Atomic and Molecular Physics (AMP)

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Syllabus of Atomic and Molecular Physics

Unit I: The Atom Model for Two Valence Electrons (15)

l-l coupling, s-s coupling, LS or Russell - Saunder's coupling; the Pauli exclusion principle, Coupling schemes for two electrons, G-factors for LS coupling, Lande interval rule, jjcoupling, branching rules, selection rules, Intensity relations.

Unit II: Zeeman Effect, Paschen-Back Effect and Stark Effect (15)

The magnetic moment of the atom, Zeeman effect for two-electrons, Intensity rules for Zeeman effect, Paschen-Back effect for two electrons, Stark effect of hydrogen, weak field Stark effect in hydrogen, strong field Stark effect in hydrogen, origin of hyperfine structure. Principles of resonance Spectroscopy (ESR and NMR)

Unit III: Microwave Spectroscopy (15)

Classification of molecules: linear, symmetric tops, spherical tops, asymmetric tops; rotational spectra: the rigid diatomic molecule, the non-rigid rotator, spectrum of a non-rigid rotator, techniques and instrumentation of microwave spectroscopy, chemical analysis by microwave spectroscopy.

Unit IV: Infra-Red Spectroscopy (15)

The vibrating diatomic molecule: the energy of a diatomic molecule, the simple harmonic oscillator, the anharmonic oscillator, the diatomic vibrating-rotator, techniques and instrumentation of infra-red spectroscopy, chemical analysis by infra-red spectroscopy.

Text books
1) Introduction to Atomic Spectra – H.E. White, Mac-Graw Hill (1934).
2) Fundamentals of Molecular Spectroscopy, 4th Edition. – C.N. Banwell, Tata MacGraw Hill (2008).

Reference books
1) Molecular Structure and Spectroscopy, G. Aruldhas, PHI Learning Pvt. Ltd. Spectra of Diatomic Molecules, Vol. I – G. Herzberg, N.J.D. van Nostrand (1950).
2) Spectroscopy, Vol. I, II and III – B.P. Straughan and S. Walker, Chapman and Hall (1976).
3) Introduction to Molecular Spectroscopy – G.M. Barrow, MacGraw Hill (1962).
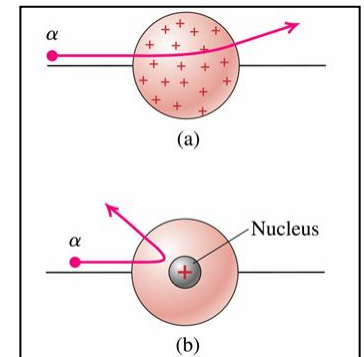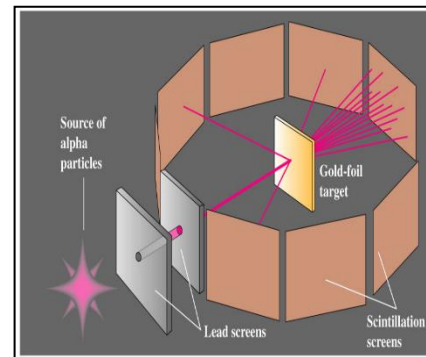4) Molecular Spectroscopy – J.M. Brown, Oxford University Press (1998).

Atomic Models

Various atomic models proposed by scientists over the last few decades are:

➢ Thomson's Plum Pudding Model
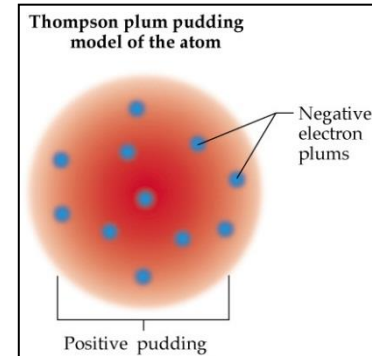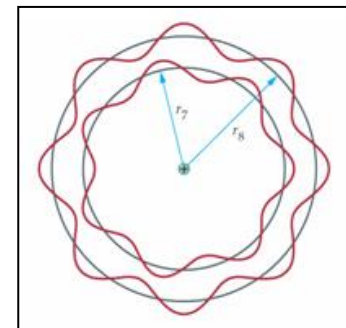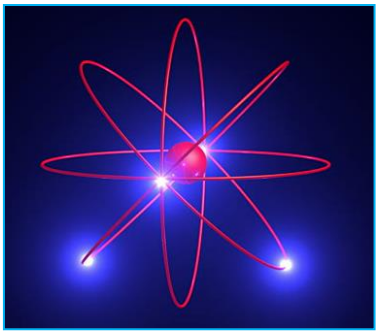
➢ Rutherford's Nuclear Model

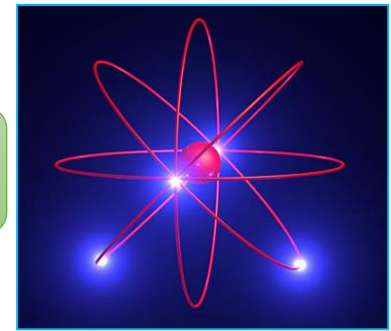➢ Bohr's Model

➢ Sommerfeld's Relativistic Model

➢ Vector Atom Model and

➢ Wave-Mechanical Model

Basic Properties of Atoms

➢ Atoms are of microscopic size, ~ 10^{-10} m.

➢ Visible light is not enough to resolve the detail structure of an atom as its size is only of the order of 100 nm.

➢ Atoms are stable

➢ Atoms contain negatively charges, electrons, but are electrically neutral. An atom with Z electrons must also contain a net positive charge of $+Ze$.

➢ Atoms emit and absorb EM radiation (in other words, atoms interact with light quite readily)

➢ Because atoms interacts with EM radiation quite strongly, it is usually used to probe the structure of an atom.

Atomic Spectra

Emission Spectral Lines
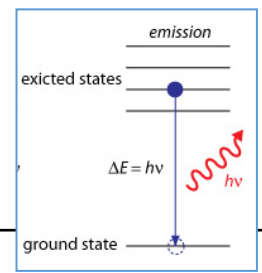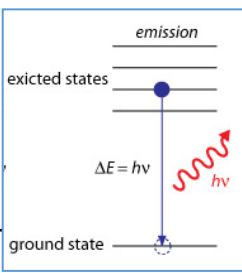
➤ Experimental fact: A single atom or molecule in a very diluted sample of gas emits radiation characteristic of the particular atom/molecule species.

➤ The emission is due to the de-excitation of the atoms from their excited states. For e.g. if heating or passing electric current through the gas sample, the atoms get excited into higher energy states.

➤ When a excited electron in the atom falls back to the lower energy states (de-excites), EM wave is emitted.

➤ The spectral lines are analysed with *spectrometer*, which give important physical information of the atom/molecules by analysing the wavelengths composition and pattern of these lines.
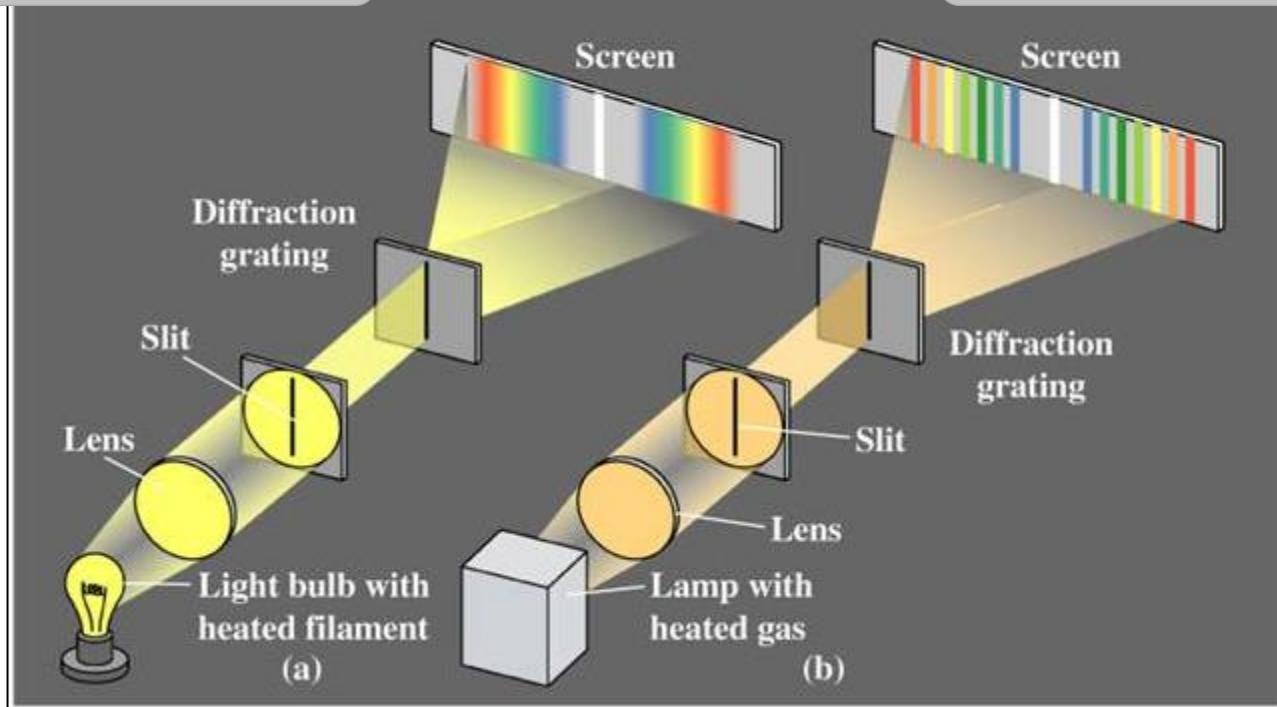
Line spectrum of an atom

The light given off by individual atoms, as in a low-pressure gas, consist of a series of discrete wavelengths corresponding to different colour.
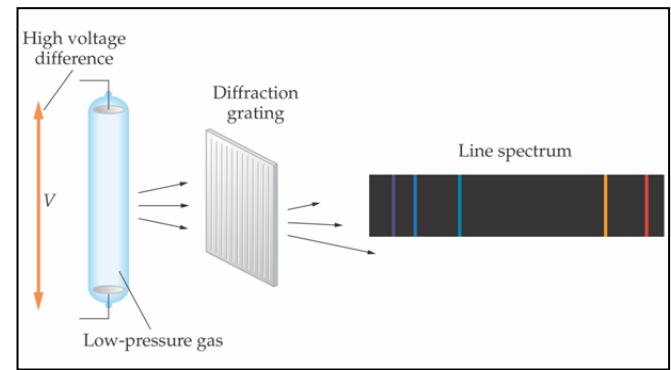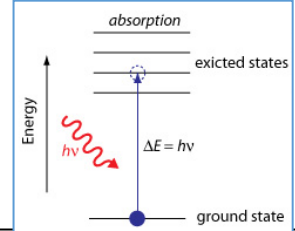

Comparing Continuous and Line Spectrum

(a) Continuous spectrum produced by a glowing light-bulb

(b) Emission line spectrum by lamp containing heated gas

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Absorption line spectrum
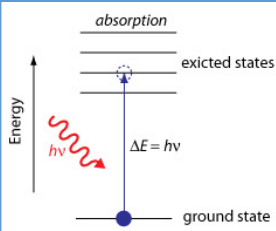
➢ We also have absorption spectral line, in which white light is passed through a gas.

➢ The absorption line spectrum consists of a bright background crossed by dark lines that correspond to the absorbed wavelengths by the gas atom/molecules.

Experimental arrangement for the observation of the absorptions lines of a sodium vapour

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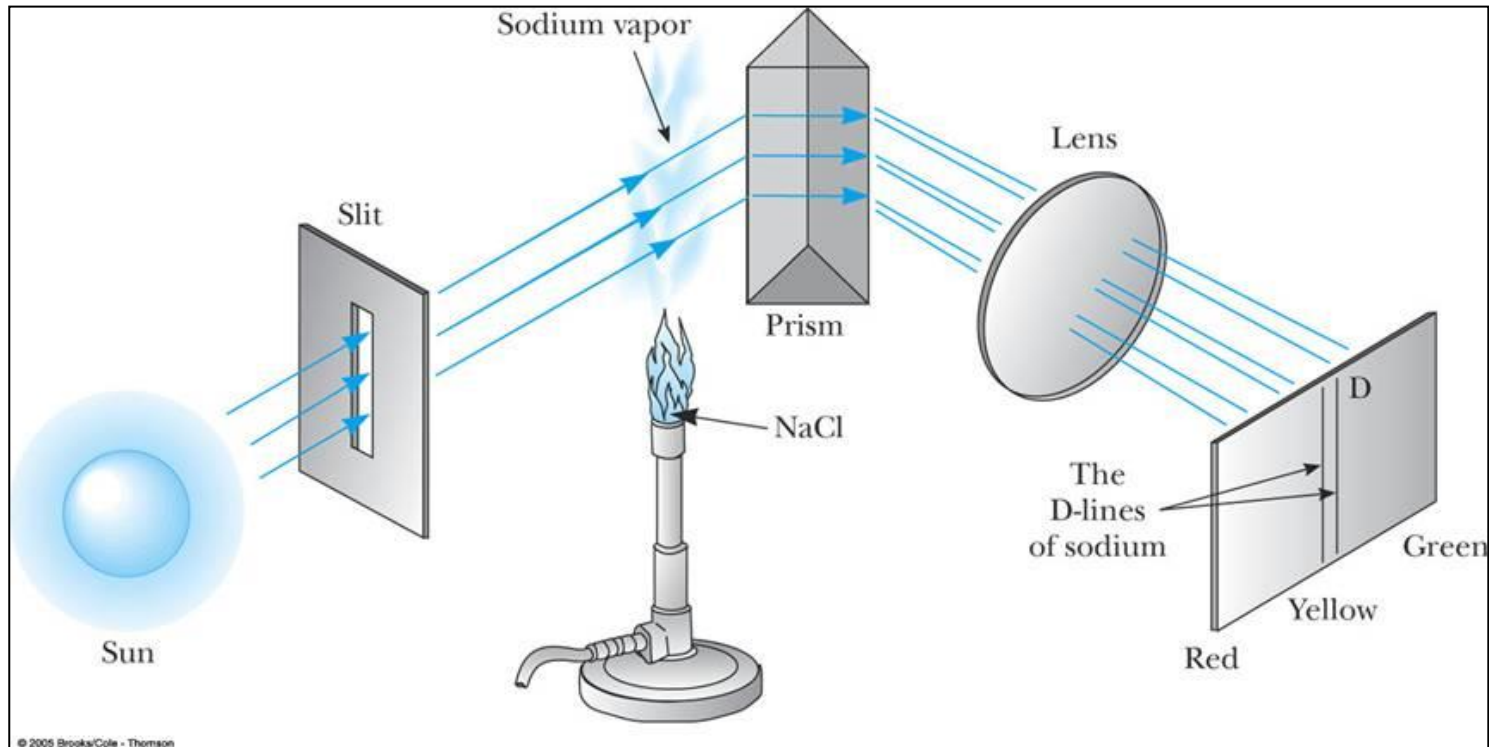
Comparing Emission and Absorption Spectrum

The emitted and absorption radiation displays characteristic discrete sets of spectrum which contains certain discrete wavelengths only

(a) shows 'finger print' emission spectral lines of H, Hg and Ne.

(b) shows absorption lines for H

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Vector Atom Model
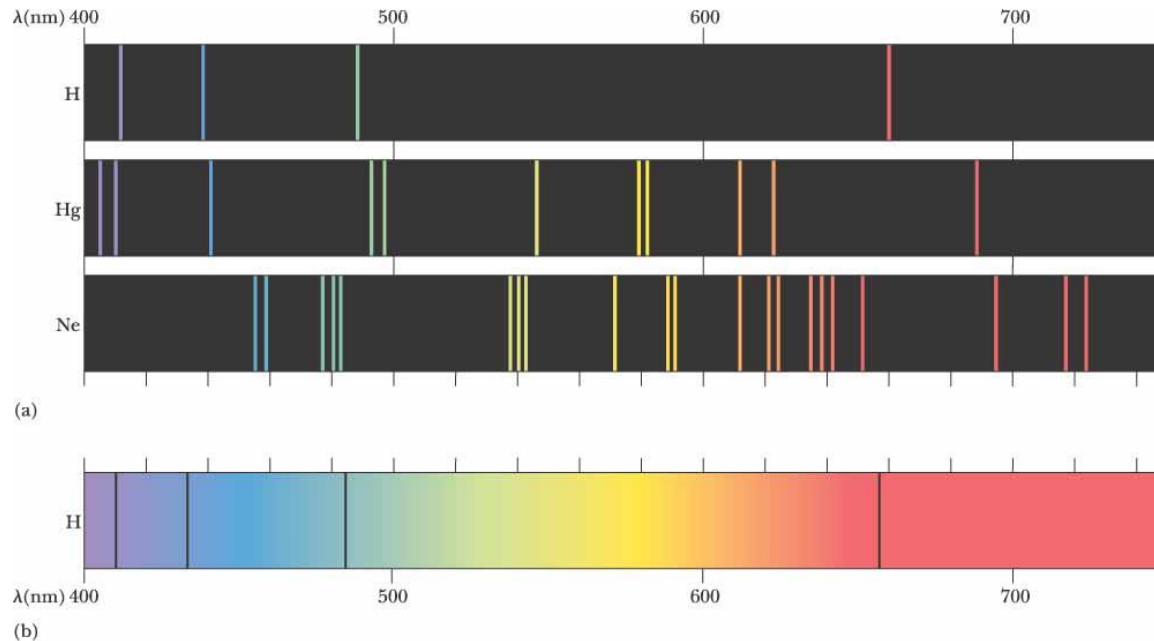
The vector atom model basically deals with the total angular momentum of an atom, which is results of the combination of orbital and spin angular momenta.
The two fundamental features of the vector atom model are
(i) Space quantization of orbits and (ii) Spinning electron hypothesis.

Space Quantization

➤ The angular momentum is a vector quantity, hence its direction must be specified to describe it completely.
➤ To specify the orientation or direction of an orbit, a reference is required.
➤ The direction of the magnetic field applied to the atom is chosen as the reference line.
➤ The phenomenon of quantization of angular momentum of electron in the direction of magnetic field B is commonly known as space quantization.

$$|L| = \sqrt{l(l+1)}\, \hbar$$

l = orbital angular momentum
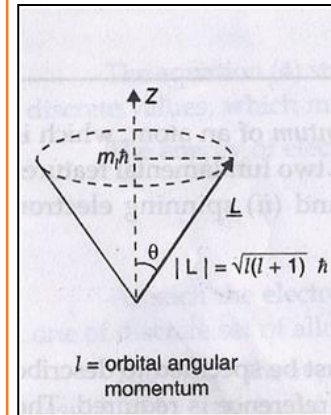
Spin Quantization

➤ Goudsmit and Uhlenbeck in 1925 proposed that electron 'spins' about an axis through its centre of mass and further it has both angular momentum and a magnetic moment.
➤ The spin of electron is analogous to the planetary motion about the Sun in our solar system.
➤ Quantum mechanical treatment has demonstrated that the spin of electron should be quantized.

The orbital and spin motions of an electron are quantized in magnitude as well as in direction. These motions are represented by quantized vectors, as such the atomic model is termed as *Vector Atom Model*

Quantum Numbers

The Bohr-Sommerfeld atomic theory uses four quantum numbers which are known as mechanical quantum numbers:

(i) Principal quantum number *(n)*

(ii) Orbital quantum number *(l)*

(iii) Spin quantum number *(s)* and

(iv) Total angular momentum quantum number *(j)*.

In addition to these, three other quantum numbers have been introduced in vector atom model which are magnetic quantum numbers:

(i) Magnetic orbital quantum number *(m_l)*

(ii) Magnetic spin quantum number *(m_s)* and

(iii) Magnetic total angular momentum quantum number *(m_j)*.

Quantum Numbers

(1) Principal Quantum Number (n):

This quantum number represents the serial number of the atomic shells starting from the innermost. The 'n' can have only positive integral values excluding zero.

$$n = 1,2,3,4, \ldots\ldots\ldots$$

Principal quantum Number :   1   2   3   4   5   6   7

Atomic Shell   :   K   L   M   N   O   P   Q

(2) Orbital Quantum Number (l):

The Orbital quantum number 'l' can have the values from *0 to (n - 1)*, where 'n' is the principal quantum number.

For example, if $n = 3$, then $l = 0, 1, 2, 3, \ldots\ldots\ldots$

Conventionally we call

$l = 0$ s electron

$l = 1$ p electron

$l = 2$ d electron

$l = 3$ f electron

(3) Spin Quantum Number (s) :

Spin quantum number 's' has only one value

i.e. $\quad s = \frac{1}{2}$

(4) Total Angular Momentum Quantum Number (j) :

The total angular momentum quantum number ' j ' is the sum of orbital angular momentum 'l' and spin quantum number 's'.

As such j can have $l \pm s$ $\quad$ or

$l \pm \frac{1}{2}$ values.

(5) Magnetic Orbital Quantum Number (m_l):

The magnetic orbital quantum number m_l can have $(2l + 1)$ values.

$$m_l = +l, (l - 1), (l - 2) \ldots\ldots 1, 0, -1, \ldots\ldots -(l-2), -(l-1), -l$$

For example, $l = 2$, m_l can have $-2, -1, 0, 1, 2$ *i.e.,* total 5 values.

(6) Magnetic Spin Quantum Number (m_s):

The magnetic spin quantum number take $(2s + 1)$ values.

We know that s = ½ and hence m_s, can take $(2 \times ½ + 1) = 2$ in total.

The values of m_s therefore are $- s$ and $+ s$ or $- ½$ and $+ ½$.

(7) Magnetic Total Angular Momentum Quantum Number (m_j)

The total momentum J of an atom is a vector quantity and is the vector sum of orbital momentum L and spin angular momentum S *i.e.,* J = L + S.

The magnetic total angular momentum quantum number take $(2j + 1)$ values.

We define quantum number m_j which is known as the magnetic total angular momentum quantum number and specify the orientation of J in space with respect to Z-axis.

$$m_j = m_l + m_s$$
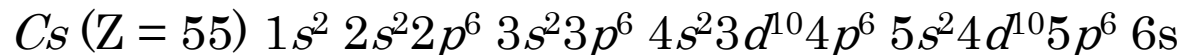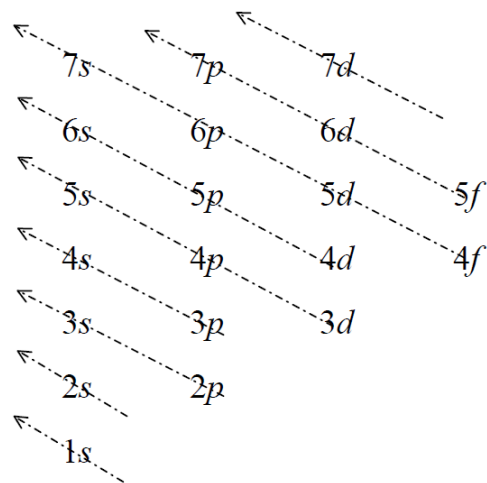
The values of m_j therefore are $- j$ and $+ j$

Maximum number of electrons in each sub-shell = $2(2l+1)$

l :	0	1	2	3
Sub-shell :	s	p	d	f
Number of electrons :	2	6	10	14

Maximum number of electrons in each shell = $2n^2$

n :	1	2	3	4
Number of electrons :	2	8	18	32

Shortcut to Write an Electronic Configuration

7s   7p   7d

6s   6p   6d

5s   5p   5d   5f

4s   4p   4d   4f

3s   3p   3d

2s   2p

1s

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

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Widely accepted scheme

Bohr	Stoner	n	L		
No. of e⁻	No. of e⁻				
8	14	4	3	———————— 4f	⎤
8	10	4	2	———————— 4d	N
8	6	4	1	———————— 4p	
8	2	4	0	———————— 4s	⎦
6	10	3	2	———————— 3d	⎤
6	6	3	1	———————— 3p	M
6	2	3	0	———————— 3s	⎦
4	6	2	1	———————— 2p	⎤ L
4	2	2	0	———————— 2s	⎦
2	2	1	0	———————— 1s	⎤ K

No. of e⁻ | No. of e⁻ | n | L

Bohr   **Stoner**

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Notations

l^*	Orbital quantum number	$\Big\}$ *One electron atom*
s^*	Spin quantum number	
L^*	$\sum l_i^*$ - many electron atom	
S^*	$\sum s_i^*$ - many electron atom	
j^*	Total angular quantum number – one electron atom	
J^*	$\sum j_i^*$ - many electron atom	

❖ Single electron states ❖ Many electron states

$s, p, d, f, ...$ for $l = 0, 1, 2, 3...$ $S, P, D, F, ...$ for $L = 0, 1, 2, 3...$

Term Value Or Term Symbols

❖ Multiciplicity of energy level $= 2S + 1$; indicated as left superscript.

e.g.

Multiplicity ($= 2S + 1$)

$$3\ ^2S_{1/2}$$

n value L value j value
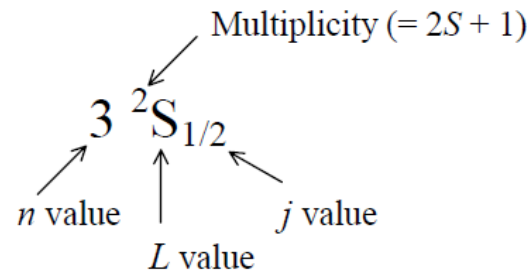
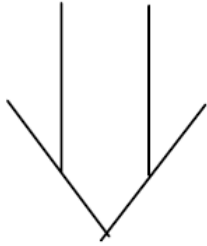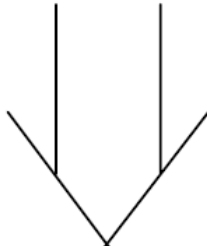|		n	L	J	S
1.	$3\ ^2S_{1/2}$	3	0	½	½
2.	$3\ ^2P_{1/2}$	3	1	½	½
3.	$4\ ^3P_0$	4	1	0	1
4.	$4\ ^1D_2$	4	2	2	0
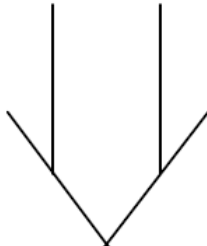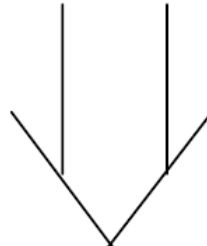
Single Valence Electron Spectra
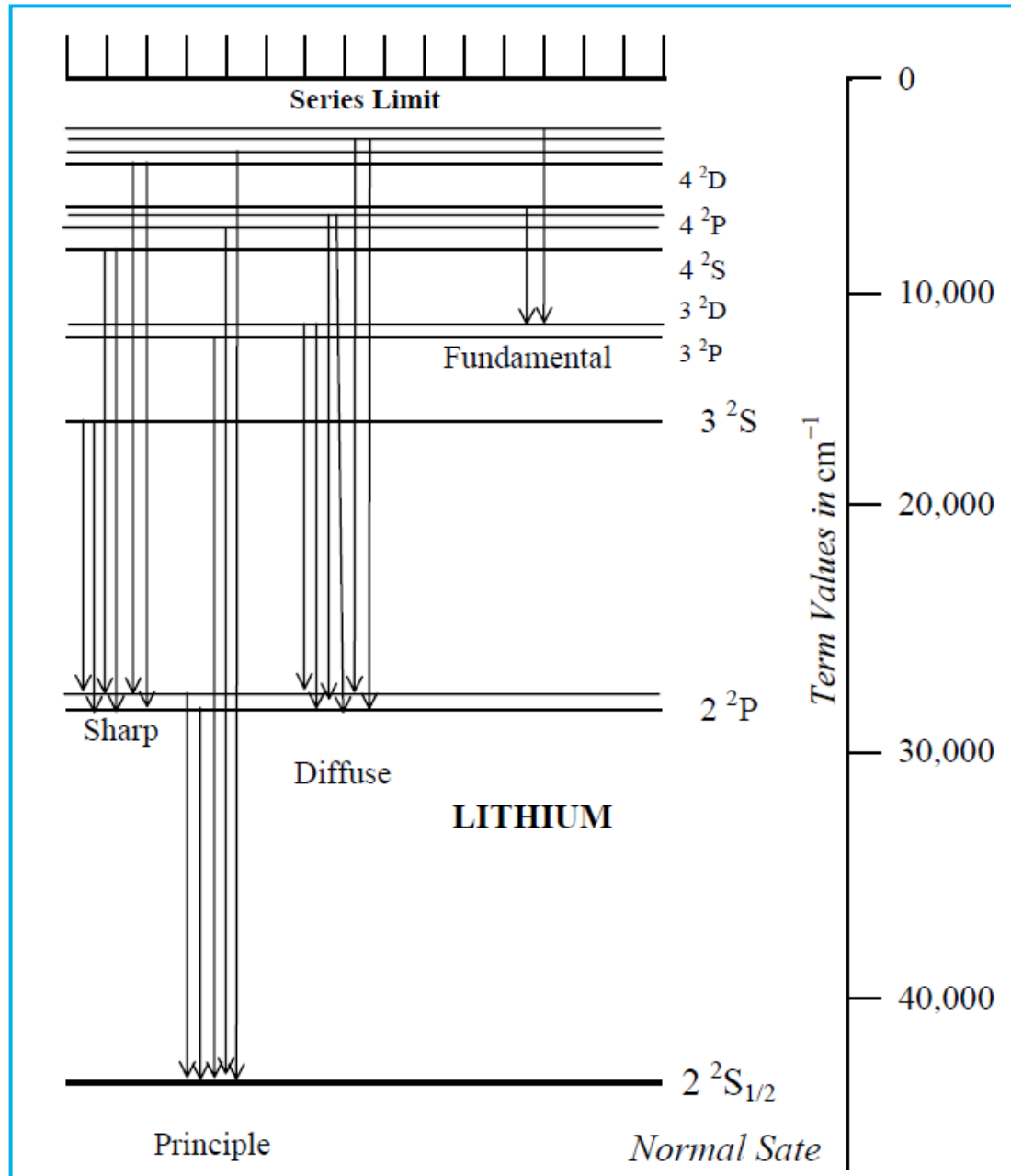### (Energy level diagrams of alkali metals)

Shell	K	L	M	N	O	P
Li $(Z=3)$	$1s^2$	$2s$				
Na $(Z=11)$	$1s^2$	$2s^2 2p^6$	$3s$			
K $(Z=19)$	$1s^2$	$2s^2 2p^6$	$3s^2 3p^6 3d^{10}$	$4s$		
Rb $(Z=37)$	$1s^2$	$2s^2 2p^6$	$3s^2 3p^6 3d^{10}$	$4s^2 4p^6 4d^{10}$	$5s$	
Cs $(Z=55)$	$1s^2$	$2s^2 2p^6$	$3s^2 3p^6 3d^{10}$	$4s^2 4p^6 4d^{10}$	$5s^2 5p^6$	$6s$

➢ Each alkali atom contains, in addition to completed subshells of electrons, one single electron in an outer shell.

➢ There is a single unbalanced electron, which is responsible for the +1 valency of the alkali metals and for the spectra.

Four chief series of spectral lines

Sharp (S)	Principle (P)	Diffuse (D)	Fundamental (F)
Various s levels	Various p levels	Various d levels	Various f levels
Lowest p level	Lowest s level	Lowest p level	Lowest d level

The energy level diagram of neutral Li

Two Valence Electron Spectra
(Energy level diagrams of IIA and IIB atoms)

4	**Be**	$1s^2\, 2s^2$
12	*Mg*	$2p^6\, 3s^2$
20	*Ca*	$3p^6\, 4s^2$
30	*Zn*	$3d^{10}\, 4s^2$
38	*Sr*	$4p^6\, 5s^2$
48	*Cd*	$4d^{10}\, 5s^2$
56	*Ba*	$5p^6\, 6s^2$
80	*Hg*	$5d^{10}\, 6s^2$

➢ It is well known that atoms like *Be*, *Mg*, *Zn*, *Cd*, *Hg*, *Ca*, *Sr*, and *Ba* (*in group IIA and IIB of periodic table*), contain two valence electrons and give rise to singlet and triplet spectra.

➢ In each type, four chief series (viz. Sharp, Principle Diffuse and Fundamental) of spectrum lines are observed.

➢ The last two "equivalent" electrons are responsible for the chemical valence of two and are responsible for the general characteristics of their optical spectra.

Observed Fine Structure:
In general, the fine structure of triplets shows the following features.
1. All members of sharp series are composed of three lines, which are equally spaced.
2. All members of principle series consist of three lines, with decreasing separations.
3. All members of diffuse and fundamental series contain six lines; three strong and three faint (satellites) lines.
The fine structure is due to the fine structure of energy levels or terms. The following notations have been adopted for the term series:

$$\text{Singlets}: \quad ^1S, \, ^1P, \, ^1D, \, ^1F$$
$$\text{Triplets}: \quad ^3S, \, ^3P, \, ^3D, \, ^3F.$$

Transitions between ^3P and ^3D term series
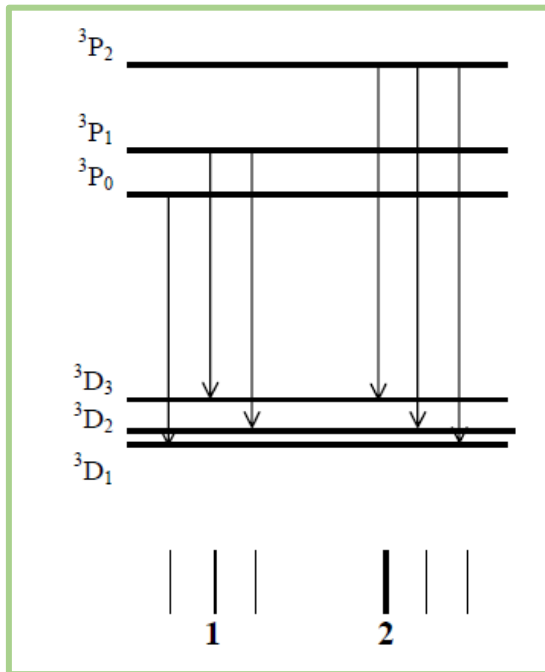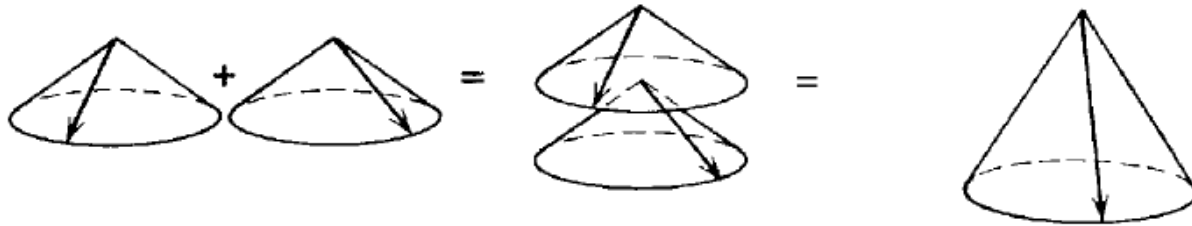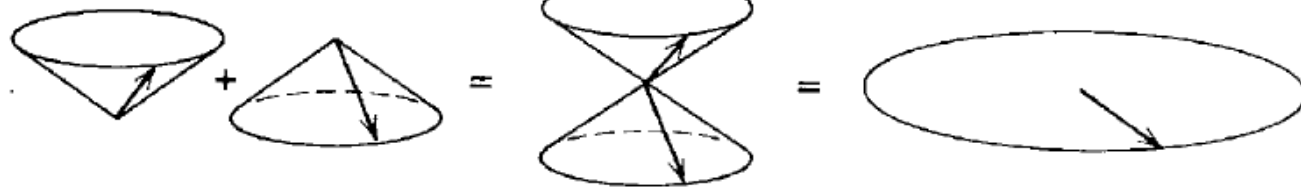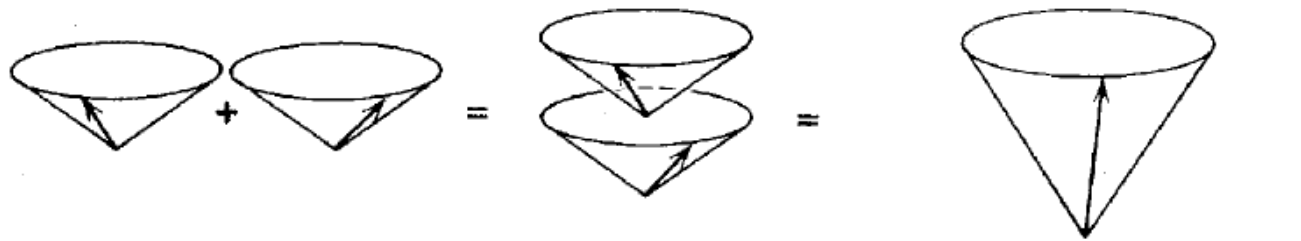

Triplet Spectral Lines

^3P intervals are wider than the corresponding ^3D intervals, which are wider than the corresponding ^3F intervals.
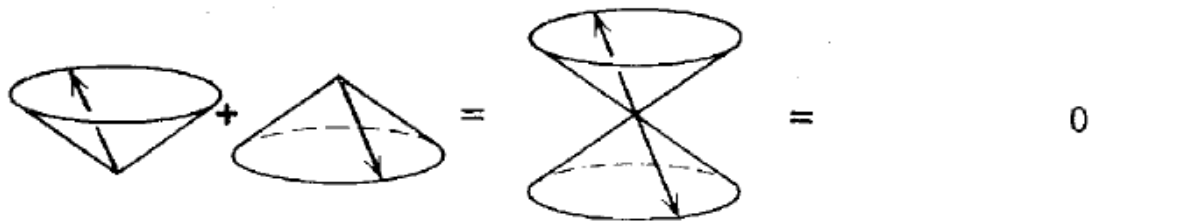
In the observed spectrum lines

1. The stronger (*in intensities*) ones arise when ΔL changes in the same direction as ΔJ.

2. The strongest line arises from the transition involving the largest L and J values.

Accordingly spectrum line **2** is the strongest and line **1** is the next stronger in intensity.

Triplet State

Singlet State