

## ZEEMAN EFFECT: WEAK FIELD

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References: Griffiths, David J. (2005), Introduction to Quantum Mechanics, 2nd Edition; Pearson Education - Problem 6.21.

We saw that the Zeeman effect can be divided into 3 cases: weak, strong or intermediate external field. We now need to consider how to calculate the effects of the external field on the energy levels.

There are effectively two magnetic dipoles in the hydrogen atom (well, 3 if you count the proton's spin, but we'll get to that later; here we're concerned only with effects on the electron): that from the orbital angular momentum and that from spin. The energy associated with a dipole  $\mu$  in an external magnetic field is

$$U = -\mu \cdot \mathbf{B}_{ext} \quad (1)$$

so the Zeeman hamiltonian component is

$$H'_Z = -(\mu_L + \mu_S) \cdot \mathbf{B}_{ext} \quad (2)$$

To work out these magnetic moments (well, the spin one, anyway) properly requires relativistic quantum theory so we'll just quote the results:

$$\mu_L = -\frac{e}{2m} \mathbf{L} \quad (3)$$

$$\mu_S = -\frac{e}{m} \mathbf{S} \quad (4)$$

If we direct  $\mathbf{B}_{ext}$  along the  $z$  axis, then

$$H'_Z = \frac{e}{2m} (L_z + 2S_z) B_{ext} \quad (5)$$

It's fairly obvious from this that  $H'_Z$  commutes with  $L_z$  and  $S_z$  and, since  $L^2$  and  $S^2$  both commute with  $L_z$  and  $S_z$  as well,  $H'_Z$  commutes with these operators also. However, if we look at the total angular momentum  $\mathbf{J} = \mathbf{L} + \mathbf{S}$ , then the operator  $J^2 = L^2 + S^2 + 2\mathbf{S} \cdot \mathbf{L}$  does *not* commute with  $L_z$  and  $S_z$  because of the  $\mathbf{S} \cdot \mathbf{L}$  term. For example,

$$[S_x L_x, L_z] = S_x [L_x, L_z] = -i\hbar S_x L_y \quad (6)$$

$$[S_x L_x, S_z] = L_x [S_x, S_z] = -i\hbar L_x S_y \quad (7)$$

and so on. This result may seem bizarre: how can  $\mathbf{L}$  and  $\mathbf{S}$  independently be conserved, yet their sum  $\mathbf{J}$  not be conserved?

To see how this works, we consider the effect of  $\mathbf{B}_{ext}$  on the two dipole moments. The external field exerts a torque on each moment, which is given by  $\mathbf{N} = \boldsymbol{\mu} \times \mathbf{B}_{ext}$ . Suppose  $\boldsymbol{\mu}$  makes an angle  $\theta$  with  $\mathbf{B}_{ext}$ . Then the magnitude of the torque is  $N = \mu B_{ext} \sin \theta$  and its direction is perpendicular to both the moment and the field. This causes  $\boldsymbol{\mu}$  to precess around  $\mathbf{B}_{ext}$  with  $\theta$  remaining constant and the azimuthal angle  $\phi$  (in spherical coordinates) changing at a constant rate. This is true for both  $\mu_L$  and  $\mu_S$ , but since the magnitudes of these moments (and the angles  $\theta$ ) will, in general, be different for the two moments, the rate of precession will vary causing the moments (and thus the angular momenta  $\mathbf{L}$  and  $\mathbf{S}$  associated with them) to point in different relative directions as time goes by. Thus the vector sum  $\mathbf{J} = \mathbf{L} + \mathbf{S}$  will vary, even though the magnitudes of  $\mathbf{L}$  and  $\mathbf{S}$  and their  $z$  components  $L_z$  and  $S_z$  remain constant.

This discussion ignores spin-orbit coupling, however. If we remove  $\mathbf{B}_{ext}$  and instead consider just the behaviour of the electron's spin magnetic moment in the field  $\mathbf{B}_L$  produced by the proton's relative orbit around it, then  $\mathbf{B}_p$  exerts a torque on  $\mu_S$  causing it to precess about  $\mathbf{B}_L$ . However, the spin also produces a magnetic field  $\mathbf{B}_S$  which exerts an equal and opposite torque on the orbital moment, with the result that  $\mu_L$  precesses about  $\mathbf{B}_S$ . In our analysis of spin-orbit coupling, we saw that  $J^2$  and  $J_z$  commute with  $H'_{so}$  while  $L_z$  and  $S_z$  do not. What is happening here is that the sum  $\mathbf{J} = \mathbf{L} + \mathbf{S}$  is constant, but  $\mathbf{L}$  and  $\mathbf{S}$  each precess about  $\mathbf{J}$  in such a way as to conserve  $J^2$  and  $J_z$ , but with varying  $L_z$  and  $S_z$ .

I have to confess that I haven't found a rigorous derivation of these results, so it's possible that they are merely classical analogies designed to make the quantum mechanics easier to understand. Since the components of angular momentum don't all have well-defined values at any given time (since they don't commute), the notion of a rigid vector precessing around an axis isn't valid anyway. If anyone knows of a better derivation or explanation, please do let me know.

The question when analyzing the Zeeman effect is which of these two processes (the external field or spin-orbit coupling) is dominant, since this affects how we do the analysis. In the weak field case, spin-orbit coupling produces a vector  $\mathbf{J}$  which will then precess about  $\mathbf{B}_{ext}$ , while in the strong

field case, the field essentially breaks the coupling between  $\mathbf{L}$  and  $\mathbf{S}$  and forces the two moments to act independently. We'll have a look at the weak field case here.

In this case, spin-orbit coupling is the dominant perturbation, with the Zeeman effect being a smaller perturbation on top of the spin-orbit perturbation. Since the spin-orbit effect is dominant, we use the eigenstates of that hamiltonian to calculate the first-order corrections due to the Zeeman effect. This isn't strictly valid since as we saw above,  $J^2$  and  $J_z$  are 'good' operators for spin-orbit coupling but not for the Zeeman effect, so technically we should use degenerate perturbation theory to calculate the latter. However, a decent approximation is to use the spin-orbit eigenstates to calculate the Zeeman corrections.

Since  $L_z$  and  $S_z$  are not 'good' operators for spin-orbit coupling, we go back to the original Zeeman hamiltonian 2 in terms of angular momenta:

$$H'_Z = \frac{e}{2m} (\mathbf{L} + 2\mathbf{S}) \cdot \mathbf{B}_{ext} = \frac{e}{2m} (\mathbf{J} + \mathbf{S}) \cdot \mathbf{B}_{ext} \quad (8)$$

The eigenstates we'll use are  $|n\ell jj_z\rangle$  so the Zeeman energy correction is

$$E_{Z1} = \langle n\ell jj_z | H'_Z | n\ell jj_z \rangle \quad (9)$$

$$= \frac{eB_{ext}}{2m} \langle n\ell jj_z | J_z | n\ell jj_z \rangle + \frac{e}{2m} \langle n\ell jj_z | \mathbf{S} \cdot \mathbf{B}_{ext} | n\ell jj_z \rangle \quad (10)$$

$$= \frac{eB_{ext}}{2m} \hbar j_z + \frac{e}{2m} \langle \mathbf{S} \cdot \mathbf{B}_{ext} \rangle \quad (11)$$

$$= \frac{eB_{ext}}{2m} \hbar j_z + \frac{e}{2m} \langle \mathbf{S} \rangle \cdot \mathbf{B}_{ext} \quad (12)$$

The first term in the second line assumes that  $\mathbf{B}_{ext}$  points along the  $z$  axis. The last term involves the average projection of  $\mathbf{S}$  onto the  $z$  axis which is, of course,  $S_z$  but this doesn't do us much good here since the states are not eigenstates of  $S_z$ . The argument at this point makes use of the fact that  $\mathbf{S}$  precesses about the fixed total angular momentum  $\mathbf{J}$  and therefore its time average is the projection of  $\mathbf{S}$  onto  $\mathbf{J}$ , since the component of  $\mathbf{S}$  perpendicular to  $\mathbf{J}$  averages out to zero. That is

$$\langle \mathbf{S} \rangle = \left\langle \frac{\mathbf{S} \cdot \mathbf{J}}{J^2} \mathbf{J} \right\rangle \quad (13)$$

so

$$E_{Z1} = \frac{eB_{ext}}{2m} \hbar j_z + \frac{e}{2m} \left\langle \frac{\mathbf{S} \cdot \mathbf{J}}{J^2} \right\rangle \langle \mathbf{J} \cdot \mathbf{B}_{ext} \rangle \quad (14)$$

$$= \frac{eB_{ext}}{2m} \hbar j_z \left( 1 + \left\langle \frac{\mathbf{S} \cdot \mathbf{J}}{J^2} \right\rangle \right) \quad (15)$$

To get the final average, we use

$$\mathbf{L} = \mathbf{J} - \mathbf{S} \quad (16)$$

$$L^2 = J^2 + S^2 - 2\mathbf{S} \cdot \mathbf{J} \quad (17)$$

$$\mathbf{S} \cdot \mathbf{J} = \frac{1}{2} (J^2 + S^2 - L^2) \quad (18)$$

or in terms of the eigenvalues

$$\langle \mathbf{S} \cdot \mathbf{J} \rangle = \frac{\hbar^2}{2} \left( j(j+1) + \frac{3}{4} - \ell(\ell+1) \right) \quad (19)$$

Putting it all together, we get

$$E_{Z1} = \frac{e\hbar B_{ext}}{2m} j_z \left( 1 + \frac{j(j+1) + \frac{3}{4} - \ell(\ell+1)}{2j(j+1)} \right) \quad (20)$$

This expression is often condensed to

$$E_{Z1} = \mu_B g_J B_{ext} j_z \quad (21)$$

$$\mu_B \equiv \frac{e\hbar}{2m} \quad (22)$$

$$g_J \equiv 1 + \frac{j(j+1) + \frac{3}{4} - \ell(\ell+1)}{2j(j+1)} \quad (23)$$

where  $\mu_B$  is called the Bohr magneton and  $g_J$  is called the Landé g-factor. Combining the Zeeman formula with the fine structure formula, we get the overall energy states of hydrogen:

$$E_n = -\frac{13.6 \text{ eV}}{n^2} \left[ 1 - \frac{\alpha^2}{4n^2} \left( 3 - \frac{4n}{j + \frac{1}{2}} \right) \right] + \mu_B g_J B_{ext} j_z \quad (24)$$

For given values of  $\ell$  and  $j$ , the Zeeman effect splits an energy level into separate levels, one for each possible value of  $j_z$ . Plotting the energy  $E_n$  versus  $\mu_B B_{ext}$  we get one straight line with slope  $g_J j_z$  for each possible value of  $j_z$ . For example, for  $n = 2$  the possibilities are

$\ell$	$j$	$j_z$	$g_J$	Energy (eV)	Slopes
0	$\frac{1}{2}$	$\pm\frac{1}{2}$	2	$-3.4 - 1.0625\alpha^2 \pm \mu_B B_{ext}$	$\pm 1$
1	$\frac{1}{2}$	$\pm\frac{1}{2}$	$\frac{2}{3}$	$-3.4 - 1.0625\alpha^2 \pm \frac{1}{3}\mu_B B_{ext}$	$\pm\frac{1}{3}$
1	$\frac{3}{2}$	$\pm\frac{1}{2}$	$\frac{4}{3}$	$-3.4 - 0.2125\alpha^2 \pm \frac{2}{3}\mu_B B_{ext}$	$\pm\frac{2}{3}$
1	$\frac{3}{2}$	$\pm\frac{3}{2}$	$\frac{4}{3}$	$-3.4 - 0.2125\alpha^2 \pm 2\mu_B B_{ext}$	$\pm 2$

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