

SPIN-ORBIT COUPLING

So far, we have written the Hamiltonian for an atom as just a sum of kinetic energy terms and terms resulting from Coulomb interactions between the particles:

$$\hat{H} = \underbrace{-\frac{\hbar^2}{2m_e} \sum_i \nabla_i^2}_{\text{Electron kinetic energy}} - \underbrace{\frac{Ze^2}{4\pi\epsilon_0} \sum_i \frac{1}{r_i}}_{\text{Attraction of electrons to the nucleus}} + \underbrace{\frac{e^2}{4\pi\epsilon_0} \sum_{i < j} \frac{1}{r_{ij}}}_{\text{Electron-electron repulsion}}$$

This Hamiltonian gives highly accurate results for H and He, but as Z increases other effects begin to become important. These effects are ultimately traced to the fact that this Hamiltonian is derived from classical mechanics and becomes incorrect as the electron velocities approach the speed of light. To correct for these deficiencies a relativistically correct quantum mechanics must be developed. [Here I'm talking about special relativity, not general relativity.] Such a theory was developed by Dirac (and others) in the 1930's.

One effect of this relativistic treatment is an additional term in the Hamiltonian given by:

$$\hat{H}_{SO} = \frac{(g_e - 1)}{2m_e^2 c^2} \sum_i \frac{\hbar}{r_i} \frac{dV_i}{dr_i} \hat{\mathbf{l}}_i \cdot \hat{\mathbf{s}}_i$$

Here g_e is a fundamental constant, given by 2.0023, m_e is the mass of the electron, c is the speed of light, $V_i(r)$ is the effective potential felt by the i th electron, due to its interaction with the nucleus and averaged over all the other electrons, and $\hat{\mathbf{l}}_i$ and $\hat{\mathbf{s}}_i$ are the orbital and spin angular momenta of electron i .

This extra term in the Hamiltonian is called the spin-orbit interaction (due to $\vec{L}_i \cdot \vec{S}_i$), and it is generally much smaller in magnitude than the electron-electron repulsion term. In the heaviest atoms, it may become more important than the electron-electron repulsion, however, so in the heavy atoms it cannot be ignored. Usually it is small enough to be treated by perturbation theory.

Even in the H-atom, the occurrence of a term proportional to $\vec{L} \cdot \vec{S}$ destroys the validity of m_l and m_s as quantum numbers, and this leads to a splitting of the atomic terms into atomic levels. In this situation, it is appropriate to speak about the values of l, s , and j , where j gives the magnitude of the vector sum of \vec{L} and \vec{S} .

In the multielectron atoms we find that a term, specified by L and S and having a degeneracy of $(2L+1)(2S+1)$, is split into levels specified by the quantum numbers l, s, J (the vector sum of L and S), and M_J . To make this more concrete, consider the $1s^2 2s^2 2p^2$ states of carbon:

3P_g state: $L=1, S=1$ $|1-1| \leq J \leq 1+1$
 $0 \leq J \leq 2$
 $J = 0, 1, 2$

$(2L+1)(2S+1) = 3 \times 3 = 9$ states

The 3P_g state is split into states labeled as $^3P_{0g}, ^3P_{1g}, ^3P_{2g}$

Each has a degeneracy of $2J+1$:

$^3P_{0g}$	$2J+1 = 1$ state	} 9 states
$^3P_{1g}$	$2J+1 = 3$ states	
$^3P_{2g}$	$2J+1 = 5$ states	

In this diagram the largest splittings are considered first. Generally, the splittings between configurations are larger than the splitting between terms arising from a given configuration. Splittings between levels arising from a given term are generally smaller still (at least in the light elements).

Hund's third rule:

The spin orbit splitting arising from a configuration with an orbital less than half-full (as in the $p^1, p^2, d^1, d^2, d^3, d^4$ configurations) is such that the lowest J -levels lie lowest in energy.

If the configuration contains a subshell that is more than half-full (as in the $p^4, p^5, d^6, d^7, d^8, d^9$ configurations), then it is the highest J -levels that lie lowest in energy.

The hole formalism:

Electron configurations that lack n electrons of having a closed subshell give the same terms as configurations which have only n electrons in that subshell.

Thus, a p^1 and a p^5 configuration give only a single 2P_n term.

A p^2 and a p^4 configuration both give only $^3P_g, ^1D_g,$ and 1S_g terms.

etc.

Thus one gets the same results working with the electrons or the missing electrons (holes).

As a final step in resolving the degeneracies of an atom application of an external magnetic field splits the levels into their $2J+1$ different M_J states, giving:

