

QUANTUM THEORY

- The hydrogen atom consists of a single electron, bound to its nucleus (single proton) by the attractive Coulomb force. The potential energy function $U(r)$ for this system is :

$$U(r) = -\frac{1}{4\pi\epsilon_0} \frac{e^2}{r},$$

e = magnitude of the charge of the electron and the proton

r = the distance between electron and the proton

$$\frac{1}{4\pi\epsilon_0} = k \quad \text{Constant}$$

- It has spherical symmetry, so that the potential energy depends on only one variable- the separation ‘ r ’ between the electron and the central proton.

The potential energy is negative for all values of r .

This is because we have (arbitrarily) chosen our zero of potential to correspond to $r = \infty$.

THE BOHR ATOM

1913: Extension of Rutherford model, with three new assumptions

1. Electrons only go in **circular** orbits due to attraction of nucleus
2. When the electron changes its configuration, energy is $E = hf = h\omega$ emitted in the form of a **single photon** of energy
3. The electrons *must* have angular momentum that is an **integer multiple of \hbar**

$$\frac{m_e}{r} \left(\frac{nh}{m_e r} \right)^2 = \frac{ke^2}{r^2}$$

$$\frac{n^2 h^2}{m_e r^3} = \frac{ke^2}{r^2}$$

Electrostatic

Attraction:

$$F = \frac{ke^2}{r^2}$$

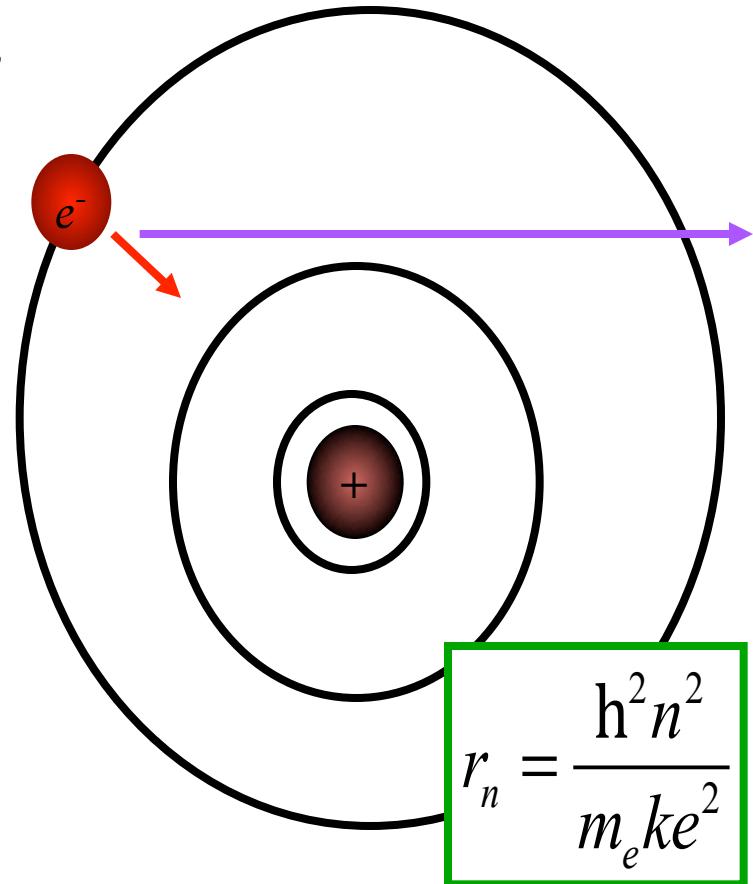
$$\text{Centripetal Force: } F = \frac{m_e v^2}{r}$$

$$L = nh = m_e vr$$

$$v = \frac{nh}{m_e r}$$

subs

$$\frac{m_e v^2}{r} = \frac{ke^2}{r^2}$$



The Bohr Atom (Cont'd)

$$\nu = \frac{nh}{m_e r}$$

$$r_n = \frac{h^2 n^2}{m_e k e^2}$$

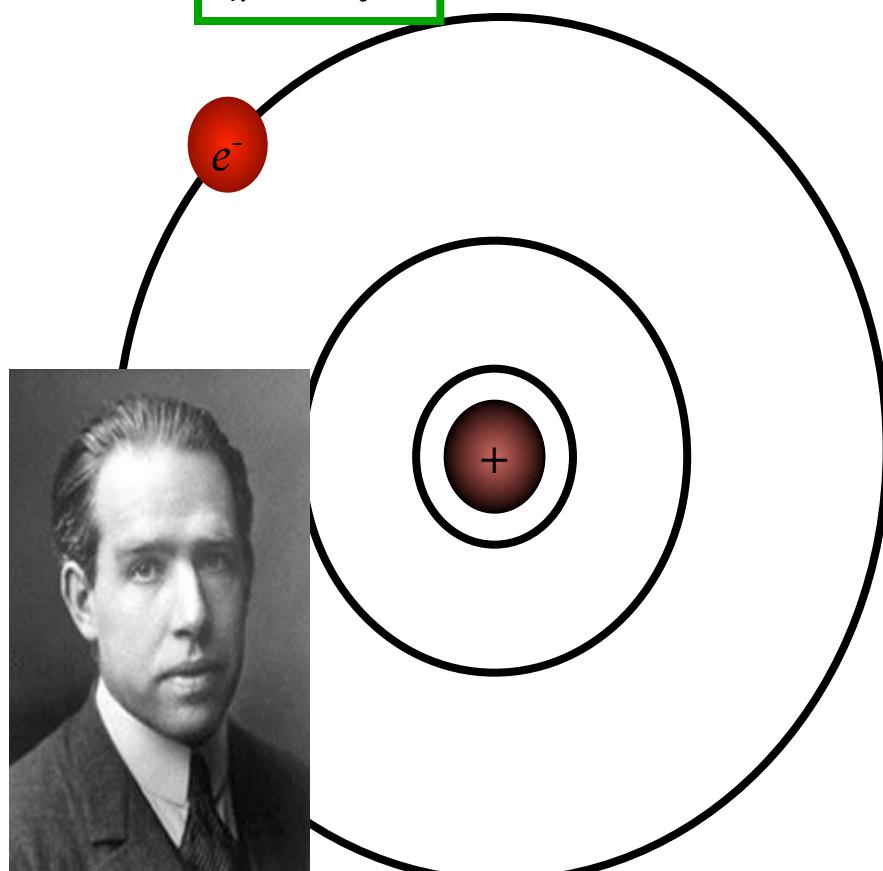
Define:
Bohr Radius

$$a_0 \equiv \frac{h^2}{m_e k e^2} = 0.05297 \text{ nm}$$

- Diameter of H-atom for $n = 1$ is 0.106 nm!

$$\nu = \frac{nh}{m_e} \left(\frac{m_e k e^2}{h^2 n^2} \right) = \frac{k e^2}{h n}$$

But wait, there's more!



The Bohr Atom (Cont'd)

$$\nu = \frac{ke^2}{hn} \quad r_n = \frac{h^2 n^2}{m_e ke^2}$$

Energy has two components:

- Kinetic energy:
- Potential energy*

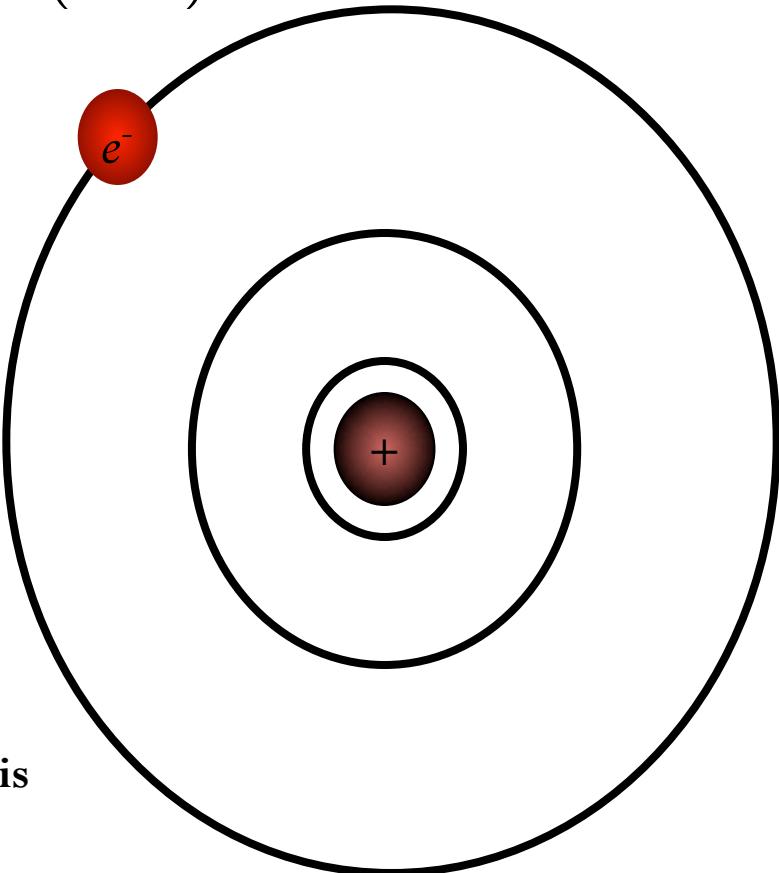
$$E_{\text{kin}} = \frac{1}{2} m_e v^2 = \frac{1}{2} m_e \left(\frac{ke^2}{hn} \right)^2 = \frac{m_e k^2 e^4}{2 h^2 n^2}$$

$$\begin{aligned} E_{\text{pot}} &= \int F dr = \int \frac{ke^2}{r^2} dr = -\frac{ke^2}{r} \\ &= -ke^2 \left(\frac{m_e ke^2}{h^2 n^2} \right) = -\frac{m_e k^2 e^4}{h^2 n^2} \end{aligned}$$

$$E = E_{\text{kin}} + E_{\text{pot}}$$

$$E = -\frac{m_e k^2 e^4}{2 h^2 n^2} = -\frac{\alpha^2 m_e c^2}{2 n^2} = -\frac{13.6 \text{ eV}}{n^2}$$

* Note: the sign of this equation assumes the force F is attractive.



Question :

Photon energy. Calculate the energy of a photon of blue light, $\lambda = 450 \text{ nm}$ in air (or vacuum).

Solution:

The photon has energy $E = hf$

Since $f = c/\lambda$, we have

$$E = hf = \frac{hc}{\lambda} = \frac{(6.63 \times 10^{-34} \text{ J}\cdot\text{s})(3.0 \times 10^8 \text{ m/s})}{(4.5 \times 10^{-7} \text{ m})} = 4.4 \times 10^{-19} \text{ J},$$

or $(4.4 \times 10^{-19} \text{ J}) / (1.60 \times 10^{-19} \text{ J/eV}) = 2.8 \text{ eV.}$

Energetics

Generally, the permitted energy state of the hydrogen atom of atomic number z and principal quantum number n is given by

$$E_n = -\frac{m_e e^4 z^2}{8\epsilon_0^2 h^2 n^2} \quad \text{J}$$

$$= -\frac{m_e e^3 z^2}{8\epsilon_0^2 h^2 n^2} \quad \text{eV}$$

For the hydrogen atom $z = 1$, the ionization potential E_i is given by

$$E_i = E_\infty - E_1 = -eV_i [\text{J}] = E_1 [\text{J}]$$

$$E_i = -V_i [\text{eV}] = E_1 [\text{eV}]$$

$$E_i = \frac{m_e e^4 z^2}{8\epsilon_0^2 h^2} \left[\frac{1}{1^2} - \frac{1}{\infty^2} \right] = \frac{m_e e^4 z^2}{8\epsilon_0^2 h^2} [\text{J}]$$

$$= \frac{m_e e^3 z^2}{8\epsilon_0^2 h^2} [\text{eV}]$$

$$-V_i = \frac{m_e e^3 z^2}{8\epsilon_0^2 h^2} \quad [\text{eV}]$$

$$V_i = -\frac{m_e e^3 z^2}{8\epsilon_0^2 h^2} \quad [\text{eV}]$$

For the hydrogen atom

$$E_1 = -\frac{m_e e^3 z^2}{8\epsilon_0^2 h^2} \quad [\text{eV}] \quad \text{and}$$

$$E_n = -\frac{m_e e^3 z^2}{8\epsilon_0^2 h^2 n^2} \quad [\text{eV}]$$

$$\Rightarrow E_n = \frac{E_1 z^2}{n^2} \quad [\text{eV}]$$

with

$$E_1 = -V_i \quad [\text{eV}]$$

$$E_n = -\frac{V_i z^2}{n^2} \quad [\text{eV}]$$

$$E_n = -\frac{13.6}{n^2} \quad [\text{eV}]$$

Holds for all hydrogenic atoms

For singly ionised Helium atom ($z = 2$),

$$E_n = \frac{-13.6 \times 4}{n^2} \text{ [eV]} = -\frac{54.4}{n^2} \text{ [eV]}$$

This is a lot of energy required.

Try that of of Li: Now!!

THE HYDROGEN SPECTRUM

The wavelengths of the hydrogen spectrum are given by the Rydberg formula

$$1/\lambda = R \left(\frac{1}{n_l^2} - \frac{1}{n_u^2} \right)$$

R is the **Rydberg Constant**

$$R = 1.0967758 \times 10^{-3} \text{ per } \text{\AA}^\circ$$

The Hydrogen Spectrum (Cont'd)

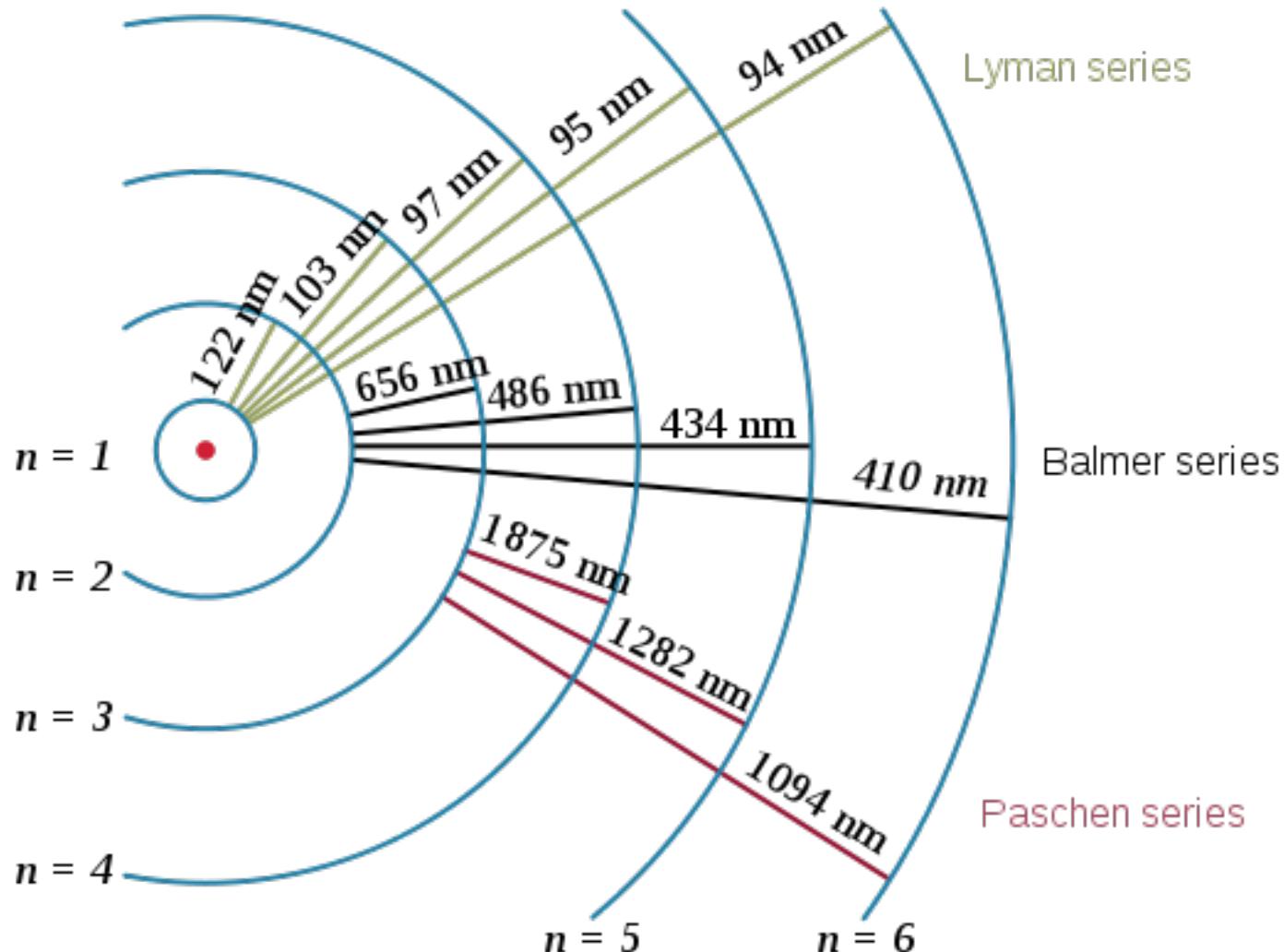
$n_l = 1$ and $n_u = 2, 3, 4 \dots$ gives the **Lyman series**
(ultraviolet region)

$n_l = 2$ and $n_u = 3, 4, 5 \dots$ gives the **Balmer series (optical region)**

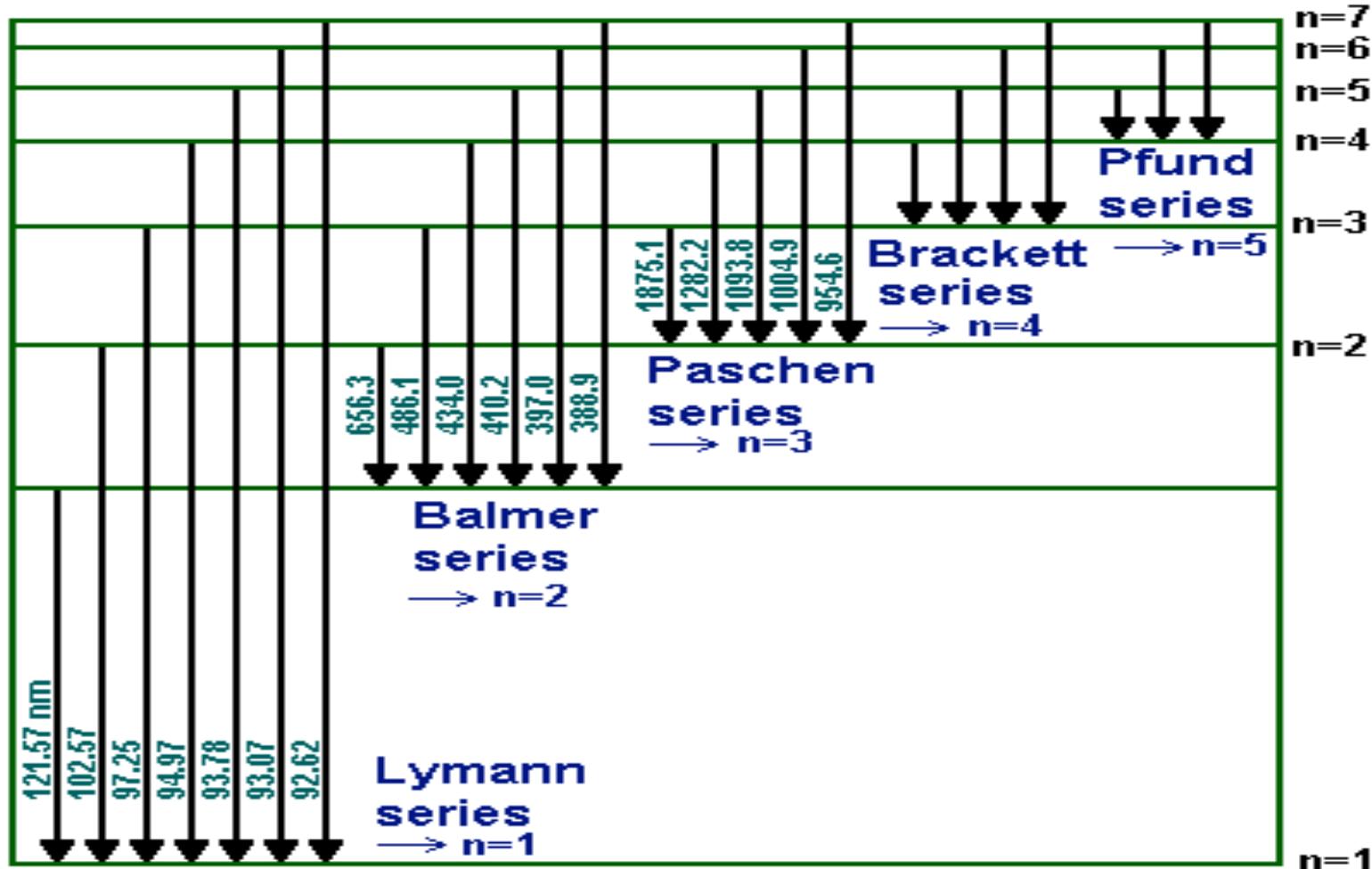
$n_l = 3$ and $n_u = 4, 5, 6 \dots$ gives the **Paschen series**
(infrared region)

$n_l = 4$ and $n_u = 5, 6, 7 \dots$ gives the **Brakett series (far infrared region)**

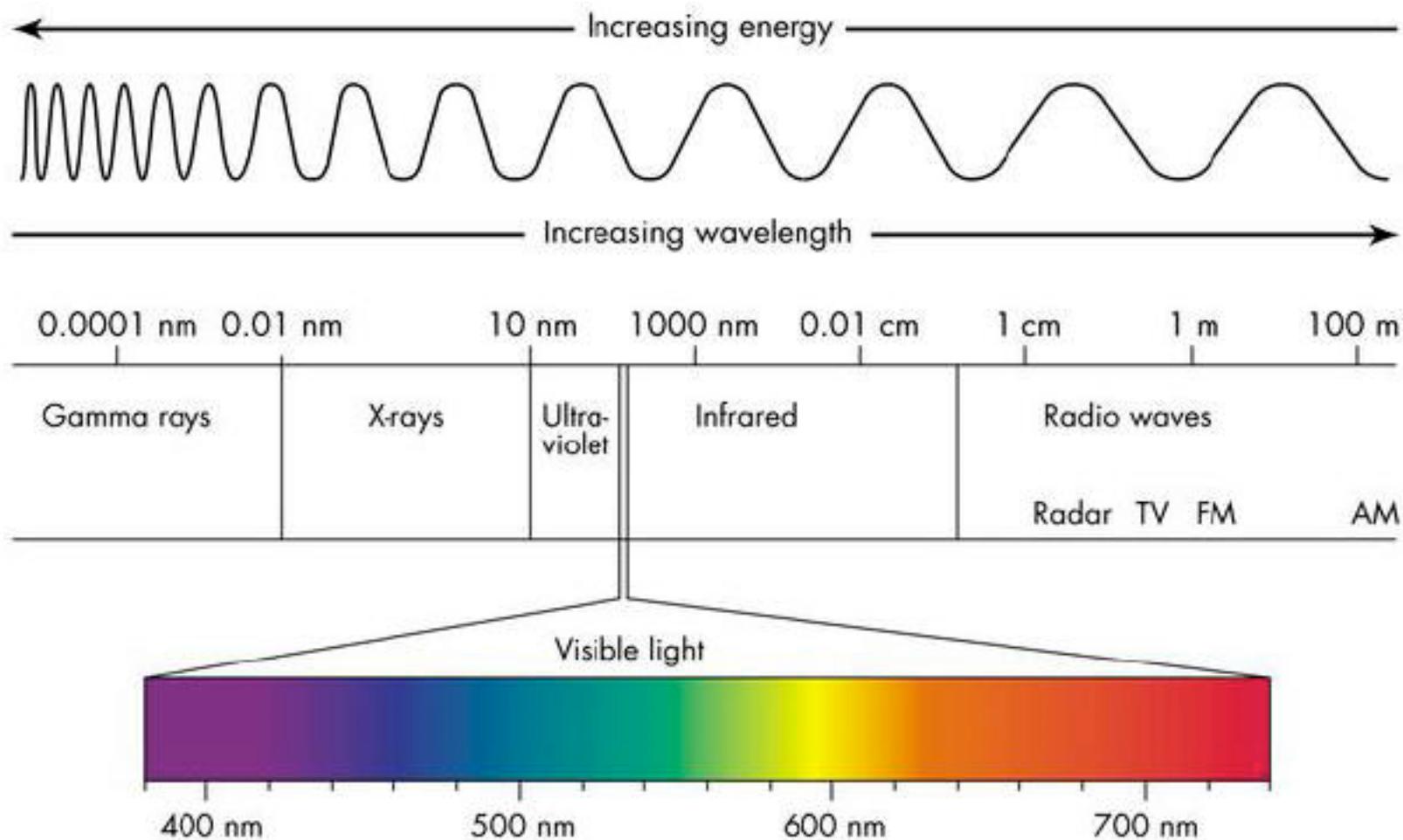
The Hydrogen Spectrum (Cont'd)



The Hydrogen Spectrum (Cont'd)



The Hydrogen Spectrum



The Electromagnetic Spectrum

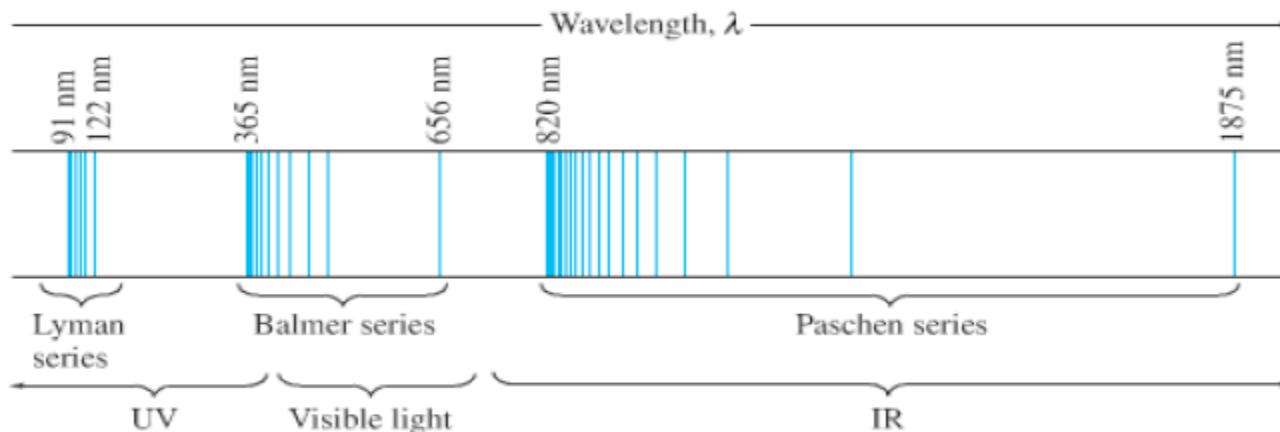
Question : **Wavelength of a Lyman line.** Use Fig. 27–27 to determine the wavelength of the first Lyman line, the transition from $n = 2$ to $n = 1$. In what region of the electromagnetic spectrum does this lie?

Solution:

In this case, $hf = E_2 - E_1 = \{-3.4 \text{ eV} - (-13.6 \text{ eV})\} = 10.2 \text{ eV} = (10.2 \text{ eV})(1.60 \times 10^{-19} \text{ J/eV}) = 1.63 \times 10^{-18} \text{ J}$. Since $\lambda = c/f$, we have

$$\lambda = \frac{c}{f} = \frac{hc}{E_2 - E_1} = \frac{(6.63 \times 10^{-34} \text{ J}\cdot\text{s})(3.00 \times 10^8 \text{ m/s})}{1.63 \times 10^{-18} \text{ J}} = 1.22 \times 10^{-7} \text{ m},$$

or 122 nm, which is in the UV region of the EM spectrum



Question :

Wavelength of a Balmer line. Determine the wavelength of light emitted when a hydrogen atom makes a transition from the $n = 6$ to the $n = 2$ energy level according to the Bohr model.

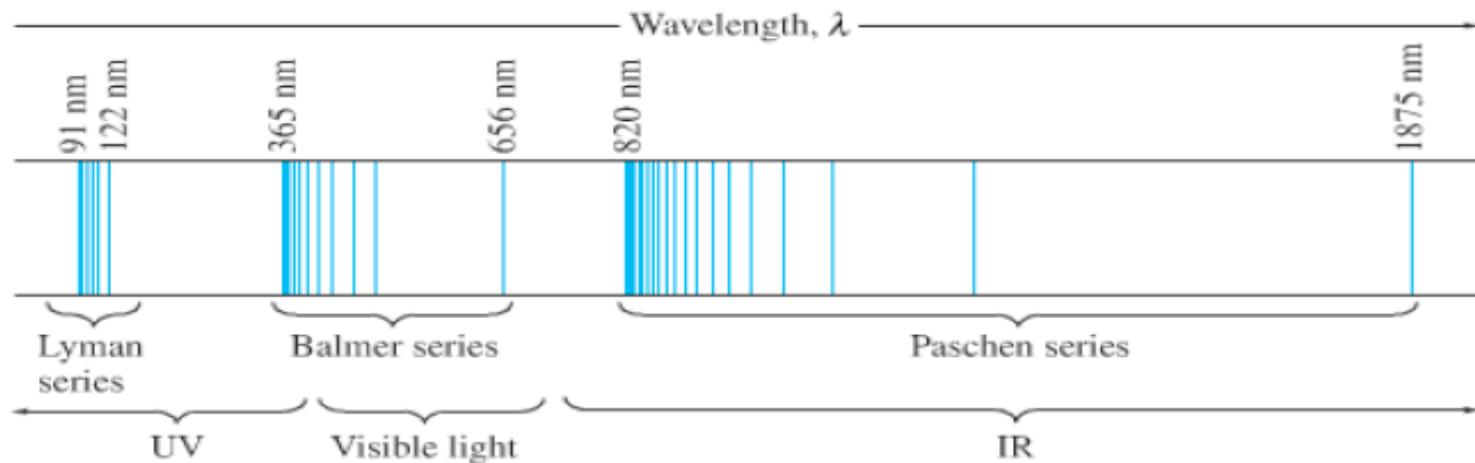
Solution:

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

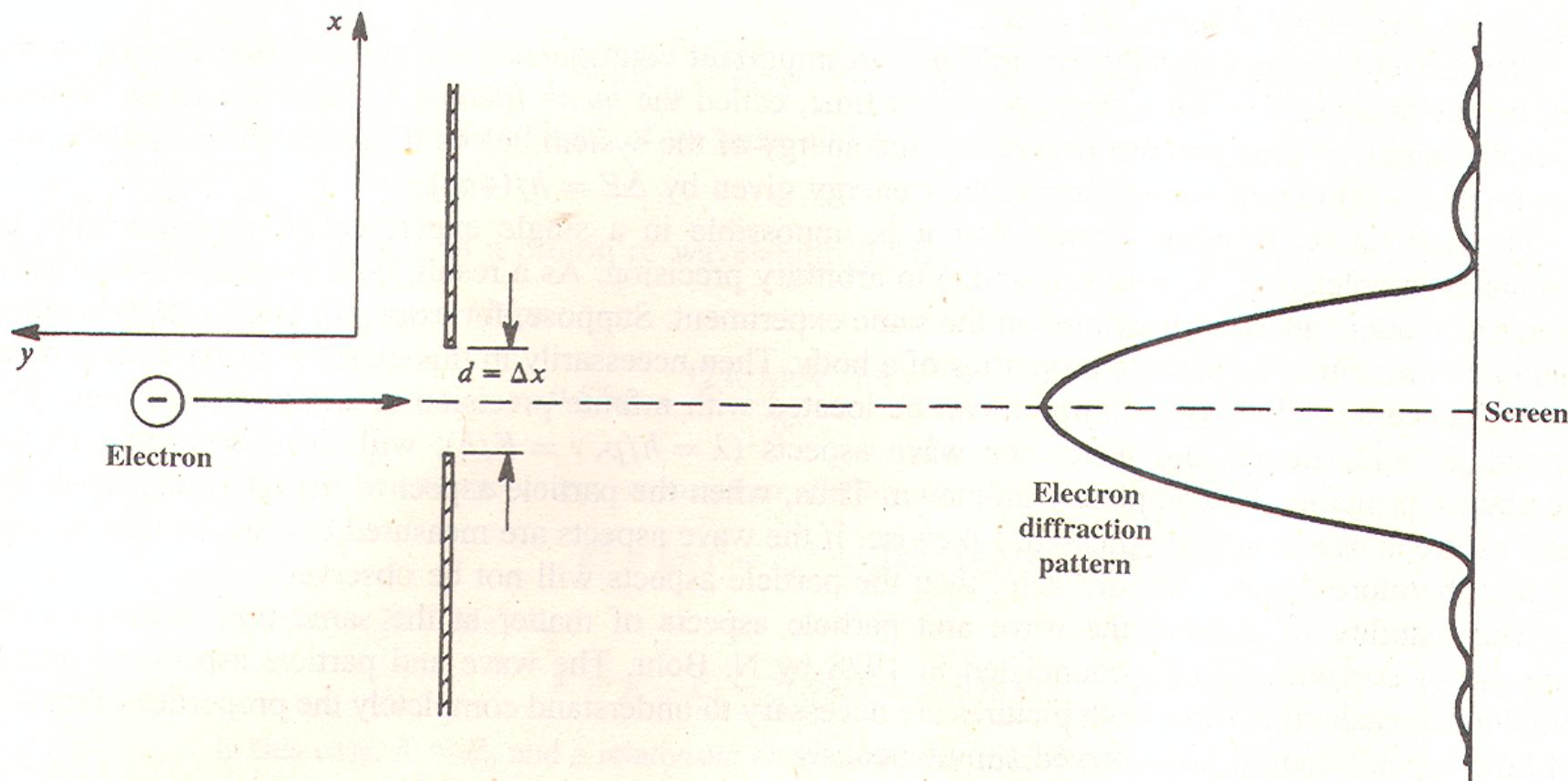
$$R = 1.097 \times 10^7 \text{ m}^{-1}.$$

$$\frac{1}{\lambda} = (1.097 \times 10^7 \text{ m}^{-1}) \left(\frac{1}{4} - \frac{1}{36} \right) = 2.44 \times 10^6 \text{ m}^{-1}.$$

$$\text{So } \lambda = 1/(2.44 \times 10^6 \text{ m}^{-1}) = 4.10 \times 10^{-7} \text{ m or } 410 \text{ nm.}$$



Heisenberg Uncertainty Principle



- The x-position of the particle, upon (and before) entering the slit will have been determined up to an *uncertainty* Δx given by $\Delta x = d$.
- The smaller we make the slit width, the smaller is the uncertainty in the x-position of the body, and hence the more precisely is its location known.
- Because of the wave nature of matter the particle will be diffracted as it passes through the slit.
- Though it is not possible to predict where on the screen it will strike, as long as the body strikes the screen *somewhere* you know that it has gone through the slit. .
- The diffraction process, however, has an effect on the momentum of the particle. .

Heisenberg Uncertainty Principle:

$$\Delta p_x \Delta x \geq \frac{h}{2\pi}$$

$$\Delta E \Delta t \geq \frac{h}{2\pi}$$

Question :

Position uncertainty of electron. An electron moves in a straight line with a constant speed $v = 1.10 \times 10^6 \text{ m/s}$ which has been measured to a precision of 0.10%. What is the maximum precision with which its position could be simultaneously measured?

Solution:

The momentum of the electron is

$$p = mv = (9.11 \times 10^{-31} \text{ kg}) \cdot (1.10 \times 10^6 \text{ m/s}) = 1.00 \times 10^{-24} \text{ kg} \cdot \text{m/s}.$$

The uncertainty in the momentum is $\Delta p = 0.0010p$.

$$\text{Hence, } \Delta p = 1.0 \times 10^{-27} \text{ kg} \cdot \text{m/s}.$$

From the uncertainty principle, the best simultaneous position measurement will have an uncertainty of

$$\Delta x \approx \frac{\hbar}{\Delta p} = \frac{1.06 \times 10^{-34} \text{ J} \cdot \text{s}}{1.0 \times 10^{-27} \text{ kg} \cdot \text{m/s}} = 1.1 \times 10^{-7} \text{ m},$$

or 110 nm.

Question :

Position uncertainty of a baseball. What is the uncertainty in position, imposed by the uncertainty principle, on a 150-g baseball thrown at (93 ± 2) mph = (42 ± 1) m/s?

Solution:

The uncertainty in the speed is $\Delta v = 1$ m/s. We multiply Δv by m to get Δp and then use the uncertainty principle, solving for Δx .

The uncertainty in the momentum is

$$\Delta p = m \Delta v = (0.150 \text{ kg})(1 \text{ m/s}) = 0.15 \text{ kg} \cdot \text{m/s}.$$

Hence the uncertainty in a position measurement could be as small as

$$\Delta x = \frac{\hbar}{\Delta p} = \frac{1.06 \times 10^{-34} \text{ J} \cdot \text{s}}{0.15 \text{ kg} \cdot \text{m/s}} = 7 \times 10^{-34} \text{ m}.$$

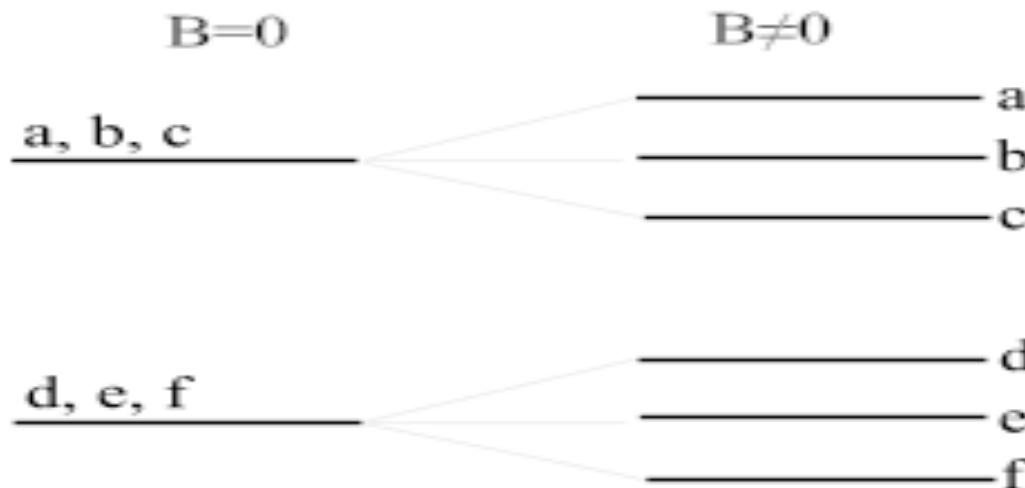
THE ZEEMAN EFFECT

The Zeeman effect is the **splitting of a spectral line into several components** in the presence of a static magnetic field.

The splitting is due to the **interaction between the magnetic field and the magnetic dipole moment associated with the orbital angular momentum**.

In most atoms, there exist **several electronic configurations** that have **the same energy(degeneracy)**, so that transitions between different pairs of configurations correspond to a **single spectral line**.

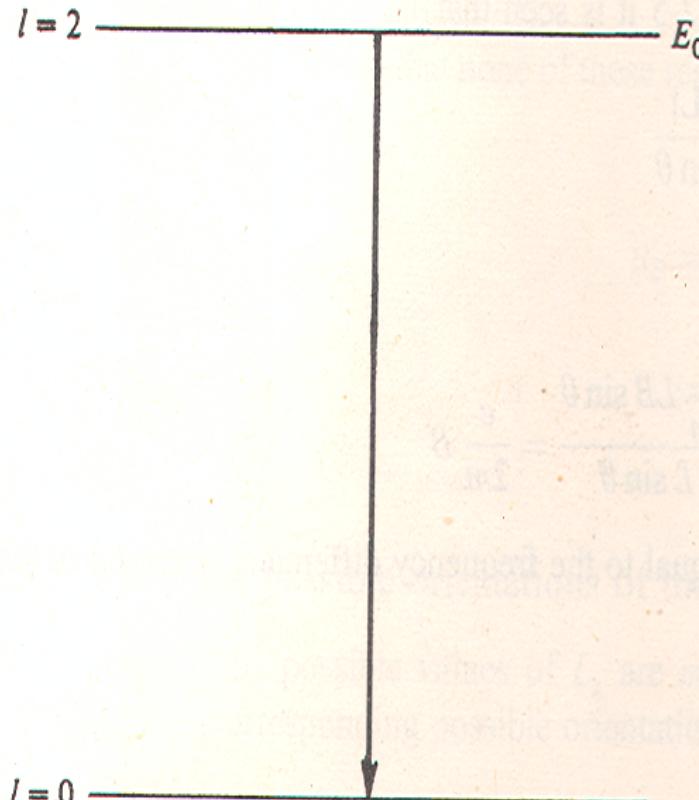
The presence of a magnetic field **breaks the degeneracy**, since it interacts in a **different way with electrons with different quantum numbers**. This modifies their energies. As a result,



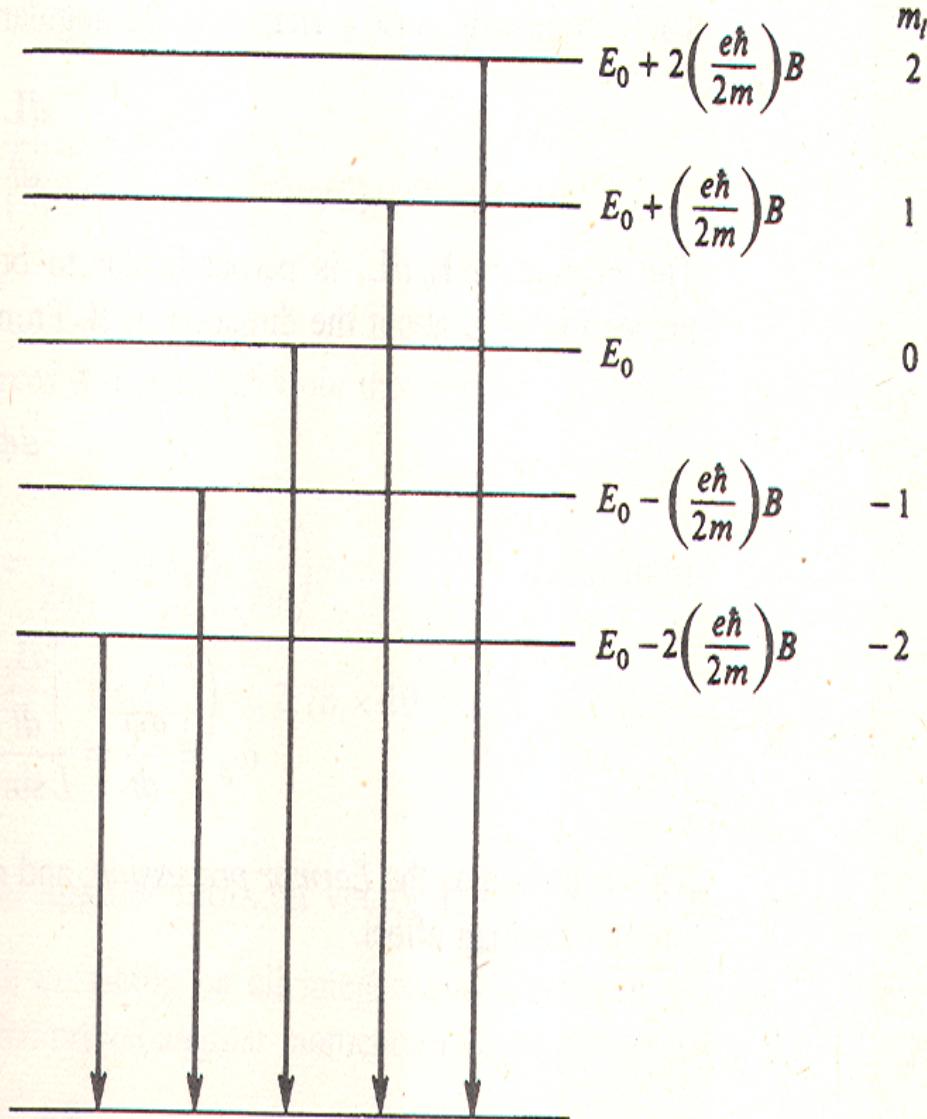
Without a magnetic field, configurations a, b and c have the same energy, as do d, e and f.

The presence of a magnetic field splits the energy levels. A line produced by a transition from a, b or c to d, e or f now will be several lines between different combinations of a, b, c and d, e, f.

Not all transitions will be possible, as regulated by the transition rules.



(a) Single transition without an external magnetic field



(b) Five transitions with an applied external magnetic field

Splitting of Spectra lines

Zeeman splitting is observed in two different cases:

- 1.when the summed spin(S) of the electrons of the atom is equal to zero, but the orbital angular momentum(L) is different than zero, $S=0$, $L \neq 0$
2. when the spin and the orbital angular momentum are different from zero and the external magnetic field is strong enough , $L \neq 0, S \neq 0$

The Zeeman effect is very important in applications such as nuclear magnetic resonance spectroscopy, electron spin resonance spectroscopy, magnetic resonance imaging (MRI) and Mössbauer spectroscopy and also used by astronomers to measure the magnetic field of the Sun and other stars.

Electrons in an Atom

- Electrons under the influence of positive charges of atomic nuclei are confined to the neighbourhood of the atomic nuclei.
- The motion of these electrons has been treated as **waves**.
- Equations that describe the **wave motions** have been applied to represent the electrons.
- Solutions to the equations lead to wave functions.
- Confinement of electron in the neighbourhood of the atomic nuclei, these solutions are associated with some integers called **quantum numbers**.
- For the descriptions of electrons in an atom, we rely on quantum numbers and **wave functions**.
- Wave functions are used to describe the shape of the electron cloud e.g. in a chemical bonding.

The Quantum Numbers n, m, l

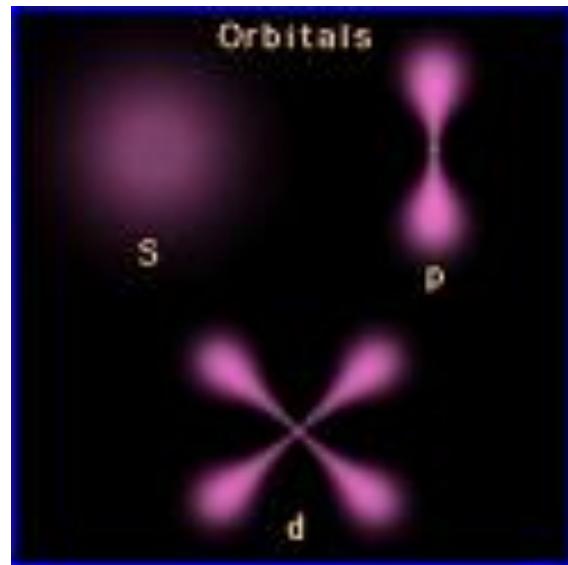
QN n

The principle quantum number n most affects the energy of the state of the electron. It gives the relative **size** and **energy** of atomic orbitals.



QN /

The angular momentum quantum number l is related to the directional property of the wave-function. It gives the **shape** of the orbitals.

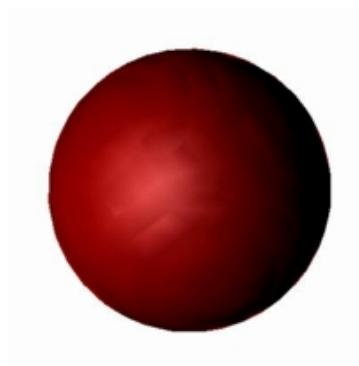


It ranges from 0 to $n-1$. For a spherical wave, $l = 0$, the number of nodal planes is equal to l .

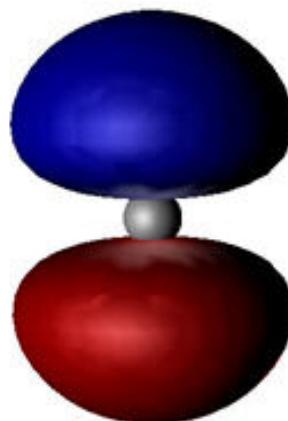
Related to l are 4 orbitals. These are the s , p , d and f orbitals.

They are described briefly as follows:

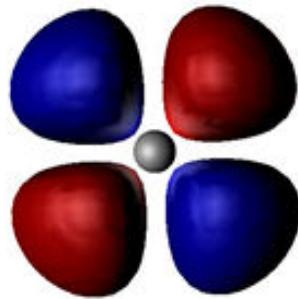
1. S orbital – 0 = “sphere”



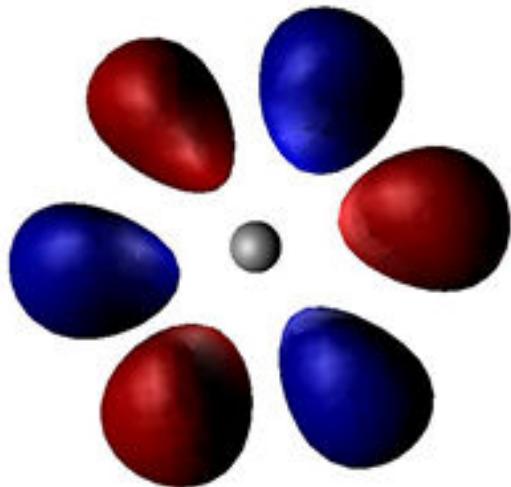
2. P orbital – 1= “polar”



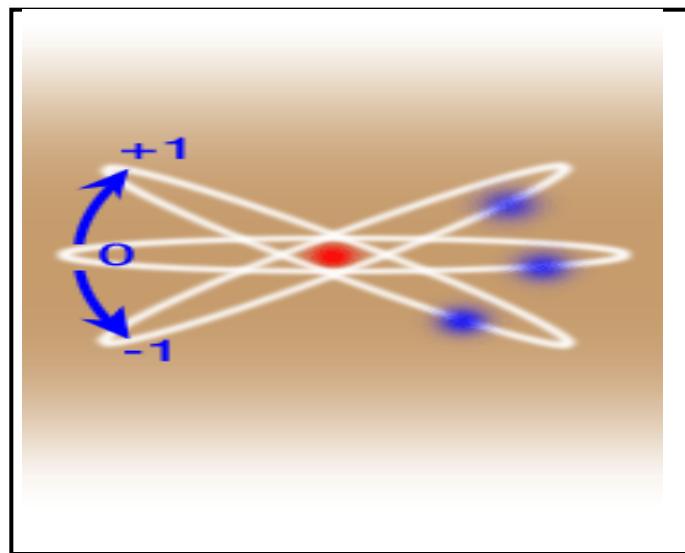
3. D orbital – 2 = “dual polar”



4. F orbital – 3 = “irregular”



The angular momentum l is further quantized by the quantum number ml based on the orientation of the orbital angular momentum. Since the orientation is related to l , ml has values ranging from $-l$ to l i.e. $-l$ - $(l-1)$, ... 0, ..., $l-1$, and l .



Rules for n,m, l

The three quantum numbers n, l, m follow the rules:

1. For the principal quantum number n (1,2,3 ...),
 - i. the azimuthal quantum number $l = 0, 1, 2, \dots, n-1$
 - ii. the magnetic quantum number $m_l = -l, -(l-1), \dots, (l-1), l$
2. Rules are algorithms, by which we generate possible quantum numbers. The lowest value of n is 1 (NOT zero). For $n = 1$, the only possible value for quantum number l is 0, and $m_l = 0$. Each set of quantum numbers is called a **state**. Thus, for $n = 1$, there is only one state (1,0,0). The states are represented by symbols, and special symbols have been used to represent the quantum number l as follows:
 - i. $l = 0, 1, 2, 3, 4, \dots$
 - ii. symbol = s, p, d, f, g, ...
 - iii. Using symbols, the valid quantum states can be listed in the following manner:

1s

2s 2p

3s 3p 3d

4s 4p 4d 4f

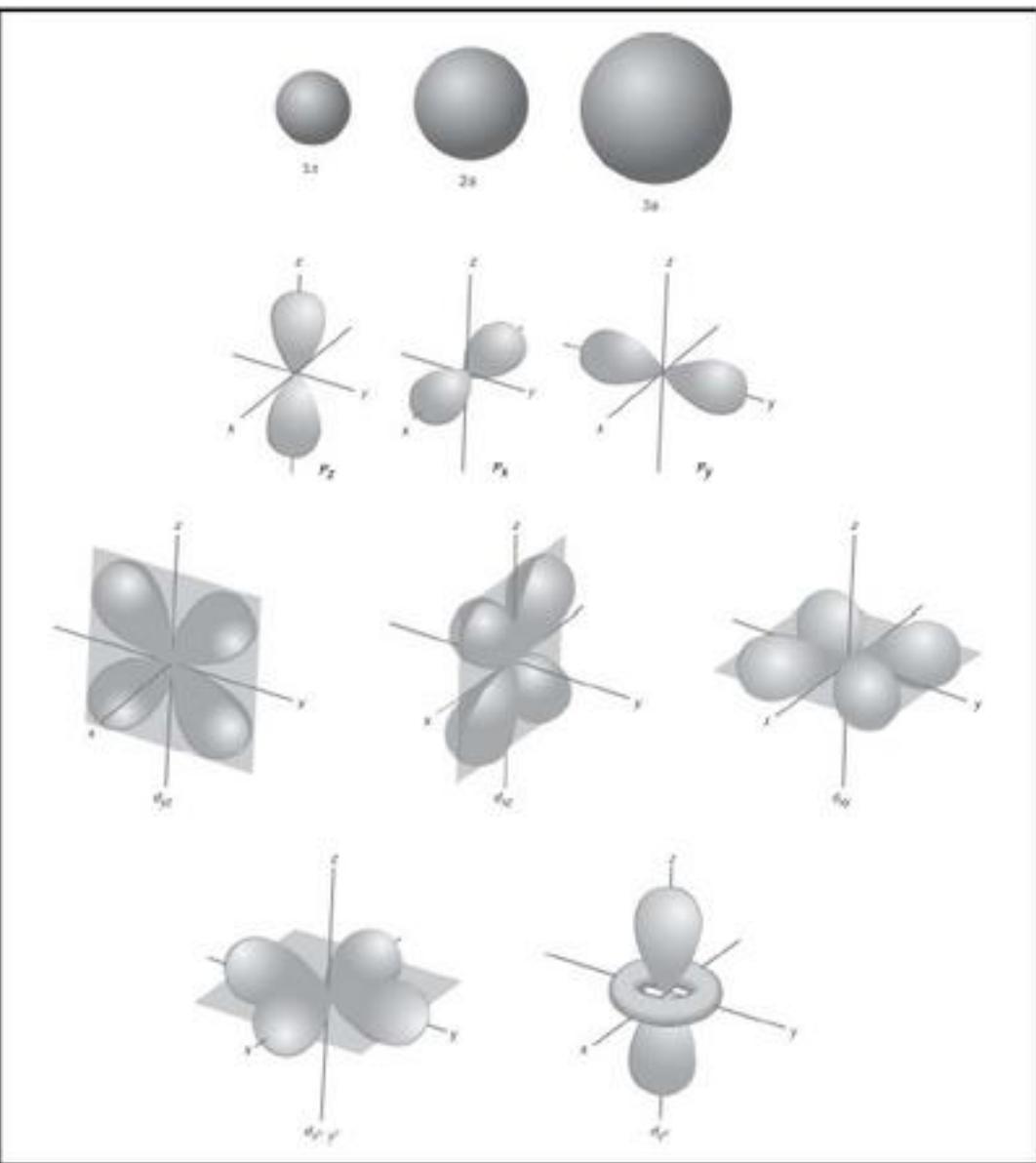
5s 5p 5d 5f 5g

6s 6p 6d 6f 6g 7h

7s 7p 7d 7f 7g 7h 8i

iv. $l = 0 \rightarrow$ s, $l = 1 \rightarrow$ p and $l = 2 \rightarrow$ d orbitals

v. There are $2l+1$ values of m_l , and thus $2l + 1$ allowed orientations or quantum states of the nucleus. All have the same energy in the absence of a magnetic field.



For hydrogen-like atoms, that are atoms or ions with one electron, the energy level is solely determined by the principle quantum number n . and the energy levels of the sub-shells np and nd etc. are the same as the ns .

Question :

How many distinct (n, l, m_l) states of the hydrogen atom with $n = 3$ are there? Find the energy of these states.

Solution:

When $n = 3$, l can be 0, 1, or 2. When $l = 0$, m_l can be only 0 (1 state). When $l = 1$, m_l can be $-1, 0$, or 1 (3 states). When $l = 2$, m_l can be $-2, -1, 0, 1$, or 2 (5 states). The total

number of (n, l, m_l) states with $n = 3$ is therefore $1 + 3 + 5 = 9$.

The energies of these states are all the same because the energy depends only on n .

$$E_3 = \frac{-13.60 \text{ eV}}{3^2} = -1.51 \text{ eV}$$

CHEMICAL BONDING

Ionic Bonding

The ionic bonding is formed if **an electron** is transferred from the less electronegative element to the more electronegative.

The ions of this elements differ by one electronic charge and are thus attracted to one another.

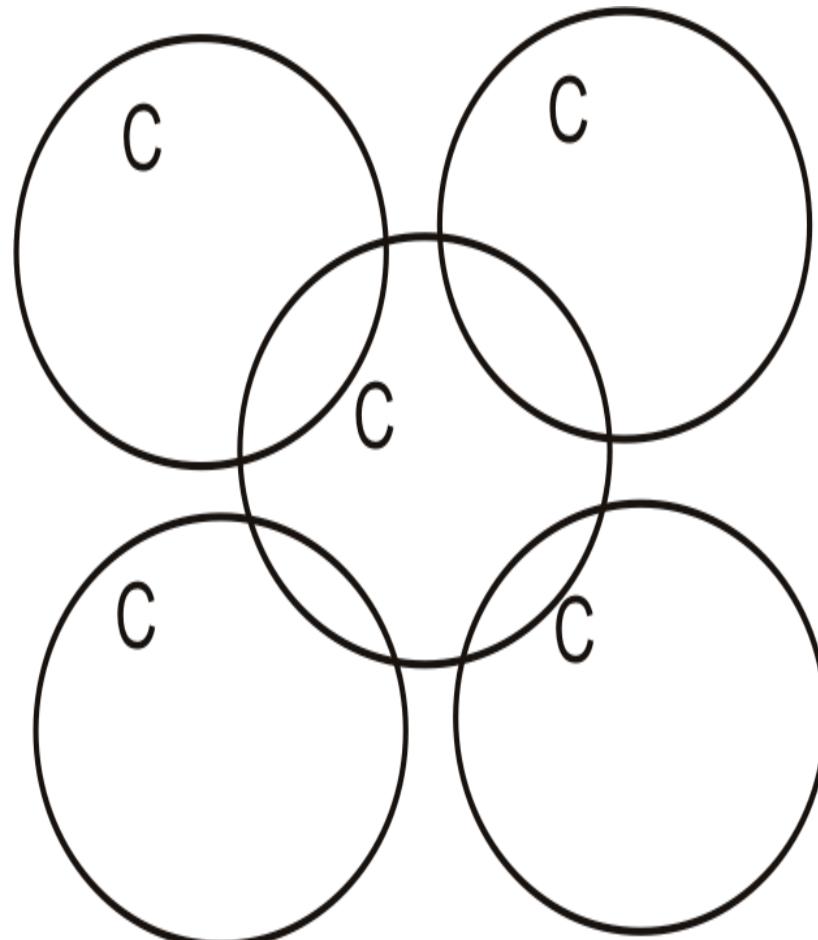
Some ions may gain or lose more than one electron.

Eg: Bonding in NaCl

Covalent Bonding

Covalent materials are formed from **bonding electron sharing between two or more atoms.**

Eg: Carbon atoms form covalent bond with other carbon atoms, because each carbon atoms has four outer electrons which can be share with other four carbon atoms



Materials such as Diamond and polyethylene are covalent material.

Van der Waal's Bond

Any two separated molecules will be attracted to one another by a **weak electrostatic force** called the Van der Waal's force.

This weak force arises from the interaction of the instantaneous electric dipole moments of the molecules. Two polar molecules with permanent electric dipole moments, eg. water molecules bond due to Van der Waal force.

At any instant more electrons may appear on one side of the molecule than the other and the center of the negative charge distribution is slightly displaced (distorted) from the positive charge on the nucleus. This give room for attraction of the electric dipoles with a weak force called the Van der Waal's force.

SPECTROSCOPY

What is It?

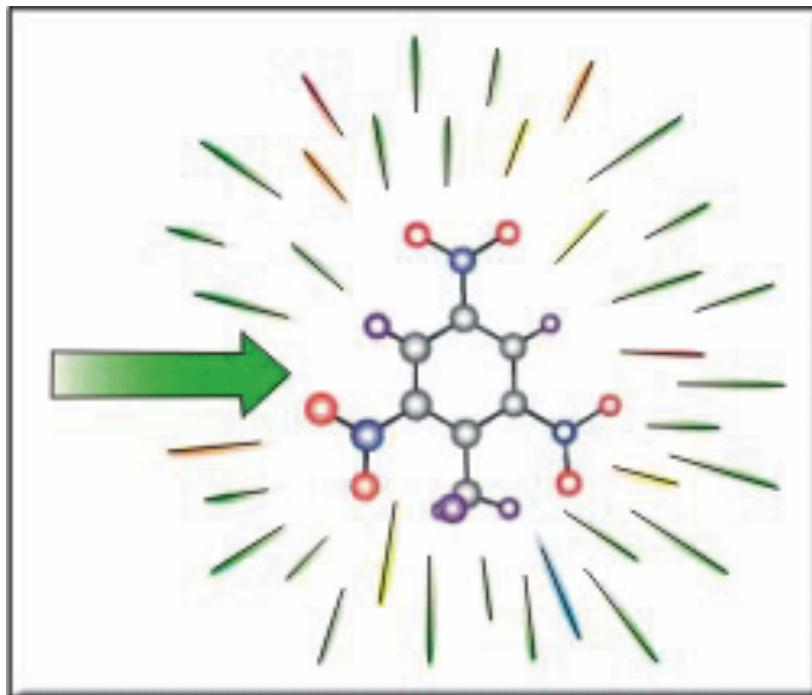
Spectroscopy is the study of how 'species' (i.e., atoms, molecules, solutions) react to light.

Some studies depend on how much light an atom absorbs and hence the need for Spectroscopy .

The electromagnetic radiation absorbed, emitted or scattered by the molecule is analyzed.

What Exactly Is Being Measured?

When Light hits a sample, it becomes excited, and forced to vibrate and move. These vibrations are measured and analysed.

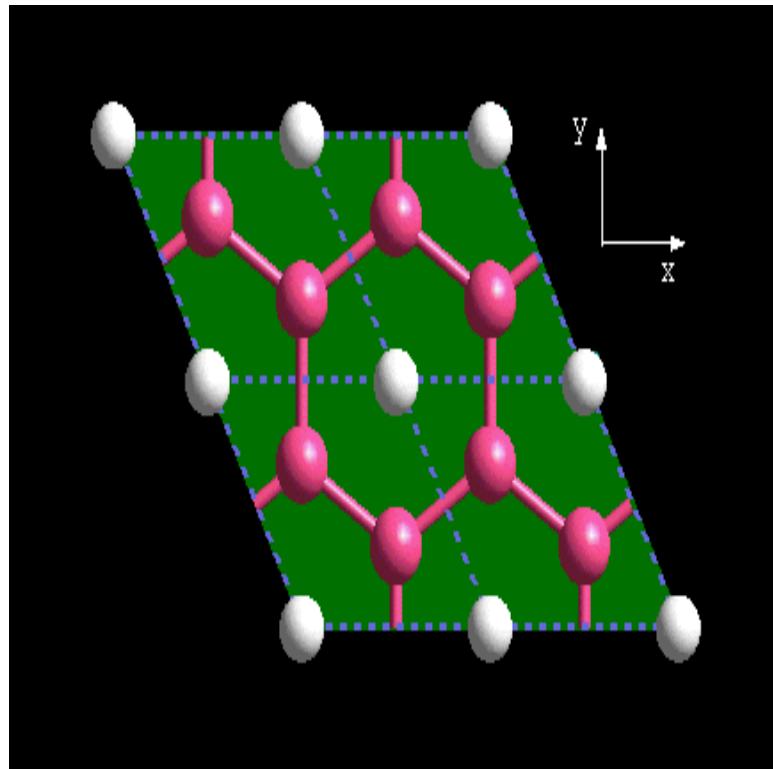


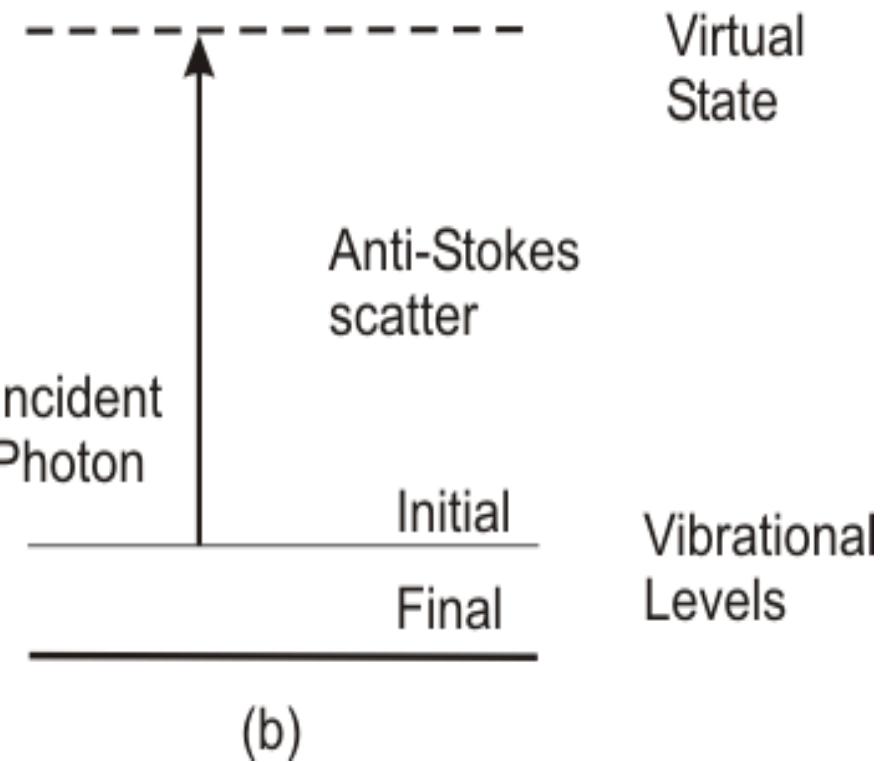
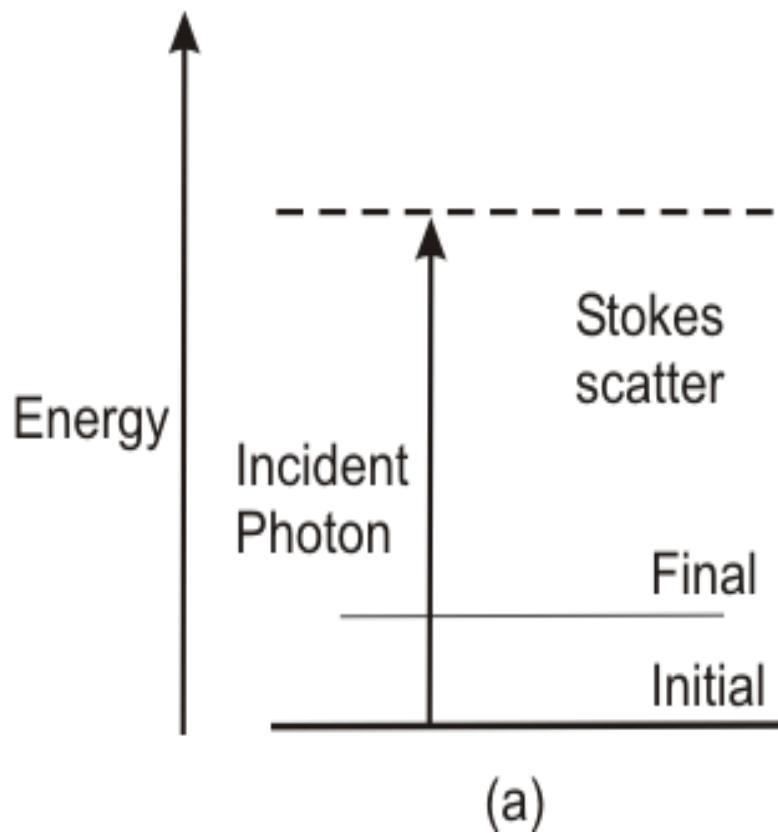
Raman Spectroscopy

Raman spectroscopy is the measure of the wavelength and intensity of inelastically scattered light.

By varying the frequency of the radiation, a spectrum can be produced, showing the intensity of the exiting radiation for each frequency.

This shows which frequencies of radiation have been absorbed by a molecule to raise it to higher energy states.

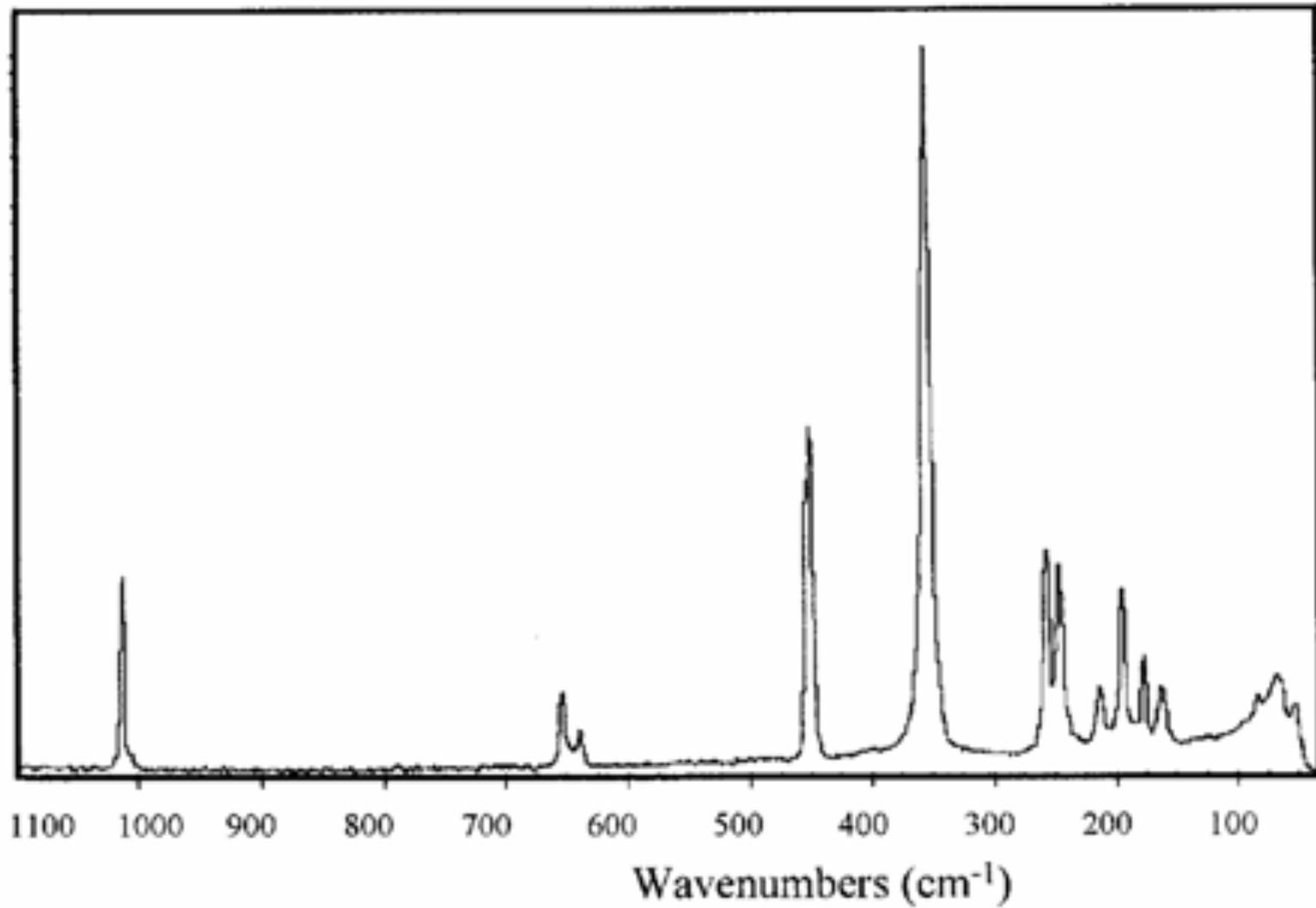




Raman Spectroscopy

- Raman spectroscopy is the measurement of the wavelength and intensity of inelastically scattered light.
- Raman spectroscopy is a two photon process.
- The Raman scattered light occurs at wavelengths that are shifted from the incident light by the energies of molecular vibrations.
- The mechanism of Raman scattering is different from that of infrared absorption, and Raman and IR spectra provide complementary information.

Raman intensity



Surface enhanced Raman scattering, SERS

- In the vicinity of a rough metal surface the Raman cross section can drastically be enhanced, by a factor of up to 10⁶. This allows very sensitive measurements of adsorbates on surfaces.
- Good substrates for SERS are gold, silver and copper.
- Two mechanisms are responsible for the enhancement:
- (1) Enhancement of the local electromagnetic field at the surface of a metal. When the wavelength of the incident electromagnetic field is close to the plasma wavelength of the metal electrons can be excited into an extended surface electronic state (surface plasmon resonance). This leads to exceptionally large local fields.
- (2) The formation of charge transfer complexes between adsorbate and surface (resonance enhancement).

End of Lecture