14.6: Addition of Angular Momentum and Term Symbols

One of the more complicated things about electronic structure is the addition of spin and “normal” orbital angular momenta. This is important because the total energy is proportional to the square of the total angular momentum. Thus far we have already introduced $\hat{L}$ and $\hat{S}$ operators and their associated l and s quantum numbers as defined previously. Now we define the total angular momentum operator $\hat{J}$:

$$\hat{J} = \hat{L} + \hat{S}$$

A pictorial representation is shown in Figure 14.13. The total angular momentum operator returns eigenvalues via:

$$\hat{J}\psi = \hbar\sqrt{j(j+1)} \cdot \psi$$

where j is the quantum number for the total angular momentum, and likewise there are sub-total angular momentum states determined by the operator $\hat{J}_z$ that has eigenvalues j_z. Similar to the m_l quantum numbers, the allowed values for j_z are:

$$j,\ j-1\ldots 0\cdots -j$$

The wavefunctions of the total angular momentum operators $\hat{J}$ and $\hat{J}_z$ are sums of the individual orbital$\times$spin states.

An atom with both orbital (l) and spin (s) momentum angular momenta is like a gyroscope that has another gyroscope on top of it. While this sounds complicated, to sum the momentum one simply uses vector addition. However, there is a problem when it comes to quantum angular momenta because the uncertainty principle dictates that the x, y and z components of either the orbital l or spin s momentum vectors are not fully known. Furthermore, we aren’t so concerned with $\hat{J}$, rather $\hat{J}^2$ as the square of the momentum gives us the energy. Fortunately, the mathematics of connecting the l orbital and s spin together to form j have been established; however this is best left to graduate-level texts on quantum mechanics. Here we will show the end result, which is that the final j quantum number results from either constructive (addition) or destructive (subtraction) of the l and s angular momenta, which when applied to the quantum numbers results in the following relationship:

$$j = l+s,\ l+s-1\ldots|l-s|$$

Take for example a hydrogen atom in a $2p^1$ excited state. Here, we have to add the spin angular momentum $s = \frac{1}{2}$ with the orbital momentum $l = 1$. As a result, we can see that there are two possible j states: $j = l+s = 1+\frac{1}{2} = \frac{3}{2}$ and $j = l-s = 1-\frac{1}{2} = \frac{1}{2}$. We can express this information in a quantity called a term symbol: ${}^{2S+1}\mathrm{L}_j$; in this example there are two possible states labeled ${}^2P_{\frac{3}{2}}$ and ${}^2P_{\frac{1}{2}}$. It is important to note that there are six possible states for the $2p^1$ electron configuration because there are two possible spins (up or down) that can go into one of three orbitals (p_x, p_y and p_z); these are depicted in Figure 14.14. As a result, there must also be six j states, and we can find them once we consider the sub-total angular momentum states j_z. For $j = \frac{3}{2}$ there are four sub-states $\left(j_z = \frac{3}{2}, \frac{1}{2}, -\frac{1}{2}, -\frac{3}{2}\right)$, while $j = \frac{1}{2}$ has two sub-states $\left(j_z = \frac{1}{2}, -\frac{1}{2}\right)$ for a total of six. It is important that we don’t “lose” states when adding them together! These states are shown to the right of Figure 14.14, where you can see that the different j states are linear combinations of the singularly filled p_x, p_y and p_z orbitals. Last, we note that these states are degenerate, however there is an effect called spin orbit coupling that energetically favors the ${}^2P_{\frac{1}{2}}$; this is explained in the next chapter.

You might be curious about the 2S+1 part of the term symbol. This is called the multiplicity, and to explain it let’s do another example of the addition of angular momentum just for spin. We run into such a problem for the excited state of helium with an electron configuration of $1s^1 2s^1$ as shown in Figure 14.15. As there is no l angular momentum, we are simply adding the two s quantum numbers, s_1 and s_2 to the total angular momentum that we call s_{tot}. Following the addition rules reveals two possibilities, one of which is: $s_{tot} = s_1 + s_2 = \frac{1}{2} + \frac{1}{2} = 1$. This configuration must have a total of three sub-s_{tot} states which are:

$$s_{tot},\ s_{tot}-1, -s_{tot} = 1,\ 0, -1$$

You may have figured out already based on the diagram that these are the triplet states, where $\uparrow\uparrow$ is for the +1 sub-s_{tot} state, $\downarrow\downarrow$ is for -1 and $\uparrow\downarrow + \downarrow\uparrow$ is for 0. Likewise there is the singlet state with a $s_{tot} = s_1 - s_2 = 0$, which has the associated spin wavefunction $\uparrow\downarrow - \downarrow\uparrow$. The singlet state cannot be degenerate. Consequently, the 2S+1 part of a term symbol is meant to convey the degeneracy expected due to spin angular momentum.