

2.19: A Shorter Critique of the Centrifugal Effect in the Hydrogen Atom

On page 174 of Quantum Chemistry & Spectroscopy, 3rd ed. Thomas Engel derives equation 9.5 which is presented in equivalent form in atomic units ($e = m_e = \hbar/2\pi = 4\pi\epsilon_0 = 1$) here.

$$-\frac{1}{2r^2} \frac{d}{dr} \left(r^2 \frac{d}{dr} R(r) \right) + \left[\frac{L(L+1)}{2r^2} - \frac{1}{r} \right] R(r) = ER(r)$$

At the bottom of the page he writes,

Note that the second term (in brackets) on the left-hand side of Equation 9.5 can be viewed as a effective potential, $V_{\text{eff}}(r)$. It is made up of the centrifugal potential, which varies as $+1/r^2$, and the Coulomb potential, which varies as $-1/r$.

$$V_{\text{eff}}(r) = \frac{L(L+1)}{2r^2} - \frac{1}{r}$$

Engel notes that because of its positive mathematical sign, the centrifugal potential is repulsive, and goes on to say,

The net result of this repulsive centrifugal potential is to force the electrons in orbitals with $L > 0$ (p, d, and f electrons) on average farther from the nucleus than s electrons for which $L = 0$.

This statement is contradicted by the radial distribution functions shown in Figure 9.10 on page 187, which clearly show the opposite effect. As L increases the electron is on average closer to the nucleus. It is further refuted by calculations of the average value of the electron position from the nucleus as a function of the n and L quantum numbers. For a given n the larger L is the closer on average the electron is to the nucleus. In other words, these calculations support the graphical representation in Figure 9.10.

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

On page 180 in Example Problem 9.2, Engel introduces the virial theorem. For systems with a Coulombic potential energy, such as the hydrogen atom, it is $\langle V \rangle = 2\langle E \rangle = -2\langle T \rangle$. We will work with the version $\langle E \rangle / \langle V \rangle = 0.5$. The values of the energy, the so called centrifugal potential energy and the Coulombic potential energy are as shown below as a function of the appropriate quantum numbers.

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

The calculations below show that the virial theorem is violated for any state for which $L > 0$.

1s	$n = 1$	$L = 0$	$\frac{E(n)}{V_{\text{centrifugal}}(n, L) + V_{\text{coulomb}}(n)} = 0.5$
2s	$n = 2$	$L = 0$	$\frac{E(n)}{V_{\text{centrifugal}}(n, L) + V_{\text{coulomb}}(n)} = 0.5$
2p	$n = 2$	$L = 1$	$\frac{E(n)}{V_{\text{centrifugal}}(n, L) + V_{\text{coulomb}}(n)} = 0.75$
3s	$n = 3$	$L = 0$	$\frac{E(n)}{V_{\text{centrifugal}}(n, L) + V_{\text{coulomb}}(n)} = 0.5$
3p	$n = 3$	$L = 1$	$\frac{E(n)}{V_{\text{centrifugal}}(n, L) + V_{\text{coulomb}}(n)} = 0.833$
1s	$n = 3$	$L = 2$	$\frac{E(n)}{V_{\text{centrifugal}}(n, L) + V_{\text{coulomb}}(n)} = 0.833$

These calculations are now repeated eliminating the centrifugal term, showing that the virial theorem is satisfied and supporting the claim that the "centrifugal potential" is actually a kinetic energy term.

$$\begin{array}{llll}
 1s & n = 1 & L = 0 & \frac{E(n)}{V_{\text{coulomb}}(n)} = 0.5 \\
 2s & n = 2 & L = 0 & \frac{E(n)}{V_{\text{coulomb}}(n)} = 0.5 \\
 2p & n = 2 & L = 1 & \frac{E(n)}{V_{\text{coulomb}}(n)} = 0.5 \\
 3s & n = 3 & L = 0 & \frac{E(n)}{V_{\text{coulomb}}(n)} = 0.5 \\
 3p & n = 3 & L = 1 & \frac{E(n)}{V_{\text{coulomb}}(n)} = 0.5 \\
 3d & n = 3 & L = 2 & \frac{E(n)}{V_{\text{coulomb}}(n)} = 0.5
 \end{array}$$

We finish by rewriting the equation at the top with brackets showing that the first two terms are quantum kinetic energy and that the Coulombic term is the only potential energy term.

$$\left[-\frac{1}{2r^2} \frac{d}{dr} \left(r^2 \frac{d}{dr} R(r) \right) + \frac{L(L+1)}{2r^2} R(r) \right] - \frac{1}{r} R(r) = ER(r)$$

In summary, the "centrifugal potential" 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.

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