

# Physics 4261: Lectures for week 5

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## 5.1 Spin-orbit coupling in alkalis

Because the alkali structure is so similar to hydrogen, the spin-orbit coupling can be computed in basically the same way. So we have  $2s_{1/2}$ ,  $2p_{1/2}$ ,  $2p_{3/2}$ , etc. To quantify the magnitude of the effect, recall that for hydrogen-like atoms the spin-orbit splitting is given by

$$\Delta E_{s-o} = \frac{Z^4 \alpha^2 hc R_\infty}{n^3 l(l+1)}.$$

The modified form for the alkalis is

$$\Delta E_{s-o, \text{alkali}} = \frac{Z^2 \alpha^2 hc R_\infty}{(n^*)^3 l(l+1)},$$

here, we made the same replacement of the quantum defect, and also we used the power  $Z^2$  to interpolate between  $Z^4$  dependence of the hydrogen-like ion (relevant near zero where the spin-orbit coupling is big), and  $Z^0$  dependence of a singly-charge atom (relevant far away and useful to determine the energy).

## 5.2 Relative intensities

Since we are moving into some spectroscopy, let's consider a simple rule for transition strengths. This is to say that the total strength of all absorption or emission lines between two states is proportional to the degeneracy of the state. This comes from the fact that the strength in the non-spin orbit coupled case all these lines are the same, and the spin-orbit coupling is a weak perturbation (usually). So an equilibrium situation involves equal populations of all the  $m_j$  levels, and hence the total transition strength will be proportional to the degeneracy.

## 5.3 Angular momentum couplings

Imagine an atom with more than one valence electron (e.g. carbon). There are now two orbital angular momenta,  $\mathbf{l}_1$  and  $\mathbf{l}_2$ , and two spins,  $\mathbf{s}_1$ , and  $\mathbf{s}_2$ . We need to figure out how to add all of these up to make the total angular momentum  $\mathbf{J}$ . There are two basic ways: either add the orbital angular momenta to make  $\mathbf{L}$ , and all spins to make  $\mathbf{S}$ . I will now attempt to motivate the interactions which lead to these couplings.

## 5.4 Spin interactions and $LS$ coupling

Let's come back to the notion of the exchange interaction between a pair of particles:

$$E_{\text{exch}} = -\frac{e^2}{4\pi\epsilon_0} \int \int \psi_1^*(r) \psi_2^*(r') \frac{1}{|\mathbf{r} - \mathbf{r}'|} \psi_1(r') \psi_2(r) d^3r d^3r'.$$

The minus sign comes from our Slater determinant, because we must be an a totally antisymmetric wavefunction with respect to Fermion exchange. However, we have to consider spin. In fact, if we have different spins, we can be in a totally anti-symmetric spin wavefunction, but a totally symmetric spatial wavefunction. For example,

$$|1s1s \uparrow\downarrow\rangle - |1s1s \downarrow\uparrow\rangle ,$$

is symmetric spatially and antisymmetric with spin. This configuration does not generate an exchange term, because the exchange flips the spin. We can also consider other states, like

$$|1s2s \uparrow\uparrow\rangle - |2s1s \uparrow\uparrow\rangle .$$

In this case, the spatial wavefunction is anti-symmetric, and the Pauli exclusion principal keeps the two identical spins apart. Of course we can also have

$$|1s2s \uparrow\downarrow\rangle - |2s1s \downarrow\uparrow\rangle ,$$

which has no exchange term. However, this is really a superposition of two states with opposite exchange integrals:

$$|(1s2s - 2s1s)(\uparrow\downarrow + \downarrow\uparrow)\rangle + |(1s2s + 2s1s)(\uparrow\downarrow - \downarrow\uparrow)\rangle$$

The point of all this is that the total spin of the system,  $\mathbf{S}$ , matters. Similar arguments exist for the total angular momentum. For example, with two electrons in a  $d$  orbital, the interaction may depend on whether they are in states with the same value of  $m$  (for example, both in  $m = 2$ ), versus one in  $m = 2$  and the other in  $m = 0$ . Thus I expect  $\mathbf{L}$ , the total orbital angular momentum operator, to matter. Absent any spin-orbit coupling, I therefore expect  $\mathbf{L}^2$  and  $\mathbf{S}^2$  to commute with the Hamiltonian, so that different values of  $S$  and  $L$  will give different energies. Now is when things are going to get really fun. Spin-orbit coupling does exist, but let's say it's small compared with the electrostatic terms. The spin-orbit Hamiltonian is

$$H_{s-o} = \beta_1 \mathbf{s}_1 \cdot \mathbf{l}_1 + \beta_2 \mathbf{s}_2 \cdot \mathbf{l}_2.$$

Now, to do perturbation theory we need to know the expectation of the operator  $\mathbf{s}_1$  in the state  $\mathbf{S}$ . It turns out, due to something called the Wigner-Eckart theorem, that the expectation value of any vector operator is proportional to the vector  $\mathbf{S}$ , since this is the only vector that can be defined. Thus, prefactors aside, the two spin-orbit terms lead to just one proportional to  $\mathbf{L} \cdot \mathbf{S}$ . Here is the basic procedure to put everything together:

1. Figure out the configuration (i.e.  $1s^2 2s^2 2p^1 3p^1$ ).
2. Figure out what the possible values of  $L$  and  $S$  are. In this case, we have  $L$  is the sum of two spin 1 particles, so  $L = 0, 1, 2$ .  $S = 0, 1$ .

3. Now couple the values of  $S$  and  $L$  to make  $J$ .
4. If the electrons are in the same state (i.e.  $1s^2 2s^2 2p^2$ ), we need to figure out which combinations of  $L$  and  $S$  are allowed by the anti-symmetrization. I find it helpful to start with the largest possible value of  $L_z$ , the total angular momentum, and within that the biggest  $S_z$ . You can count total states and use the  $n$  choose  $k$  formula to find the total size of the Hilbert space. Then subtract out the configurations as you find them. So biggest is  $L_z = 2$ , which forces  $L = 2, S = 0$ . Then  $L_z = 1$ , which has four ways, one from  $L = 2$  is used up by three more from  $L = 1, S = 1$ . Then finally  $L_z = 0$ , which has 5 ways, 4 we counted already, and the fifth must be  $L = 0, S = 0$ .
5. These states are represented by a term symbol  $^{2S+1}L_J$ , where  $L$  is usually a capital letter  $S, P, D$ , etc. So carbon has  $^1D_2, ^3P_2, ^3P_1, ^3P_0, ^1S_0$ , and these are pronounced “singlet D two”, “triplet P two”, etc.

## 5.5 The $jj$ coupling scheme

In the previous, we coupled orbital angular momenta to make  $L$  before adding spin-orbit coupling because it was assumed spin-orbit is a weaker effect. This is true for light atoms but less so for heavy ones, and particularly for atoms in different sub-shells. Let's talk about the  $nsnp$  configuration. If we did  $LS$  coupling, we'd have  $L = 1$  obviously, and we'd have  $S = 1$  or  $S = 0$ . So we'd have  $^3P_2, ^3P_1, ^3P_0$ , and  $^1P_1$ . Now if we do  $jj$  coupling, we first add together spin and orbit in the  $s$  state, which leaves  $j_1 = 1/2$ . Then we have two values of  $j_2$ , namely  $j_2 = 3/2$  and  $j_2 = 1/2$ . This gives us two states written as  $(1/2, 1/2)$  and  $(1/2, 3/2)$ . The adding the total angular momentum gives  $(1/2, 1/2)_0, (1/2, 1/2)_1, (1/2, 3/2)_1$ , and  $(1/2, 3/2)_2$ . Note that there are always the same number of each  $J$  state, just in different terms! Also, note that the  $(1/2, 1/2)_1$  and  $(1/2, 3/2)_1$  both include some amount of spin singlet and triplet. This is important, as there is no perfect  $LS$  scheme, in reality all couplings fall somewhere in between the  $LS$  and  $jj$  limits, in the intermediate coupling scheme. So a little bit of  $^1P_1$  can mix with  $^3P_1$ , which allows so-called intercombination transitions. Since electric dipoles do not affect spin, we cannot move between singlet and triplet otherwise. So,  $^3P_1$  states have a weak intercombination transition, whereas  $^3P_0$  and  $^3P_2$  states are extremely long lived.

## 5.6 The interval rule

Back in the  $LS$  scheme, we finally add  $L$  and  $S$  together to make  $J$ . The value of the  $\mathbf{L} \cdot \mathbf{S}$  term comes out as  $2\mathbf{L} \cdot \mathbf{S} = \mathbf{J}^2 - \mathbf{L}^2 - \mathbf{S}^2$ . This can tell us about the spacing of the levels: level  $J$  is spaced apart from level  $J - 1$  by an amount  $J(J + 1) - (J - 1)J = 2J$ . So the spacing between  $J = 2$  and  $J = 1$  is twice that between  $J = 1$  and  $J = 0$ . This is called the interval rule. Note that it does not apply in the intermediate coupling scheme, so this is a way to check how well the  $LS$  coupling applies.