Spin-orbit coupling

Atomic states with the same n and l values but different j values have slightly different energies because of the interaction of the spin of the electron with its orbital motion. This is called the *spin-orbit effect*.

The resulting splitting of the spectral lines such as that resulting from the splitting of the $2P$ level in the transition $2P \to 1S$ in hydrogen is called *fine-structure splitting*. We can understand the spin-orbit effect qualitatively from a simple Bohr model as shown in Figure 1.

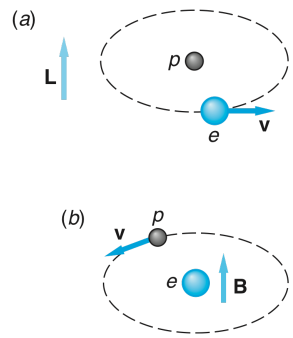

Figure 1: (a) An electron moving about a proton with angular momentum **L** up. (b) The magnetic field **B** seen by the electron due to the apparent (relative) motion of the proton is also up.

In this picture, the electron moves in a circular orbit with speed v around a fixed proton. In the figure, the orbital angular momentum L is up. In the frame of reference of the electron, the proton moves in a circle around it, thus making a circular loop current that produces a magnetic field B at the position of the electron. The direction of B is also up, parallel to L.

The interaction between the electron's spin magnetic moment and this magnetic field leads to the phenomenon of spin-orbit coupling. The magnetic potential energy associated with the spin-orbit interaction is

$$\Delta E_s = -\vec{\mu_s} \cdot \vec{B} = -\mu_s B \cos\theta$$

where θ is the angle between $\vec{\mu_s}$ and $\vec{B}$. The quantity $\mu_s \cos\theta$ is the component of $\vec{\mu_s}$ parallel to $\vec{B}$. In the case fo the spin magnetic moment of the electron, this component is equal to Bohr magneton ($\pm\mu_B$) which is equal to $\pm\frac{e\hbar}{2m}$.

$$\therefore \Delta E_s = -\mu_s B \cos\theta = \pm\mu_B B$$

Depending upon the orientation of its spin vector, the energy of an electron in a given atomic quantum state will be higher or lower by $\mu_B B$ than its energy in absence of spin-orbit coupling. The result is the splitting of every quantum state intro two separate sub-states. Hence every spectral line splits intro two component lines.

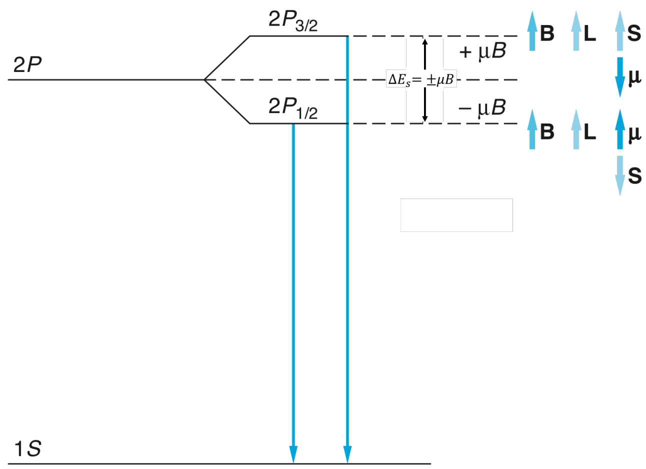

Figure 2: Fine-structure energy-level diagram. On the left, the levels in the absence of a magnetic field are shown. The effect of the magnetic field due to the relative motion of the nucleus is shown on the right. Because of the spin-orbit interaction, the magnetic field splits the $2P$ level into two energy levels, with the $j = 3/2$ level having slightly greater energy than the $j = 1/2$ level. The spectral line due to the transition $2P \to 1S$ is therefore split into two lines of slightly different wavelengths.

Notice that there is one exception. When an electron is in s state, $l = 0$ and as a result the magnetic field at the site of the electron is zero. Since $B = 0$, ΔE_s is also *zero* and therefore there is no fine structure splitting for this state.

Zeeman Effect

The *Zeeman effect* is the splitting of atomic energy levels and the associated spectral lines when the atoms are placed in a magnetic field. When the splitting occurs intro two or three lines, it is called *normal Zeeman effect*. The splitting of spectral line into more than three components in *weak magnetic field* is called *anomalous Zeeman effect*.

Expression for the Zeeman shift Consider an electron in the atom moving in a circular orbit of radius r with a linear velocity v and angular velocity ω. Let e be the charge of electron and m be its mass.

The centripetal force on the electron towards the centre in the absence of the magnetic field is

$$F = \frac{mv^2}{r} = m\omega^2 r \tag{1}$$

Now let an external magnetic field B is applied in a direction perpendicular to the plane of the orbits. Then an additional radial force of magnitude Bev acts on the electron.

Let $\delta\omega$ be the change in angular velocity caused by the field. For the circular motion in the *clockwise* direction, the additional radial force is directed away from the center.

Therefore,

$$F - Bev = m\left(\omega + \delta\omega\right)^2 r$$

$$m\omega^2 r - Be\omega r = m(\omega^2 + 2\omega\delta\omega + \delta\omega^2)r$$

$$-Be\omega r = 2mr\omega\delta\omega \qquad \text{(neglecting } \delta\omega^2 \text{)}$$

$$\delta\omega = -\frac{Be}{2m}$$

Similarly for the circular motion in the *anticlockwise* direction, the additional radial force is directed towards the center. Therefore, $\delta\omega = +\frac{Be}{2m}$

Combining both cases,

$$\delta\omega = \pm\frac{Be}{2m} \tag{2}$$

If ν be the frequency of orbiting of the electron,

$$\omega = 2\pi\nu \quad \Rightarrow \quad \delta\omega = 2\pi\delta\nu \quad \Rightarrow \quad \delta\nu = \frac{\delta\omega}{2\pi}$$

Therefore the change in frequency of spectral line is given by

$$\delta\nu = \pm\frac{Be}{4\pi m} \tag{3}$$

If ν and λ are the frequency and wavelength of the original line

$$c = \lambda\nu \quad \Rightarrow \nu = \frac{c}{\lambda} \quad \Rightarrow \delta\nu = -\frac{c}{\lambda^2}\delta\lambda \quad \Rightarrow \delta\lambda = -\frac{\lambda^2}{c}\delta\nu \quad \Rightarrow \delta\lambda = \pm\frac{\lambda^2}{c}\frac{Be}{4\pi m}$$

This is called *Zeeman shift*. Therefore the expression for *Zeeman shift* is

$$\delta\lambda = \pm\frac{Be\lambda^2}{4\pi mc} \tag{4}$$