Physics 4261: Lectures for week 6

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6.1 Hyperfine splitting

Thus far we have only considered the nucleus as being an electric charge. However, the nucleus also carries a spin, as does the electron. The nucleus interacts with the magnetic field by the formula

$$-g_I \mu_N \mathbf{I} \cdot \mathbf{B},$$

where $\mu_N = \mu_B m_e / M_p$, and g_I is a fudge factor that we leave to nuclear physicists to figure out. This moment can couple to the magnetic field produced by the electron. Let's make a simple estimation, assuming the nucleus is fixed. We have two ways to do this. For s states, we don't worry about magnetic field produce by the orbital angular momentum of the electron, and only worry about the electron's spin. In this case we consider only the region very near the nucleus, as the nucleus itself is extremely small. Considering the electron's wavefunction to define a magnetization density

$$\mathbf{M} = -g_s \mu_B \mathbf{s} |\psi(r)|^2.$$

Now, from E&M, we know that inside a uniformly magnetized sphere, we have a field $\mathbf{B} = 2/3\mu_0 \mathbf{M}$. This same argument shows zero field in the empty region of a hollow sphere (analogous to, but not the same as, the zero field inside a hollow charged sphere). Thus, we get an electron field of

$$\mathbf{B}_e = -\frac{2}{3}\mu_0 g_s \mu_B |\psi(0)|^2 \mathbf{s},$$

leading to a hyperfine interaction

$$H_{\text{HFS}} = g_I \mu_N \frac{2}{3}\mu_0 g_s \mu_B |\psi(0)|^2 \mathbf{I} \cdot \mathbf{s}.$$

Now let's make some gestures in the direction of the case $l \neq 0$. In this case, the field of the electron can be computed from the formula,

$$\mathbf{B}_e = \frac{\mu_0}{4\pi}\left\{\frac{-e\mathbf{v} \times \mathbf{r}}{r^3} - \frac{\boldsymbol{\mu}_e - 3(\boldsymbol{\mu}_e \cdot \hat{\mathbf{r}})\hat{\mathbf{r}}}{r^3}\right\},$$

where the first term is the orbital magnetic field (Biot-Savart law) and the second term is the magnetic dipole of the spin. At this point, we wave our hands, and argue that all of these terms depend on μ_B and $1/r^3$, and the angular momentum, so we get some interaction (to do it right we would be doing some difficult angular integrals)

$$H_{\text{HFS}} \propto g_I \mu_N \mu_0 \mu_B \left\langle \frac{1}{r^3} \right\rangle \mathbf{I} \cdot \mathbf{J},$$
$$H_{\text{HFS}} = A\mathbf{I} \cdot \mathbf{J}.$$

With $l = 0$, we had $\mathbf{J} = \mathbf{s}$, so in fact the interaction will always involve $\mathbf{I} \cdot \mathbf{J}$. Like fine structure, we have a $1/r^3$ dependence, but we lack a dependence on the nuclear charge Z, instead depending on nuclear moment. Therefore, we expect a Z dependence instead of a Z^2 dependence. This is a pretty crude approximation, but something to keep in mind, and in general it's true that high-Z atoms have more hyperfine splitting. Note also that the interval rule should apply to hyperfine splitting, although interactions which are higher powers of $\mathbf{I} \cdot \mathbf{J}$ are also allowed if we consider quadrupolar nuclei. To find the spectrum of hyperfine interactions, as before consider the operator $\mathbf{F} = \mathbf{I} + \mathbf{J}$.

6.2 Other nuclear effects

The nucleus has other small effects on the electronic structure. These sometimes lead to isotope shifts, for example between hydrogen and deuterium, but isotope shifts are present in nearly all species. One of these effects is of course the reduced mass effect. Another effect is nuclear size, which gives a small correction to the Coulomb potential at short range. For hydrogen, and highly charge hydrogen-like atoms, these effects can be quantified because exact results for transitions can be calculated.

6.3 Zeeman effect

We now consider, in a quantum mechanical way, the effect of a magnetic field on our atom. We are going to work within perturbation theory, so our first assumption is that the principal quantum number and orbital angular momentum quantum numbers are not affected by the magnetic field. Next we observe that the z-axis angular momentum operator F_z (or J_z) remains a good quantum number, since rotation around the magnetic field is still a symmetry of the system (note we are putting the field on the z axis by convention). Since we are working within perturbation theory, let's consider first the effect of magnetic fields on spins and orbital angular momenta directly. Now, we now that electrons and nuclei couple to the field via

$$H_e = g_s \mu_B s_z B, \qquad H_n = -g_I \mu_N I_z B.$$

What about orbital angular momentum? We derived a classical result earlier, but let's do a quantum treatment. To add magnetic field to the Schrödinger equation, we replace $\mathbf{p}$ by $\mathbf{p} + e\mathbf{A}$, where $\mathbf{A}$ is the vector potential of the field. We will work in the so-called symmetric gauge, so that

$$A_x = -\frac{B_0}{2} y, \qquad A_y = \frac{B_0}{2} x, \qquad A_z = 0.$$

You can see that $\nabla \times \mathbf{A} = \mathbf{B} = B\hat{z}$. Now,

$$\begin{aligned}(\mathbf{p} + e\mathbf{A})^2 &= \frac{p^2}{2m} + \frac{e^2A^2}{2m} - \frac{p_x eBy}{2m} + \frac{p_y eBx}{2m}, \\ &= \frac{e\hbar}{2m}\mathbf{l} \cdot \mathbf{B} = \mu_B \mathbf{l} \cdot \mathbf{B} = \mu_B l_z B.\end{aligned}$$

So the orbital angular momentum couples to the magnetic field with the Bohr magneton. To illustrate the general principle we are going to consider $l = 0$ and $s = j = 1/2$. We fill use more pertrubation results, and you will start to see how perturbations can be really helpful in tackling the harder problem. By hard problem, I mean that the Hamiltonian now includes a whole bunch of angular momentum operators dotted to each other, and to the external field, and very few of these commute. In general denote each angular momentum by $\mathbf{j}_n$, we have a massive Hamiltonian:

$$H = \sum_u g_u \mathbf{j}_u \cdot \mathbf{B} + \sum_{<uv>} c_{uv} \mathbf{j}_u \cdot \mathbf{j}_v$$

That's why we need to simplify and use approximations.

6.4 The Zeeman and hyperfine Hamiltonian

Let's work the case of ^{6}Li, where $I = 1$ and $S = J = 1/2$. Our Hamiltonian is,

$$\begin{aligned}H &= g_s \mu_B B J_z - g_I \mu_N B I_z + A_{\text{HF}} \mathbf{J} \cdot \mathbf{I}, \\ &= \frac{g_s\mu_B - g_I\mu_N}{2}(J_z + I_z)B + \frac{g_s\mu_B + g_I\mu_N}{2}(J_z - I_z)B + A_{\text{HF}}\mathbf{J} \cdot \mathbf{I}, \\ &= g_- B(J_z - I_z) + g_+ B(J_z + I_z) + A_{\text{HF}} \mathbf{J} \cdot \mathbf{I}.\end{aligned}$$

Note that **F** is no longer a good operator, as it does not commute with the $J_z - I_z$ terms. So this will be a trickier problem, but not one that is too difficult to solve. We will consider it in two different limits and then develop an exact solution.

6.4.1 Strong-field limit

Sometimes known as the Paschen-Back effect, let's take $g_- B$ to be larger than A_{HF}. Then the good quantum numbers are m_J and m_I. By "good quantum numbers" I mean the eigenvalues of a "good" set of mutually commuting operators. Any such set will be a valid description of the basis, but the "good" ones will be eigenstates of the largest energy scale in the problem. The first two terms of the Hamiltonian can be computed, the state $|m_J, m_I\rangle$ has energy $E = g_- B(m_J - m_I) + g_- B(m_J + m_I)$. But what of the third term? Recall that

$$\mathbf{J} \cdot \mathbf{I} = J_z I_z + \frac{1}{2} J_+ I_- + \frac{1}{2} J_- I_+.$$

We note that in this case, there is no degeneracy between states which are connected by the ladder operators, since then differn in the value of $m_J - m_I$ and $g_- B$ is large. Then it is easy to see that

$$\begin{aligned}\langle m_J, m_I | \, H \, | m_J, m_I \rangle &= g_- B(m_J - m_I) + g_+ B(m_J + m_I) + A_{\text{HF}} m_J I_J \\ &\quad + A_{\text{HF}} \langle m_J, m_I | \, J_+ I_- \, | m_J, m_I \rangle + A_{\text{HF}} \langle m_J, m_I | \, J_- I_+ \, | m_J, m_I \rangle \,,\end{aligned}$$

but the last two terms are zero,

$$\begin{aligned}
\langle m_J, m_I | \, H \, | m_J, m_I \rangle &= g_- B(m_J - m_I) + g_+ B(m_J + m_I) + A_{\mathrm{HF}} m_J I_J, \\
\langle m_J, m_I | \, H \, | m_J, m_I \rangle &= g_s \mu_B B m_J - g_I \mu_N B m_I + A_{\mathrm{HF}} m_J I_J, \\
\langle m_J, m_I | \, H \, | m_J, m_I \rangle &\approx g_s \mu_B B m_J + A_{\mathrm{HF}} m_J I_J,
\end{aligned}$$

where in the last step I ignored the small nuclear moment.

6.4.2 Weak-field limit

On the other hand let's take A_{HF} much larger than $g_- B$. In this case F and m_F are the good quantum numbers, and the state $|F, m_F\rangle$ has energy $E = A_{\mathrm{HF}}/2\,[F(F+1) - J(J+1) - I(I+1)] + g_+ B(m_F)$. The perturbation term is

$$\langle F, m_F | \, H' \, | F, m_F \rangle = g_- B \, \langle F, m_F | \, J_z - I_z \, | F, m_F \rangle \, .$$

How should we calculate such a thing? It turns out to be easiest to come back to our old friends the raising and lowering operators. A note first about notation, we have a state $|F, m_F\rangle$, and in general, this state can be written as a combination of m_J and m_I values, as

$$|F, m_F\rangle = \alpha \, | J, m_J, I, m_I \rangle + \beta \, | J, m_J', I, m_I' \rangle + \gamma \, | J, m_J'', I, m_I'' \rangle + \cdots \, ,$$

and the Clebsch-Gordon coefficients, instead of being Greek letters, are denoted

$$\langle J, m_J, I, m_I | F, m_F \rangle \, .$$

Now take as an example the case of $J = 3/2$, and $I = 1$ (the $2p_{3/2}$ excited state of ^{6}Li for example). In this case we know $F = 5/2, 3/2, 1/2$. Let's say we want to know about the $F = 3/2$ case. We write all possible values of m_J and m_I for the maximum m_F state:

$$\left| \frac{3}{2}, \frac{3}{2} \right\rangle = \alpha \left| \frac{3}{2}, \frac{3}{2}, 1, 0 \right\rangle + \beta \left| \frac{3}{2}, \frac{1}{2}, 1, 1 \right\rangle \, .$$

Then apply the F_+ operator, knowing we will get zero,

$$F_+ \left| \frac{3}{2}, \frac{3}{2} \right\rangle = \sqrt{2}\alpha \left| \frac{3}{2}, \frac{3}{2}, 1, 1 \right\rangle + \sqrt{3}\beta \left| \frac{3}{2}, \frac{3}{2}, 1, 1 \right\rangle = 0.$$

Thus, we can solve for α and β, normalizing to get $\alpha = \sqrt{3/5}$, $\beta = -\sqrt{2/5}$. There is some sign ambiguity, but for expectation values it does not matter. From here we can read out that $\left\langle \frac{3}{2}, \frac{3}{2} \right| J_z \left| \frac{3}{2}, \frac{3}{2} \right\rangle = 3/2(3/5) + 1/2(2/5) = 11/10$. A useful fact is that $\langle F, m_F | \, J_z \, | F, m_F \rangle$ is always linearly proportional to m_F, so that

$$\left\langle \frac{3}{2}, -\frac{3}{2} \right| J_z \left| \frac{3}{2}, -\frac{3}{2} \right\rangle = -11/10,$$

$$\left\langle \frac{3}{2}, \frac{1}{2} \right| J_z \left| \frac{3}{2}, \frac{1}{2} \right\rangle = 11/30.$$

Putting it all together, that gives

$$\begin{aligned}
\langle F, m_F | \, H \, | F, m_F \rangle = \frac{A_{\mathrm{HF}}}{2} [F(F+1) - J(J+1) - I(I+1)] + g_+ B m_F + \\
\sum_{m_J, m_I} \langle J, m_J, I, m_I | \, | F, m_F \rangle \, g_- B(m_J - m_I).
\end{aligned}$$