33-756 Homework 5

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1. Corrections to the Hydrogen Atom

In class, we said that there are two other corrections (aside from spin-orbit) which contribute at order v^2/c^2. Let us consider the correction to the kinetic energy

$$H_{\text{KE}} = -\frac{\vec{\mathbf{p}}^4}{8m^3c^2}.$$

Calculate the shift in the $n = 1$, $l = 0$ level.

$$\Delta E_{\text{KE}}^{100} = -\frac{1}{8m^3c^2} \langle \psi_{100} | \vec{\mathbf{p}}^4 | \psi_{100} \rangle$$

However, rather than evaluate the momentum operator to the fourth power in spherical coordinates, we can rewrite this perturbation as

$$\begin{aligned} -\frac{\vec{\mathbf{p}}^4}{8m^3c^2} &= -\frac{1}{2mc^2}\left(\frac{\vec{\mathbf{p}}^2}{2m}\right)^2 = -\frac{1}{2mc^2}\left(H_0 + \frac{e^2}{r}\right)^2 \\ &= -\frac{1}{2mc^2}\left(H_0^2 + \frac{2e^2H_0}{r} + \frac{e^4}{r^2}\right) \end{aligned}$$

Using this, we can write the energy shift as

$$\Delta E_{\text{KE}}^{100} = -\frac{1}{2mc^2}\left(E_n^2 + 2e^2E_n\left\langle\frac{1}{r}\right\rangle + e^4\left\langle\frac{1}{r^2}\right\rangle\right)$$

From class, online, or through a thorough proof involving the Hellmann-Feynman theorem, we could show that the expectation value for $\frac{1}{r}$ is

$$\left\langle\frac{1}{r}\right\rangle = \frac{1}{a_0}$$

and

$$\left\langle\frac{1}{r^2}\right\rangle = \frac{2}{a_0^2}$$

Plugging all of this in, we find that

$$\Delta E_{\text{KE}}^{100} = -\frac{5}{8}mc^2\alpha^4$$

Now consider the $n = 2$ level. Ignoring spin, this level has four degenerate states. We showed in class that in such cases we may need to use degenerate perturbation theory where we diagonalize the perturbing Hamiltonian. However, this is not necessary if the Hamiltonian has no non-vanishing, off-diagonal matrix elements. Why is this true?

From perturbation theory, the first-order correction to the perturbed wave function is

$$\left|\psi_n^{(1)}\right\rangle = \sum_{m\neq n} \frac{\left\langle \psi_m^{(0)} \middle| V \middle| \psi_n^{(0)} \right\rangle}{E_n^{(0)} - E_m^{(0)}} \left|\psi_m^{(0)}\right\rangle$$

If all of the off-diagonal matrix elements vanish, the numerator will be zero, since these are the off-diagonal elements of the Hamiltonian (since it's a sum over $m \neq n$). Therefore, for such Hamiltonians, there is no first-order correction to the wave function.

Determine whether or not H_{KE} has non-vanishing, off-diagonal matrix elements within the $n = 2$ system. That is, determine the selection rules for this operator. Can it change l or m?

Since $\vec{\mathbf{p}}^4$ is a scalar under rotations, $\left[\vec{\mathbf{p}}^4, \vec{\mathbf{L}}^2\right] = \left[\vec{\mathbf{p}}^4, L_z\right] = 0$. Therefore

$$\begin{aligned} \langle n'l'm'|\left[H_{\mathrm{KE}}, \vec{\mathbf{L}}^2\right]|nlm\rangle &= \langle n'l'm'|H_{\mathrm{KE}}\vec{\mathbf{L}}^2|nlm\rangle - \langle n'l'm'|\vec{\mathbf{L}}^2 H_{\mathrm{KE}}|nlm\rangle \\ 0 &= \hbar^2\left((l(l+1)) - (l'(l'+1))\,\langle n'l'm'|H_{\mathrm{KE}}|nlm\rangle\right) \end{aligned}$$

The nonzero matrix elements are possible when $l'(l'+1) = l(l+1)$. Solving for this, we find $l = l'$. This selection rule gives "on-diagonal" matrix elements only, and so far, there are no nonzero off-diagonal elements.
Next

$$\begin{aligned} \langle n'l'm'|[H_{\mathrm{KE}}, L_z]|nlm\rangle &= \langle n'l'm'|H_{\mathrm{KE}L_z}|nlm\rangle - \langle n'l'm'|L_z H_{\mathrm{KE}}|nlm\rangle \\ 0 &= \hbar(m - m')\,\langle n'l'm'|H_{\mathrm{KE}}|nlm\rangle \end{aligned}$$

Again, the selection rule is $m = m'$, so there are no non-vanishing, off-diagonal matrix elements.

Next, consider the Darwin term which arises from the fact that the electron has a finite Compton wavelength.

$$H_{\mathrm{D}} = \frac{\pi e^2 \hbar^2}{2m^2c^2}\delta^3(\vec{\mathbf{R}})$$

Calculate the shift in the $n = 1$ energy level. If we consider the $n = 2$ state, are there any non-vanishing, off-diagonal matrix elements? Calculate the shift in the p-wave orbitals.

$$\Delta E_{\mathrm{D}}^{100} = \frac{\pi e^2\hbar^2}{2m^2c^2}\left\langle \delta^3(\vec{\mathbf{R}})\right\rangle_{100}$$

and

$$\left\langle \delta^3(\vec{\mathbf{R}})\right\rangle_{100} = \frac{1}{\pi a_0^3}\int e^{-2\frac{r}{a_0}}\delta(r)\,\mathrm{d}r = \frac{1}{\pi a_0^3}e^{-2\frac{0}{a_0}} = \frac{1}{\pi a_0^3}$$

where $a_0 = \frac{\hbar^2}{me^2}$, so

$$\Delta E_{\mathrm{D}}^{100} = \frac{e^8 m}{2c^2\hbar^4} = \frac{1}{2}mc^2\alpha^4$$

For the $n = 2$ state, there are no non-vanishing, off-diagonal matrix elements because all of the p-wave orbitals have wave functions $\psi \propto re^{-\frac{r}{2a_0}}$, so they vanish at the origin. While this is not true for the $2s$ state, the only non-zero matrix element will be on the diagonal for that state, since the r-dependence in the p-wave orbitals will cause the whole term to be zero. Therefore,

$$\Delta E_{\mathrm{D}}^{21\{-1,0,1\}} = 0$$

Now we would like to determine the net shift in the $n = 1$ state. Collect your results from this problem to determine the net change in the $n = 1$ state. Present your answer in eV. Why is it OK to ignore the spin coupling for this state?

$$\Delta E_{\mathrm{KE}}^{100} + \Delta E_{\mathrm{D}}^{100} = \left(-\frac{5}{8} + \frac{1}{2}\right) mc^2\alpha^4 = -\frac{1}{8}mc^2\alpha^4 \approx 510,998\frac{\mathrm{eV}}{c^2}c^2\left(\frac{1}{137}\right)^4 = 0.00145056\mathrm{eV}$$

We can ignore the spin coupling because the Hamiltonian is proportional to $\vec{\mathbf{J}}^2 - \vec{\mathbf{L}}^2 - \vec{\mathbf{S}}^2$ and for the $1s$ state, $l = 0$, $\vec{\mathbf{J}}^2\,|1s\rangle \propto \frac{1}{2}\left(\frac{1}{2}+1\right)|1s\rangle = \vec{\mathbf{S}}^2\,|1s\rangle$ so the $\vec{\mathbf{J}}^2 - \vec{\mathbf{S}}^2$ term will vanish. For higher energy states, we need to take into account the different ways of adding angular momentum and spin to form total angular momentum, but for the $1s$ state, there is no angular momentum except for spin.

2. Clebsch-Gordan Coefficients

Consider adding two spins, one of 3/2 and the other 1/2. Calculate all of the Clebsch-Gordan coefficients.

From group theory, we know that

$$\frac{3}{2}\otimes\frac{1}{2} = \left(\frac{3}{2}+\frac{1}{2}\right)\oplus\left(\frac{3}{2}-\frac{1}{2}\right) = 2\oplus 1$$

since in general, $J_1 \otimes J_2 = (J_1 + J_2) \oplus (J_1 + J_2 - 1) \oplus \cdots \oplus (J_1 - J_2)$. We first identify the highest states in both bases:

$$|2,2\rangle = \left|\frac{3}{2},\frac{3}{2}\right\rangle \otimes \left|\frac{1}{2},\frac{1}{2}\right\rangle \equiv \left|\frac{3}{2},\frac{3}{2}\right\rangle\left|\frac{1}{2},\frac{1}{2}\right\rangle$$

Next, we act the lowering operator on both sides:

$$J_-\,|2,2\rangle = \hbar\sqrt{(J+M)(J-M+1)}\,|2,2-1\rangle = \hbar\sqrt{(4)(1)}\,|2,1\rangle = 2\hbar\,|2,1\rangle$$

$$j_-\left|\frac{3}{2},\frac{3}{2}\right\rangle\left|\frac{1}{2},\left|\frac{1}{2}\right\rangle\right\rangle + \left|\frac{3}{2},\frac{3}{2}\right\rangle j_-\left|\frac{1}{2},\frac{1}{2}\right\rangle = \hbar\left(\sqrt{3}\left|\frac{3}{2},\frac{1}{2}\right\rangle\left|\frac{1}{2},\frac{1}{2}\right\rangle + \left|\frac{3}{2},\frac{3}{2}\right\rangle\left|\frac{1}{2},-\frac{1}{2}\right\rangle\right)$$

so

$$|2,1\rangle = \frac{\sqrt{3}}{2}\left|\frac{3}{2},\frac{1}{2}\right\rangle\left|\frac{1}{2},\frac{1}{2}\right\rangle + \frac{1}{2}\left|\frac{3}{2},\frac{3}{2}\right\rangle\left|\frac{1}{2},-\frac{1}{2}\right\rangle$$

We can continue using ladder operators to get the rest of the $J = 2$ states:

$$J_-\,|2,1\rangle = \sqrt{6}\hbar\,|2,0\rangle$$

$$\frac{\sqrt{3}}{2}j_-\left|\frac{3}{2},\frac{1}{2}\right\rangle\left|\frac{1}{2},\frac{1}{2}\right\rangle + \frac{1}{2}j_-\left|\frac{3}{2},\frac{3}{2}\right\rangle\left|\frac{1}{2},-\frac{1}{2}\right\rangle + \frac{\sqrt{3}}{2}\left|\frac{3}{2},\frac{1}{2}\right\rangle j_-\left|\frac{1}{2},\frac{1}{2}\right\rangle + \frac{1}{2}\left|\frac{3}{2},\frac{3}{2}\right\rangle j_-\left|\frac{1}{2},-\frac{1}{2}\right\rangle$$
$$= \sqrt{3}\hbar\left|\frac{3}{2},-\frac{1}{2}\right\rangle\left|\frac{1}{2},\frac{1}{2}\right\rangle + \frac{\sqrt{3}}{2}\hbar\left|\frac{3}{2},\frac{1}{2}\right\rangle\left|\frac{1}{2},-\frac{1}{2}\right\rangle + \frac{\sqrt{3}}{2}\hbar\left|\frac{3}{2},\frac{1}{2}\right\rangle\left|\frac{1}{2},-\frac{1}{2}\right\rangle + 0$$
$$= \sqrt{3}\hbar\left[\left|\frac{3}{2},-\frac{1}{2}\right\rangle\left|\frac{1}{2},\frac{1}{2}\right\rangle + \left|\frac{3}{2},\frac{1}{2}\right\rangle\left|\frac{1}{2},-\frac{1}{2}\right\rangle\right]$$

Therefore,

$$|2,0\rangle = \frac{1}{\sqrt{2}}\left[\left|\frac{3}{2},-\frac{1}{2}\right\rangle\left|\frac{1}{2},\frac{1}{2}\right\rangle + \left|\frac{3}{2},\frac{1}{2}\right\rangle\left|\frac{1}{2},-\frac{1}{2}\right\rangle\right]$$

Next, $J_-\,|2,1\rangle = \sqrt{6}\hbar\,|2,-1\rangle$ and

$$\begin{aligned}
&\frac{1}{\sqrt{2}}\left[j_-\left|\frac{3}{2},-\frac{1}{2}\right\rangle\left|\frac{1}{2},\frac{1}{2}\right\rangle + j_-\left|\frac{3}{2},\frac{1}{2}\right\rangle\left|\frac{1}{2},-\frac{1}{2}\right\rangle + \left|\frac{3}{2},-\frac{1}{2}\right\rangle j_-\left|\frac{1}{2},\frac{1}{2}\right\rangle + \left|\frac{3}{2},\frac{1}{2}\right\rangle j_-\left|\frac{1}{2},-\frac{1}{2}\right\rangle\right]\\
&= \frac{\hbar}{\sqrt{2}}\left[\sqrt{3}\left|\frac{3}{2},-\frac{3}{2}\right\rangle\left|\frac{1}{2},\frac{1}{2}\right\rangle + 2\left|\frac{3}{2},-\frac{1}{2}\right\rangle\left|\frac{1}{2},-\frac{1}{2}\right\rangle + \left|\frac{3}{2},-\frac{1}{2}\right\rangle\left|\frac{1}{2},-\frac{1}{2}\right\rangle + 0\right]\\
&= \frac{\hbar}{\sqrt{2}}\left[\sqrt{3}\left|\frac{3}{2},-\frac{3}{2}\right\rangle\left|\frac{1}{2},\frac{1}{2}\right\rangle + 3\left|\frac{3}{2},-\frac{1}{2}\right\rangle\left|\frac{1}{2},-\frac{1}{2}\right\rangle\right]
\end{aligned}$$

Therefore

$$|2,-1\rangle = \frac{1}{2}\left|\frac{3}{2},-\frac{3}{2}\right\rangle\left|\frac{1}{2},\frac{1}{2}\right\rangle + \frac{\sqrt{3}}{2}\left|\frac{3}{2},-\frac{1}{2}\right\rangle\left|\frac{1}{2},-\frac{1}{2}\right\rangle$$

The lowest state with $J=2$ can be deduced by the same reasoning as with the highest state:

$$|2,-2\rangle = \left|\frac{3}{2},-\frac{3}{2}\right\rangle\left|\frac{1}{2},-\frac{1}{2}\right\rangle$$

For $J=1$, we first start an arbitrary state with $M = m_1 + m_2 = 1$:

$$|1,1\rangle = \alpha\left|\frac{3}{2},\frac{1}{2}\right\rangle\left|\frac{1}{2},\frac{1}{2}\right\rangle + \beta\left|\frac{3}{2},\frac{3}{2}\right\rangle\left|\frac{1}{2},-\frac{1}{2}\right\rangle$$

We want this to be orthogonal to $|2,1\rangle$, so

$$|1,1\rangle = -\frac{1}{2}\left|\frac{3}{2},\frac{1}{2}\right\rangle\left|\frac{1}{2},\frac{1}{2}\right\rangle + \frac{\sqrt{3}}{2}\left|\frac{3}{2},\frac{3}{2}\right\rangle\left|\frac{1}{2},-\frac{1}{2}\right\rangle$$

Applying the lowering operator gives us $J_-\,|1,1\rangle = \sqrt{2}\hbar\,|1,0\rangle$ and

$$\begin{aligned}
&-\frac{1}{2}j_-\left|\frac{3}{2},\frac{1}{2}\right\rangle\left|\frac{1}{2},\frac{1}{2}\right\rangle + \frac{\sqrt{3}}{2}j_-\left|\frac{3}{2},\frac{3}{2}\right\rangle\left|\frac{1}{2},-\frac{1}{2}\right\rangle - \frac{1}{2}\left|\frac{3}{2},\frac{1}{2}\right\rangle j_-\left|\frac{1}{2},\frac{1}{2}\right\rangle + \frac{\sqrt{3}}{2}\left|\frac{3}{2},\frac{3}{2}\right\rangle j_-\left|\frac{1}{2},-\frac{1}{2}\right\rangle\\
&= -\hbar\left|\frac{3}{2},-\frac{1}{2}\right\rangle\left|\frac{1}{2},\frac{1}{2}\right\rangle + \frac{3}{2}\hbar\left|\frac{3}{2},\frac{1}{2}\right\rangle\left|\frac{1}{2},-\frac{1}{2}\right\rangle - \frac{1}{2}\hbar\left|\frac{3}{2},\frac{1}{2}\right\rangle\left|\frac{1}{2},-\frac{1}{2}\right\rangle + 0\\
&= -\hbar\left|\frac{3}{2},-\frac{1}{2}\right\rangle\left|\frac{1}{2},\frac{1}{2}\right\rangle + \hbar\left|\frac{3}{2},\frac{1}{2}\right\rangle\left|\frac{1}{2},-\frac{1}{2}\right\rangle
\end{aligned}$$

so

$$|1,0\rangle = \frac{1}{\sqrt{2}}\left[-\left|\frac{3}{2},-\frac{1}{2}\right\rangle\left|\frac{1}{2},\frac{1}{2}\right\rangle + \left|\frac{3}{2},\frac{1}{2}\right\rangle\left|\frac{1}{2},-\frac{1}{2}\right\rangle\right]$$

Finally, for the $|1,-1\rangle$ state, I don't want to work out the whole thing again. Technically all three of these can be solved by orthogonality:

$$|1,-1\rangle = -\frac{\sqrt{3}}{2}\left|\frac{3}{2},-\frac{3}{2}\right\rangle\left|\frac{1}{2},\frac{1}{2}\right\rangle + \frac{1}{2}\left|\frac{3}{2},-\frac{1}{2}\right\rangle\left|\frac{1}{2},-\frac{1}{2}\right\rangle$$

Now that we know all the states, we can read out the (nonzero) Clebsch-Gordan coefficients:

$$\begin{aligned}
C^{2,2}_{\frac{3}{2},\frac{3}{2},\frac{1}{2},\frac{1}{2}} &= C^{2,-2}_{\frac{3}{2},-\frac{3}{2},\frac{1}{2},-\frac{1}{2}} && && &&= 1\\
C^{2,1}_{\frac{3}{2},\frac{1}{2},\frac{1}{2},\frac{1}{2}} &= C^{2,-1}_{\frac{3}{2},-\frac{1}{2},\frac{1}{2},-\frac{1}{2}} &&= C^{1,1}_{\frac{3}{2},\frac{3}{2},\frac{1}{2},-\frac{1}{2}} &&= -C^{1,-1}_{\frac{3}{2},-\frac{3}{2},\frac{1}{2},\frac{1}{2}} &&= \sqrt{\frac{3}{4}}\\
C^{2,1}_{\frac{3}{2},\frac{3}{2},\frac{1}{2},-\frac{1}{2}} &= C^{2,-1}_{\frac{3}{2},-\frac{3}{2},\frac{1}{2},\frac{1}{2}} &&= -C^{1,1}_{\frac{3}{2},\frac{1}{2},\frac{1}{2},\frac{1}{2}} &&= C^{1,-1}_{\frac{3}{2},-\frac{1}{2},\frac{1}{2},-\frac{1}{2}} &&= \frac{1}{2}\\
C^{2,0}_{\frac{3}{2},-\frac{1}{2},\frac{1}{2},\frac{1}{2}} &= C^{2,0}_{\frac{3}{2},\frac{1}{2},\frac{1}{2},-\frac{1}{2}} &&= -C^{1,0}_{\frac{3}{2},-\frac{1}{2},\frac{1}{2},\frac{1}{2}} &&= C^{2,0}_{\frac{3}{2},\frac{1}{2},\frac{1}{2},-\frac{1}{2}} &&= \sqrt{\frac{1}{2}}
\end{aligned}$$