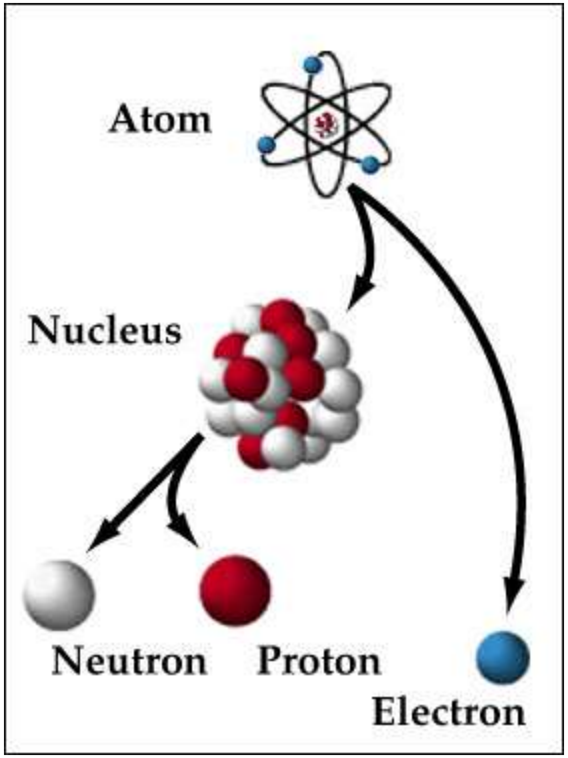
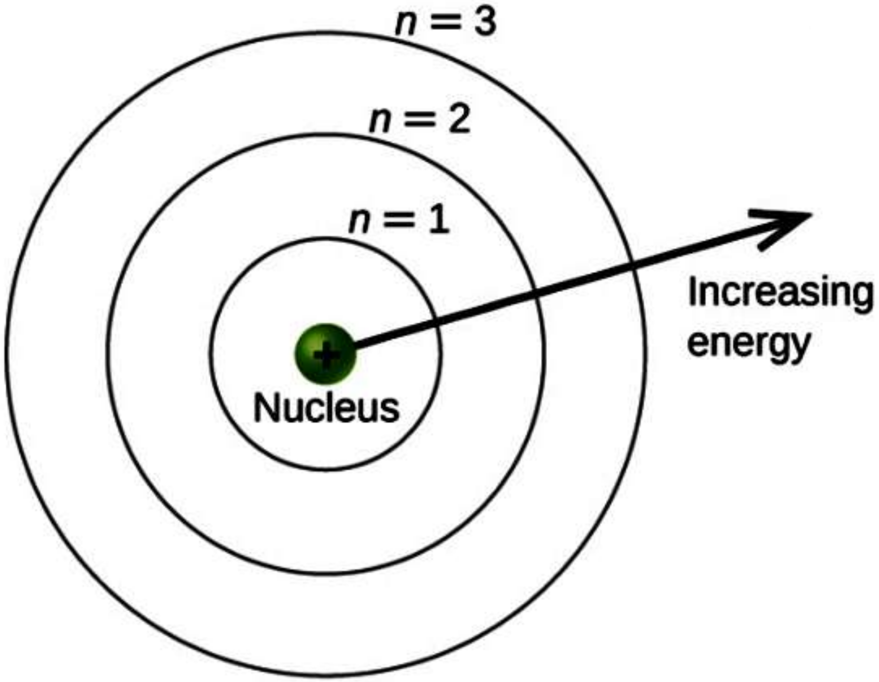
QUANTUM SPECTRA OF ELECTRON IN ATOMS

$$\Delta x \,.\, \Delta px \geq h/2\pi$$

1. **Principle of quantum number (n)**
2. **Orbital quantum number (l)**
3. **Magnetic orbital quantum number (m_l)**
4. **Magnetic spin quantum number (m_s)**

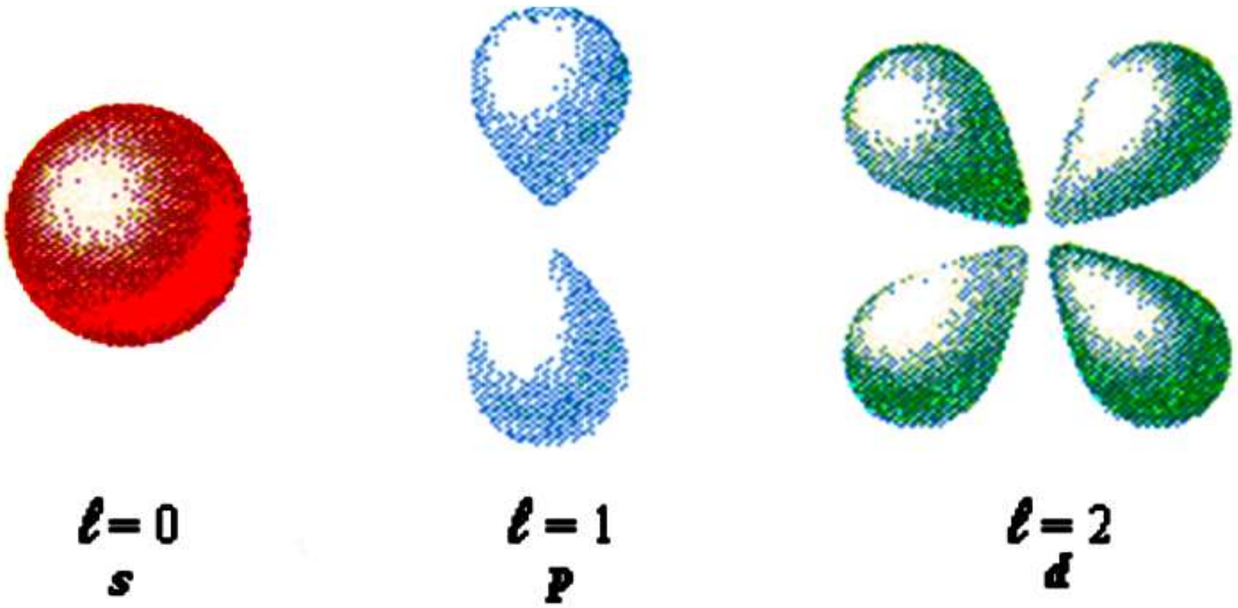


1. Principle of quantum number (n)



n =1, 2, 3,4, … etc.,

2. Orbital quantum number (l)



If n =1; l=0

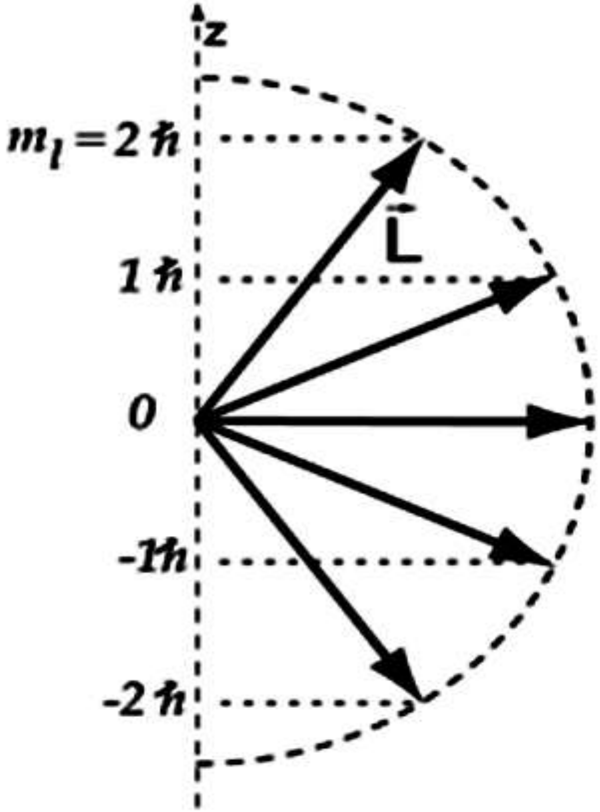
n =2; l=0, 1

n =3; l=0, 1, 2

l = 0 1 2 3 4

Notations = s p d f g

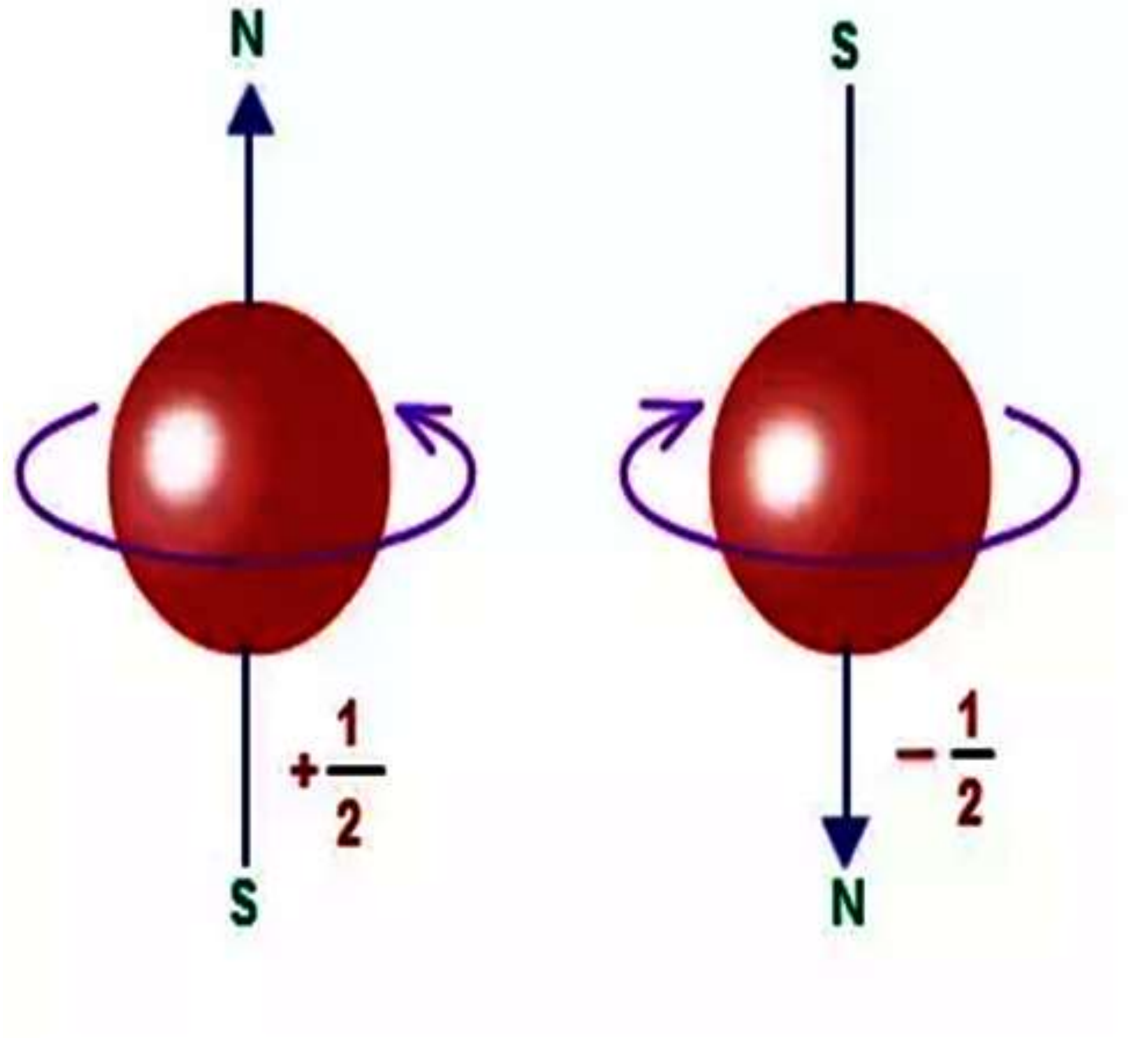
3. Magnetic orbital quantum number (m_l)



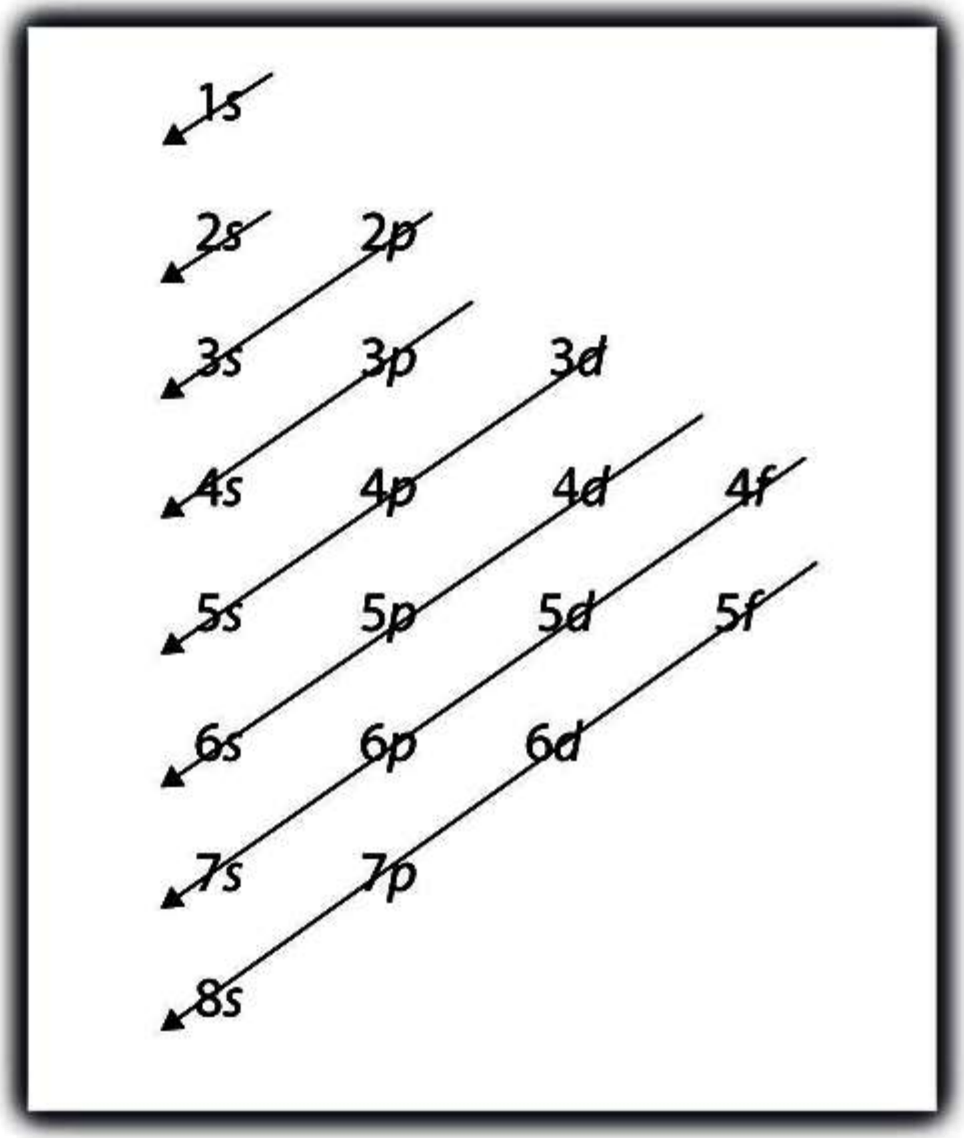
m_l can take the values

$-l, -l+1, -l+2, \ldots\ldots.-1,0,1,\ldots\ldots..l-2, l-1, l$

4. Magnetic spin quantum number (m_s)

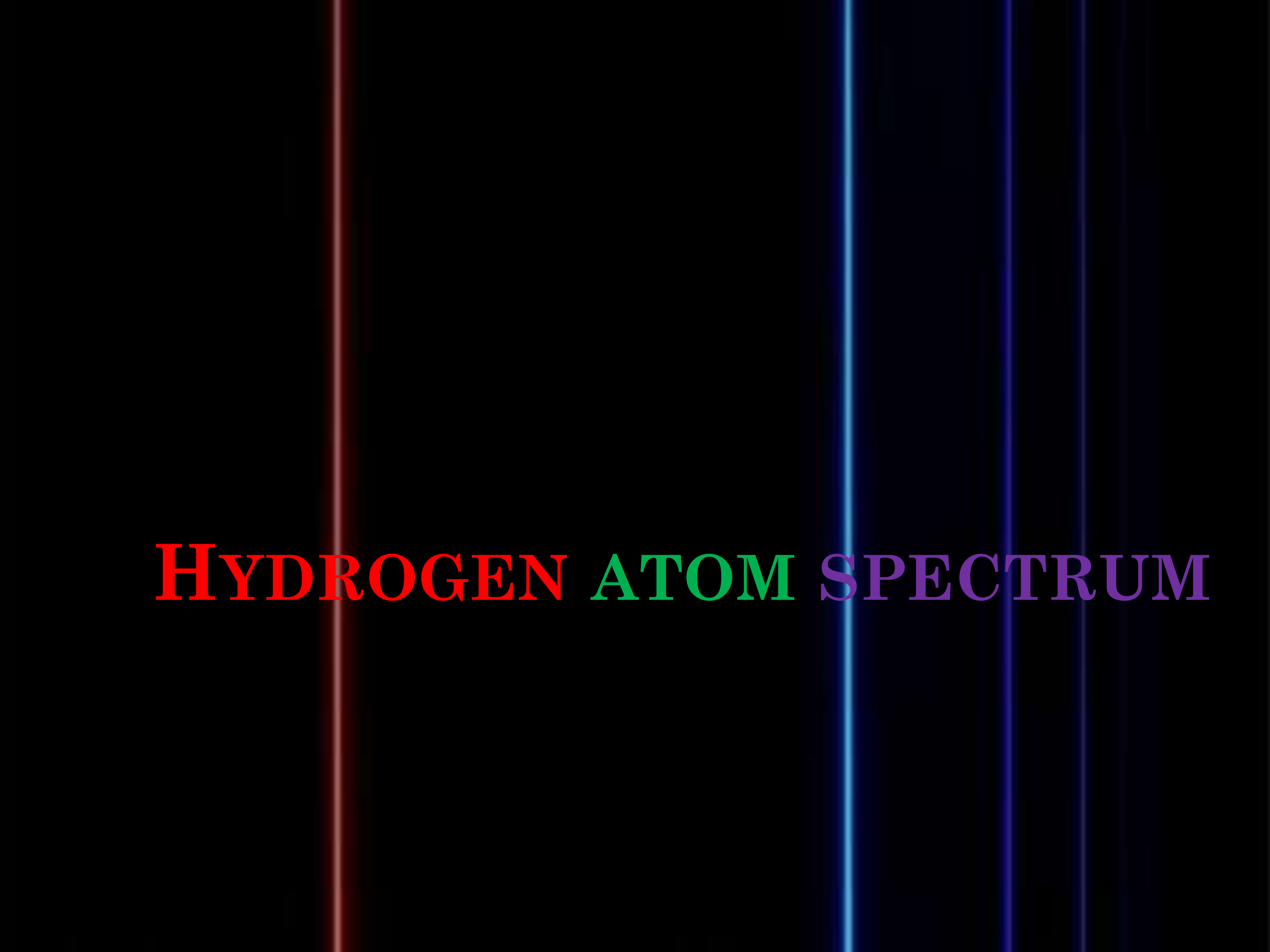


Pauli's exclusion Principle



$$\Delta E = h\nu$$

$$C = \nu\lambda$$

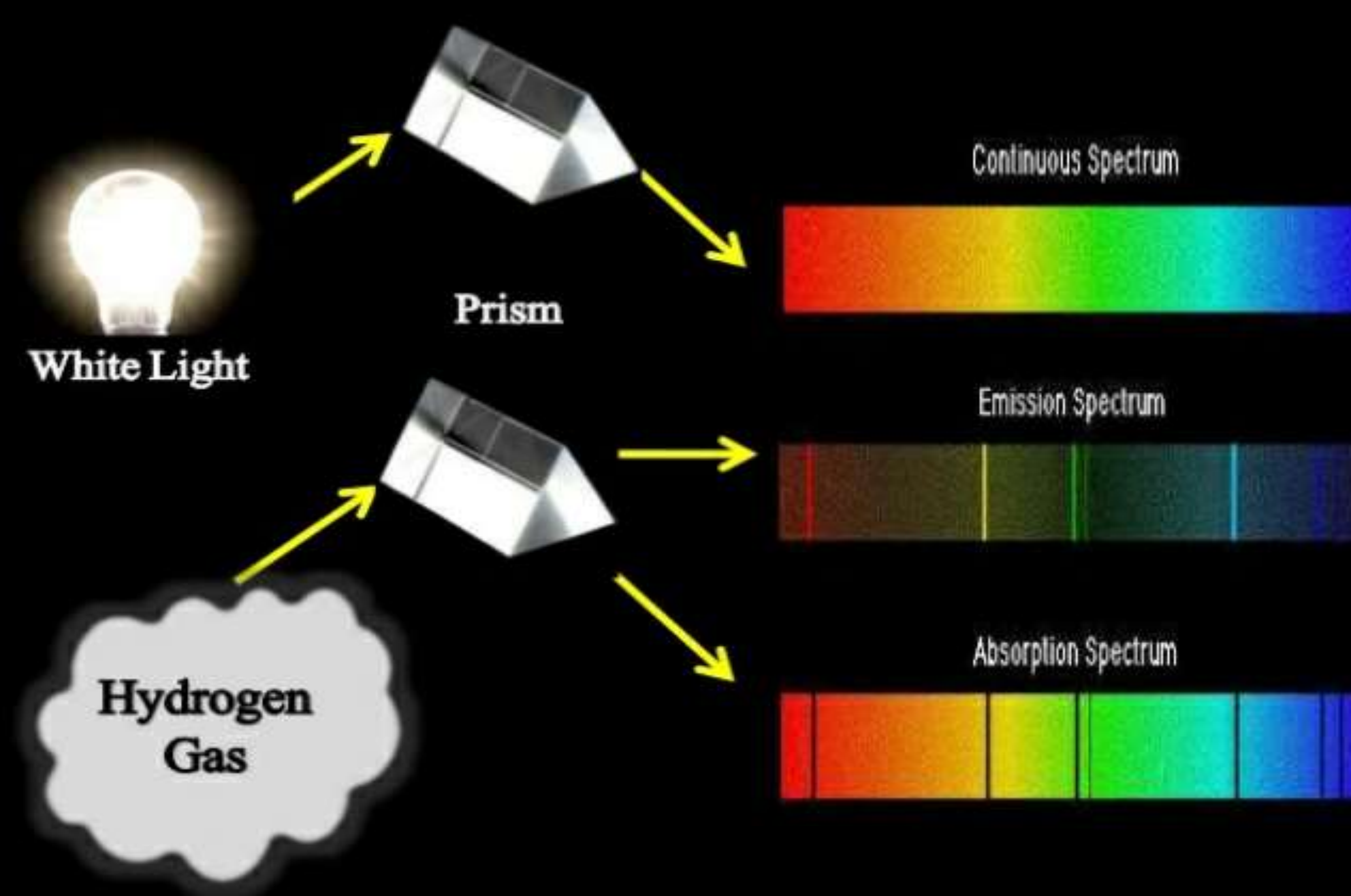


Hydrogen atom spectrum

INTRODUCTION

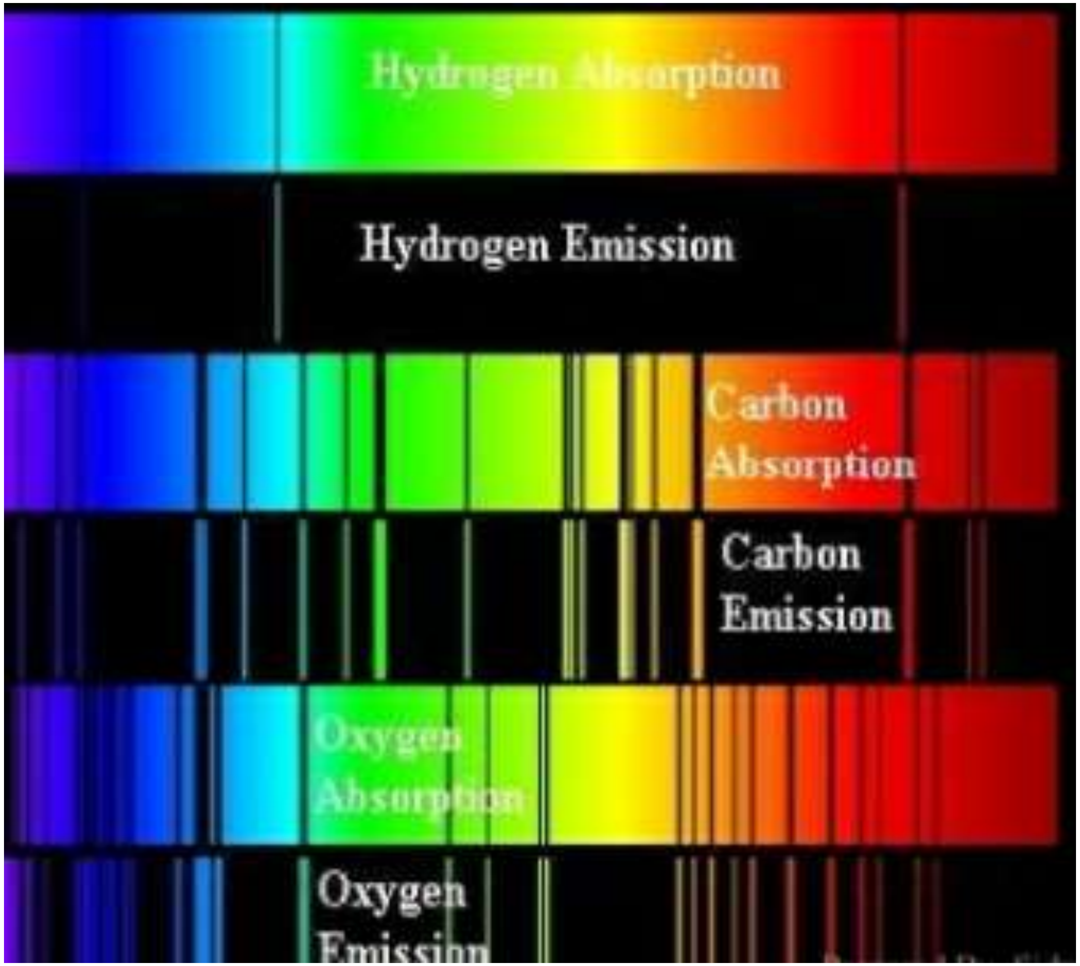
- The emission spectrum of atomic hydrogen has been divided into a number of spectral series, with wavelengths given by the Rydberg formula.
- These observed spectral lines are due to the electron making transitions between two energy levels in an atom.
- The classification of the series by the Rydberg formula was important in the development of quantum mechanics.
- The spectral series are important in astronomical spectroscopy for detecting the presence of hydrogen and calculating red shifts.

Cont…


White Light
Prism
Hydrogen Gas
Continuous Spectrum
Emission Spectrum
Absorption Spectrum

Cont…

- ✓ Atomic Spectrum – Finger Print of an Atom

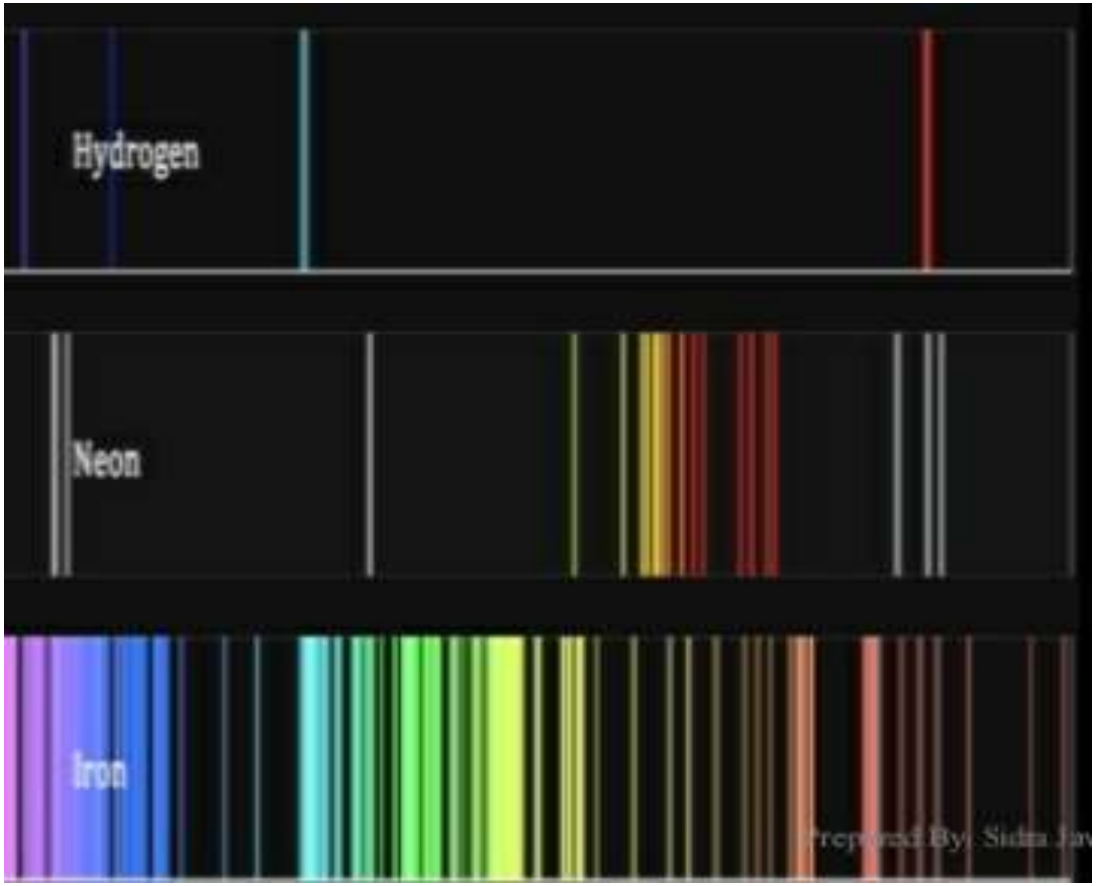


- ✓ Each element gives off its own characteristic colours

- ✓ Can be used to identify the atom

Cont…

- ❖ **Atomic Spectrum- Finger Prints of an Atom**



- ❖ **These are called line emission spectra**

DESCRIPTIONS

- The frequency of the emitted radiations can be found from the following relation

$$hf = E_{n2} - E_{n1}$$

Now,

$$E_{n2} = -\frac{mZ^2e^4}{8\varepsilon_o^2h^2}\frac{1}{n_2^2} = -\frac{me^4}{8\varepsilon_o^2h^2}\frac{1}{n_2^2}$$

Here Z=1

$$E_{n1} = -\frac{me^4}{8\varepsilon_o^2h^2}\frac{1}{n_1^2}$$

$$hf = -\left[\frac{me^4}{8\varepsilon_o^2h^2}\frac{1}{n_2^2}\right] - \left[-\left(\frac{me^4}{8\varepsilon_o^2h^2}\right) - \frac{1}{n_1^2}\right]$$

$$hf = \frac{me^4}{8\varepsilon_o^2h^2}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

Cont…

$$f = \frac{me^4}{8\varepsilon_o^2 h^3}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

Now c $= f\lambda,$

where c is the velocity of light

Hence $f = \frac{c}{\lambda}$

$$\frac{c}{\lambda} = \frac{me^4}{8\varepsilon_o^2 h^3}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

$$\frac{1}{\lambda} = \frac{me^4}{8\varepsilon_o^2 h^3 c}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

Let, $R = \frac{me^4}{8\varepsilon_o^2 h^3 c}$ **= 10.97 X 10^6 m^{-1}**

= Rydberg's constant

Cont…

$$\frac{1}{\lambda} = R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

$$\nu = R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

For Hydrogen Atom

- **The different series observed in hydrogen spectrum are as under.**
  - **1. Lyman Series**
  - **2. Balmer Series**
  - **3. Paschen Series**
  - **4. Backett Series**
  - **5. Pfund Series**

1. Lyman Series

Here $n_1 = 1$ and $n_2 = 2,3,4,5,\ldots\ldots$

$$\nu = R\left(\frac{1}{1^2} - \frac{1}{n_2^2}\right) \quad ; \qquad n = 2,3,4,5,\ldots$$

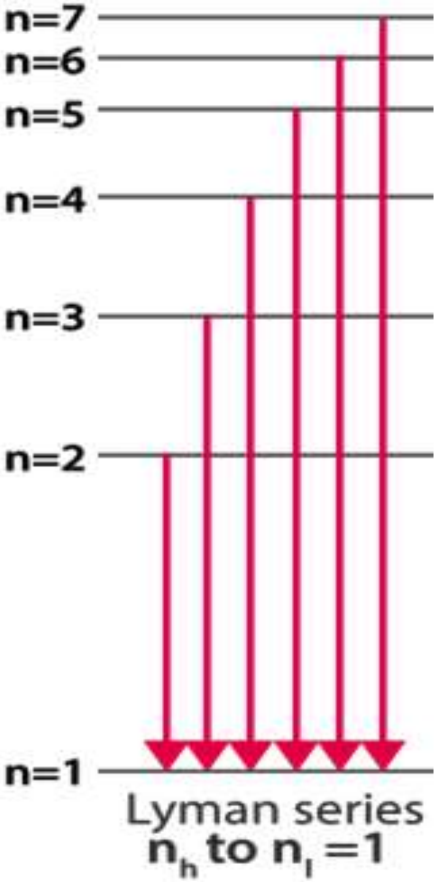


Fig. Energy level diagram Lyman Series

2. Balmer Series

Here $n_1 = 2$ and $n_2 = 3,4,5,6,\ldots\ldots$

$$\nu = R\left(\frac{1}{2^2} - \frac{1}{n_2^2}\right) \quad ; \qquad n = 3,4,5,6,\ldots$$

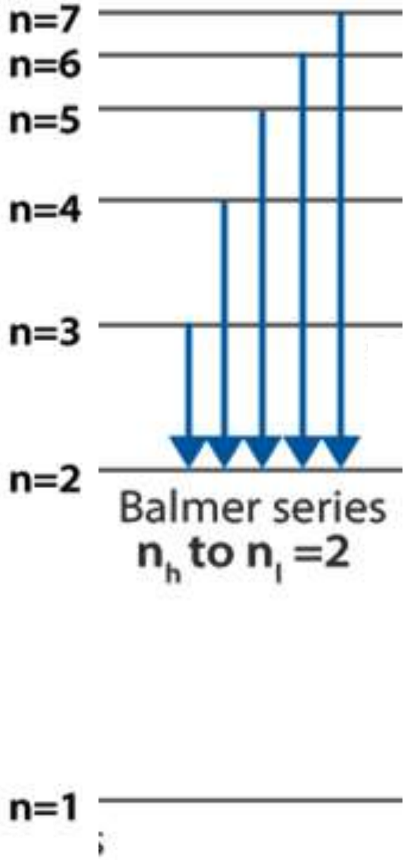
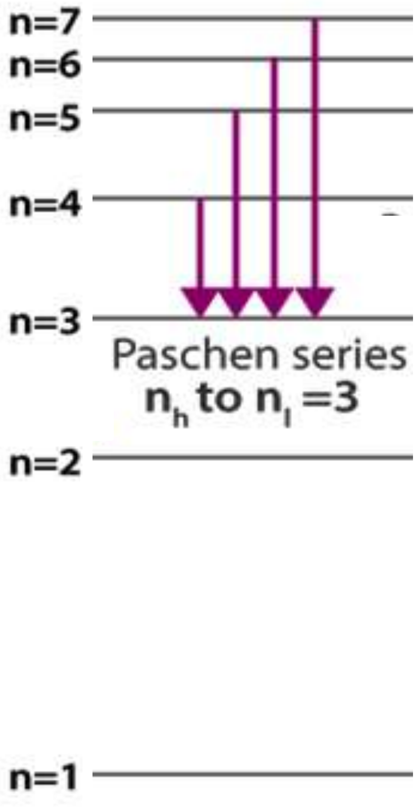


Fig. Energy level diagram for Balmer Series

3. Paschen series

Here $n_1 = 3$ and $n_2 = 4,5,6,7,\dots$



$$\nu = R\left(\frac{1}{3^2} - \frac{1}{n_2^2}\right) ; \quad n = 4,5,6,7,\dots$$

Fig. Energy level diagram for Paschen Series

4. Brackett Series

Here $n_1 = 4$ and $n_2 = 5,6,7,8,...$

$$\nu = R\left(\frac{1}{4^2} - \frac{1}{n_2^2}\right) \; ; \quad n = 5,6,7,8,...$$

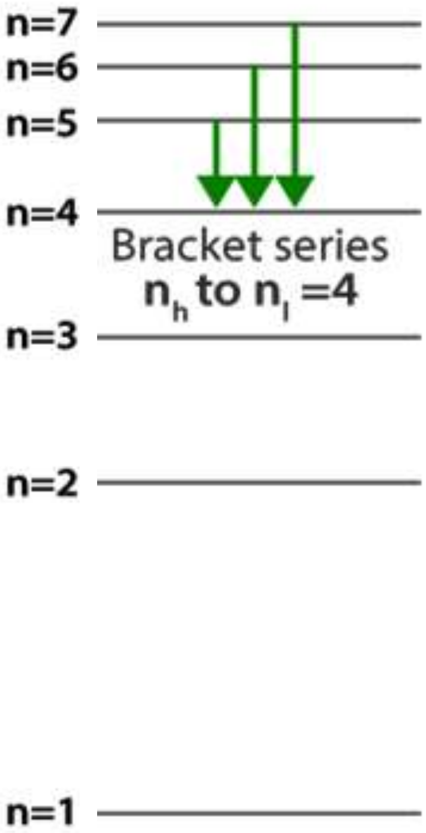
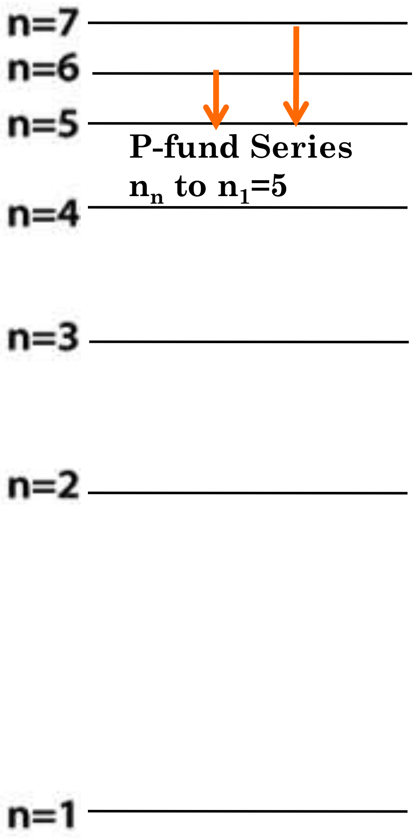


Fig. Energy level diagram for Brackett Series

5. Pfund Series

Here $n_1 = 5$ and $n_2 = 6,7,8,9,\ldots$



$$\nu = R\left(\frac{1}{5^2} - \frac{1}{n_2^2}\right) ; \quad n = 6,7,8,9,\ldots$$

Fig. Energy level diagram for P-fund Series

Different Series in H_2 atom

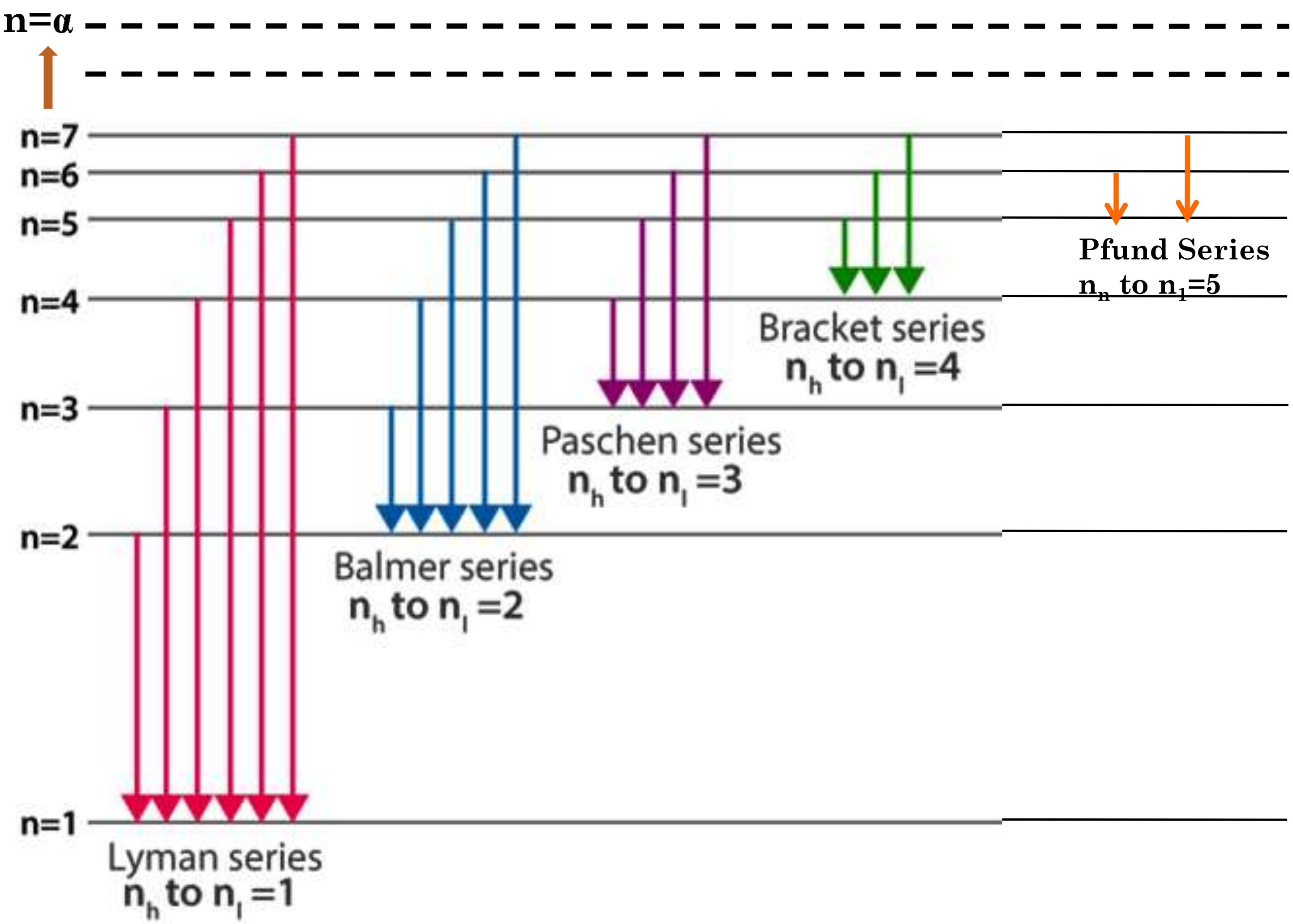


Fig. Energy level diagram for the H_2 atom

Cont…

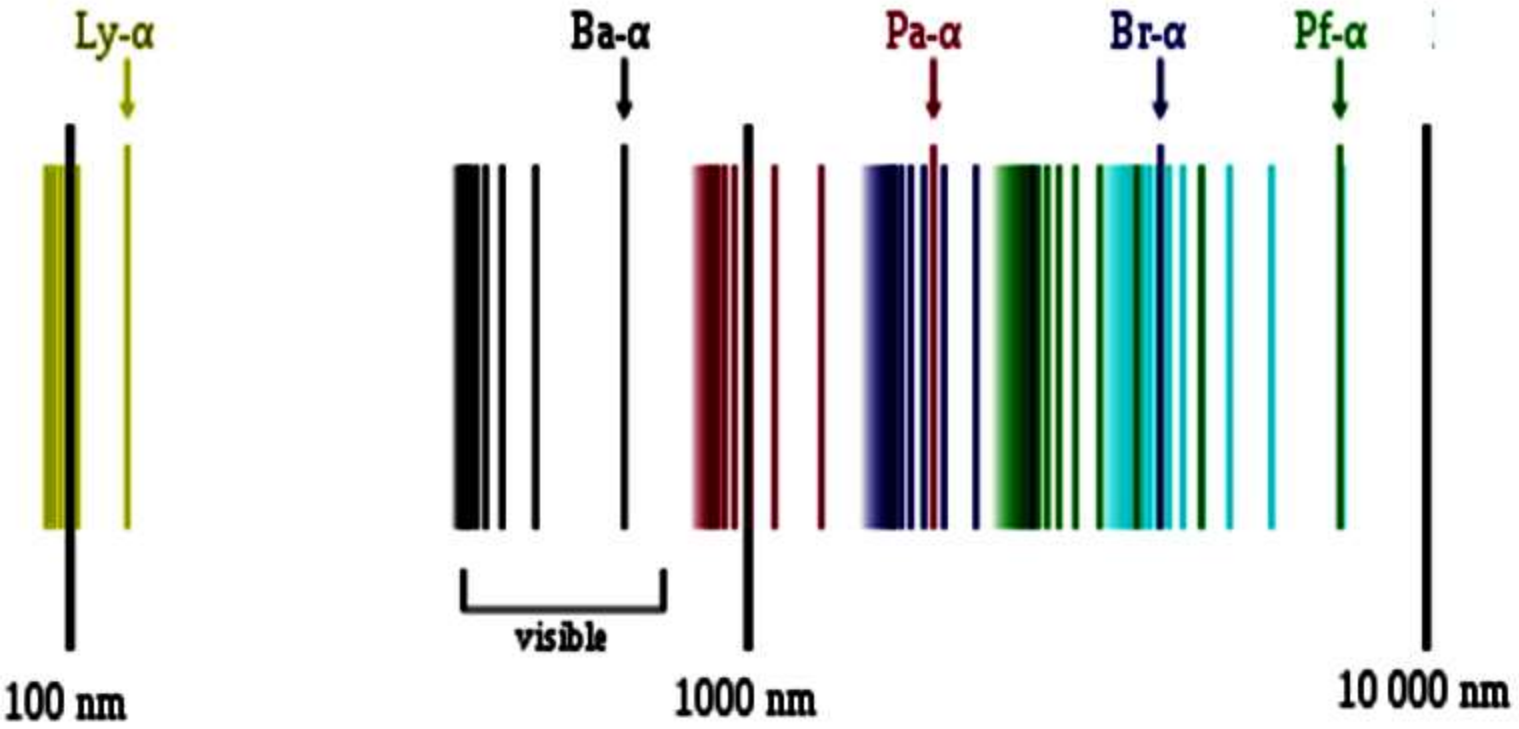


Fig. **Experimentally observed H_2 atom spectrum**

Cont…

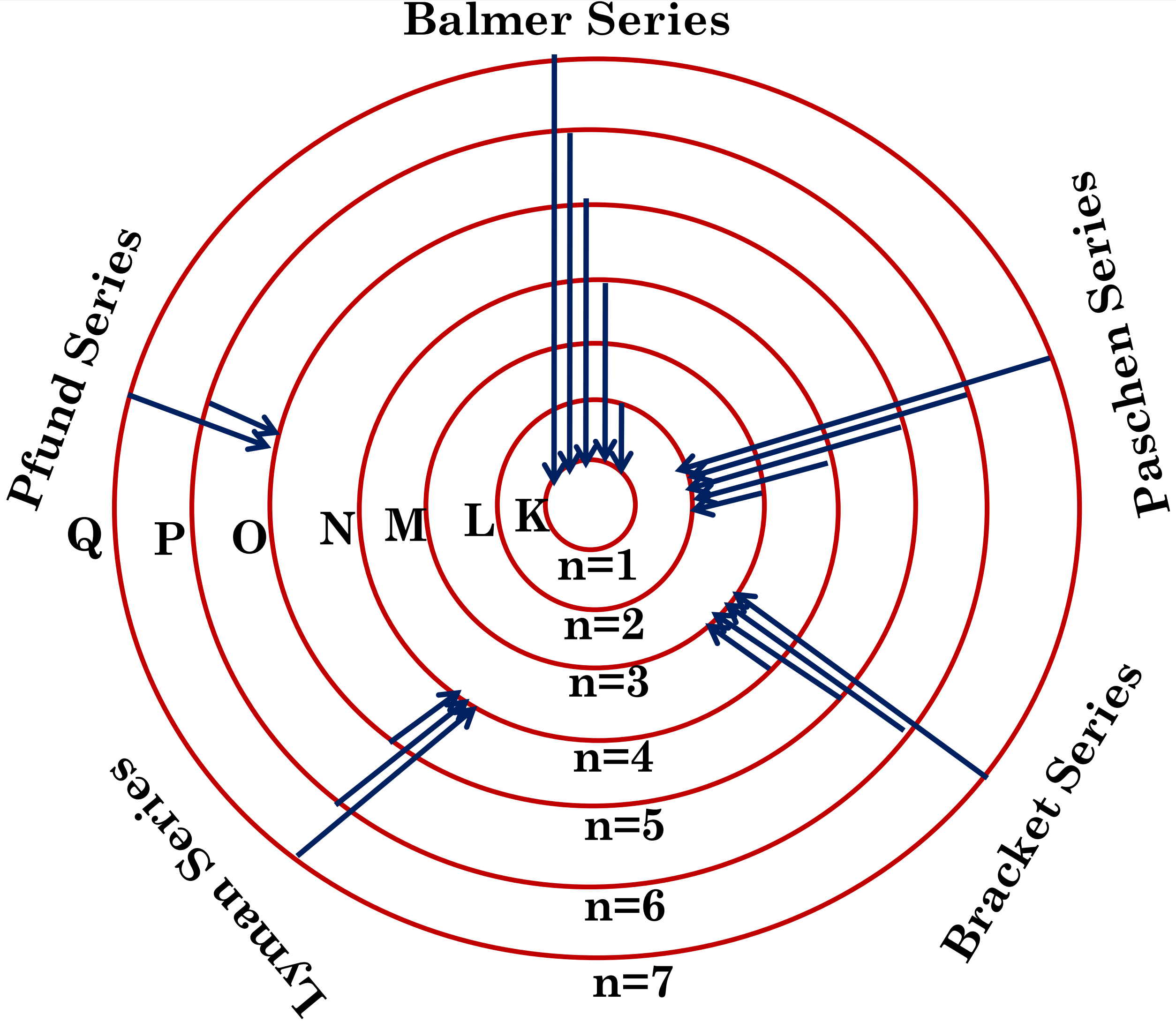
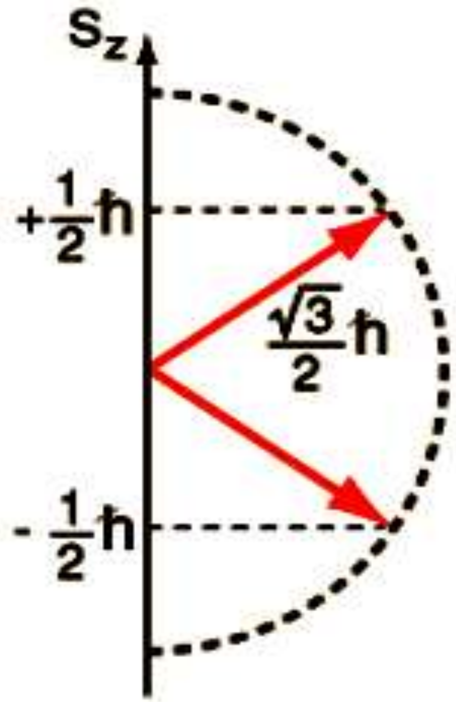


Fig. Diagram showing the origin of the series spectrum of H_2 atom

Electron Spin

- Electron spin is a quantum property of electrons.
- It is a form of angular momentum.
- The magnitude of this angular momentum is permanent.
- If the electron spins clockwise on its axis, it is described as spin-up; counterclockwise is spin-down.



Cont…

- Spin “up” and “down” allows two electrons for each set of spatial quantum numbers.

$$n, \ell, m_\ell$$

- An electron spin s = 1/2 is an intrinsic property of electrons.
- Electrons have intrinsic angular momentum characterized by quantum number 1/2.
- In the pattern of other quantized angular momenta, this gives total angular momentum

$$S = \sqrt{\frac{1}{2}\left(\frac{1}{2}+1\right)}\hbar = \frac{\sqrt{3}}{2}\hbar$$

- The resulting fine structure which is observed corresponds to two possibilities for the z-component of the angular momentum.

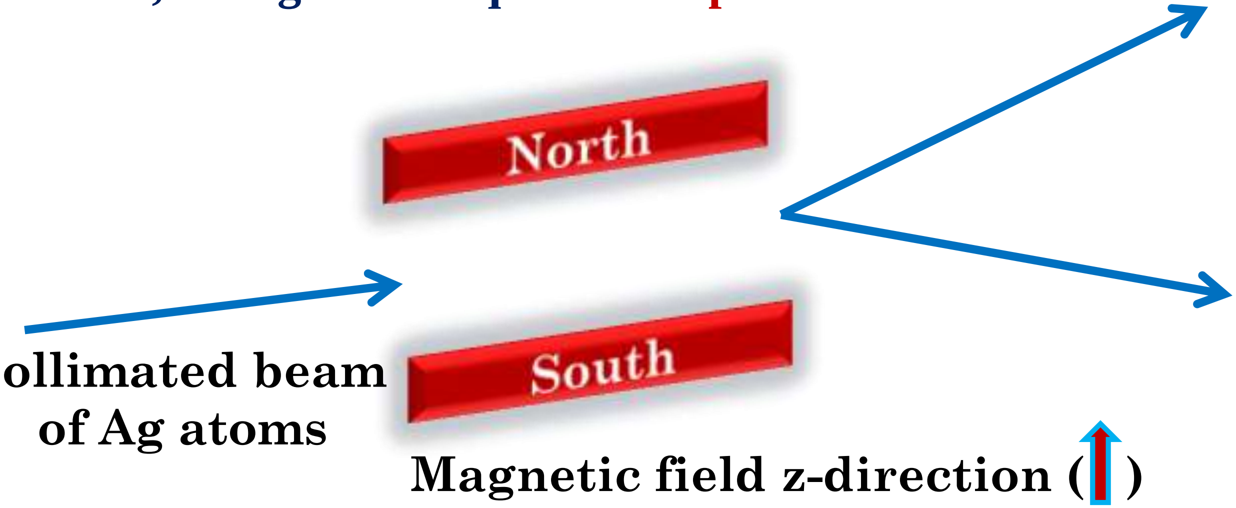
$$S_z = \pm\frac{1}{2}\hbar$$

- This causes an energy splitting because of the magnetic moment of the electron

$$\mu_S = -\frac{e}{2m}gS$$

Stern – Gerlach Experiment

- The Stern–Gerlach experiment demonstrated that the spatial orientation of angular momentum is quantized.
- Thus an atomic-scale system was shown to have intrinsically quantum properties.
- In the original experiment, silver atoms were sent through a spatially varying magnetic field, which deflected them before they struck a detector screen, such as a glass slide.
- Particles with non-zero magnetic moment are deflected, due to the magnetic field gradient, from a straight path.
- The screen reveals discrete points of accumulation, rather than a continuous distribution, owing to their quantized spin.

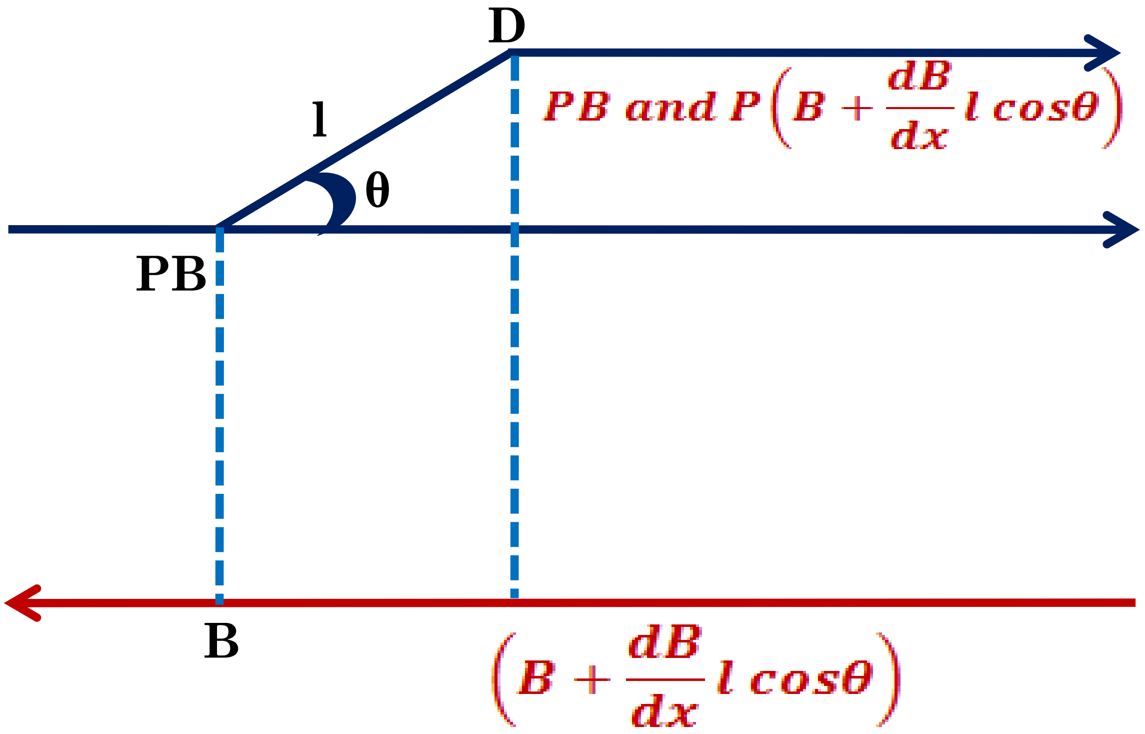


Collimated beam
of Ag atoms

Magnetic field z-direction (↑)

Cont…

- Let the magnetic field varying alone the x-direction
- So the field gradient is dB/dx and is $+^{ve}$
- CD is the atomic magnet with inclined at the angle θ
- to the field direction.



Cont…

- The field strength at the pole C is B
- The field strength at the another pole D is $\left(B + \frac{dB}{dx} l\, cos\theta\right)$
- The forces on the two poles are $PB \text{ and } P\left(B + \frac{dB}{dx} l\, cos\theta\right)$
- The atomic magnet experiences not only a torque $(=P_l B = \mu_S B)$ but also a translatory force

$$F_x = \frac{dB}{dx} P_l cos\theta$$

$$F_x = \frac{dB}{dx} \mu_s cos\theta \qquad (1)$$

P – Pole strength
l – Length,
M - Dipole moment

Cont...

- ❑ Let

  V-velocity of the atomic magnet of mass m as it enters the field

  L-length of the path of the atom in the field

  t-time of travel of the atom through the field = L/V

- ❖ The accelerations given to the atom along the field direction,

  by the translatory force F_x ❖ $= F_x/m$ (2)

- ❖ The displacement of the atom along the field

  direction on emerging out of the field = α

$$\alpha = \frac{1}{2}\left(\frac{F_x}{m}\right) t^2 = \frac{1}{2}\left(\frac{F_x}{m}\right)\frac{L^2}{r^2}$$

Cont…

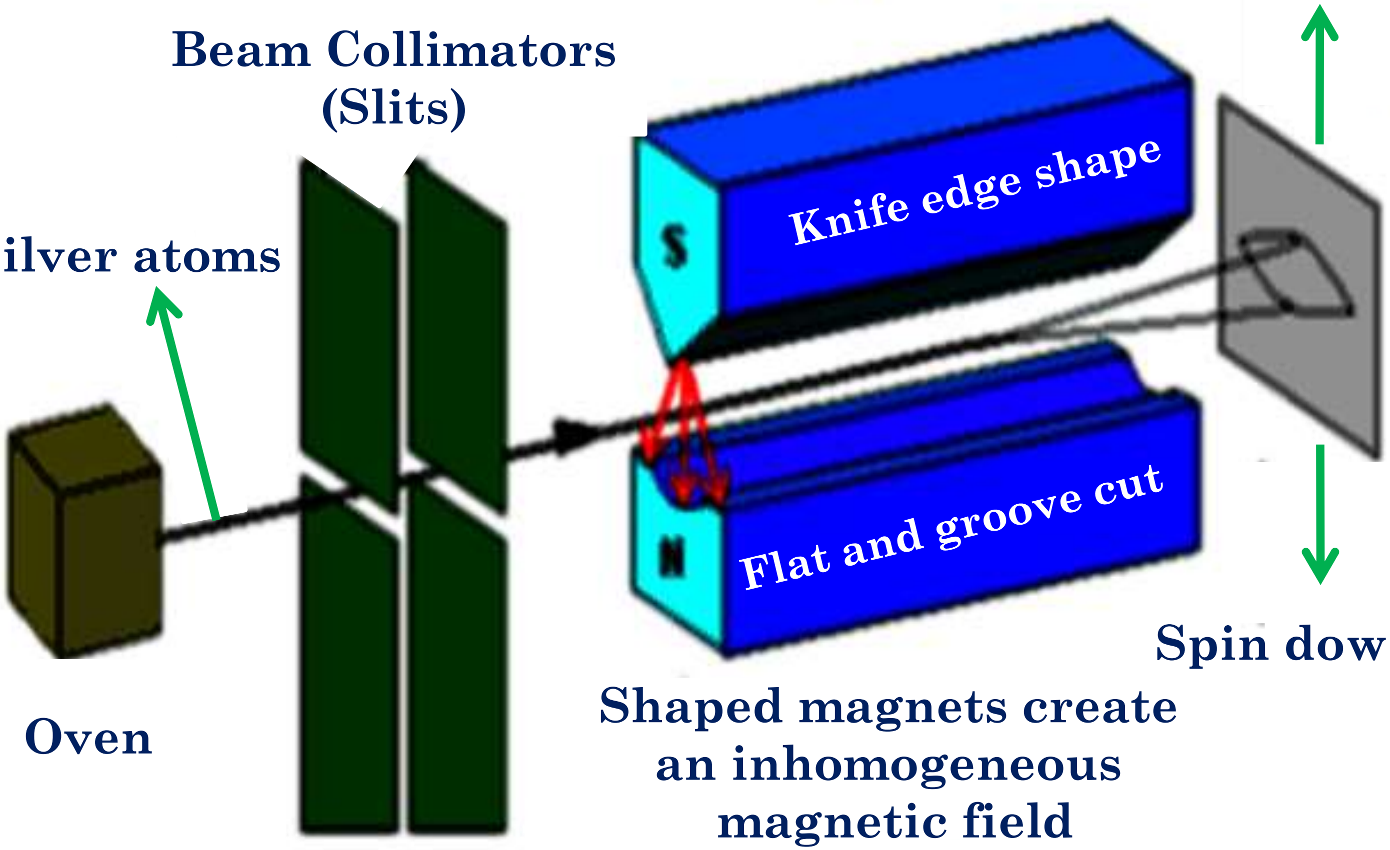
$$\alpha = \frac{1}{2}\frac{dB}{dx}\frac{\mu_s \cos\theta}{m}\frac{L^2}{r^2} \qquad \text{———} \qquad (3)$$

If μ is resolved component of the magnetic moment in the field direction, $\mu = \mu_s \cos\theta$

Therefore,

$$\alpha = \frac{1}{2}\frac{dB}{dx}\frac{\mu}{m}\frac{L^2}{r^2} \qquad \text{———} \qquad (4)$$

Cont...



Spin up atoms

Beam Collimators (Slits)

Silver atoms

Spin down atom

Oven

Shaped magnets create an inhomogeneous magnetic field

Fig. Experimental Arrangement

Cont...

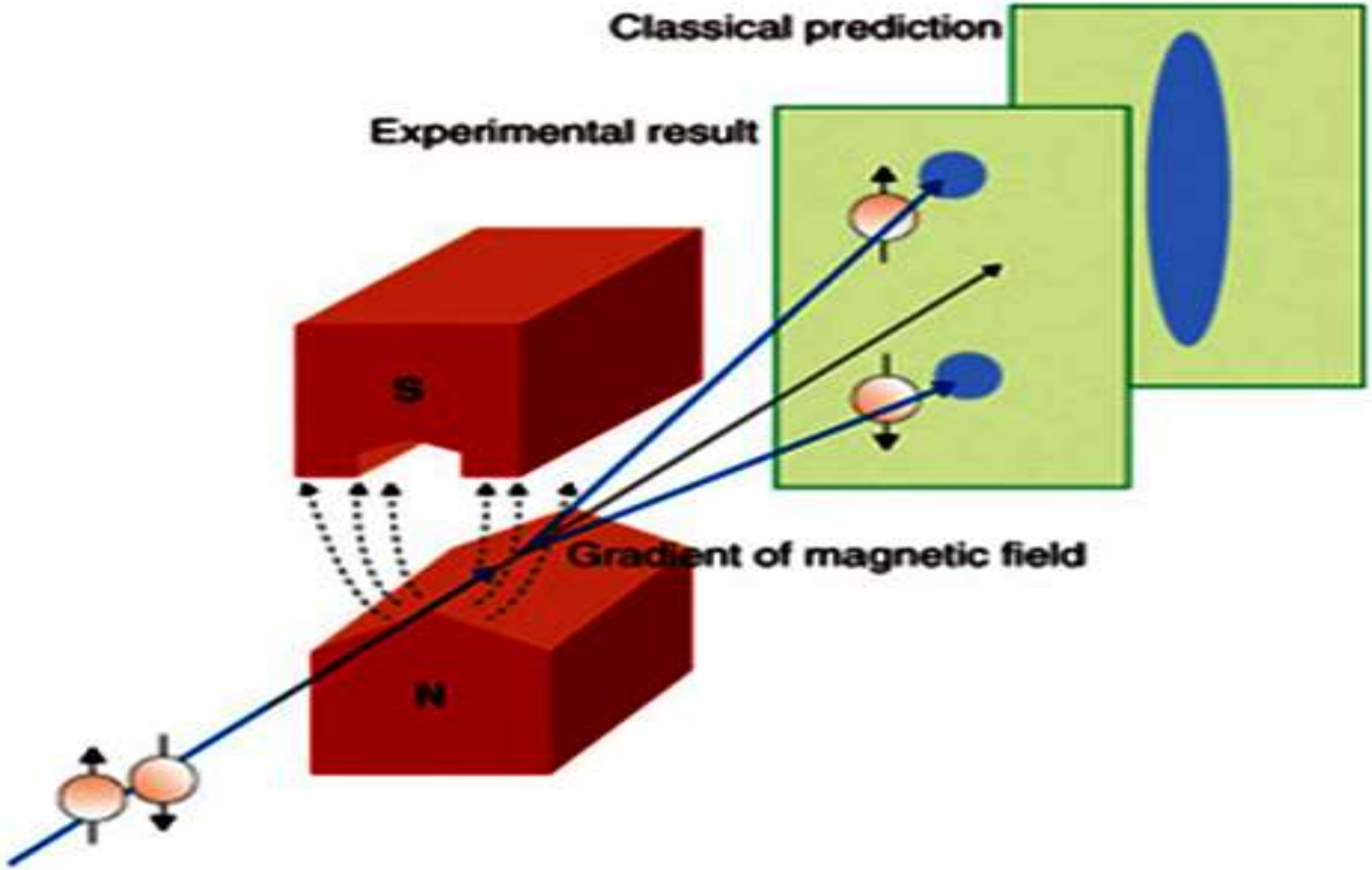


Fig. Experimental observations

Spin-Orbit Interaction

- This is equivalent to a current loop with current I given by

$$I = \frac{Ze}{2T} = \frac{Ze}{2\pi r/v} = \frac{Zev}{2\pi r}$$

- The magnetic field due to such a current loop is

$$B_{int} = \frac{\mu_o I}{2r} = \frac{\mu_o Zev}{4\pi r^2}$$

- Here B $_{int}$ represents the integral magnetic field arising in the atom as explained above

- In vector notation

$$B_{int} = \frac{\mu_o Ze(\vec{r} \times \vec{v})}{4\pi r^2 |\vec{r}|}$$

$$B_{int} = \frac{\mu_o Ze}{4\pi m r^3} (\vec{r} \times m\vec{v})$$

$$B_{int} = \frac{\mu_o Ze}{4\pi m r^3} \vec{L} = \frac{Ze}{4\pi \varepsilon_o m c^2 r^3} \vec{L}$$

Cont…

Using

$$\mu_o = \frac{1}{\varepsilon_o c^2}$$

$$E_m = -\vec{\mu}_s \,.\, \vec{B}_{int}$$

$$\vec{\mu}_s = -g_s \frac{\mu_B}{\hbar} \vec{S}$$

$$E_m = g_s \frac{\mu_B}{\hbar} \vec{S}\,\vec{B}_{int}$$

$$= \frac{g_s\, \mu_B\, Ze}{4\pi\varepsilon_o mc^2 r^3 \hbar} \vec{S}.\vec{L}$$

$$= \frac{Ze^2}{4\pi\varepsilon_o mc^2 r^3} \vec{S}.\vec{L}$$

Cont…

Using

$$\mu_B = \frac{e\hbar}{2m}$$

$$g_s = 2$$

$$E_m = \frac{Ze^2}{4\pi\varepsilon_o mc^2r^3}\,\vec{S}.\vec{L}$$

$$\vec{j}.\vec{j} = J^2 = \left(\vec{L} + \vec{S}\right) = L^2 + S^2 + \vec{L}.\vec{S} + \vec{S}.\vec{L}$$

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

$$\vec{S}.\vec{L} = \frac{J^2 - L^2 - S^2}{2}$$

Coupling Scheme

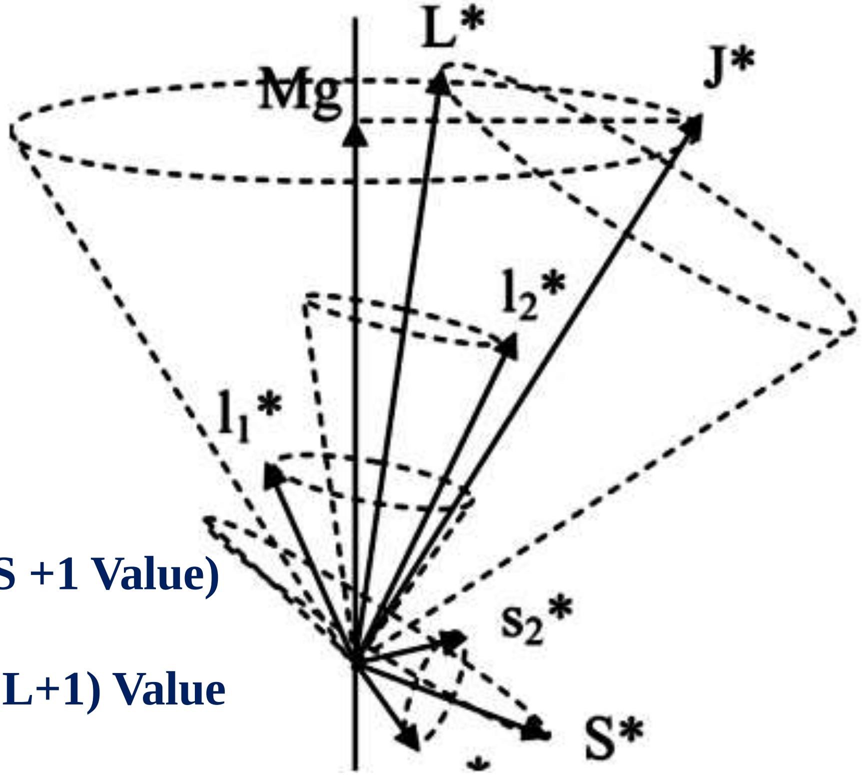
Two types of scheme have been developed

1. **L-S Coupling**
2. **J-J Coupling**

1. L-S Coupling

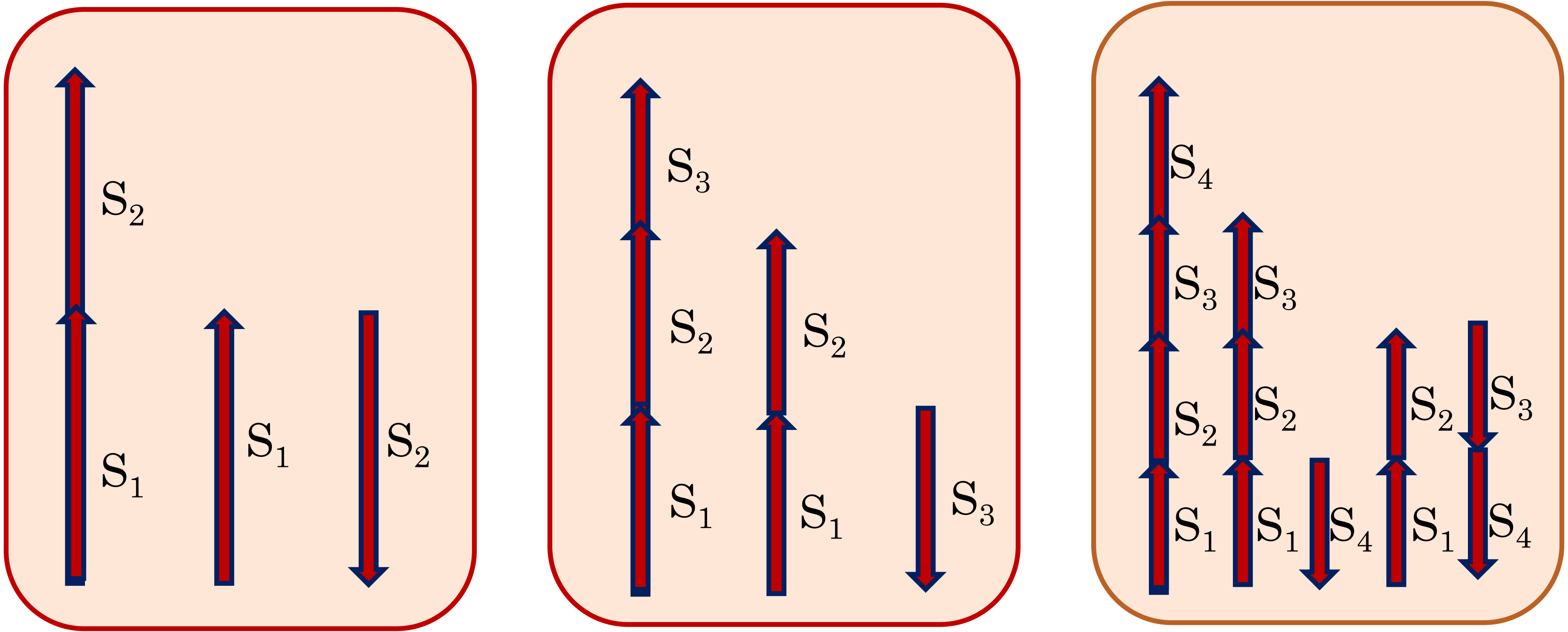
$L = \mathscr{E} l_i$ $S = \mathscr{E} s_i$

$J = L+S$



- ✓ **When L > S, J Can have (2S +1 Value)**
- ✓ **When L < S, J Can have (2L+1) Value**
- ✓ **L = 0,J=S**

Cont…



2 Electrons	3 Electrons	4 Electrons
S = 1,0	S = 3/2, 1/2	S = 2,1,0

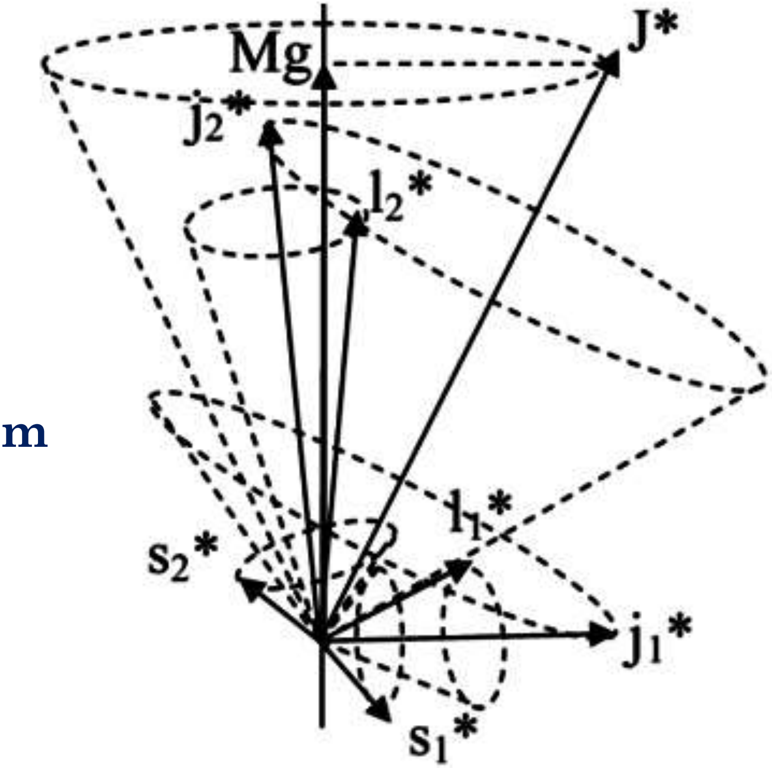
Cont…

2. J-J Coupling

- **From Figure vector are, $j_i = l_i + s_i$**

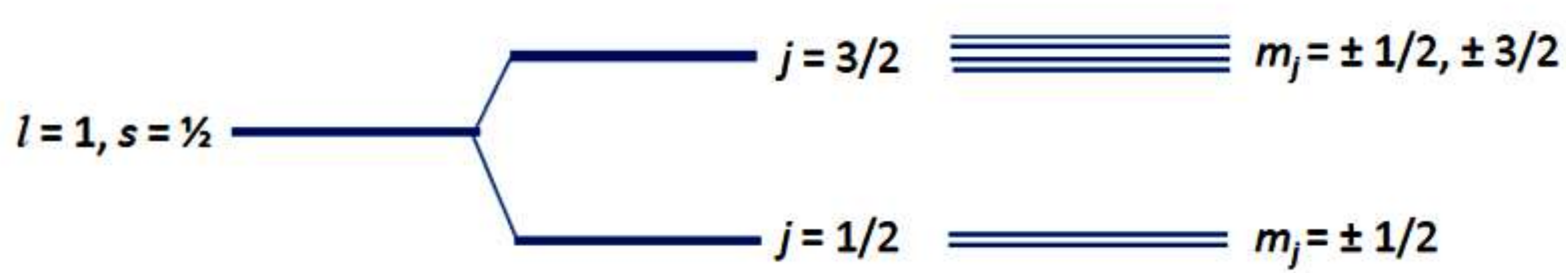
- **j gives the total angular momentum J of the atom**

- **Thus $J = \mathcal{E} j_i$**



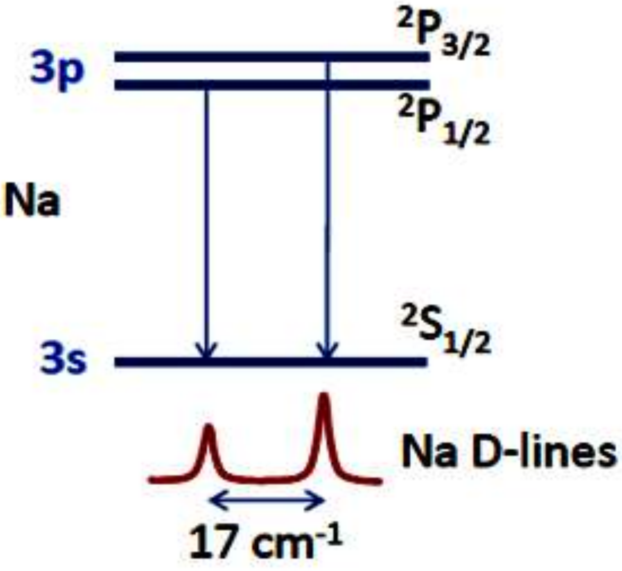
Fine Structure

- Spin-Orbit coupling gives rise to splitting in spectra called Fine Structure

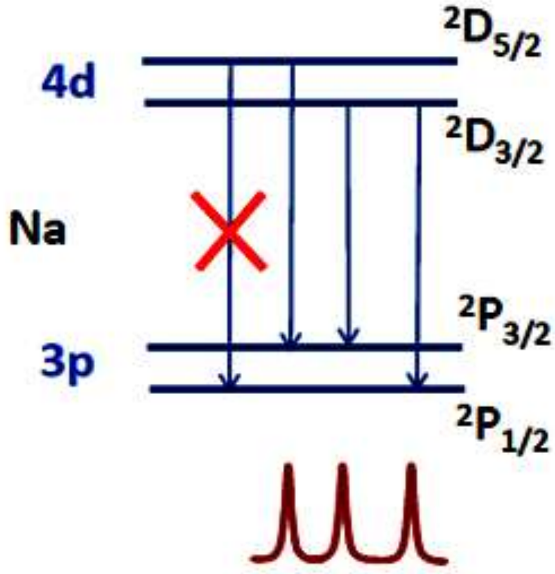


- Selection Rule Δj = 0, ±1 (But $\neq$ 0) arises from conservation of angular momentum.

E.g.1.



E.g.2.



Spectroscopic terms and selection rules

Spectroscopic terms:

Terms, Configurations, and Levels

- **The outermost electron in an atom or ion is the one that usually undergoes transitions, and so the state of that electron describes the state of the atom or ion.**
- **The configuration describes the n and *l* values for all the electrons in an atom.**
- **For example, the ground state of Boron has a $1s^2 2s^2 2p$ configuration, with 2 electrons filling the n=1 level (*l*=0), 2 electrons in the n=2, *l*=0 *s* orbital, and the fifth electron beginning to populate the 2*p* orbital.**
- **The *level* is the set of 2J+1 states with specific values of L, S, and J.**
- **The difference in the energy between two levels gives the wavelength or frequency of an atomic transition.**

Cont…

- The *term* is the set of levels characterized by a specific S and L.
- The ground state of Boron has a $^2P_{1/2}$ term.
- Closed shells always have a $^1S_0$ term.
- Atoms whose outer electrons have l=0,1,2,3,4 are referred to as S, P, D, F, G terms, respectively (Note that an electron with l=0 is called an *s* electron; lower case terms refer to individual electrons.
- For example, In the ground state, Boron has 4 *s* electrons (2 in the n=1 level and 2 in the n=2 level) and one *p* electron. The ground state term of the atom is P.
- Warning: The *s* in an *s* electron has nothing to do with the quantum number s.
- This is a carryover from early spectroscopic nomenclature (sharp, principal, diffuse, and fundamental bands, with G following F alphabetically) for alkali atoms, those with a closed shell of electrons plus a single valence electron, such as Li, Na, K, Mg -II, Ca-II.

Cont…

Free ion Spectroscopic Term for d^n Configurations

- **Electron – electron repulsions cause a given electron configuration to be split into terms**
- **Terms: Energy levels of atoms or ions that arise due to inter-electronic repulsion**

Configuration	Russel-Saunders Terms
d^0 , d^{10}	^1S
d^1, d^9	^2D
d^2, d^8	^3F, ^3P, ^3G, ^1D, ^1S
d^3, d^7	**^4F**, ^4P, ^2H, ^2G, ^2F, ^2D, ^2D, ^2P
d^4, d^6	**^5D**, ^3H, ^3G, ^3F, ^3F, ^3D, ^3P, ^3P, ^1I, ^1G, ^1F, ^1D, ^1D, ^1S, ^1S
d^5	**^6S**, ^4G, ^4F, ^4D, ^4P, ^2I, ^2H, ^2G, ^2G, ^2F, ^2F, ^2D, ^2D, ^2D, ^2P, ^2S

- **Ground State terms are highlighted in bold**

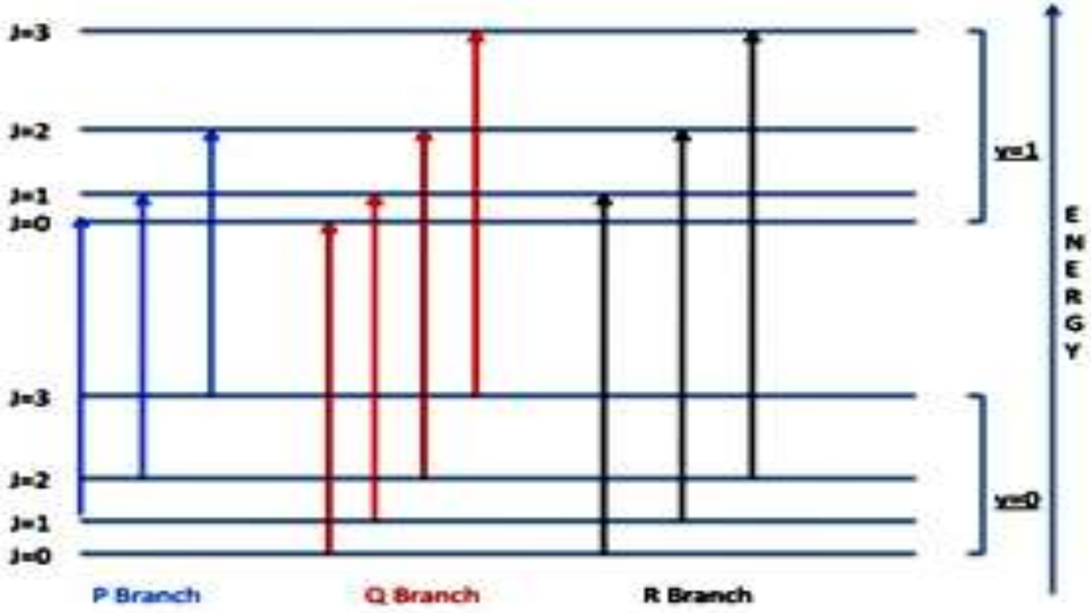
Cont…

Selection Rules:

- In complex ions, there are an enormous number of possible transitions.
- Not all of these possible transitions are observed.
- This is because some transitions are more likely than others.
- Selection rules were arrived at empirically to describe those changes in quantum numbers that were observed (permitted transitions) and those which did not (forbidden transitions).
- The basic selection rules, which strictly apply only to simple configurations which obey strict L-S coupling .
- The levels of L and S do not affect each other.
- This lack of interaction is known as L-S coupling.
- In complex atoms or ions, levels of L and S can interact, leading to a breakdown in L-S coupling.

Cont...

- When this happens, L and S are no longer interpretable in terms of angular momenta.), are: $\Delta L = 0, +/- 1$, $\Delta l = 1$, $\Delta J = 0, +/- 1$, except that J=0 -> J=0 is forbidden. $\Delta S = 0$
- $\Delta M = 0, +/- 1$, except that M=0 -> J=0 is forbidden if $\Delta J=0$.
- As the atoms become more complex, strict L-S coupling fails to hold, and these selection effects become weaker.
- Permitted lines are those whose transition probability is high.



Schematic diagram of P, Q, and R branch transitions

Hyperfine Structure

- Atomic nuclei radii of the order of 10^{-4} Å
- The nuclei heavier than electron
- Nuclei to be positive point charges of infinite mass
- Michelson, Fabry and Perot are explained about hyperfine effects
- They produce shifts of the electron energy levels < fine structure
- Hyperfine components are observed using a high resolution interferometer
- Pauli's attributed the hyperfine structure to an angular momentum of the nucleus of the atom
- Orbitals and spin angular momentum of electron could explain completely the fine structure of spectral lines.
- Hyperfine structure is caused by the properties of the nucleus

Alkali type spectra

- Therefore they give alkali spectra

- In general, the wave number of the same series in alkali spectra

  is written as, $$\bar{\gamma} = \frac{1}{\lambda} = R\left[\frac{1}{(p-\alpha)^2} - \frac{1}{(q-\beta_\alpha)^2}\right]$$

- Where alpha and β are characteristic constants for the element,

  p- are the fixed Term

  q- are the running Term

- The various series found in the alkali spectra are the following:

Cont...

1.Principal series

$$p = 1 \ \& \ q \geq 2$$

$$\bar{\gamma} = R\left[\frac{1}{(1-\alpha)^2} - \frac{1}{\left(q-\beta_p\right)^2}\right]$$

2. Sharp series

$$p = 2 \ \& \ q \geq 2$$

$$\bar{\gamma} = R\left[\frac{1}{(2-\alpha)^2} - \frac{1}{(q-\beta_s)^2}\right]$$

3. Diffuse series

$$p = 2 \ \& \ q \geq 3$$

Cont…

4. Fundamental or Bergmann Series

Here,

$$p = 2 \;\&\; q \geq 3$$

Here

β_p, β_s, β_d, and β_f are the characteristics of Principal, Sharp, Diffuse and Fundamental series respectively.

Equivalent Electron

- Among the values of *L* and *S* obtained from the general rules for addition of angular momenta are those which correspond to states forbidden by the Pauli principle.

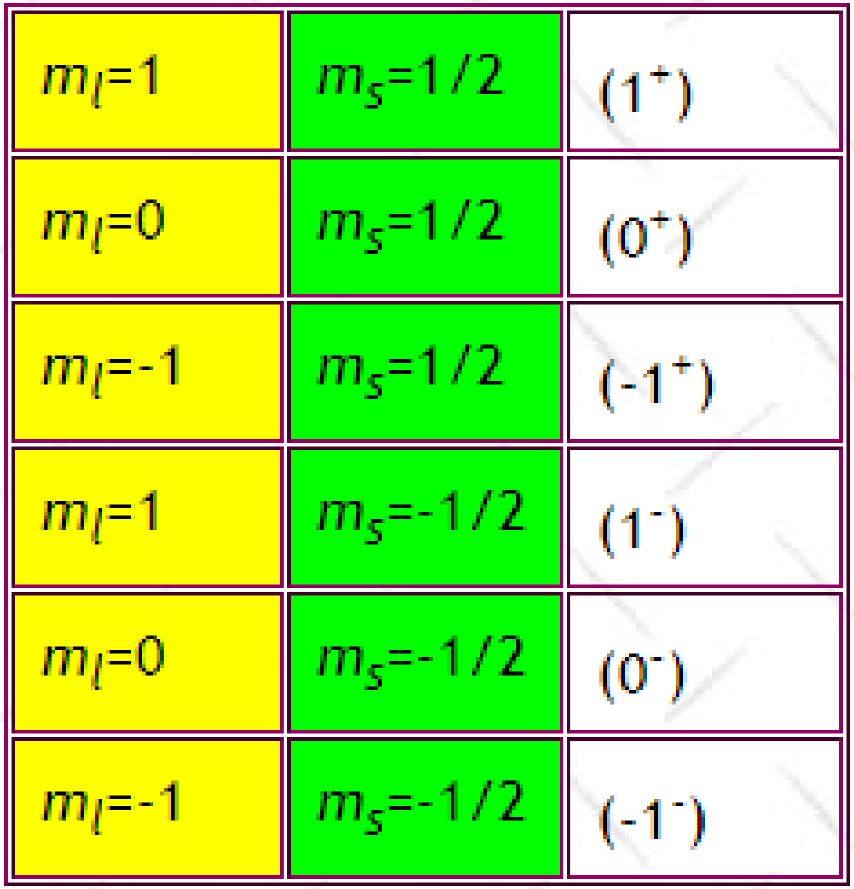
Examples:

- Configuration np^2For each electron the following values are possible:

$$m_l=1,0,-1, \quad m_s=1/2,-1/2$$

Combining the different values of m_l and m_s, we obtain the following possible states:

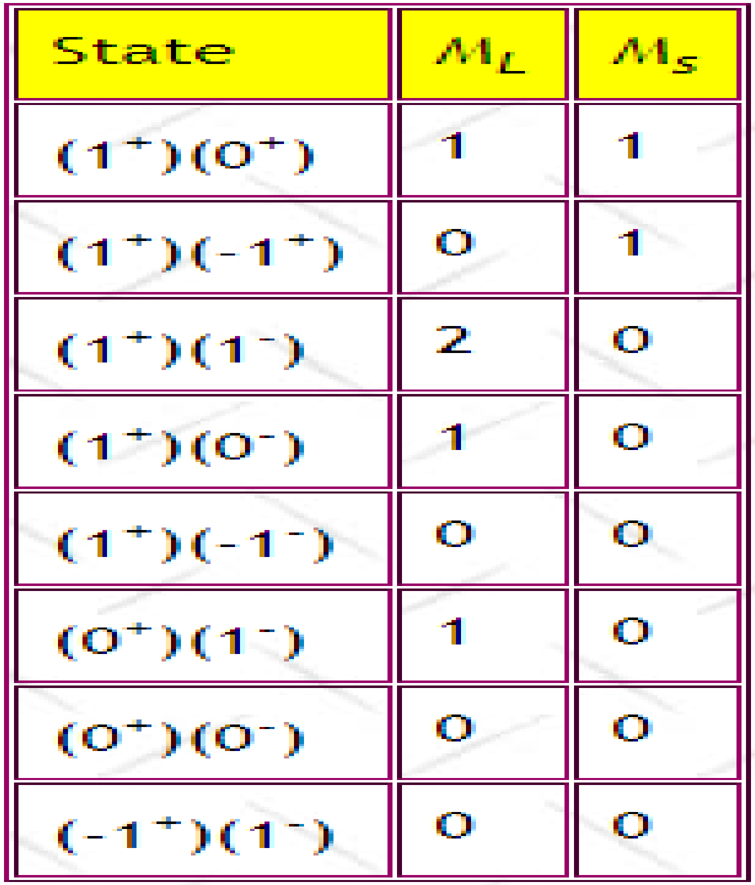
Cont...



$m_l=1$	$m_s=1/2$	(1^+)
$m_l=0$	$m_s=1/2$	(0^+)
$m_l=-1$	$m_s=1/2$	(-1^+)
$m_l=1$	$m_s=-1/2$	(1^-)
$m_l=0$	$m_s=-1/2$	(0^-)
$m_l=-1$	$m_s=-1/2$	(-1^-)

Cont…

- In each of these states there cannot be more than one electron.
- The following states with non-negative values of M_L and M_s are possible.



State	M_L	M_s
$(1^+)(0^+)$	1	1
$(1^+)(-1^+)$	0	1
$(1^+)(1^-)$	2	0
$(1^+)(0^-)$	1	0
$(1^+)(-1^-)$	0	0
$(0^+)(1^-)$	1	0
$(0^+)(0^-)$	0	0
$(-1^+)(1^-)$	0	0

Cont…

- ☐ **State with negative values of M_L and M_s need not be written out.**
  - ❖ **The presence of the M_L=2, M_s=0 term shows that a ^1D term is among the possible terms.**
  - ❖ **To this term we must further assign states with M_L=1, M_s=0 and M_L=0, M_s=0.**
  - ❖ **Among the states left is a state with M_L=1, M_S=1.**
  - ❖ **This and states with M_L=1, M_S=0, and M_L=0, M_S=1, and M_L=0, M_S=0 yield the ^3P term.**
  - ❖ **The only remaining state has M_L=0, M_S=0.**
  - ❖ **It corresponds to the ^1S term.**

Cont…

- Thus only three terms are possible, ^1D, ^3P, and ^1S for the configuration np^2.

- The possible terms for the configuration np^3 are ^4S, ^2P, and ^2D.

- The possible terms for the configuration np^4 are ^1D, ^3P, and ^1S, the same terms as for the configuration np^2.

Hund’s Rule

RULE 1: The term with maximum multiplicity lies lowest in energy.

- The lowest energy atomic state is the one that maximizes the sum of the S for all the electrons in the open sub shell.
- Consider the ground state of silicon.
- The electronic configuration of Si is $1s^2 2s^2 2p^6 3s^2 3p^2$ (see spectroscopic notation).
- We need to consider only the outer $3P^2$ electrons, for which it can be shown (see term symbols) that the possible terms allowed by the Pauli exclusion principle are 1D, 3P, and 1S.
- Hund's first rule now states that the ground state term is ^{3}P, which has S=1.
- The superscript 3 is the value of the multiplicity = 291=3.
- The diagram shows the state of this term with ML=1 and Ms= -1.

Cont...

RULE 2: **For a given multiplicity, the term with the largest value of L lies lowest in energy.**

- For a given multiplicity, the term with the largest value of the total orbital angular momentum quantum number L has the lowest energy.
  (Ti, Z=22)

- Electron configuration $Is^2 2s^2 2p\ ^6 3s\ ^2 3p^6 3d^2 4s^2$ Open shell $3d^2$ and the allowed terms include three singlet's (1S, 1D, and 1G) and two triplets (3P and 3F).

- We deduce from Hund's rule that the ground state is one of the two triplets, and from the Hund's second rule that the ground state is 3F (with L=3) rather than 3P 9with L=1).

- There is no 3G term since its (ML=4, Ms=1) state would require two electrons each with (ML=2, Ms= +1/2), in violation of the Pauli principle.

Cont…

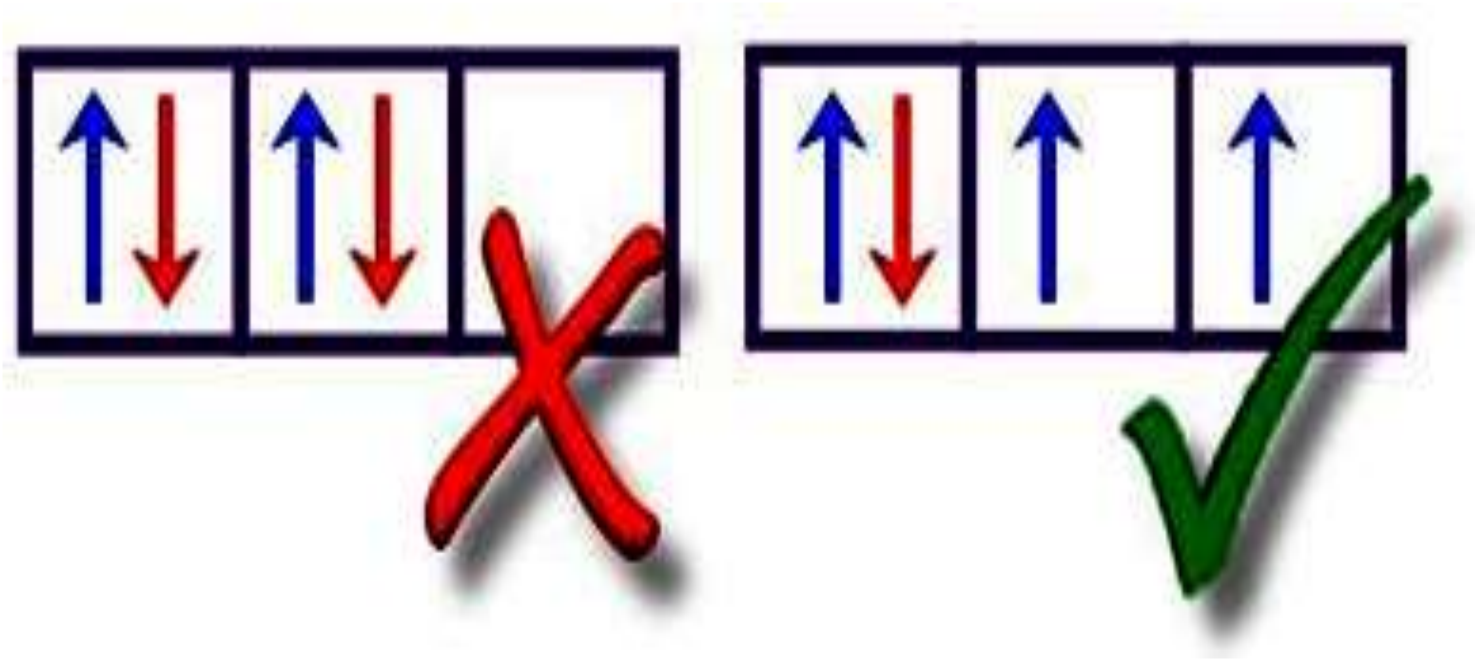
RULE 3: **For atoms with less than half-filled shells, the level with the lowest value of J lies lowest in energy.**

- This rule consider the energy shifts due to spin orbit coupling.
- In this case where the spin orbit coupling is weak compared to the residual electrostatic interaction of L and S are still good quantum numbers and the splitting is given by:
- The 3P lowest energy term is Si consist of three levels, With only two of six possible electrons in the shell, it is less than half-full and thus 3Po is the ground state.
- For sulfur (S) the lowest energy term is again 3P with spin-orbit levels but now there are four of six possible electrons in the shell so the ground states is $3P^2$.

Cont…

Pictorial representations of Hund's rule:

- ✓ **Within a sublevel, place one electron per orbital before pairing them**
- ✓ **"Empty Bus Seat Rule"**



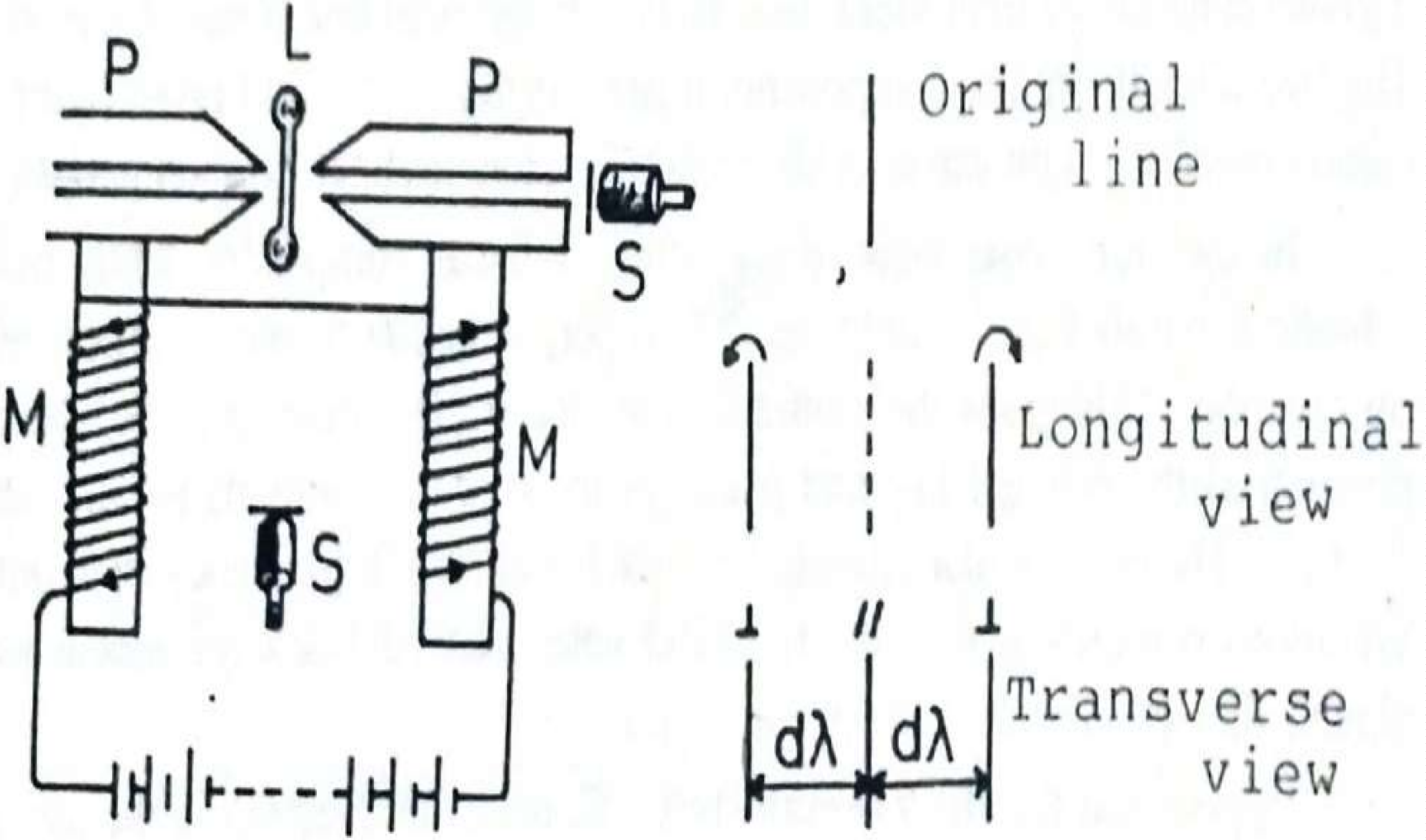
Topic: Zeeman Effect

- **Zeeman effect is a <u>magneto-optical</u> phenomenon**

- **The splitting of spectral line 2 or 3 ; Zeeman effect**

- **The splitting of spectral line more than 3; Anamalous Zeeman effect**

Experimental Arrangement:



Zeeman effect may be observed in two ways:

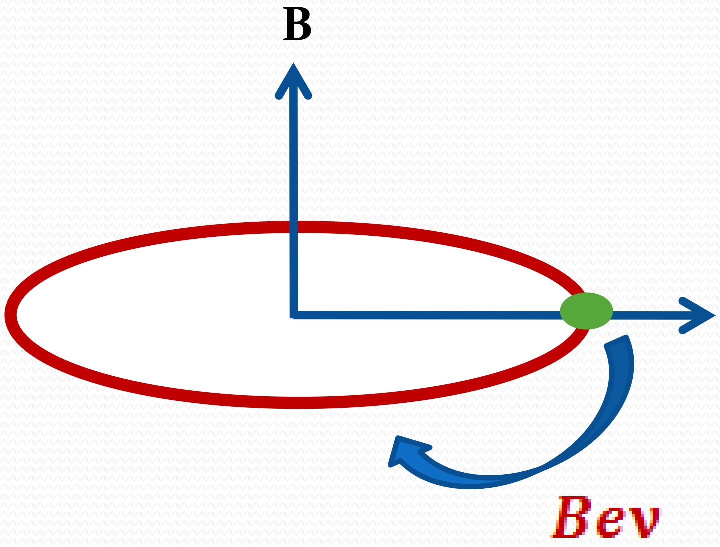
1. **Normal Longitudinal Zeeman effect**

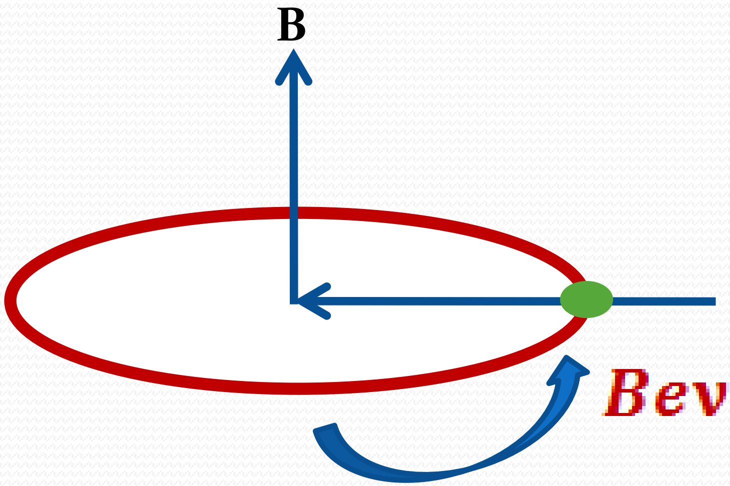
2. **Normal Transverse Zeeman effect**

Expression for the Zeeman Shift:

The centripetal force on the electron towards the centre in the absence of the magnetic field

$$F = \frac{mv^2}{r} = m\omega^2 r \text{ \_\_\_\_\_\_\_\_\_\_ } (1)$$





Let $\delta\omega$

be the change in angular velocity

The circular motion in the clockwise direction,
the additional radial force is directed away from the centre

$$F - Bev = m(\omega + \delta\omega)^2 r \qquad \_\_\_\_\_\_\_\_\_\_ (2)$$

$$m\omega^2 r - m(\omega + \delta\omega)^2 r = Be\omega r$$

$$m\omega^2 r - m[(\omega^2 + (\delta\omega)^2) + 2\omega\delta\omega]r = Be\omega r$$

$$m\omega^2 r - m\omega^2 r - m(\delta\omega)^2 r - 2m\omega r\delta\omega = Be\omega r$$

Neglecting $(\delta\omega)^2$

$$-2mr\omega\delta\omega = Be\omega r$$

$$\delta\omega = -\frac{Be}{2m} \qquad \_\_\_\_\_\_\_\_\_\_ (3)$$

- For the circular motion in the anticlockwise direction,
  the additional radial force in directed towards the centre

$$F + Bev = m(\omega + \delta\omega)^2 r$$

$$m\omega^2 r + m(\omega + \delta\omega)^2 r = Be\omega r$$

$$m\omega^2 r + m[(\omega^2 + (\delta\omega)^2) + 2\omega\delta\omega]r = Be\omega r$$

$$m\omega^2 r + m\omega^2 r + m(\delta\omega)^2 r + 2m\omega r\delta\omega = Be\omega r$$

Neglecting $(\delta\omega)^2$

$$2mr\omega\delta\omega = Be\omega r$$

$$\delta\omega = \frac{Be}{2m} \qquad \text{———— (4)}$$

$$\delta\omega = \pm\frac{Be}{2m} \qquad \underline{\hspace{4cm}}\ (5)$$

$$\omega = 2\pi\nu$$

$$\delta\omega = 2\pi\delta\nu$$

$$\delta\nu = \frac{\delta\omega}{2\pi} \qquad \underline{\hspace{4cm}}\ (5\text{-a})$$

Equation 5 Substitute in equation 5(a)

$$\delta\nu = \pm\frac{\mathrm{Be}}{2m2\pi} = \pm\frac{\mathrm{Be}}{4\pi\mathrm{m}}$$

Change in frequency of spectral line =

$$\delta\nu = \pm\frac{\mathrm{Be}}{4\pi\mathrm{m}} \qquad \underline{\hspace{4cm}}\ (6)$$

If ν and λ are the frequency and wavelength of the original line,

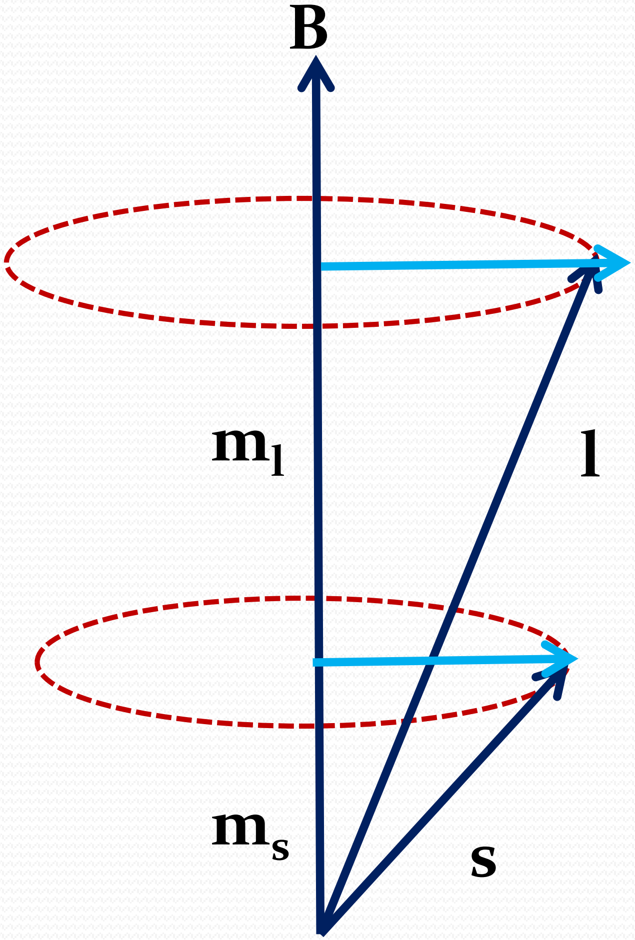
$$\pm\frac{Be}{4\pi m} = \frac{c}{\lambda^2}\delta\lambda$$

$$\frac{c}{\lambda^2}\delta\lambda = \pm\frac{Be}{4\pi m}$$

$$\delta\lambda = \pm\frac{Be\lambda^2}{4\pi mc}$$

Therefore the Zeeman Shift= $\delta\lambda = \pm\frac{Be\lambda^2}{4\pi mc}$ ———————— **(7)**

Paschen-Back Effect



Statement:

Explain:

Hence

$$\Delta E = (\Delta E)_l + (\Delta E)_s$$

$$= B\, eh/4\pi m\, [\, l \cos(l,B) + 2S \cos(S,B)$$

$$= eh/4\pi m\;\; B\, (m_l + 2m_s)$$

In terms of frequency change

Here, $E=h\nu$

$$\Delta\nu = eB/4\pi m\;\; \Delta(m_l + 2m_s)$$

$\nu=E/h$

- The quality (ml + ms) is known as the strong field quantum number and is evidently an integer

Now Since $\Delta m_l = 0, \pm 1, \Delta m_s = 0$

So, $\Delta(m_l + 2m_s) = 0 \text{ or } \pm 1$

- Hence in a strong magnetic field, a given spectral line will split into three components only and this is the usual characteristic of the normal zeeman effect

Stark Effect

Statement:

- The stark effect is the electrical analogue of the Zeeman effect
- Splitting of spectral lines when we apply the external electric field

Experimental:

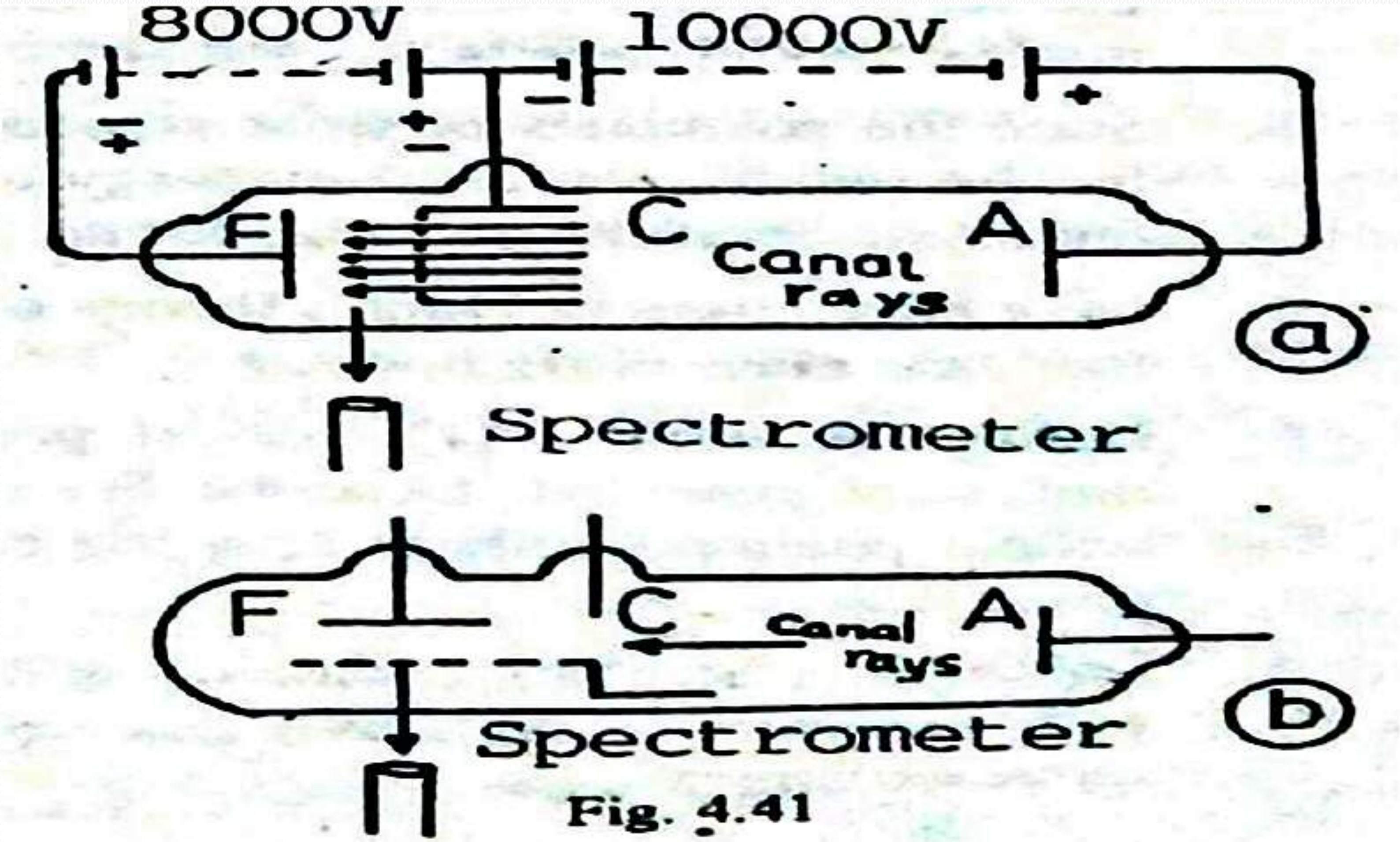


Fig. 4.41

Results

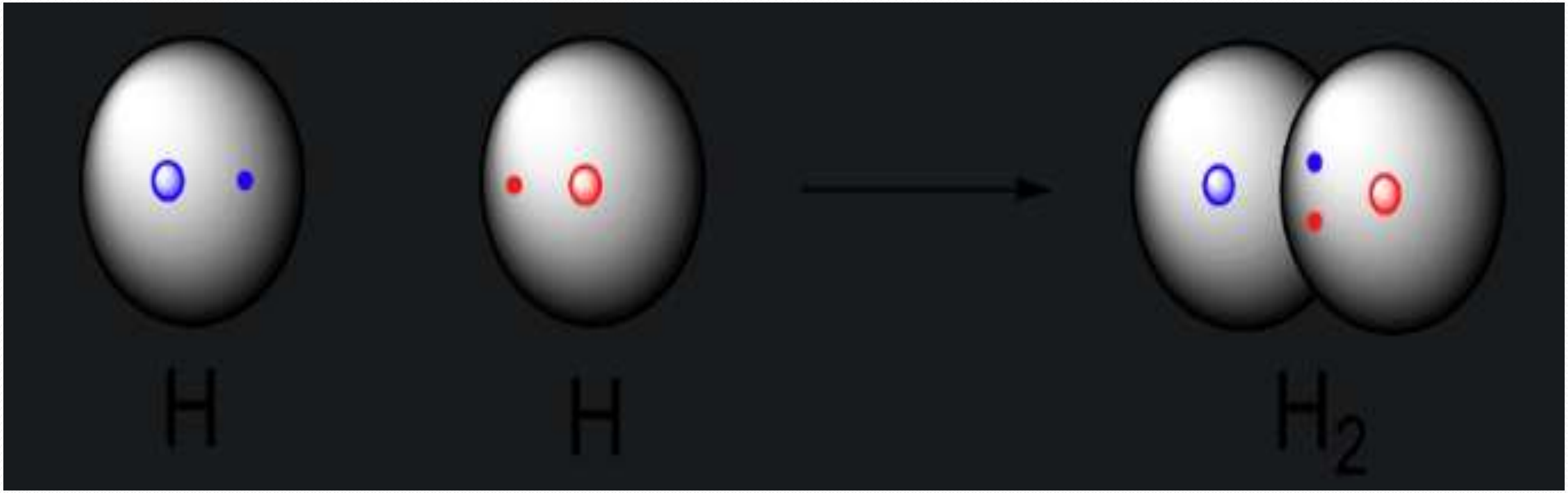
The results obtained with Balmer Series and discussed below:

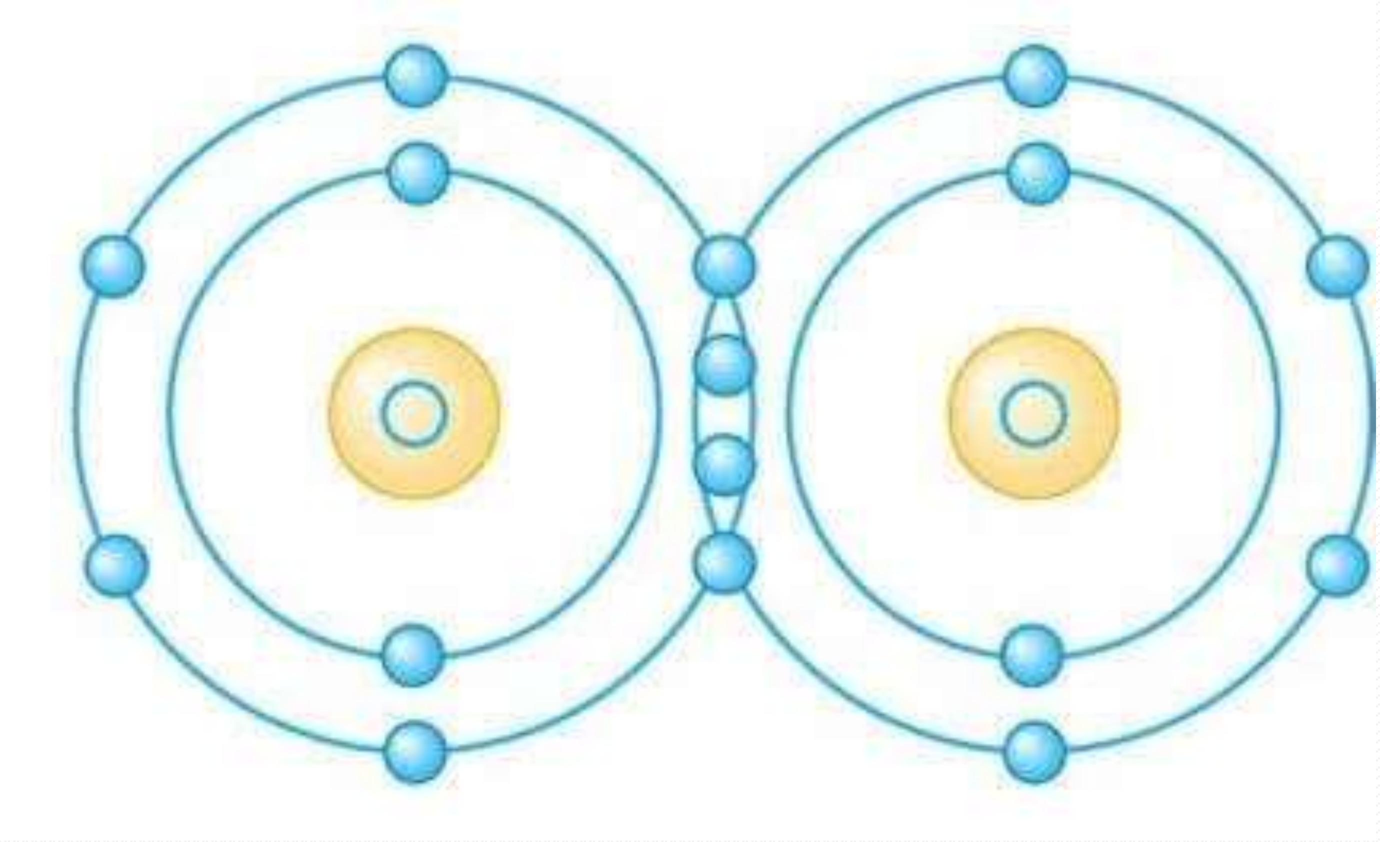
1. **Every line is split up into a number of sharp components and the the resolution number of lines and the total width of the pattern increase with n**
2. **Observation perpendicular to the direction of the electric field**

3. **Up to fields of about 10^7 v/m, the resolution increases in proportion to the field strength(E). (First Order Stark Effect).**

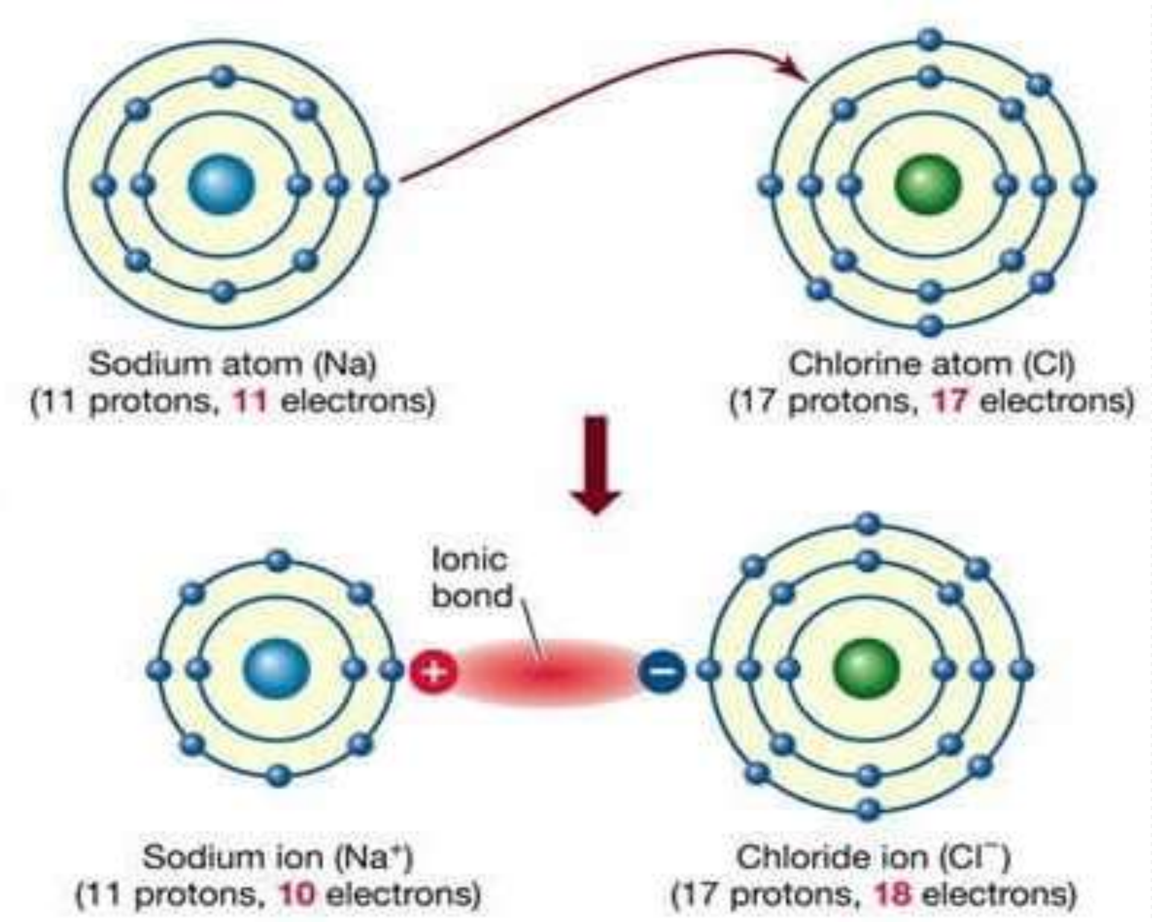
When E exceeds 10^7v/m, there are shifts in the line patterns which are proportional to E2 (Second Order Stark Effect)

Covalent Interaction or Covalent Bonding





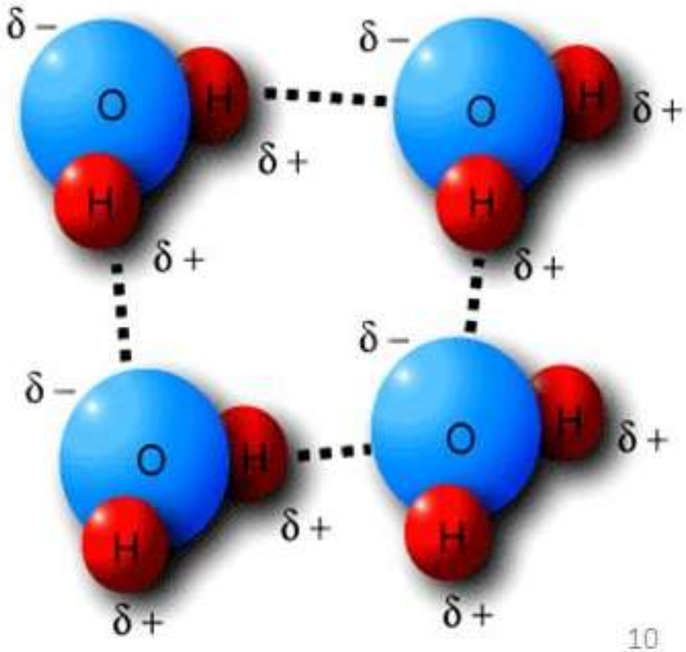
Ionic Interaction or Ionic Bonding



Van der Waals Bonding (or) Van der Waals Interaction

- When ionic and covalent bonds are present, there is some imbalance in the electrical charge of the molecule. Take water as an example. Research has determined the hydrogen atoms are bonded to the oxygen atoms at an angle of 104.5°. This angle produces a positive polarity at the hydrogen-rich end of the molecule and a negative polarity at the other end.

- A result of this charge imbalance is that water molecules are attracted to each other. This is the force that holds the molecules together in a drop of water



Microwave Spectroscopy

- A range of the spectrum of electromagnetic waves.
- The approximate wave length range is 1 mm to 10 m
- The approximate frequency range is $10^7 – 10^{12}$ Hz.

- **Linear Molecules**
- **Symmetric Tops**
- **Spherical Tops**
- **Asymmetric Tops**

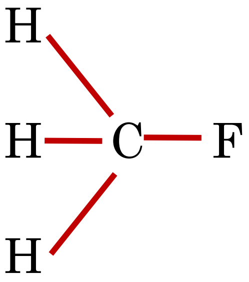
1. Linear Molecules:

$H - Cl$

$O - C - S$

$I_B = I_C = I_A = 0$

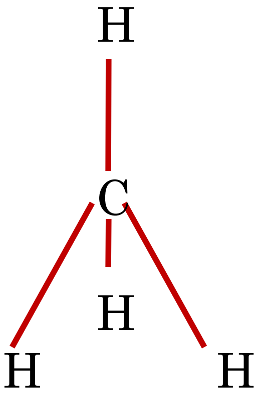
2. Symmetric Tops:



$I_B = I_C \pm I_A$

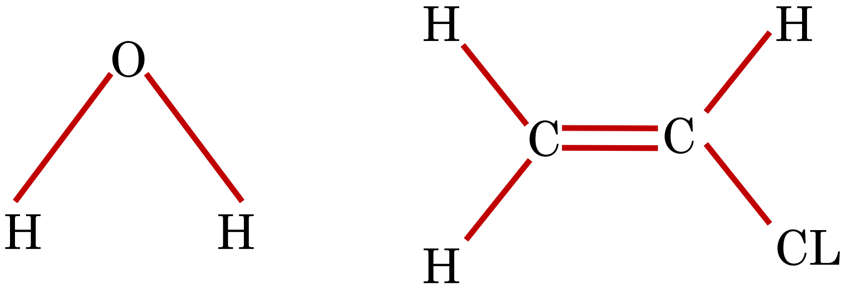
$I_A \pm 0$

3. Spherical Tops:



$I_A = I_B = I_C$

4. Asymmetric Tops:

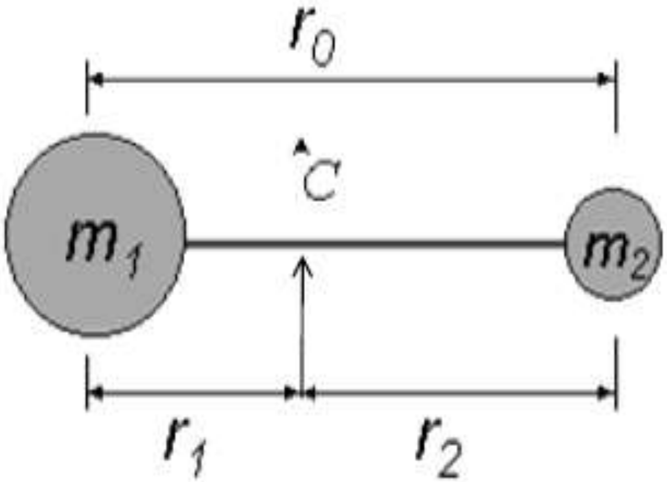


$I_B \pm I_C \pm I_A$

IR Spectroscopy

- It is a region of the spectrum of electromagnetic waves.
- The approximate wavelength range is $10^{-6} – 10^{-8}$ cm.
- The be approximate frequency range is $10^{12} – 10^{15}$ Hz

Rotation Spectra of Diatomic molecule



$I_B = I_C$ and $I_A = 0$

C – centre of gravity

express I via m_1, m_2 and r_0

from
$$m_1 \cdot r_1 = m_2 \cdot r_2 \qquad (1)$$
$$r_1 + r_2 = r_0 \qquad (2)$$
$$I = m_1 \cdot r_1^2 + m_2 \cdot r_2^2 \qquad (3)$$

$$\Rightarrow \quad I = \frac{m_1 \cdot m_2}{m_1 + m_2} \cdot r_0^2 = \mu \cdot r_0^2$$

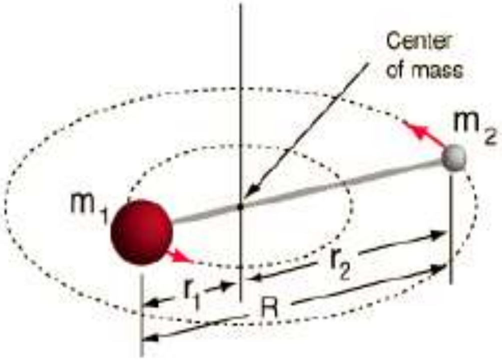
img003

μ - reduced or effective mass

units: $kg \cdot m^2 = kg \cdot m^2$

Simplest Case: Diatomic or Linear Polyatomic molecules

Rigid Rotor Model: Two nuclei are joined by a weightless rod



From solution of Schrodinger equation; $E_J = \frac{h^2}{8\pi^2 I} J(J+1)$

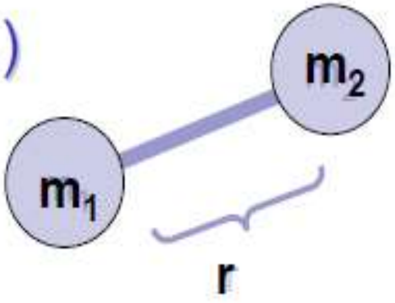
E_J = Rotational energy of rigid rotator (in Joules)

J = Rotational quantum number (J = 0, 1, 2, …)

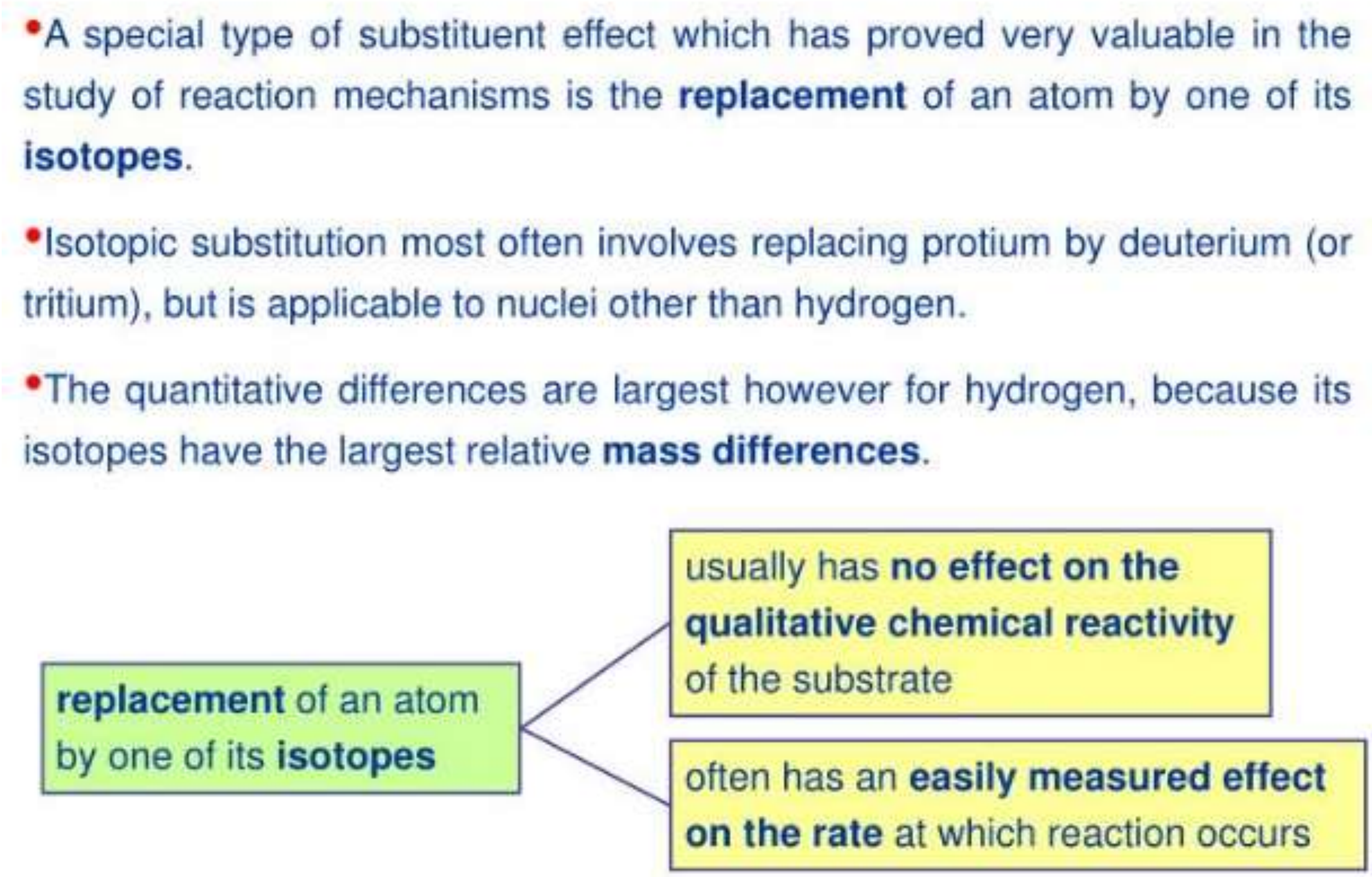
I = Moment of inertia = μr^2

μ = reduced mass = $m_1 m_2 / (m_1 + m_2)$

r = internuclear distance (bond length)



The effect of isotopic substitution



- A special type of substituent effect which has proved very valuable in the study of reaction mechanisms is the **replacement** of an atom by one of its **isotopes**.
- Isotopic substitution most often involves replacing protium by deuterium (or tritium), but is applicable to nuclei other than hydrogen.
- The quantitative differences are largest however for hydrogen, because its isotopes have the largest relative **mass differences**.

replacement of an atom by one of its **isotopes**

usually has **no effect on the qualitative chemical reactivity** of the substrate

often has an **easily measured effect on the rate** at which reaction occurs

Cont…

Considering Carbon monoxide

^{16}C ^{12}O to ^{13}C ^{16}O

$B > B^1$

^{13}C molecule with a prime

The first rotational absorption of ^{12}C ^{16}O to be at 3.8422 cm^{-1}

The first rotational absorption of ^{13}C ^{16}O to be at 3.67337 cm^{-1}

The values of B determined from these figures are: $B = 1.92118$ cm^{-1}

and $B^1 = 1.83669$ cm^{-1}

Cont…

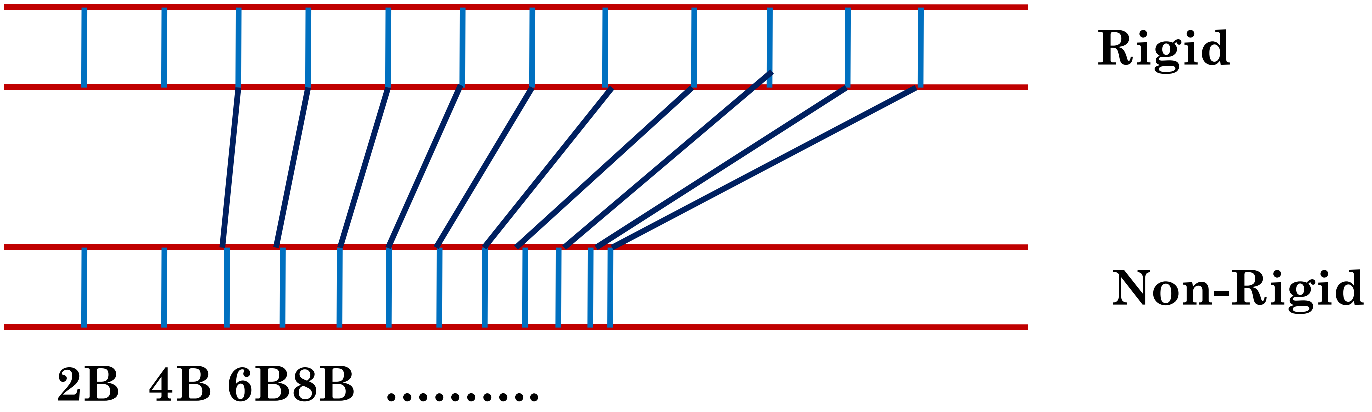
Where the prime refers to the heavier molecules,

we have immediately:

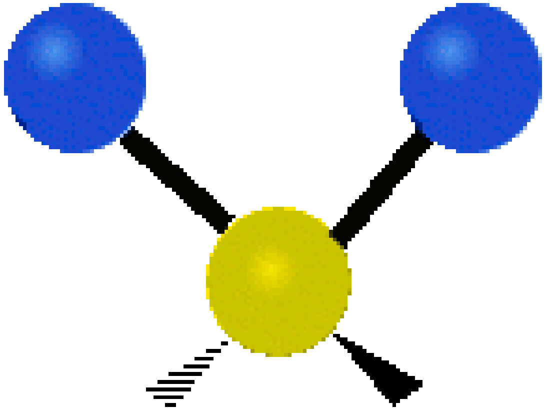
$$\frac{B}{B^1} = \frac{h}{8\pi^2 I_c} \cdot \frac{8\pi^2 I_c^1}{h} = \frac{I^1}{I} = \frac{\mu^1}{\mu} = 1.046$$

The effect of isotopic substitution

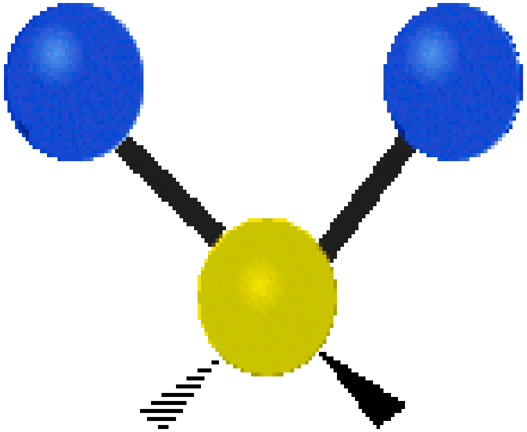
Definition



Symmetric top and Asymmetric top molecules



Symmetric



Asymmetric

Consider Methyl Fluoride (CH_3F)
K = -2, -1 (or) 0.
In general , Total angular momentum J,
we see that k can take values:
K= J, J-1, J-2, ……,0, …….- (J-1), -J ------------------(1)

Cont…

Symmetric Top Molecules:

$\Sigma_{J,K} = E_{j,K} / hc = BJ(J+1) + (A\text{-}B)k^2/cm$ -------------(2)

Where as before,

$B = h / 8\pi^2 I_B C$ and $A = h / 8\pi^2 I_A C$

The selection rules for this molecule may be showed to be ;

$\Delta J = \pm 1$ (as before) and $\Delta K = 0$

Cont…

$$\Sigma_{J+1,\, k} - \Sigma_{j,k} = \bar{U}J,K$$

$$= B(J + 1)(J + 2) + (A-B)K^2 – [BJ(J + 1) + (A-B)K^2]$$

$$= 2B(J+1 \quad \text{cm-1} \text{ ----------------}(3)$$

Asymmetric top molecules:

- ✓These molecules having three different moments of inertia, also have much more complicated rotational energy levels and spectra
- ✓No simple general equations can be derived for them
- ✓They are usually treated by approximation methods, much computation being required before agreement between observed and calculated spectra is achieved
- ✓This methods have been very successful for small molecule and much accurate bond length and bond angle beta have been derived
- ✓From this table some examples are included

Experimental Technique

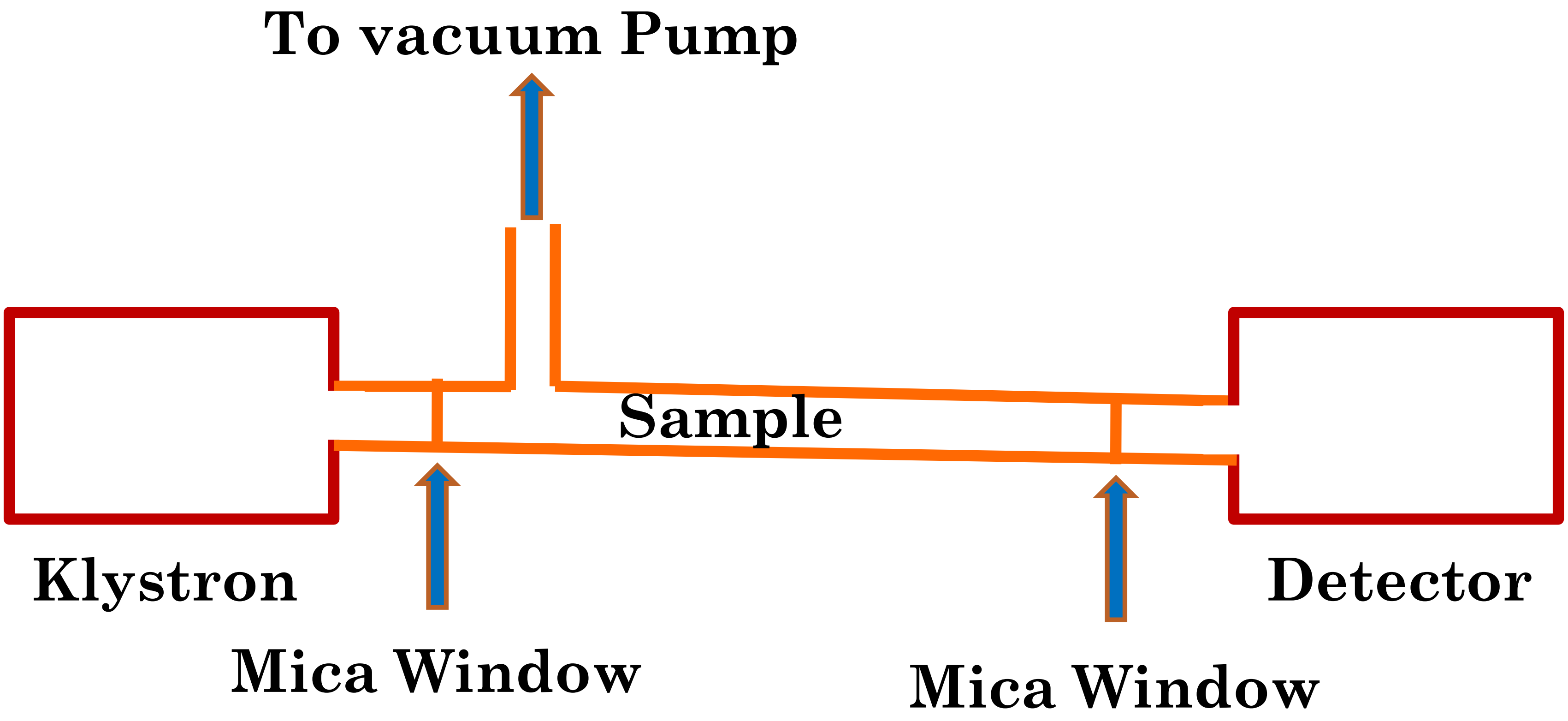


Fig. Schematic Diagram of a microwave spectrometer

Cont…

1.The Source and monochromator

2. Beam detection

3.Sample and Sample space

4. Detector

LASER

INTRODUCTION:

In 1958, Townes and Schawlow worked out the principle of Laser. Some devices have been developed which emit light radiations which are not only coherent in phase but also in direction of emission and state of polarisation. Such devices are known as Lasers. The acronym refers to Light Amplification by stimulated emission of radiation. The range of operation was first in the near infrared region and visible region and has been extended now to the ultraviolet region also.

PRINCIPLE OF LASER:

Let us consider an assembly of atoms of some kind that have metastable states of excitation energy $h\nu$. Suppose we somehow raise a majority of the atoms to the metastable level. If we now shine light of frequency ν on the assembly, there will be more induced emission from the metastable level than induced absorption by the lower level. The result will be an amplification of the original light. This is the concept that underlies the operation of the Laser.

INDUCED ABSORPTION, SPONTANEOUS EMISSION AND STIMULATED EMISSION

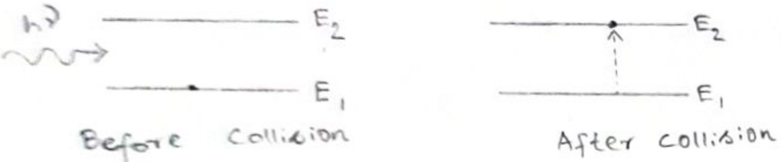
Three kinds of transition involving electromagnetic radiation are possible between two energy levels, E_1 and E_2 in an atom.

Induced absorption:

i) If the atom is initially in the lower state E_1, it can be raised to E_2 by absorbing a photon of Energy $E_2 - E_1 = h\nu$. This process is called induced absorption. Einstein postulated that the induced absorption transition rate was proportional to the number of atoms with electrons in the lower state and to the density of radiation energy incident on these atoms or

$$\left(\frac{dN_{12}}{dt}\right)_I = B_{12}\rho_{21}N_1 \longrightarrow ①$$

Induced absorption



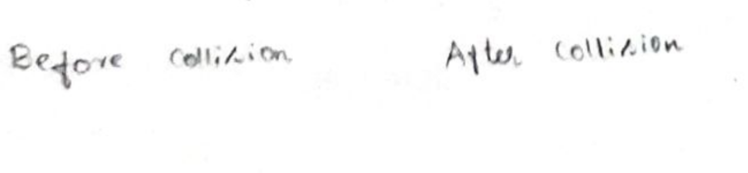
where N_1 is the number of atoms with electrons in the $n=1$ state

ρ_{21} is the density of electromagnetic radiation with energy equal to the energy difference between the two states

B_{12} is the Einstein Co-efficient for induced absorption.

Spontaneous Emission:

ii) If the atom is initially in the upper state E_2, it can drop to E_1 by emitting a photon of energy $h\nu$, this is Spontaneous emission.

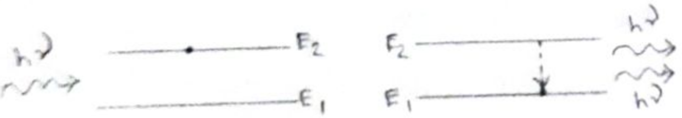


Einstein postulated that the spontaneous emission transition rates were proportional to the number of atoms with electrons in the upper state or

$$\left(\frac{dN_{21}}{dt}\right)_s = A_{21} N_2 \rightarrow ②$$

Stimulated Emission:

iii) Einstein Suggested that under certain conditions, it is possible to force an excited atom to emit a photon by another matching photon. According to Einstein, an atom in an excited energy state may, under the influence of the electromagnetic field of a photon of frequency ν incident upon it, jump to a lower energy state, emitting an additional photon of same frequency ν. Thus now two photons instead of one move on. In short, the excited atom emits light waves instep with the incoming wave and increases its intensity. This is known as stimulated emission of radiation.



The radiated light waves are exactly in phase with the incident ones. So the result is an enhanced beam of coherent light.

The transition rate for stimulated emission is proportional to N_2 and to the density of radiation incident on the atoms with energy equal to the energy difference between the two states or

$$\left(\frac{dN_{21}}{dt}\right)_s = B_{21}\,\rho_{21}\,N_2 \rightarrow ③$$

where B_{21} is the Einstein co-efficient for stimulated emission. After making the above assumptions, Einstein showed that for thermal equilibrium the co-efficients of induced absorption and stimulated emission are equal.

$$B_{21} = B_{12} \rightarrow ⑭$$

He also showed that the relationship between the co-efficient of spontaneous emission and the co-efficient of stimulated emission is $\frac{A_{21}}{B_{21}} = \frac{8(E_2-E_1)}{h^2c^3} \rightarrow ⑤$

where (E_2-E_1) is the energy difference between the two states.

POPULATION INVERSION :

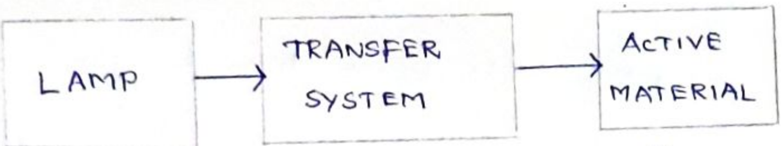
Under ordinary conditions of thermal equilibrium, the number of atoms in the higher energy state is considerably smaller than the number in the lower energy state. By Boltzmann law $\frac{N_2}{N_1} = e^{-(E_2-E_1)/KT}$ ie) $N_2 < N_1$. Hence there is very little stimulated emission compared with absorption. Let by some means, the atoms be initially excited so that there are more atoms in the higher energy state E_2 than in the lower energy state E_1. We then have $N_2 > N_1$. This is known as population Inversion.

PUMPING PROCESS :

The process by which population inversion is achieved is known as pumping process. The pumping is achieved through following two ways.

i) optically pumping : In optically pumping, energy in the form of light radiation is absorbed by the active material and thereby that energy pumps into the upper pump level. This method is particularly suited for Solid state (eg. Ruby or neodymium) and liquid lasers. In liquid and solids pumplevel is a band rather than a level. Hence it is in a position to absorb a sizable fraction of pumping light.

This figure gives a Schematic representation of optical pumping system. Light is allowed to fall from powerful lamp to active material through a optical system.



The light sources used for optical pumping are a) low pressure (100 Torr) Xe flash lamps (for pulsed Lasers) and b) Tungsten iodine krypton or high pressure mercury capilliary lamps (for CW lasers). In Xe flash lamps electrical energy stored in Capacitor bank is discharged into the flash lamp. The discharge is initiated by a high voltage trigger pulse to an auxiliary electrode and thus pulse preionises the gas. The lamp then provides the flash of light for the duration equal to the time constant (equal to the product of storage capacitance and resistance of the lamp). The time Constant Varies from few micro-Seconds to few-hundred Seconds. In both active material is in the form of cylinder having diameter 6mm to 1cm order and length ranging from few Centimeters to tens of Centimeter.

<u>Electrical pumping</u>: Electric pumping is used for gas and semiconductor lasers. In this case pumping is achieved by allowing a current of suitable value to pass through

the gas. It results into the generation of ions and electrons. the electrons are accelerated by the electric field and acquire enough additional kinetic energy from the field to excite the neutral atom by collisions. In this impact excitation process the movement of ions is less significant than that of the electrons. The electrons have larger kinetic energy then corresponding ion energy. The electron energy is characteristic by effective electron temperature T_e.

Electric pumping takesplace through following two processes:

i) In this, excitation takes place by electron impact

$$e + X \rightarrow X^* + e$$

where X and X^* represent the ground and excited state of same atom, respectively. This is known as collision of first kind. This type of process takes place in the gas Consisting of only one species.

ii) For a gas consisting of two species excitation occurs due to the collision of atoms of different species such as

$$X^* \times Y \rightarrow X + Y^*$$

Called collision of second kind. In this process it is assumed that energy difference ΔE is lessthan kT. Further, this type of process is preferred way of pumping atom Y, if upperstate of X is a metastable.

IMPORTANCE OF METASTABLE STATE :-

The existence of metastable level is of paramount importance for laser action to occur. The relatively long life time provides mechanism helpful to achieve population inversion. Because of strong interatomic coupling, most of the excited atoms decay through non-radiative way and have short life times and broad line widths. A few atoms of Selected atoms give rise to radiative transitions. In terms of Selection rules metastable level is one from which all dipole transition to lower energy states are forbidden.

Thus in the absence of metastable level, the excited atom will directly return to the groundstate through Spontaneous emission, or through intermediate level or by phonon-emission. Hence the existence of metastable level is a must.

TYPES OF LASERS

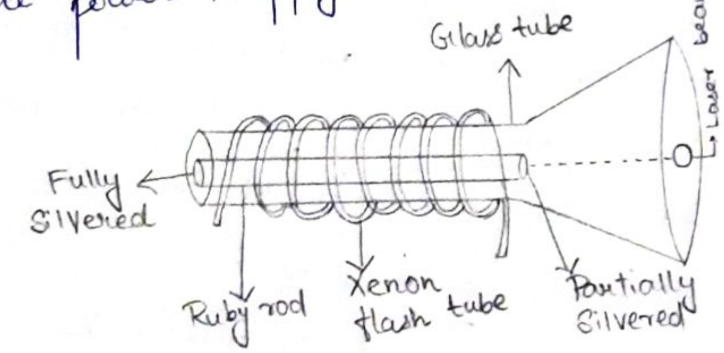
i) **RUBY LASER**: In 1960 T. H. Maiman demonstrated First Laser action by using ruby crystal. Ruby is made of Aluminium oxide (saphire) Al_2O_3 with a small percentage (0.05%) of Cr^{+3} replacing Al^{+3}. This is done by adding small amounts of Cr_2O_3 in the melt of highly purified Al_2O_3. The chromium ions imparts pink colour to the ruby. The chromium ions are responsible for the emission of light by ruby.

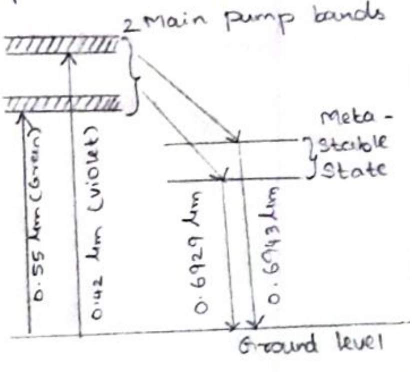
construction: It is a cylindrical ruby rod of about 0.8 cm in diameter and about 15 cm in length. The ends are flat to better than $\lambda/10$ and parallel to within 2 Second of an arc. It is made up of fully reflecting plate at the left and partially reflecting at the right. The cylindrical surface is fine ground to prevent total internal reflection.

The cr ions are excited from level E_1 to level E_3 by the absorption of light of wavelength 550 nm from the Xenon flash tube. The excited ions quickly undergo non-radiative transitions with a transfer of energy to the lattice thermal motion, to the level E_2. The E_2 level is a metastable state with a lifetime of about 3×10^{-3} Sec. Now the population of the E_2 level becomes greater than that of the E_1 level. Thus "population inversion" is achieved.

Some photons are produced by spontaneous transition from E_2 to E_1 and have a wavelength of 694.3 nm. The ends of the rubyrod act as reflecting mirrors. Therefore photons that are not moving parallel to the ruby rod escape from the side, but those moving parallel to it are reflected back and forth. These stimulate the emission of similar other photons. The chain reaction quickly develops a beam of photons all moving parallel to the rod, which is monochromatic and is coherent. When the beam develops sufficient intensity it emerges through the partially silvered end.

Once all the chromium ions in the metastable level have returned to ground level, the laser action stops. It is then necessary to send one more flash of pumping radiation through the rod. Thus the ruby Laser operates only in pulses. This Laser is also called three level Laser. Pumping is done by Xenon flash lamp operated by a seperate power supply.



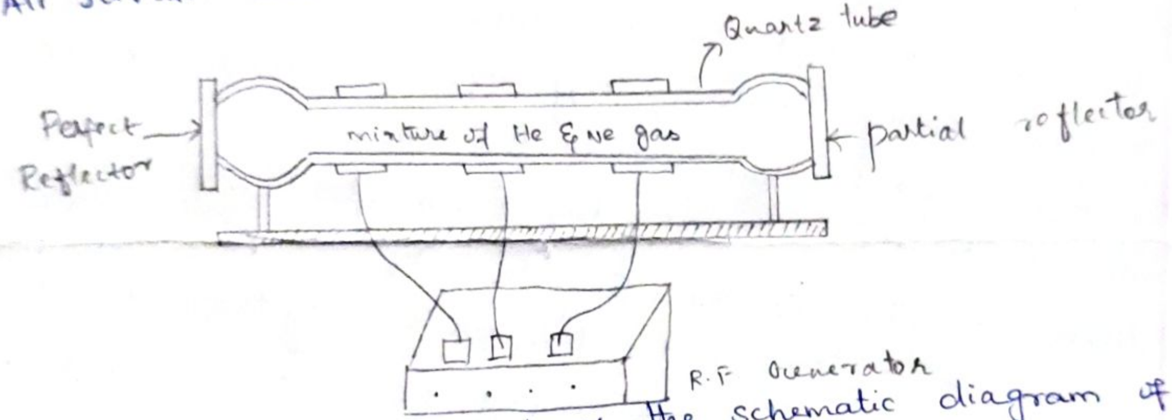


Uses of Ruby laser: Pulsed ruby laser is used Successfully for precision welding and drilling of metal, for drilling of industrial diamonds, for repairing of detached retinas in opthamalogy and for holography and photography of moving objects.

Disadvantages of Three level System:

In the three level systems the terminal level is ground level and hence more than half of the atoms are to be transferred to the level 2. This requires more inversion power. But as N_2-N_1 is small, power required to maintain the inversion is small. The presence of large number of atoms in level 2 gives rise to large number of spontaneous radiationless transitions. The energy is usually carried by lattice phonons. The three level system has got low efficient.

HELIUM-NEON GAS LASER: This Laser was worked first by Ali Javan and his Co-workers in Bell Laboratory in USA.

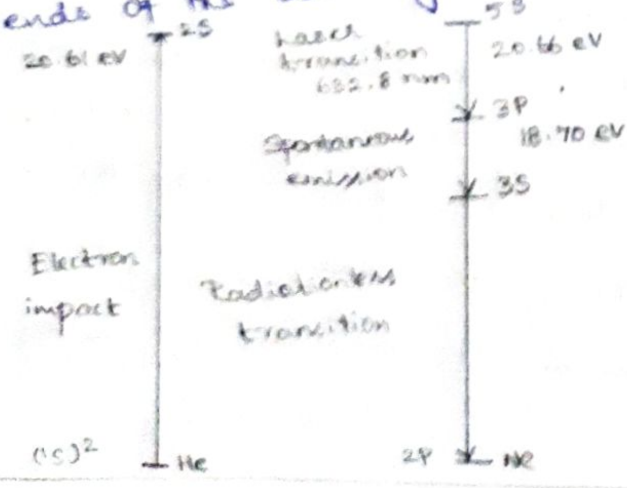


This figure shows the schematic diagram of a He-Ne laser. The laser tube is approximately 5 mm in diameter and 0.5 m long. It contains a helium-neon mixture in the ratio 5:1 at a total pressure of about 1-2 mm of mercury ~~1 torr~~. The tube has parallel mirrors, one of them partly transparent, at both ends. The spacing of the mirrors is equal to an integral number of half wavelengths of the laser light. The He-Ne mixture contained in the gas discharge tube is ionized by passing a dc current through the gas. He atoms are excited very efficiently by electron impact into the 2s level, while the neon atoms are much less readily excited by the electrons. This excited 2s state of helium is relatively long lived. The energy of this level is almost the same as the energy of the

5s level, in Neon. Hence the energy of the Helium atoms is easily transferred to the neon atoms when they collide. This preferential transfer of the neon atoms to the 5s state results in a population inversion between the 5s and 3p states. The purpose of the He atoms is thus to help achieve a population inversion in the Ne atoms. The spontaneous transitions from the 5s state to the 3P state, produce photons of wavelength 632.8 nm, which then trigger stimulated transitions. Photons travelling parallel to the tube are reflected back and forth between the mirror placed at the ends, and rapidly build up into an intense beam which escapes through the end with the lower reflectivity. The Brewster end windows allow light of one polarisation to pass through without any reflection losses. Because the electron impacts that excite the He and Ne atoms occur all the time, a He-Ne laser operates continuously. This laser is also called four level laser.

In the case of four level system as the terminal level is almost empty, few atoms raised to level 2 from ground level suffices for population inversion. Thus laser action in four level is sustained only with small pump power and small pump rate.

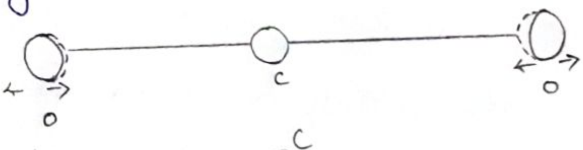
One disadvantage of using internal mirror is that mirrors are usually eroded by the gas discharge and have to be replaced. By using these external mirrors, the ends of the discharge tube also cause a loss due to reflection.



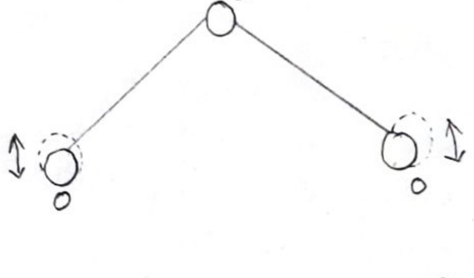
CARBONDIOXIDE LASER :

This is a class of vibrational rotational lasers.
The active material is a mixture of CO_2, molecular N_2 and He.
Oscillation takes place between the two Vibrational
levels of CO_2, while N_2 and He employed to increase the
For a given electronic configuration in a molecule, there are a no of vibrational levels.
efficiency of laser actions. The electric discharge that
Further for each vibrational level there are a no of rotational levels.
excites the most gas laser is a glow discharge, or an
arc that is maintained by an anode and a cathode at
a end of a long thin plasma or discharge tube. All
such lasers operate at a pressure well below atmosp-
heric pressure. The CO_2 lasers are either CW or pulsed
or Q switched.

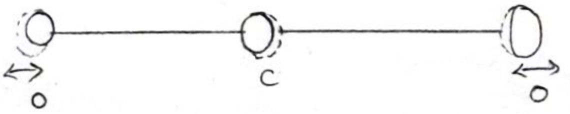
In CO_2 there are three distinct mode of Vibration
i) Symmetric stretching mode (ν_1) ii) bending mode (ν_2)
and iii) asymmetric stretching mode (ν_3). The level is thus
described by a set of three quantum numbers. A quantum



Symmetric Stretching mode



Bending mode

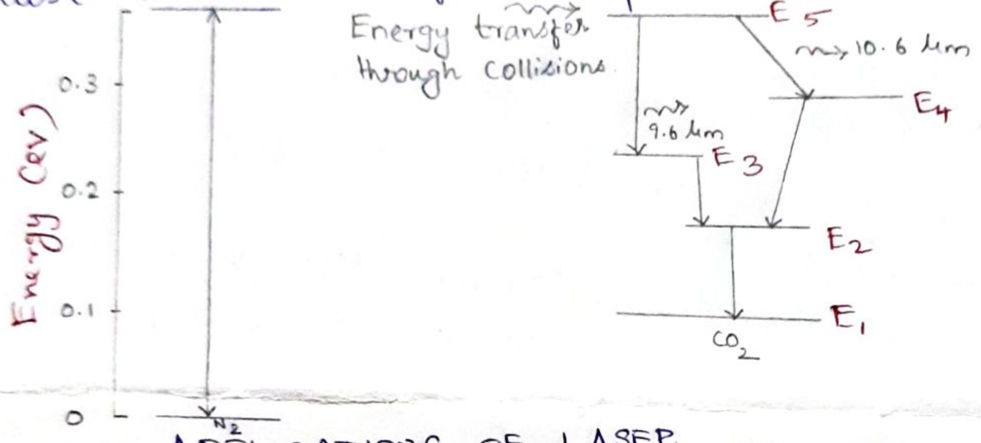


Asymmetric stretching mode

number gives vibrational quantum number in given mode.
Superscript on the bending quantum number characterises
angular momentum of the given mode about the axis
of CO_2 molecule. The energy level diagram is shown in
the above figure. Laser action takes place between the

$00^{0}1$ and $10^{0}0$ levels ($\lambda = 10.6\ \mu m$) and $00^{0}1$ and $02^{0}0$ ($\lambda = 9.6\ \mu m$). The $00^{0}1$ level is very efficiently pumped by two processes i) electron collisions with CO_2 molecules and ii) resonant energy transfer from N_2 molecule. Both the processes are equally efficient.

The CO_2 laser actually is most powerful laser which gives about 1 MW continuous output power with 15-20 percent efficiency. These lasers are in use for cutting metal and fabric and for welding metals. They must also be useful in optical radar systems.



APPLICATIONS OF LASER

Lasers have found use and applications in almost all the fields of science and technology. Some of the important applications may be described as under.

i) Chemical applications:

Laser beams are used to

a) accelerate some chemical reaction

b) create new chemical compounds by destroying atomic bonds between molecules.

ii) Industrial applications:

a) Using high power lasers. we can weld or melt any material.

b) We can also make very small holes in the hard materials (diamonds and hard steels) that cannot be done by mechanical drilling.

c) It can be used to test quality of the materials.

iii) Scientific and Engineering applications:

a) Since laser light can stay on at a single frequency it can be modulated to transmit hundreds of messages at a time on radio television and telephone.

b) Communication between planets is possible with Laser.

c) Since the laser light waves are not absorbed by water it is possible to establish under water communication between submarines.

d) Using Laser we can get three-dimensional photography

e) Laser can be used for forecasting earthquake.

f) Computer print outs are done with Laser printers.

iv) Military applications:

The laser is being developed to serve as a war weapon. A powerful beam can destroy in a few seconds big size objects like airplanes missile etc by Pointing the laser beam into them (Since Laser beam being highly energetic).

Laser beam can determine precisely the distance, Velocity and direction as well as the size and form of distant objects by means of the reflected signal as in radar. It is known as Ladar (Laser Rador)

v) Biological applications:

a) Drill minute holes without damaging the cell itself.

b) carry out minute micro-surgical operations wit
in cells.

vi) Medical applications:

It is used for

a) treatment of detached retinas

b) performing human and animal cancers, eye and Skin tumors.

PROPERTIES OF LASER

The Properties of Laser are

i) The light is very nearly monochromatic

ii) A laser beam diverges hardly at all substances.

iii) The light is coherent with the waves all exactly in phase with one another.

iv) The beam is extremely intense.

Disadvantages of Laser.

i) Laser treatment is costly

ii) Needs proper Safety guards.