Review Session Problems 2

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November 9, 2024

Exercise 1. When we solve the hydrogen atom, we assume that the nucleus is a point charge. In this problem, we will compute the approximate change to the energy levels due to the finite size of the nucleus. This is called the **volume effect**. Model the nucleus as a uniform sphere of radius $r_0 A^{1/3}$, where $A^{1/3}$ is the number of nucleons (so this works for e.g. deuterium) and $r_0 = 1.3 \cdot 10^{-13}$ cm.

a) What is the potential $V(r)$?
Hint: Outside the nucleus, $V(r)$ is just the Coulomb potential. Inside the nucleus, use Gauss' law to determine $V(r)$.

b) What is H', where H^0 is the hydrogen atom hamiltonian?

c) Argue that the $\ell = 0$ states are only slightly affected by this perturbation.
Hint: Think about the small r behavior of the wavefunctions for s-states vs. $\ell > 0$ states.

d) Calculate the correction to the energy levels for all states with $\ell = 0$. Note that

$$R_{n0}(0) = \frac{2}{(na_0)^{3/2}},$$

where $a_0 = \hbar^2/me^2$.

e) For hydrogen, calculate the correction to the $n = 1$ and $n = 2$ states in eV.

f) Fine structure is of order $\alpha^4 mc^2$. Compare the magnitude of the volume effect to that of fine structure.

a) Outside the atom, the potential is just the Coulomb potential $-Ze^2/r$. Inside the atom, Gauss' law says that

$$4\pi Q = \oint \mathbf{E} \cdot \mathrm{d}\mathbf{a},$$

where the charge at radius $r < R = r_0 A^{1/3}$ is

$$Q = Ze\frac{r^3}{R^3}.$$

Thus,

$$E(r) = Ze\frac{r}{R^3}$$

inside the atom. To find the potential, we need to take

$$e\int \mathbf{E}\cdot \mathrm{d}\boldsymbol{\ell} = \int_\infty^R \frac{Ze^2}{r^2} + \int_R^r \frac{Ze^2 r}{R^3} = -\frac{3Ze^2}{2R} + \frac{Ze^2r^2}{2R^3}.$$

Thus,

$$V(r) = \begin{cases} -\frac{3Ze^2}{2R} + \frac{Ze^2r^2}{2R^3}, & r < R \\ -\frac{Ze^2}{r}, & r \geq R \end{cases}.$$

b) Note that the unperturbed potential is $-e^2/r$ for all r, so that the perturbed potential is

$$H' = \begin{cases} -\frac{3Ze^2}{2R} + \frac{Ze^2r^2}{2R^3} + \frac{Ze^2}{r}, & r < R \\ 0, & r \geq R \end{cases}.$$

c) The small r behavior of $R(r)$ is given by $R(r) \sim r^\ell$. Hence, $\ell > 0$ states are concentrated away from the origin, and so will not be very strongly affected by the size of the nucleus. On the other hand, $\ell = 0$ states have a more uniform distribution, so they are much more affected.

d) Since R is tiny, we can approximate $R_{n0}(r)$ to be $R_{n0}(0)$ for $r < R$; indeed, this follows from the small r behavior of the wavefunction $R(r) \sim r^\ell$. Furthermore, the $\ell = 0$ states are not degenerate, so we can use first order nondegenerate perturbation theory. Lastly, notice that since we have Z protons, the Bohr radius is scaled as $a_0 \to a_0/Z$; hence, $R_{n0}(0) \to Z^{3/2}R_{n0}(0)$Thus,

$$\begin{aligned}\langle H'\rangle =& \frac{4Z^4e^2}{(na_0)^3}\int_0^R \left(-\frac{3}{2}R + \frac{r^2}{2R^3} + \frac{1}{r}\right) r^2\,\mathrm{d}r \\ =& \frac{2Z^4}{5(na_0)^3}e^2R^2 \\ \approx& \frac{A^{2/3}Z^4}{n^3}\cdot 10^{-8}\text{ eV}.\end{aligned}$$

e) For hydrogen, $A = 1$, so we get that the corrections are $\sim 10^{-8}$ eV for the $n = 1$ state and $\sim 10^{-9}$ eV for the $n = 2$ state.

f) $\alpha \sim \frac{1}{137}$, $mc^2 \sim 511$ keV, so $\alpha^4 mc^2 \sim 1.45 \cdot 10^{-3}$ eV, which is 5 orders of magnitude greater than the volume effect!

Exercise 2. Explain the physical origins of

a) fine structure

b) Lamb shift

c) hyperfine structure.

a) This is due to 1) a relativistic correction and 2) the spin-orbit coupling between the spin of the electron and the orbital angular momentum of the proton (which creates a magnetic dipole moment). It is of order $\alpha^4 mc^2$.

b) This is due to the quantization of the electromagnetic field; it's of order $\alpha^5 mc^2$.

c) This is due to the coupling between the spin of the proton and of the electron; it's of order $\frac{m}{m_p}\alpha^4 mc^2$. Notice that since $m/m_p \sim 1/2000$, this effect is *weaker* than the Lamb shift.

Exercise 3. *Griffiths 8.19* Find the lowest bound on the ground state of hydrogen using the variational principle and an exponential trial wavefunction,

$$\psi(\mathbf{r}) = Ae^{-br^2},$$

where A is determined by normalization and b is a variational parameter. Express your answer in eV.

First, we calculate A. We can totally ignore the angular part of the integration, since any integration constant can be absorbed into A anyway. We thus get

$$\int_0^\infty |A|^2 e^{-2br^2} r^2 \,\mathrm{d}r = |A|^2 \frac{\sqrt{\pi}}{4(2b)^{3/2}},$$

so

$$|A|^2 = \frac{4(2b)^{3/2}}{\sqrt{\pi}}.$$

The hydrogen atom hamiltonian is

$$H = -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0 r}.$$

Note that it's important that we have the laplacian here, so the derivative with respect to r is not just $\partial^2/\partial r^2$. Acting on $\psi(r)$ with this hamiltonian, we get

$$-\frac{\hbar^2}{2m}A\left(2br^2 - 3\right)2be^{-br^2} - \frac{e^2}{4\pi\varepsilon_0 r}Ae^{-br^2}.$$

We want to calculate $\langle\psi|H|\psi\rangle$ to use the variational principle. We thus calculate

$$\langle\psi|H|\psi\rangle = -\frac{\hbar^2}{2m}|A|^2\int_0^\infty 2br^2 e^{-2br^2}(2br^2 - 3)\,\mathrm{d}r - \frac{e^2}{4\pi\varepsilon_0}|A|^2\int_0^\infty re^{-2br^2}\,\mathrm{d}r.$$

The first integral has two terms, each of which is a gaussian integral. You can look up how to do these online or just plug them into e.g. Mathematica.

Note that gaussian integrals follow from the following calculation. Let

$$I = \int_{-\infty}^{\infty} \mathrm{d}x e^{-ax^2}.$$

First, we can do a change of variables $x \to x/\sqrt{a}$, so that

$$I = \frac{1}{\sqrt{a}} \int_{-\infty}^{\infty} \mathrm{d}x e^{-x^2}.$$

Then consider

$$I^2 = \frac{1}{a} \int_{-\infty}^{\infty} \mathrm{d}x e^{-(x^2+y^2)}.$$

We can set $r^2 = x^2 + y^2$, change to polar coordinates, and find

$$I^2 = \frac{2\pi}{a} \cdot \frac{I}{2},$$

where we get $I/2$ because the integration bounds for r are from 0 to ∞. Since I converges and is nonzero, we have

$$I = \sqrt{\frac{\pi}{a}}.$$

If we want to calculate integrals of the form

$$\int_0^{\infty} x^{2n} e^{-ax^2}\,\mathrm{d}x,$$

we can differentiate our form for I with respect to a:

$$\frac{\mathrm{d}}{\mathrm{d}a} I = -\int \mathrm{d}x\; x^2 e^{-ax^2} = -\frac{\sqrt{\pi}}{2a^{3/2}}.$$

Similarly, differentiating twice with respect to a, we get

$$\frac{\mathrm{d}^2}{\mathrm{d}a^2} I = \int_{-\infty}^{\infty} \mathrm{d}x\; x^4 e^{-ax^2} = \frac{3\sqrt{\pi}}{4a^{5/2}}.$$

Returning to our calculation, we see that the second integral is easy, since the derivative of e^{-2br^2} is $-4bre^{-2br^2}$, while the other two integrals are given by the calculations above. The result is

$$\begin{aligned}\langle\psi|H|\psi\rangle &= -\frac{\hbar^2}{2m} \cdot \frac{4(2b)^{3/2}}{\sqrt{\pi}} \cdot 2b \left(\frac{3\sqrt{\pi}}{8(2b)^{5/2}} \cdot 2b - \frac{3\sqrt{\pi}}{4(2b)^{3/2}} \right) - \frac{e^2}{4\pi\varepsilon_0} \cdot \frac{4(2b)^{3/2}}{\sqrt{\pi}} \cdot \frac{1}{4b} \\ &= -\frac{\hbar^2}{2m} 2b \left(\frac{3}{2} - 3 \right) - \frac{e^2}{4\pi\varepsilon_0} \cdot \sqrt{\frac{8b}{\pi}} \\ &= \frac{3\hbar^2}{2m} b - \frac{e^2}{2\pi^{3/2}\varepsilon_0} \sqrt{2b}.\end{aligned}$$

Now, we want to minimize $\langle\psi|H|\psi\rangle$ to get the best possible bound on the ground state energy. Hence, take the derivative with respect to b and set it equal to 0, so that

$$\frac{3\hbar^2}{2m} = \frac{e^2\sqrt{2}}{4\pi^{3/2}\varepsilon_0\sqrt{b}} \Longrightarrow$$
$$\Longrightarrow b = \left(\frac{me^2\sqrt{2}}{6\pi^{3/2}\hbar^2\varepsilon_0}\right)^2.$$

Plugging this back in, we find

$$\langle\psi|H|\psi\rangle = -\frac{me^4}{12\pi^3\hbar^2\varepsilon_0^2}.$$

Plugging in some numbers, we get

$$E_g \le -11.66 \text{ eV},$$

which is spectacularly close to the actual answer -13.6 eV.

Exercise 4. *Griffiths 9.18* When we turn on an external electric field, it should be possible to ionize the electron in an atom. A crude model for this is to suppose that a particle is in a very deep, one-dimensional finite square well from $x = -a$ to $x = a$.

a) What is the energy of the ground state, measured up from the bottom of the well? Assume that $V_0 \gg \hbar^2/ma^2$.

b) Introduce the perturbation $H' = -\alpha x$, where $\alpha \equiv eE_{\text{ext}}$. Assume that $\alpha a \ll \hbar^2/ma^2$, and sketch the total potential, noting that the electron can tunnel out in the direction of positive x.

c) Calculate

$$\gamma = \frac{1}{\hbar}\int |p(x)|\,\mathrm{d}x,$$

and estimate the time it would take for the particle to escape,

$$\tau = \frac{2x_1}{v}e^{2\gamma},$$

where x_1 is the distance the electron must travel to reach the tipping point of the potential and v is the speed of the electron.

d) Plug in some numbers, e.g. $V_0 = 20$ eV, $E_{\text{ext}} = 7\cdot 10^6$ V/m, $a = 10^{-10}$ m. Calculate τ, and compare it to the age of the universe.

a) In the limit $V_0 \gg \hbar^2/ma^2$, this is just the ground state energy of the *infinite* square well of width $2a$, which is

$$\frac{\hbar^2\pi^2}{8ma^2}.$$

b) The potential is

$$V(x) = \begin{cases} -\alpha x, & x \in (-a, a) \\ V_0 - \alpha x, & x > a \end{cases}.$$

This is a square well with a bottom that slopes downwards from left to right with a slope of $-\alpha$, and a top beginning at $x = a$ that slopes down from V_0 with a slope of $-\alpha$. A particle of energy E could then tunnel out after the point $x_0 = (V_0 - E)/\alpha$.

c) The limits of integration are from a to x_0, and $p(x) = \sqrt{2m(V_0 - E - \alpha x)}$. Thus,

$$\gamma = \frac{2\sqrt{2m}}{3\hbar\alpha}(V_0 - \alpha a - E)^{3/2}.$$

Since $V_0 \gg \alpha a + E$, we get that

$$\gamma \approx \frac{2\sqrt{2m}}{e\hbar\alpha} V_0^{3/2}.$$

To compute τ, assume that all energy is kinetic, so that $v = \pi\hbar/(2ma)$, using the ground state energy above. We also have that x_1 is just $x_0 - a$, so that $\tau \sim 10^{49}$ s, which is 32 orders of magnitude greater than the age of the universe.