Electronic Spectra of Atoms

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I. Spin Orbit Coupling

A. Origin

- **Electron has spin angular momentum and moving charges generate magnetic fields, so an electron has a magnetic moment.**
- **An electron with orbital angular momentum also possesses a magnetic moment.**
- **These interact to give spin-orbit coupling, the magnitude of which depends on the relative orientations of spin and orbital magnetic moments.**

B. Total Angular Momentum of One Electron

- **Vector sum gives total angular momentum.**
- **Value is $j = l \pm s$ or $j = l \pm ½$**

- **Quantum mechanical calculations lead to the fact that there are different energies for a particular configuration based on the spin-orbit coupling.**

Example: What would be the splitting of the spectra resulting from the excited state for the potassium atom [Ar]$5p^1$.

Answer: Since l=1 for p level and s=½ so j=3/2 and ½ and the spectra should be split into two lines.

C. Term symbols

Term symbols such as ${}^2P_{3/2}$ convey the information given above for the spin-orbit interaction.

(1) The letter (S, P, D) indicates the total orbital angular momentum

(2) The left superscript in the term symbol gives the multiplicity of the term

(3) The right superscript on the term symbol is the value of the total angular momentum quantum number J

We shall now break each one down.

D. Total Orbital Momentum

When several electrons are present, it is necessary to judge how their individual angular momenta add together. The total angular momentum L is obtained by coupling the individual orbital angular momenta. For two electrons:

$$L = |l_1 - l_2| \text{ to } l_1 + l_2$$

- **Example: For two p electrons, L = 2, 1, 0. Hence a p^2 configuration can give rise to D, P and S terms. They differ in energy on account of the different electrostatic interactions between the electrons arising from their different orbital occupations.**

- **Example: For three electrons we use two series in succession – first we couple two electrons, and then we couple the third to each combined state. For a p^2 we have L' = 2,1,0 so we couple the third electron to each of these states. With L'=2 we get L=3,2,1; with L' = 1 we get L=2,1,0; with L'=0 we get L=1. The overall result is L=3,2,2,1,1,1,0; one F state, two D states, three P states and one S state.**

- **Remember that what we are doing is getting the vector sum of the angular momenta!**

D. Multiplicity

When there are several electrons to be taken into account, we must assess the total spin angular momentum S. For two electrons:

$$S = |s_1 + s_2| \text{ to } |s_1 - s_2|$$

- **Example: For two electrons, S = 1, 0.**

- **Example: For three electrons, couple the third electron to the S values of the first two. Thus S = 3/2 and ½ from coupling the third electron to S'=1, and S = ½ from coupling the third electron to S'=0.**

The multiplicity of a term is the value of 2S + 1. When S = 0 (as for a closed shell) the electrons are all paired and there is no net spin: this gives a singlet term, such as ^1S. [Try not to confuse the S of the term symbol with the S for the total spin angular momentum – it's very difficult to keep them straight in the beginning] A single electron gives rise to a double term such as ^2S. With two unpaired electrons, S=1 and the multiplicity is 3.

E. Total Angular Momentum and Russell-Saunders Coupling

The total angular momentum quantum number j tells us the relative orientation of the spin and orbital angular momenta of a single electron. The total angular momentum J does the same for several electrons. If there is a single electron outside a closed shell then J=j.

Example: The [Ne]$3p^1$ configuration has l=1 and therefore j=3/2 and ½; the ^2P term has two levels, $^2P_{3/2}$ and $^2P_{1/2}$.

If there are several electrons outside a closed shell we have to consider the coupling of all the spins and all the orbital angular momenta. This is a nasty problem that can be simplified by the use of the <u>Russell-Saunders coupling scheme</u>.

Russell Saunders Coupling

We imagine that all the orbital angular momenta of the electrons couple to give some total L and that all the spins are similarly coupled to give some total S. Only then do we imagine the momenta coupling through the spin-orbit interaction. The permitted values of J are:

$$J = |L-S| \text{ to } L + S$$

For the ^3D term of the configuration [Ne]$2p^1 3p^1$, the permitted values of J are 3,2,1 because L=2 and S=1. This gives three levels, $^3D_3$, $^3D_2$, and $^3D_1$.

A. How to determine term symbols

- **Write the configurations but ignore inner closed shells.**
- **Couple the orbital momenta to find L.**
- **Couple the spins to find S.**
- **Couple L and S to find J.**
- **Express the term as $^{2S+1}\{L\}_J$, where L is the appropriate letter.**

Example: Find the term symbol for the ground configuration of Na. Answer $^2S_{1/2}$.

Example: Find the term symbols for the configuration of $2s^1 2p^1$. Answer $^3P_2$, $^3P_1$, $^3P_0$, $^1P_1$.

Selection Rules

Spectral transitions can be specified using term symbols. For example, the transitions giving rise to the yellow sodium doublet are:

$3p^1\ \ {}^2P_{3/2} \rightarrow 3s^1\ \ {}^2S_{1/2}$ and $3p^1\ \ {}^2P_{1/2} \rightarrow\rightarrow 3s^1\ \ {}^2S_{1/2}$

We have seen that selection rules arise from the conservation of angular momentum during a transition and from the fact that a photon has a spin of 1. They can be expressed in terms of the term symbols, because the latter carry information about angular momentum.

$\Delta S = 0$ $\Delta L = 0, \pm 1$ with $\Delta l = \pm 1$
$\Delta J = 0, \pm 1$ but $J = 0$ cannot combine with $J = 0$.

The rule about $\Delta S = 0$ stems from the fact that light does not affect the spin directly. The rule about ΔL and Δl

expresses the fact that the orbital angular momentum of an individual electron must change (so $\Delta l = \pm 1$), but whether or not this results in an overall change of orbital momentum depends on the coupling.

These rules are applicable to light atoms. In very heavy atoms the rules may not apply for all transitions as other coupling comes into play.