

## **Lecture 18 Title : Fine Structure : multi-electron atoms**

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In this lecture we will concentrate on the fine structure of the multielectron atoms.

As discussed in the previous lecture that the fine structure arises due to spin orbit coupling.

Here we will discuss about the spin orbit coupling in case of more than one electron and their effect on terms transitions.

The Hamiltonian for the multielectron atoms

$$H = H^* + H_1 + H_{Spin-Orbit}$$

$$\text{where } H^* = -\frac{\hbar^2}{2m_e} \sum_{i=1}^N \nabla_i^2 + \sum_{i=1}^N U(r_i)$$

$$\text{where } \sum_i U(r_i) = -\sum_{i=1}^N \frac{Ze^2}{r_i} + \left\langle \sum_{i<j}^N \frac{e^2}{r_{ij}} \right\rangle$$

$$\text{and } H_1 = \sum_{i<j}^N \frac{e^2}{r_{ij}} - \left\langle \sum_{i<j}^N \frac{e^2}{r_{ij}} \right\rangle \quad \text{Non-Spherical part only}$$

$$H_{Spin-Orbit} = A_{SO} \sum l_i \cdot \sum s_i$$

The Spin-orbit interaction couples the total spin and total orbital angular momentum (L) to form the total angular momentum  $J$ .

The figure-18.1 represents the vector diagram and accordingly we write

$$\vec{J} = \vec{L} + \vec{S} \quad (\text{for one electron atoms}).$$

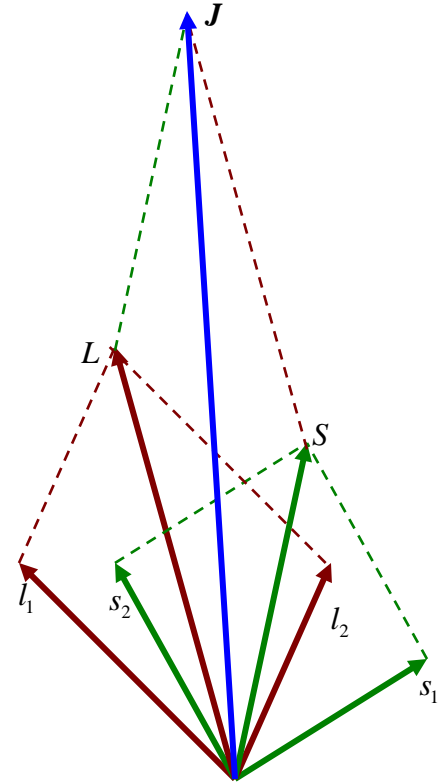


Figure 18.1

Because of this coupling, the one electron wavefunctions

$|L m_l\rangle |S m_s\rangle$  which are the eigenfunctions of  $H_{CentralField} + \sum_{i,j} \frac{e^2}{r_{ij}}$

are no more the eigenfunctions of the total Hamiltonian  $H$ .

$$H = H_{CF} + \sum_{i,j} \frac{e^2}{r_{ij}} + AL.S$$

$$|l_1 m_{l_1} s_1 m_{s_1}\rangle |L m_L\rangle |J m_J\rangle$$

$$|l_1 m_{l_2} s_2 m_{s_2}\rangle |S m_s\rangle$$

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The eigenfunctions of the  $H$  will be  $|J m_J\rangle$  which are the coupled wavefunctions and can be derived from the uncoupled wavefunctions  $|L m_l\rangle |S m_s\rangle$ , as described in previous lectures.

According to the coupling of angular momentum the value of  $J = L + S, \dots, |L - S|$  and the notation is  $^{2S+1}L_J$  where  $L = 0, 1, 2, 3, \dots$  are  $S, P, D, F$  respectively.

So the perturbation energy

$$\Delta E_{so} = \langle J m_J | A_{so} \vec{L} \cdot \vec{S} | J m_J \rangle$$

Now,  $\vec{J} = \vec{L} + \vec{S}$

$$J^2 = L^2 + S^2 + 2\vec{L} \cdot \vec{S}$$

$$\vec{L} \cdot \vec{S} = \frac{1}{2} [J^2 - L^2 - S^2]$$

And thus, the energy correction due to the spin-orbit interaction is

$$\Delta E_{so} = \langle J m_J | A_{so} \vec{L} \cdot \vec{S} | J m_J \rangle = \frac{A_{so}}{2} [J(J+1) - L(L+1) - S(S+1)] \dots \dots \dots (18.1)$$

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$2S + 1$  is the known as *multiplicity*. Indicates the degeneracy of the level due to spin.

If  $S = 0 \Rightarrow$  multiplicity is 1: *singlet* term.

If  $S = 1/2 \Rightarrow$  multiplicity is 2: *doublet* term.

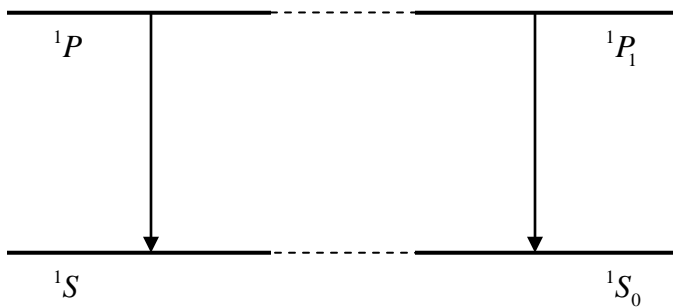
If  $S = 1 \Rightarrow$  multiplicity is 3: *triplet* term and so on.

In the following we will discuss the effect of spin-orbit interaction on terms to terms transitions.

### Singlet levels

$$S = 0 ; \quad \vec{J} = \vec{L} + \vec{S} = \vec{L}$$

$$\Delta E_{SO} = \frac{A_{SO}}{2} [J(J+1) - L(L+1)] = 0$$



Selection Rules :  $\Delta l = \pm 1, \Delta L = 0, \pm 1, \Delta S = 0, \Delta J = 0, \pm 1$

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Doublet levels

Transition from  ${}^2D$  to  ${}^2P$

For  ${}^2D$   $L=2$ ,  $S=\frac{1}{2}$ ,  $J=\frac{5}{2}, \frac{3}{2}$

Using equation-18.1

$$\Delta E_{SO} \left( {}^2D_{5/2} \right) = \frac{A'_{SO}}{2} \left[ \frac{5}{2} \left( \frac{5}{2} + 1 \right) - 2(2+1) - \frac{1}{2} \left( \frac{1}{2} + 1 \right) \right] = A'_{SO}$$

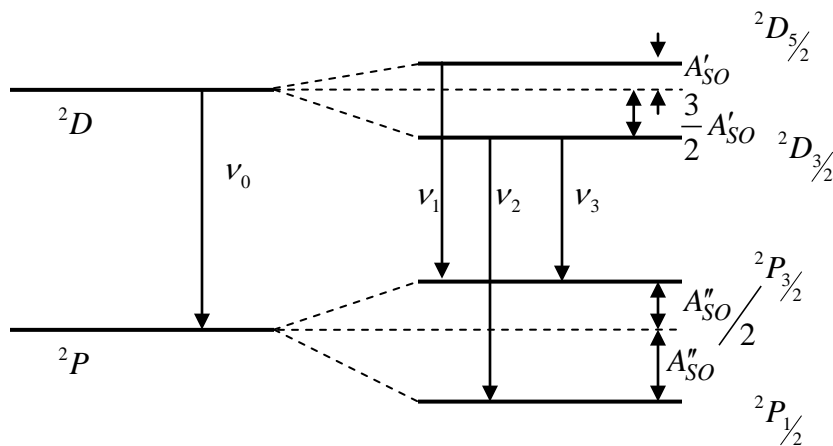
$$\Delta E_{SO} \left( {}^2D_{3/2} \right) = \frac{A'_{SO}}{2} \left[ \frac{3}{2} \left( \frac{3}{2} + 1 \right) - 2(2+1) - \frac{1}{2} \left( \frac{1}{2} + 1 \right) \right] = -\frac{3}{2} A'_{SO}$$

For  ${}^2P$   $L=1$ ,  $S=\frac{1}{2}$ ,  $J=\frac{3}{2}, \frac{1}{2}$

$$\Delta E_{SO} \left( {}^2P_{3/2} \right) = \frac{A''_{SO}}{2} \left[ \frac{3}{2} \left( \frac{3}{2} + 1 \right) - 1(1+1) - \frac{1}{2} \left( \frac{1}{2} + 1 \right) \right] = A''_{SO}/2$$

$$\Delta E_{SO} \left( {}^2P_{1/2} \right) = \frac{A''_{SO}}{2} \left[ \frac{1}{2} \left( \frac{1}{2} + 1 \right) - 1(1+1) - \frac{1}{2} \left( \frac{1}{2} + 1 \right) \right] = -A''_{SO}$$

So the construction of energy levels



It is important to know the degeneracy lifted by this spin-orbit interaction. The degeneracy for

$$^2D \text{ level is } 10 \left[ (2L+1)(2S+1) = (2 \cdot 2 + 1)(2 \cdot \frac{1}{2} + 1) = 10 \right]$$

When this level splits into  $^2D_{5/2}$  and  $^2D_{3/2}$ , then

$^2D_{5/2}$  the degeneracy is 6 because  $J = 5/2, m_J = 5/2, 3/2, 1/2, -1/2, -3/2, -5/2$ . All  $m_J$  levels will be degenerate. The  $m_J$  degeneracy will not be lifted until the external magnetic field is applied.

Similarly,  $^2D_{3/2}$  the degeneracy is 4 because  $J = 3/2, m_J = 3/2, 1/2, -1/2, -3/2$ .

$$\text{The degeneracy for } ^2P \text{ level is } 6 \left[ (2L+1)(2S+1) = (2 \cdot 1 + 1)(2 \cdot \frac{1}{2} + 1) = 6 \right]$$

When this level splits into  $^2P_{3/2}$  and  $^2P_{1/2}$

$^2P_{3/2}$  the degeneracy is 4 because  $J = 3/2, m_J = 3/2, 1/2, -1/2, -3/2$ . All  $m_J$  levels will be degenerate. The  $m_J$  degeneracy will not be lifted until the external magnetic field is applied.

Similarly,  $^2P_{1/2}$  the degeneracy is 2 because  $J = 1/2, m_J = 1/2, -1/2$ .

We will discuss the later the effect of magnetic field on these levels.

Transitions : as shown in the adjacent figure-18.2

$$\text{For transition } 1 \rightarrow \nu_1 = \nu_0 + A'_{so} - A''_{so}/2$$

$$\text{For transition } 2 \rightarrow \nu_2 = \nu_0 - \frac{3}{2} A'_{so} + A''_{so}$$

$$\text{For transition } 3 \rightarrow \nu_3 = \nu_0 - \frac{3}{2} A'_{so} - A''_{so}/2$$

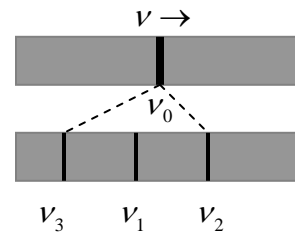


Figure 18.2

In general  $A''_{so} > A'_{so}$  so transition pattern will be  $\nu_2 > \nu_1 > \nu_3$ .

${}^3D \rightarrow {}^3P$  transition

$$\text{For } {}^3D \text{ term} \quad \begin{array}{l} S=1 \\ L=2 \end{array} \quad \text{So,} \quad \begin{array}{l} J=3, 2, 1 \\ {}^3D_3, {}^3D_2, {}^3D_1 \end{array}$$

$$\text{For } {}^3P \text{ term} \quad \begin{array}{l} S=1 \\ L=1 \end{array} \quad \begin{array}{l} J=2, 1, 0 \\ {}^3P_2, {}^3P_1, {}^3P_0 \end{array}$$

Now, let us calculate the perturbation energies for these levels using equation-18.1. We take the spin-orbit constants  $A_2$  and  $A_1$  for  ${}^3D$  and  ${}^3P$  respectively.

$$\Delta E_{SO}({}^3D_3) = \frac{A_2}{2} [12 - 6 - 2] = 2A_2, \quad \Delta E_{SO}({}^3D_2) = \frac{A_2}{2} [\cancel{6} - \cancel{6} - 2] = -A_2$$

$$\Delta E_{SO}({}^3D_1) = \frac{A_2}{2} [\cancel{6} - 6 - \cancel{2}] = -3A_2$$

$$\Delta E_{SO}({}^3P_2) = \frac{A_1}{2} [6 - 2 - 2] = A_1, \quad \Delta E_{SO}({}^3P_1) = \frac{A_1}{2} [\cancel{6} - 2 - \cancel{2}] = -A_1$$

$$\Delta E_{SO}({}^3P_0) = \frac{A_1}{2} [0 - 2 - 2] = -2A_1$$

Transition energies are

$$\nu_1 = \nu_0 + 2A_2 - A_1$$

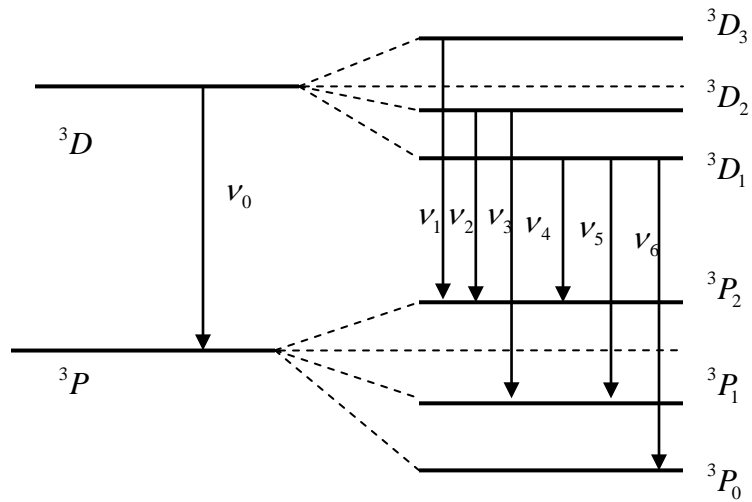
$$\nu_2 = \nu_0 - A_2 - A_1$$

$$\nu_3 = \nu_0 - A_2 + A_1$$

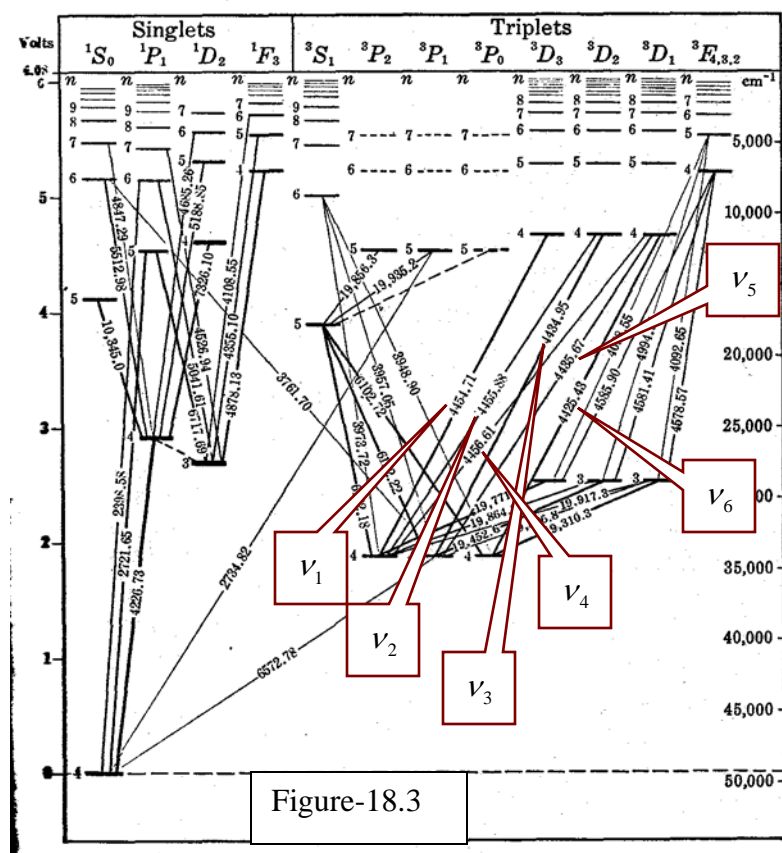
$$\nu_4 = \nu_0 - 3A_2 - A_1$$

$$\nu_5 = \nu_0 - 3A_2 + A_1$$

$$\nu_6 = \nu_0 - 3A_2 + 2A_1$$



The Observed transition of Calcium is given in this figure below.



Observed transitions	Observed transitions (nm)	Observed transitions (cm⁻¹)	Calculated transitions (cm⁻¹)
$\nu_1 = \nu_0 + 2A_2 - A_1$	445.47	22448.20	22447.46
$\nu_2 = \nu_0 - A_2 - A_1$	445.59	22442.16	22442.16
$\nu_3 = \nu_0 - A_2 + A_1$	443.50	22547.91	22547.91
$\nu_4 = \nu_0 - 3A_2 - A_1$	445.66	22438.63	22438.63
$\nu_5 = \nu_0 - 3A_2 + A_1$	443.57	22544.36	22544.38
$\nu_6 = \nu_0 - 3A_2 + 2A_1$	442.54	22596.68	22597.26

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From transitions  $\nu_2$  and  $\nu_3$

$$E_0 - A_2 - A_1 = 22442.16$$

$$E_0 - A_2 + A_1 = 22547.91$$

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$$2A_1 = 22547.9 - 22442.26$$

$$= 105.7$$

$$A_1 = 52.875 \text{ cm}^{-1}$$

From transitions  $\nu_2$  and  $\nu_4$

$$E_0 - 3A_2 - A_1 = 22438.63$$

$$E_0 - A_2 - A_1 = 22442.16$$

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$$2A_2 = 22442.16 - 22438.63$$

$$\Rightarrow A_2 = \frac{3.53}{2} = 1.765 \text{ cm}^{-1}$$

$$\text{And } \nu_0 = 22496.8 \text{ cm}^{-1}$$

The other transitions calculated from these values are given in the table.

Let us take another example, the transitions of Copper  $[3d^9 4s 4p] \text{ } ^4\mathbf{F} \rightarrow [3d^9 4s 5s] \text{ } ^4\mathbf{D}$

$$\text{For } ^4D \text{ term} \quad \begin{array}{l} S = 3/2 \\ L = 2 \end{array} \quad \text{So,} \quad \begin{array}{l} J = 7/2, 5/2, 3/2, 1/2 \\ ^4D_{7/2}, ^4D_{5/2}, ^4D_{3/2}, ^4D_{1/2} \end{array}$$

$$\text{For } ^4F \text{ term} \quad \begin{array}{l} S = 3/2 \\ L = 3 \end{array} \quad \begin{array}{l} J = 9/2, 7/2, 5/2, 3/2 \\ ^4F_{9/2}, ^4F_{7/2}, ^4F_{5/2}, ^4F_{3/2} \end{array}$$

For  $^4F$

$$\Delta E(J = \frac{9}{2}) = \frac{A_1}{2} \left[ \frac{9}{2} \cdot \frac{11}{2} - 3 \cdot 4 - \frac{3}{2} \cdot \frac{5}{2} \right] = \frac{9}{2} A_1$$

$$\Delta E(J = \frac{7}{2}) = \frac{A_2}{2} \left[ \frac{63-63}{4} \right] = 0$$

$$\Delta E(J = \frac{5}{2}) = \frac{A_1}{2} \left[ \frac{35-63}{4} \right] = -\frac{A_1}{2} \cdot \frac{28}{4} = -\frac{7}{2} A_1$$

$$\Delta E(J = \frac{3}{2}) = \frac{A_1}{2} \left[ \frac{15-63}{4} \right] = -\frac{A_1}{2} \cdot \frac{48}{4} = -6A_1$$

For  $^4D$

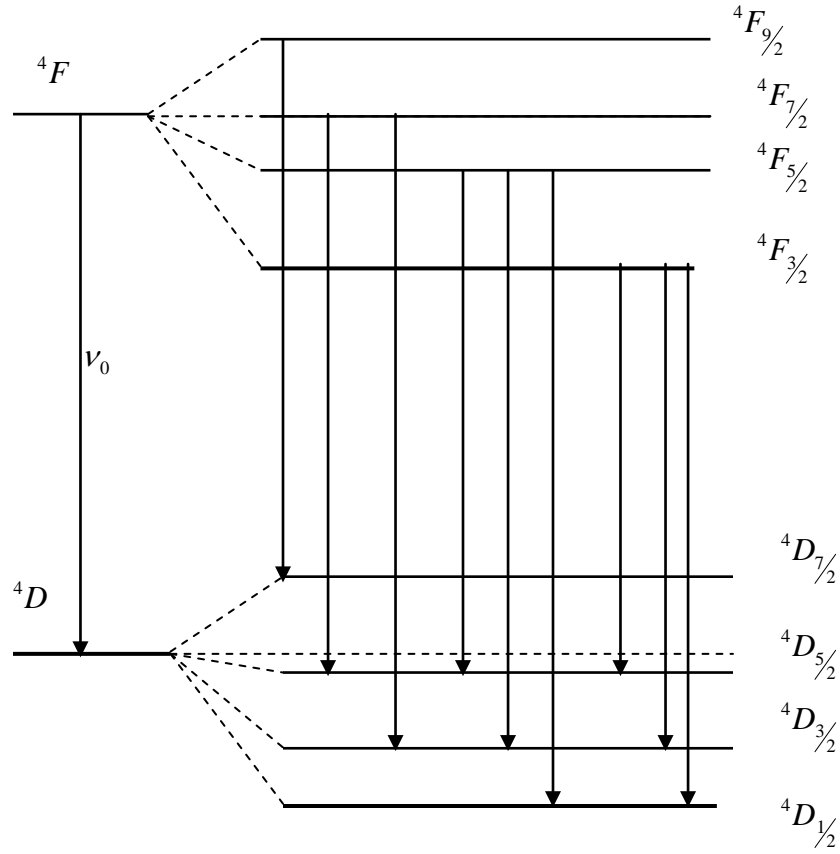
$$\Delta E(J = \frac{7}{2}) = \frac{A_2}{2} \left[ \frac{63-39}{4} \right] = \frac{A_2}{2} \cdot \frac{24}{4} = 3A_2$$

$$\Delta E(J = \frac{5}{2}) = \frac{A_2}{2} \left[ \frac{35-39}{4} \right] = \frac{A_2}{2} \cdot \frac{4}{4} = -\frac{A_2}{2}$$

$$\Delta E(J = \frac{3}{2}) = \frac{A_2}{2} \left[ \frac{15-39}{4} \right] = -\frac{A_2}{2} \cdot \frac{24}{4} = -3A_2$$

$$\Delta E(J = \frac{3}{2}) = \frac{A_2}{2} \left[ \frac{3-39}{4} \right] = -\frac{A_2}{2} \cdot \frac{36}{4} = -\frac{9}{2} A_2$$

The constructed energy level diagram is shown in this figure below.



Selection rules: derived from Wigner-Eckart theorem discussed earlier

$\Delta l = \pm 1$ ,  $\Delta S = 0$ ,  $\Delta J = 0, \pm 1$ . The  $J = 0 \rightarrow J = 0$  is forbidden.

The transition energies are

$$(1) \quad \bar{\nu}(4F_{9/2} \rightarrow 4D_{7/2}) = \nu_0 - 3A_2 + \frac{9}{2}A_1$$

$$(2) \quad \bar{\nu}(4F_{7/2} \rightarrow 4D_{7/2}) = \nu_0 - 3A_2$$

$$(3) \quad \bar{\nu}(4F_{7/2} \rightarrow 4D_{5/2}) = \nu_0 + \frac{A_2}{2}$$

$$(4) \quad \bar{\nu}(4F_{5/2} \rightarrow 4D_{7/2}) = \nu_0 - \frac{7}{2}A_1 - 3A_2$$

$$(5) \quad \bar{\nu}(4F_{5/2} \rightarrow 4D_{5/2}) = \nu_o - \frac{7}{2}A_1 + \frac{A_2}{2}$$

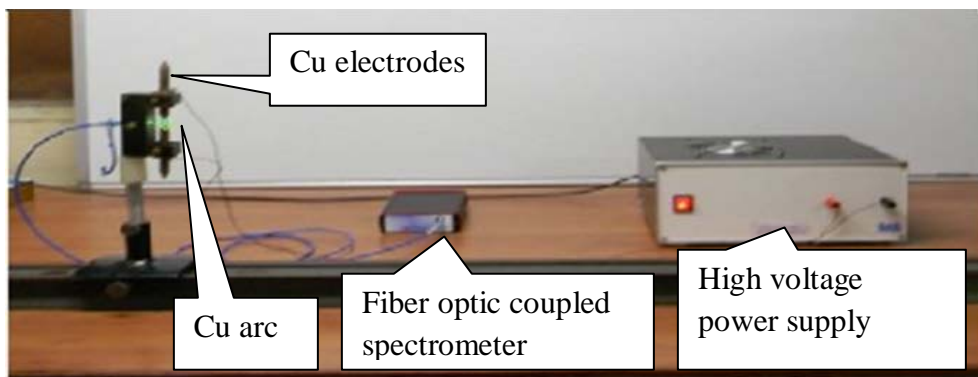
$$(6) \quad \bar{\nu}(4F_{5/2} \rightarrow 4D_{3/2}) = \nu_o - \frac{7}{2}A_1 + 3A_2$$

$$(7) \quad \bar{\nu}(4F_{3/2} \rightarrow 4D_{5/2}) = \nu_o - 6A_1 + \frac{A_2}{2}$$

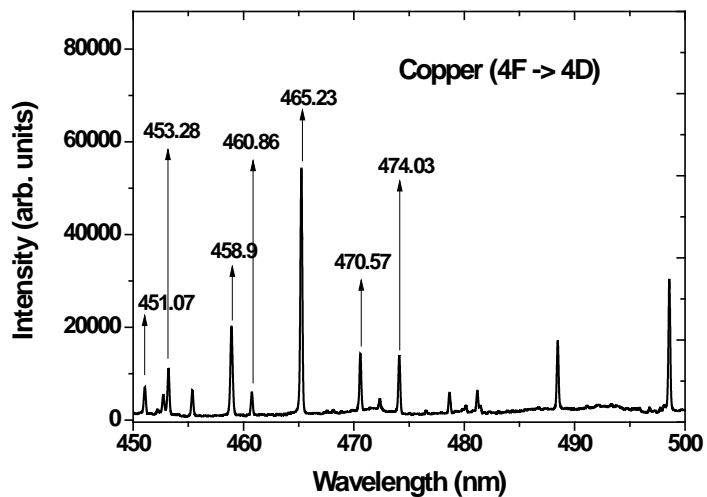
$$(8) \quad \bar{\nu}(4F_{3/2} \rightarrow 4D_{3/2}) = \nu_o - 6A_1 + 3A_2$$

$$(9) \quad \bar{\nu}(4F_{3/2} \rightarrow 4D_{1/2}) = \nu_o - 6A_1 + \frac{9}{2}A_2$$

The experimental set up for recording the copper  $^4F \rightarrow ^4D$  spectrum.



The copper  $^4F \rightarrow ^4D$  spectrum.



Assigning the observed three transitions as follows.

Transitions	Observed wavelength (nm)	Observed transition energy (cm <sup>-1</sup> )
$4F_{7/2} \rightarrow 4D_{5/2}$	458.90	21791.2
$4F_{9/2} \rightarrow 4D_{7/2}$	465.23	21494.7
$4F_{3/2} \rightarrow 4D_{1/2}$	470.57	21250.8

So we have three equations below to solve for obtaining three parameters.

$$\nu_o - 3A_2 + \frac{9}{2}A_1 = 21494.7$$

$$\nu_o - 3A_2 = 21250.8$$

$$\nu_o + \frac{A_2}{2} = 21791.2$$

From these above equations, we get

$$\nu_o + \frac{A_2}{2} = 21791.2$$

$$\nu_o - 3A_2 = 21250.8$$

$$\frac{7}{2}A_2 = 540.4$$

$$A_2 = \frac{540.4 \times 2}{7} = 154.4 \text{ cm}^{-1}$$

$$\nu_o = 21250.8 + 3 \times 154.4 = 21714$$

$$\frac{9}{2}A_1 = 21494.7 - 21250.8 = 243.9$$

$$A_1 = \frac{243.9 \times 2}{9} = 54.2 \text{ cm}^{-1}$$

Transitions	Transition energy	Calculated transition energy (cm <sup>-1</sup> )	Calculated transitions (nm)	observed transitions (nm)
${}^4F_{9/2} \rightarrow {}^4D_{7/2}$	$\nu_o - 3A_2 + \frac{9}{2}A_1$	21494.7	465.23	465.23
${}^4F_{7/2} \rightarrow {}^4D_{7/2}$	$\nu_o - 3A_2$	21250.8	470.57	470.57
${}^4F_{7/2} \rightarrow {}^4D_{5/2}$	$\nu_o + \frac{A_2}{2}$	21791.2	458.90	458.90
${}^4F_{5/2} \rightarrow {}^4D_{7/2}$	$\nu_o - \frac{7}{2}A_1 - 3A_2$	21061.1	474.8	474.03
${}^4F_{5/2} \rightarrow {}^4D_{5/2}$	$\nu_o - \frac{7}{2}A_1 + \frac{A_2}{2}$	21601.5	462.93	460.86
${}^4F_{5/2} \rightarrow {}^4D_{3/2}$	$\nu_o - \frac{7}{2}A_1 + 3A_2$	21987.5	454.80	453.28
${}^4F_{3/2} \rightarrow {}^4D_{5/2}$	$\nu_o - 6A_1 + \frac{A_2}{2}$	21464.8	465.88	-----
${}^4F_{3/2} \rightarrow {}^4D_{3/2}$	$\nu_o - 6A_1 + 3A_2$	21850.8	457.65	-----
${}^4F_{3/2} \rightarrow {}^4D_{1/2}$	$\nu_o - 6A_1 + \frac{9}{2}A_2$	22082.4	452.84	451.07

## **Summary of Atomic Energy levels**

### **Gross structure of the atomic energy levels:**

It covers largest interactions within the atom:

- (a) Kinetic energy of electrons in their orbits.
- (b) Attractive electrostatic potential between positive nucleus and negative electrons
- (c) Repulsive electrostatic interaction between electrons in a multi-electron atom.

These interactions give energies in the 1-10 eV range and upwards. It determine the spectrum range whether a photon is IR, visible, UV or X-ray.

### **Fine structure:**

Spectral lines often come as multiplets. E.g.,  $H\alpha$  line.

This smaller interactions within atom, called spin-orbit interaction.

The origin of this interaction is

Electrons in orbit about nucleus give rise to magnetic moment which interacts with spin of the electrons. This introduces splitting of the energy levels and produces small shift in energy.

### **Hund's rule :**

- (1) Of the terms given by equivalent electrons, those with greatest multiplicity lie deepest, and of these the lowest is that with the greatest L
- (2) Multiplets formed equivalent electrons are regular when less than half the shell is occupied, but inverted when more than half shell is occupied.

## Recap

In this lecture we have seen the effect of spin orbit coupling on the fine structure of the multielectron atoms.

We have discussed the transitions between the various spin multiplicity energy levels, sometime called as multiplets.

We have also gone through the experiments in the copper transitions and also learnt how to assign the transitions.

We also learnt how to evaluate the spin-orbit constant term for a level from the observed transitions.