

## 8.6: Atomic Spectroscopy

The complex spectra of atoms can be understood using term symbols, as they contain all of the symmetry and quantum number values needed. The selection rules for systems that are well described by **Russell-Saunders coupling** are

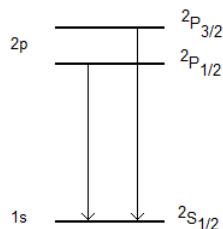


Figure 8.6.1

$$\Delta S = 0$$

$$\Delta L = 0, \pm 1 \text{ (but not } 0 \leftrightarrow 0)$$

$$\Delta J = 0, \pm 1 \text{ (but not } 0 \leftrightarrow 0)$$

Consider a  ${}^2P \leftarrow {}^2S$  transition. An energy level diagram for such a transition is shown to the right.

The selection rules predict two lines will be observed in the spectrum. The splitting between the lines will be related to the spin-orbit coupling constant in the upper state. Note that for this transition,  $\Delta S = 0$  and  $\Delta L = +1$ . (In spectroscopy recall that changes are always calculated as the upper state value minus the lower state value as in  $\Delta L = L' - L''$ ). The two lines predicted have  $\Delta J = 0$  and  $+1$  as depicted in the diagram.

Things get more complex for larger values of  $L$  and  $S$ . For example, consider the transition between a  ${}^3D$  state and a  ${}^3P$  state (with the  ${}^3D$  state as the upper state and both states increasing in energy with increasing  $J$ .)

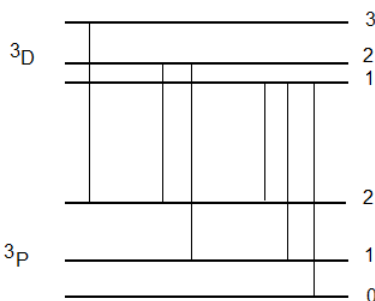


Figure 8.6.2

For this transition, six lines are predicted. The pattern formed by the lines can vary based on the relative values of the spin-orbit coupling constants in each level. In general, the upper state will have the lower spin-orbit coupling constant, as electronic excitation quenches spin-orbit coupling.

### Landé Interval Rule

The **Landé Interval Rule** describes the magnitude of the splittings in a term manifold. For example, it is predicted that the splitting pattern in a  $3P$  state is

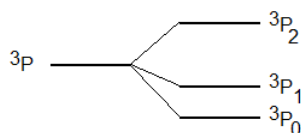


Figure 8.6.3

The splitting between the  ${}^3P_2$  level and the  ${}^3P_1$  level is twice as large as that between the  ${}^3P_1$  component and the  ${}^3P_0$  component. In general, the Landé Interval Rule can be stated

$$E_{J+1} - E_J = hcA(J+1)$$

where A is the **spin-orbit splitting constant** for the level. The Landé Interval Rule works well for small splittings, where the spin-orbit interaction can be treated as a perturbation to the Hamiltonian. There will generally be small deviations from the interval rule, especially when relativistic effects become important. The Landé Interval can be used to interpret the complex splitting patterns that can be seen in some atomic spectra.

### The Deslandres Table

A very useful tool that can be used in spectroscopy is the **Deslandres table**. In such a table, transitions are arranged according to upper and lower state combinations in such a way as to accentuate the differences in energy between quantum levels. For example, consider the following energy level diagram for  ${}^3D-{}^3P$  transition, where the six transitions have been labeled a-f for convenience.

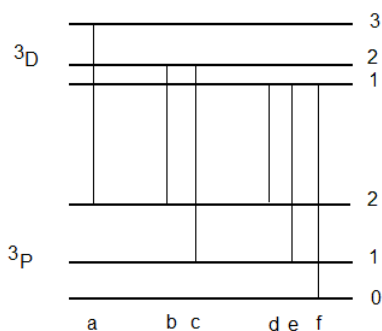


Figure 8.6.4

Looking at the diagram, it should be clear that the difference in energy between lines b and c must be identical to that between lines d and e, since both differences give the difference in energy between the  $J = 2$  and  $J = 1$  components of the  ${}^3P$  level. Similarly, the difference in energy between lines b and d must be equal to that between lines c and e, as that is the difference in energy between the  $J = 2$  and  $J = 1$  levels in the  ${}^3D$  state.

A Deslandres table summarizes the information in the energy level diagram and also incorporates the values of the measured lines in the spectrum. Symbolically, the Deslandres table for the above transition would look as follows

		${}^3D$				
		3	$3A'$	2	$2A'$	1
${}^3P$	2	a	$a - b$	b	$b - d$	d
	$2A''$			$c - b$		$e - d$
	1	–		c	$c - e$	e
	$A''$					$f - e$
	0	–		–		f

The table contains not only the line frequencies, but also the differences between them. It is the constancy of differences that confirms the assignment of the spectrum.

#### ✓ Example 8.6.1

consider the following data for a  ${}^3D-{}^3P$  transition. Assign the lines and calculate the spin-orbit coupling constants for both the upper and lower states based on your assignments.

Line	Freq ( $\text{cm}^{-1}$ )
1	18492.74

Line	Freq ( $\text{cm}^{-1}$ )
2	18511.98
3	18525.82
4	18540.84
5	18542.36
6	18545.06

The stick spectrum (simulated spectrum, with transitions indicated as sticks instead of lines with a definite line shape and without intensity data indicated) looks as follows.

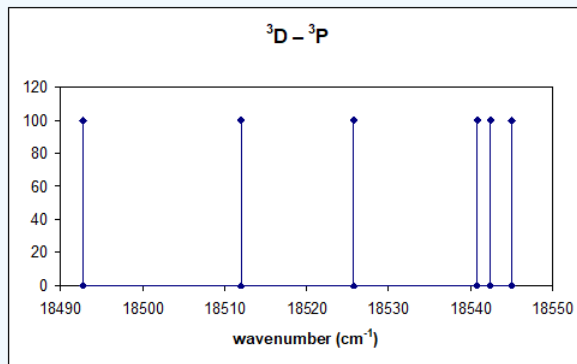


Figure 8.6.5

### Solution

It would be difficult to assign the spectrum simply based on the pattern seen above. In some cases, the spectral pattern can be quite complex! A couple of things can be inferred, however, based on the energy level diagram above.

The smallest energy transition is for  ${}^3D_1 - {}^3P_2$  and

the largest energy transition is either  ${}^3D_1 - {}^3P_0$  or  ${}^3D_2 - {}^3P_1$  (depending on the relative magnitudes of the spin-orbit splittings.)

Based on these observations, we can assign the 18492.74 line.

If 18545.06  $\text{cm}^{-1}$  is the  ${}^3D_1 - {}^3P_0$  transition, then the difference should be  $3A''$ . This predicts a lower level spin-orbit-coupling constant of  $A'' = 17.44 \text{ cm}^{-1}$ . And there must be a line at 18527.62  $\text{cm}^{-1}$ . But there is no such line! Hence, the highest energy transition is not the  ${}^3D_1 - {}^3P_0$  transition. It must be the  ${}^3D_2 - {}^3P_1$  transition instead!

If the 18542.36  $\text{cm}^{-1}$  line is the  ${}^3D_1 - {}^3P_0$  transition, a value of  $A'' = 16.54 \text{ cm}^{-1}$  is predicted. This predicts a line at 18525.82  $\text{cm}^{-1}$  which does exist! (This is idealized theoretical data for demonstration purposes. The Landé interval rule does not always hold as strongly as that.) The difference between the  ${}^3D_2 - {}^3P_1$  transition and the  ${}^3D_1 - {}^3P_1$  transition is 19.24  $\text{cm}^{-1}$ . In order to maintain a constant set of differences, there must be a line at 18511.98  $\text{cm}^{-1}$ , which there is. This is assigned as the  ${}^3D_2 - {}^3P_2$  transition. The only remaining line is 18540.84  $\text{cm}^{-1}$ , which is assigned as the  ${}^3D_3 - {}^3P_2$  transition. The final Deslandres table looks as follows.

		${}^3D$				
		3	$3A'$	2	$2A'$	1
${}^3P$	2	18540.84	28.86	18511.98	19.24	18492.74
	$2A''$			33.08		33.08
	1	--		18545.06	19.24	18525.82
	$A''$					16.54
	0	--		--		18542.36

In conclusion, angular momentum coupling schemes can be used to describe the states in a polyelectronic atom. These states can be used to predict the spectroscopy of these systems. In the next chapter, we will apply a number of the principles developed in this chapter in order to understand the electronic structure of diatomic molecules. This has important ramifications on both spectroscopy and bonding in these molecules, and also forms a foundation for how we think about electronic structure in larger molecules.

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