\sin(\theta)}\frac{d}{d\theta}\left(\sin(\theta)\frac{d}{d\theta}\Psi(r,\ \theta,\ \phi)\right) - \frac{1}{2r^2\sin(\theta)^2}\frac{d^2}{d\phi^2}\Psi(r,\ \theta,\ \phi) - \frac{1}{r}(r,\ \theta,\ \phi)$$
$$= E\Psi(r,\ \theta,\ \phi)$$

and its eigenfunctions are identical to those reported in this critique using the one-dimensional radial equation and its eigenfunctions.

Some authors call $\frac{L(L+1)}{2r^2}$ a centrifugal barrier because for L > 0 it prevents the electron from being very close the nucleus, without also noting that the greater the value of L the closer the electron is on average to the nucleus as this equation $r(n, L) = \frac{3n^2 - L(L+1)}{2}$ clearly shows. The radial distribution functions for n = 2, 3 and 4 clearly show this dual effect: as L increases for a given n the average distance to the nucleus decreases as does the electron density in the region nearest the nucleus. The maximum value of the radial distribution function for the highest L state is indicated on each graph.

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