

Class 36: Zeeman effect, Fine structure

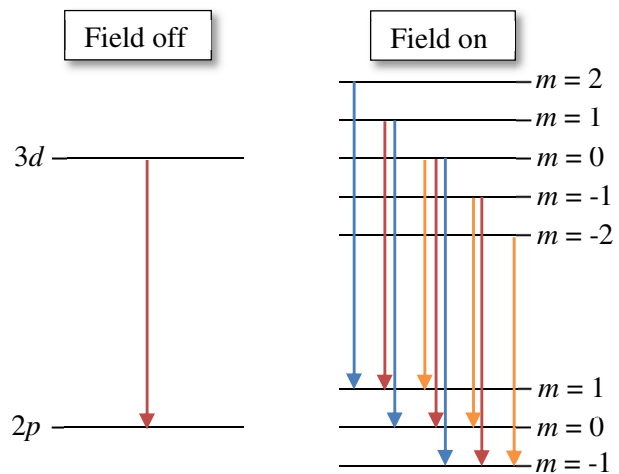
The Zeeman effect

If a hydrogen atom is placed in a uniform magnetic field \mathbf{B} , there is an additional term in the potential energy, $-\mathbf{m} \cdot \mathbf{B}$. Taking the z -axis to be aligned with the magnetic field, the energy levels are

$$E_{nlm} = E_n + m\mu_B B, \quad (36.1)$$

where E_n are the energy levels in the absence of magnetic field. Thus the presence of the magnetic field removes some of the degeneracy of the energy levels. For example if $n = 2$, and $l = 1$, the energies are $E_{21,-1} = E_2 - \mu_B B$, and $E_{210} = E_2$, and $E_{211} = E_2 + \mu_B B$. In a radiative transition from the $n = 2$ state to the $n = 1$ state, the energy of the photon will depend on the on the magnetic quantum number in the $n = 2$ state. Hence the spectral line will be split into three components with the frequency separation between components being proportional to the magnetic field strength. This effect is called the Zeeman effect.

Problem 7.24. Consider the normal Zeeman effect applied to the $3d$ to $2p$ transition. (a) Sketch an energy-level diagram that shows the splitting of the $3d$ and $2p$ levels in an external magnetic field. Indicate all possible transitions from each m_l state of the $3d$ level to each m_l stated of the $2p$ level. (b) Which transitions satisfy the $\Delta m_l = \pm 1$ or 0 selection rule? (c) Show that there are only three different transition energies?



(a) and (b). The $3d$ to $2p$ transition is a transition from a state with quantum numbers $n = 3, l = 2$ to a state with $n = 2, l = 1$. The change in m has to be -1 , or 0 or $+1$. The diagram shows the energy level splitting and the allowed transitions. The different colored arrows show the 3 different photon energies.

(c) Because the additional energy due to external field is

$$U = \mu_B B m_l,$$

we see that the splitting in transition energies is

$$\Delta U = \mu_B B \Delta m_l.$$

Since the selection rule allows only 3 values for the change in magnetic quantum number, there are only three different transition energies.

Note in the above discussion, the presence of electron spin has been neglected. Because it is the total angular momentum, $\mathbf{J} = \mathbf{L} + \mathbf{S}$, that is conserved, the spin and orbital angular momentum do not need to point in the same direction. In fact, \mathbf{S} and \mathbf{L} both precess about the direction of \mathbf{J} , which itself precesses about the direction of \mathbf{B} . When the electron spin is taken into account, the energy of interaction with the magnetic field is

$$\Delta E = g_L m_j \mu_B B, \quad (36.2)$$

where m_j is the quantum number associated with the z -component of the total angular momentum and the **Landé g-factor** is

$$g_L = 1 + \frac{j(j+1) + s(s+1) - l(l+1)}{2j(j+1)}. \quad (36.3)$$

The presence of electron spin gives rise to the **anomalous Zeeman effect** in which there is a greater variety of splitting patterns, including non-uniform spacing of the spectral lines.

Fine structure

High resolution spectra show that lines have what is called **fine structure**. For example, the H_α line is actually a number of closely spaced lines, spread in wavelength over ≈ 0.02 nm. There are a number of effects which contribute to modifying the energies from the Bohr model predictions. One effect is due to special relativity. The relativistic energy of a particle is related to its momentum by

$$E = \sqrt{E_0^2 + (cp)^2}, \quad (36.4)$$

where E_0 is the particle's rest energy. If $cp \ll E_0$, we can approximate the energy by the first few terms of a series expansion

$$E = E_0 \sqrt{1 + \left(\frac{cp}{E_0}\right)^2} = E_0 \left(1 + \frac{1}{2} \left(\frac{cp}{E_0}\right)^2 - \frac{1}{8} \left(\frac{cp}{E_0}\right)^4 + \dots \right), \quad (36.5)$$

The second term in the series is the non-relativistic kinetic energy, which is used in deriving the Schrödinger equation. For the H atom, the next term provides a small perturbation to the Hamiltonian (energy operator)

$$\Delta E = -\frac{1}{8} m_e c^2 \left(\frac{p}{m_e c} \right)^4. \quad (36.6)$$

Using the relation $p^2/(2m_e) = E - V(r)$, the relativistic corrections to the energy levels are found to be

$$\delta E_{nl}^{(rel)} = \frac{\alpha^2}{n} \left(\frac{1}{l+1/2} - \frac{3}{4n} \right) E_n. \quad (36.7)$$

For the H atom ground state the relativistic correction is -9.1×10^{-4} eV.

The second effect that modifies the energy levels is called spin-orbit coupling. For $l \neq 0$, in a frame moving with the electron, the positively charged nucleus moves in an orbit and provides a magnetic field at the location of the electron. Due to its magnetic dipole moment, the electron has additional term in its potential energy which involves the scalar product of the orbital angular momentum and the electron spin angular momentum. This spin-orbit coupling term is

$$H_{so} = -\frac{1}{2} k e^2 \left(\frac{g_e}{2m_e^2 c^2} \right) \frac{\mathbf{L} \cdot \mathbf{S}}{r^3}, \quad (36.8)$$

where r is the radius of the orbit.

We can find the expectation value of $\mathbf{L} \cdot \mathbf{S}$ by considering the total momentum operator $\mathbf{J} = \mathbf{L} + \mathbf{S}$. We note that

$$\mathbf{J} \cdot \mathbf{J} = (\mathbf{L} + \mathbf{S}) \cdot (\mathbf{L} + \mathbf{S}) = \mathbf{L} \cdot \mathbf{L} + 2\mathbf{L} \cdot \mathbf{S} + \mathbf{S} \cdot \mathbf{S}. \quad (36.9)$$

Applying this operator to a hydrogen wave function we get

$$\langle \mathbf{L} \cdot \mathbf{S} \rangle = \frac{\hbar^2}{2} [j(j+1) - l(l+1) - s(s+1)] = \frac{\hbar^2}{2} \left[j(j+1) - l(l+1) - \frac{3}{4} \right], \quad (36.10)$$

where use has been made of $s = 1/2$.

The expectation value of the r^{-3} factor can be shown to be

$$\left\langle \frac{1}{r^3} \right\rangle = \frac{1}{(na_0)^3} \frac{1}{l \left(l + \frac{1}{2} \right) (l+1)}. \quad (36.11)$$

The net effect of the relativistic, spin-orbit coupling, and a third correction called the Darwin term (that arises because the electron cannot be confined to a point and must be treated as fuzzy ball of radius equal to the electron Compton wavelength) is that

$$\delta E_{nj} = \frac{\alpha^2}{n} \left(\frac{1}{j+1/2} - \frac{3}{4n} \right) E_n, \quad (36.12)$$

where $j = 1/2$ if $l = 0$ and $j = l \pm 1/2$ if $l > 0$. Note that this expression does not depend on l . Hence the splitting of the energy levels of a state of given n and l arises from the direction of the electron spin.

The $H\alpha$ line is produced by transitions from the $n = 3$ state to the $n = 2$ state. Because the photon has intrinsic spin, the change in l is restricted to be ± 1 . The table shows the allowed quantum numbers in a transition and the corresponding energies, in eV. We see that there are 4 distinct transition energies.

n	l	j	E_n	δE_{nl}	n	l	j	E_n	δE_{nl}
3	2	$2\frac{1}{2}$	-1.5109	$-2.236 \cdot 10^{-6}$	2	1	$1\frac{1}{2}$	-3.3996	$-1.132 \cdot 10^{-5}$
3	2	$1\frac{1}{2}$	-1.5109	$-6.708 \cdot 10^{-6}$	2	1	$\frac{1}{2}$	-3.3996	$-5.660 \cdot 10^{-5}$
3	1	$1\frac{1}{2}$	-1.5109	$-6.708 \cdot 10^{-6}$	2	0	$\frac{1}{2}$	-3.3996	$-5.660 \cdot 10^{-5}$
3	1	$\frac{1}{2}$	-1.5109	$-2.012 \cdot 10^{-5}$	2	0	$\frac{1}{2}$	-3.3996	$-5.660 \cdot 10^{-5}$
3	0	$\frac{1}{2}$	-1.5109	$-2.012 \cdot 10^{-5}$	2	1	$1\frac{1}{2}$	-3.3996	$-1.132 \cdot 10^{-5}$
3	0	$\frac{1}{2}$	-1.5109	$-2.012 \cdot 10^{-5}$	2	1	$\frac{1}{2}$	-3.3996	$-5.660 \cdot 10^{-5}$

The shifts in the photon energies are $9.084 \cdot 10^{-6}$, $4.989 \cdot 10^{-5}$, $3.648 \cdot 10^{-5}$ and $-8.800 \cdot 10^{-6}$ eV. The separation between the lines is of order $6 \cdot 10^{-5}$ eV, which corresponds to a wavelength separation of ≈ 0.02 nm.