

Atomic Physics

14 The Zeeman effect

We have now finished our discussion of a free atom or ion, that is, one with no external influences on it. [Problem (hard): is it possible that there is substructure within the hyperfine levels of an atom?] We now turn to the influence of external things such as magnetic and electric fields, and electromagnetic radiation.

When an atom is placed in a uniform magnetic field B , the transitions are observed to split into several components. This is called the Zeeman effect. When the field is large (exactly how large will be seen below) the way the components vary with B changes and this regime is called the Paschen-Back effect.

14.1 Weak B field

We will calculate the weak-field Zeeman effect as if we are treating LS coupling, but the treatment will be completely general. The result for any other angular momentum coupling $j_1 j_2$ is obtained by substituting j_1 for L and j_2 for S , and putting in the correct g -factors. We will look at how this works in the case of hyperfine structure in the next section.

An external magnetic field will interact primarily with the net magnetic dipole moment μ of an atom if it has one. [Problem: is it possible for an atom to have zero magnetic dipole moment?] The interaction Hamiltonian is therefore

$$H = -\mu \cdot \mathbf{B} \quad (138)$$

14.1.1 Normal Zeeman effect

First consider the case of an LS coupled atom in a singlet state, $S = 0$. Then

$$\mu = -g\mu_B \mathbf{L} \quad (139)$$

For $S = 0$ the total magnetic moment is $\mathbf{J} = \mathbf{L}$. Before the field is applied \mathbf{J} and therefore here \mathbf{L} is a constant of the motion. Choosing the z axis to lie along \mathbf{B} , we obtain

$$-\mu \cdot \mathbf{B} = -\mu_z B = g\mu_B B L_z \quad (140)$$

and the effect is

$$\Delta E = \hbar L M_L |g\mu_B B L_z| L M_L \rangle = g\mu_B B M_L \quad (141)$$

The \mathbf{L} vector which was fixed in space is now precessing about \mathbf{B} , but clearly L_z is still a constant of the motion.

The energy level L is now split into $2L + 1$ levels (corresponding to the different values of M_L) separated by $\mu_B B$ (since $g_l = 1$).

A radiative transition involves transitions between two different states. If these are both singlets, then both will have the same Zeeman splitting $\mu_B B$ and the resulting pattern of emitted frequencies is called the Normal Zeeman effect. Owing to conservation of angular momentum, the atom's angular momentum projection on the z axis can change by at most ~ 1 when it emits or absorbs a photon by electric dipole radiation (see also section 15). The three possible types of transition $M'_L = M_L + 1$, $M'_L = M_L$ and $M'_L = M_L - 1$ have frequencies shifted with respect to the zero-field frequency by $+\mu_B B$, 0 , and $-\mu_B B$ respectively.

14.1.2 Zeeman effect

The fact that g_s is not equal to 1 means that the Zeeman effect is much richer when $S \neq 0$. Because the classical model of angular momentum only allows $g = 1$, this more general case was originally called 'anomalous', although it is in fact the more typical case, so we tend to drop the adjective 'anomalous' nowadays in the laboratory, though the word lives on in textbooks and final questions.

It is rather nice to see what happens when both \mathbf{L} and \mathbf{S} are involved. The magnetic dipole moment operator for an LS coupled atom of total angular momentum \mathbf{J} is

$$\boldsymbol{\mu} = -(g_l \mu_B \mathbf{L} + g_s \mu_B \mathbf{S}). \quad (142)$$

Note that since $g_s \neq g_l$, $\boldsymbol{\mu}$ is not parallel to \mathbf{J} . The Zeeman interaction Hamiltonian is

$$H = -\boldsymbol{\mu} \cdot \mathbf{B} = g_l \mu_B B \hat{L}_z + g_s \mu_B B \hat{S}_z \quad (143)$$

where we have chosen the z axis to be along the \mathbf{B} field (we are always free to do this).

You might expect that the energy shift is given by

$$\delta E = g_l \mu_B B M_L + g_s \mu_B B M_S \quad (144)$$

but we have to remember that in LS coupling M_L and M_S are not good quantum numbers. \mathbf{L} and \mathbf{S} are precessing about \mathbf{J} in the vector model, and since \mathbf{J} is not along \mathbf{B} the z -components of \mathbf{L} and \mathbf{S} are not constants of the motion. All this is simply lots of ways of saying that the energy eigenstates of the atom, before the perturbation is applied, are not eigenstates of L_z or S_z ; they are eigenstates of L^2 , S^2 , J^2 and J_z .

In first order perturbation theory we are calculating, therefore,

$$\delta E = \langle LSJM_J | g_l \mu_B B \hat{L}_z + g_s \mu_B B \hat{S}_z | LSJM_J \rangle. \quad (145)$$

Taking the \hat{L}_z part first, use the following observation from the vector model: \mathbf{L} is precessing rapidly about \mathbf{J} , so the mean value of L_z is found by first projecting \mathbf{L} onto \mathbf{J} , and then taking the component of this vector along the z -direction. The expressions for the classical vectors are as follows: the size of the component of \mathbf{L} along \mathbf{J} is $\mathbf{L} \cdot \mathbf{J} / J$. The direction of this projected vector is along \mathbf{J} , so to get its z component we need to multiply its length by J_z / J . Hence when \mathbf{L} precesses about \mathbf{J} the mean value of L_z is $(\mathbf{L} \cdot \mathbf{J}) J_z / J^2$.

The exact result for the quantum operators is:

$$\langle LSJM_J | \hat{L}_z | LSJM_J \rangle = \frac{\langle LSJM_J | \hat{\mathbf{L}} \cdot \hat{\mathbf{J}} | LSJM_J \rangle \langle LSJM_J | \hat{J}_z | LSJM_J \rangle}{\langle LSJM_J | \hat{\mathbf{J}} \cdot \hat{\mathbf{J}} | LSJM_J \rangle} \quad (146)$$

—the classical vector model serves simply to show that this expression is reasonable, but at this level we have to quote the quantum operator expression without any more complete proof¹. In order to bring out the form of this result, I will write it again without the state labels, but one should be aware nonetheless of what type of angular momentum state we are considering:

$$\langle \hat{L}_z \rangle = \frac{\langle \hat{\mathbf{L}} \cdot \hat{\mathbf{J}} \rangle \langle \hat{J}_z \rangle}{\langle \hat{\mathbf{J}} \cdot \hat{\mathbf{J}} \rangle} \quad [\text{for } |LSJM_J\rangle] \quad (147)$$

All the expectation values here are trivial to evaluate in the state under consideration:

$$\langle LSJM_J | \hat{J}_z | LSJM_J \rangle = M_J \quad (148)$$

$$\langle LSJM_J | \hat{\mathbf{J}}^2 | LSJM_J \rangle = J(J + 1) \quad (149)$$

$$\langle LSJM_J | \hat{\mathbf{L}} \cdot \hat{\mathbf{J}} | LSJM_J \rangle = \frac{1}{2} (J(J + 1) + L(L + 1) - S(S + 1)) \quad (150)$$

where for the last result we used

$$\begin{aligned} \mathbf{J} &= \mathbf{L} + \mathbf{S} \\ \Rightarrow (\mathbf{J} - \mathbf{L})^2 &= \mathbf{S}^2 \\ \Rightarrow \mathbf{J}^2 + \mathbf{L}^2 - 2\mathbf{L} \cdot \mathbf{J} &= \mathbf{S}^2 \\ \Rightarrow \mathbf{L} \cdot \mathbf{J} &= \frac{\mathbf{J}^2 + \mathbf{L}^2 - \mathbf{S}^2}{2} \end{aligned}$$

which is an exact relationship between the operators. Therefore we have

$$g_l \mu_B B \langle \hat{L}_z \rangle = g_l \mu_B B \frac{\langle \hat{\mathbf{J}}^2 + \hat{\mathbf{L}}^2 - \hat{\mathbf{S}}^2 \rangle}{2J(J + 1)} M_J \quad (151)$$

The treatment of the \hat{S}_z part in (145) goes on exactly corresponding lines; it is easy to see that the result is as before except that L and S are swapped. Since the overall result is proportional to M_J , we define a Landé factor g_J for the total J by the expression

$$\Delta E = \mathbf{h} - \boldsymbol{\mu} \cdot \mathbf{B} = g_J \mu_B B M_J \quad [\text{definition of } g_J] \quad (152)$$

and putting it all together we have

$$g_J = g_L \frac{J(J + 1) + L(L + 1) - S(S + 1)}{2J(J + 1)} + g_S \frac{J(J + 1) + S(S + 1) - L(L + 1)}{2J(J + 1)} \quad (153)$$

If we put $g_L = 1$ and $g_S = 2$ this expression can be simplified somewhat:

$$g_J = \frac{3J(J + 1) - L(L + 1) + S(S + 1)}{2J(J + 1)} \quad (154)$$

It is useful to notice the following simple cases:

- when $S = 0, g = 1$ (since purely orbital)
- when $L = 0, g = 2$ (since purely spin)
- when $S = L, g = 3/2$

¹ The standard proof invokes the Wigner Ekart theorem, it is outlined in Woodgate.

It is also worth noticing that our derivation was quite general to obtain the net g factor when two angular momenta of known g factors are coupled together. For example, we can see immediately that the Zeeman effect of a hyperfine structure level in IJ coupling is $g_F \mu_B M_F$ with

$$g_F = g_J \frac{F(F+1) + J(J+1) - I(I+1)}{2F(F+1)} - g_I \frac{m_e}{m_p} \frac{F(F+1) + I(I+1) - J(J+1)}{2F(F+1)}, \quad (155)$$

where the factor m_e/m_p allows for the fact that g_I is defined with a scale factor of μ_N rather than μ_B , and the minus sign comes from the different sign convention in the definition of g_I compared with g_J .

You should derive g_I and examine carefully the Zeeman splittings for some example cases such as the transitions $^2S_{1/2} \rightarrow ^2P_{3/2}$ and $^3P_1 \rightarrow ^3P_2$. Make sure you understand not only the energy level splittings, but also how all the transition frequencies in the Zeeman spectrum arise, bearing in mind that only $\Delta M_J = \pm 1, 0$ transitions arise.

14.1.3 Directional dependence and polarization of the emitted light

When you look at the light emitted along the direction of the magnetic field \mathbf{B} , you don't see all the components of the Zeeman spectrum! The ones corresponding to $\Delta M = 0$, the so-called π components, are not there. Yet they are there when you look in any direction perpendicular to the magnetic field lines (together with the $\Delta M = \pm 1$ components which are called σ_{\pm}). What is going on? ...In a $\Delta M = 0$ transition, the atomic charge distribution is oscillating along the magnetic field direction, and therefore the emitted light is polarized parallel to \mathbf{B} . But light is a transverse oscillation: light can't propagate in the direction along which its electric field is oscillating. The intensity of the π light therefore falls gradually to zero as a function of angle out of the plane perpendicular to \mathbf{B} .

Meanwhile the $\Delta M = \pm 1$ transitions are associated with rotation of the atomic charge distribution in the plane perpendicular to \mathbf{B} . The light comes out in all directions but oscillates always in this plane. Looking along the plane, therefore, we see linear polarization in the plane, i.e. perpendicular to the π polarization. Looking perpendicular to the plane, i.e. along \mathbf{B} , we see circular polarization. That is, the $\Delta M = +1$ transition gives right-handed circular polarization, $\Delta M = -1$ gives left-handed circular polarization. [Problem: if you look at the Zeeman spectrum in a direction perpendicular to \mathbf{B} , and slowly rotate a linear polarizer in front of your eye, what do you expect to observe?]

Uses of the Zeeman effect

With modern computers we can make a fair stab at calculating atomic structure from scratch, but the problem is so complicated for some atoms that even this is only moderately successful. Historically, the problem of working out the identities of all the different atomic energy levels from the observed spectral lines was like trying to deduce the structure of a piano from the noise it makes when thrown down stairs. The Zeeman effect is a very powerful tool in this analysis. Merely by counting components in the Zeeman spectrum one can make a pretty fair guess at the values of J for the two levels involved in the transition. The relative positions of the Zeeman lines then lead rapidly to confirming J and identifying L and S , or indeed to concluding that LS coupling is not a good approximation. One of the problems gives you some practice at such a piece of detective work.

Nowadays, the mere identities of atomic levels are not exactly hot news, but occasionally we need to know the details of some particular transition, in order to use it for some purpose, and the vast majority of transitions in all but the most simple atoms will (rightly) forever remain uncalculated and unobserved until they are needed. The Zeeman effect therefore retains its old usefulness as an identifier of levels.

However, the more common uses of the Zeeman effect are as a diagnostic of magnetic fields in an inaccessible environment such as the atmosphere of a star or the inside of a tokamak fusion reactor,

and as a tool for manipulating atoms. The Zeeman effect is used for example to define an axis in space so that atoms in atomic clocks don't wander in direction. It is also a central ingredient in other magnetic resonance experiments. A more ingenious use is in atom traps, where a magnetic field gradient provides a force to confine cold atoms. A Zeeman effect which varies with position is also used in one laser cooling method to compensate for the changing Doppler effect when atoms are slowed down to very low speeds by laser light.

14.2 Strong B field: Paschen-Back effect

The above perturbation theory is valid as long as the Zeeman shift ΔE is small compared to the separation of the energy eigenstates before the perturbation was applied. This is typically ok for fine structure splittings (~ 100 GHz so $B \lesssim 7$ Tesla is 'small'), but not always for hyperfine structure (~ 100 MHz so $B \lesssim 0.007$ Tesla required for 'small').

If the Zeeman effect dominates the fine structure, then we have to apply the perturbations in reverse order, i.e. first Zeeman, then spin-orbit. The result for Zeeman splitting is then as given in equation (144) since now we can argue that M_L and M_S are well-defined. This situation is called the Paschen-Back effect. The angular momentum vectors \mathbf{L} and \mathbf{S} now precess independently about the magnetic field direction. In the Paschen-Back situation, spin-orbit coupling produces a further (comparatively small) shift proportional to $\hbar^2 M_L M_S \langle \mathbf{L} \cdot \mathbf{S} \rangle = M_L M_S$.

In going from weak to strong field, the good quantum numbers therefore change from L, S, J, M_J to L, S, M_L, M_S : note that the net angular momentum along the z direction is a constant of the motion at all field strengths, this can be underlined by referring to a quantum number M which is equal to M_J at small B and to $M_L + M_S$ at large B .

Similar arguments apply to the case of the Zeeman effect in hyperfine structure. The case where $J = 1/2$ can be solved exactly, leading to the Breit-Rabi formula, valid for all field strengths:

$$\Delta E(F, M_F) = g_I \mu_B B M_F + \frac{\Delta E_0}{2} \left(\frac{-1}{2I+1} \pm \sqrt{1 + \frac{4M_F}{2I+1} x + x^2} \right) \quad (156)$$

$$\text{where } x = (g_J - g_I) \mu_B B / \Delta E_0 \quad (157)$$

You might like to amuse yourself by plotting this formula by computer (or by hand) so as to see the behaviour of the hyperfine levels in hydrogen, for example, which are crucial in the hydrogen maser (see section 16).

14.3 External electric field: the Stark effect (off syllabus)

A uniform external electric field \mathbf{E} will also perturb an atom. The details are somewhat different since the atom does not have an electric dipole moment before the field is applied: rather, the field polarizes the atom. See textbooks for details.

The oscillating electric field of a light wave produces an oscillating electric dipole moment in an atom, and an associated shift called the a.c. Stark shift, or light shift. This is a versatile tool for laser-manipulation of atoms (both cooling and trapping), but is beyond the level of these notes.

14.4 Main points

$H = -\boldsymbol{\mu} \cdot \mathbf{B}$; normal Zeeman effect giving three transition lines; anomalous Zeeman effect: vector model description; derivation of g factor in LS coupling; how the transitions divide up into several components; polarization of the light; Paschen-Back effect in strong fields; uses of the Zeeman effect: identifying levels, probing magnetic fields, manipulating atoms.



