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THE IIT - JEE SECRET

JEE MAINS AND JEE ADVANCED

PHYSICAL CHEMISTRY

VOL - I

SIERRA INNOVATIONS
Private Limited

Contents

ATOMIC STRUCTURE

Dalton's Atomic Theory -

① Atom is the smaller individual part of matter which take part in chemical reactions.
② Atom is neither created nor destroyed.
③ Atom of same element are similar in size, mass & other properties.
④ Atoms of different elements have different size mass & other properties.
⑤ Atoms of different or same element take part in chemical rx^n's and form molecule in simplest ratio.

Drawbacks -

① Atom is divisible & it can be divided into sub atomic partice.

② Atoms of Isotopes have different at mass, even they belong to same nature of element. $^1H_1$, $^2H_1$, $^3H_1$ (Isotopes)

③ Atoms of isotobes has same atomic mass, even they belong to different nature of element.

④ In non-Stiochiometric compounds, the ratio of different atoms is not simplest, that means different from expected Simplest ration.

Similarly, total energy (TE)

$$\frac{1}{2} m_e v_2^2 + \frac{1}{2} m v_1^2 - \frac{Kze^2}{r}$$

$$\frac{1}{2} \frac{Kze^2}{r^2} \times (r_2 + r_1) - \frac{Kze^2}{r^2}$$

$$= \frac{-Kze^2}{2r}$$

$\therefore$ TE $= -13.6$

★ The difference between stationary & non-stationary nucleus will be significant only when μ & m_e differ appreciably which will occur when M_{nu} & m_e are comparable $\left(\mu = \frac{m_e \times M_{Nu}}{M_{nu} + m_e} \right)$

★ The energies of the shell in case of isotopes (Z same) is dependent on mass on nucleus only when nucleus is considered non stationary.

Q. When Bohr's model is analysed for stationary & non-stationary nucleus following formulas are observed in case of SN

$$r = .529 \times \frac{n^2}{Z} \text{ Å}$$

$$V_e = 2.18 \times 10^6 \times \frac{Z}{n} \text{ m/s}$$

$$T.E = -13.6 \times \frac{Z^2}{n^2} \text{ eV}$$

Whereas in case of NSN

$$r = .529 \times \frac{n^2}{Z} \times \frac{m_e}{\mu}$$

$$V_e = 2.18 \times 10^6 \times \frac{Z}{n} \times \frac{\mu}{m_e}$$

$$TE = -13.6 \times \frac{Z^2}{n^2} \times \frac{\mu}{m_e} \; eV$$

using above info. & fact that $\mu = \frac{m_e M_{Nu}}{m_e + M_{Nu}}$,

answer the questions, that follows-

Note (given)

$$\boxed{m_e = \frac{1}{1837} m_p} \qquad m_p = m_n$$

Q. For a hypothetical atom, obey Bohr's model the nuclear charge = +e & charge on the particle revolving = -e mass of revolving particle is half of mass of nucleus, then calculate T.E. of the system?

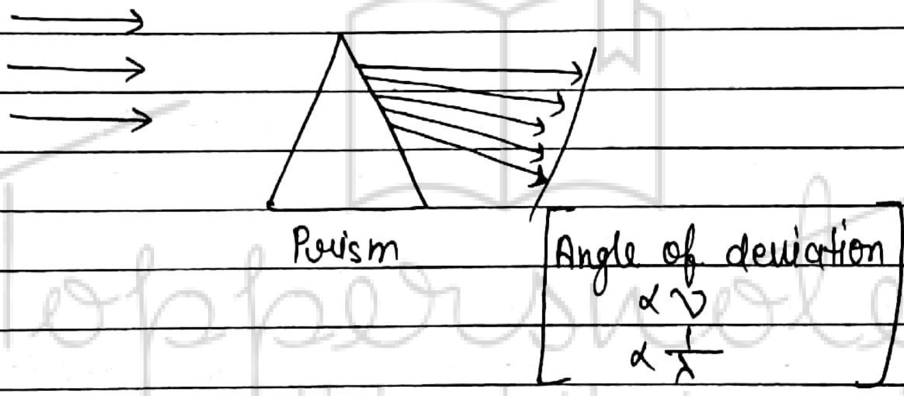
Ans.- $\mu = \frac{m_e . M_{nu}}{m_e + M_{nu}} = \frac{m_{rp} \, r^2 \, \cancel{m_{rp}}}{3 \cancel{m_{rp}}}$

$$= \frac{2 m_{rp}}{3}$$

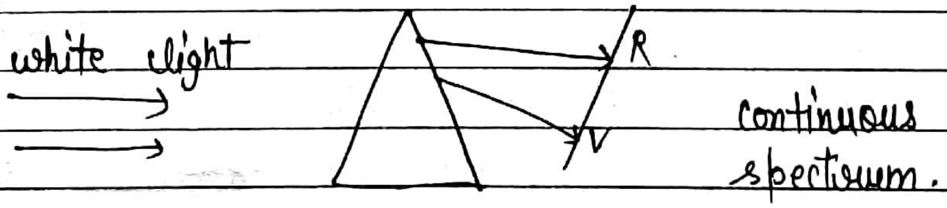
$$TE = -13.6 \times \frac{2}{3}$$

ATOMIC SPECTRUM

Spectrum consists of various electromagnetic radiations arranged in increasing / decreasing order of frequencies or wavelength. It can be obtained when electromagenetic radiation are passed through a prism.



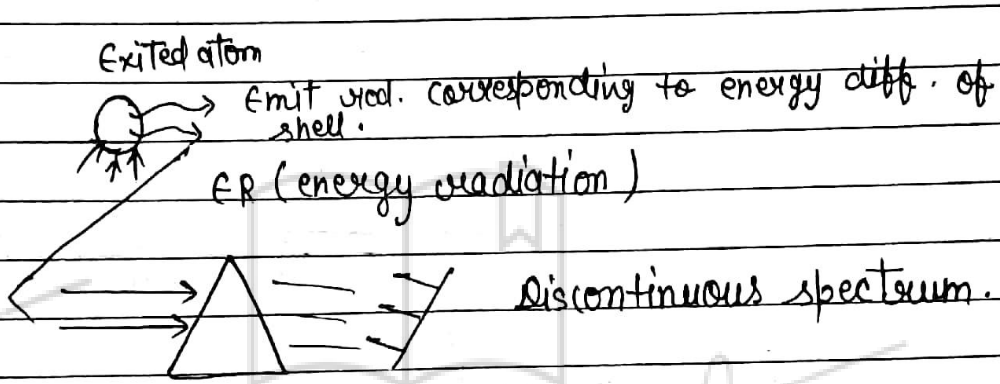
If a white light is used, then a continuous spectrum is obtained on the photographic plate.



However, when spectrum obtained from atom is analysed, the spectrum observed is different. The "atomic spectrum" can be analysed by two mothods :-

① Emission Spectrum
② Absorption spectrum.

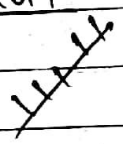
Analysis of emission spectrum



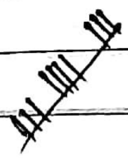
Since the emitted radiations from excited atom will be dependent on energy difference of the shell of that particular atom. Therefore, only specific radiations are emitted and hence, the spectrum obtained is a discontinuous spectrum.

Depending upon the type of atom (Z<10, Z>10 or molecule), the spectrum observed are

① LINE SPECTRUM (Z<10)

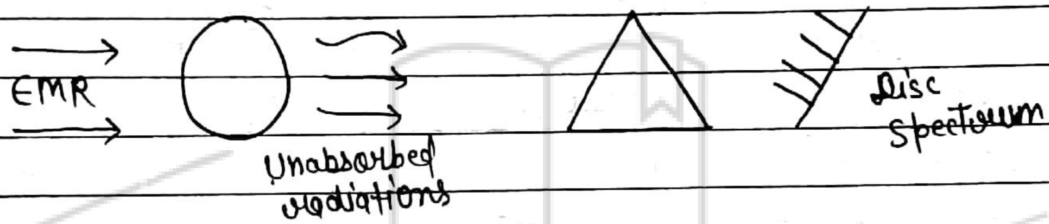


② BAND SPECTROM (Z>10)



⇒ The atomic spectrum is a characterist property of the element can be used to identify any element.

Analysis of absorption spectrum



In the above case, all the deviations subjected are not absorbed & the unabsorbed radiations are analysed.
The missing wavelengths in the spectrum will correspond to the energy difference of the atom. The spectrum is disconcinuas spectrum.
Implies that -
If emission spectrum has B, G & Y line in visible region, then in the absorption spectrum of the same element, using white light, all the wavelengths except B, G & Y will be present.

★ Although the atomic spectrums are discontinuous, however, after a particular energy value the spectrum will become continuous.

DE - BROGLIE'S DUAL NATURE

When photo electric effect was observed using electro magnetic radiations, the results led to the conclusion that light behaves as a stream of energy bundles or particles known as photons which on collision with electron transfer energy to the $e^{\ominus}$, thus photo electric effect demonstrates partical nature of light or EMR However, it was also observed that light behaves as a wave also since it shows wave effects like interference or diffraction.

On the basis of above observations de-broglie concluded that light or EMR exhibit dual nature (particle nature & wave nature) which can be related as shown below-

$$E_p = \frac{hc}{\lambda} \quad —①$$

Since, photons are considered to be bundles of energy. Therefore if "m" is the mass associated with photons then

$$E_p = mc^2 \quad -②$$

from ① & ② $\therefore mc^2 = \frac{hc}{\lambda}$

$$mc = \frac{h}{\lambda}$$

particle nature $\therefore$ $\boxed{p = \frac{h}{\lambda}}$ — wave nature

p = momentum

$p = mv_c$

The above eqn can be used to calculate-

① momentum associated with any wave (given λ).

② Associate mass of the photon.

The above expression was extended for all the moving particles & it was concluded that-
" Any moving particle (with some mass & velocity) has a wave nature associated with its motion, which is inversely proportional to its particle nature. The two nature can be related by the expression-

$$\boxed{\lambda_{DB} = \frac{h}{p} \quad \text{or} \quad \lambda_{DB} = \frac{h}{mv}}$$

λ is known as de-broglie wave

POINTS TO REMEMBER

① The de-broglie wave does not represent motion of particle as a wave, but is used only to explain experiments where wave nature is required.

② The de-broglie wave is not an EM wave and hence frequency of de broglie wave will not be equal to $\frac{c}{\lambda_{DB}}$

$$v_{DB} \neq \frac{c}{\lambda_{DB}}$$

Also velocity of particle will not be equal to velocity of wave.
Therefore, only wavelength of DB wave can be calculated.

③ Which nature will be significant will be dependent on relative magnitudes of momentum and λ.
If λ is high, then wave nature will be ~~subt~~ substantial.

④ The de-broglie wavelength can be experimentally determined & verified for small sized particles using diffraction experiments.

Q. Calculate de-broglie wavelength for
(i) a ball of mass 200 gms moving with a speed of 6.6×10^2 m/s.

(ii) a proton of mass 1.67×10^{-24} gms moving with a velocity of 6.64×10^{3} m/s.

Comment which will have a significant wave nature?

$h = 6.64 \times 10^{-34}$ (SI)

Ans (i) $\lambda_{DB} = \frac{h}{mv}$

$\lambda_{DB} = \frac{6.64 \times 10^{-34}}{\cdot 2 \times 6.64 \times 10^{2}}$

$\boxed{\lambda_{DB} = \cdot 5 \times 10^{-35} \text{ m}}$

(ii) $\lambda_{DB} = \frac{6.64 \times 10^{-34}}{1.67 \times 10^{-27} \times 6.64 \times 10^{3}}$

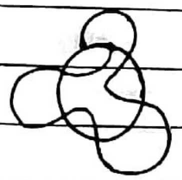
$\boxed{\lambda_{DB} = \frac{1}{1.67} \times 10^{-10} \text{ m}}$

Note: It can be concluded that the wave nature asociated with normal mass particle will be insignifcant and hence wave nature will be influential only for microsopic particles like protons and electrons.

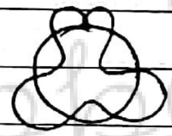
EXPLAINATION OF QUANTISATION OF ANGULAR MOMENTUM USING DE-BROGLIE'S DUAL NATURE

As per de-broglie's, only those orbits should be permissible in which "wave represented by electron" gets completed.

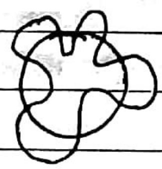
eg -



non-permissible orbit



non-permissible orbit



permissible orbit

Therefore, if there are "n" waves.

$\Rightarrow \quad 2\pi r = n \lambda$ - de-broglie's

(n = no of waves)

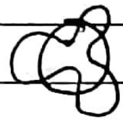
$= n \times \frac{h}{mv} \Rightarrow \boxed{mvr = \frac{nh}{2\pi}}$

(n = no of shells)

$\therefore$ angular momentum is quantised.

* also, no. of waves in any orbit is equal to shell no.

∴ 3rd orbit ⇒



HEISENBERG'S UNCERTAINITY PRINCIPAL

As per Heisenberg's principle, it is impossible to determine both position as well as momentum of any particle simultaneously and accurately. (there would be some uncertainity or error that would be involved in measurement of the two parameters).

Mathematically,

$$\Delta x \cdot \Delta p \geq \frac{h}{4\pi}$$

or $\Delta x \cdot \Delta p \geq \frac{\hbar}{2}$ $\left(\hbar = \frac{h}{2\pi}\right)$

Δx is uncertainity or error in position & Δp is uncertainity in momentum

where uncertainity will either be directly mentioned or can be calculated with appropriate data.

eg-

Q.1 A particle is confined in a region of length 10^{-10} m. If the mass of the particle is 6.64×10^{-30} kg, then calculate uncertainity in momentum, position & velocity?

Ans. $l = 10^{-10}$ m

$\boxed{\Delta x = 10^{-10}}$ (uncertainity cannot exceed actual dimension of the parameter)

$$\Delta x \cdot \Delta p = \frac{h}{4\pi}$$

$$\Delta p = \frac{h}{4\pi 10^{-10}} = \frac{6.64 \times 10^{-24}}{4\pi} \text{ Kgm. m/s}$$

$$\boxed{\Delta p = \frac{6.64 \times 10^{-24}}{4\pi}} \text{ Kgm. m/s}$$

The above value is the minimum uncertainity in momentum.

$$\Delta p = m \Delta v$$

$$\Delta v = \frac{\Delta p}{m} = \frac{6.64 \times 10^{-24} \; 10^{6}}{4\pi \times 6.64 \times 10^{-24}}$$

$$\boxed{\Delta v = \frac{10^{6}}{4\pi}}$$

Q. Show that, an e^- cannot at be present inside the nucleus (10^{-15} m) using Heisenberg's uncertainity principal ($m_e = 9.1 \times 10^{-31}$ kg)

Ans. $\Delta x = 10^{-15}$ m

$$\Delta x \cdot m \Delta v \geq \frac{h}{4\pi}$$

$10^{-15} \cdot 9.1 \times 10^{-31} \cdot \Delta v > 10^{-34} \times 10^{+12}$

$\Delta v_{min} > 10^{2}$

Since maximum uncertainery in velocity possible's is 3×10^{8} m is-

e^- cannot be confined in such a small space.

Q. A particle of mass 200g has a position respresented by-

① Position = 10m ± 10Å

② Position = 10 m ± 0.001%

③ Position varying from 10m → 10.0001m calculate Δx, Δp & Δv of particle.

Ans. ① $\Delta x = 10 Å$ ② $\frac{.001}{100} \times 10 = 10^{-4}$ ③ .0001 m

$\Delta x \cdot \Delta p > \frac{h}{4\pi}$

$\Delta p = \frac{h}{40\pi}$

$10 \times 10^{-10} \times 2 \times \Delta v = \frac{h}{4\pi}$

$\Delta v = \frac{h}{4\pi \times 2 \times 10^{-16}}$

now same