Review Session Problems Solutions

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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

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

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

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

Thus,

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

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

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

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 7.45.*** **Stark Effect in Hydrogen.** When an atom is placed in a uniform electric field $\mathbf{E}_{\text{ext}}$, 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 $H^0 = \frac{p^2}{2m} - \frac{e^2}{4\pi\varepsilon_0}\frac{1}{r}$.

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, $\psi_{200},\ \psi_{21m}$, 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

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

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

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

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

$$\begin{bmatrix} 0 & \xi \\ \xi & 0 \end{bmatrix}. \tag{1}$$

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

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

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 relaistic 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

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

a) 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.

b) 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.

c) Find all eight levels for the $n = 2$ states of hydrogen perturbed by H^1.
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.

d) Expand the results of (c) for small x, and show that they agree with the energy levels for the weak field Zeeman effect. Do the same for large x, and show that they agree with the energy levels for the strong field Zeeman effect.

a)

	L^2	L_X	L_y	L_z	S^2	S_x	S_y	S_z	J^2	J_X	J_y	J_z
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

b) It looks like the n, ℓ, j, m_j basis is the best choice here, since the only off-diagonal elements will be for different values of j. Since $j \in \left\{\frac{1}{2}, \frac{3}{2}\right\}$, there are $4 \cdot 4 = 16$ off-diagonal elements, where the first 4 is from $j = 1/2$ (2 from $\ell = 0$ and 2 from $\ell = 1$) and the second 4 from $j = 3/2$ (when ℓ can only be 1).

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 $H_Z \propto J_z + S_z$).

$$\begin{bmatrix}
E_{\text{FS}} - \frac{\alpha^2 x}{2} & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & E_{\text{FS}} + \frac{\alpha^2 x}{2} & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & E_{\text{FS}} - \frac{\alpha^2 x}{6} & 0 & 0 & -\frac{\alpha^2 x}{3\sqrt{2}} & 0 & 0 \\
0 & 0 & 0 & E_{\text{FS}} + \frac{\alpha^2 x}{6} & 0 & 0 & -\frac{\alpha^2 x}{3\sqrt{2}} & 0 \\
0 & 0 & 0 & 0 & E_{\text{FS}} - \alpha^2 x & 0 & 0 & 0 \\
0 & 0 & -\frac{\alpha^2 x}{3\sqrt{2}} & 0 & 0 & E_{\text{FS}} - \frac{\alpha^2 x}{3} & 0 & 0 \\
0 & 0 & 0 & -\frac{\alpha^2 x}{3\sqrt{2}} & 0 & 0 & E_{\text{FS}} + \frac{\alpha^2 x}{3} & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & E_{\text{FS}} + \alpha^2 x
\end{bmatrix},$$

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

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

We can change our basis to obtain the following matrix instead

$$\begin{bmatrix}
E_{\text{FS}} - \frac{\alpha^2 x}{2} & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & E_{\text{FS}} + \frac{\alpha^2 x}{2} & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & E_{\text{FS}} - \alpha^2 x & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & E_{\text{FS}} + \alpha^2 x & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & E_{\text{FS}} - \frac{\alpha^2 x}{6} & -\frac{\alpha^2 x}{3\sqrt{2}} & 0 & 0 \\
0 & 0 & 0 & 0 & -\frac{\alpha^2 x}{3\sqrt{2}} & E_{\text{FS}} - \frac{\alpha^2 x}{3} & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & E_{\text{FS}} + \frac{\alpha^2 x}{3} & -\frac{\alpha^2 x}{3\sqrt{2}} \\
0 & 0 & 0 & 0 & 0 & 0 & -\frac{\alpha^2 x}{3\sqrt{2}} & E_{\text{FS}} + \frac{\alpha^2 x}{6}
\end{bmatrix},$$

Note that the order of our basis is now

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

Since this matrix is block diagonal with the largest size of a minor 2×2, we need only compute eigenvalues and eigenvectors of (2×2)-matrices. In particular, the eigenvalues are the first 4 terms on the diagonal, and the eigenvalues of the other two (2×2)-minors of the above matrix. So the first four eigenvalues are.

$$-\frac{5\alpha^2}{128} - \frac{\alpha^2 x}{2}$$
$$-\frac{5\alpha^2}{128} + \frac{\alpha^2 x}{2}$$
$$-\frac{\alpha^2}{128} - \alpha^2 x$$
$$-\frac{\alpha^2}{128} + \alpha^2 x.$$

The next four are

$$\alpha^2\left(-\frac{3}{128}-\frac{x}{4}-\frac{1}{64}\sqrt{1+32x\left(-\frac{1}{3}+8x\right)}\right)$$
$$\alpha^2\left(-\frac{3}{128}-\frac{x}{4}+\frac{1}{64}\sqrt{1+32x\left(-\frac{1}{3}+8x\right)}\right)$$
$$\alpha^2\left(-\frac{3}{128}+\frac{x}{4}-\frac{1}{64}\sqrt{1+32x\left(\frac{1}{3}+8x\right)}\right)$$
$$\alpha^2\left(-\frac{3}{128}+\frac{x}{4}+\frac{1}{64}\sqrt{1+32x\left(\frac{1}{3}+8x\right)}\right)$$

A plot of the solutions is below.

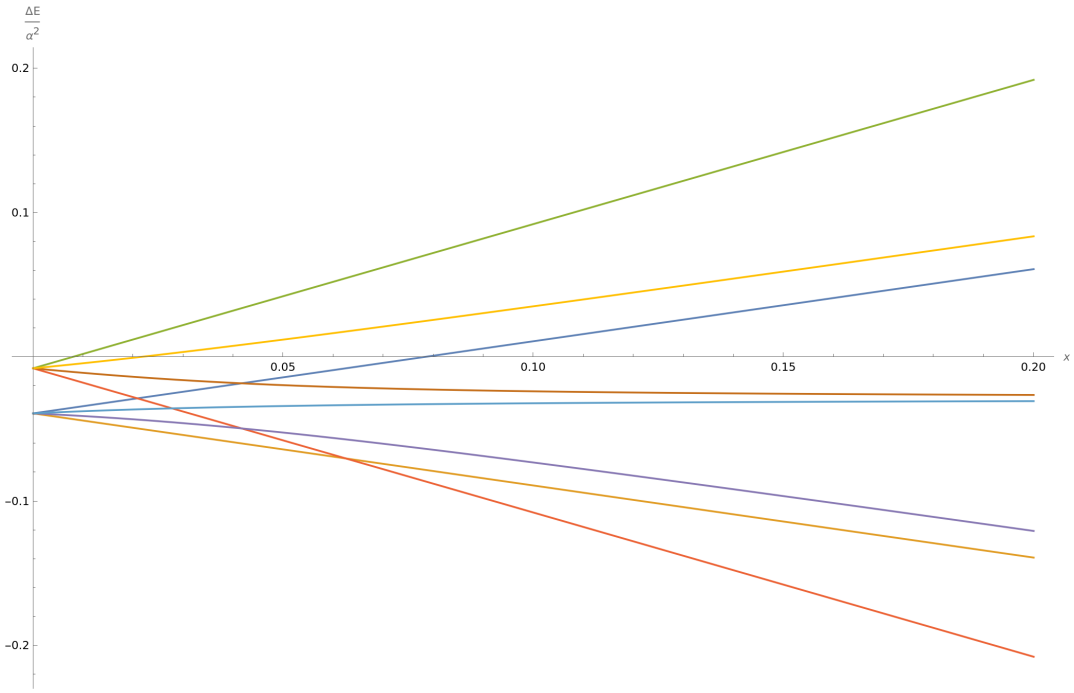

Figure 1: These energy shifts are measured relative to the $n = 2$ unshifted hydrogenic energies, which are all $-1/2 \cdot 2^2$ in atomic units. The top lines (those originating at the higher value of $\Delta E/\alpha^2$ at $x = 0$) correspond to the $j = 3/2$, $\ell = 1$ states, while the bottom lines 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.

d) 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 expand the eigenvalues for small x to find the same eigenvalues as for the Zeeman correction plus the fine structure correction. This only needs to be done for the four eigenvalues with square roots:

$$-\frac{3}{128} - \frac{x}{4} - \frac{1}{64}\sqrt{1 + 32x\left(-\frac{1}{3} + 8x\right)} \approx -\frac{3}{128} - \frac{x}{4} - \frac{1}{64}\left(1 - \frac{16x}{3}\right) = -\frac{5}{128} - \frac{x}{6}$$

$$-\frac{3}{128} - \frac{x}{4} + \frac{1}{64}\sqrt{1 + 32x\left(-\frac{1}{3} + 8x\right)} \approx -\frac{3}{128} - \frac{x}{4} + \frac{1}{64}\left(1 - \frac{16x}{3}\right) = -\frac{1}{128} - \frac{x}{3}$$

$$-\frac{3}{128} + \frac{x}{4} - \frac{1}{64}\sqrt{1 + 32x\left(\frac{1}{3} + 8x\right)} \approx -\frac{3}{128} + \frac{x}{4} - \frac{1}{64}\left(1 + \frac{16x}{3}\right) = -\frac{5}{128} + \frac{x}{6}$$

$$-\frac{3}{128} + \frac{x}{4} + \frac{1}{64}\sqrt{1 + 32x\left(\frac{1}{3} + 8x\right)} \approx -\frac{3}{128} + \frac{x}{4} + \frac{1}{64}\left(1 + \frac{16x}{3}\right) = -\frac{1}{128} + \frac{x}{3}$$

Clearly, these match the ΔE values above.

We will do the strong field Zeeman splitting in the case that we can ignore H_{FS} entirely. In this case, we have the eigenvalues (α^2 omitted everywhere)

$$\begin{matrix} -\frac{x}{2} \\ \frac{x}{2} \\ -x \\ x \\ -\frac{x}{2} \\ 0 \\ 0 \\ \frac{x}{2}, \end{matrix}$$

where the last four follow from expanding

$$\sqrt{1 + 32x\left(\pm\frac{1}{3} + 8x\right)} \approx \sqrt{32 \cdot 8x^2} = 16x.$$

These agree with the strong Zeeman effect when we ignore fine structure.