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## Quantum numbers associated with vector atom model:

**Principal quantum number:** we that  $n$  is number of orbit in which electron revolving called principal quantum number. Orbit is also called shells. For shell  $n=1,2,3,-----$  denoted by K,L,M,N---. The total number of electrons accommodated in each shell  $= 2n^2$

**Orbital quantum number:** Given shell divided into number of subshells. Orbital quantum number is denoted by  $l$ , gives no. Of subshells in which electron is revolving. It take  $l=0,1,2,-----(n-1)$ . The total number of electrons accommodated in each subshell shell  $= 2(2l+1)$ .

**Spin quantum number:** Electron have also spin motion denoted by  $s=+1/2,-1/2$ .

**Total angular momentum quantum number:** Sum of orbital quantum number and spin quantum number.  $j=l+s$ .

In presence of magnetic field three more quantum number associated with electron is Magnetic orbital quantum number, Magnetic spin quantum number, Magnetic total angular momentum quantum number.

Every electron in an atom has its own unique set of four quantum numbers  $n, l, m_l, m_s$ . This set of quantum numbers specifies the state of an electron in an atom which is called quantum state of an electron.

## Arrangement of electrons in shells and subshells:

Principle orbit or shell		Subshell			s or m <sub>s</sub>	No. of electrons accommodated	Total no. of electrons in		Electronic configuration
n	symbol	l = 0, 1, 2 ----- (n-1)	symbol				Subshell 2(2l+1)	Shell 2n <sup>2</sup>	
1	K	0	s				0	+1/2, -1/2	
2	L	0	s	0	+1/2, -1/2	2	2	8	2s <sup>2</sup> 2p <sup>6</sup>
		1	p	-1	+1/2, -1/2	2	6		
				0	+1/2, -1/2	2			
				+1	+1/2, -1/2	2			
3	M	0	s	0	+1/2, -1/2	2	2	18	3s <sup>2</sup> 3p <sup>6</sup> 3d <sup>10</sup>
		1	p	-1	+1/2, -1/2	2	6		
				0	+1/2, -1/2	2			
				+1	+1/2, -1/2	2			
		2	d	+2	+1/2, -1/2	2	10		
				-1	+1/2, -1/2	2			
				0	+1/2, -1/2	2			
				+1	+1/2, -1/2	2			
				+2	+1/2, -1/2	2			

- An atom of an element is represented by its electronic configuration. For that we start from K shell (n=1) from left, then L shell etc. in order and for each shell we write subshell possible in the order s, p, d, f with number of shell as prefix and write the number of electrons as superscript of subshell symbol. Consider electronic configuration of Na, its atomic number is 11  
(i. e. z=11)  $1s^2 2s^2 2p^6 3s^1$
- If a shell contains the maximum number of electrons possible, it is said to be closed. Electronic configuration of Na =  $\boxed{1s^2 2s^2 2p^6} 3s^1$ .
- In this case first orbit (n=1) and second orbit (n=2) contains maximum electrons, hence they are closed. Third orbit is incomplete because it consists of only one electron. The electron outside the closed shell is called valence electron or optical electron.

Spectra produced by all elements (atoms) are discrete lines (wavelengths).

The simplest spectrum is produced by hydrogen atom which has only one orbital electron ( $z=1$ ) and hydrogen Spectra was explained theoretically by Bohr.

Alkali metals have  $ns^1$  configuration i.e. there is only one electron outside filled configuration. This last  $ns^1$  electron called valence electron is responsible for emission or absorption of radiation i.e. for optical transition and hence for observed optical Spectra.

- Spectral notations and optical spectral series for doublet structure,

For writing the atomic states, it is necessary to know the orbital angular momentum  $L$ , spin angular momentum  $S$  and the total angular momentum  $J$  of the atom. The total angular momentum  $J$  of an atom is sum of orbital and spin angular momentum it is given as,  $\vec{J} = \vec{L} + \vec{S}$ .

Where,  $\vec{L} = \sum \vec{l}_i$  is the orbital angular momentum of an atom; it is vector addition of total orbital angular momentum vector  $\vec{l}_i$  of all the electrons and  $\vec{S} = \sum \vec{s}_i$  is the total spin angular momentum of an atom; it is vector addition of spin angular momentum vector  $\vec{s}_i$  of all the electrons in the atom. The addition of the total orbital angular momentum of an electron in atom and total spin angular momentum of an electron in an atom gives total angular momentum  $\vec{J}$ . This type of coupling of  $\vec{L}$  and  $\vec{S}$  for determination of  $\vec{J}$  is called L-S or Russell-Saunders coupling.

The total angular momentum vector  $\vec{J}$  characterized by total angular momentum quantum number  $j$ . The total angular momentum vector  $\vec{J}$  is also quantized, hence according to quantum mechanically  $\vec{J} = \sqrt{j(j+1)} \frac{h}{2\pi}$ . The total number of allowed values of  $\vec{J}$  for the given  $\vec{L}$  and  $\vec{S}$  are

$$J = (L + S), (L + S - 1), \dots, (L - S + 1), (L - S)$$

For example, let  $L = 3$  and  $S = \frac{3}{2}$  then  $J = \frac{9}{2}, \frac{7}{2}, \frac{5}{2}, \frac{3}{2}$ ; it means that there are  $(2S+1)$

i. e.  $(2 * \frac{3}{2} + 1) = 4$  different values of  $J$  (4 different states of the atom).

The multiplicity of the atomic state (term) is given by value of  $(2S+1)$ . The multiplicity

$(2S+1)=1$ , represents the singlet energy level ( $S=0$ )

$(2S+1)=2$ , represents the doublet energy level ( $S=1/2$ )

$(2S+1)=3$ , represents the triplet energy level ( $S=1$ )

The atomic states are denoted by the capital letters S, P, D, F, G ----- etc., which corresponds to the  $L=0, 1, 3, 4, \text{-----}$  resp. The atomic state is denoted using the term symbol as

$$^{(2S+1)}L_J,$$

where,

$(2S+1)$  is the multiplicity (here S is the resultant spin momentum of atom),

L is the resultant angular momentum of atom. For  $L=0$ , S-state;  $L=1$ , P-state;  $L=2$ , D-state and so on.

and J takes  $(2S+1)$  values from  $(L + S), (L + S - 1), \text{---} (L - S + 1), (L - S)$

**1) Let us consider hydrogen atom in ground state ( $z=1$ )**

$$n = 1, l = 0, m_l = 0, m_s = \frac{1}{2}$$

**Therefore, state of an atom  $^{(2S+1)}L_J$  will be  $^2S_{1/2}$  ; and it is read as doublet S half.**



2) Similarly suppose  $L = 3$ , and  $S = \frac{3}{2}$

then the values of  $J = \frac{9}{2}, \frac{7}{2}, \frac{5}{2}, \frac{3}{2}$  [ and  $J$  takes  $(2S+1)$  values from  $(L + S), (L + S - 1), \dots, (L - S + 1), (L - S)$  ]

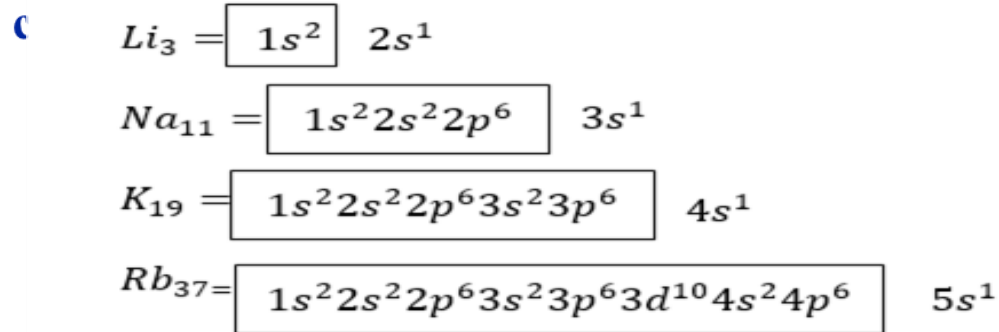
Therefore, for  $L=3$  indicates F state as  ${}^2F_{\frac{9}{2}, \frac{7}{2}, \frac{5}{2}, \frac{3}{2}}$  ;

The atomic states  ${}^2F_{\frac{9}{2}}, {}^2F_{\frac{7}{2}}, {}^2F_{\frac{5}{2}}, {}^2F_{\frac{3}{2}}$ . All these states are doublets. The atomic state

${}^2F_{\frac{7}{2}}$  can be read as doublet F seven halves and so on.

In general, atomic level is described as  $n^{(2S+1)}L_J$ , where  $n$  is principal quantum number.

Optical spectral series for doublet structure : **We know that in alkali metals there is only one electron in the outermost subshell, all other electrons form a closed shell. The electronic**



**The electrons in closed shell do not contribute to total angular momentum. The outermost subshell  $s^1$  electrons is the valance electron and is responsible for optical spectra of alkalis. Hence this electron is called optical electron.**

**In normal state of alkali metals, there is one electron in S-orbit i. e.  $l=0$ . Therefore, corresponding energy state is designated as S state or  $n \ ^rS_J$  state.**

**Where n is principal quantum number,**

**$r = 2S + 1$  is multiplicity**

**For alkali metal,  $r = 2S + 1 = 2 \times \frac{1}{2} + 1 = 2$ , Therefore, for alkali metal energy state is  $n \ ^2S_J$**

When energy supplied to alkali atoms, then S electron goes to higher permitted orbits P, D, F, ----- . Therefore, corresponding state (term) of the atom is designated as  $^2P$ ,  $^2D$ ,  $^2F$  etc. *resp.* According to Bohrs frequency condition, when electron jumps from a higher level to a lower level, the energy difference is emitted as radiation of frequency  $\nu$  i. e. it emits spectral line of radiation. According to Rydberg and others observation in alkali spectra, there are four groups or series of spectra. Under low resolution, spectral lines are close doublets in these series.

The spectrum of alkali metals (e.g. Na) consists of several series of spectral lines. When the spectral lines are examined with high resolving power instrument, many of them to consist of doublets i. e. very close two lines, such line is said to exhibit a fine structure. The spectral lines of alkali elements were classified into four series

- i) Sharp series
- ii) Principle series
- iii) Diffuse series
- iv) Fundamental series

- **Sharp series:**

This series of sharp spectral lines occurs due to transition from ns level to lowest p level. e. g.  $Na_{11}$  electronic configuration is  $1s^2 2s^2 2p^6 3s^1$ . Hence lowest state is 3S and excited states are 3P, 4S, 4P, 4D, 5S, 5P, 5D, 5F..... etc. Therefore Na atom emits sharp series due to transition

$3P \leftarrow nS$ . Where,  $n = 4, 5, 6, \dots$  . (Transitions involve a fixed state 3P and running state nS).

- **Principle series**

This is prominent i. e. intense spectral lines occur due to transition from np level to lowest s level. e. g. For Na atom principal series is represented by transition

$3S \leftarrow nP$ . Where,  $n = 3, 4, 5, 6, \dots$  . e. g. Na yellow D-lines

- **Diffuse series**

The spectral lines in this series are diffuse i. e. rather wide. This series for Na corresponds to the transition

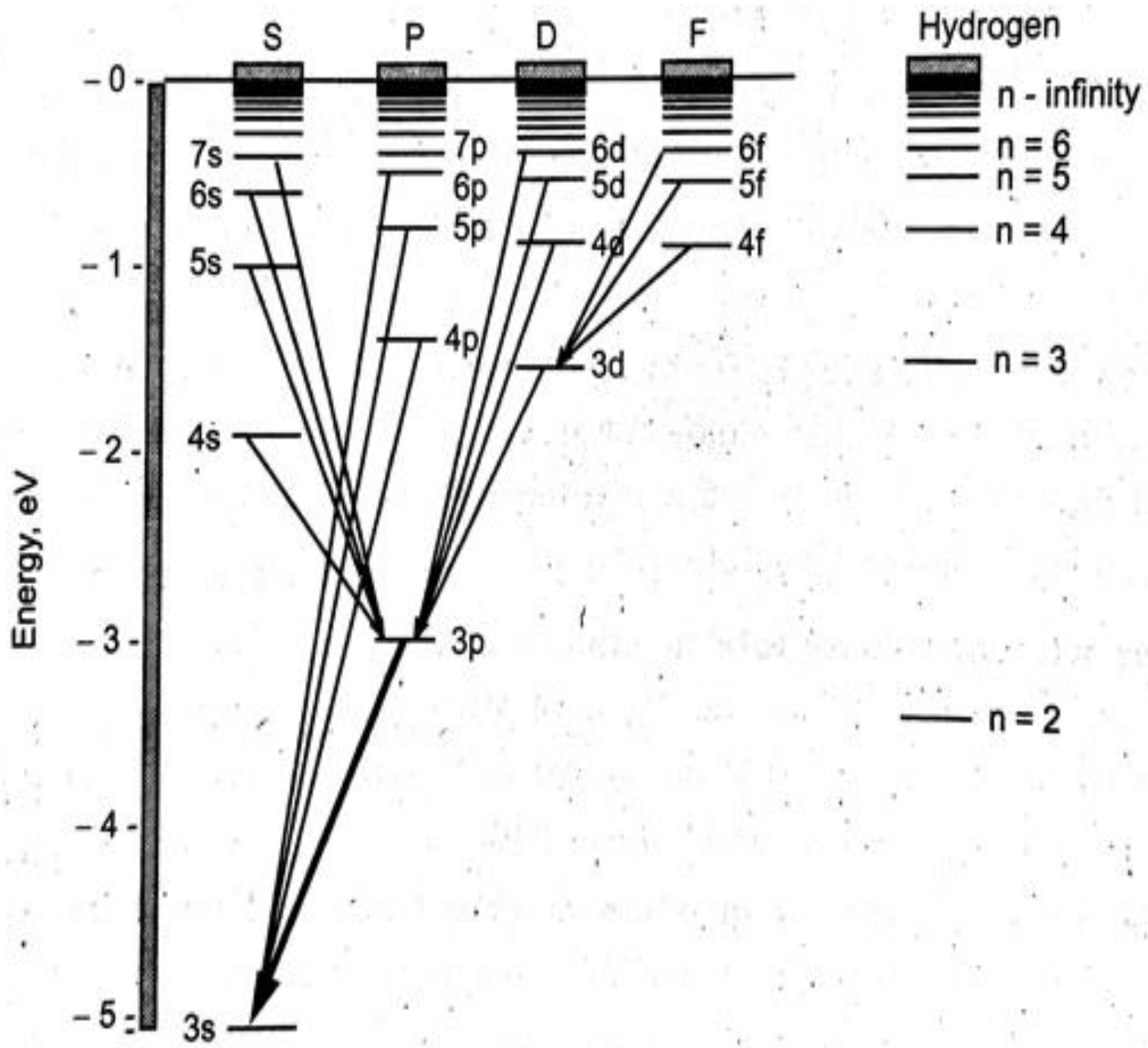
$3P \leftarrow nD$ , Where,  $n = 3, 4, 5, 6, \dots$  .

- **Fundamental series**

This series was occur in Na due to transition

$3d \leftarrow nF$ , Where,  $n = 4, 5, 6, \dots$  .

The energy levels of normal sodium atom and comparison with hydrogen is as shown in figure below



## Spectrum of sodium and its doublet fine structure

The structure of sodium (or alkali metals) is similar to that of hydrogen. Sodium has 11 electrons. The electronic configuration of the normal sodium atom is  $1s^2 2s^2 2p^6 3s^1$ . Here K and L shells are completely filled. The last level 3s is partially filled. The electrons in this level plays a part in optical spectrum of sodium atom. The optical 3s electron of sodium atom when excited, jumps to higher energy states such as are 3P, 4S, 4P, 4D, 5S, 5P, 5D, 5F...etc. depending upon the amount of excitation energy. When this electron returns to ground state gives rise to spectral series. These electron transitions are responsible for different lines observed in sodium spectrum.

When sodium atoms are excited, they give rise to a spectrum which contains four prominent series as

- i) Sharp series due to transition  $3P \leftarrow nS, n \geq 4$
- ii) Principal series due to transition  $3S \leftarrow nP, n \geq 3,$
- iii) Diffuse series due to transition  $3P \leftarrow nD, n \geq 3,$
- iv) Fundamental series due to transition  $3D \leftarrow nF, n \geq 4$



{ Multiplicity factor (spin quantum number  $S = \frac{1}{2}$ ),  $r = 2S + 1 = 2 \times \frac{1}{2} + 1 = 2$ ,

**For S state**  $L = 0$ ,  $J = L + S = 0 + \frac{1}{2} = \frac{1}{2}$  ∴ There are one values of  $J$ . Therefore S-state is a single state and Hence it is written as  $2S_{\frac{1}{2}}$

**For P state**  $L = 1$ ,  $J = L + S = 1 + \frac{1}{2} = \frac{3}{2}$  ;

$$J = L - S = 1 - \frac{1}{2} = \frac{1}{2}$$

There are two values of  $J$ . Therefore P-state is a doublet state and Hence it is written as  $2P_{\frac{3}{2}}$  and  $2P_{\frac{1}{2}}$

**For D state**  $L = 2$ ,  $J = L + S = 2 + \frac{1}{2} = \frac{5}{2}$  ;

$$J = L - S = 2 - \frac{1}{2} = \frac{3}{2}$$

There are two values of  $J$ . Therefore D-state is a doublet state and Hence it is written as  $2D_{\frac{5}{2}}$  and  $2D_{\frac{3}{2}}$

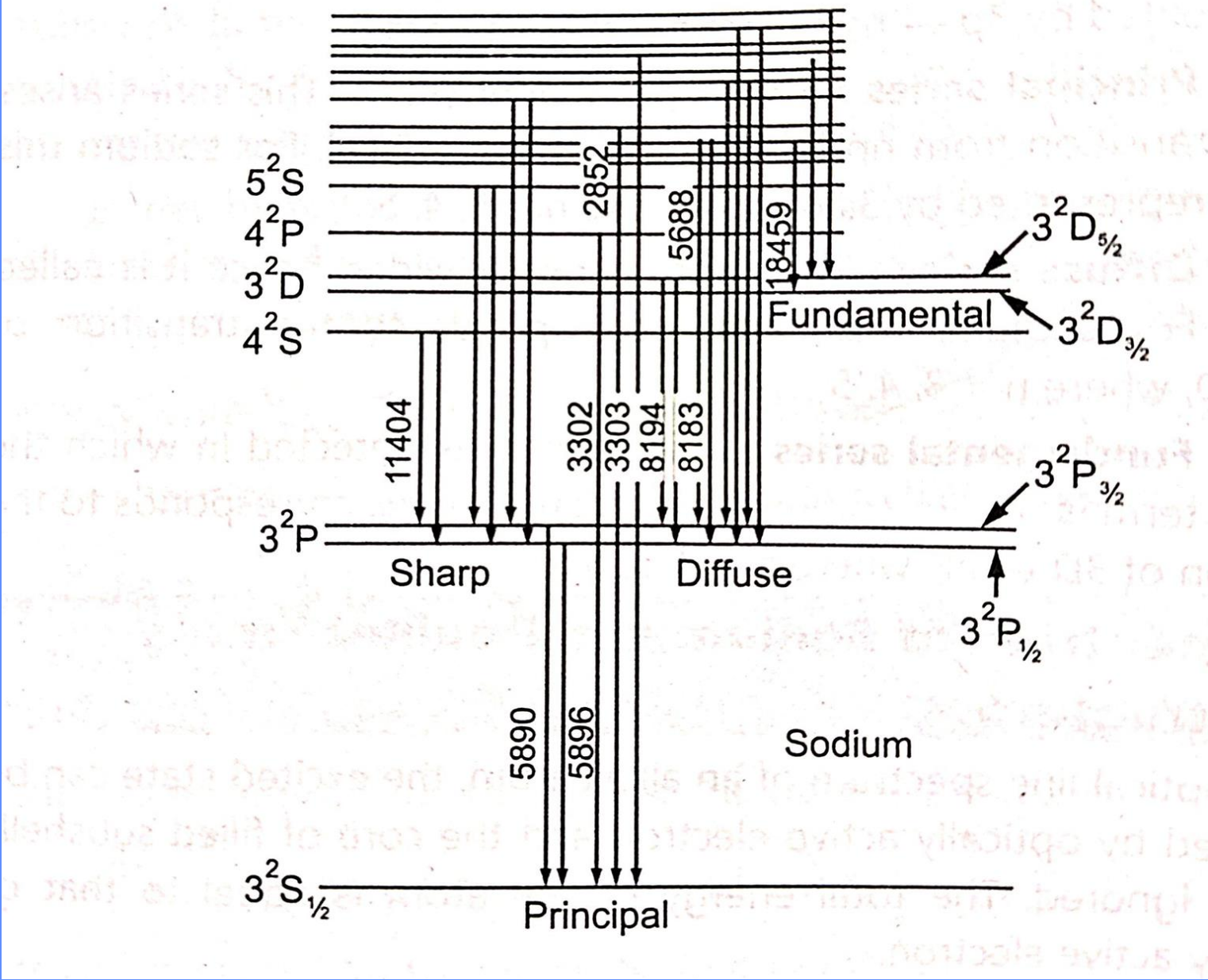
**For F state**  $L = 3$ ,  $J = L + S = 3 + \frac{1}{2} = \frac{7}{2}$  ;

$$J = L - S = 3 - \frac{1}{2} = \frac{5}{2}$$

There are two values of  $J$ . Therefore F-state is a doublet state and Hence it is written as  $2F_{\frac{7}{2}}$  and  $2F_{\frac{5}{2}}$

The spectral lines in alkali elements shows a doublet, triplet lines in series (Sharp series, Principal series- doublet line spectra; Diffuse, fundamental lines-triplet line spectra) are due to transition from energy levels in which P, D, F, G are doublet except S levels(S-singlet) }.

Transitions of spectral lines in energy level diagram of sodium atom is as shown in figure below.





Spectrum of sodium shows that some lines consist of doublets as well as triplet (Sharp series, Principal series- doublet lines; Diffuse, fundamental lines-triplet lines). In principal series of Na consists of two lines very close and separated by about  $6 \text{ \AA}$  ( $D_1 - 5896 \text{ \AA}$  and  $D_2 - 5890 \text{ \AA}$ ). These lines are due to transition from P state to lowest S state.

Following figure shows principal series doublets.

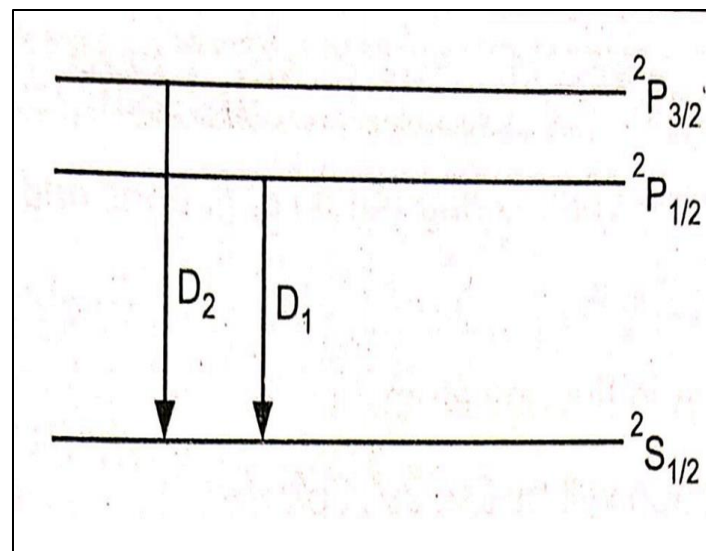
Therefore, two transitions are possible

$$3 \text{ } ^2P_{\frac{1}{2}} \rightarrow 3 \text{ } ^2S_{\frac{1}{2}}$$

which produces  $D_1 - 5896 \text{ \AA}$  lines &

$$3 \text{ } ^2P_{\frac{3}{2}} \rightarrow 3 \text{ } ^2S_{\frac{1}{2}} \quad \text{which produces}$$

$D_2 - 5890 \text{ \AA}$  lines.



**The study of spectra of alkali metals shows some salient features,**

**i) The spectral lines are close doublets called fine structure.**

**ii) The doublet separation increases with atomic number.**

**iii) For given alkali element the doublet separation decreases with increase in  $n$ .**

**iv) For given  $n$ , the doublet separation decreases with increase in  $l$ . i. e. P doublets are wider than D doublets and so on is as shown in fig. below.**

**v) S-levels are single i.e. they do not show doublets.**

