

## 15.4: Spin-Orbit Coupling

A curious thing about the hydrogen atom is that the 2p states always appear split *even if no magnetic field has been applied!* This phenomenon originates from the fact that any electron in a  $l > 0$  state has orbital rotation that creates a magnetic field, just as discussed in the previous section. This field then acts upon the intrinsic magnetism of an electron, which exists due to its spin angular momentum. Essentially, they are like little bar magnets. Thus, the orbital and spin magnetic fields can either be aligned (higher energy) or not (lower energy). This effect is called spin-orbit coupling and is depicted in Figure 15.5.

The Hamiltonian for this interaction can be derived from the Einstein's theory of relativity:

$$\hat{H}_{SO} = -\frac{\mu_B}{\hbar m_e c^2} \frac{1}{r} \frac{\partial \hat{V}}{\partial r} \hat{L} \cdot \hat{S}$$

where  $\mu_B = 9.274 \text{ J} \cdot \text{T}^{-1}$  is the Bohr magneton that describes the magnetic moment of an electron due to orbital or spin angular momentum. The constants and gradient of the potential are generally lumped into a constant "A" such that  $\hat{H}_{SO} \sim A \cdot \hat{L} \cdot \hat{S}$ . The dot product of the two operators is defined as any standard vector:  $\hat{L} \cdot \hat{S} = \hat{l}_x \cdot \hat{s}_x + \hat{l}_y \cdot \hat{s}_y + \hat{l}_z \cdot \hat{s}_z$ . However, we cannot use this expression because the uncertainty principle dictates that we cannot know the x, y, and z components of angular momentum simultaneously. As a result, we employ an alternative strategy where we calculate the total angular momentum using the  $\hat{J}$  operator, where  $\hat{J} = \hat{L} + \hat{S}$ . We encountered the issue of addition of angular momentum in Ch. 14, so you might want to review that section. Regardless, the operator  $\hat{J}^2$  contains the  $\hat{L} \cdot \hat{S}$  dot product:

$$\hat{J}^2 = (\hat{L} + \hat{S})^2 = \hat{L}^2 + \hat{S}^2 + 2\hat{L} \cdot \hat{S}$$

We can rearrange the above to show that:  $\hat{L} \cdot \hat{S} = \frac{1}{2} \{ \hat{J}^2 - \hat{L}^2 - \hat{S}^2 \}$ , where the  $\hat{J}$ ,  $\hat{L}$ , and  $\hat{S}$  operators return their respective quantum numbers ( $j$ ,  $l$  and  $s$ ) such that the interaction is:

$$E_{SO} = \frac{A}{2} \cdot \{ j(j+1) - l(l+1) - s(s+1) \}$$

This spin-orbit energy is a unique function of the electronic configuration of an atom or molecule. To understand exactly how this works we will provide an example for a hydrogen atom with a  $2p^1$  electron configuration, i.e.  $l = 1$  and  $s = \frac{1}{2}$ . As discussed in Ch. 14 the  $l$  and  $s$  angular momenta add to produce two possible  $j$  states:

$$j = |l + s| = \frac{3}{2} \text{ or } j = |l - s| = \frac{1}{2}$$

Term symbols ( $^{2S+1}L_j$ ) distinguish between the two as having  $^2P_{\frac{3}{2}}$  and  $^2P_{\frac{1}{2}}$  electronic configurations. Spin-orbit coupling raises the energy of the  $^2P_{\frac{3}{2}}$  state:

$$E_{SO} = A \cdot \left\{ \frac{3}{2} \left( \frac{3}{2} + 1 \right) - 1(1+1) + \frac{1}{2} \left( \frac{1}{2} + 1 \right) \right\} = \frac{A}{2} \cdot \left\{ \frac{15}{4} - \frac{8}{4} - \frac{3}{4} \right\} = \frac{A}{2}$$

while the  $^2P_{\frac{1}{2}}$  state is pushed downhill:

$$E_{SO} = A \cdot \left\{ \frac{1}{2} \left( \frac{1}{2} + 1 \right) - 1(1+1) - \frac{1}{2} \left( \frac{1}{2} + 1 \right) \right\} = \frac{A}{2} \cdot \left\{ \frac{3}{4} - \frac{8}{4} - \frac{3}{4} \right\} = -A$$

Consequently the otherwise degenerate  $^2P_{\frac{3}{2}}$  and  $^2P_{\frac{1}{2}}$  configurations are split as shown in Figure 15.6. Also shown is how the spin-orbit effect is observed from the  $H_\alpha$  fluorescence which is the target of astronomers for charting the galaxy.

Hydrogen's spin-orbit coupling is very small and can only be observed with a fine spectrometer. However, the spin-orbit Hamiltonian's A constant is a function of the gradient of the Coulombic potential energy:  $\frac{\partial \hat{V}}{\partial r}$ , which in turn is proportional to the atomic number (Z) of an element as  $Z^4$ . This has two effects; one is that the spin-orbit energy becomes overwhelmingly strong for high Z elements. Second, the spin-orbit effect means that the total wavefunction cannot have the orbital and spin wavefunctions separated as:  $\psi_{total} \neq \psi_{space} \cdot \psi_{spin}$ . This introduces significant problems when trying to classify these atoms using term symbols

and order their energy levels. Unfortunately this is very difficult to deal with, and the development of theoretical calculations that incorporate spin-orbit effects is a topic of current research.

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