7.13: LS-coupling

Each of the several electrons in an atom has an orbital angular momentum $\mathbf{l}$ and a spin angular momentum $\mathbf{s}$, and there are numerous conceivable ways in which the various angular momenta can be coupled together to result in the total electronic angular momentum of the atom. (The total angular momentum of the atom may also include a small contribution from the nucleus. This contribution is usually quite tiny, but measurable. We'll ignore it for the time being; in any case, many nuclides (including most of those that have even numbers of protons and neutrons) have zero nuclear spin.

One of the simplest coupling schemes is called *LS-coupling* (or sometimes Russell-Saunders coupling). In this scheme (which may be regarded as one extreme of a host of conceivable coupling schemes), all the orbital angular momenta $\mathbf{l}$ of the several electrons are strongly coupled together to form the total electronic orbital angular momentum of the atom, which is denoted by $\mathbf{L}$. This can be represented symbolically by

$$\sum \mathbf{I} = \mathbf{L}. \tag{7.13.1}$$

The summation indicated is a vector summation.
The magnitude of $\mathbf{L}$ is $\sqrt{L(L+1)}\,\hbar$, and L can have nonnegative integral values, 0, 1, 2, 3, etc.

Similarly, all the spin angular momenta $\mathbf{s}$ of the several electrons are strongly coupled together to form the total electronic spin angular momentum of the atom, which is denoted by $\mathbf{S}$. This can be represented symbolically by

$$\sum \mathbf{s} = \mathbf{S} \tag{7.13.2}$$

The magnitude of $\mathbf{S}$ is $\sqrt{S(S+1)}\,\hbar$. If there is an even number of electrons in the atom, S can have nonnegative integral values. If there is an odd number of electrons in the atoms, the value of S is a positive odd integral number times $1/2$, such as $1/2,\ 3/2,\ 5/2$… etc.

The total electronic orbital angular momentum of the atom, $\mathbf{L}$, then couples weakly to the total electronic spin angular momentum of the atom, $\mathbf{S}$, to form the total (orbital plus spin) electronic angular momentum of the atom, denoted by $\mathbf{J}$. This is denoted symbolically by

$$\mathbf{L} + \mathbf{S} = \mathbf{J} \tag{7.13.3}$$

The magnitude of $\mathbf{J}$ is $\sqrt{J(J+1)}\,\hbar$. If there is an even number of electrons, J can take any of the $2\min\{L, S\} + 1$ nonnegative integral values from $|L-S|$ to $L+S$. If there is an odd number of electrons, J can have any of the $2\min\{L, S\} + 1$ odd-half-integral values from $|L-S|$ to $L+S$. The z-component of $\mathbf{J}$ is $M\hbar$. If J is integral (i.e. if there is an even number of electrons), M can have any of the $2J+1$ integral values from $-J$ to $+J$. If J is odd-half-integral, M can have any of the $2J+1$ odd-half-integral values from $-J$ to $+J$.

In many of the lighter elements near the beginning of the periodic table, the coupling of the angular momenta is close to that of ideal LS-coupling. There are appreciable departures from this simple scheme higher up in the periodic table. We shall discuss other coupling schemes a little later.