

Review Session Problems Solutions

Jacob Erlikhman

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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

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

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

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

Thus,

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

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

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

- 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 $a_0 \rightarrow a_0/Z$; hence, $R_{n0}(0) \rightarrow Z^{3/2} R_{n0}(0)$. Thus,

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

- 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 7.45. Stark Effect in Hydrogen. When an atom is placed in a uniform electric field \mathbf{E}_{ext} , the energy levels are shifted. This is known as the **Stark effect**. You'll analyze the Stark effect for the $n = 1$ and $n = 2$ states of hydrogen. Suppose $\mathbf{E}_{\text{ext}} = E_{\text{ext}} \hat{z}$, so that

$$H' = eE_{\text{ext}}r \cos \theta$$

is the perturbation of the hamiltonian for the electron, where $H^0 = \frac{p^2}{2m} - \frac{e^2}{4\pi\epsilon_0} \frac{1}{r}$.

- a) Show that the ground state energy is unchanged at first order.
- b) How much degeneracy does the first excited state have? List the degenerate states.
- c) Determine the first-order corrections to the energy. Into how many levels does E_2 split?

Hint: All W_{ij} are 0 except for two, and you can avoid doing all of the zero integrals in this problem by using symmetry and selection rules. You'll need the following

$$\psi_{210} = \frac{1}{2\sqrt{6}} a^{-3/2} \frac{r}{a} e^{-r/2a} \sqrt{\frac{3}{4\pi}} \cos \theta$$

$$\psi_{200} = \frac{1}{\sqrt{2}} a^{-3/2} \left(1 - \frac{r}{2a}\right) e^{-r/2a} \frac{1}{2\sqrt{\pi}}.$$

- d) What are the “good” wavefunctions for (b)? Find the expectation value of the electric dipole moment in each of these states.
- a) The ground state is spherically symmetric, so clearly $\langle H' \rangle = 0$. (Also, you can recall that Y_{00} is a constant).
 - b) There are 4 degenerate states, ψ_{200} , ψ_{21m} , where $m \in \{-1, 0, 1\}$.

- c) First, note that all diagonal elements are 0. This is because a diagonal element will have an even angular part, cosine is even, and the measure will have a sine, which is odd. Since the integral is over an even interval, it will integrate to 0. The integral of ψ_{200} with any of the $m \neq 0$ states will be 0, since the integral of $e^{\pm i\varphi}$ will be 0. Likewise, this kills the integrals of ψ_{210} with any of the $m \neq 0$ states. Finally, we're left with the integral of ψ_{211} with ψ_{21-1} . But this will be 0 by the selection rule that $\ell + \ell'$ must be odd for the matrix element of an operator with odd parity (like $z = r \cos \theta$). We are thus left with one integral, that between the two states given in the hint. Let's do this integral. It will equal

$$\begin{aligned} & \frac{eE_{\text{ext}}}{16a^4\pi} \cdot 2\pi \int_0^\pi d\theta \int_0^\infty dr r^4 \left(1 - \frac{r}{2a}\right) e^{-r/a} \cos^2 \theta \sin \theta = \\ & = \frac{eE_{\text{ext}}}{8a^4} \cdot \frac{2}{3} \int_0^\infty dr r^4 \left(1 - \frac{r}{2a}\right) e^{-r/a}. \end{aligned}$$

The integral over r can be done by noticing the following.

$$\int_0^\infty dr r^n e^{-r/a} = -a r^n e^{-r/a} \Big|_0^\infty + a n \int_0^\infty dr r^{n-1} e^{-r/a}.$$

Notice that the boundary term vanishes, and we get the same integral multiplied by an with the exponent of r reduced by 1. Repeating this process, we'll be left with

$$a^n n! \int_0^\infty e^{-r/a} = a^{n+1} n!.$$

Thus, our original integral is equal to

$$\frac{eE_{\text{ext}}}{12a^4} (4!a^4 - 60a^4) = -3aeE_{\text{ext}}.$$

Denoting $\xi \equiv -3aeE_{\text{ext}}$, we want to find the eigenvalues of a 4×4 matrix all of whose terms are 0 except for a 2×2 minor which is of the form

$$\begin{bmatrix} 0 & \xi \\ \xi & 0 \end{bmatrix}. \quad (1)$$

The eigenvalues of this matrix are $\pm\xi$, and its eigenvectors are

$$\begin{aligned} \begin{bmatrix} 1 \\ 1 \end{bmatrix} &\leftrightarrow \xi \\ \begin{bmatrix} 1 \\ -1 \end{bmatrix} &\leftrightarrow -\xi. \end{aligned}$$

Thus, the energy E_2 splits into *three* energies. One corresponds to the states ψ_{2lm} which aren't ψ_{210} or ψ_{200} . These states have the same energy as for unshifted hydrogen. $\psi_{210} + \psi_{200}$ has energy which is shifted up by ξ , while $\psi_{210} - \psi_{200}$ has energy shifted down by ξ (so up by $3aeE_{\text{ext}}$).

- d) The good wavefunctions are given in the previous paragraph. To find $\langle ez \rangle$, the expectation value of the electric dipole, we again have to compute some integrals. But since $z = r \cos \theta$, we have already done them in (c)! Consider first

$$\frac{1}{\sqrt{2}}(\psi_{210} + \psi_{200}).$$

Then, since $H' = ezE_{\text{ext}}$, we have

$$\begin{aligned}\langle ez \rangle &= \frac{1}{E_{\text{ext}}} \langle \psi_{210} | H' | \psi_{200} \rangle \\ &= -3ae.\end{aligned}$$

On the other hand, if we instead consider the state

$$\frac{1}{\sqrt{2}}(\psi_{210} - \psi_{200}),$$

we get $\langle ez \rangle = 3ae$.

Exercise 4. Zeeman Effect. In this problem you will do a realistic calculation of the effect of magnetic fields on the $n = 2$ states of hydrogen. We will allow the magnetic field to *take on any value*, so that we won't assume that the Zeeman term is necessarily small or large in comparison to the fine structure terms. It will be helpful to use units where $m = \hbar = c = 1$, called **atomic units**. It will also be helpful to use the dimensionless variable

$$x = \frac{B}{B_1},$$

where B is the external magnetic field and B_1 is α times the strength $B_0 = 1$ magnetic field in atomic units,

$$\begin{aligned}B_1 &= \frac{e^7 m^2}{\hbar^5 c} \\ &= \alpha B_0 \\ &= \alpha \frac{m^2 e^5}{\hbar^4}.\end{aligned}$$

Note that I am using gaussian units for the formulas above.

For this problem, the hamiltonian H^0 is the hydrogen atom hamiltonian and

$$H^1 = H_r + H_{\text{SO}} + H_Z.$$

- Make a table which shows which of the operators $L^2, L_x, L_y, L_z, S^2, S_x, S_y, S_z, J^2, J_x, J_y, J_z$ commute with H^0 and which commute with H^1 .
- Use the table from (a) to find a basis in the 8-dimensional subspace of the $n = 2$ degenerate energy levels of H^0 for which the perturbing hamiltonian will be as diagonal as possible.
Hint: After choosing this basis, there should be only 16 off-diagonal matrix elements which you need to calculate.

- Hints:* You will need to use a Clebsch-Gordan table to calculate some of the matrix elements. You are allowed to (and should!) use a computer algebra program (e.g. Mathematica) to calculate the eigenvalues and eigenvectors of the 8×8 matrix you obtain while solving this problem.

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|----|----------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| | | L^2 | L_X | L_y | L_z | S^2 | S_x | S_y | S_z | J^2 | J_X | J_y | J_z |
| a) | H_r | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y |
| | H_{SO} | Y | N | N | N | Y | N | N | N | Y | Y | Y | Y |
| | H_D | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y |
| | H_Z | Y | N | N | Y | Y | N | N | Y | N | N | N | Y |

- c) The 8×8 matrix is below, where the basis is

$$\{|\ell, j, m_j\rangle\} = \{|0, 1/2, -1/2\rangle, |0, 1/2, 1/2\rangle, |1, 1/2, -1/2\rangle, |1, 1/2, 1/2\rangle, \\ |1, 3/2, -3/2\rangle, |1, 3/2, -1/2\rangle, |1, 3/2, 1/2\rangle, |1, 3/2, 3/2\rangle\}.$$

Note that the matrix elements are in this order, e.g. $|0, 1/2, -1/2\rangle$ corresponds to the first column/row. The way you calculate these matrix elements is by using the Clebsch-Gordan table for $\ell = 1$ and $s = 1/2$, which allow you to write the states as a linear combination of the eigenvectors of S_z (since $H_Z \propto J_z + S_z$).

[illegible]

where

$$E_{\text{FS}} = \frac{\alpha^2}{2 \cdot 2^4} \left(\frac{3}{4} - \frac{2}{j + 1/2} \right)$$

is the fine structure correction. Since this depends only on j , in the first 4 terms of the diagonal it is

$$E_{\text{FS}} = -\frac{5\alpha^2}{128}.$$

In the last 4 terms, it is

$$-\frac{\alpha^2}{128}.$$

Now, the weak Zeeman energy correction (not including the fine structure correction) in atomic units is

$$\Delta E = \alpha^2 x m_j \begin{cases} 1, & j = \frac{1}{2}, \ell = 0 \\ \frac{1}{3}, & j = \frac{1}{2}, \ell = 1 \\ \frac{2}{3}, & j = \frac{3}{2}, \ell = 1 \end{cases}.$$

We can then plug the matrix we obtained into Mathematica to get the eigenvalues, which I'm not going to write down (the expressions are a bit unwieldy). We can expand the eigenvalues for small x to find the same eigenvalues as for the Zeeman correction plus the fine structure correction. See the accompanying Mathematica notebook. A plot of the solutions is below.

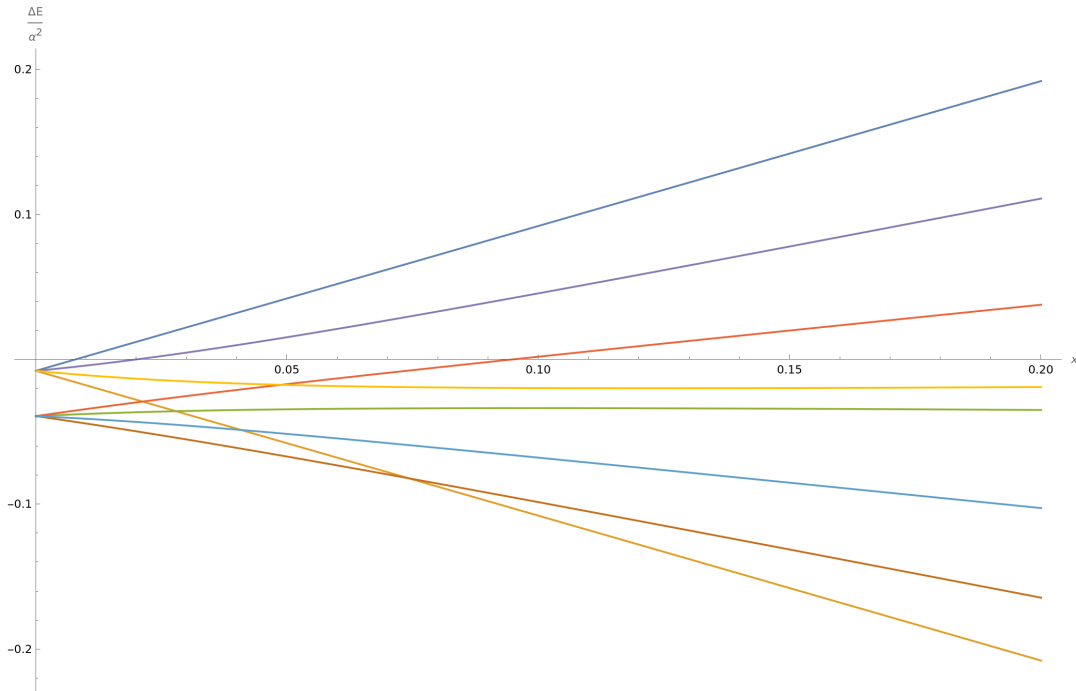


Figure 1: These energy shifts are measured relative to the $n = 2$ unshifted hydrogenic energies, which are all $-1/2 \cdot 2^2$ in atomic units. The top lines (those originating at the higher value of $\Delta E/\alpha^2$ at $x = 0$) correspond to the $j = 3/2$, $\ell = 1$ states, while the bottom lines correspond to the $j = 1/2$ states. Note that the energy levels cross as x increases. The fine structure splitting is overwhelmed by the Zeeman splitting at relatively small values (i.e. $x \approx 0.03$ instead of $x \approx 1$, as one might have expected) due to the quantum numbers introducing additional dimensionless factors which naive scaling arguments would ignore. Note that $x \approx 0.03$ corresponds to a magnetic field of about 0.4 T, which is accessible in modern laboratories.