D.B.F. Dayanand College of Arts and Science, Solapur

Department of Physics

Presented by: Dr. S. G. Pawar

Dayanand E Pathshala Physics

SUBJECT	PHYSICS
PAPER NO & TITLE	Paper – XV Atomic Physics, Molecular Physics and Quantum Mechanics
MODULE TITLE	Atomic Spectra
MODULE TAG	DAYA_B.Sc.III_PHY_P-XV_AS

Dr. S. G. Pawar

Assistant Professor,

Department of Physics

D.B.F. Dayanand College of Arts and Science, Solapur

Email: shaileshgpawar@gmail.com

PHYSICS

21/07/2020

Paper – XV Atomic Physics, Molecular Physics and Quantum Mechanics

Module.1: Atomic Spectra – I (2020-21)

CONTENT

1. Learning Outcomes

1.1 Electronic Configuration of Alkali Metals

1.2 Spectral Notations

1.3 Alkali Spectra

1.4 Doublet Fine Structure of Alkali Metals

1.5 Spectrum of Sodium

1.6 Summary

Dr. S. G. Pawar, Department of Physics

1. Learning Outcomes

Dr. S. G. Pawar, Department of Physics

- **In this module,**
- You shall to depict state of an atom using spectral notation.
- Four groups of series of alkali spectra
- Doublet fine structure of alkali metals
- Spectrum of Sodium

1.1 Electronic Configuration of Alkali Metals

Alkali metals have one electron outside the completely filled subshell called valence electron. Hence, they are said to have ns^1 configuration. This electron is responsible for emission or absorption of radiation.

The electronic configuration of alkali metals is as follows:

(i) Li Z = 3 $1s^2\ \mathbf{2s^1}$

(ii) Na Z = 11 $1s^2\ 2s^2\ 2p^6\ \mathbf{3s^1}$

(iii) K Z = 19 $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ \mathbf{4s^1}$

(iv) Rb Z = 37 $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^6\ \mathbf{5s^1}$

(v) Cs Z = 55 $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^6\ 5s^2\ 4d^{10}\ 5p^6\ \mathbf{6s^1}$

The electronic configuration of alkali metals look like the core of an inert gas is surrounded by an s electron as follows:

$$\mathrm{Li} = [\mathrm{He}] + 2s^1$$

$$\mathrm{Na} = [\mathrm{Ne}] + 3s^1$$

$$\mathrm{K} = [\mathrm{Ar}] + 4s^1$$

$$\mathrm{Rb} = [\mathrm{K}] + 5s^1$$

$$\mathrm{Cs} = [\mathrm{Xe}] + 6s^1$$

The valence electron in alkali metals hence behave like an orbiting electron in the hydrogen atom. Hence alkali metals have hydrogen like spectra. Their spectrum is also referred to as one electron spectra.

Dr. S. G. Pawar, Department of Physics

1.2 Spectral Notations

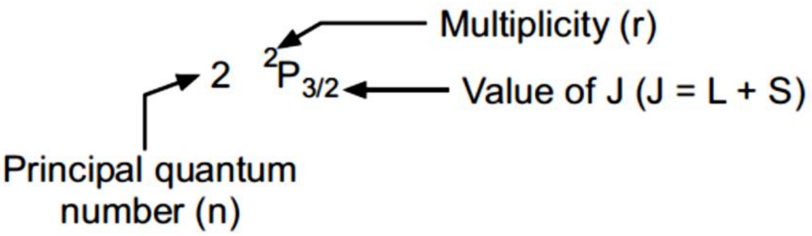
The state of an atom can be mentioned using the values of L, S, J and multiplicity (r). For atoms the levels L = 0, 1, 2, 3, 4 … correspond to S, P, D, F … etc.

The small letters show the state of electron, while the capital letters L, S and J show the state of atom as a whole. But for one valence electron system, L, S and J are same as *l*, *s* and *j* respectively.

But for many valence electron systems, the vectors L, S and J are the sum of *l*, *s* and *j* respectively for different free electrons.

Dr. Department of Physics

e.g. For $L = 1$, $S = \frac{1}{2}$ and $J = \frac{3}{2}$, notations are given as



Here the value of L is given by capital letter.

The state $3^2S_{1/2}$ is read as three doublet ess one half. The multiplicity ($r = 2s + 1$) gives the number of energy states available for excited electron. i.e. number of states available for transition.

e.g. (i) In case of one electron system,

$r = 2s + 1 = 2\left(\frac{1}{2}\right) + 1 = 2$, hence multiplicity is two. Therefore single electron system always gives rise to double state with exception of ground state, corresponding to

$$J = \left(L + \frac{1}{2}\right) \quad \text{and} \quad J = \left(L - \frac{1}{2}\right)$$

i.e. For $L = 0$, $\quad J = \frac{1}{2}$ or $J = -\frac{1}{2}$

The net angular momentum of an electron is always positive. Therefore the possibility of $J = -\frac{1}{2}$ is ruled out.

That means for $L = 0$, $J = +\frac{1}{2}$ only.

Therefore the ground state of single electron system is always singlet.

(i) In case of two electrons system, $S = 0$ or 1.

Therefore the state is either singlet or triplet.

(ii) For three electrons system, $S = \frac{1}{2}$ or $\frac{3}{2}$ and hence state is doublet or quartet.

The complete notations of the levels are as follows :

Table 1.2

Level	L	S	Multiplicity 2S + 1	J	Full notation
S	0	$\pm\frac{1}{2}$	2	$\frac{1}{2}$	${}^2S_{1/2}$
P	1	$\pm\frac{1}{2}$	2	$\frac{3}{2}, \frac{1}{2}$	${}^2P_{3/2}$, ${}^2P_{1/2}$
D	2	$\pm\frac{1}{2}$	2	$\frac{5}{2}, \frac{3}{2}$	${}^2D_{5/2}$, ${}^2D_{3/2}$
F	3	$\pm\frac{1}{2}$	2	$\frac{7}{2}, \frac{5}{2}$	${}^2F_{7/2}$, ${}^2F_{5/2}$

1.3 Alkali Spectra

According to Bohr's frequency condition, when the valence electron jumps from a higher level to a lower level, the energy difference is emitted as radiation of frequency (u), such that

$$h\upsilon = E_{higher} - E_{lower}$$

From the observations of alkali spectra by Rydberg and others, it is found that there are four groups of series of spectra. Under low resolution, spectral lines are close doublets in these series.

(i) Sharp series:

This type of series arises from the transitions from nS-level (exclusive of lowest) to the lowest P levels.

(ii) Principal series:

This series corresponds to transitions from nP levels to the lowest S level. The energy of the lowest s level is lowest possible value of energy and it represents the ground state of the atom.

(iii) Diffuse series:

This type of series arises from the transitions between various nD levels to lowest P levels.

(iv) Fundamental (or Bergmann series):

The fundamental series arises because of the transition from various nF levels to the lowest D levels.

Dr. S. G. Pawar, Department of Physics

e.g. **Spectral series for Na :**

Sharp series	nS → 3P,	n = 4, 5, 6 …
Principal series	nP → 3S,	n = 3, 4, 5 …
Diffuse series	nD→ 3P,	n = 3, 4, 5 …
Fundamental series	nF → 3D,	n = 4, 5, 6 …

Spectral series for Li :

Sharp series	nS → 2P,	n = 3, 4, 5 …
Principal series	nP → 2S,	n = 2, 3, 4 …
Diffuse series	nD→ 2P,	n = 3, 4, 5 …
Fundamental series	nF → 3D,	n = 4, 5, 6 …

1.4 Doublet Fine Structure of Alkali Metals

The lines of optical spectra emitted by alkali atoms show a fine structure splitting. The spectral lines are close doublet and hence called fine structure.

An analysis of alkali spectra shows that the S levels are single but all other P, D, F are doublet levels. This is due to electron spin orbit interaction. (The spin magnetic moment of the optically active electrons interact with the internal magnetic field created by motion of electron through the nuclear field.)

Due to this interaction,

$$J = L + S$$

where J = Total angular momentum

L = Orbital angular momentum

S = Spin angular momentum.

The spin orbital angular momenta are parallel and anti-parallel.

Therefore, $L = J \pm S = L \pm 1/2$

The double possibility for the setting of the spin with respect to orbit results in a splitting of each energy level (l-level) into two. One corresponds to $J = L + ½$ and other corresponds to $J = L - ½$ with the exception of s level for $L = 0$.

In each doublet level the component corresponding to the smaller value of J lies deeper being more stable. It is stable because the spin magnetic moment μs of the electron lines up in the direction of magnetic field –B produced due to orbital motion of the electron in the field of nucleus and –B is in the same direction as the orbital angular momentum –l.

Thus $J = L - ½$ are more stable than $J = L + ½$ and lie deeper.

Dr. S. G. Pawar, Department of Physics

The lines of optical spectra emitted by alkali atoms show a fine structure splitting as shown in Fig. 1.3.

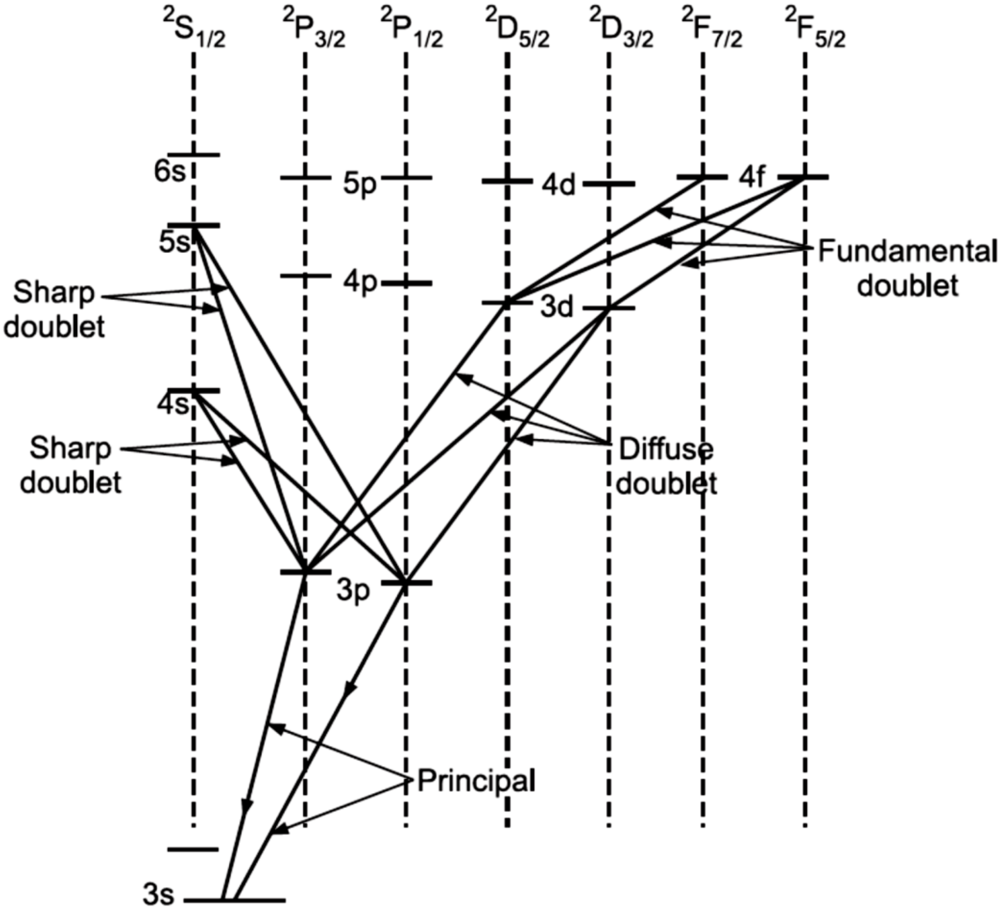


Fig. 1.3 : Fine structure splitting of alkali levels

Each line of sharp and fundamental series is doublet. The lines of diffuse and fundamental series show a three-component fine structure and are called compound doublet (not triplets). The fine structure in the lines of fundamental series is negligible.

Dr. S. Physics

The study of spectra of alkali metals reveals the following salient features:

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

(ii) The doublet separation increases with increasing atomic number.

(iii) For a given alkali (element), the doublet separation decreases with increase in n i.e., ongoing to higher number of series. (iv) For a given n, the doublet separation decreases with increase in *l* i.e. P doublets are wider than D doublets etc. as shown in

Fig. 1.4.

Department of Physics

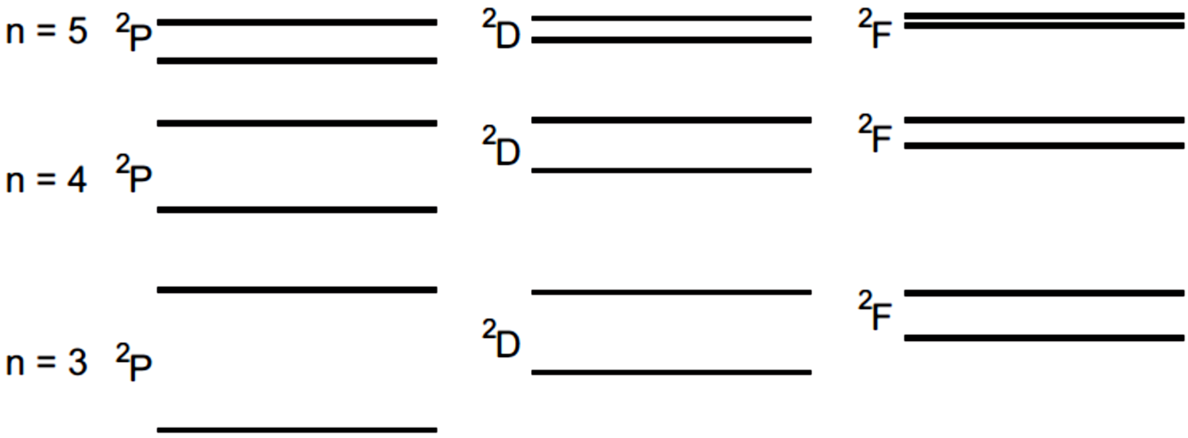


Fig. 1.4 : Schematic representation of doublet term separation

1.5 Spectrum of Sodium

The optical 3S electron of sodium when excited, jumps to higher energy states, such 3P, 4S, 3D, 5S, 4D … etc. depending upon the amount of excitation energy. According to Bohr-Sommerfeld theory and quantum mechanical theory, all sub-states belonging to a given n (principal quantum number) in hydrogen have same value of energy. But this *l* degeneracy is removed in a multi-electron system because of shielding of nuclear charge and penetration of atomic core.

The term value is, $T = \frac{RZ_0^2}{n_{eff}^2}$

where, Z_0 - Effective nuclear charge outside the core

n_{eff}^2- Effective quantum number

As Z_0 is greater than one and $n_{eff} < n$, the term value is increased. As a result energy levels in alkali atoms lie lower than the corresponding hydrogen levels. For large value of n, corresponding levels approach the hydrogen levels. However, all alkali levels lie below the corresponding hydrogen level.

Dr. S. G. Pawar, Department of Physics

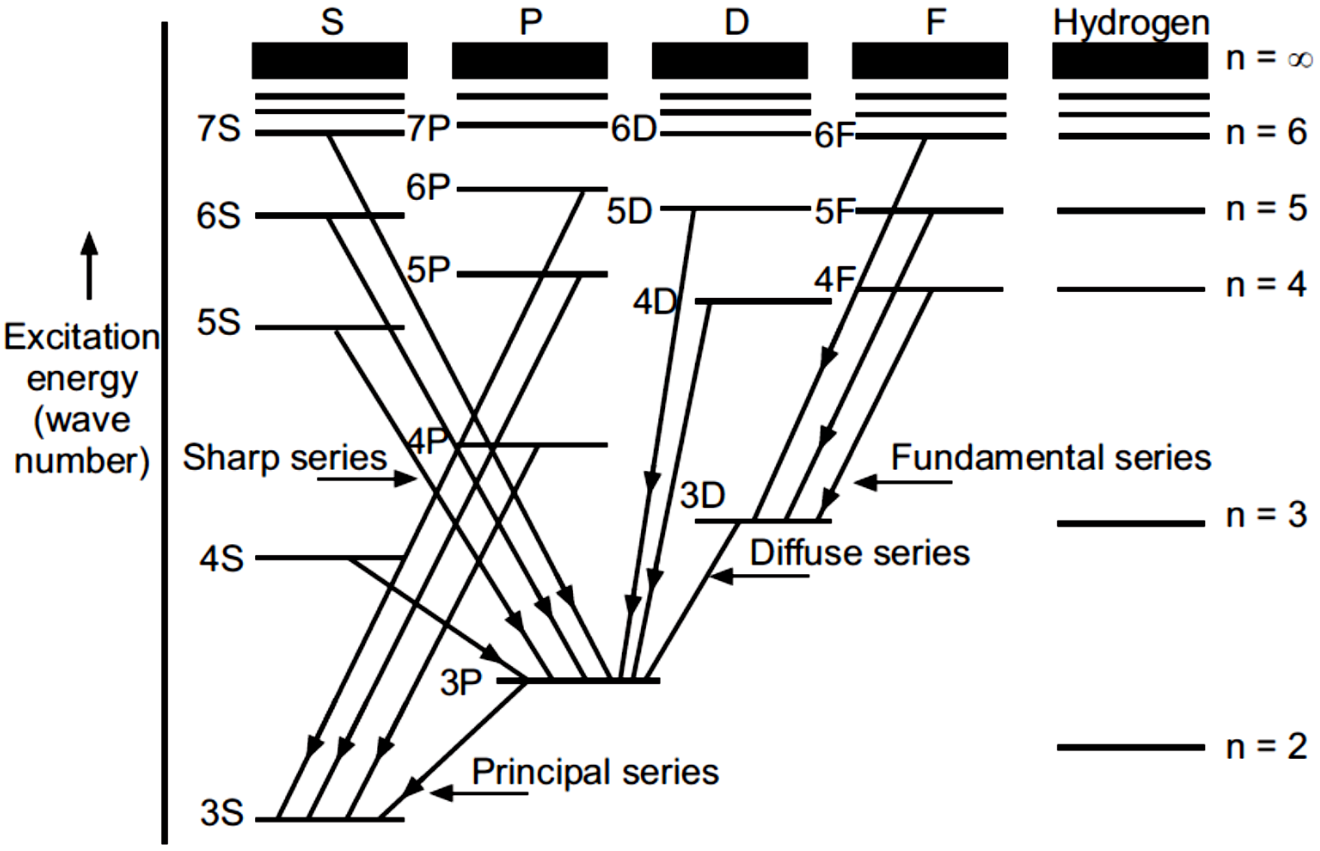


Fig. 1.5 : Spectrum of Sodium

Dr. S. G. Pa

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

(i) Sharp series due to transitions ($nS \rightarrow 3P, n \geq 4$).

(ii) Principal series due to transitions ($nP \rightarrow 3S, n \geq 3$).

(iii) Diffuse series due to transitions ($nD \rightarrow 3P, n \geq 3$).

(iv) Fundamental series due to transitions ($nF \rightarrow 3D, n \geq 4$).

The lines of sharp series are relatively sharp; hence the name is sharp series. The lines of P series are observed in both absorption and emission spectra of sodium, hence name principal series. The diffuse series lines are somewhat diffused; hence the name diffuse. The frequencies of fundamental series are in infra-red region and very close to the 'fundamental hydrogen atom', hence called fundamental.

It may also be noted from Fig. 1.5 that sharp and diffuse series have same convergence limit i.e. 3P state. The wave number difference in the limit 3P and 4S is the wave number of first line in principal series. Similarly, the wave number difference between fundamental series limit (3D) and diffuse series (3P) is equal to the wave number of first line in diffuse series.

Dr. S. G. Pawar, Department of Physics

1.6 Summary

- The alkali metal spectrum is referred as one electron spectra or hydrogen like spectra.
- Single electron system always gives rise to double state (doublet) with exception of ground state which is always singlet.
- From the observations of alkali spectra by Rydberg and others, it is found that there are four groups of series of spectra as Sharp series, Principal series, Diffuse series and Fundamental series. Under low resolution, spectral lines are close doublets in these series.
- The lines of optical spectra emitted by alkali atoms show a fine structure splitting. The spectral lines are close doublet and hence called fine structure.
- The levels J = L −½ are more stable than J = L + ½ and lie deeper.

Dr. S. G. Pawar, Department of Physics

Exercise

Problem 1.1 : *What are the term symbols for (i)* $S = \frac{1}{2}$ *and* $L = 2$ *?*

Solution : Given : (i) $S = \frac{1}{2}$ and L = 2 correspond to 'D' orbital.

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

The spin multiplicity,

$$(2S + 1) = 2 \times \frac{1}{2} + 1 = 1 + 1 = 2$$

∴ The term symbol is $^2D_{5/2}$.

(ii) $S = 1$ *and* $L = 1$.

Solution : Given : S = 1, L = 1 correspond to 'P' orbital.

$$J = L + S = 1 + 1 = 2$$

The spin multiplicity $(2S + 1) = 2 \times 1 + 1 = 2 + 1 = 3$

∴ The term symbol is $^3P_2$.

(iii) $S = \frac{3}{2}$ *and* $L = 1$.

Solution : Given : $S = \frac{3}{2}$ and L = 1 correspond to 'P' orbital.

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

The spin multiplicity $(2S + 1) = 2 \times \frac{3}{2} + 1 = 3 + 1 = 4$

∴ The term symbol is $^4P_{5/2}$.

Problem 1.2 : *Determine the L, S and J values for given term symbols*

(i) ${}^{2}P_{3/2}$.

Solution : $$J = \frac{3}{2}$$

The spin multiplicity (2S + 1) = 2.

$$\therefore \quad S = \frac{2-1}{2} = \frac{1}{2}$$

$$\therefore \quad S = \frac{1}{2}$$

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

The values are $S = \frac{1}{2}$, $J = \frac{3}{2}$ and $L = 1$

(ii) ${}^{3}S_{1}$.

Solution : J = 1.

The spin multiplicity (2S + 1) = 3.

$$\therefore \quad 2S + 1 = 3$$

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

$$\therefore \quad S = 1$$

$$J = L + S \quad \therefore\ L = J - S = 1 - 1 = 0$$

∴ The values are S = 1, L = 0 and J = 1.

Homework

Dr. S. G. Pawar, Department of Physics

Multiple Choice Questions:

1. The magnitude of spin quantum number is always ……
   a) 1/ 2
   b) 1
   c) − 1 /2
   d) −1
2. Elements with configuration ns^1 for last orbit are called ……
   a) alkali metals
   b) alkaline earth metals
   c) halogen
   d) inert gases
3. The nP → 2S transitions for $n \geq 2$ correspond to …… series of Li.
   a) diffuse
   b) fundamental
   c) sharp
   d) principal
4. The ground state of single electron system always give rise to ……
   a) Singlet
   b) Doublet
   c) triplet
   d) quartet

5. The orbital quantum number l=2 corresponds to the ………… Orbital.
   a) s
   b) p
   c) d
   d) f
6. Following is the electronic configuration of ……… alkali metal.
   $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^1$
   a) Li
   b) K
   c) K
   d) Rb
7. Due to spin orbit interaction …………… Shows doublet levels.
   a) s
   b) s,p
   c) s, p, d
   d) p, d, f
8. In the spectra of Na, the ………… and ………… Series have same convergence.
   a) sharp, diffuse
   b) fundamental, sharp
   c) principal, sharp
   d) principal, diffuse

Dr. S. G. Pawar, Department of Physics

9. Determine the values of L, S and J for term symbol $^2P_{3/2}$.
   a) S = ½, J = 3/2, L=1
   b) S = ½, J = 3/2, L=2
   c) S = 1, J = 3/2, L=0
   d) S = ½, J = 3/2, L=0
10. What is the term symbol for S = ½ and L = 3.
   a) $^2F_{7/2}$
   b) $^2P_{3/2}$
   c) $^2D_{5/2}$
   d) $^4P_{5/2}$

Dr. S. G. Pawar, Department of Physics

Answer Key			
1. a	**2.** a	**3.** d	**4.** a
5. c	**6.** d	**7.** d	**8.** a
9. a	**10.** a		

References and Know More

1. Atomic Spectra – H.E. White
2. Atomic and Molecular Spectra – Rajkumar

Ctrl + Click Following links to Know More

https://www.youtube.com/watch?v=eKRYsvYLcxQ

Dr. S. G. Pawar, Department of Physics

Feedback

1) How was the learning experience?

Outstanding/ Excellent / Nice /Good/Fair

2) Which aspect do you like most?

Introduction/Concept/Diagrams/Exercise

3) Anything else to be added?

Applications/Problems/Illustrations/Notes/Videos

4) Which point was not up to the mark and need revision?

Introduction/Concept/Diagrams/Exercise

5) Suggestions if any:

……………………………………………………………………………

Name of the student and class: ……………………………………

……………………………………………………………………………..

Dr. S. G. Pawar. Department of Physics