1. Hyperfine Hydrogen, but Twice the Fun

“Heavy hydrogen” is a common name for the hydrogen isotope deuterium, $^2\text{H}$, in which the proton in the nucleus is joined by a neutron. This has no effect on the Coulomb interaction that dominates atomic structure, but there are smaller, subtle effects, such as a slightly different reduced mass. A much more interesting effect is a large change in the hyperfine splitting of the atomic ground state. Following the steps from class, or section 6.5 in the text, calculate the wavelength (in cm) of the photon emitted during a hyperfine transition in the $^2\text{H}$ ground state. You will need to know that the deuterium nucleus (the ‘deuteron’) has a spin of 1, a mass equal to twice the proton mass, and a $g$-factor of 1.71.

**SOLUTION**

In this problem, we estimate the size of the hyperfine splitting for “heavy hydrogen,” or deuterium. The energy level structure for deuterium is basically just the same as for “regular” hydrogen, so the deuterium ground state, for example, will have $n = 1$ and $\ell = 0$. Following exactly the same arguments used in class (in practice, doing nothing more than switching subscript ‘$p$’ to ‘$d$’) this means that for deuterium

$$E_{\text{hf}}^1 = \frac{-2\mu_0}{3} \frac{1}{\pi a_0^3} \left( -\frac{g_e e}{2m_e} S_e \right) \cdot \left( \frac{g_d e}{2m_d} S_d \right) = \frac{\mu_0 g_d e^2}{3\pi m_e m_d a_0^3} \langle S_e \cdot S_d \rangle$$

where I used $g_e \approx 2$. Using $\mu_0 = 1/(c^2\epsilon_0)$, $k \equiv 1/(4\pi\epsilon_0)$, and the definition of $a_0$, we can rewrite this as

$$E_{\text{hf}}^1 = \frac{4 g_d \hbar^2}{3 m_d m_e^2 c^2 a_0^4} \langle S_e \cdot S_d \rangle \equiv \frac{E_{\text{hf}}^{(d)}}{\hbar^2} \langle S_e \cdot S_d \rangle$$

Before evaluating the constant out front, we can work out the result for the spin-spin expectation value. If we define the total atomic spin operator $S \equiv S_e + S_d$, then we can use our now ‘standard’ trick to evaluate the dot product, i.e.,

$$S_e \cdot S_d = (1/2) [S^2 - S_e^2 - S_d^2]$$
To find the expectation value of the operators on the right-hand side, we know the electron has \( s_e = 1/2 \), so \( \langle S_e^2 \rangle = s_e(s_e + 1)\hbar^2 = (3/4)\hbar^2 \). Similarly, the deuteron has \( s_d = 1 \), so \( \langle S_d^2 \rangle = s_d(s_d + 1)\hbar^2 = 2\hbar^2 \). Finally, we use our rules for adding angular momentum to realize that the total spin \( s \) can be either 1/2 or 3/2, and so \( \langle S^2 \rangle = (3/4)\hbar^2 \) or \((15/4)\hbar^2\), respectively. Altogether, this means that

\[
\langle S_e \cdot S_d \rangle = \frac{\hbar^2}{2} \times \begin{cases} 
3/4 - 2 - 3/4 = -2 & \text{for } s = 1/2 \\
15/4 - 2 - 3/4 = 1 & \text{for } s = 3/2
\end{cases}
\]

To work out the constant, we could just plug in a whole bunch of numbers and grind it out; or we could be clever and see how it differs from the equivalent constant for hydrogen. By inspection, we see that

\[
E_{hf}^{(d)} = \frac{g_d m_p a_p^4}{g_p m_d a_d} \times E_{hf}^{(p)}
\]

To this level of accuracy, we can take \( a_d = a_p \), as there is only a reduced mass correction here, so a 1:2000 size effect. For hydrogen, the constant \( E_{hf}^{(p)} \) is given in Eq. 6.93 in the text, once we include the extra factor of \( \hbar^2 \) from our spin-spin expectation value. We find

\[
E_{hf}^{(d)} = \frac{1.71}{5.59} \frac{1}{2} (5.88 \times 10^{-6} \text{ eV}) = 8.99 \times 10^{-7} \text{ eV}
\]

and so we conclude that for deuterium

\[
E_{hf} = (8.99 \times 10^{-7} \text{ eV}) \times \begin{cases} 
-1 & \text{for } s = 1/2 \\
+1/2 & \text{for } s = 3/2
\end{cases}
\]

From this, we see that the hyperfine (or spin-spin) interaction in atomic deuterium leads to an energy splitting of the ground state given by

\[
\Delta E \equiv (E_{hf}^{1})_{s=3/2} - (E_{hf}^{1})_{s=1/2} = (3/2)(8.99 \times 10^{-7} \text{ eV}) = 1.35 \times 10^{-6} \text{ eV}
\]

Our last step is to convert this energy splitting into the corresponding wavelength for a photon that makes this transition. Using \( E_{\gamma} = h\nu \), and \( \lambda = c/\nu \), we see that

\[
\lambda = \frac{hc}{E_{\gamma}} = \frac{1240 \text{ eV} \cdot \text{nm}}{1.35 \times 10^{-6} \text{ eV}} = 9.19 \times 10^{8} \text{ nm} = 91 \text{ cm}
\]

Thus, the photon emitted in this process is 4-5 times lower in energy than the photon emitted in the analogous process in ‘regular’ hydrogen, and hence has a wavelength 4-5 times longer. Taking a step back, note that these photons have a wavelength that is close to a meter long! They would diffract (in principle) going through a picket fence.
2. SHO Me the Functional!

Consider the 1-D SHO, described by the familiar Hamiltonian:

\[ H = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{1}{2}m\omega^2 x^2 \]

We know that the true wave function for the ground state is a Gaussian, with tails extending well into the kinematically forbidden regions. Suppose we didn’t know this, and we guessed that the wave function must “turn off” at some point, just as for the infinite square well. Thus, we might consider a function of the form

\[ \phi_c(x) = \begin{cases} 
(c^2 - x^2)^2 & \text{for } |x| \leq c \\ 
0 & \text{for } |x| \geq c 
\end{cases} \]

Treating \( c \) as an adjustable parameter, calculate a best-guess for the energy of the SHO ground state, and compare this to the actual value for \( E_0 \).

**SOLUTION**

There’s not a lot of “prep work” to do here – this is mostly an exercise in just going through all the steps required to carry out a variational calculation, in a system (1-D SHO) for which we already know the correct answer. In this case, we use as our trial wave function \( \phi_c(x) \) as specified above. To evaluate the functional \( E[\phi_c] \), we first need to calculate the expectation value of the SHO Hamiltonian in this trial state. We examine the operation

\[
\hat{H} \phi_c(x) = -\frac{\hbar^2}{2m} \frac{d^2\phi_c}{dx^2} + \frac{1}{2}m\omega^2 x^2 \phi_c \\
= -\frac{\hbar^2}{2m} \left[ \frac{d^2}{dx^2} (c^2 - x^2)^2 - \alpha^2 x^2 (c^2 - x^2)^2 \right] \\
= -\frac{\hbar^2}{2m} \left[ -4c^2 + 12x^2 - \alpha^2 (c^4 x^2 - 2c^2 x^4 + x^6) \right] \\
= \frac{\hbar^2}{2m} \left[ \alpha^2 x^6 - 2\alpha^2 c^2 x^4 + (\alpha^2 c^4 - 12) x^2 + 4c^2 \right]
\]

where in the second line I introduced the constant \( \alpha \equiv m\omega/\hbar \). With this evaluated, we now multiply on the left by \( \phi_c^* \) (which equals \( \phi_c \)) to get

\[
\phi_c^* \hat{H} \phi_c = \frac{\hbar^2}{2m} \left[ x^4 - 2c^2 x^2 + c^4 \right] \left[ \alpha^2 x^6 - 2\alpha^2 c^2 x^4 + (\alpha^2 c^4 - 12) x^2 + 4c^2 \right] \\
= \frac{\hbar^2}{2m} \left[ \alpha^2 x^{10} - 4\alpha^2 c^2 x^8 + (6\alpha^2 c^4 - 12) x^6 - (4\alpha^2 c^6 - 28c^2) x^4 + (\alpha^2 c^8 - 20c^4) x^2 + 4c^6 \right]
\]
Now we must integrate the above expression from \(-c\) to \(+c\), giving us
\[
\langle \phi_c | H | \phi_c \rangle = \frac{\hbar^2}{2m} \left[ \alpha^2 c^4 \frac{c^11}{11} - 4\alpha^2 c^2 \frac{c^9}{9} + (6\alpha^2 c^4 - 12)\frac{c^7}{7} \right.
\]
\[
- (4\alpha^2 c^6 - 28c^2)\frac{c^5}{5} + (\alpha^2 c^8 - 20c^4)\frac{c^3}{3} + 4c^7 \right]
\]
\[
= 2\alpha^2 c^4 \frac{\hbar^2}{2m} \left[ \left( \frac{1}{11} - \frac{4}{9} + \frac{6}{7} - \frac{4}{5} + \frac{1}{3} \right) - \left( \frac{12}{7} - \frac{28}{5} + \frac{20}{3} - 4 \right) \right]
\]
\[
= 2\alpha^2 \frac{\hbar^2}{2m} [\alpha^2 c^4 \kappa_1 - \kappa_2]
\]
where the constants \(\kappa_1\) and \(\kappa_2\) can be read off from the previous expression.

The next step is to do a similar integral for the denominator of our functional. The integrand is somewhat easier, and we find
\[
\phi_c^* \phi_c = (x^2 - c^2)^4 = x^8 - 4c^2 x^6 + 6c^4 x^4 - 4c^6 x^2 + c^8
\]
and so
\[
\langle \phi_c | \phi_c \rangle = 2c^9 \left( \frac{1}{9} - \frac{4}{7} + \frac{6}{5} - \frac{4}{3} + 1 \right) = 2c^9 \kappa_3
\]
We now have all the pieces we need to calculate the functional \(E[\phi_c] = E(c)\). We have
\[
E(c) = \frac{\langle \phi_c | H | \phi_c \rangle}{\langle \phi_c | \phi_c \rangle} = \frac{\hbar^2}{2m} \frac{\alpha^2 c^4 \kappa_1 - \kappa_2}{c^2 \kappa_3} = \frac{\hbar^2}{2m} \left[ (\kappa_1/\kappa_3)\alpha^2 c^2 - (\kappa_2/\kappa_3)c^{-2} \right]
\]
To find the minimum in the energy \(E(c)\), we set \(dE/dc = 0\), giving us
\[
(\kappa_1/\kappa_3)\alpha^2 (2c) - (\kappa_2/\kappa_3)(-2c^{-3}) = 0
\]
Solving for \(c\) and evaluating our constants gives us
\[
\alpha^2 c^4 = -\kappa_2/\kappa_1 = 33 \quad \Rightarrow \quad \alpha c^2 = \sqrt{33}
\]
Our last step is to insert this value back into our expression for \(E(c)\). After pulling out a common factor of \(\alpha\), simplifying the dimensioned quantities out front, and evaluating the constants \(\kappa_j\), we obtain our final result that:
\[
E(c)_{\text{min}} = \frac{\hbar^2}{2m} \alpha \left[ (\kappa_1/\kappa_3)\alpha c^2 - (\kappa_2/\kappa_3)(\alpha c^2)^{-1} \right]
\]
\[
= \frac{\hbar \omega}{2} \left[ (1/11)\sqrt{33} - (-3)(1/\sqrt{33}) \right]
\]
\[
= \frac{\hbar \omega}{2} \left[ 2\sqrt{33}/11 \right] \approx 1.0445 \frac{\hbar \omega}{2}
\]
So, this was a pretty good guess! After doing some ugly (but trivial) integrals, we could determine the SHO ground state energy to within about 5% of its true value (and we note that, as required, we were 5% too high). Cutting off the tails of the wave function in the kinematically “forbidden” regions is not well-motivated quantum mechanically, but it doesn’t seem to screw up our ground state energy estimate too badly!
3. **Try to be Vary Linear**

Consider a potential well that grows linearly with $x$ when $x > 0$, but goes to infinity for all $x < 0$, *i.e.*, a potential of the form

$$V(x) = \begin{cases} +\infty & \text{for } x < 0 \\ \kappa x & \text{for } x > 0 \end{cases}$$

Using variational techniques, estimate the ground state energy using the trial function

$$\phi_\alpha(x) = xe^{-\alpha x^2}$$

Argue qualitatively why you would expect this trial function to be better (*i.e.*, yield a better estimate for the ground state energy) than the simple exponential function

$$\phi_\beta(x) = xe^{-\beta x}$$

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**SOLUTION**

This problem is pretty straightforward: given a potential $V(x)$ and a trial wave function, estimate the ground-state energy of this system. We use as our trial function

$$\phi_\alpha(x) = xe^{-\alpha x^2}$$

This seems like a reasonable choice: the function has a ‘tail’ at large $x$ due to the exponential term, yet the multiplicative factor of $x$ drives the function to zero at the origin, thus satisfying our asymptotic boundary conditions. The function is also ‘node-less,’ making it a good candidate for the lowest energy state. Brimming with confidence, we now pound out the explicit form for the energy functional, defined by

$$E[\phi_\alpha] = \frac{\langle \phi_\alpha | \hat{H} | \phi_\alpha \rangle}{\langle \phi_\alpha | \phi_\alpha \rangle}$$

Working on the denominator first, we have

$$\langle \phi_\alpha | \phi_\alpha \rangle = \int_0^\infty |\phi_\alpha(x)|^2 dx = \int_0^\infty x^2 e^{-2\alpha x^2} dx$$

where the limits of integration account for the fact that the wave function must vanish wherever $V(x) \to \infty$. As a definite integral, this expression is easily evaluated and we get

$$\langle \phi_\alpha | \phi_\alpha \rangle = \frac{\sqrt{\pi}}{4 \cdot (2\alpha)^{3/2}} = \frac{1}{8\alpha} \sqrt{\frac{\pi}{2\alpha}}$$
Turning now to the numerator, we know that for $x > 0$

$$\hat{H} = \frac{\vec{p}^2}{2m} + \hat{V}(x) = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \kappa x$$

For the kinetic energy term, we must take a few derivatives, which yields

$$\phi''_\alpha \equiv \frac{d^2}{dx^2} \left( xe^{-\alpha x^2} \right) = [4\alpha^2 x^3 - 6\alpha x] e^{-\alpha x^2}$$

and so we find

$$\langle \phi_\alpha | \hat{H} | \phi_\alpha \rangle = -\frac{\hbar^2}{2m} \int_0^\infty \left[ 4\alpha^2 x^4 - 6\alpha x^2 - (2m\kappa/\hbar^2) x^3 \right] e^{-2\alpha x^2} dx$$

We look up a few more definite integrals of $x^n$ times a gaussian, and find

$$\langle \phi_\alpha | \hat{H} | \phi_\alpha \rangle = -\frac{\hbar^2}{2m} \left[ 4\alpha^2 \frac{3\sqrt{\pi}}{8} \left( \frac{1}{2\alpha} \right)^{5/2} - 6\alpha \frac{\sqrt{\pi}}{4} \left( \frac{1}{2\alpha} \right)^{3/2} - \frac{2m\kappa}{\hbar^2} \cdot \frac{1}{2} \left( \frac{1}{2\alpha} \right)^2 \right]$$

$$= \frac{\hbar^2}{2m} \left[ \frac{3\sqrt{\pi}}{8\sqrt{2\alpha}} + \frac{3\sqrt{\pi}}{4\sqrt{2\alpha}} + \frac{m\kappa}{4\hbar^2\alpha^2} \right]$$

$$= \frac{\hbar^2}{2m} \left[ \frac{3\sqrt{\pi}}{8\sqrt{2\alpha}} + \frac{m\kappa}{4\hbar^2\alpha^2} \right]$$

Combining this with our expression for the denominator, we see

$$E[\phi_\alpha] = E(\alpha) = \frac{\hbar^2}{2m} \left[ \frac{3\sqrt{\pi}}{8\sqrt{2\alpha}} + \frac{m\kappa}{4\hbar^2\alpha^2} \right] \cdot \frac{8\alpha\sqrt{2\alpha}}{\sqrt{\pi}} = \frac{\hbar^2}{2m} \left[ 3\alpha + \frac{2\sqrt{2m\kappa}}{\hbar^2 \sqrt{\pi} \alpha} \right]$$

where I have made the $\alpha$ dependence obvious. This is important, because our next step is to minimize this function w.r.t. the parameter $\alpha$. Doing so, we find that

$$\frac{dE}{d\alpha} = \frac{\hbar^2}{2m} \left[ 3 - \frac{\sqrt{2m\kappa}}{\hbar^2 \sqrt{\pi} \alpha \sqrt{\alpha}} \right] = 0$$

and so

$$\alpha \sqrt{\alpha} = \frac{\sqrt{2m\kappa}}{3\hbar^2 \sqrt{\pi}} \quad \Rightarrow \quad \alpha = \left[ \frac{2m^2\kappa^2}{9\pi\hbar^4} \right]^{1/3}$$

Almost done! Armed with our optimal value for $\alpha$, we now insert this back into our expression for the energy, and find that for this trial function

$$E_{\text{min}} = \frac{\hbar^2}{2m} \left\{ 3 \left[ \frac{2m^2\kappa^2}{9\pi\hbar^4} \right]^{1/3} + \frac{2\sqrt{2m\kappa}}{\hbar^2 \sqrt{\pi}} \left[ \frac{9\pi\hbar^4}{2m^2\kappa^2} \right]^{1/6} \right\}$$
\[ E_{\text{min}} = \frac{\hbar^2}{2m} \left\{ \left[ \frac{6m^2\kappa^2}{\pi \hbar^4} \right]^{1/3} + \left[ \frac{48m^2\kappa^2}{\pi \hbar^4} \right]^{1/3} \right\} \]

\[ = \frac{\hbar^2}{2m} \left[ \frac{m^2\kappa^2}{\pi \hbar^4} \right]^{1/3} \cdot 6^{1/3} \cdot (1 + 2) \]

\[ = 3 \left[ \frac{3h^2\kappa^2}{4\pi m} \right]^{1/3} = \left( \frac{81}{4\pi} \right)^{1/3} \left[ \frac{h^2\kappa^2}{m} \right]^{1/3} = 1.861 \ldots \left[ \frac{h^2\kappa^2}{m} \right]^{1/3} \]

Thus, our best guess for the lowest energy eigenvalue for this system is

\[ E_{\text{g.s.}} \leq 1.86 \left[ \frac{h^2\kappa^2}{m} \right]^{1/3} \]

But given how much effort is involved in determining these estimates for \( E_{\text{g.s.}} \), is there any way we could guess in advance that \( \phi_\alpha \), for example, would do a better job than \( \phi_\beta \)? In this case, we can. For wave functions that extend into kinematically forbidden regions, we know that if the potential \( V(x) \) is constant, then the correct asymptotic behavior is purely exponential. Here, the potential increases linearly with \( x \), so \( (V - E) \) gets larger and larger as \( x \to \infty \). This means the wave function must die off faster than exponentially, so a tail that goes as \( e^{-\alpha x^2} \) would be a better guess than a pure exponential. In practice, the best option would be to consider the full differential equation in the asymptotic limit, and use those solutions as our trial function.

4. More Gaussians, More Variations

(a) Assuming that the orbital angular momentum \( \ell \) is zero for the ground state of the hydrogen atom, estimate the energy of this state, using a trial function of the form

\[ \phi_c(r) = e^{-cr^2} \]

Compare the answer you get to the actual ground state energy. (b) Without doing any calculations, discuss what your answer would have been if you had instead used a trial function of the form

\[ \phi_c(r) = e^{-cr} \]

SOLUTION

(a) For a state in hydrogen with no angular momentum (\( \ell = 0 \)), we know that the wave function must be purely radial, and that the radial wave function \( R(r) \) must be an eigenfunction of the Hamiltonian

\[ \hat{H} = -\frac{\hbar^2}{2m} \frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{d}{dr} \right) - \frac{ke^2}{r} \]
Rather than solving this equation, we try a wave function of the form $\phi_c(r) = e^{-cr^2}$.

To make our best prediction of the ground state energy, we must minimize the energy functional $E[\phi_c]$, so we start by examining the operation of $\hat{H}$ on our trial wave function:

$$\hat{H} \phi_c(r) = -\frac{\hbar^2}{2m} \frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{d}{dr} e^{-cr^2} \right) - \frac{ke^2}{r} e^{-cr^2}$$

$$= -\frac{\hbar^2}{2m} \frac{1}{r^2} \frac{d}{dr} \left( -2cr^3 e^{-cr^2} \right) - \frac{ke^2}{r} e^{-cr^2}$$

$$= -\frac{\hbar^2}{2m} \frac{1}{r^2} \left( 4c^2 r^4 e^{-cr^2} + (-6cr^2) e^{-cr^2} \right) - \frac{ke^2}{r} e^{-cr^2}$$

$$= -\frac{\hbar^2}{2m} e^{-cr^2} \left[ 4c^2 r^2 - 6c + \frac{2mk^2 e^2}{\hbar^2} \right]$$

With this operation worked out, we can now set up the integral for the numerator of $E[\phi_c]$:

$$\langle \phi_c | \hat{H} | \phi_c \rangle = -\frac{\hbar^2}{2m} \int_0^\infty e^{-2cr^2} \left[ 4c^2 r^2 - 6c + \frac{2mk^2 e^2}{\hbar^2} \right] r^2 dr$$

$$= -\frac{\hbar^2}{2m} \int_0^\infty e^{-2cr^2} \left[ 4c^2 r^4 - 6cr^2 + \frac{2mk^2 e^2}{\hbar^2} r \right] dr$$

As an indefinite integral, this would be a mess! The definite integrals, though, are straightforward, since they are all of the variety:

$$I_n \equiv \int_0^\infty z^n e^{-az^2} dz = \frac{\Gamma[(n+1)/2]}{2a^{(n+1)/2}}$$

where the Gamma function $\Gamma(x)$ can be evaluated easily for integer and half-integer arguments if we use the rules that

$$\Gamma(1) = 1 \quad \Gamma(1/2) = \sqrt{\pi} \quad \Gamma(z) = (z-1) \Gamma(z-1) \quad \text{for any } z$$

These tell us that $\Gamma(n) = (n-1)!$ for integer $n$, and $\Gamma(3/2) = \sqrt{\pi}/2$, etc.

We now have all the tools we need to do the integrals. We find

$$\langle \phi_c | \hat{H} | \phi_c \rangle = -\frac{\hbar^2}{2m} \int_0^\infty e^{-2cr^2} \left[ 4c^2 r^4 - 6cr^2 + \frac{2mk^2 e^2}{\hbar^2} r \right] dr$$

$$= -\frac{\hbar^2}{2m} \left[ 4c^2 \frac{\Gamma(5/2)}{2(2c)^{5/2}} - 6c \frac{\Gamma(3/2)}{2(2c)^{3/2}} + \frac{2mk^2 e^2 \Gamma(1)}{\hbar^2} \frac{1}{2(2c)} \right]$$

$$= -\frac{\hbar^2}{2m} \left[ \frac{3}{8} \sqrt{\frac{\pi}{2c}} - \frac{3}{4} \sqrt{\frac{\pi}{2c}} + \frac{mke^2}{\hbar^2} \frac{1}{2c} \right]$$

$$= \frac{\hbar^2}{2m} \left[ \frac{3}{8} \sqrt{\frac{\pi}{2c}} - \frac{mke^2}{2\hbar^2 c} \right]$$
We use the same set of integrals to evaluate the denominator of our functional as well:

\[ \langle \phi_c | \phi_c \rangle = \int_0^\infty r^2 e^{-2cr^2} \, dr = \frac{\Gamma(3/2)}{2(2c)^{3/2}} = \frac{1}{8} \sqrt{\frac{\pi}{2c^3}} \]

Combining these last two results, we see

\[ E[\phi] = E(c) = \frac{\hbar^2}{2m} 8 \sqrt{\frac{2c^3}{\pi}} \left[ 3 \sqrt{\frac{\pi}{2c} - \frac{mke^2}{2h^2} \frac{1}{c}} \right] = \frac{3h^2}{2m} c - 2ke^2 \sqrt{\frac{2}{\pi}} c^{1/2} \]

We now minimize this function by setting \( dE/dc \) to 0, which yields

\[ \frac{dE}{dc} = \frac{3h^2}{2m} - ke^2 \sqrt{\frac{2}{\pi}} c^{-1/2} = 0 \]

so

\[ c = \left[ ke^2 \sqrt{\frac{2}{\pi}} \cdot \frac{2m}{3h^2} \right]^2 = \frac{8}{9\pi} \left( \frac{mke^2}{h^2} \right)^2 \]

Our last step is to use this value for \( c \) in our function \( E(c) \) to obtain a “best guess” of the ground state energy of the hydrogen atom:

\[ E_{\text{min}} = \frac{3h^2}{2m} c - 2ke^2 \sqrt{\frac{2}{\pi}} c^{1/2} \]

\[ = \frac{3h^2}{2m} \cdot \frac{8}{9\pi} \left( \frac{mke^2}{h^2} \right)^2 - 2ke^2 \sqrt{\frac{2}{\pi}} \cdot \frac{2\sqrt{2}}{3\sqrt{\pi}} \left( \frac{mke^2}{h^2} \right) \]

\[ = \frac{4}{3} \left( \frac{mk^2e^4}{\pi h^2} \right) - \frac{4}{3} \frac{2}{\pi} \left( \frac{mk^2e^4}{h^2} \right) \]

\[ = -\frac{4}{3} \left( \frac{mk^2e^4}{\pi h^2} \right) \]

To compare this more directly with the true ground state energy \( E_{gs} \), we rearrange a few constants and express our result in the form

\[ E_{\text{min}} = -\frac{8}{3\pi} \cdot \frac{1}{2} mc^2 \left( \frac{k^2e^4}{h^2c^2} \right) = -\frac{8}{3\pi} \cdot \frac{1}{2} mc^2 \alpha^2 = \frac{8}{3\pi} E_{gs} \]

and so

\[ E_{\text{min}} \approx 0.849 \, E_{gs} \]

So, this wasn’t such a great guess for a trial function after all! Because the energy is negative (bound state), our guess must be more positive, i.e., smaller in magnitude, and indeed it is ... by about 15%. A much better guess would have been to ...

(b) ... consider a trial wave function of the form \( \phi_c(r) = e^{-cr} \). Note that this function is of the correct form, i.e., the true solution is \( R_{10} \propto e^{-cr} \), so minimizing \( E \) in this case would yield a value for \( c \) which reproduces the correct ground state energy.
5. Beware of Massive Photons!

Please do Problem 7.14, found on page 310 in the text. It would be great if everyone could choose “a trial wave function of your own devising,” but I suspect the grader would not be thrilled. So let’s all agree to use something resembling the hydrogen ground state, that is, use

\[ \phi(x) = Ae^{-r/b} \]

and treat \( b \) as an adjustable parameter. Note that in the limit of the photon mass \( m_\gamma \to 0 \), we would expect \( b \to a_0 \), the Bohr radius. Make sure that this is indeed the case for your solution.

SOLUTION

In this problem, Griffiths states without proof a very profound result: if nature had given us a “Coulomb-like” interaction mediated by a massive particle, rather than by a massless photon, the potential for this interaction would have a Yukawa form, i.e.,

\[ V(r) = V(r) = -ke^2 \frac{e^{-\mu r}}{r} \]

where \( \mu \equiv mc/\hbar \) and \( m \) is the mass of the exchanged particle. Using this as the potential energy term in our Hamiltonian, we can estimate the ground state energy of hydrogen. We want a trial wave function similar to the “true” hydrogen ground state, so we use

\[ \phi(x) = Ae^{-r/b} \]

We first work out the normalization constant \( A \) – but we already did this back in Ch. 4, where we found \( A = 1/\sqrt{\pi b^3} \) (see Eq. 4.80). We also don’t have to re-evaluate the kinetic energy of this system (only the potential energy is different) and so the expectation value of the kinetic energy is given by (Eq. 4.191) \( \langle T \rangle_{\phi} = \hbar^2/2mb^2 \). So the only ‘work’ we need to do is find the expectation value of the new potential energy. Setting this up as usual:

\[
\langle V \rangle_{\phi} = \langle \phi | V | \phi \rangle = \int \left( \frac{1}{\sqrt{\pi b^3}} e^{-r/b} \right) \left( -ke^2 \frac{e^{-\mu r}}{r} \right) \left( \frac{1}{\sqrt{\pi b^3}} e^{-r/b} \right) d^3r
\]

\[=-ke^2 \frac{4\pi}{b^3} \int_0^\infty e^{-2r/b} \frac{e^{-\mu r}}{r^2} r^2 dr = -\frac{4ke^2}{b^3} \int_0^\infty e^{-(\mu+2/b)r} r^2 dr \]

\[=-\frac{4ke^2}{b^3} \left( \frac{1}{(\mu+2/b)^2} \right) = -\frac{ke^2}{b} \left[ \frac{1}{2} + \frac{\mu b}{2} \right]^{-2} \]

For this last expression, we were motivated by the idea that eventually we will want to treat \( \mu \) (or, more precisely, \( \mu b \)), as a small quantity, so this gets us closer to a ‘1 + \epsilon’ form. We now add these results together to find

\[ E[\phi] = \langle H \rangle_{\phi} = \langle T \rangle_{\phi} + \langle V \rangle_{\phi} = \frac{\hbar^2}{2mb^2} - \frac{ke^2}{b} \left[ 1 + \frac{\mu b}{2} \right]^{-2} \]
Armed with $E(b)$, we now minimize this function by setting its derivative w.r.t. $b$ to zero:

$$\frac{d E_\phi}{db} = -\frac{\hbar^2}{mb^3} + \frac{ke^2}{b^2} \left[1 + \frac{\mu b}{2}\right]^{-2} + \frac{\mu ke^2}{b} \left[1 + \frac{\mu b}{2}\right]^{-3}$$

We have to re-arrange this just a bit to arrive at the result

$$\frac{(1 + 3\mu b/2)}{(1 + \mu b/2)^3} b = \frac{\hbar^2}{mke^2} = a$$

This is nice! (Sort of.) The “$a$” here is the standard Bohr radius, so we again have an expression where in the limit $m_\gamma \to 0$, so $\mu \to 0$, we see that $b \to a$, as it should in order to regain the correct result for the hydrogen atom.

On the downside, we now have to solve a cubic equation for $b$. This isn’t so bad, because we eventually want to treat $\mu b$ as a small parameter, so we may as well start now. We can “solve” for $b$ by expanding in powers of $(\mu b)$; working to order $(\mu b)^2$ gives us

$$b = a \left[1 + \frac{\mu b}{2}\right]^3 \left[1 + \frac{3\mu b}{2}\right]^{-1}$$

and, because we see that $b = a$ to order $(\mu b)^2$, we can express $b$ simply as

$$b = a \left[1 + \frac{3}{4}(\mu a)^2\right]$$

Our last step is to use this value for $b$ to estimate the ground state energy. Inserting this into our functional $E_\phi$ and working consistently to order $(\mu b)^2 = (\mu a)^2$, we have

$$E_\phi = \frac{\hbar^2}{2mb^2} - \frac{ke^2}{b} \left[1 + \frac{\mu b}{2}\right]^{-2}$$

This looks pretty ugly . . . until we think about the constants more closely, and realize that $\hbar^2/(2ma^2) = ke^2/(2a) = -E_1$. Using this, the above reduces to

$$E_\phi = -E_1 \left[1 - \frac{3}{2}(\mu a)^2\right] + 2E_1 \left[1 - (\mu a)\right] = E_1 \left[1 - 2(\mu a) + \frac{3}{2}(\mu a)^2\right]$$

Again, as $(\mu a) \to 0$, we better regain the hydrogen ground state energy!