Doublet Fine Structure

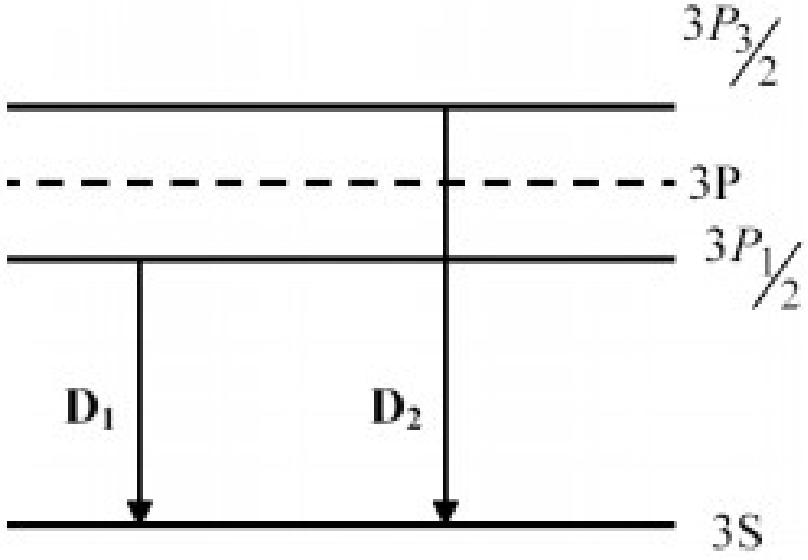
Doublet Fine Structure

Each member of some of the series in the alkali metals is a closed doublet whereas in alkaline earth it is closed triplet.

Sodium yellow line, corresponding to 3p → 3s transition, is a close doublet with separation of 6 Å.

Potassium has a doublet separation of 34 Å and so on.

(Li, Na, K, Rb, Cs, Fr)



Find structure intervals

- Doublet separation increases with atomic number.

- Doublet separations in ionized alkaline earth are larger than the corresponding doublets in the alkaline metal.

- Within each element doublet separations decrease in going to higher members of a series.

- Within each element P doublets are wider than D doublet of the same n and D doublet are wider than F doublets of the same n.

Only the S-terms are singlet.

All the other terms P, D, F etc. are doublets. Such doublet structure in energy is observed for all the atoms possessing a single valence electron i.e., in the outer most shell. Usually the doublet spacing is small and hence it is called fine structure.

To explain this feature Uhlenback and Goudsmith first proposed the hypothesis of electron spin.

The mechanism responsible for doublet splittng in S-O interaction, each energy level has got a spin multiplicity (2s+1)=2 as s=1/2

Spin is essentially a quantum phenomenon. The spin of the electron is found to be 1/2 ħ and

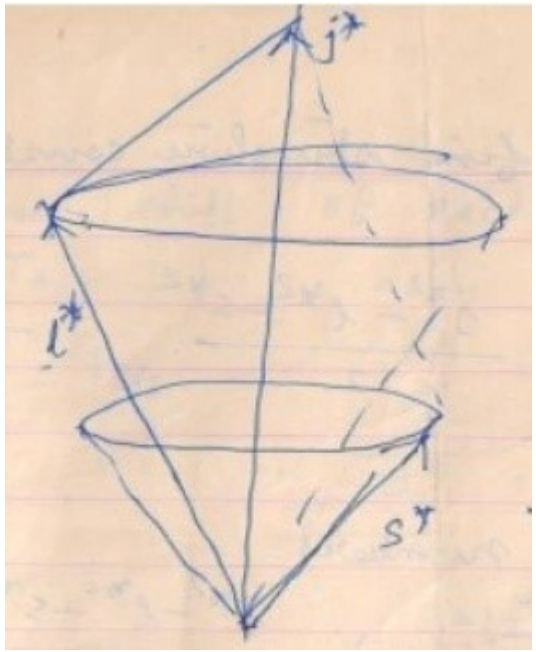
$$S^2 = s(s+1)\hbar^2$$

For spectra of atomic systems containing only one electron notation

s	is replaced by S	^2S
p	is replaced by P	^2P
d	is replaced by D	^2D
f	is replaced by F	^2F

Small subscript 2 in front of each term indicates that the level in question, including S level has doublet properties, and belongs to a doublet system.

In the field free space both orbit and spin are free to move so that l* and s* will precess around their resultant j*. By the law of conservation of angular momentum angle between l* and s* remains fixed.



Due to orbit-spin interaction in a single electron system an energy level is split into two according to the following scheme

$$\Gamma = a\,\frac{j^{*2} - l^{*2} - s^{*2}}{2} = a\,l^{*}s^{*}\cos l^{*}s^{*}$$

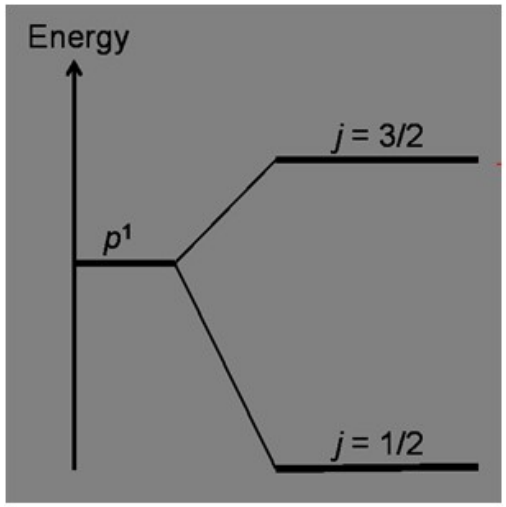
For s orbit $l = 0,\ l = 0, \gg \Gamma = 0$

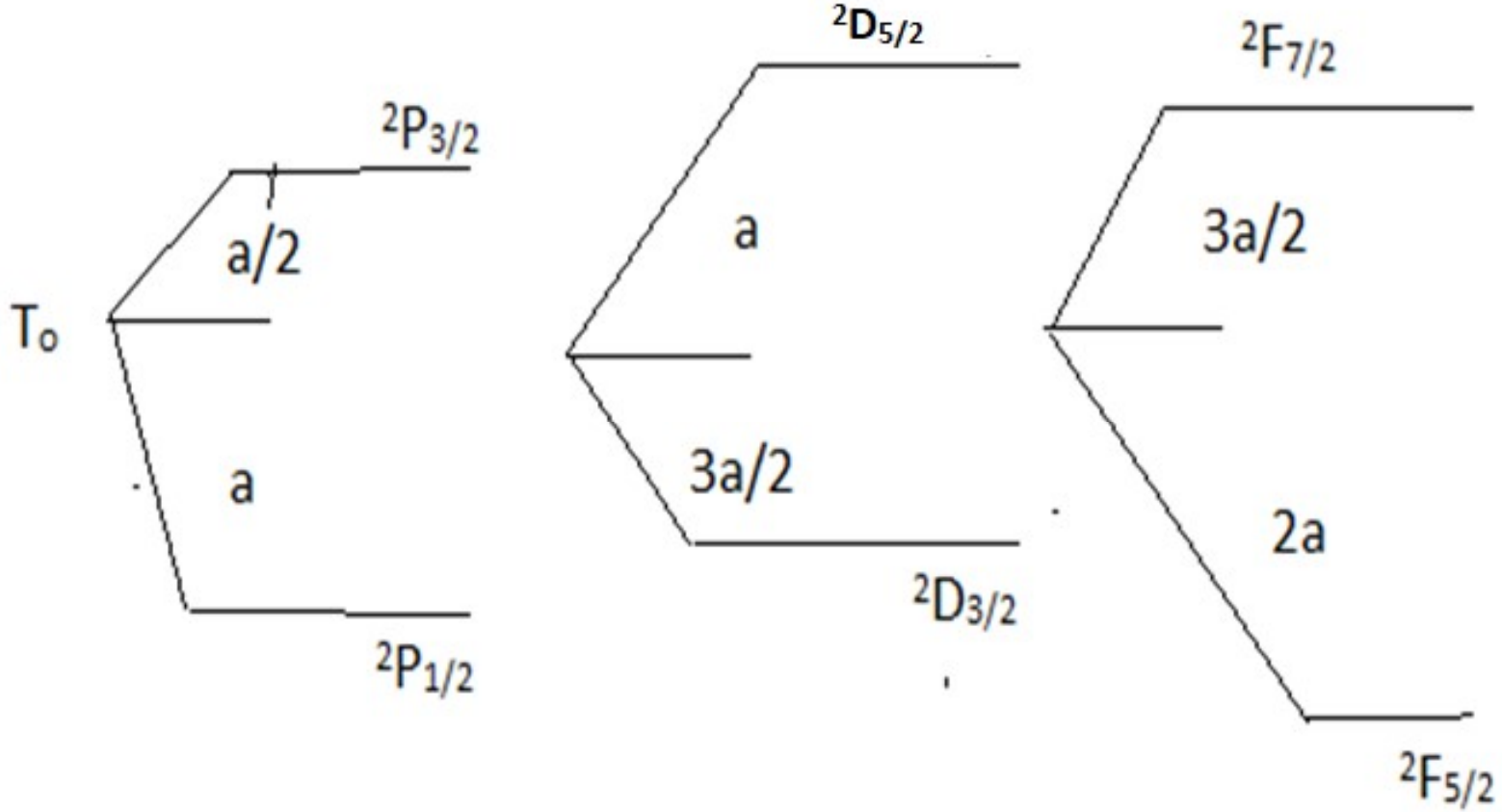
For p orbit $l = 1, s = \frac{1}{2} \gg j = \frac{1}{2}, \frac{3}{2} \gg l^* = \sqrt{1(1+1)} = \sqrt{2}$

$$s^* = \sqrt{\frac{1}{2}\left(\frac{1}{2}+1\right)} = \sqrt{\frac{3}{4}} \qquad i^* = \sqrt{\frac{3}{4}}, \qquad \sqrt{\frac{3}{2}\times\frac{5}{2}}$$

$$For\ j = \frac{1}{2}, \qquad \Gamma = a\frac{\frac{3}{4} - 2 - \frac{3}{4}}{2} = -a$$

$$For\ j = \frac{3}{2}, \qquad \Gamma = \frac{\frac{15}{4} - 2 - \frac{3}{4}}{2} = \frac{a}{2}$$



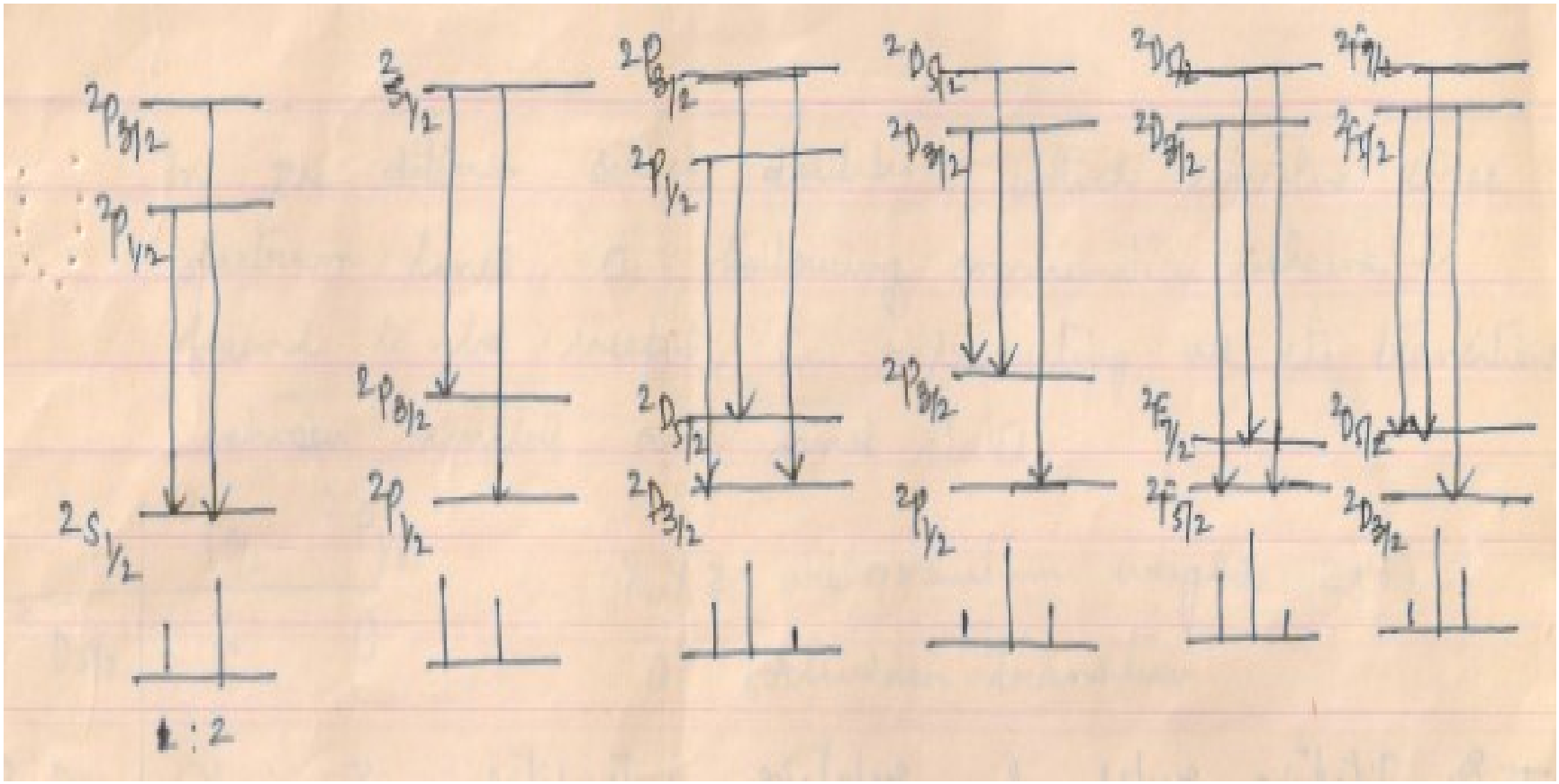

$^2P_{3/2}$
a/2
T_o
a
$^2P_{1/2}$
$^2D_{5/2}$
a
3a/2
$^2D_{3/2}$
$^2F_{7/2}$
3a/2
2a
$^2F_{5/2}$

Selection rules for fine structure doublet

In order to distinguish between two fine structure levels having same n and l values, half integral subscripts (**j** or **J**) are used.

For transition of an electron from one energy state to another, definite selection rules are in operation. These are based on experimental results. Total quantum number has no restriction and may change by any number.

$\Delta l = \pm 1$ $\Delta j = 0, \pm 1$



λ (5890 Å) **$3^2S_{1/2}$ -------- $3^2P_{3/2}$**

Combination between ^2P and ^2S always give rise to fine structure doublet, where as all other combinations give rise to a doublet and one satellite.

In designating any spectrum line lower state is written first followed by higher state.

Intensity Rules

Intensity rules are best stated in terms of quantum numbers of electrons in the initial and final states involved.

- Strongest lines in any doublet arise from transition in which j and l change in the same way.
- When there is more than one line in the same doublet, line involving largest j values is the strongest.

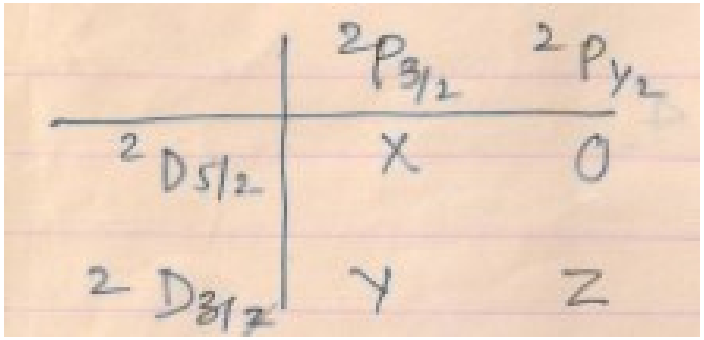
Quantitative rules for relative intensities

1. Sum of the intensities of those lines of a doublet which come from a common initial level is proportional to the quantum weight of that level.

2. Sum of the intensities of those lines of a doublet which end on a common level is proportional to the quantum weight of that level.

3. The quantum weight of a level is given by (2j+1). This (2j+1) is the number of Zeeman level into which a level j is split when the atom is placed in a magnetic field.

In the diffuse series doublet, which involves three spectrum lines, the following combination scheme is found to be useful in representing all the transitions between initial and final states.



X, Y, Z are quantum weights **2j+1**, and **0** represents forbidden transition.

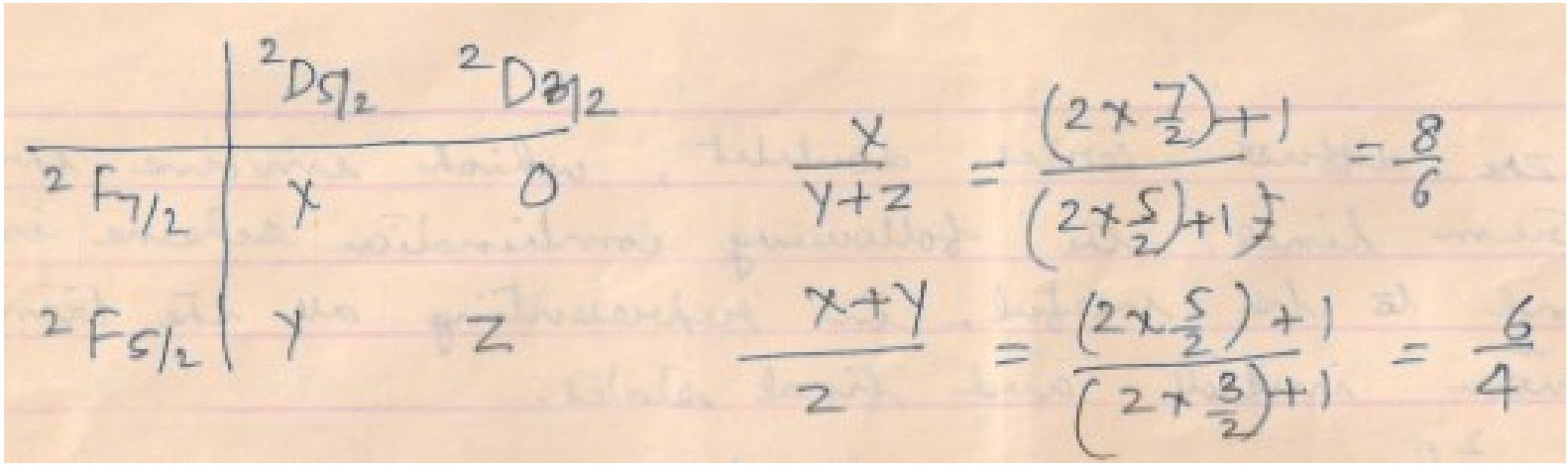
$$\frac{Sum\ of\ lines\ starting\ from\ {}^2D_{5/2}}{Sum\ of\ lines\ starting\ from\ {}^2D_{3/2}} = \frac{X}{Y+Z} = \frac{2\times\left(\frac{5}{2}\right)+1}{2\times\left(\frac{3}{2}\right)+1} = \frac{6}{4} = \frac{3}{2}$$

$$\frac{Sum\ of\ lines\ ending\ on\ {}^2P_{3/2}}{Sum\ of\ lines\ ending\ on\ {}^2P_{1/2}} = \frac{X+Y}{Z} = \frac{2\times\left(\frac{3}{2}\right)+1}{2\times\left(\frac{1}{2}\right)+1} = \frac{4}{2} = \frac{2}{1}$$

Smallest whole numbers which satisfy these equations are

X = 9, Y = 1, Z = 5

If the **^{2}D** terms are very close together so that the observed lines do not resolve the satellite from the main line, the two line have the intensity ratio $\frac{9+1}{5} = \frac{2}{1}$



Smallest numbers satisfying these equations are

X = 20, Z = 14, Y = 1

Prof. Narendra Kumar Pandey
Department of Physics
University of Lucknow
Lucknow-226007
Email: profnarendrapandey137@gmail.com