Quantum mechanism in
Chemistry, 2nd edition
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CHM 303

Quantum Chemistry

Historical Development

(1) The Origin Of Quantum Mechanics

The motion of material bodies i.e objects possessing the properties of mass are governed by the laws of Newton.

Such objects are generally often reperred to as particles even though, the term may seem inappropriate for bodies as large as howlage ships, car, passenger plane or any other massive object.

Newtons theory was able to explain the motion of a pendulum, the trajectory of a canon ball, and orbit of the planet in a specified state parameter

It is also able to predict the motion of these bodies in any other state parameters (speed & position)

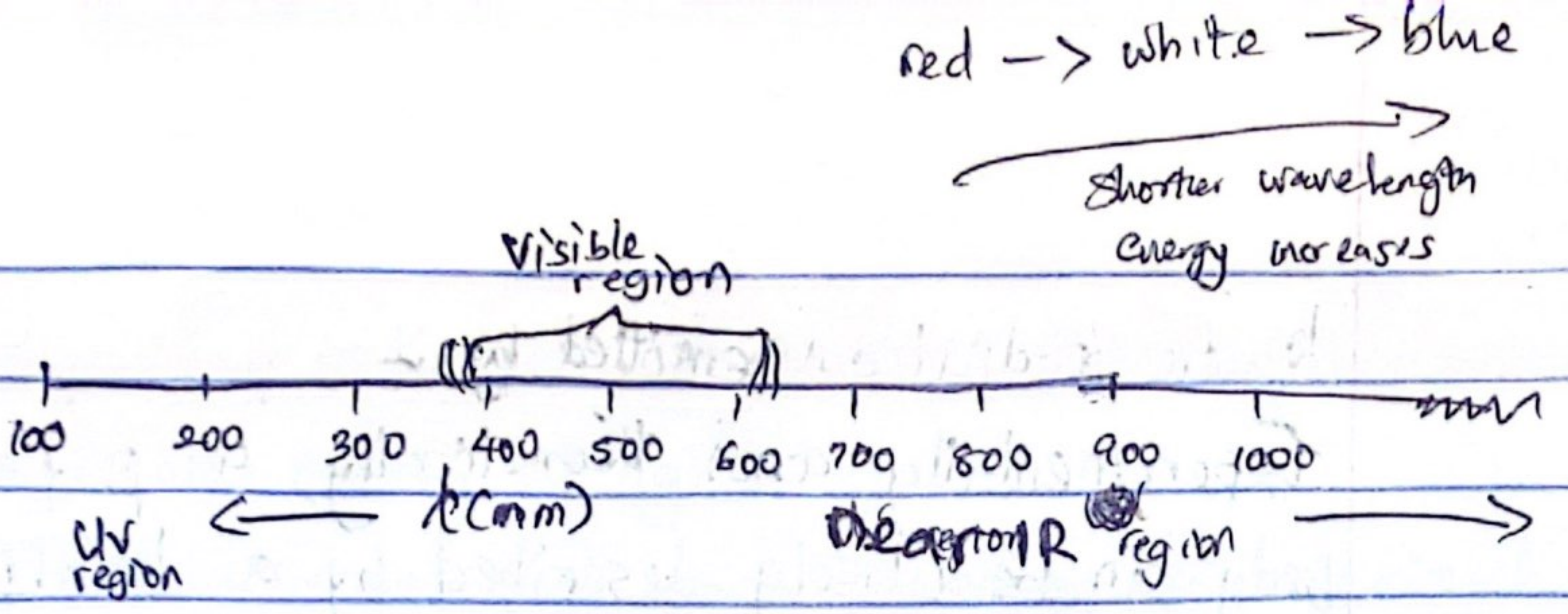
He was able to do this with the invention ~~of~~ the concept of mass and force. These laws of Newton forms the foundation for classical mechanics.

As earlier noted, classical mechanics can adequately explain ~~clas~~ experimental result on the macro scale (large sized particles). However, on the atomic and sub atomic scales, it fails woefully.

Therefore, to understand the behaviour of atomic and Sub atomic, particles, there is need for a new mechanics. Classical mechanics was dominant until the end of 19th century, when investigations to know how to know the wavelength of radiation emitted by a hot solid varies with the intensity were being carried out.

The Newton's concept of force & mass could not provide any explanation to the behaviour of the radiation. Newton had earlier favoured a model that pictured radiation (light) as massless particles called corpuscles (Huygens' wave model). The Huygens' wave model was accepted then because it could readily explain ~~phenomenon~~ phenomena like interference, refraction and diffraction. But still, the underline nature of Huygens' wave was a mystery

(ii) Black Body Radiation: A hot body may cool by emitting heat in the form of electromagnetic radiation. At moderate temperatures, this radiation is primarily at wavelength longer than visible light, i.e infrared,



At higher temperature, the radiant energy shifts shorter wavelength and the body will glow red. At still higher temperature, the emitted radiation appears white, then blue. In addition to the shift shorter wavelength, the total energy emitted increases with temperature The total energy at all wavelength emitted per unit area per unit time (e) is related to temperature by the Steffan-Boltzmann Law equation.

$$e(T) = \sigma T^4 \quad \text{.....} \ ①$$

σ = Stefann Boltzmann constant 5.67×10^{-8} watt $m^{-2} K^{-4}$

In 1859, German physicsist, Gustav Robert Kirchoff (1824-1887). This man concieved a substance that will absorb all frequencies of radiation falling into it; It will reflect none of it and will appear black.
Such an idealized object known as a black body would be in perfect equilibrium, such that the radiations striking it would be equal in intensity.

to the radiation emitted by it
Experimentally and theoretically, a perfect black body can be closely described by a hohlraum.
It has a cavity with black walls inside a solid material

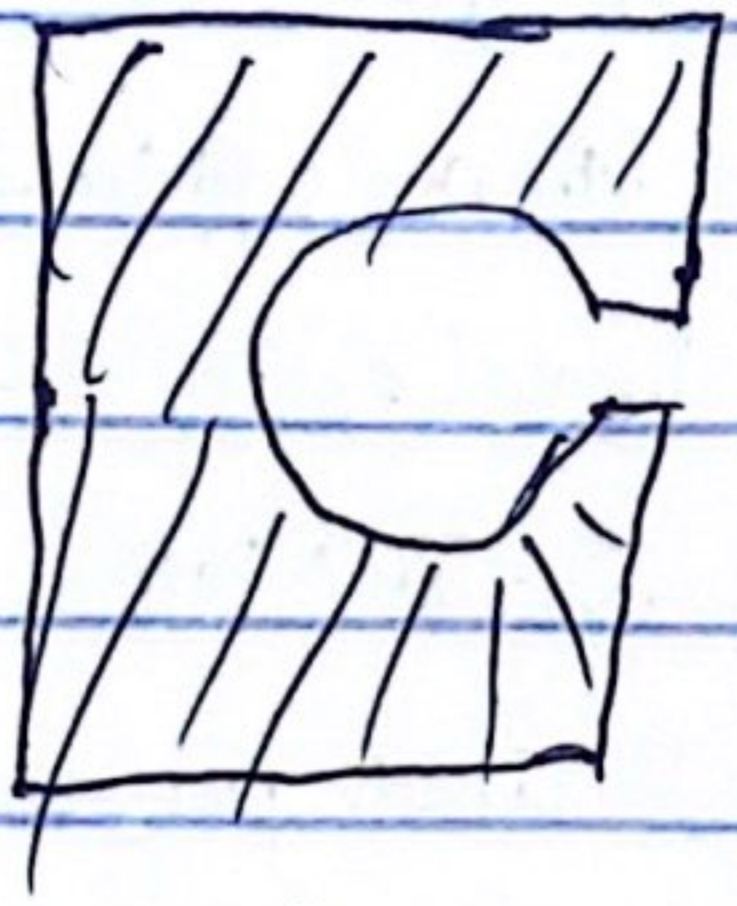


fig 1: A haulraum, a cavity with black walls inside a solid material.

~~The explanation of the black body~~

Experimentally and theoretically, a perfect black body can be closely described by a hohlraum which is a solid hollow chamber with black cavity wall.

The explanation of the blackbody radiation pattern was a major problem for physicsist on the 19th century and one of the problems that gave birth to the quantum theory

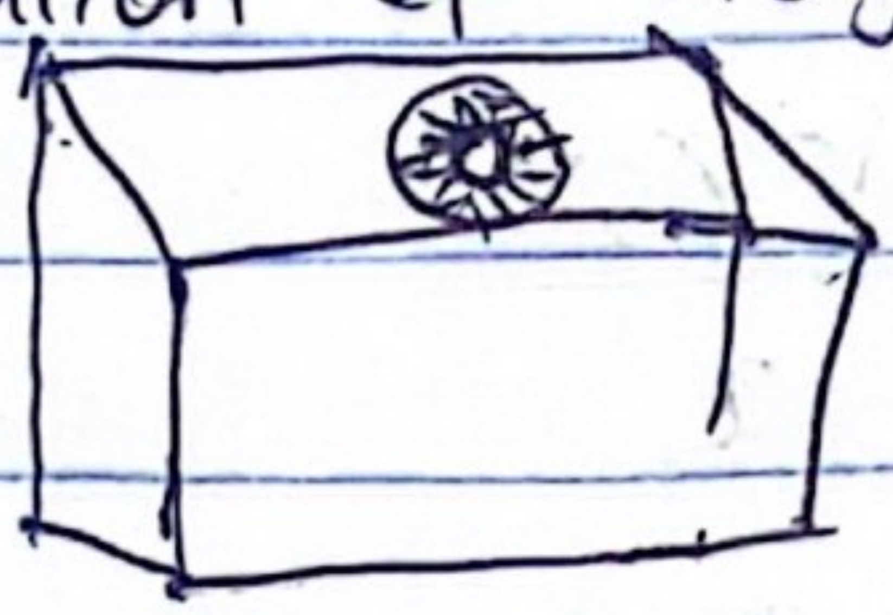
Rigourous treatment of this phenomenon assumed that the radiation in the hohlraum is a gas of massless particle called photons.

This idea is a reincanation of the Newton's ~~poposcular~~ corpuscular theory of light.

It is assumed that each photon is characterized by fequency ν and has an energy, given by

$$E_{(photon)} = h\nu \quad \text{.....} ②$$

The radiant energy in hohlraum was studied via a small hole in the side. Some result of the frequency distribution of energy in fig 2



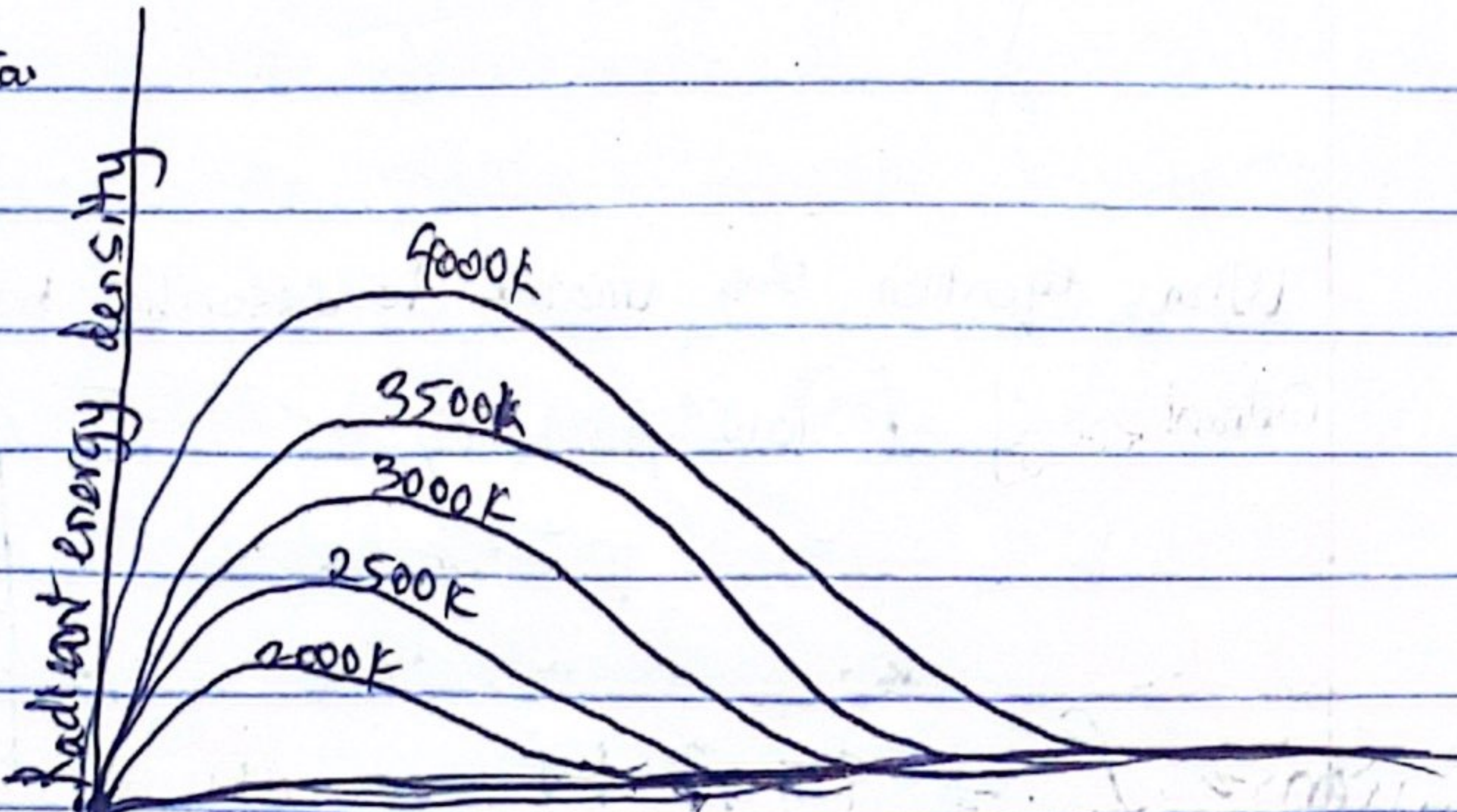


Fig 2: Radiant energy from blackbody at various temperature versus ν/T

Note the jump from each level of temperature to another level which corrobate the idea of quantization.

The above experimental result are well described in eqn 3 given in 1900 by German physicsist by Max, Kahl, Ernest, Ludwig, planck (1858-1947).

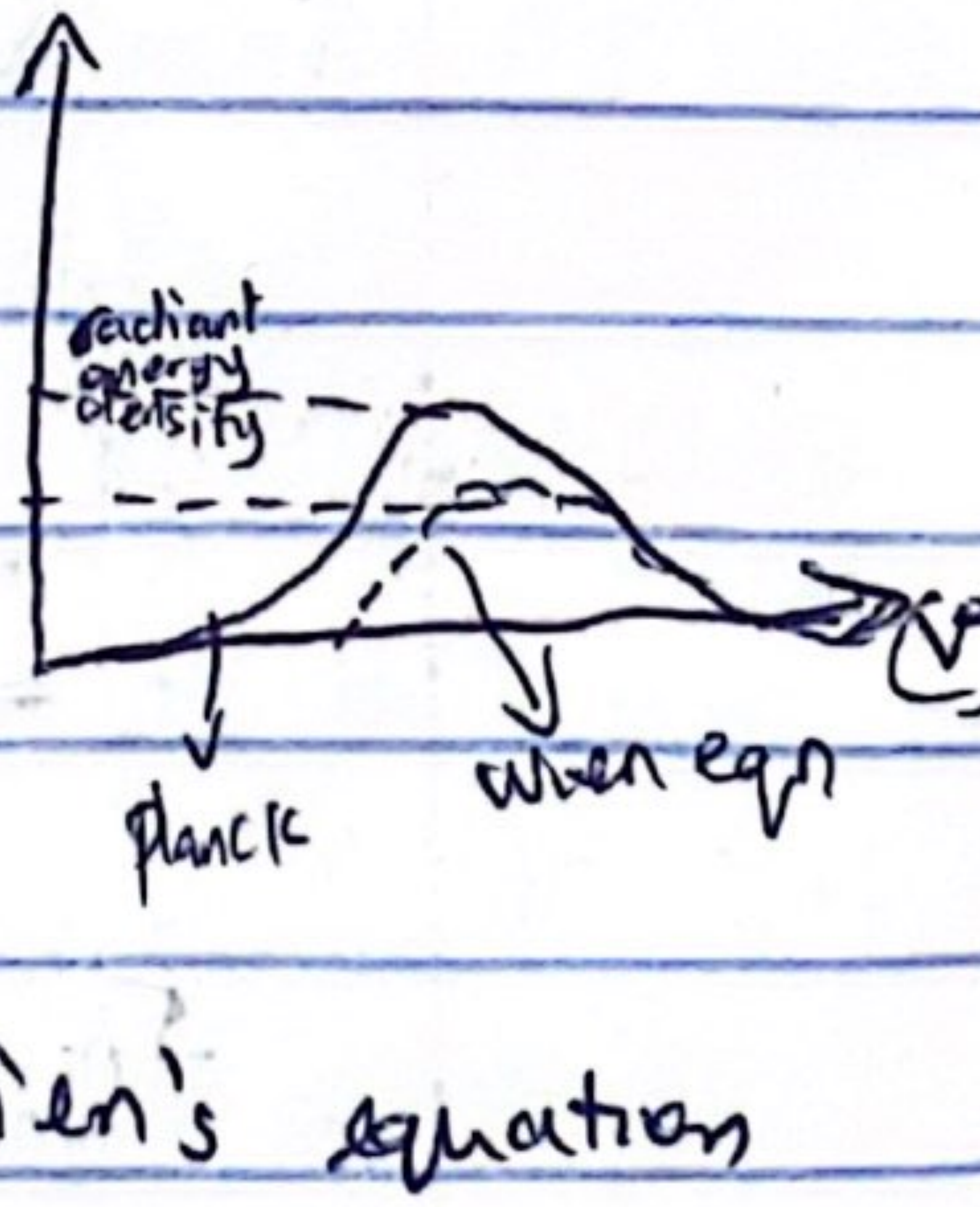
Planck equation

$$\rho_v = \frac{8\pi v^2}{c^3}\frac{hv}{e^{\left(\frac{hv}{k_B T}\right)}-1} = \frac{8\pi v^2}{c^3}\frac{hv}{e_{xp}^{\frac{hv}{k_B T}}-1} \quad \text{......} ③$$

K_B = boltzmann constant

ρ_v	λ (nm)	v (s^{-1}
y_1	200	x_1
	300	x_2

Wien equation was unable to describe behaviour of radiant energy at low frequency



$$\text{wiens} = \rho_v = \frac{8\pi v^2}{c^3}\frac{hv}{e^{\frac{hv}{k_B T}}} \quad \text{...} (4)$$

planck derived his expression from wien's equation which is eqn (4), by adding a negative unity in the denominator. He found a need to do this

* hot objects emits IR radiation

after Heinrich Reuban's (1865 - 1922) and Ferdinard Kurlbaum (1857 - 1929) in 1900 carried out similar measurement as Wien's for a wider frequency range, further into the IR region. (i.e, to lower frequency region than the previous).

They found that although, wien's formular gave excellent agreement at higher frequencies, but at lower frequencies, he predicted radiant energy densities that were too low with the discrepancies becoming greater as the frequency was lowered. The planck's expression eqn (3) provided the solution to this discrepancy. At higher frequencies, where unity in the denominator is insignificant and can be neglected, the planck's equation reduces to Wien's equation.

The solution to the black body radiation, triggered the idea of ~~quatum~~ energy ~~radiation~~ quantization, which is the primary foundation of quatum theory

(iii) Bohr's Atomic Theory: First and foremost, there was a problem with the structure of atom which the early scientist knew could not be solved using the classical mechanism

The triumph of quatum theory on the structure of atom problem was first noted on the work of the Danish physissit, Neil's Henrik ~~Harg~~ David Bohr (1885 - 1962).

Bohr, based his theory on the nuclear model proposed in 1911 by Ernest Rutherford (1871 - 1937) who proposed that an atom is composed of a dense positively charged nucleus, not only that, the electrons revolves around this dense positively charged nucleus, and the size of the atom is determined by the size of the electronic orbit.

The simplest atom, hydrogen, consists of a nucleus having a single positive charge and a single orbiting electron. However, a more careful look at this model (Rutherford model) reveals a formidable problem in the realm of classical physics. If the negative electron is orbiting about the positive nucleus, a dipole which oscillate at the frequency of rotation is created.

Maxwell's theory and the experiment of Hertz showed that an oscillating dipole must emit radiation at the frequency of oscillation. We do practically see the implication of the works of these two people oscillating dipole emits radiation at the frequency of oscillation

application of maxwell theory and the experiment of Hertz

(maxwell and Hertz) everytime we listen to the radio or watch the television.

The continua radiative loss of energy by the oscillating electron is expected to cause it to spiral inward and collapse into the nucleus. This obviously put grey marks on the Rutherford nuclear model, making it general acceptability difficult.

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Bohr resolved this difficulty by combining Rutherford's concept of the nuclear atom with planck's concept of quantization from the black body model and some important new ideas of his own. He brought the bold idea that electrons are revolving round the nucleus in a radiationless orbit.

~~He~~ sets aside many of the most fundamental classical mechanics and came up with the following assumptions known as the Bohr's theory

(i) Electrons revolves round the nucleus in a circular orbit and do not radiate energy.

ii The laws of classical mechanics hold, except that radiation due to acceleration does not occur

iii The angular momentum of the electron is quantized in unit of $\frac{h}{2\pi}$. i.e, electrons may only have angular momentum $= \frac{nh}{2\pi}$, where, n takes only integer values such as 1, 2, 3...... ∞. That is, whole numbers.

Bohr was led to this postulate by assuming that, in the limit of large angular momentum (i.e large value of n), the classical emission frequency must become equal to the electron orbital frequency as required by the laws of classical electrodynamics.

This assupmption is now called the Bohr's correspondence principle.

The Bohr's correspondence principle simply states that in the limit of large n, the prediction of quantum mechanics must be equal to the prediction of classical mechanics.

iv The potential energy is couloumbic. ~~With~~ With the above four assumptions, Bohr was able to qualitatively predict the spectrum for any hydrogen-like atom containing only one electron. e.g hydrogen itself, He^{+}, Li^{2+}

The Bohr atomic model essentially contains a rotating particle (the electron) and the massive, stationary object at the origin called the nucleus. ~~A~~

According to the second assumption, where it states that the laws of classical mechanics hold, the Hamiltonian equations $(H = \underset{= \text{total energy}}{KE} + \overset{P.E}{V})$ for this system holds, with which the electronic motions and energy can be described. The fourth assumption tells us that the potential energy is columbic:

$$V(R) = \frac{Ze(-e)}{4\pi\varepsilon_0 R} = \frac{-Ze^2}{4\pi\varepsilon_0 R} \quad \ldots\ldots(5)$$

Where Z = atomic no of atom or ion

$Q(q)$ = magnitude of chargo

ε_0 = Permitivity

R = distance

By the third assumption, the angular momentum P_θ can be written as eqn (6)

$$P_\theta = \frac{nh}{2\pi} \quad \text{for } n = 1, 2 3 \dots \infty \quad \dots (6)$$

If the orbit is circular as the first assumption implies, the net radiant force, which is (F_R) must be zero, Otherwise, the electron would not stay at the same radius as it rotates about the nucleus. Therefore, from the Hamiltonian's equation of motion for electron, we can write that

$$\frac{-P_\theta^2}{MR^3} + \underbrace{\frac{\partial V(R)}{\partial R}}_{\text{Coulombic force}} = -\frac{dP_R}{dt} = -F_R = -(\text{radial force}) = 0 \quad \dots (7)$$

$$F \propto \frac{q_1 q_2}{R^2} \Rightarrow F = \frac{K q_1 q_2}{R^2}$$

$$P_\theta = mvR$$

$$P_\theta^2 = m^2 v^2 R^2$$

angular momentum

Assignment

show that centripetal force $\frac{mv^2}{R}$ is equal to $\frac{P_\theta^2}{mR^3}$

If you rearrange eqn (7)

$$\frac{P_\theta^2}{mR^3} = \frac{\partial V_{(R)}}{\partial R} \quad \ldots\ldots ⑧$$

where P_θ, m, R and V are angular momentum, particle mass, radial and potential energy (coulombic) functions ~~where P_θ~~, respectively

$$\frac{P_\theta^2}{mR^3} = \frac{m^2v^2R^2}{\cancel{m}R^3} = \frac{mv^2}{R} \text{ (centripetal force)}$$

Substituting eqn 5 & 6 into eqn (8)

$$\frac{n^2h^2}{4\pi^2 m R^3} = \frac{\overset{\text{atomic number}}{Z}e^2}{4\pi\varepsilon_0 R^2} \quad \ldots\ldots ⑨$$

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solving eqn (9) for the R of the circular orbit, we obtain;

$$R = \frac{n^2 h^2 \varepsilon_0}{Z e^2 \pi m} = \frac{n^2}{Z}\left[\frac{4\pi\varepsilon_0 \hbar^2}{e^2 m}\right] \ldots (10) \qquad \left(\hbar = \frac{h}{2\pi}\right)$$

$$\Rightarrow \frac{n^2}{Z} a_0$$

where $\hbar = \frac{h}{2\pi}$ which can be evaluated as

$$\frac{h}{2\pi} = \frac{6.62608\times10^{-34}\,Js}{2\times3.1415927} \Rightarrow \hbar = 1.05457\times10^{-34}\,Js$$

The quantity inside the square bracket in eqn (10) has the unit of distance and it is given the symbol a_0. It is called the Bohr radius. And its value is

$$a_0 = \left[\frac{4\pi\varepsilon_0\hbar^2}{e^2 m}\right] = \frac{4\times3.1415927\times(1.05457\times10^{-34})^2 \times 8.854190\times10^{-12}\,J^{-1}C^2m^{-1}}{(1.60217\times10^{-19}C)^2\times 9.10930\times10^{-31}\,k}$$

$$\Rightarrow a_0 = 5.29175\times10^{-11}\,m \text{ (Bohr radius)}$$

Eqn (10) was a stunning result showing that not all radii for the circular orbit are permitted.
The electrons can rotate only circular orbit whose radii

are $\frac{a_0}{Z}, \frac{4a_0}{Z}, \frac{9a_0}{Z}, \frac{16a_0}{Z}, \ldots, \frac{n^2a_0}{Z}$

as shown in the figure below

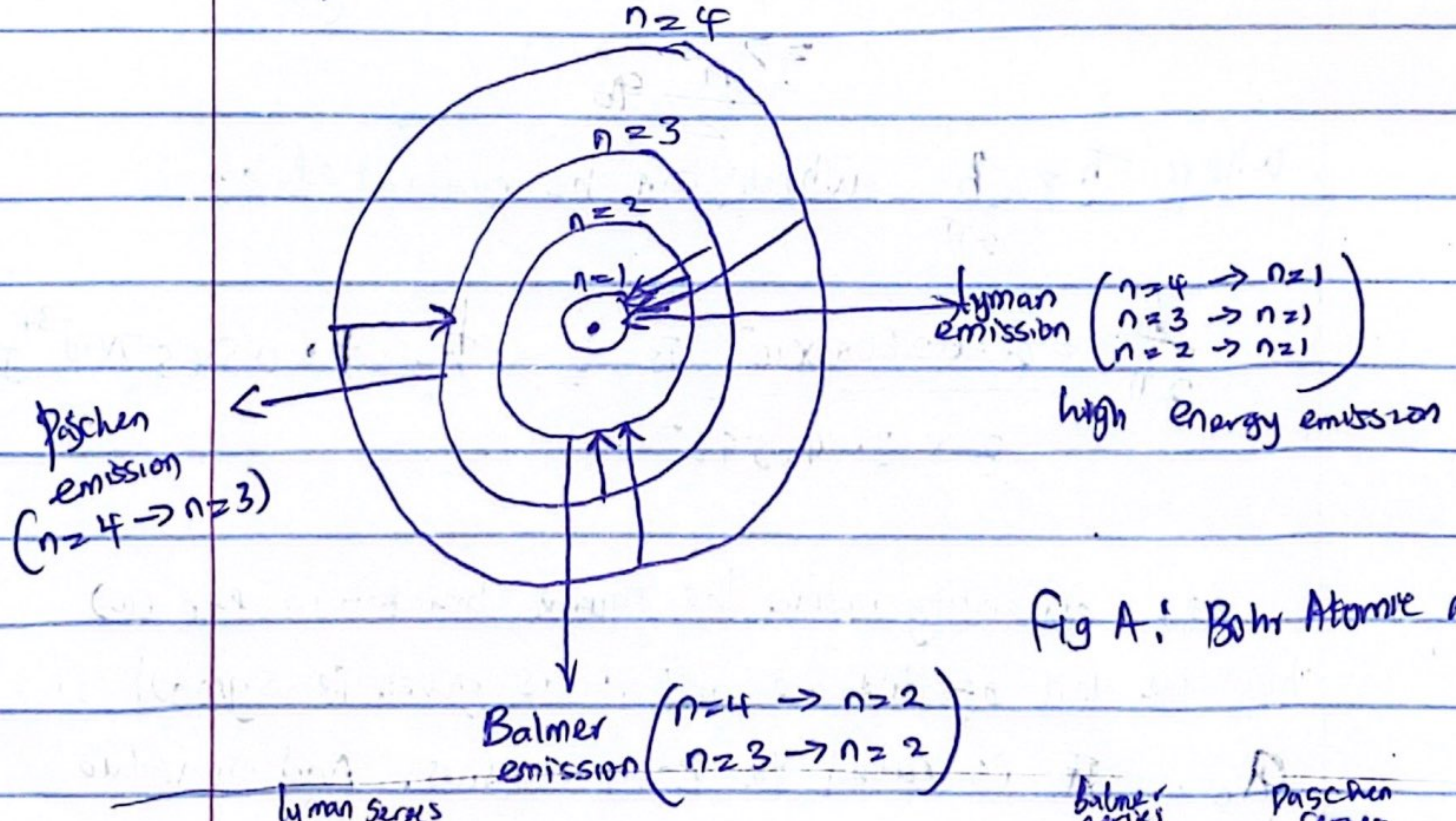


Fig A: Bohr Atomic model

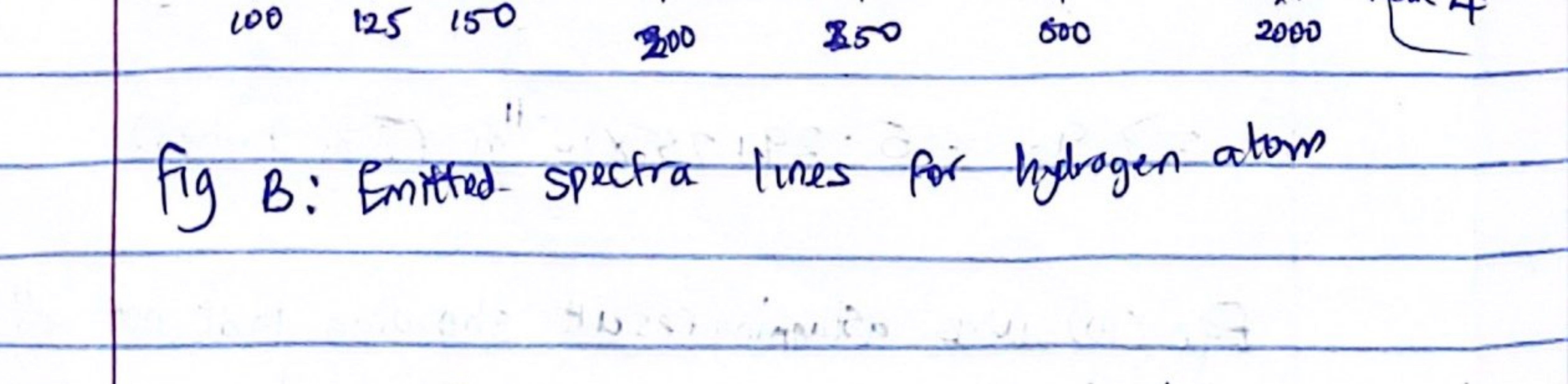


Fig B: Emitted spectra lines for hydrogen atom

Note that the spectral lines were not drawn to scale
For the hydrogen atom, $Z = 1$ the smallest possible radius
is a_0. With the possible orbital radii known, the
total energy of the system can now be obtained directly
by substituting eqn (10) into the general Halmitonian
equation

$$H = \overset{KE}{T} + \overset{P\text{-}E}{V_{(R,\theta)}} = E \text{ (eigen value)}$$

$$\underset{\text{(eigen value)}}{E} = \frac{\overset{\text{linear KE}}{P_R^2}}{2m} + \frac{\overset{\text{angular KE}}{P_\theta^2}}{2mR^2} + V_{(R,\theta)} \quad \cdots\cdots (11)$$

momentum

$$\left(\begin{array}{l} P = mv, \quad P^2 = m^2v^2 \\ KE = \frac{1}{2}mv^2 = \frac{P^2}{2m} \end{array} \right)$$

$$P_\theta = mvR$$

$$\frac{P_\theta^2}{2mR^2} = \frac{m^2v^2R^2}{2mR^2}$$

$$\frac{P_\theta^2}{2mR^2} = \frac{1}{2}mv^2$$

Where the first, 2nd and 3rd terms of the right handside
of eqn (11) represent the K.E of the tangential

linear motion of the electron, KE of the circular motion of the electron and the PE between the electron and the positive nucleus, respectively.

Since the circular orbit ensures that linear momentum (P_R) equals to zero, therefore, $\frac{P_R^2}{2m} = 0$.

$$\therefore E = \frac{P_\theta^2}{2mR^2} + V_{(R,\theta)} = \frac{P_\theta^2}{2mR^2} + V_{(R)} \quad \ldots\ldots (12)$$

V depends only on R.

Substituting eqn (5) & (6) into eqn (12)

$$E = \frac{n^2\hbar^2}{2mR^2} - \frac{Ze^2}{4\pi\varepsilon_0 R} \quad \ldots\ldots (13)$$

Inserting the value of R from eqn (10) into (13)

$$E = \frac{-Z^2e^4m}{32\pi^2 n^2\hbar^2\varepsilon_0^2} \quad \ldots\ldots (14)$$

Writing eqn (13) in form of Bohr's radius

$$E_n = -\frac{Z^2e^2}{8\pi n^2\varepsilon_0 a_0} \quad \ldots\ldots (15)$$

Note that the subscript n on E in eqn (15) emphasizes that energy depends upon the value of n which is a quantization paramater.

The result of Bohr's theory was a quantized energy for hydrogen-like atoms

For the hydrogen atom itself with $Z=1$, the energies only take values such as

$$E_1 = \frac{-e^2}{8\pi\varepsilon_0 a_0},\quad E_2 = -\frac{e^2}{8(4)\pi\varepsilon_0 a_0},\quad E_3 = \frac{-e^2}{8(16)\pi\varepsilon_0 a_0},\ \ldots,\ E_n$$

Bohr also recegnize that the spectral emission lines from hydrogen atoms were due to transitions, from higher energy state to lower energy state.

fig 3 also depicted this, the energy difference, ΔE between the states shown will have to be equal to the energy of the emitted radiation, which by planck's theory is $h\nu = \frac{hc}{\lambda}$.

Therefore for a given transition between an upper hydrogen state with $n = n_u$ and a lower state with $n = n_L$, eqn (15)

$$\Delta E(n_u, n_L) = E_u - E_L = \frac{-e^2}{8\pi\varepsilon_0 a_0}\left[\frac{1}{n_u^2} - \frac{1}{n_L^2}\right] = h\nu \quad \text{......} (16)$$

The predicted Spectral frequency will then be

$$\nu = \frac{-e^2}{8h\pi\varepsilon_0 a_0}\left[\frac{1}{n_u^2} - \frac{1}{n_l^2}\right] = \frac{e^2}{8h\pi\varepsilon_0 a_0}\left[\frac{1}{n_l^2} - \frac{1}{n_u^2}\right] \quad \ldots\ldots (17)$$

$$\bar{\nu} = \frac{1}{\lambda} \; ; \; \Delta E = h\bar{\nu} = \frac{hc}{\lambda} = hc\bar{\nu}$$

$$\frac{1}{\lambda} = \bar{\nu} = \frac{e^2}{8hc\pi\varepsilon_0 a_0}\left[\frac{1}{n_l^2} - \frac{1}{n_u^2}\right] \quad \ldots\ldots \text{(18)}$$

The calculated value of constant outside the square bracket in eqn (18) is

$$\frac{e^2}{8hc\pi\varepsilon_0 a_0} = 1.09738 \times 10^7 \, m^{-1} = 109738 \, cm^{-1}$$

(Rydberg constant)
(R_H)

(as bohr radius used when $z = 1$)

Thus, the Bohr model predicts that the emitted wavelength/energy for hydrogen atom from upper state (u) to lower state (l) will be

$$\bar{\nu} = 109738\left(\frac{1}{n_l^2} - \frac{1}{n_u^2}\right] cm^{-1} \quad \ldots\ldots \text{(19)}$$

If eqn (19) is corrected for reduced mass effect, the predicted Rydberg constant becomes 109 677 cm^{-1} which is in close agreement with the experimentally observed result (109,737 cm^{-1})

In the electronic transition, electron is moved apart and proton in the spectrum

Bohr actually reported a value of R_H to 103500 cm^{-1}, because the fundamental contants were not accurately know in 1913. Bohr recieved a nobel prize for this work in 1922. The model however, failed to predict the emission lines for many electron atom.

This failure was first attributed to the assumption that the electron orbit is circular, but when elliptical ~~body~~ Orbit was used, the result was only slightly improved

Another complaint about Bohr's theory, although a minor one, is the closely spaced lines, within the line spectra observed for the hydrogen atom, under high magnetic field called fine structure. ~~And~~ this called the zeeman's effect.

(4) Wave-Particle Duality 20/11/24

De Broglie's Hypothesis

The particle nature of light is illustrated more vividly by compton effect – the elastic scattering of light by electrons

Photon of light, which is $\frac{h\nu}{c}$

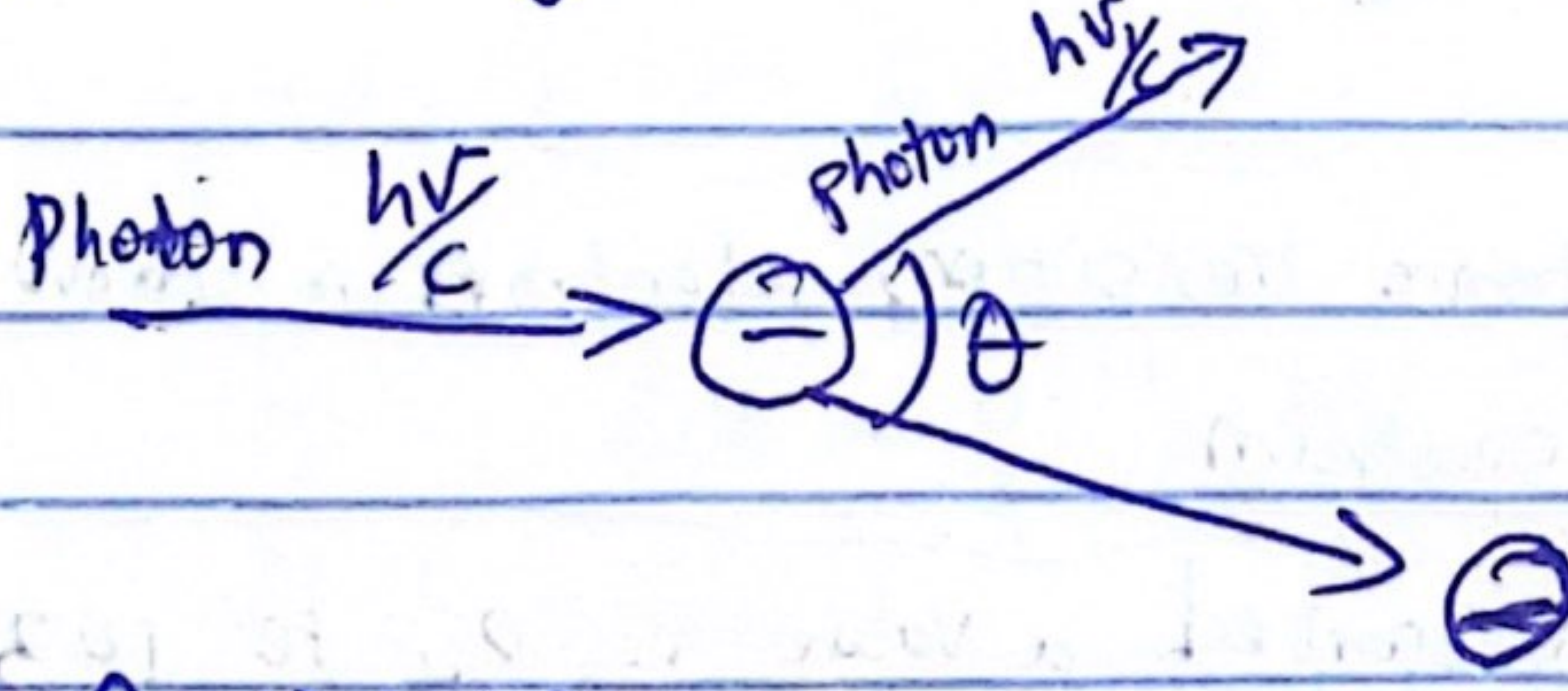


fig 4: The compton effect.

The interaction of a photon and an electron is rather like the collision of two Billard balls. The electron gains some energy, and the photon's loss of energy is reflected by change in frequency in accordance with eqn (20)

$$\text{Energy of photon} = h\nu = \text{.....} \quad (20)$$

Furthermore, to explain the angles of scattering, θ, in accordance with the law of conservation of momentum, it is required to assume that the photon has a momentum

$$\text{Momentum of a photon} = \frac{h\nu}{c} \quad \text{....} \ (21)$$

Eqn (12) proofs that electromagnetic radiation (light) has both wave like and particle-like characteristics. This is referred to as wave - particle duality

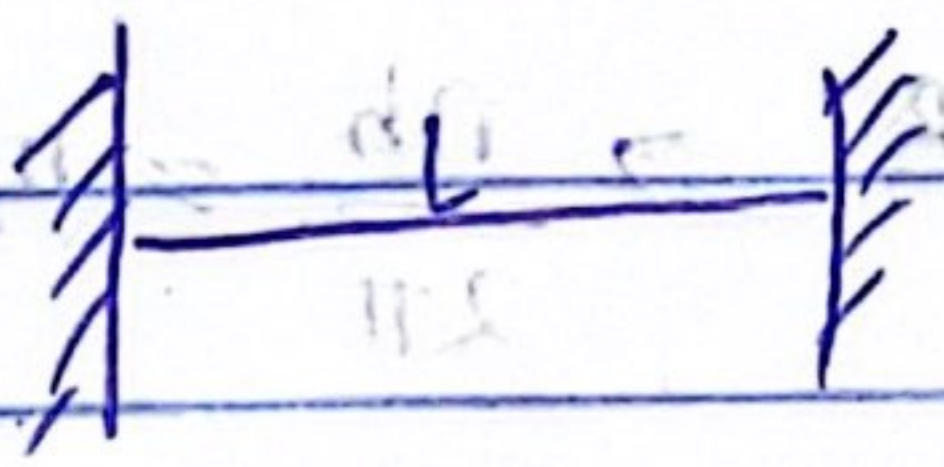
Question

How did Bohr arrive at integer value for the quantized energy?

Integers occur naturally when wave motion is subjected to boundary conditions. For example, standing waves on a string of length L, attached at each end to stationary wall, may have only wavelength given by; ~~$\lambda = \frac{2L}{n}$~~

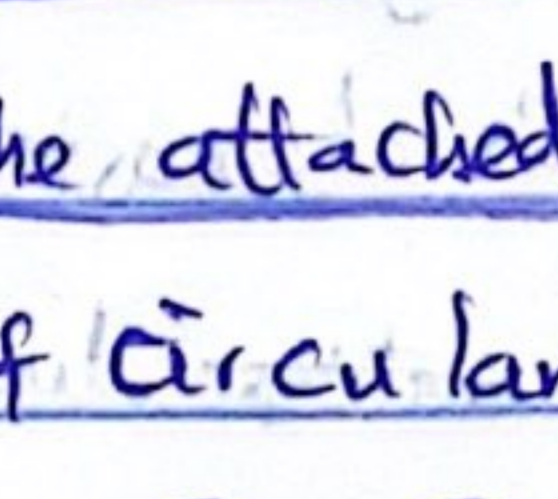
$$\lambda = \frac{2L}{n} \quad \ldots\ldots (22)$$

where n is an integer.



Any other wavelengths within the domain of eqn (22) would require the value of L to change by moving the positions of the attached ends of the string

For waves of circular ring, similar boundary conditions suffice



$$\lambda = \frac{\text{Circumference}}{\text{integer}} = \frac{2\pi R}{n} \quad \ldots\ldots (23)$$

De Broglie's hypothesis States that an object of mass m, travelling with a velocity, v is associated with wavelength, given by $\frac{h}{mv}$

$$\lambda = \frac{h}{mv} = \frac{h}{p} \text{ ......} 24$$

p ↓ momentum

Assuming an electron of mass, m_e and combining eqn (24) with the condition of the standing wave on a ring

$$\lambda = \frac{2\pi R}{n} = \frac{h}{mv}$$

$$\Rightarrow nh = m_e v \cdot 2\pi R \Rightarrow \frac{nh}{2\pi} = m_e v R$$

$$\Rightarrow n\hbar = p_\theta \leftarrow \text{angular momentum} \text{ ----} (25)$$

Eqn (25) is Bohr's hypothesis of the quantization of angular momentum, which demostrates that Bohr effectively assumed a ~~wave-like nature~~ wave-particle duality nature for the electron.

De Broglie's hypothesis has received numerous confirmations by electron and neutron diffraction experiments.

Principles and Concept of Quantum Chemistry

① Operator algebra: An algebra is a set of rules for manipulating ~~fig~~ Symbols. ordinary algebra defines the procedures for manipulating real numbers, with operations Such as addition at multiplication.

Extensions of the real number concept to complex numbers, vectors or matrices requires new set of rules, i.e an algebra of their own.

In quantum mechanical operations, we deal with Symbols. Each of this symbols represents a rule for transforming functions into new functions.

If $\hat{\alpha}$ is an operator that transforms a function $f(x)$ into the function $g(x)$, the Symbolic representation called the Operator equation is;

$$\hat{\alpha} f(x) = g(x) \cdots\cdots (26)$$

Example

(I) Let $\underset{\text{an operator}}{\hat{d}} \overset{\text{defined as}}{=} \frac{d}{dx}$ operates on a function $f(x)$

$$\Rightarrow \hat{d} f(x) = \frac{d}{dx} f(x)$$

If $f(x) = e^{-x^2}$

$$\Rightarrow \frac{d}{dx} e^{-x^2} = -2x e^{-x^2} \leftarrow \text{new function}$$

to operate on

② $\hat{x}, \quad f(x) = e^{-x^2}$

$\hat{x} f(x) = x \cdot e^{-x^2}$ ← new function

③ $\hat{i}\, f(x)$, $f(x) = x$

inversion operator
(when operates on a function, it multiplies it with opposite of the sign)

$\hat{i} f(x) = -x$

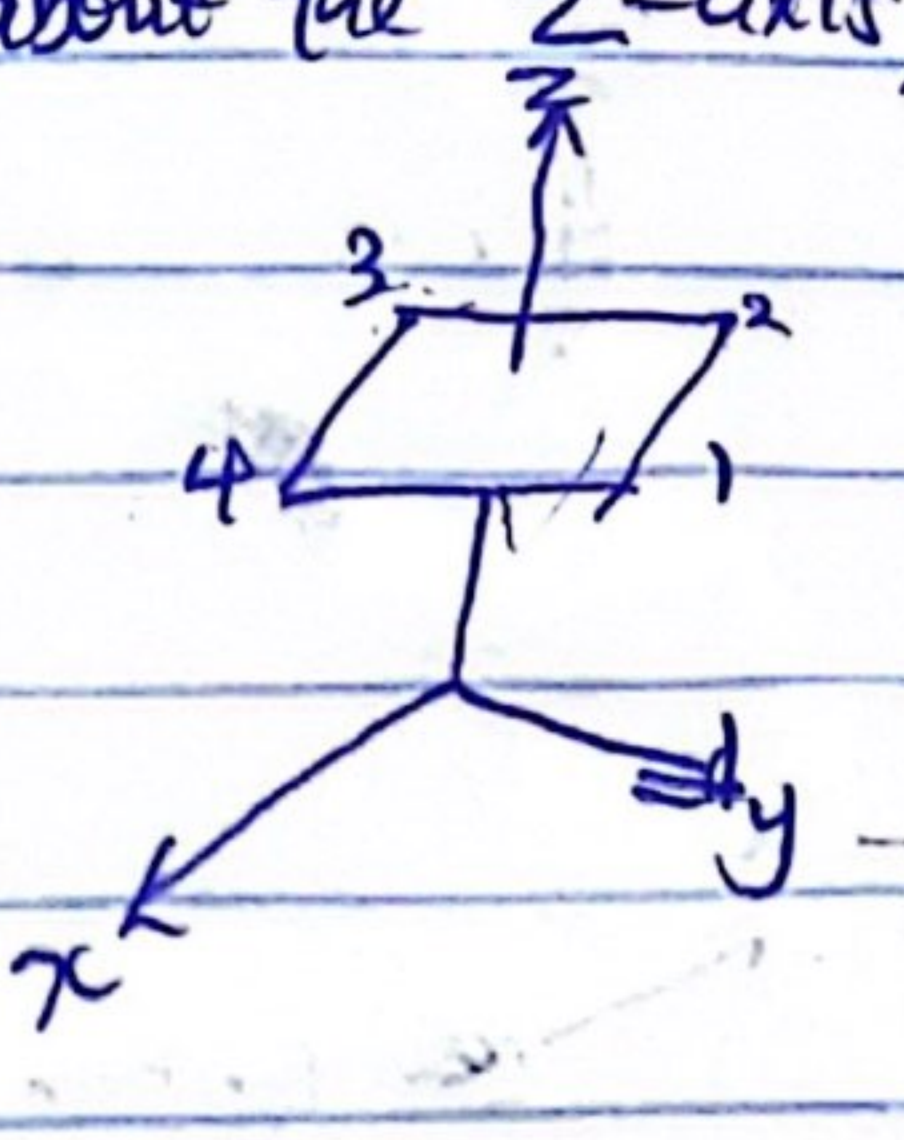
$f(x, y, z)$

$\hat{i}\, f(x, y, z) = f(-x, -y, -z)$

④ $f(x) = x^2 - 3x + 5$

$\hat{i} f(x) = x^2 + 3x + 5$

* $\hat{C}_4$ which means you rotate the function by 90° about the z-axis, ~~this has the effect~~



$x \to y$
$y \to -x$

The effect of this is that x changes to minus, z remains unchanged [illegible] y also changes to [illegible] y

Exampu

① $f(x,y) = xy + y$ y.

$\hat{C}_4 f(x,y) = -xy - x$

② $f(x,y,z) = xy - xz + yz$

21-11-2024

for $\hat{C}_4 = x \to y$
$y \to -x$
$z \to z$

③ Transform using $\hat{C}_4$ rotation

① $f(x,y,z) = xy - xz + yz$
$(y)(-x) - (yz) + (-x)(z)$
$-xy - yz - xz$

② $f(x,y,z) = x^2y + xz + y^2z$
$\Rightarrow y^2(-x) + y(z) + (-x)^2 z$
$= -xy^2 + yz + x^2 z$

Rules of Operation

(1) Equality: For two operators $\hat{\alpha}$ and $\hat{\beta}$ to be equal

$$\left.\begin{array}{l}\hat{\alpha} f(x) = g(x) \\ \hat{\beta} f(x) = g(x)\end{array}\right\} \text{ the same } F(x)$$

Then, $\hat{\alpha} = \hat{\beta}$ the f(x) and the result must be the same.

(2) Addition: Given two operators such that when operated on a fuction f(x) obtain a new function g(x);

$$\hat{\alpha} f(x) = g(x)$$

and, $\hat{\beta} f(x) = h(x)$

Adding the two

$$\hat{\alpha} + \hat{\beta} f(x) = \hat{\alpha} f(x) + \hat{\beta} f(x) = g(x) + h(x)$$

i.e, the distribution law is obeyed

These set of operators are linear operators.

Linear operators are a class of operators that obey the distribution law with respect to addition of functions, i.e

$$\hat{\alpha}(f(x) + g(x)) = \hat{\alpha} f(x) + \hat{\alpha} g(x)$$

Examples of linear and non linear Operator

$\hat{d} = \frac{d}{dx}$, $\hat{x}$, i (linear

The operator for square root is not linear

because, $\sqrt{f(x) + g(x} \neq \sqrt{f(x)} + \sqrt{g(x)}$

(3.) Multiplication: The symbol $\hat{\alpha}\cdot\hat{\beta}$ means operate first with $\hat{\beta}$ and on the result obtained with $\hat{\alpha}$. The operator $\hat{\alpha}^2$ or $\frac{d^2}{dx}$, $\hat{\beta}^2$, means tat you operate with the operator twice

Example

Find $d^2 f(x)$ for $f(x) = \sin 3x$

$$\frac{d^2}{dx^2} f(x) = \frac{d^2}{dx^2}\sin 3x = \frac{d}{dx}\cdot\frac{d}{dx}\sin 3x = \frac{d}{dx} 3\cos 3x = \underline{-9\sin 3}$$

In many cases, the order of operation matters, i.e operators do not necessarily comute

i.e $\hat{\alpha}\hat{\beta} \neq \hat{\beta}\hat{\alpha}$, and $\hat{\alpha}\hat{\beta} - \hat{\beta}\hat{\alpha} \neq 0$

What this inequality means is that the $\hat{\alpha}\cdot\hat{\beta} f(x)$ and $\hat{\beta}\hat{\alpha} f(x)$ do not necessarily give the same result

Example

Consider $\hat{x}$ and $\hat{d}$ on the $f(x) = e^{-x^2}$

If the order of operation is to use $\hat{d}$ first such that, $\hat{x}\hat{d}f(x) = x(-2xe^{-x^2}) = -2x^2e^{-x^2}$

But, if we reverse the order of operation, an entirely different ~~operation~~ result is obtained

$$\hat{d}\hat{x}f(x) = \frac{d}{dx}(xe^{-x^2}) = -2x^2e^{-x^2} + e^{-x^2}$$

$$\Rightarrow (1-2x^2)e^{-x^2}$$

(4) Division; Division is not defined for operators, excep in the following sense, if $\hat{\alpha} f(x) = g(x)$, there may exist some operator β that reverses this transformation, such that

$$\hat{\beta}\, g(x) = f(x)$$

In such a case, we may state that $\hat{\beta} = \alpha^{-1}$ which mathematically implies that

$$\hat{\beta} = \frac{1}{\hat{\alpha}} \Rightarrow \hat{\alpha}\hat{\beta} = 1 //$$

(5) Commutators: ~~We can define~~ Commutator is usually symbolized as $[\hat{\alpha}, \hat{\beta}] = \hat{\alpha}\hat{\beta} - \hat{\beta}\hat{\alpha}$.

$[\hat{\alpha}, \hat{\beta}] f(x)$ for an arbituary function $f(x)$ operated on by this Commutation, you obtain a result such that &

$$[\hat{\alpha}, \hat{\beta}] f(x) = (\hat{\alpha}\hat{\beta} - \hat{\beta}\hat{\alpha})\, f(x))$$

$$= \hat{\alpha}(\hat{\beta} f(x)) - \hat{\beta}(\hat{\alpha} f(x))$$

$= g(x) = 0$ for commutativity

$\Rightarrow g(x) \neq 0$ for non commutativity.

✱ You must know the Order

Example

The commutator of operator $\hat{x}$ and $\hat{d}$ is the most important one for our purposes and we will see later that it has an important physical significance. We need to find the result of $[\hat{d},\hat{x}]f(x)$

$$[\hat{d},\hat{x}]f(x) = \hat{d}\hat{x}f(x) - \hat{x}\hat{d}f(x)$$

$$= \frac{d}{dx}(xf) - x\frac{d}{dx}f$$

$$\Downarrow$$

$$\frac{d}{dx}(xf) = x\frac{df}{dx} + f\frac{dx}{dx} = x\frac{d}{dx}f + f$$

$$\therefore [\hat{d},\hat{x}]f(x) = \cancel{x\frac{d}{dx}f} + f - \cancel{x\frac{d}{dx}f}$$

$$[\hat{d},\hat{x}]f(x) = f \;//$$

$$\therefore \left[\frac{d}{dx}, x\right] = 1 \;//$$

✱ In a similar fashion, derive the commutation

$$[\hat{d}^2,\hat{x}] = 2\hat{d}$$

Eigen Value Equation

The general operator equation $\hat{\alpha} f(x) = g(x)$, has a important special case in which the new function defers from the old one only by multiplication by a constant

$$\hat{\alpha} f(x) = \overset{\text{eigen value}}{a} \underbrace{f(x)}_{\text{eigen function to } \hat{\alpha}} \quad \cdots\cdots (27)$$

(1) e.g

$$\frac{d}{dx} e^{-x} = -e^{-x}$$

$$= \underbrace{-1}_{\text{eigen value}} \cdot \underbrace{e^{-x}}_{\text{eigen function}}$$

(2) $f(x) = 7e^{-3x}$, $\frac{d}{dx}$, Verify if $f(x)$ is an eigen function to the operator $\frac{d}{dx}$

$$\frac{d}{dx} f(x) = \frac{d}{dx} 7e^{-3x} = -21e^{-3x} \Rightarrow \underbrace{-3}_{\text{eigen value}} \cdot \underbrace{7e^{-3x}}_{\text{eigen function}}$$

Compound Operators

Operators such as those illustrated above, can be combined to form compound operators, one example for which this is important is $\hat{h} = \hat{x}^2 - \hat{\partial}^2 = x^2 - \frac{d^2}{dx^2}$.

Another example is the laplacian operator;

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \cdots\cdots (28)$$

Often, the laplacian operator in spherical polar coordinate shall be used

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} + \frac{1}{r^2 \sin\theta} \cdot \frac{\partial}{\partial\theta} \cdot \sin\theta \frac{\partial}{\partial\theta} + \frac{1}{r^2\sin^2\theta} \cdot \frac{\partial^2}{\partial\phi^2} \cdots\cdots (2$$

Example

When using compound operators of the type found in eqn (29), the right to left rule must be followed strictly. The first term of eqn (29) operating on the function e^{ar}

$$\frac{1}{r^2}\left\{\frac{\partial}{\partial r}\left[r^2\left(\frac{\partial}{\partial r}e^{ar}\right)\right]\right\} = \frac{1}{r^2}\left[\frac{\partial}{\partial r} ar^2 e^{ar}\right]$$

$$= \frac{1}{r^2}\left(2are^{ar} + a^2r^2e^{ar}\right)$$

$$= \left(\frac{2a}{r} + a^2\right)e^{ar}$$

Do you notice that this not an eigen value equation?

Question

$$\hat{h} = \hat{x}^2 - \frac{d^2}{dx}, \quad f(x) = e^{-\frac{x^2}{2}}$$

The operator $\hat{h}$ defined above is?

solution

$$\hat{h} = x^2 e^{-\frac{x^2}{2}} - \frac{d}{dx}\left(\frac{d}{dx}\left(e^{-x^2/2}\right)\right)$$

$$\hat{h} = x^2 e^{-\frac{x^2}{2}} - \frac{d}{dx}\left(-x e^{-\frac{x^2}{2}}\right)$$

$$\hat{h} = x^2 e^{-\frac{x^2}{2}} - \left(-e^{-\frac{x^2}{2}} + x \cdot \left(-xe^{-x^2/2}\right)\right)$$

$$\hat{h} = x^2 e^{-x^2/2} - \left(-e^{-x^2/2} + x^2 e^{-x^2/2}\right.$$

$$\hat{h} = \cancel{x^2 e^{-x^2/2}} + e^{-x^2/2} - \cancel{x^2 e^{-x^2/2}}$$

$$\hat{h} = 1 e^{-x^2/2}$$

eigen value = 1, eigen function = $e^{-x^2/2}$

25-11-2024

$\psi = 0$ → trival function

$\psi = 2 \quad \psi = e^{kx}, \; k = 0$

Simultaneous Eigen Function

If each operator has a set of functions — is it possible that some functions will be eigen functions of two different operators?

Theorem: Two operators that do not commute may not have a complete set of functions that are eigen functions of both.

Conversely, if the operators do commute, such a set of simultaneous eigen function will exist. However, it should be noted that all possible eigen functions of an operator, need not be eigen functions of another, ~~of another~~ commuting operator; but some will be so.

Proof: Suppose that two operators ($\hat{\alpha}$ and $\hat{\beta}$) both have some non-trival eigen function ψ. For the two operators ($\hat{\alpha}$ & $\hat{\beta}$), the eigen value equations are;

$$\alpha\psi = a\psi \quad \text{-----(i)}$$

$$\beta\psi = b\psi \quad \text{-----(ii)}$$

E.g You operate on the first equation with β and the second op~~erator~~ with α

$$\hat{\beta}(\alpha\psi) = ba\psi \quad \text{---(iii)}$$

$$\hat{\alpha}(\beta\psi) = ab\psi \quad \text{----(iv)}$$

Substracting the two equations, we have;

(iii) and (iv)

$\hat{\alpha}(\hat{\beta}\psi) - \hat{\beta}(\hat{\alpha}\psi) = (ab - ba)\psi$

Since a & b are constant

$ab - ba = 0$; we can then write;

$$(\hat{\alpha}\beta - \hat{\beta}\alpha)\psi = 0.$$

$$[\hat{\alpha}, \hat{\beta}]\psi = 0 \quad \ldots\ldots (30)$$

There, eqn 30 is proved for a non-trival set of a Such simultaneous eigen function to exist as long as the operators commute

Ladder Operator

Another type of commutation, is one that is of the form $[\hat{\alpha}, \hat{\beta}] = K\hat{\beta}$ ----- ③1

Where K is a constant.

Such operators have the property that the operator $\hat{\beta}$ is a generator for the eigen functions of $\hat{\alpha}$

This can be proved by assuming that ψ is an eigen function to $\hat{\alpha}$, so that

$$\hat{\alpha}\psi = a\psi$$

Since $\hat{\alpha}$ and $\hat{\beta}$ do not commute, ψ cannot be eigen function of β. But, if we ~~decide~~

ψ = psi. α = Fi/phi

to operate $\hat{\beta}$ on ψ, we give

$$\beta\psi = \phi$$

Here ϕ is some new function

Is ϕ an eigen function of $\hat{\alpha}$?

To find out, we operate $\hat{\alpha}$ on Φ

$$\hat{\alpha}\Phi = \hat{\alpha}(\hat{\beta}\psi)$$

The commutation eqn (31) allows us to write

$$\hat{\alpha}\beta - \hat{\beta}\alpha = k\hat{\beta} \Rightarrow \hat{\alpha}\beta = \beta\hat{\alpha} + k\hat{\beta}$$

$$\Rightarrow \hat{\alpha}(\hat{\beta}\psi) = \hat{\beta}(\hat{\alpha}\psi) + k(\hat{\beta}\psi)$$

We know that $\hat{\alpha}\psi = a\psi$, then,

$$\hat{\alpha}(\hat{\beta}\psi) = \hat{\beta}(a\psi) + k(\beta\psi)$$

$$\hat{\alpha}(\hat{\beta}\psi) = a(\hat{\beta}\psi) + k(\hat{\beta}\psi)$$ From ($\beta\psi = \phi$)

$$\alpha\phi = a\Phi + k\phi$$

$$\alpha\phi = (a+k)\phi$$

∴ ϕ is an eigen function of $\hat{\alpha}$
With eigen value $a+k$

Assignment (to be submitted)

Repeat this procedure to show that

$$\beta\phi = \beta^2\psi$$ with eigen value $a+2k$

This will show that $\hat{\beta}$ generates a ladder of eigen functions for $\hat{\alpha}$ and the relationship of Commutato to "quantization" may be starting to become apparent

Questions

(1) a Show that

$f_1(x) = e^{-x^2/2}$ is an eigen function of $\hat{h} = x^2 - d$

(b) Show that it is also an eigen function of

$\hat{A} = x - \hat{d}$

(ii) $f_2(x) = 2xe^{-x^2/2}$, show that it is an eigen function of

$\hat{h} = \hat{x}^2 - \hat{d}^2$

(iii) Find the result of the commutator $[\hat{h}, \hat{A}]$

Postulates of Quantum Theory

Postulate approach often begins the treatment of problems by giving series of statements that are not necessarily self evident or obvious that are only presumed to be true.

This statements are expected to be experimentally investigated, and ~~they are~~ their "proof" is the ability to explain the experimental observation

Assigenment (to be Submitted)

~~Question~~ (i) What is the difference between postulate, ~~and~~ hypotheses and theory.

~~(ii) What is the differences between theory and law.~~

First Postulate in Quatum Theory; Postulate 1

The physical state of a particle/system is described as fully as possible by an appropriate wave function (or state function) which could be $\psi(x, y, z, t)$ in space and time (t)

By the first postulate, the wave function is expected to contain all the information that can be known and should be known, about the particle or system.

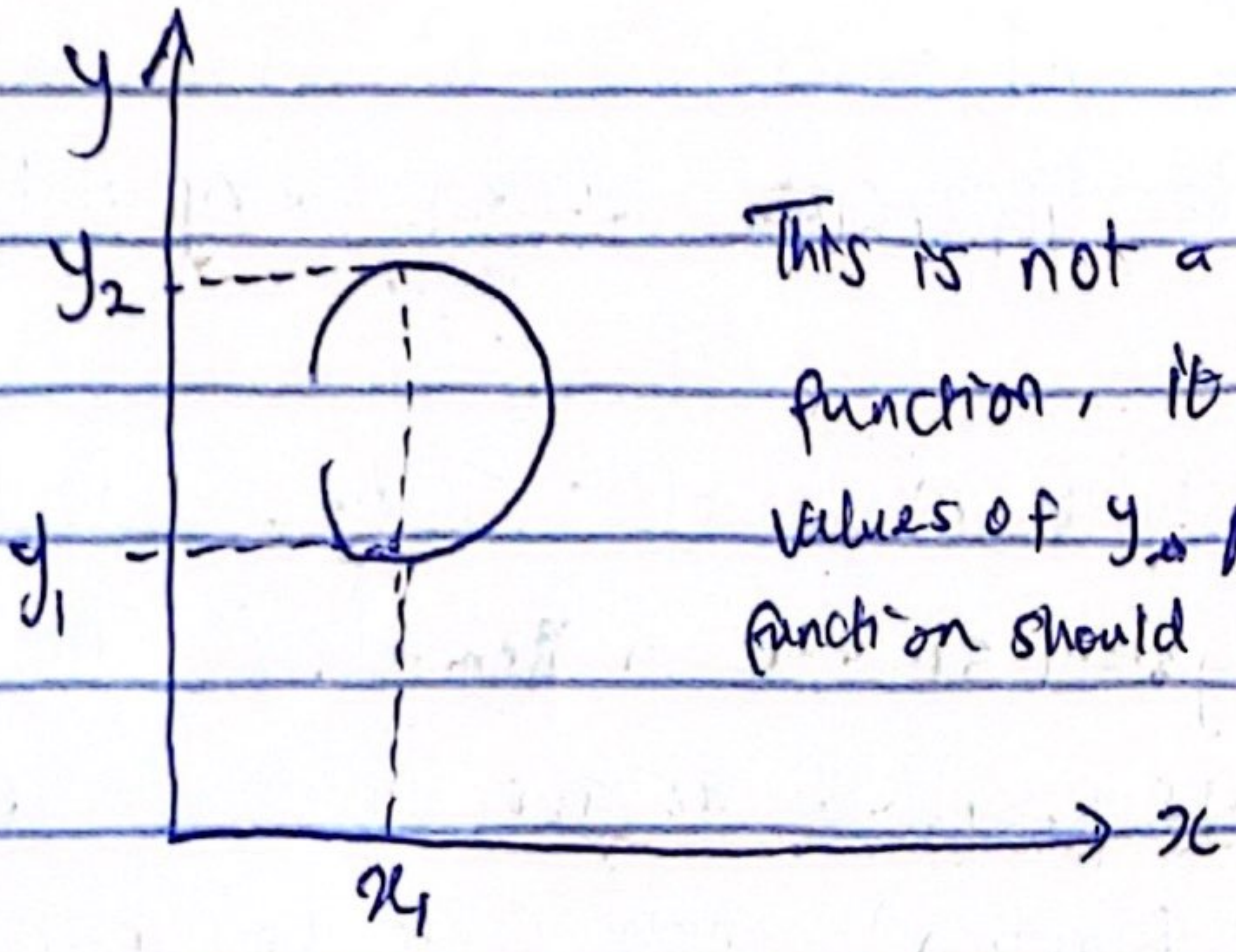
The following are the conditions that a wave function ~~sho~~ must satisfy to be appropriate to describe a relevant system.

wave function is a single word

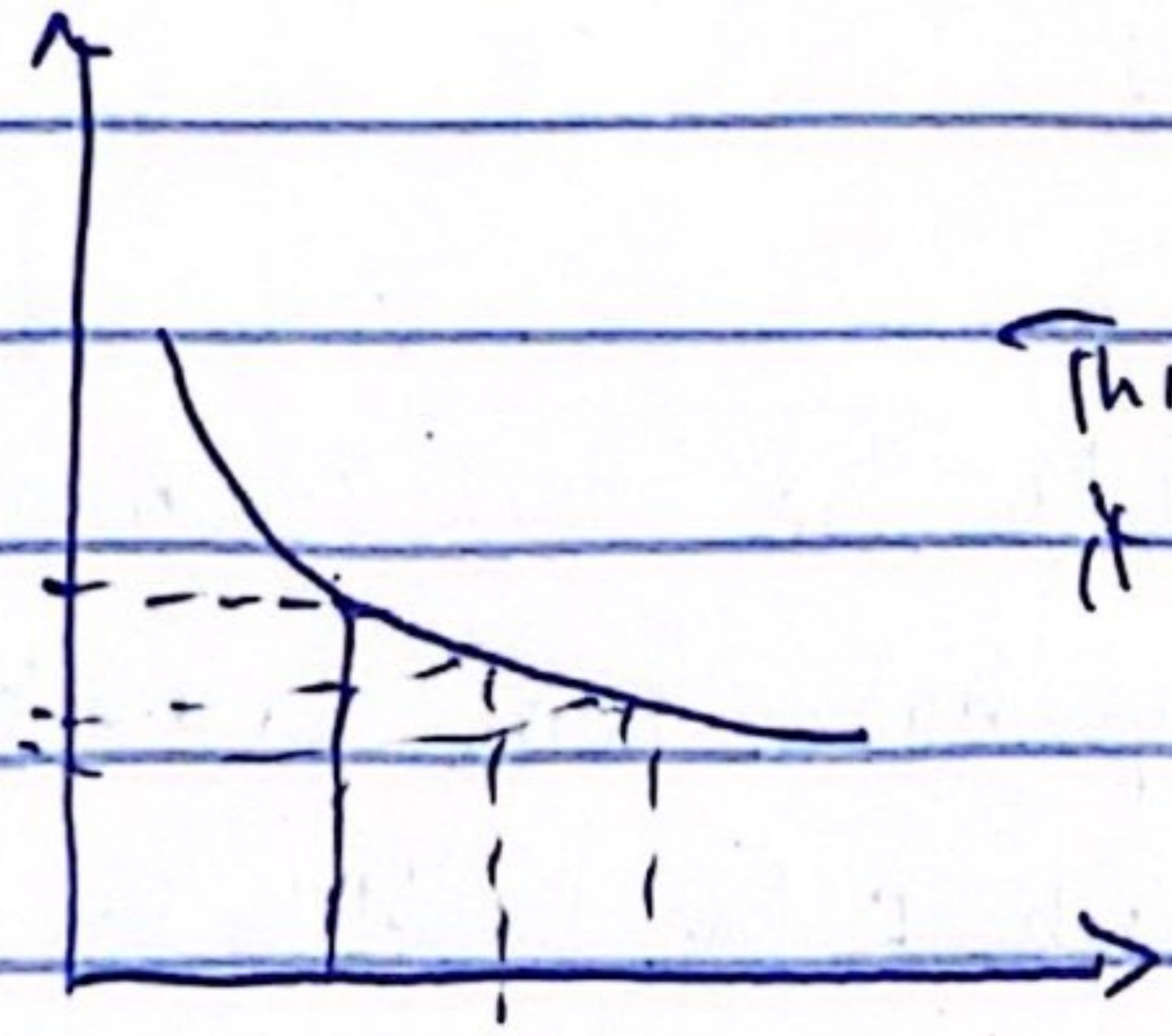
Single valued is a single word

(a) Like all functions, ~~wave function~~ wavefunction must be Single-valued. This means that at any point in space and time. The square of the wave function may have only one possible numerical value, i.e, it should not be a function with the following graphical property

Question: What are four ways of representing a function?



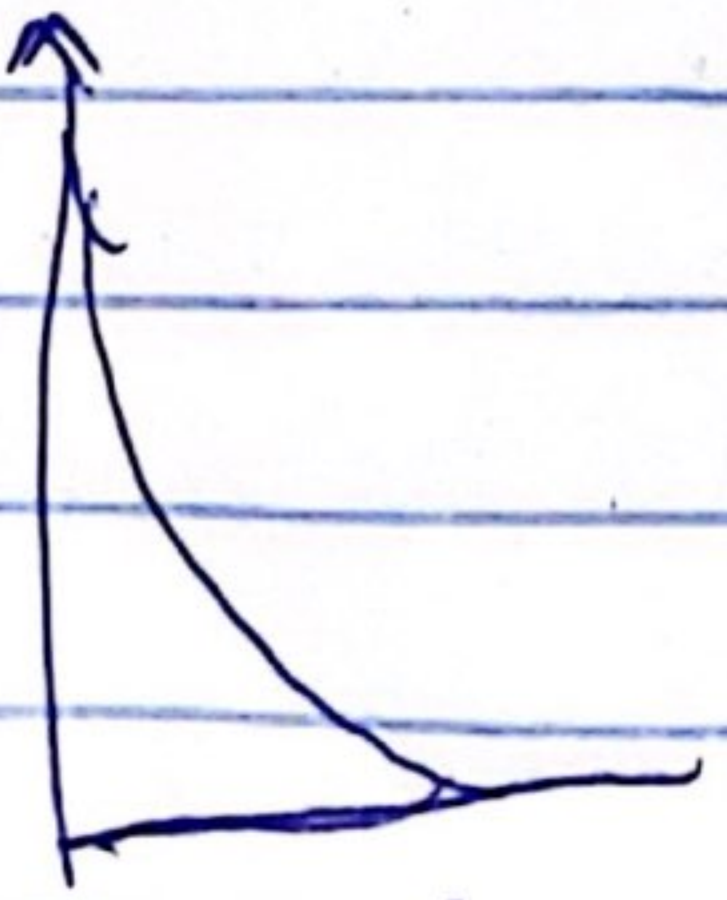
This is not a good wave function, it has two values of y. A good wave function should be single valued.



This is a good wave function, it is single valued

(b) A wavefunction must be finite and continuous at all point in space, i.e, it should not be a function with the following graphical pattern

e.g a straight line graph is continuous



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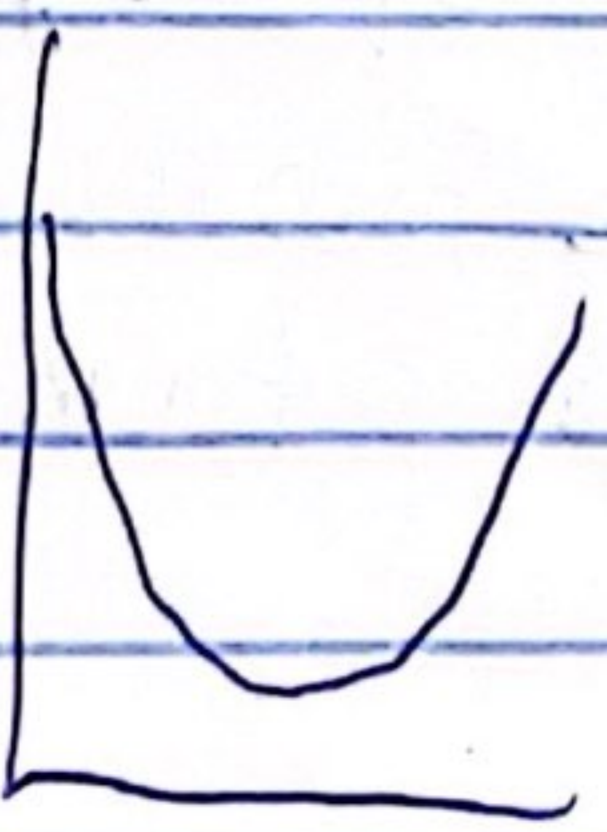

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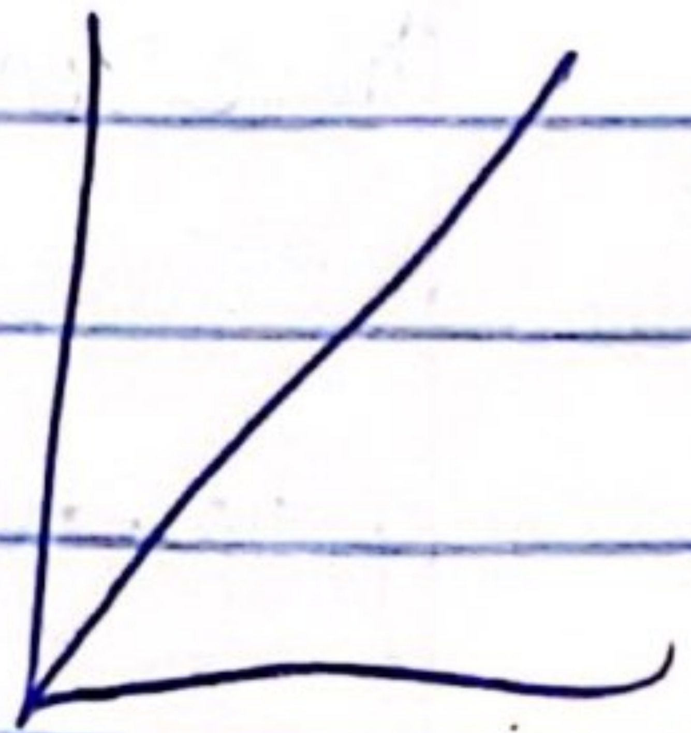

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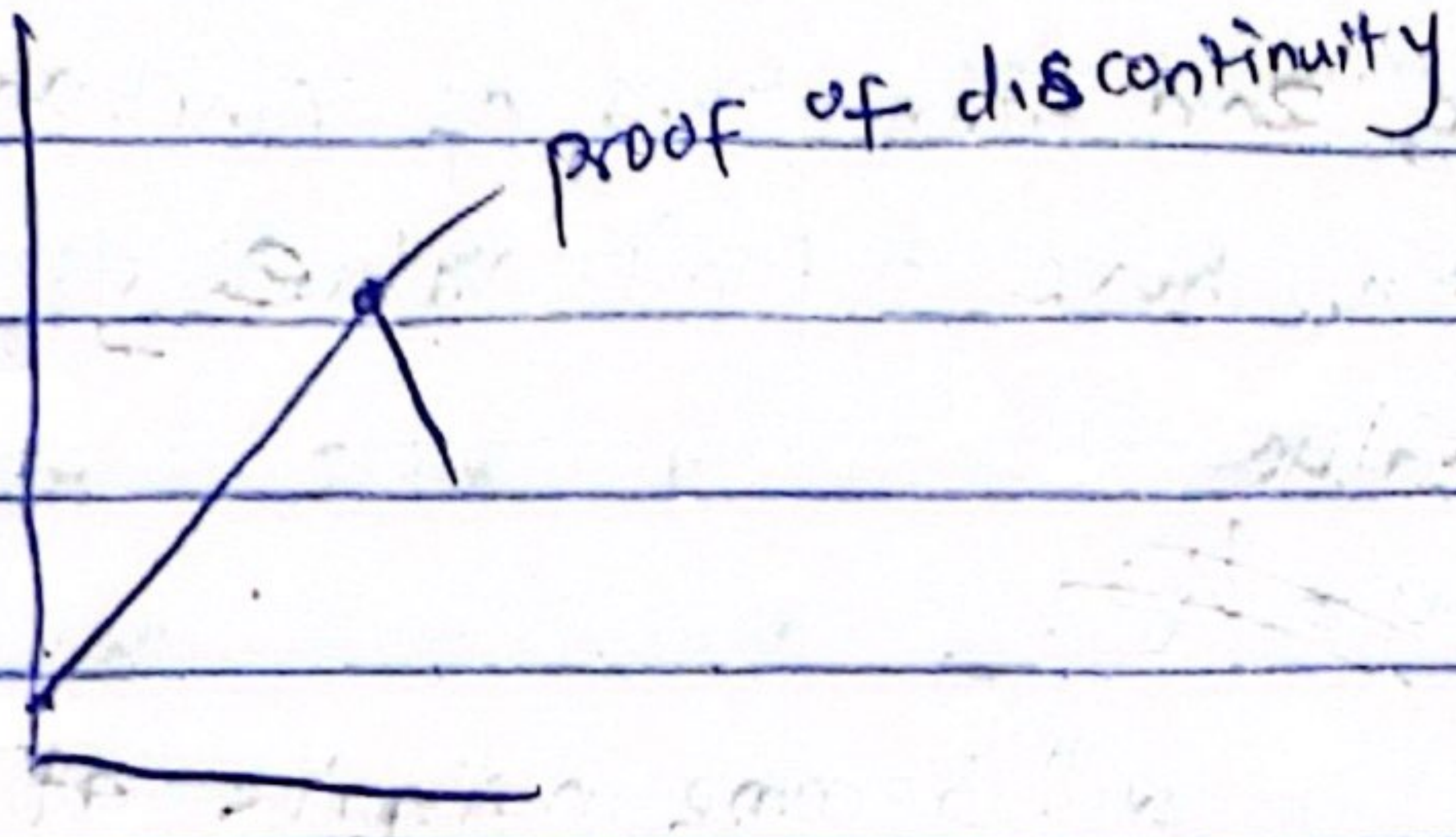

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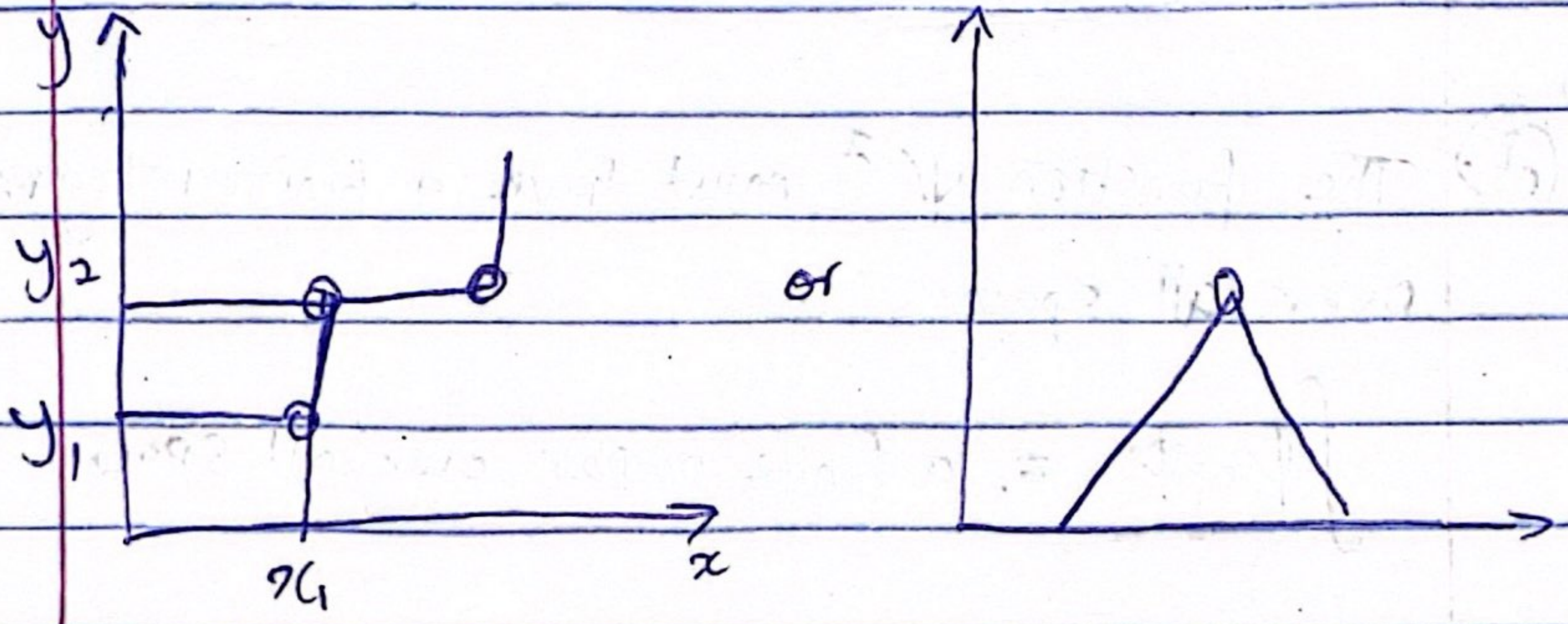

Finite means there must be a finite value, (∞ means infinite)

~~e.g #~~ Single valued — one value

① The wave function first and second derivature must be finite and continuous.

e.g $f(x) = 2x^2$, $\frac{d}{dx} = 4x$, $\frac{d^2}{dx} = 4$

A trival example is to assume that the wave function

$y = x^3$

$\frac{dy}{dx} = 3x^2$ and $\frac{d^2y}{dx^2} = 6x$

Both the 1st & 2nd derivatives of function y are continuous and we have a finite values y at a particular x-value

A function like ~~$y = 1/x^3$~~

$$y = \frac{1}{x^3 + 3x^2}$$ will become infinite at $x = 0$

and so will not be fit for a wave function.

(d) The function ψ^2 must have a finite integral over all space

$$\int \psi \cdot \psi$$ = a finite number over all space

For a single particle, integral "all space" means in Cartesian coordenate

$$\int_{-\infty}^{+\infty} dx \int_{-\infty}^{+\infty} dy \int_{-\infty}^{+\infty} |\psi|^2 dz$$ = a finite value

In spherical polar coordinate integral all space for (r, θ, ϕ)

$$\int_{0}^{2\pi} d\phi \int_{0}^{\pi} \sin\theta \, d\theta \int_{0}^{\infty} |\psi|^2 r^2 dr =$$ a finite number

Since a function (generally), is not altered in its essential nature when multiplied by a constant, it's always possible to scale the wave function so that the "finite number" which is the output of the integral of the square of the wave function, can be equal to 1.

e.g $\int_{\text{over all space}} |\psi^2| \, dx = 2/3$

(They always want the integral of the square of the wavefu to be 1 because of probability

$$N^2 \int_{\text{over al space}} |\psi|^2 \, di = 2/3$$

where $N^2 = 3/2$

~~It~~e's

We can then write,

$$N^2 \int_{\text{all space}} \psi^2 \psi \, di = 1 \ldots\ldots (32)$$

Normalization costant

N in eqn (32) is called the normalization constant. When this is done, the wave function is said to be normalized.

The practical meaning of this is that the probability which is the square of the wavefunction of

(202) (202)

i

finding the location of an electron, atom, ion, molecule, etc, anywhere in space is certainly **1**.

Question:

Assuming $\psi = x$, normalize the wave function within the region of $0 \leq x \leq 1$

$$N^2 \int \psi^2 = 1$$

$$\int_0^1 x^2 \, dx$$

$$\Rightarrow \left[\frac{x^3}{3}\right]_0^1$$

$$\Rightarrow \left[\frac{1^3}{3}\right] - 0$$

$$\Rightarrow \frac{1^3}{3} = \frac{1}{3}$$

$$N^2 = \frac{3}{1}$$

$$N = \pm\sqrt{3}$$

28 - 11 - 2024

Postulate 2:

Every physical observable is represented by a linear operator. Observable can be describeds as properties that can be measured and determined through experiment.

In classical mechanics the principal variables are the position (x, y, z) and the velocity (v) or momentum p (mv), vectors. They are vector quantities.

The same is true for quantum mechanical "observables" except that momentum is more useful, than velocity. ~~except that momentum is~~

For these observables, the basic operators are;

① position: x, y, z

② Linear momentum: $P_x = \frac{\hbar\partial}{i\partial x} = -ih\frac{\partial}{\partial x}$; $P_y = \frac{h\partial}{i\partial y} = -i\hbar\frac{\partial}{\partial y}$;

$$P_z = \frac{h\partial}{i\partial z} = -ih\frac{\partial}{\partial z} \quad \text{----} (33)$$

where $i = \sqrt{-1}$

③ Angular momentum: $L_x = -i\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)$

matrix representation;

$$L = -i\hbar\begin{vmatrix} \hat{i} & \hat{j} & \hat{k} \\ x & y & z \\ \frac{\partial}{\partial x} & \frac{\partial}{\partial y} & \frac{\partial}{\partial z} \end{vmatrix},$$

$$L_y = -ih\left(x\frac{\partial}{\partial z} + z\frac{\partial}{\partial x}\right);$$

$$L_z = -ih\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right.$$

$\frac{\hbar\partial}{i\partial x} = ih\frac{\partial}{\partial x}$

(4) Kinetic Energy: $E_K = \frac{p^2}{2m} = \frac{1}{2m}\left(p_x^2 + p_y^2 + p_z^2\right)$

$$= \frac{1}{2m}\left[\left(-i\hbar\frac{\partial}{\partial x}\right)^2 + \left(-i\hbar\frac{\partial}{\partial y}\right)^2 + \left(-i\hbar\frac{\partial}{\partial z}\right)^2\right]$$

$$= \frac{i\hbar^2}{2m}\nabla^2 = \frac{-\hbar^2}{2m}\nabla^2 = \frac{-h^2}{8\pi^2 m}\nabla^2$$

(5) Potential Energy: It is a function of x, y, z depending on the system under consideration. $V_p(x, y, z)$

(6) Total Energy (Time-dependent): $E = E_K + V_p$;

$$H_t = \frac{-h}{2\pi i}\frac{\partial}{\partial t}$$

(7) Total Energy (Conservative System): $\hat{H} = \frac{-\hbar}{8\pi^2 m}\nabla^2 + V_p(x, y, z)$

There are other important observables, such as dipole moments and magnetic moments. Operators that represents physical Observables are called Hamitian operator

Postulate 3:

The measurement of a physical observable will give a result that is one of the eigen values of a corresponding (appropriate) operator for that observable.

This immediately raises the possibility of quantization, since only certain values (eigen values) are possible.

Suppose that operator α representing some physical quantity A_i has a set of eigen functions $\{\psi_i\}$ with eigen value $\{a_i\}$, according to the equation

$$\alpha \psi_i = a_i \psi_i \quad \ldots\ldots (34)$$

Any measurement of A must give as a result, one of the set of eigen value.

~~The Hamiltonian~~

The Hamiltonian

The most useful of the physical observative is the total energy E. It operator is called Hamiltonian and it given the symbol $\hat{H}$.

The eigen value equation for this operator is called Schrodinger equation

$$\hat{H}\psi = E\psi \quad \ldots (35)$$

$$\left[\frac{-h^2}{8\pi^2 m}\nabla^2 + V_p(x,y,z)\right]\psi = E\psi \quad \ldots (36)$$

The eigen values of the Hamitonian operator $(\hat{e_i})$ are the allowed energy of the system; according to posulate 3, only these values will be found if the energy of the system "measured".

Average Value Theorem

Assumption: If a wave function is an eigen function of a particular operator, then a measurement of the corresponding physical property will give us an answer, the eigen value.

But, if the wave function (ψ) is not an eigen function of a particular operator ($\hat{\alpha}$), measurement will give one of the eigen values of that operator, even though we may not be able to determine which one of the eigen values

The average value that will be obtained from repeated measurement can be calculated. This quantity is denoted by $\langle \alpha \rangle$ and also called the expected value and it is calculated by finding the integral over all space of the s~~quare~~ wave function and conjugate of the wave function

$$\langle \hat{\alpha} \rangle = \int_{\substack{\text{all} \\ \text{space}}} \psi^* (\hat{\alpha}\,\psi)\, d\tau \quad \text{---} \; 37$$

assuming that ψ is normalized

* only use conjugate only if it's complex function

$$\psi = e^{ix}$$

$$\langle \alpha \rangle = \int e^{-ix} (\hat{\alpha} e^{ix}) dx$$

$$\langle P_x \rangle = \int e^{-ix} \left(-i\hbar \frac{d}{dx} e^{ix}\right) dx \rightarrow \text{soln.}$$

$$\langle P_x \rangle = \int e^{-ix} (-i\hbar (ie^{ix})) dx$$

$$\langle P_x \rangle = \int e^{-ix} (-i \cdot i (\hbar e^{ix})) dx$$

$$\langle P_x \rangle = \int e^{-ix} (1 \cdot \hbar e^{ix}) dx$$

$$\langle P_x \rangle = \hbar \int e^{-ix} \cdot e^{ix} dx$$

$$\langle P_x \rangle = \hbar \int e^{-ix+ix}$$

$$\langle P_x \rangle = \hbar \int e^{0} \Rightarrow \langle P_x \rangle = \hbar x + C$$

2-12-2024

Orthogonality

Recall that we mentioned that operators that can represent physical variable (observables) is called Hermitian operator. The eigen function of a Hermitian operator have an important property which is they form a complete orthogonal set.

For Ψ_1 and Ψ_2 are orthogonal (i-e if Ψ_1 and Ψ_2 are members of the set). This equation must hold;

$$\int_{\text{all space}} \Psi_1^* \Psi_2 \, d\tau = 0 \quad \ldots\ldots (38)$$

In summary, two functions, Ψ_1 and Ψ_2, are orthogonal if the integral of the complex conjugate of one multiplied by the other is zero, according to eqn (38).

As we have already seen above, this integral can be normalized. When $\Psi_1 = \Psi_2$, we can write

$$\int \Psi_1^* \Psi_2 \, d\tau = \begin{cases} 1 & \text{if } 1 = 2 \\ 0 & \text{if } 1 \neq 2 \end{cases} \quad \ldots\ldots (39)$$

The above combination is called which is eqn (39) is called an orthonormal set

$$\int_{\text{all space}} \Psi^2 \, d\tau = 1 \Rightarrow \text{orthonormal set}$$

(wave function already normalized)

~~We can write~~ Complete set of function (completeness of functions) means that we can expresss a function as a linear combination of the orthonormal

Set.

$\Psi = \Sigma_n C_n \psi$

$\Psi = C_1\psi_1 + C_2\psi + C_2\psi + \dots + C_n\psi$ .....(40)

Where C_n are constants

Show that the function $\sin\phi$ and $\cos\phi$ defined for the interval $0 \leq \phi < 2\pi$ are orthogonal to each other.

$$\int_0^{2\pi} \sin\phi \cos\phi = 0 \quad \text{(orthogonal Condition)}$$

let $u = \cos\phi$

$$\frac{du}{d\phi} = -\sin\phi, \quad d\phi = \frac{du}{\sin\phi}$$

$$\Rightarrow -\int_0^{2\pi} \sin\phi \cdot \cos\phi \frac{du}{\sin\phi} = -\int_0^{2\pi} \cos\phi\, du$$

$$\Rightarrow -\int_0^{2\pi} u\,du = \frac{-u^2}{2} = \left[-\frac{\cos^2 u}{2}\right]_0^{2\pi}$$

$$= -\frac{1}{2} + \frac{1}{2} = 0$$

Measurement and Uncertainty

Earlier, we raised two possibilities for the result of the measurement of physical observable:

(i) The wave function is an eigen function of the operator, representing the observable

(ii) The wave function is not an eigen function (average value thes,

In the first case, every measurement will give the same answer - the eigen value.

In the second case, different answers will be obtained for ~~different~~ every measurement, and the observable will be obtained by finding the average of all possible measurement using the average value equation in eqn (37)

For the second case, it should be noted that there is some uncertainty in the observable, since none of the result of the seperate measurement can be ascertain as the true value.

Suppose a quantity (A) was measured and the average $\langle A \rangle$ and the variance (σ_A^2) were obtained. The Variance can be related to the average value by eqn (41)

$$\sigma_A^2 = \langle A^2 \rangle - \langle A \rangle^2 \quad \cdots\cdots (41)$$

These when applied in quantum mechanics, the average Value according to eqn (37) will give

$$\langle \hat{\alpha}^2 \rangle = \int \psi^* (\hat{\alpha}^2 \psi) \, di \cdots\cdots (42)$$

$$\langle \hat{\alpha} \rangle = \int \psi^* (\hat{\alpha} \psi) \, di$$

For the other quantity $\langle \hat{\alpha} \rangle^2$, then square the

The uncertainty will be defined as the standard deviation of the measurement. For the observable (A) Physical quantity represented by the operator $\hat{\alpha}$, The Uncertainty will be

$$\sigma_A = \pm \sqrt{\langle A^2 \rangle - \langle A \rangle^2}$$

04-12-2024

Heisenberg's Uncertainty Principle

Suppose we have two physical ~~properties~~ quantities A and B represented by operator $\hat{\alpha}$.

Ai operator $\hat{\alpha}$ with eigen function $\{\psi_i\}$ (eigen values a_i)

Bi Operator $\hat{\beta}$ with eigen function $\{\phi_i\}$ (eigen values b_i)

As discussed earlier, these sets of eigen function can be the same only if the operators commute.

If the system is ~~in~~ a state represented by the functions ψ_i, a measurement of A will give the result a_i, then a measurement of B will give a result of the allowed values $\{b_j\}$

The superposition principle requires that the wavefunction ψ_1 can be expanded in terms of the eigen function of $\hat{\beta}$

$$\psi_1 = \sum_j c_{ij} \phi_j$$

The average value theorem gives

$$\langle \hat{\beta} \rangle = \int \psi_i^* (\hat{\beta} \psi_i) \, di$$

$$= \int \sum_j (c_{ij} \phi)^* \cdot \beta \left(\sum_k c_{ik} \phi_k \right) di$$

Since the ϕ function are eigen function of β, this ~~operator~~ equation becomes

$$\langle \hat{\beta} \rangle = \int \sum_j (c_{ij} \phi_j)^* \left(\sum_k b_k c_{ik} \phi_k \right) di$$

$$= \sum_j \sum_k C^*_{ij} C_{ij} b_k \int \phi^*_j \, \phi_k \, di$$

Remember/recall that the set $\{\phi_j\}$ is orthonormal, so only the terms with $j = k$ gives a non-zero result while terms with $j \neq k$ gives zero.

Therefore,

$$\langle \beta \rangle = \sum_j C^*_{ij} C_{ij} b_j = \sum_j |C_{ij}|^2 b_j$$

The coefficient $|C_{ij}|^2 = C^*_{ij} C_{ij}$ is therefore the probability that a particular value (b_j) will be obtained for measurement of B when the system is in a state represented by ψ_i which is the state for which the measured value A is a_i with α as the operator.

Now, supposing we measure B and get a result b_i, it is an indication that the system is in the state represented by ϕ_i. If you now measure A when the system is in a state represented by function ϕ_i, the superposition principle can be used in reverse to show that,

$$\phi_i = \sum_j C_{ij} \psi_j$$

(9.4) .....

The measurement ~~of~~ A will now be subjected to the statistical uncertainties that previously applied to B.

\# All these ~~the~~ operations / transformations are for commuting operators.

05 - 12 - 2024

What happens when the operators do not commute?

There is a fundamental incompatibility in the measurement of physical variables that are represented by non commuting operator, which is - a measurement of one causes an uncertainty in the other.

This idea was new ~~known~~ and peculiar to quantum mechanics. Before the advent of quantum theory, it was a common knowledge that physical measurement contain some degree of uncertainty, but it had been assumed that it was merely a limitation imposed by the experimental method, apparatus ~~or both~~, or even human error or all.

For quantum mechanics, this limitation is, in most cases, fundamental and unavoidable. The product of the uncertainty of two physical quantities, A and B can shown to be

$$\sigma_A \cdot \sigma_B \geq \frac{1}{2} \left| \langle [\hat{\alpha}, \hat{\beta}] \rangle \right| \quad \cdots\cdots (44)$$

For a normalized wave function ψ

$$\langle [\hat{\alpha}, \hat{\beta}] \rangle = \int \psi^* (\hat{\alpha}\hat{\beta} - \hat{\beta}\hat{\alpha}) \psi \, d\tau$$

Eqn (45) is the general statement of the Heisenberg's uncertainty principle. The uncertainty principle is commonly used for two non commuting ~~c~~operators, the position (x), and the corresponding momentum p_x

Using the operators as defined in postulate 2, the commutator can readily be calculated

$$[\hat{p}_x, \hat{x}] = \hat{p}_x \hat{x} - \hat{x} \hat{p}_x = \frac{\hbar}{i}\left[\frac{d}{dx}x - \frac{x\,d}{dx}\right]f$$

$$\Rightarrow \frac{h}{i}\left[\frac{d}{dx}xf - \frac{x\,d}{dx}f\right]$$

~~$\Rightarrow \frac{h}{i}\left[\frac{d}{dx}f + \frac{x\,df}{dx} - \left(f\frac{dx}{dx} + x\frac{df}{dx}\right)\right.$~~

$$\Rightarrow \frac{h}{i}\left[f\frac{dx}{dx} + x\frac{df}{dx} - \frac{x\,df}{dx}\right)$$

$$\Rightarrow \frac{h}{i}f = \frac{h}{i} = -ih$$

The magnitude of this quantity because $[\hat{p}_x, \hat{x}]$ is $\hbar$

$$|[p_x, x]| = \hbar \quad \ldots (46)$$

Let $z = a + ib$

$$|z| = [(a+ib)(a-ib)]^{1/2}$$

$$|z| = (a^2 + b^2)^{1/2}$$

Atople.

C

Thus, eqn (44), with A representing p_x and B representing x

$$\sigma_{p_x} \cdot \sigma_x \geq \frac{1}{2} \hbar$$

$$\sigma_{p_x} \cdot \sigma_x \geq \frac{\hbar}{2}$$

The Free Particle.

We will now apply the postulates to some simple systems that are related to some important Chemical problems.

The simplest application is to a particle of mass m moving freely in on dimension, which we will take to be x direction. This is known as the free particle problem in one dimension i.e in one dimensional free particles.

Since the particle is moving freely with no forces acting on it, the potential energy V_p is constant throughout its motion and we take it to be zero.

The total energy is therefore the kinetic energy, ordinarily $(\frac{1}{2}mv_x^2)$, which is $\frac{p_x^2}{2m}$ where p_x is the momentum the total energy in Hamiltonian form is thus $\frac{p_x^2}{2m}$

$$\hat{H} = \frac{P_x^2}{2m} \quad \cdots\cdots (47)$$

P_x as earlier noted can be represented in quantum mechanics by

$$\hat{H} = \frac{P_x^2}{2m} = \frac{(-i\hbar \frac{d}{dx})^2}{2m} = \frac{-\hbar^2}{2m}\frac{d^2}{dx^2} = \frac{-h^2}{8\pi^2 m}\frac{d^2}{dx^2}$$

The eigen function - eigen value equation for the total energy of a free particle will be;

$$H\psi = E\psi$$

Where ψ is the wave function that describes the state of the free particle and E is the energy (eigen value) of the moving particle.

The we can write the complete eigen function - eigen value equation as;

$$\frac{-h}{8\pi^3 m}\frac{d^2}{dx^2}\psi = E\psi$$

$$\frac{d^2\psi}{dx^2} = \frac{-8\pi^2 m E\psi}{h^2}$$

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2 m}{h^2}E\psi = 0 \quad \cdots\cdots (48)$$

There are two solutions to the differential eqn (48)

~~$\psi = Ae^{i}$~~

$$\psi_1 = Ae^{i\frac{\sqrt{8\pi^2 mE'x}}{h}}$$

$$\psi_2 = Be^{-i\frac{\sqrt{8\pi^2 mE'x}}{h}}$$

where A and B are constants

The fact that these are solutions may be easily verified by Substituting them into eqn (48)

The relatively probability density of the particle is

$$|\psi|^2 = \psi^*\psi$$

$$|\psi_1|^2 = \psi_1^*\psi_1$$

$$= Ae^{i\frac{\sqrt{8\pi^2 mE'x}}{h}} \times Ae^{-i\frac{\sqrt{8\pi^2 mE'x}}{h}}$$

$$= A \times A = |A|^2 \quad \text{---} (49)$$

Both quantities are independent of x, So that there is an equal probability of finding the particle ~~distance~~ at any distance along the x-axis

The particle is therefore non localized

Find the eigen value for a free particle system

$$\psi = Ae^{i(8\pi^2 mE)^{1/2} x/h}$$

$$P_x = \frac{h}{2\pi i}\frac{d}{dx}$$

$$\frac{h}{2\pi i}\frac{d}{dx}\varphi = P\psi$$

$$\frac{h}{2\pi i}\frac{d}{dx}Ae^{i(8\pi^2 mE)^{1/2}\frac{x}{h}}$$

$$\frac{h}{2\pi i}\cdot A\cdot i(8\pi^2 mE)^{1/2}\cdot\frac{1}{h}\cdot e^{i(8\pi^2 mE)^{1/2}\cdot\frac{x}{h}}$$

$$\Rightarrow = PAe^{i(8\pi^2 mE)^{1/2}\frac{x}{h}}$$

where $P = \frac{\cancel{h}}{2\pi \cancel{i}}\cdot\cancel{i}(8\pi^2 mE)^{1/2}\cdot\frac{1}{\cancel{h}}$

$$P = \frac{1}{2\cancel{\pi}}\cdot\sqrt{8mE}\cdot\cancel{\pi} \Rightarrow P = \frac{\sqrt{8mE}}{2} = \frac{\sqrt{8mE}}{\sqrt{4}}$$

$$\Rightarrow P = \sqrt{\frac{8mE}{4}} \Rightarrow \pm\sqrt{2mE} \quad \text{....(57)}$$

P = allowed momentum

This solutions corresponds to the classical values

P_x is positive if the particle is moving in one

XPS - Xray photoelectron spectroscopy

direction and negative if it is moving in the other direction. For this case, there is no quantization, and we can give the particle any energy we like.

An example of a free particle is an electron that has been separated from an atom, after which its energy will no longer be quantized

One Dimensional Box

The mathematical difficulty of a quantum mechanical problem, depends primarily on a potential function; The case of $V=0$, the free particle, is therefore is simplest. This problem is most straight forward, but for our purposes, most interesting. We will now consider when the particle is free only in some finite region of Space - "the box". One important application of this problem, is the calculation of the energy and related quantities (such as heat capacity and entropy) for the translational motions of gas in a rigid wall container ("a box")

It also serves as a good illustration of the quantum principles and as vehicle ("quantization") to introduce some new valuable idea

Although the one dimensional box is not physically realistic, it is a good place to start because it is very simple, and it forms the basis for a more realistic 3D Problem

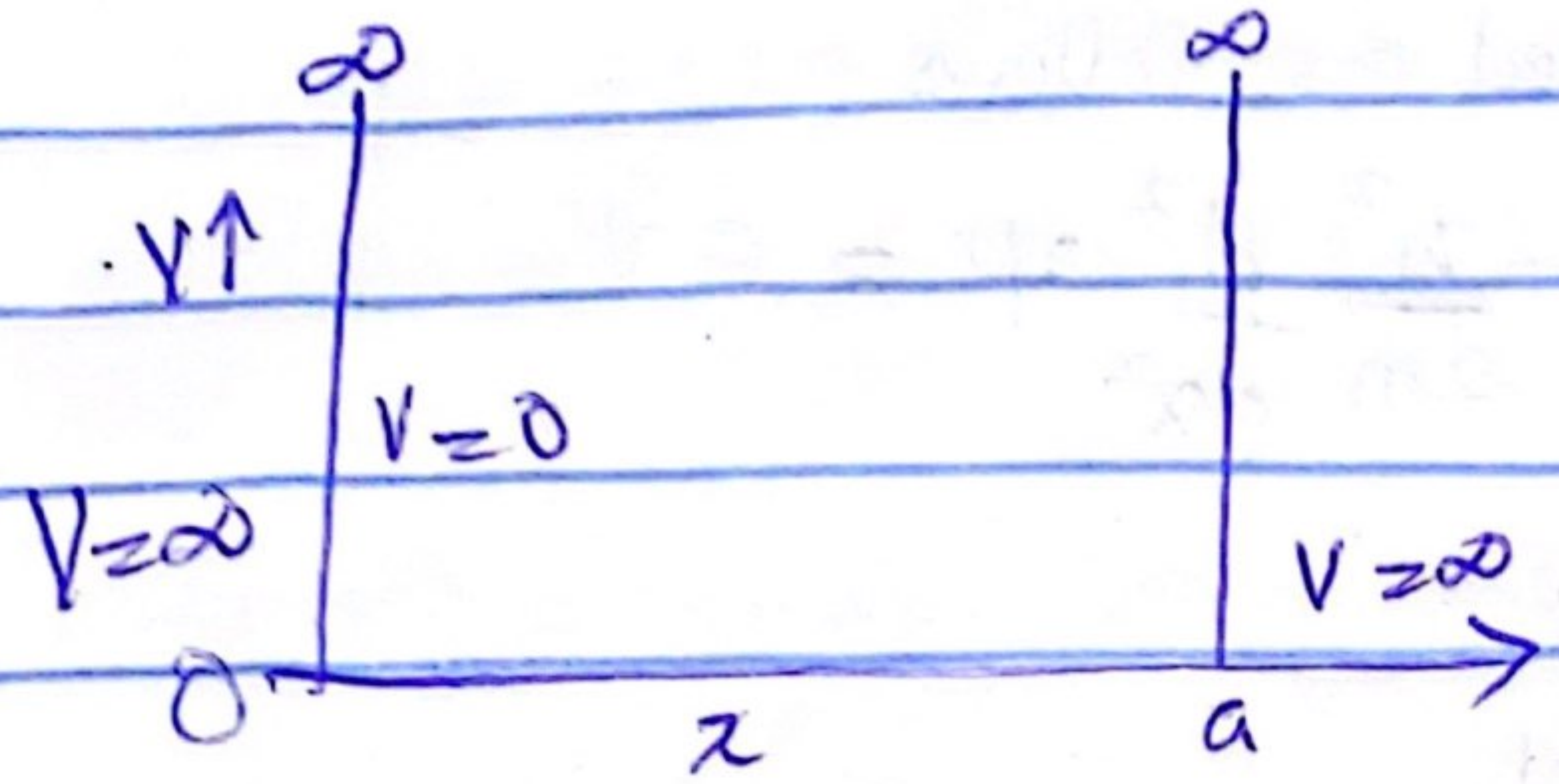

fig5: potential energy for particle in a box

The potential V is zero for some finite region, i.e $0 < x < a$ and infinitely large elsewhere. Suppose that the PE of a particle as shown in fig 5. is zero for $0 < x < a$, and large elsewhere.

This idea is somewhat unrealistic since it requires that the force, $f = -\frac{dv}{dx}$ be infinite at the edges of the box ($x = 0$ \$ ~~x~~ $= a$); and no system has been shown to have an infinite force, even the gravitational pull can be overcome with a escape velocity which is $\sqrt{2gR}$; nonetheless, there is a lot we can learn from solving this particular Problem.

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In the regions where $V = \infty$, the wave function (ψ) will be zero; i.e, the particle is never there at all. The solutions for the region $0 < x < a$ where $V = 0$ can be determined as follows

$$\hat{H}\psi = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi = E\psi$$

Recall;

$$\hat{H}\psi = E\psi$$

$$\hat{H} = KE + V$$

$$\hat{H} = \frac{P_x^2}{2m} + V$$

where $P_x = \frac{\hbar}{i}\frac{d}{dx} \Rightarrow P_x^2 = \frac{\hbar^2}{i^2}\frac{d}{dx} = -\hbar^2\frac{d^2}{dx^2}$

$$\Rightarrow \hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V$$

i.e. $\hat{H}\psi = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi = E\psi$

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi = E\psi$$

$$\frac{d^2}{dx^2}\psi = -\frac{2mE}{\hbar^2}\psi \quad \text{...(52)}$$

Functions that can give us back its function after differentiating twice are e^{kx}, $\cos kx$, $\sin kx$

But only $\sin kx$ can be used because after differentiating twice, it gives zero (at the boundary) when $x = 0$.

If $\psi = \sin kx$

$$\frac{d^2}{dx^2}(\sin kx) = \frac{d}{dx}(k\cos kx) = -k^2 \sin kx$$

$$\Rightarrow k^2 = \frac{2mE}{\hbar^2}$$

Since ka

$\psi = A\sin kx$ @ $x = a$, $= 0$.

$\sin ka = 0$, $ka = \pi, 2\pi, 3\pi \cdots n\pi$

$\therefore k = \frac{n\pi}{a}$, where $n = 1, 2, 3 \cdots \infty$

The boundary conditions are also met when $n = 0$. But then, ψ will be equal to zero everywhere in the box, i.e the particle does not exist and that is not what we want to achieve

Recall that $k^2 = \frac{2mE}{\hbar^2}$

$$\frac{n^2\pi^2}{a^2} = \frac{2mE}{\frac{h^2}{4\pi^2}} \Rightarrow \frac{n^2\pi^2}{1 \times a^2} = \frac{8mE\pi^2}{h^2}$$

$E = n^2h^2$

$$\Rightarrow E = \frac{n^2 h^2}{8 m_e}$$

$$\psi = A \sin kx$$

$$\psi_n = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right) \Uparrow \text{normalize}$$

Calculate the energy for an electron in a 1-bohr box

Solution

The energy of electron in a one-dimensional

$$E_n = \frac{\hbar^2}{m_e a_0^2}, \quad E_n = \frac{n^2 h^2}{8 m a^2}$$

$$\frac{E_n}{E_n} = \frac{n^2 \pi^2}{2} \frac{1}{(m/m_e) \cdot \left(\frac{a}{a_0}\right)^2}$$

$$m_e = m, \quad a = a_0$$

$$\frac{E_n}{E_n} = \frac{n^2 \pi^2}{n} = \frac{1^2 \cdot \pi^2}{2} = \frac{\pi^2}{2} = 4.9348 \text{ Hartree}$$

Thus, the energy is 4.9348 Hartree, which can also be expressed as 2.15×10^{17} J, 1.296×10^{7} J/mol or 134 eV, is a sizable amount of energy.

For the more massive proton, the mass will be

$m = 1896\, m_e$

The ground state where($n=1$, (1-bohr wide), energy state is much less;

The Value is 0·00269 Hartree (far less Compared to that of electron), 7057 J/mol, 0-00731eV

An electron in a larger box also has less energy. In a 10-bohr box, the energy of an electron is 0·0493 Hartree, 130 KJ/mol, and 1·34 eV.

By the time one gets to macroscopic-size masses or boxes, the minimum energy is too small to be meaningful. For example, with 1g in a 1cm box, the energy ~~an electron~~ is 3-3 × 10^{-37} J/mol

So, quantization is only applicable to tinest of the tinest particle, not macroscopic

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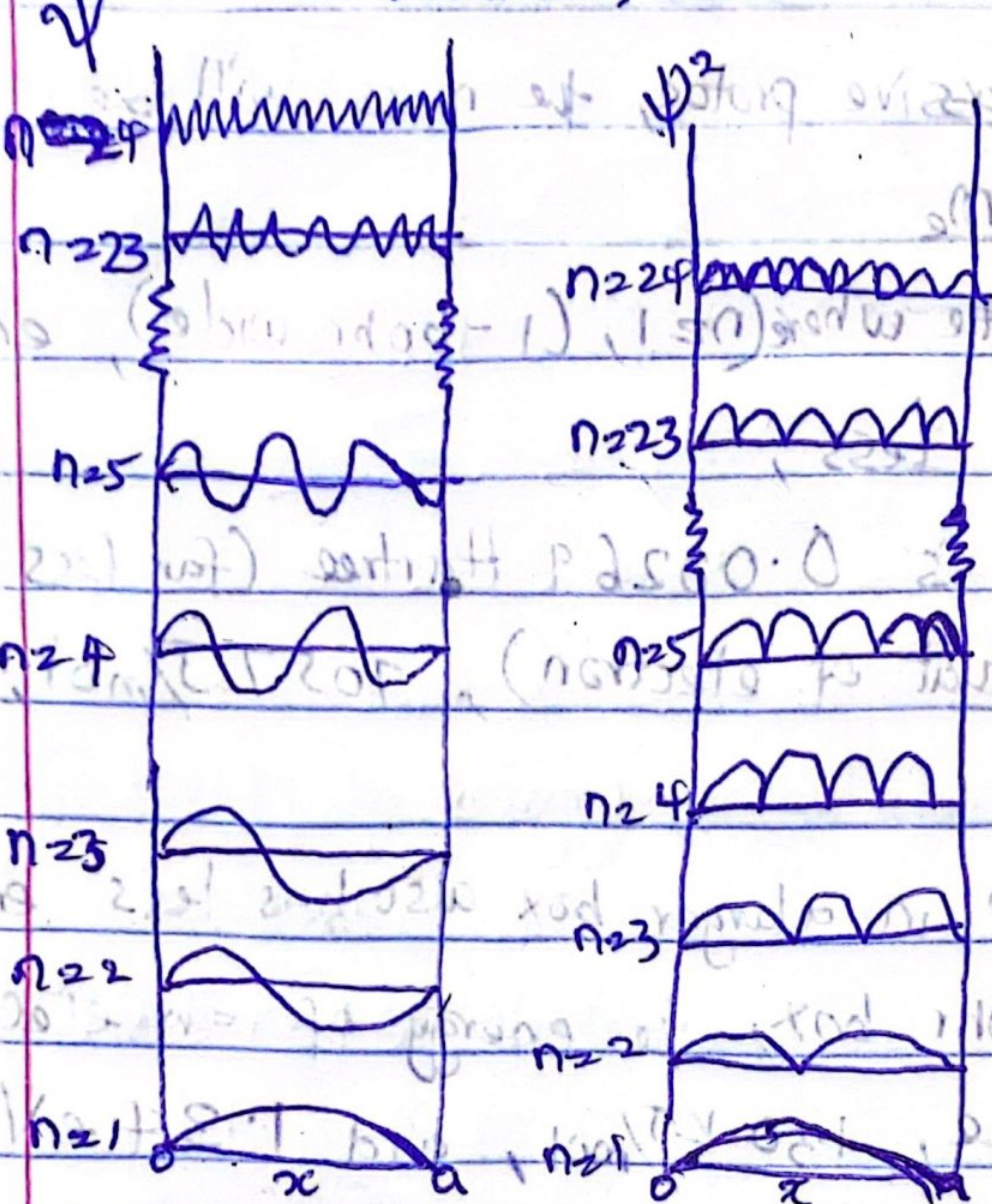


fig 6. Particle in a box wave function.

On the right, we have the probability (ψ^2) of the Wavefunction. ~~Note that as quan~~

Note that as the quantum becomes large, your macroscopic expectation that the particle should, with equal probability, be in any portion of the box is approached more closely.

The Quantum Mechanical solution for the particle in the box is complete at this point, but what have we learned?

Since the Wave function presumably "knows" everything that can be known about the system. Let us ask

Some questions. Where is the particle?

We would expect from our experience with macroscopic objects that it could be anywhere in the box with equal probability. But quantum mechanics says that the probability is equal to ψ^2 (square of the wave function) as seen in fig 6 which is by no means uniform.

For $n=1$ state, the probability is greatest on the center, for $n=2$, the probability is greatest at $x = a/4$ and $\frac{3}{4}a$ but is zero at $a/2$ (there is a node at the center of the box for this state, i.e $n=2$). For larger quantum numbers, the probability becomes more uniform and closer to our expectations. This is an example of the Bohr's correspondence principle which states that quantum mechanics approaches classical mechanics in the limit of large quantum numbers.

~~For large quanta~~

Another classical expectation is that the energy is not quantized, or if it is quantized, the energy levels are to close to be observed seperately.

However, the one-dimensional particle in a box model fails this test because the energy level seperation increases with large quantum numbers. As a result, the Bohr correspondence principle is not obeyed.

$$E = \frac{n^2h^2}{8ma^2} \quad n=1 \text{ and } n=2$$

$$\Delta E = \frac{2^2h^2}{8ma^2} - \frac{h^2}{8ma^2}$$

$$= \frac{24^2h^2}{8ma^2} - \frac{23^2h^2}{8ma^2}$$

This problem is an example of the artificial limitation created by placing the particle in one-dimensional box. The problem will disappear when the more realistic 3(D) box is considered.

We next enquire about some other properties of the particle in 1D box. Suppose we are interested in measuring the component of momentum in x-direction for a set of identical systems, in which the particle is known to be in the lowest energy state, the appropriate operator to use in the calculation of the expected result is

$$P_x = -i\hbar\frac{d}{dx}, \quad \psi = A\sin\left(\frac{n\pi x}{a}\right)$$

$$P_x\psi = -i\hbar\frac{d}{dx}A\sin\left(\frac{n\pi x}{a}\right)$$

$$= i\hbar A n\frac{\pi}{a}\cos\left(\frac{n\pi x}{a}\right)$$

It is clear that the wave function is not an eigen function of P_x; therefore, according to the understanding of the average value theorem, a series of measurement of P_x will not yield the same result.

So, we must use the average value theorem to calculate the expectation value of P_x

$$\langle P_x \rangle = \int_0^a \psi \hat{P}_x \psi \, dx = \int_0^a A \sin\left(\frac{n\pi x}{a}\right) \cdot -i\hbar \frac{d}{dx} A \sin\left(\frac{n\pi x}{a}\right)$$

$$= \cancel{\int} \left[\frac{2}{a}\right] \int_0^a \sin\left(\frac{n\pi x}{a}\right) \cdot -\frac{i\hbar n\pi}{a} \cos\left(\frac{n\pi x}{a}\right) dx$$

$= 0$ …… (5-[illegible])

Let us probe this result further. Accordingly, the average of the large number of pairs on the set of identical system is zero

Suppose one now considers the square of the momentum in the x-direction, the appropriate operator becomes

~~$-i^2\hbar^2 \frac{d^2}{dx^2} = \hbar^2 \frac{d^2}{dx^2}$~~

$$P_x^2 = (-i)^2 \hbar^2 \frac{d^2}{dx^2} = -\hbar^2 \frac{d^2}{dx^2}$$

$$= -\hbar^2 \frac{d^2}{dx^2} A \sin\left(\frac{n\pi x}{a}\right) = + \frac{\hbar n^2 \pi^2}{a^2} \sin\left(\frac{n\pi x}{a}\right)$$

ψ (wave function) is thus, an eigen function of P_x^2, and a series of measurement of P_x^2 on a set of identical system will always give the same result, namely the eigen value.

$$P_x^2 = \frac{\hbar^2 n^2 \pi^2}{a^2} \ldots *$$

$$\frac{P_x^2}{2m} = KE = E$$

$$P_x^2 = 2mE$$

$$P_x^2 = \frac{\hbar^2 n^2 \pi^2}{a^2} = 2mE$$

$$P_x = \sqrt{\frac{n^2 \hbar^2 \pi^2}{a^2}} = \sqrt{2mE}$$

$$P_x = \frac{n\hbar\pi}{a} = \pm\sqrt{2mE} \ldots (55)$$

The results calculated in eqn (54) and (53) presents an interesting dilemma. The result of eqn (54) indicates that the average value of the momentum is zero and the result of eqn (55) indicates that the momentu must be either $+(2mE)^{1/2}$ or $-(2mE)^{1/2}$

A single measurement of P_x will give one of this value. What the mean value postulate state is that, if one makes a large member of measurement of P_x will end up with ~~P_x~~

$P_x = -\sqrt{2mE}$ as often as $+\sqrt{2mE}$, and the average value of P_x will be zero.

The important point is that we never know in advance whether the result will give a $(+)$ or a $(-)$ $\sqrt{2mE}$.

It can therefore be said that an uncertainty exists in our knowledge of the momentum and the magnitude of this uncertainity is equal to $2\sqrt{2mE}$

In a similar manner, we can argue that if we know that the particle is in state ψ_n, the only thing that can be said about the position of the particle is that it is somewhere in the box. i.e. our uncertainty in the x-coordinate of the particle is the length of the box, ~~the zero~~

It is of interest to calculate the product of our uncertainties in the position and the momentum of a particle in a box.

$$\Delta x \cdot \Delta p_x \geq a \cdot 2\sqrt{2mE} \geq 2\cancel{a} \cdot \frac{n\pi\hbar}{\cancel{a}} \geq \cancel{2}n\pi \cdot \frac{h}{\cancel{2\pi}}$$

$$\geq nh$$

The products of the uncertainties will have its smallest value when $n = 1$ and thus we obtain the result that

$\Delta x \cdot \Delta P_x \geq nh$

$\Delta x \cdot \Delta p_x \simeq h$ ....(56)

This is a form of the Heisenberg uncertainty principle which states that the simultaneous measurement of both the position and momentum of a particle cannot be made to an accuracy greater than Planck's constant, h

Planck's constant is a very small number, however, and it is clear why the uncertainty principle is of no consequence in measurement and systems of large dimensions and/or systems containing particles with large masses.

The Harmonic oscillator

The total energy of a molecule or an object may be approximated as the sum of energies associated with its translational, rotational, Vibration and electronic motion

Translational energy is the Kinetic energy of motion of the object as a whole. It can be taken as the energy of a particle in a box

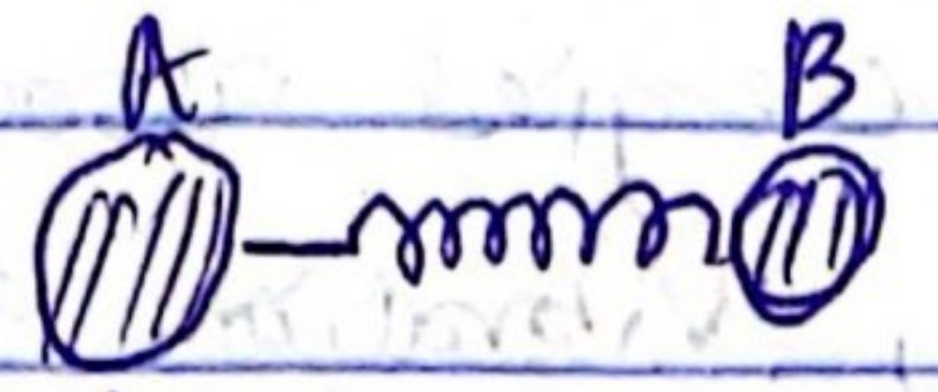
Rotational energy levels of a diatomic molecule can be approximated by those of a rigid particle rotor.

The electronic energy is often approximated with a model that treats the nuclear and electron as point masses and seperates the motion of the two Point objects. i.e, the Born - Oppenheimer

The lowest field vibrational energy level of a diatomic molecule can be approximated by the levels of a Harmonic Oscillator.

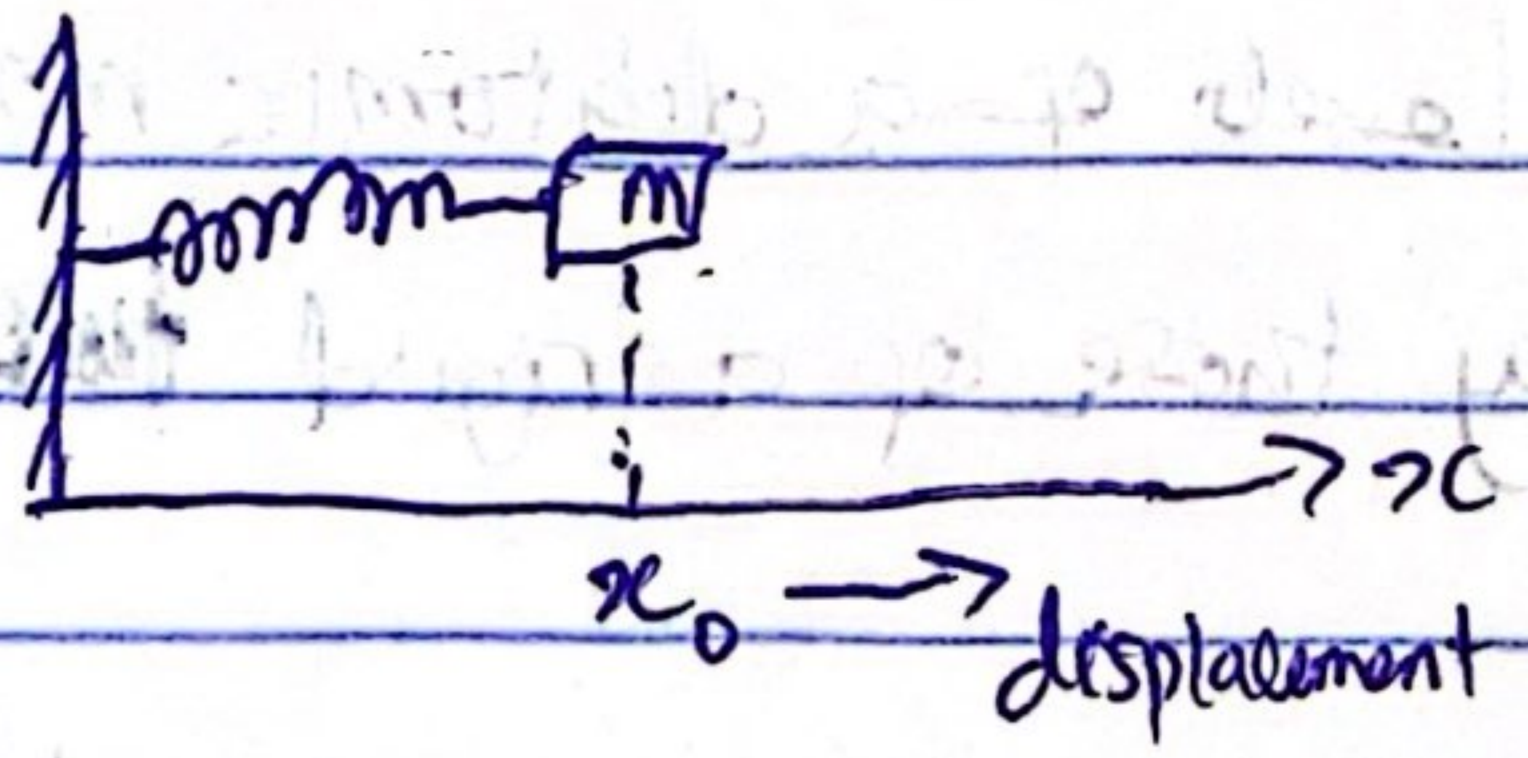
A Harmonic osscillator is a good model for molecular vibrations. A typical Harmonic oscillator, is a mass (m) attached to a rigid wall by a spring.

Another example of a Harmonic oscillator is a diatomic molecule, which could be envisioned as a two point masses



$H_a - H_B$

Classical Mechanical Treatment of ~~a~~ One-Dimensional Harmonic Oscillator



According to Hooke's law the force (f) that is holding or keeping mass (m) towards the origin is proportional to the displacement of the particle from its origin

$$F_x \propto -x$$

$$F_x = -kx \quad \text{---} ①$$

where k is called the force constant

It should be noted that the stiffer the spring, the greater the value of k and vice versa

According to Newton ~~motion~~ law of motion, we remember that $F = ma$

$$\therefore -kx = m\frac{d^2x}{dt^2} \quad \text{---} ②$$

Which we can rearrange;

$$\frac{d^2x}{dt^2} + \frac{k}{m}x = 0 \ \dots\dots (3)$$

The general solution to eqn (3) is

$$x(t) = A\sin(\omega t) + B\cos(\omega t) \ \text{----} (4)$$

which can as well be expressed as

$$x(t) = x_0 \sin(\omega t + \phi) \ \text{---} \ ⑤$$

Where x_0 and ϕ are constants of integration.

It can be proven from eqn (5) that

$$\omega = \sqrt{\frac{k}{m}} \ \text{---} (6)$$

From eqn (5)

$$\frac{dx}{dt} = x_0 \omega \cos(\omega t + \phi)$$

$$\frac{d^2x}{dt^2} = -x_0 \omega^2 \sin(\omega t + \phi)$$

$$\frac{d^2x}{dt^2} + x_0 \omega^2 \sin(\omega t + \phi)$$

where ω is the angular frequency of oscillation which is related to the vibrational frequency as

$$-kx = \frac{dv}{dx}$$

$$-kx\int dx = \int dv$$

$$\omega = 2\pi v = \sqrt{\frac{k}{m}}$$

$$\left.\begin{aligned} v &= \frac{1}{2\pi}\sqrt{\frac{k}{m}} \\ k &= 4\pi^2 v^2 m \end{aligned}\right\} (7)$$

The force (F) is also related to the potential energy V as

$$F = -\frac{dV}{dx} \quad \text{----} \quad (8)$$

From which it can be established that

$$V = \frac{1}{2}kx^2 \quad \text{...} \quad (9)$$

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Equation (9) is a parabolic equation in which x is the displacement from equilibrium

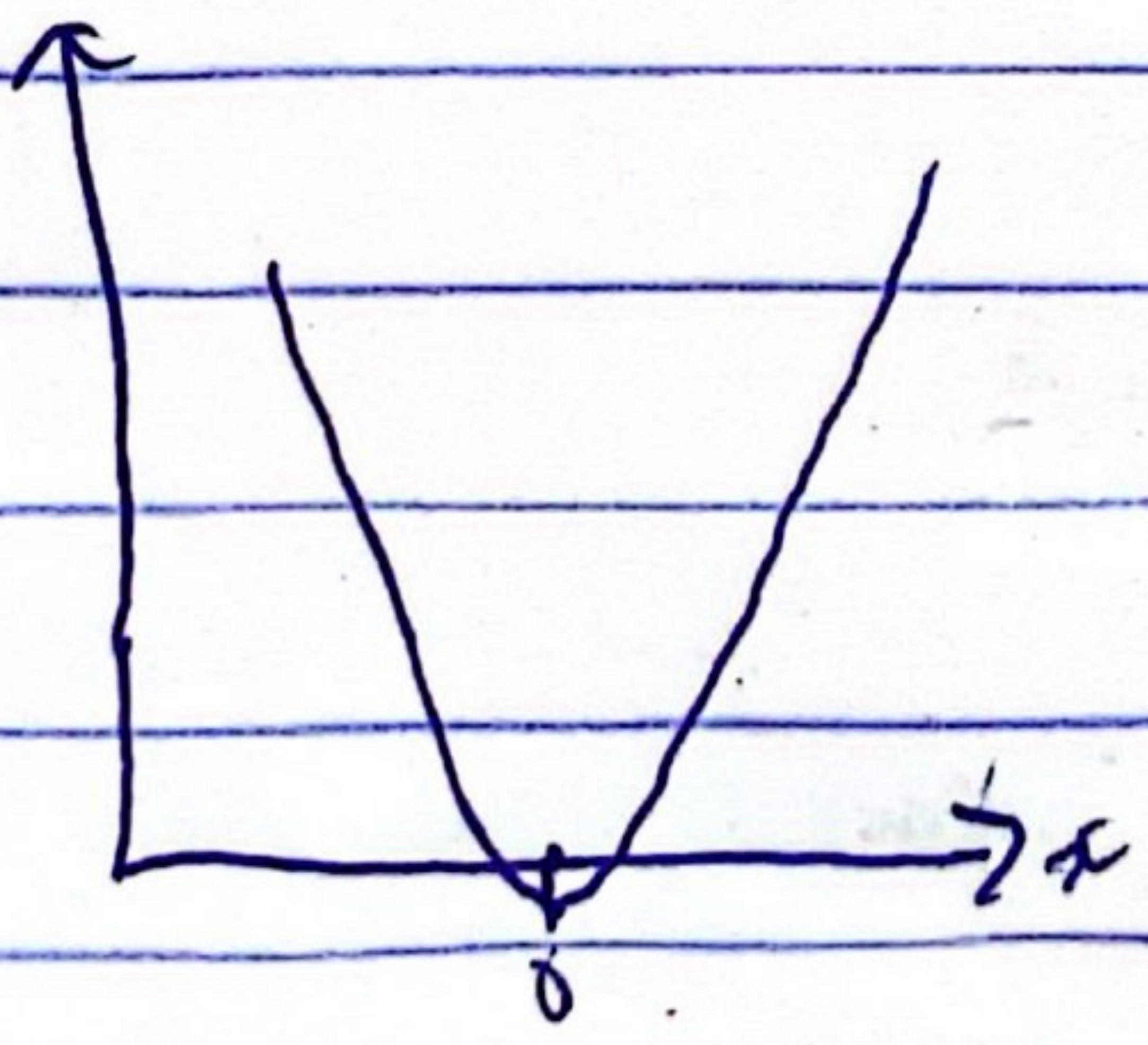


fig 2:- parabolic potential energy curve.

The narrowness of the curve depends on the ~~force~~ force constant. The larger the value of V_1, the narrower the potential well, i.e the stiffer the spring, the smaller the displacement by constant applied force.

The potential V in equation (9) can be expressed in terms of mass, m, of the body as

$$V = 2\pi V^2 m x^2 \text{ -------(10)}$$

The kinetic energy, T of the oscillator is given as

$$T = \frac{1}{2}mv^2 = \frac{1}{2}m\left(\frac{dx}{dt}\right)^2 \text{ ----(11)}$$

Therefore, the total energy is the sum of KE & PE

$$E = T + V = \frac{1}{2}kx_0^2 = 2\pi^2 V^2 m x_0^2 \text{ .....(12)}$$

Where x_0 is the amplitude of oscillation

Quiz

Given that $V = \frac{1}{2}kx^2$ and $T = \frac{1}{2}mv^2 = \frac{1}{2}m\left(\frac{dx}{dt}\right)^2$ for an harmonic oscillator of mass, m and spring constant k. Show that the total energy, E of the oscillation is;

$E = \frac{1}{2}kx_0^2$, where x_0 is the amplitutude of oscillation.

(Hint: use the trigonometry identity; $\sin^2 A + \cos^2 B = 1$ and ~~Ga~~ $x(t) = x_0 \sin(wt + \phi)$)

$$E = T + V$$

$$E = \frac{1}{2}mv^2 + \frac{1}{2}kx^2 = \frac{1}{2}kx_0^2\sin^2(wt+\phi)$$

$$\frac{1}{2}m\left(\frac{dx}{dt}\right)^2 = \left[x_0 w\cos(wt+\phi)\right]^2$$

$$T = \frac{1}{2}m x_0^2 w^2 \cos^2(wt+\phi)$$

Given that $E = \frac{1}{2} K x_0^2 \sin^2(\omega t + \phi) + \frac{1}{2} m x_0^2 \omega^2 \cos^2(\omega t + \phi)$

$E = \frac{1}{2} K x_0^2 [\sin^2(\omega t + \phi) + \cos^2(\omega t + \phi))$, $\therefore \boxed{E = \frac{1}{2} k x_0^2}$

Eqn (12) reveals that the total energy is equal to the square of amplitude

Quantum-Chemical Treatment of a One-Dimensional Harmonic Oscillator.

We recall the kinetic energy operator

$$\hat{T} = \frac{-\hbar^2}{2m}\frac{d^2}{dx^2} \; ; \quad \hat{V} = 2\pi^2 \nu^2 m x^2$$

The Harmonic oscillator Hamiltonian could be sum of kinetic energy operator, which becomes;

$$\hat{H} = \hat{T} + \hat{V} = \frac{-\hbar^2}{2m}\frac{d^2}{dx^2} + 2\pi^2\nu^2 m x^2 \text{......} (13)$$

We can now write the simplest form of the schrodinger equation

$$\hat{H}\psi = E\varphi$$

Substituting for H

$$\left[\frac{-\hbar^2}{2m}\frac{d^2}{dx^2} + 2\pi^2\nu^2 m x^2\right]\psi = E\psi$$

$$\frac{-\hbar^2 d^2}{2m\,dx^2}\psi + \left(E - 2\pi^2\nu^2 m x^2\right)\varphi = 0$$

$$\frac{d^2\varphi}{dx^2} + \frac{2m}{\hbar^2}\left[E - 2\pi^2\nu^2 m x^2\right]\psi = 0 \quad \ldots\ldots (15)$$

Obviously, the solution to eqn (15) cannot be a sine or cosine function. Since, the sine or cosine function of the second term cannot be differentiated twice to give the same function multiplied by a constant.

Let us try an exponential or a Guassian function as a solution for eqn (15)

Assume $f(x) = e^{-\frac{\alpha x^2}{2}}$ ...(16) is the solution to eqn (15)

By differentiating equation (16) twice, we have;

$$f''(x) = -\alpha e^{-\alpha x^2/2} + \alpha^2 x^2 e^{-\frac{\alpha x^2}{2}} \quad \ldots (17)$$

$$f''(x) + \alpha e^{-\frac{\alpha x^2}{2}} - \alpha^2 x^2 e^{-\frac{\alpha x^2}{2}} = 0$$

$$\frac{d^2 f(x)}{dx^2} + \alpha e^{-\frac{\alpha x^2}{2}} - \alpha^2 x^2 e^{-\frac{\alpha x^2}{2}} = 0 \quad \ldots (18)$$

$$\frac{d f(x)}{dx^2} + \alpha f(x) - \alpha^2 x^2 f(x) = 0 \quad \ldots (19)$$

Re-expressing eqn 15; $\frac{d^2\varphi}{dx^2} + \frac{2mE}{\hbar^2}\varphi - \frac{4\pi^2\nu^2 m^2 x^2}{\hbar^2}\psi = 0$ ...(19a

Comparing eqn (19) and (19a)

$$\alpha = \frac{2mE}{\hbar^2} \; ; \; \alpha^2 = \frac{4\pi^2\nu^2 m^2}{\hbar^2} \quad \ldots (20)$$

from eqn (20) ;

$$\alpha = \frac{2mE}{\hbar^2} \; \& \; \alpha = \frac{2\pi\nu m}{\hbar} \; \therefore$$

$$\therefore \frac{2mE}{\hbar^2} = \frac{2\pi\nu m}{\hbar}$$

$$\Rightarrow E = \pi\hbar\nu \qquad \text{Since } \hbar = \frac{h}{2\pi}$$

$$E = \frac{\cancel{\pi} h\nu}{2\cancel{\pi}} = \cancel{k} \Rightarrow \frac{1}{2} h\nu \quad \ldots (21)$$

Equation (21) is the lowest state energy of a simple harmonic oscillator.

Question

Given that $\overset{\text{wave function}}{x(t)} = A\sin(\omega t + \phi)$, show that

$$\underset{\text{momentum}}{p(t)} = m\omega A\cos(\omega t + \phi)$$

19th December 2024

We can give eqn (15) a more interesting mathematical treatment by showing the equation analytically. The analytical solution requires a power series solution for f(x) in the form

$$f(x) = \sum_{n=0}^{\infty} C_n x^n \quad ---- (22)$$

This eqn (22) is a two - term recurssion equation

$$C_{n+2} = \frac{\left[\alpha + 2\alpha n - \frac{2mE}{\hbar^2}\right] C_n}{(n+1)(n+2)} \quad --- (23)$$

For which, the general solution of the harmonic oscillator schrodinge equation could be written as

$$\left.\begin{aligned} \Psi_{even} &= e^{-\alpha x^2/2} \sum_{n=0,2,\ldots}^{\infty} C_n x^n \\ \text{and } \Psi_{odd} &= e^{\frac{\alpha x^2}{2}} \sum_{n=1,3,\ldots}^{\infty} C_n x^n \end{aligned}\right\} (24)$$

Which could be combined as

$$\Psi = A e^{-\frac{\alpha x^2}{2}} \sum_{l=0}^{\infty} C_{2l+1} x^{2l+1} + B e^{-\frac{\alpha x^2}{2}} \sum_{l=0}^{\infty} C_{2l} x^{2l} \quad --- (25)$$

Where A & B are arbituary constant.

The wave function in eqn (25) becomes infinite as x goes to infinity and thus, it will not be quadratically integrable. Therefore, we need to ensure that ψ goes to zero as x becomes very large. For this to happen, the coefficient of C_n in the two term recurssion eqn (23) must become zero for some values of n, Say $n = v$

Therefore, we can write that the coefficient equals zero at $n = v$

i.e, $$\frac{\alpha + 2\alpha n - \frac{2mE}{\hbar^2}}{(n+1)(n+2)} = 0 \quad @ \; n = v \quad \text{....}(26)$$

for which $$\alpha + 2\alpha v - \frac{2mE}{\hbar^2} = 0 \quad \text{....}(27)$$

Previously; $\alpha = \frac{2\pi v m}{\hbar}$, $n = v$

$$\frac{2mE}{\hbar^2} = \frac{2\pi v m}{\hbar} + \frac{2 \times 2\pi v m . v}{h}$$

$$\Rightarrow \frac{2mE}{\hbar^2} = (2v+1)\left[\frac{2\pi v m}{\hbar}\right]$$

$$\therefore E = \left(v + \frac{1}{2}\right)hv \quad \text{....}(28)$$

OR

$$E_n = \left(n + \frac{1}{2}\right)hv \quad \text{.......}(28a)$$

For $n = 0, 1, 2, \ldots$

$E_0 = \frac{1}{2}h\nu$ $E_2 = 5/2\, h\nu$

$E_1 = \frac{3}{2}h\nu$

Which shows that the stationary state energy level of quatum harmonic oscillator are equally spaced For eqn (28a), the energy of state $n+1$ is;

$$E_{n+1} = (n+1) + \frac{1}{2}$$

Such that $\Delta E = E_{n+1} - E_n$

$$\Delta E = h\nu \text{ ..... } (29)$$

The ground state energy of quantum harmonic oscillator is not zero, i.e, even at $n = 0$, $E \neq 0$. That is, the zero point energy of a quantum harmonic oscillator E_0 is not zero

$$E_0 = \frac{1}{2}h\nu \neq 0$$

The following conclusions could be drawn;

(i) The harmonic oscillator energy are quantized

(ii) The harmonic oscillator depends on the vibrational quatum number n.

(iii) The ground state or lowest energy of harmonic oscillator is not zero

(iv) The harmonic oscillator are equally spaced

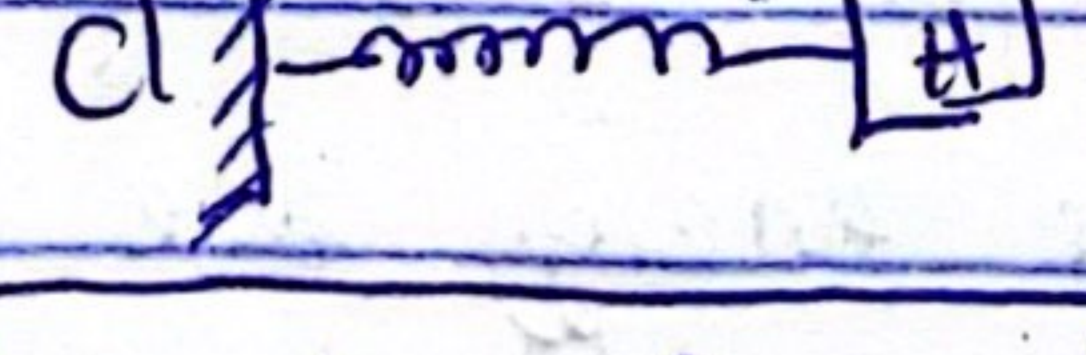
Harmonic

(1) The energy of a classical simple harmonic oscillator is given by; -

$E = \frac{p^2}{2m} + \frac{1}{2}w^2x^2$. Where p = momentum, m = mass, w = angular frequency

What is the largest value of $|x|$ if $E = \frac{1}{2}\hbar w$

(2) Consider an HCl molecule in which H–Cl chemical bond could be considered to behave as a classical simple harmonic oscillator, such that, H atom moves in a vibrational motion relative to Cl atom which acts like an anchor. Given that the force constant K for $^{1}H\,^{35}Cl$ is $516.3\ Nm^{-1}$



Calculate the classical vibrational frequency of H–Cl bond [$m_H = 1.7\times10^{-27}$ kg, $m_{Cl} = 5.9\times10^{-26}$ kg

The Harmonic- Oscillator Wave function

The general solution of the harmonic oscillator schrödinger wave equation expressed in eqn (25) has been made to break up after a finite number of times given odd and even function

$$\psi_n = \begin{cases} e^{-\frac{\alpha x^2}{2}}\left[C_0 + C_2 x^2 + C_4 x^4 + \cdots + C_n x^n\right] & \text{even } n \\ e^{-\frac{\alpha x^2}{2}}\left[C_1 x + C_3 x^3 + C_5 x^5 + \cdots + C_n x^n\right] & \text{odd } n \end{cases} \cdots (30)$$

Let's express the wave function for the lowest three terms

① $n = 0$ (ground state)

$$\psi_0 = C_0 e^{-\frac{\alpha x^2}{2}}$$

The Value of C_0 can be formed by normalization

$$\int_{-\infty}^{+\infty} \psi_0^* \psi \, d\tau = 1 = \int_{-\infty}^{+\infty} |C_0|^2 e^{-\alpha x^2} dx = 1 \cdots (31)$$

$$|C_0|^2 \int_{-\infty}^{\infty} e^{-\alpha x^2} dx = 1$$

Note: for an even function; $f(-x) = f(x)$ and $e^{-\alpha x^2}$ is an even function since $e^{-a(-x)^2} = e^{-\alpha x^2}$

By normalization

Note: Even functions

$$\int_{-a}^{+a} f(x)\,dx = \int_{a}^{0} f(x)\,dx + \int_{a}^{+a} f(x)\,dx$$

and $$\int_{-a}^{0} f(x)\,dx = \int_{0}^{+a} f(x)\,dx$$

$$\therefore \int_{0}^{+a} f(x)\,dx = 2\int_{0}^{+a} f(x)\,dx$$

Therefore,

$$|C_0|^2 \int_{-\infty}^{\infty} e^{-\alpha x^2}\,dx = \int_{-\infty}^{0} |C_0|^2 e^{-\alpha x^2} + \int_{0}^{\infty} |C_0|^2 e^{-\alpha x}$$

$$= 1$$

$$\Rightarrow 2|C_0|^2 \int_{0}^{+\infty} e^{-\alpha x^2}\,dx = 1$$

Use: $$\int_{0}^{+\infty} e^{-bx^2}\,dx = \frac{1}{2}\left(\frac{\pi}{b}\right)^{1/2} \; ; \; b > 0$$

$$\cancel{2}|C_0|^2 \cdot \frac{1}{\cancel{2}}\left(\frac{\pi}{\alpha}\right)^{1/2} = 1$$

$$|C_0|^2 = \left(\frac{\alpha}{\pi}\right)^{1/2}$$

$$C_0 = \left(\frac{\alpha}{\pi}\right)^{1/4}$$

(i) Such that the explicity form Ψ_0 is;

(b) $n = 0$; Ψ_0

$$\psi_0 = \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha x^2/2}$$

(a) $n = 1$; $\psi_1 = C_1 x e^{-\alpha x^2/2}$

$$\int_{-\infty}^{+\infty} \psi_1^* \psi_1 \, d\tau = 1 \Rightarrow \int_{-\infty}^{\infty} |C_1|^2 x^2 e^{-\alpha x^2} dx = 1$$

using $\int_0^{+\infty} x^2 e^{-bx^2} dx = \frac{1}{4}\left(\frac{\pi}{b^3}\right)^{1/2}$

$$2 C_1^2 \cdot \frac{1}{4}\left(\frac{\pi}{\alpha^3}\right)^{1/2} = 1$$

$$\Rightarrow C_1 = \left(\frac{4\alpha^3}{\pi}\right)^{1/4}$$

$$\therefore \psi_1 = \left[\frac{4\alpha^3}{\pi}\right] x e^{-\alpha x^2/2}$$

(iii) $n = 2$;

$$\psi_2 = C_2 x^2 e^{-\alpha x^2/2} + C_0 e^{-\alpha x^2/2}$$

$$\psi_2 = [C_0 + C_2 x^2] e^{-\alpha x^2/2}$$

$$\psi_2 = \frac{1}{\sqrt{8}} \left(\frac{\alpha}{\pi}\right)^{1/4} (4\alpha x^2 - 2) e^{-\alpha x^2/2}$$

From the first three lowest state, the general expression can be expressed as

$$\psi_n = \left(\frac{1}{2^n n!}\right)^{1/2} \cdot \left(\frac{\alpha}{\pi}\right)^{1/4} H_n(\alpha^{1/2} x) \, e^{-\alpha x^2/2}$$

where;

$$\left.\begin{aligned} & H_{n+1} = 2y H_n - 2n H_{n-1} \\ & \text{and } y = \alpha^{1/2} x \\ & \text{and } H_0 = 1 \end{aligned}\right\} \text{Hermite polynomials}$$

Therefore, the wave function of the ground state of an Harmonic oscillator;

i.e, $n = 0$; $\psi_0 = \left(\frac{1}{2^0 0!}\right)^{1/2} \cdot \left(\frac{\alpha}{\pi}\right)^{1/4} \cdot H_0(\alpha^{1/2} x) \, e^{-\alpha x^2/2}$

$$= \left(\frac{\alpha}{\pi}\right)^{1/4} \cdot e^{-\alpha x^2/2}$$

when $n = 1$; $\psi_1 = \left(\frac{1}{2^1 \cdot 1!}\right)^{1/2} \left(\frac{\alpha}{\pi}\right)^{1/4} \cdot H_1(\alpha^{1/2} x) \, e^{-\frac{\alpha x^2}{2}}$

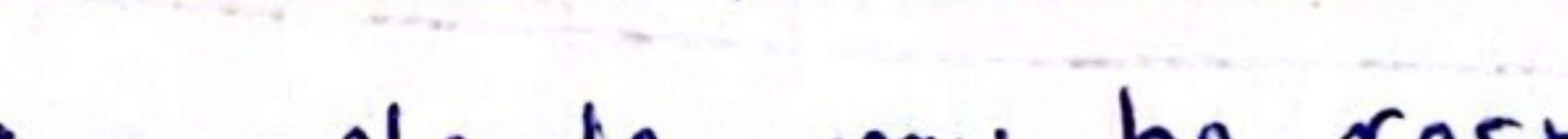
$H_1(\alpha^{1/2} x) = 2y H_0 - 2 \cdot (0) H_{0-1}$

$H_1(\alpha^{1/2} x) = 2\alpha^{1/2} x$

$$\psi_1 = \frac{1}{\sqrt{2}} \left(\frac{\alpha}{\pi}\right)^{1/4} 2\alpha^{1/2} x \cdot e^{-\frac{\alpha x^2}{2}}$$

Harmonic oscillator for diatomic molecules.

A diatomic molecule may be respresent such that m_A is very large compared to m_B, where we can have displacement of m_A, m_B along the x-axis, such that equilibrium of the bond length of a diatomic molecule behave like an harmonic oscila



Therefore, by considering the relative masses of the two bodies / considering the relative motion of the system, the mass m in the Hamitonian eqn could be replaced by the reduced mass μ,

And the Halmitonian equatio will become

$$\hat{H} = \frac{-\hbar^2}{2\mu} \frac{d^2}{dx^2} + 2\pi^2 \nu^2 \mu x^2$$

And the oscillation frequency (ω)

$$\omega = \sqrt{\frac{K}{M}}$$

and the linear frequency (ν)

$$\nu = \frac{1}{2\pi}\sqrt{\frac{K}{N}}$$

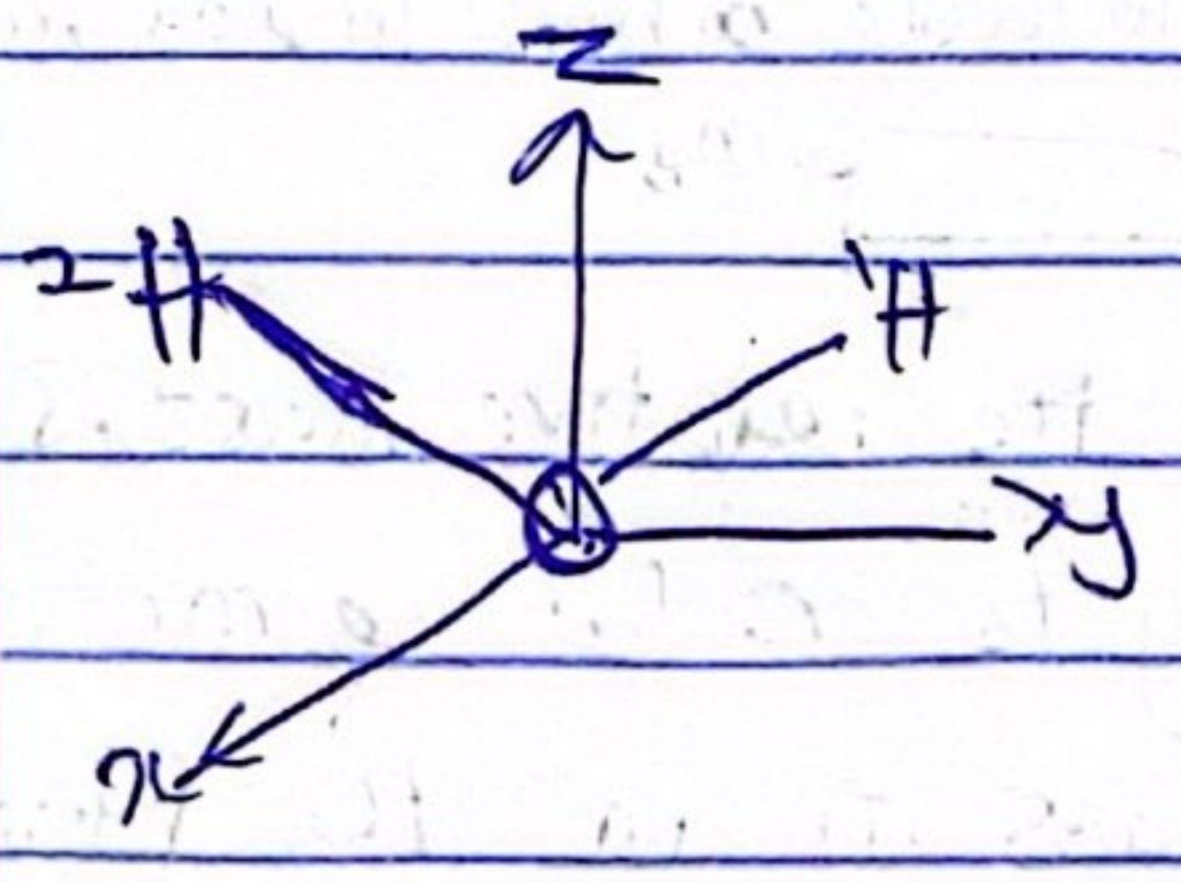
Such is the energy of the ~~diatomic~~ harmonic oscillator lies in the diatomic molecule,

$$\therefore E = \frac{1}{2}h\nu = \frac{h}{\cancel{2}}\left(\frac{K}{N}\right)$$

* The vibrational frequency of HCl is 8.963×10^{15} H
Calculate the force constant.

Coordinate System

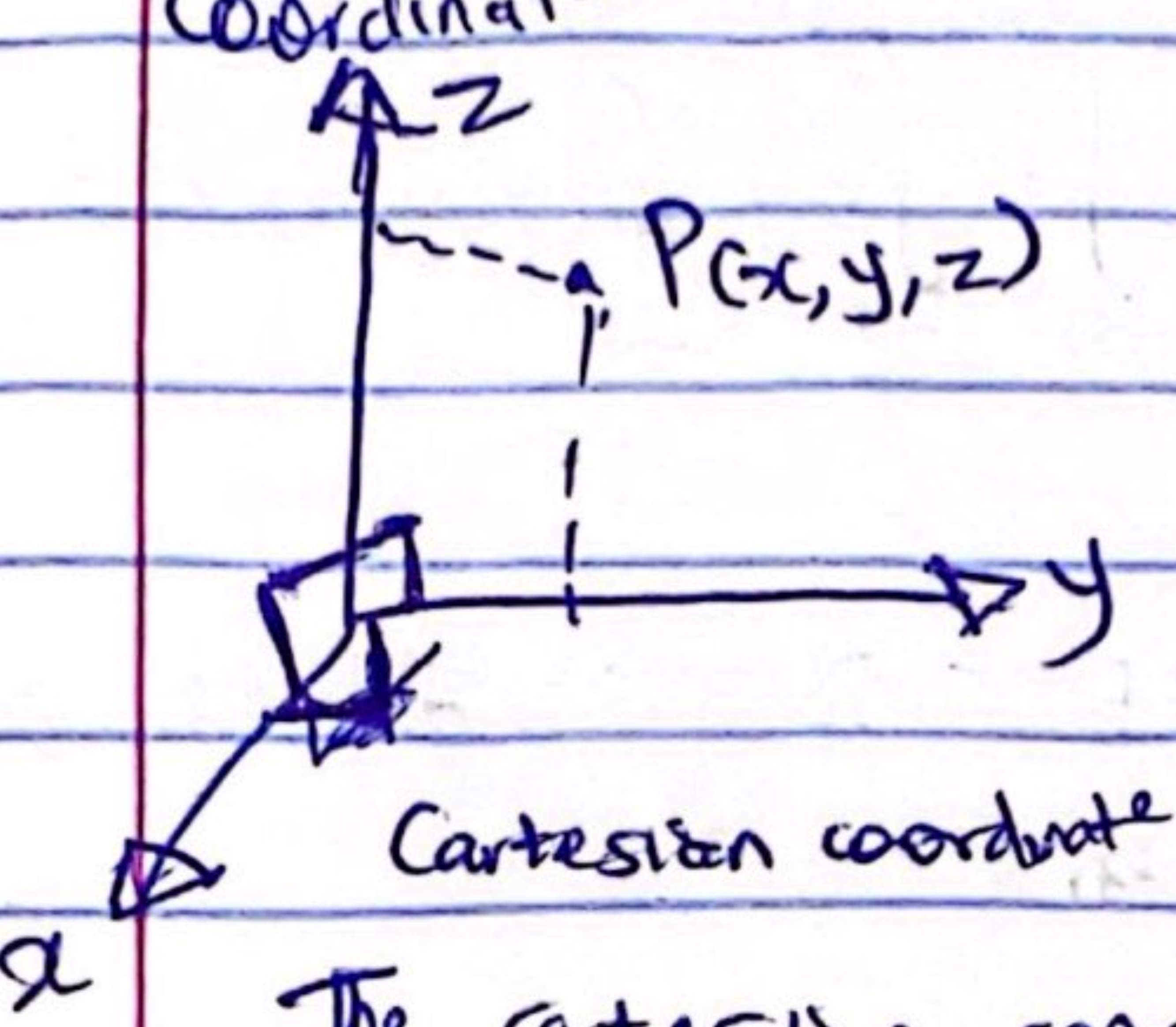
H_2O



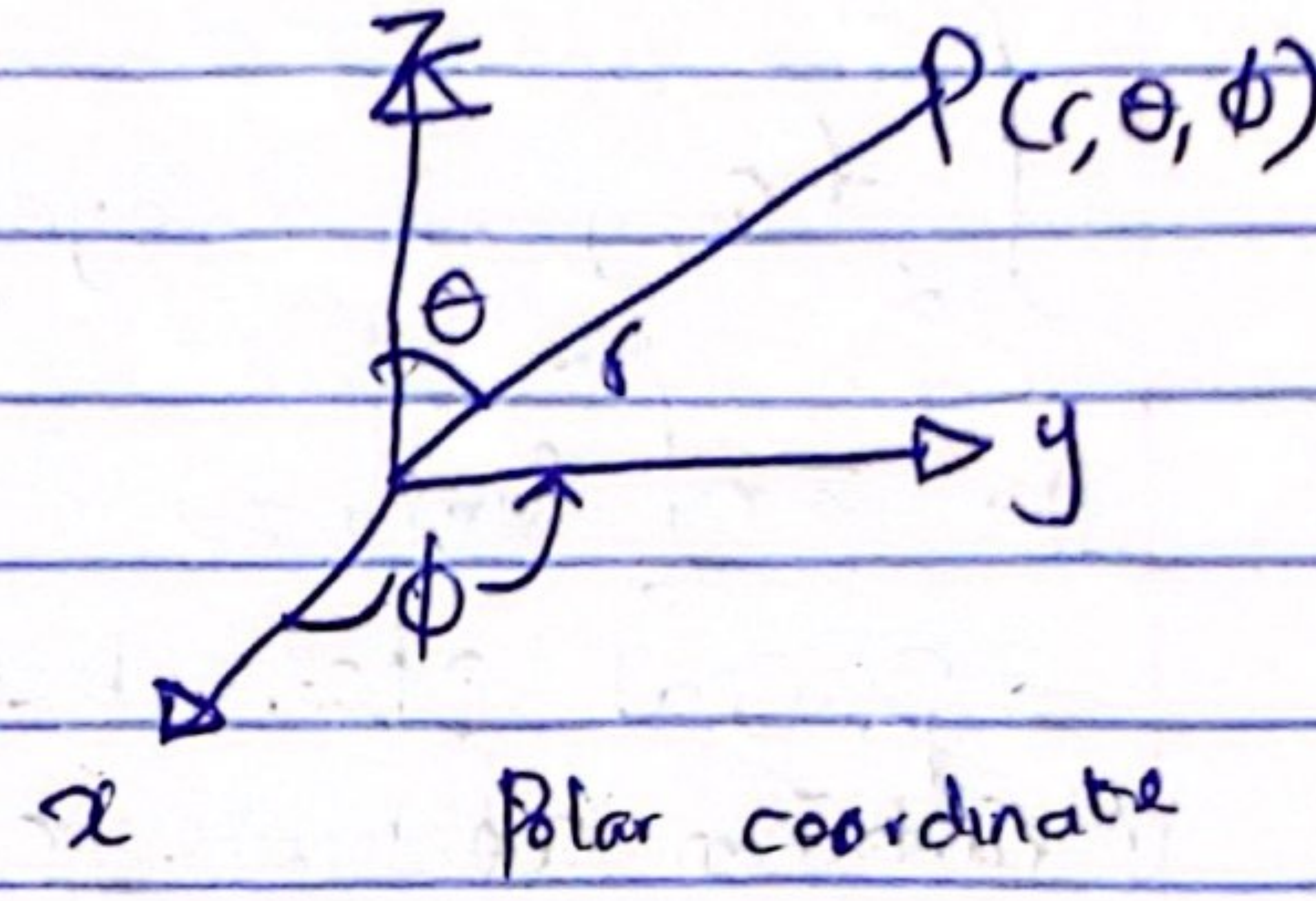
The two important coordinate systems are

(I) Cartesian coordinate
(II) Polar coordinate.

so that if you have a particle P at the point P(x, y, z), we can transform this coordinate



Cartesian coordinate



Polar coordinate

The cartesian coordinate system specifies the position of the point in space by given three numbers that are the projections of points on the orthogonal axis (x, y, z)

x, y, z coordinate can be likened to the right hand system such that the fingers of the right hand are folded in the direction x to y, while the thumb is pointing in the positive z-direction. The volume of a cubic element with infinitesimal side length dx, dy and dz is defined as

$d\tau = dx\,dy\,dz$

This called the volume element.

The integral of the function x, y, and z over all Space employs the Volume element such that

$$\int_{-\infty}^{+\infty} f(x, y, z)\, dx\,dy\,dz = \int_{-\infty}^{+\infty} dx \int_{-\infty}^{+\infty} dy \int_{-\infty}^{+\infty} f(x,y,z)\, dz$$

$$= \int_{-\infty}^{+\infty} f(x, y, z)\, d\tau$$

Physical Observables of a particle can be expressed in Cartesian coordinate system

ⓐ Position vector

$$\vec{r} = (x, y, z)$$

ⓑ velocity vector: $\vec{v} = (v_x, v_y, v_z)$

ⓒ momentum vector:

$$\vec{P} = (p_x, p_y, p_z)$$

Polar or Spherical coordinate are expressed in terms of the distance r of the position of a particle from the origin and its direction in space from the origin, where θ and ϕ specifies the direction $P(r, \theta, \phi)$

Such that r by Pythagoras theorem,

$$r = \sqrt{(x^2 + y^2, z^2)}$$

$$\theta = \cos^{-1}\left(\frac{z}{r}\right)$$

$\phi = \tan^{-1}(y/x)$ for $\vec{P} = P_x + P_y + P_z$

Transformation of cartesian to polar coordinate;

$$(x, y, z) \rightarrow (r, \theta, \phi)$$

$$r^2 = x^2 + y^2 + z^2 \quad \ldots\ldots ①$$

$$\cos\theta = \frac{z}{r}$$

$$\tan\phi = y/x$$

$$z = r\cos\theta, \quad x\sin\phi = y\cos\phi$$

$$x = \frac{y\cos\phi}{\sin\phi} = y\cot\phi$$

If you substitute x and z in eqn (1)

$$r^2 = y^2\cot^2\phi + y^2 + r^2\cos^2\theta$$

$$r^2 = y^2(1 + \cot^2\phi) + r^2\cos^2\theta$$

$$r^2 - r^2\cos^2\theta = y^2(1 + \cot^2\phi)$$

$$r^2(1 - \cos^2\theta) = y^2(1 + \cot^2\phi)$$

$$r^2\sin^2\theta = \frac{y^2}{\sin^2\phi}$$

$$y = r\sin\theta\sin\phi$$

$$x = r\sin\theta\cos\phi$$

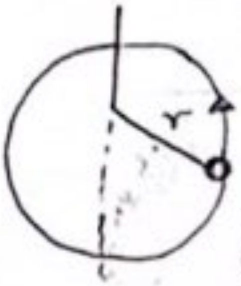
$$z = r\cos\theta$$

Angular Momentum

⑨

→ the quantum theory of angular momentum is an ~~important~~ essential feature for many areas of chemistry and physics, including atomic structure and spectroscopy, molecular dynamics, theory of nuclear structure, rotational/microwave spec., nmr etc.

Let us consider the rotation of a particle about a fixed point:



Linear momentum is given by: $P = mv$. Let ν_{rot} be the freq. of ~~rotation~~ rotation (cycles/sec). The speed of the particle then is $v = 2\pi r \nu_{rot} = r\omega_{rot}$ where $\omega_{rot} = 2\pi\nu_{rot}$ (angular freq.) is in radians/sec. The kinetic energy of the revolving particle is:

~~K.E~~ $$K = \frac{1}{2}mv^2 = \frac{1}{2}mr^2\omega^2 = \frac{1}{2}I\omega^2$$

where $I = mr^2$ ⇒ the moment of inertia.

By comparing the first and last expressions for the K.E above; the correspondences that arise are: $\omega \leftrightarrow v$ as $I \leftrightarrow m$, where ω & I are angular quantities and v and m are linear quantities.

Based on these correspondences, there should be a quantity $I\omega$ corresponding to the linear momentum mv:

$$\therefore \quad L = I\omega = mr^2\left(\frac{v}{r}\right) = mvr$$

L ⇒ angular momentum, and it is a fundamental quantity associated with rotating systems.

Then: $K = \frac{1}{2}mv^2 = \frac{(mv)^2}{2m} = \frac{p^2}{2m}$ —— linear system.

and $K = \frac{I\omega^2}{2} = \frac{(I\omega)^2}{2I} = \frac{L^2}{2I}$ ⟹ rotating system

The correspondences btw linear and rotating systems are summarized as

Linear motion	Angular motion
Mass (m)	moment of inertia (I)
Speed (v)	Angular speed (ω)
Momentum $(p = mv)$	Angular momentum $(L = I\omega)$
Kinetic Energy $\left(K = \frac{mv^2}{2} = p^2/2m\right)$	Rotating K.E $\left(K = \frac{I\omega^2}{2} = \frac{L^2}{2I}\right)$

The components of the ~~vectorial quant~~ angular momentum operator are:

$$L_x = yp_z - zp_y \; ; \; L_y = zp_x - xp_z , \; L_z = xp_y - yp_x$$

i.e.

$$\hat{L}_x = -i\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)$$

$$\hat{L}_y = -i\hbar\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right)$$

$$\hat{L}_z = -i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)$$

⇒ Find out the spherical polar coordinate equivalents.

Show that $\hat{L}_x$ & $\hat{L}_y$; $\hat{L}_y, \hat{L}_z$, $\hat{L}_z, \hat{L}_x$ do not commute

The Particle on a Ring

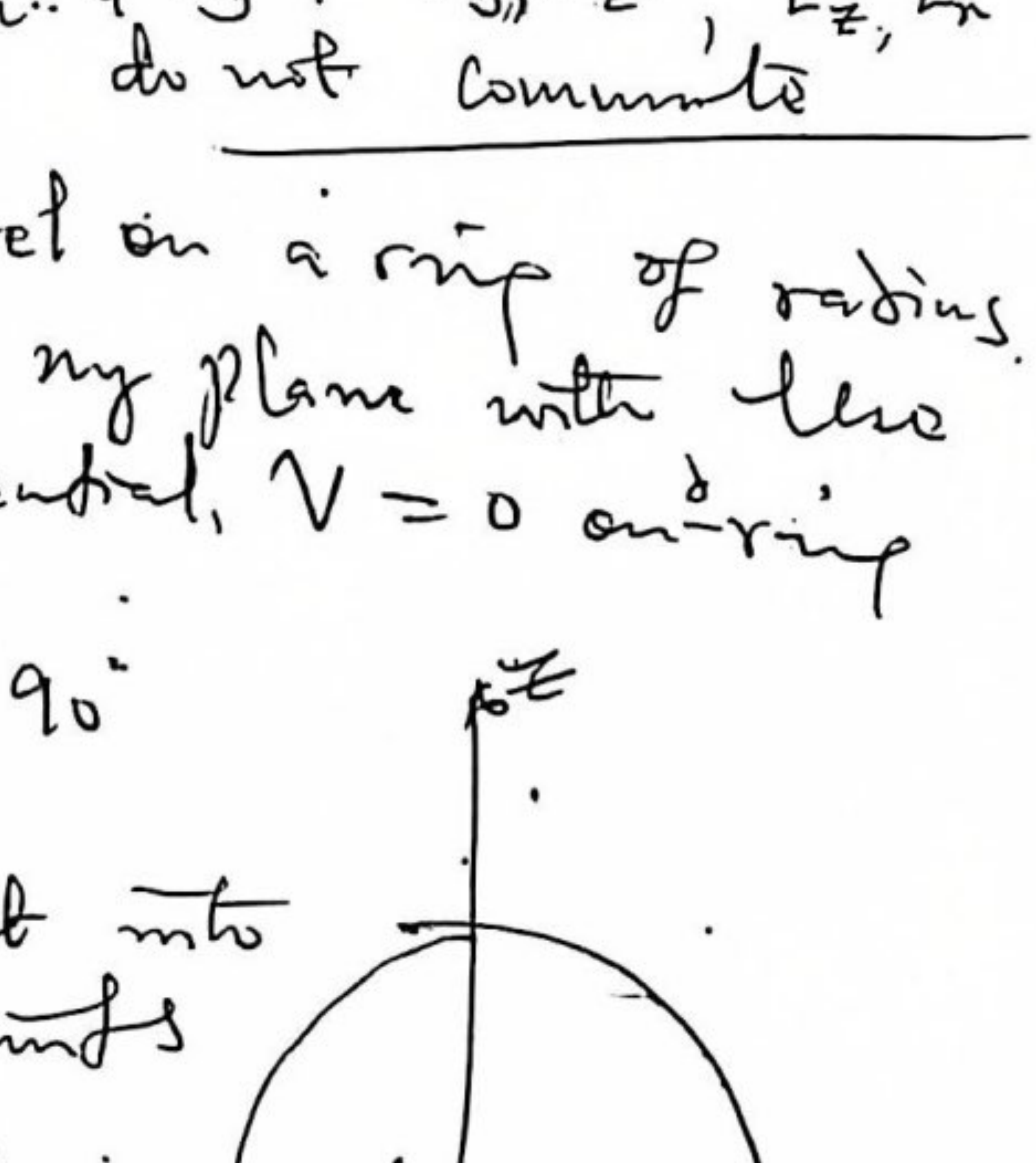
Consider a mass μ confined to travel on a ring of radius R; let us place the ring in the xy plane with the center at the origin: the potential, $V = 0$ on-ring and infinite otherwise

$$\begin{cases} V = 0 & r = R, \theta = 90^\circ \\ V = \infty & \end{cases}$$

This is effectively a 1D-"box" bent into a circle. The angular momentum points in the z-direction, so only L_z is nonzero and K.E $= L_z^2/2I$ while $I = MR^2$. On the circle, the $V = 0$, so, $E_{cl} = L_z^2/2I$

⇓

Classical Energy



Ⓒ

and the Hamiltonian is: $\hat{H} = \frac{\hbar^2}{2I}\hat{L}_z^2 = -\frac{\hbar^2}{2I}\frac{d^2}{d\phi^2}$

{~~Since~~: $\hat{L}_z = i\frac{\partial}{\partial\phi}$ in $\hbar$ units}

⇒ the Schrödinger eqn is; $\frac{\hbar^2}{2I}\frac{\partial^2\psi}{\partial\phi^2} = E\psi$

Note the mathematical similarity of this eqn to the equation for the particle in a box!

$$\psi = \begin{cases} \cos m\phi \\ \sin m\phi \\ e^{im\phi} \end{cases}$$ where m is a real const

Since these three solutions are not independent {i.e. $e^{im\phi} = \cos m\phi + i\sin m\phi$; $\cos m\phi = \frac{e^{im\phi} + e^{-im\phi}}{2}$; $\sin m\phi = \frac{e^{im\phi} - e^{-im\phi}}{2i}$}

Let $\psi = Ae^{im\phi}$ {A ⇒ normalization const}

For the restrictions of m: ~~the~~ ψ must be single valued:

i.e. $\psi(\phi) = \psi(\phi + 2\pi) \Rightarrow e^{im\phi} = e^{im(\phi+2\pi)}$

$$e^{2\pi im} = 1$$

Using $e^{2\pi im} = \cos 2\pi m + i\sin 2\pi m = 1$

this is true for integer values of m.

$m = 0, \pm 1, \pm 2, \pm 3 ----$

The energy is calculated from the Schrödinger eqn:

$$\hat{H}\psi = E\psi$$

$$\frac{\hbar^2}{2I}\frac{d^2 e^{im\phi}}{d\phi^2} = \frac{m^2\hbar^2 e^{im\phi}}{2I}$$

$$\therefore \quad E_m = \frac{m^2\hbar^2}{I} = \frac{m^2h^2}{8\pi^2 I}$$

(d)

NOTE: + & -ve quantum nos m with the same magnitude have the same energy, so all fns except $m=0$ are doubly degenerate.

The normalized wave function is:

$$\psi_m = \frac{1}{\sqrt{2\pi}} e^{im\phi} \quad (m = 0, \pm 1, \pm 2 \ldots)$$

Exc. Given $\psi = Ae^{im\phi}\{0 < \phi < 2\pi\}$ for a particle on a ring. Find the normalization const. A.

$$\Rightarrow \int_0^{2\pi} |\psi^* \psi| d\tau = 1 \Rightarrow \int_0^{2\pi} |A|e^{-im\phi} |A| e^{im\phi} d\phi = 1$$

$$\Rightarrow |A|^2 \int_0^{2\pi} d\phi = 1 \Rightarrow |A|^2 [2\pi] = 1$$

$$\therefore A = \frac{1}{\sqrt{2\pi}}$$

Hence, the normalized wavefunction is:

$$\psi = \frac{1}{\sqrt{2\pi}} e^{im\phi}$$

$$\underline{m = 0, \pm 1, \pm 2, \ldots}$$

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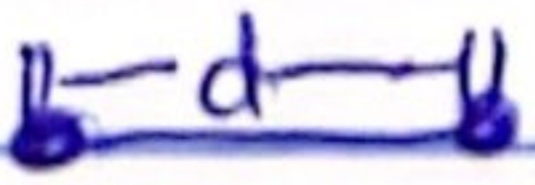
Two Particle Rigid Rotor

Consider a two particle System, with the particles hold at a fixed distance d, by a rigid massless rod.

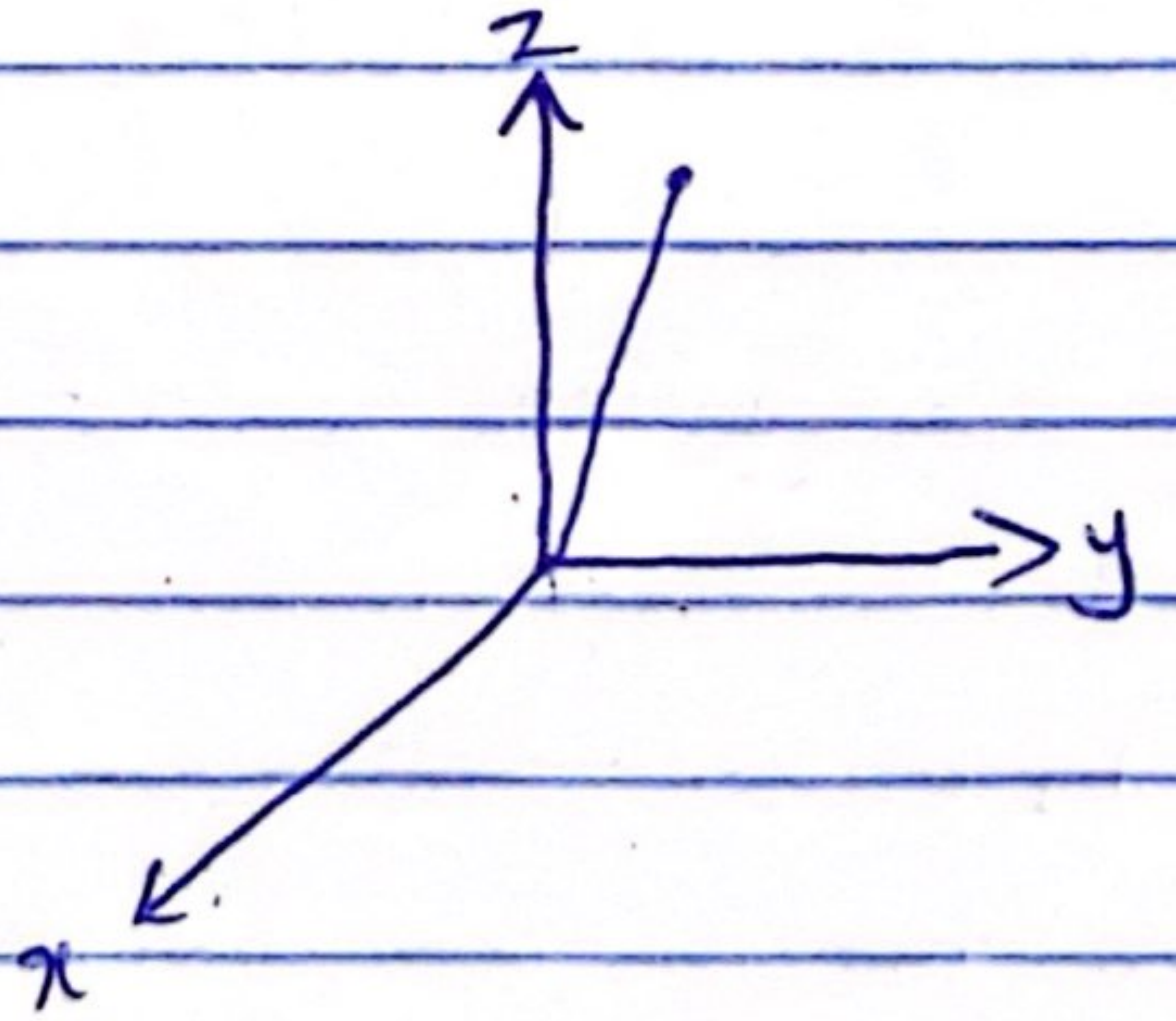


The energy of the rotor is entirely K.E, ie rotational energy, thus the PE, of the rotor V = 0

The Hamiltonian for the rotor;

$$\hat{H} = \frac{-\hbar^2}{2M}\nabla^2$$ where M is the reduced mass of the two particle.

It is therefore be more convenient in using relative spherical coordinate (r, θ, ϕ)



Using the vector r in the figure above, the magnitude $\vec{r}$ ~~is~~ equal to distance d between the particle Since m_1 and m_2 are fixed, their constraints to remain at a fixed distance apart, then the rigid rotor is like fictitious object or

Particle of mass μ on the coordinate that is conditioned to move on the surface of a sphere of radius $r = d$.

The laplacian operator (∇) for a spherical coordinate system is defined as,

$$\nabla^2 = \frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} - \frac{1}{r^2\hbar^2}\hat{L}^2$$

Since the radian coordinate is constant, the wave-function for the particle will be a function of θ and ϕ only. Hence, the first two terms of the laplacian operator will go to zero when operating on the wave function, i.e,

$$\frac{\partial}{\partial r}\psi(\theta,\phi) = 0 \quad \text{and} \quad \frac{\partial^2}{\partial r^2}\psi(\theta,\phi) = 0$$

Hence, $\nabla^2 = -\frac{1}{d^2\hbar^2}\hat{L}^2$

By substituting for laplacian operator, in the Hamiltonian, we can write that

$$\hat{H} = \frac{1}{2\mu d^2}\hat{L}^2 \quad \ldots (49)$$ since $\hat{H} = -\frac{\hbar^2}{2\mu}\nabla^2$

Recall, that the eigen function for the square of the angular momentum ($\hat{L}^2$) are spherical harmonics of the form

$$\psi = R(r)\, Y_l^m(\theta, \phi)$$

$$\hat{L}^2 \cong l(l+1)\hbar^2$$

The eigen function for the schrodinger wave equation;

$$\psi = Y_J^m(\theta, \phi)$$

where J = rotational angular momentum quatum number

For the schrodinger wave equation

$$\hat{H}\psi = E\psi$$

$$\frac{1}{2Md^2}\hat{L}^2\, Y_J^m(\theta, \phi) = E\, Y_J^m(\theta, \phi)$$

since $\hat{L}^2 = J(J+1)\hbar^2$

Substitution for $\hat{L}^2$ gives

$$\frac{1}{2Md^2} J(J+1)\hbar^2\, Y_J^m(\theta, \phi) = E\, Y_J^m(\theta, \phi)$$

Therefore $E = \dfrac{J(J+1)\hbar^2}{2Md^2}$; $J = 0, 1, 2 \ldots.$ ——— (56)

In equation 56, the energy levels, depends on J only, but the eigen function depends on J and $\hat{m}$, where $m\hbar$ is the z component of the rigid rotor angular momentum.

This means that each specified J level has $(2J+1)$ ~~of~~ degeneracy

The moment of Inertia (I) we recall is defined as

$$I = \sum_{i=1}^{n} m_i r_i^2$$

height

m ~~= mass of a~~ particle

r_1

m_1 = mass of the i^{th} particles

r_1 = distance of the particle to the axis along the perpendicular direction

For a two particle rigid rotor, we can write that

$$I = m_1 r_1^2 + m_2 r_2^2$$

$d = r_1 + r_2$ and r_1 & r_2 are measured from the centre of mass, M

$$m_1 r_1 = m_2 r_2$$

$\therefore$ $I = M d^2$ &

$$E_J = \frac{J(J+1)\hbar^2}{2I} \quad \text{for } J = 0, 1, 2, \ldots$$

At the lowest level, $J = 0$, for the particle rigid rotor, $E_0 = 0$, therefore, the Zeroth point rotational energy for a rigid rotor is equal to zero, unlike that of harmonic oscillator

The rotational level of a diatomic molecule Can be well-approximated by the 2-particle rigid rotor energy. It turns out that a well defined rotational energy is obtained only for $I \neq 0$ and transitions are defined only when $I \neq 0$

For $J = 0$, $E_0 = 0$

For $J = 1$, $E_1 = \frac{\hbar^2}{I}$

$J = 2$, $E_2 = \frac{3\hbar^2}{I}$

$J = 3$, $E_3 = \frac{6\hbar^2}{I}$

Therefore $$\Delta E_{(J+1)\to J} = \frac{(J+1)\hbar^2}{I}$$

for $J = 0, 1, 2 \ldots$

Note that when a diatomic molecule absorbs or emit radiation, the allowed pure rotational transition are those of $\Delta J = \pm 1$

Moreso, a particle must have a non-zero dipole moment in order to show a pure rotational spectrum

We consider the transition of J → J+1 for which the spectrum frequency is

$$\nu = \frac{\Delta E}{h}$$

$$\nu = \frac{(J+1)\hbar^2}{Ih} = \frac{(J+1)\hbar^2}{4\pi^2 I h} = \frac{(J+1)h}{4\pi^2 I} \quad (64)$$

Eqn (64) can be rewritten as

$$\nu = 2(J+1)\frac{h}{8\pi^2 I}$$

$$\Rightarrow \nu = 2(J+1)B$$

$$\therefore B = \frac{h}{8\pi^2 I}$$ (rotational constant) of the molecule

The Hydrogen Atom

The hydrogen atom as a nucleus consists of a heavy essentially motionless proton which may as well be regarded as the origin having charge, e together with a much lighter electron having a charge e^- that orbit around it bound by the mutual attraction of opposite charges. The movement of electron around this orbit is like that of a particle on a ring

From columb's law, the potential energy, V can be expressed as

$$V(r) = \frac{-e^2}{4\pi\varepsilon_0} \cdot \frac{1}{r} \quad \ldots (67)$$

Where r = electron-nucleus distance and

ε_0 = permittivity of the Vacuum

And the total energy Hamiltonian can be expressed as

$$\hat{H} = -\frac{\hbar^2}{2M}\nabla^2 + V(r)$$

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

And M is the reduced mass for the electron-nucleus system

In other words

$$\frac{1}{M} = \frac{1}{m_e} + \frac{1}{m_N} \quad \ldots (68)$$

We know that $M_p \approx 2000 \times m_e$

$$\therefore \frac{1}{\mu} \approx \frac{1}{m_e} \quad \therefore \quad m_e \approx \mu$$

we recall that

$$\nabla^2 = \frac{\partial^2}{\partial r^2} + \frac{\partial}{r}\frac{\partial}{\partial r} - \frac{1}{r^2}\frac{\hat{L}^2}{\hbar^2}$$

Which suggests that the Hamiltonian for the hydrogen atom commutes with the square of the angular momentum operator and also with the z component of the angular momentum operator

$$\left.\begin{array}{l} [\hat{H}, \hat{L}^2] = 0 \\ [\hat{H}, L_z] = 0 \end{array}\right\} \quad \cdots (10)$$

Recall

$\hat{L}^2 = L(L+1)\hbar^2$ For hamiltonian for a hydrogen atom, we could express the hamiltonian as

$$\hat{H} = \frac{-\hbar^2}{2m}\frac{d^2}{dr^2} + \left[\frac{-e^2}{4\pi\varepsilon_0}\cdot\frac{1}{r} + \underbrace{\frac{\hbar^2 L(L+1)}{2m r^2}}_{\text{Centrifugal component}}\right] \cdots (11$$

Let the radial part of the wave function

$$u(r) = rR(r)$$

then

$$-\frac{\hbar^2 d^2u}{2m\,dr^2} + \left[\frac{-e^2}{4\pi\varepsilon_0 r} + \frac{\hbar^2}{2m}\frac{L(L+1)}{r^2}\right]u = Eu \quad (12)$$

It is bound system Cos electron [illegible] Molecule is a bound system

In order to solve eqn (72), we will approach a solution that afford substitution for K

Let $$K = \frac{\sqrt{-2mE}}{\hbar} \ldots (72a)$$

For bound state, we know that E is $-$ve, then K will be real.

$$\frac{1}{K^2}\frac{d^2u}{dr^2} = \left[1 - \frac{me^2}{2\pi\varepsilon_0\hbar^2 K}\cdot\frac{1}{(Kr)} + l(l+1)\left(\frac{1}{Kr}\right)^2\right]u \ldots (73)$$

Eqn (73) can be further simplified as

Let $$\left[\rho = Kr,\ \rho_0 = \frac{me^2}{2\pi\varepsilon_0\hbar^2 K}\right] \ldots (74)$$

Upon substitution

$$\frac{d^2u}{d\rho^2} = \left[1 - \frac{\rho_0}{\rho} + l(l+1)\cdot\frac{1}{\rho^2}\right]u \ldots (75)$$

which can be solved approximately by examining the asymptotic form as

(i) as $\rho \to \infty$; eqn 75 reduces to $\frac{d^2u}{d\rho^2} = u \ldots (76)$

The solution to eqn (76) is in the form,

$$u(\rho) = Ae^{-\rho} + Be^{\rho} \ldots (77)$$

(diverge)

The Second term eqn (77) becomes very large as $\rho \to \infty$

u(ρ) will diverge

Meanwhile, we need $u(\rho)$ to converge, but if $\rho \to \infty$,

Therefore $B = 0$, for convergence

~~u(ρ) will diverge~~

$\therefore \; u(\rho) = Ae^{-\rho}$ (for large ρ)

Since we previously defined $\rho = Kr$;

and $K = \frac{\sqrt{-2me}}{\hbar}$

$$U(r) = Ae^{\left(-\frac{\sqrt{-2me}}{\hbar}\right)r} = Ae^{-i\left(\frac{\sqrt{2me}}{\hbar}\right)\cdot r} \quad \ldots\ldots (79)$$

(ii) As $\rho \to 0$, eqn (75) reduces to

$$\frac{d^2u}{d\rho^2} = \frac{l(l+1)}{\rho^2}u \quad \ldots (80)$$

It should be noted that equation (80) is only valid for ρ not exactly equal to zero

The general solution for eqn (80) is in the form

$$u(\rho) = C\rho^{(l+1)} + De^{-1} \quad \ldots (81)$$

The second term is eqn 80 goes up as ρ tends to zero

Therefore $D = 0$, for convergence

u(ρ) = Cρ^{l+1} (for small ρ)

$$u(\rho) = C\rho^{l+1} \text{ (for small } \rho) \quad \ldots 82)$$

$$\cancel{u(r)} = C\left[i\,\frac{\sqrt{2me}}{\hbar}\cdot r\right]^{l+1} \quad \ldots (83)$$

Hence, the wavefunction for the hydrogen system is defined as

$$U(\rho) = U(\rho)_\infty - U(\rho)_0 \cdot V(\rho) \cdots 84$$

$V(\rho)$ is introduced to take care of asymptotic assumptions.

Solution to this could be approached via power series expansion and recurrsion relation When ~~are~~ [illegible] afford

$\rho_0 = 2n$ with n being the principal quantum number

Since $E = \frac{\hbar k^2}{2m} = \frac{-me^4}{8\pi^2\varepsilon_0^2\hbar^2\rho_0^2}$

Substitution for ρ gives

$$E_n = -\left(\frac{m}{2\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_0}\right)^2\right]\frac{1}{n^2}$$

For $n = 1$ (1st energy level)

$$E_1 = \frac{-m}{2\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_0}\right)^2$$

$$E_n = \frac{E_1}{n^2}, \quad n = 1, 2, 3 \ldots \ldots \quad (85)$$

Eqn (85) is the famous Bohr's formular, Substitution into which $E_1 = -13.6$ eV and that is for the ground state energy of an hydrogen atom, also called the binding energy

Anti Symmetry Principle

In classical mechanics, each point of the particle trageotoring is described by its position and linear momentum coordinate.

Identical particles can be distinguished by distinct trajectories. However, electrons can be assigned individual trajectory due to the uncertainty principle that states that position and momentum can not be simultaneously specified.

Each electron of an atom or even a molecule is assigned four variables which comprise three spatial coordinates that specify the position vector and the spin variable that can take the value of alpha

s - spin variable α ($m_s = +\frac{1}{2}$)

β ($m_s = -\frac{1}{2}$)

It will represent the set of this variable by S. The wave function for 2 electron system could be written as $\Psi(S_1, S_2)$

Consider the exchange or permutation operator ($\hat{P}$) that interchanges all four coordinate of electron 1 and 2, we can say that;

$$\hat{P}_{12}\Psi(S_1, S_2) = \Psi(S_2, S_1)$$

Applying this operator twice has no net effect

$$\hat{P}^2_{12}\psi(S_1,S_2) = \hat{P}_{12}[\hat{P}_{12}\psi(S_1,S_2)] = \underset{\text{Permutation operator}}{\hat{P}_{12}}\psi(S_2,S_1) = \psi(S_1,S_2)$$

Therefore, the eigen value of the $\hat{P}^2 = 1$, and consequently the eigen value of the permutation operator

$$\hat{P} = +1, -1$$

to However, only -1 is consistent with experimental data for electrons. So we can say;

$$\hat{P}_{12}\psi(S_1,S_2) = -\psi(S_1,S_2)$$

Therefore $\psi(S_2,S_1) = -\psi(S_1,S_2)$

And the wave function is said to be antisymmetric with respect to interchange of coordinate of two electron including the spin coordinate.

This called antisymmetric principle

* orbital is a mathematical function describing the position of an electron in space

18th January

If $s_2 = s_1$

Then, $\psi(s_1, s_1) = -\psi(s_1, s_1)$

which consequently implies that

$$\psi(s_1, s_1) = 0 \quad ; \quad |\psi(s_1, s_1)|^2 = 0$$

The implication of this is that two electrons with the same spin will have zero probability of being found at the same point. This consequence of the anti-symmetry principle is called the Pauli Exclusion Principle.

We said previously that each electron function is a product of spatial and the spin function

$$\psi_a(s_1) = \phi_a(r_1)\,\sigma(1)$$

where $\sigma = \alpha$ or β function

Each one electron spatial factor for function $\phi_a(r_1)$ is called an orbital and the product of a spatial factor and the corresponding spin factor is called a spin orbital

The overall wavefunction for many electron system must have both antisymmetric part and symmetric part

For example, for a two electron system, we can write the spin orbital as

$$\psi_a = \phi_{12}^{\alpha\alpha} \quad \text{or} \quad \psi_b = \phi_{21}^{\alpha\alpha}$$

The overall wave function is ~~ca~~ linear combination of these two

i.e $\psi' = \psi_a - \psi_b$ → unnormalized

By putting the normalization factor, Let the normalization factor be A

$$\psi' = A(\psi_a - \psi_b)$$

By imposing the normalization condition, we have;

$$\int |\psi'|^2 d\tau = 1$$

$$\int (A\psi_a - A\psi_b)^2 d\tau = 1$$

$$\int \underbrace{|A\psi_a|^2}_{A^2} - 2\underbrace{|A|^2\psi_a\psi_b}_{\text{orthogonal}} + |A\psi_b|^2 d\tau = 1$$

Since one electron functions are orthonormal, we have

$$2|A|^2 = 1$$

$$A = \frac{1}{\sqrt{2}}$$

The overall antisymmetric wave function will therefore be

$$\therefore \psi' = \frac{1}{\sqrt{2}}(\psi_a - \psi_b)$$

where: $\psi_a = \phi_1(1)\alpha(1)\phi_2(2)\alpha(2)$

$\psi_b = \phi_2(1)\alpha(1)\phi_1(2)\alpha(2)$

Hence, $\psi' = \frac{1}{\sqrt{2}}\left[\phi_1(1)\alpha(1)\phi_2(2)\alpha(2) - \phi_2(1)\alpha(1)\phi_1(2)\alpha(2)\right]$

This can be put into a Slater Determinant

$$\psi' = \frac{1}{\sqrt{2}}\begin{vmatrix} \phi_1(1)\alpha(1) & \phi_2(1)\alpha(1) \\ \phi_1(2)\alpha(2) & \phi_2(2)\alpha(2) \end{vmatrix}$$

where; $\phi_{12}^{\alpha\alpha}$ = product of the 1st diagonal element

$\phi_{21}^{\alpha\alpha}$ = product of the 2nd diagonal element

$$\psi' = \phi_{12}^{\alpha\alpha} - \phi_{21}^{\alpha\alpha}$$

Note that $\psi' = \frac{1}{\sqrt{2}}\left[\underbrace{\phi_1(1)\phi_2(2) - \phi_2(1)\phi_1(2)}_{\text{antisymmetric}}\right]\underbrace{\alpha(1)\alpha(2)}_{\text{symmetric}}$

For a three electron system, the product of the three spin orbital would be:

$$\psi_a(1)\cdot\psi_b(2)\cdot\psi_c(3)$$

Which can be interchanged, such that ~~$\psi' = \psi_a(1)\psi_b(2)\psi_c(3)$~~

$$\psi' = \psi_a(1)\psi_b(2)\psi_c(3) - \psi_a(2)\psi_b(1)\psi_c(3)$$
$$+ \psi_a(2)\psi_b(3)\psi_c(1) - \psi_a(3)\psi_b(2)\psi_c(1) + \psi_a(3)\psi_b(1)\psi_c(2)$$
$$- \psi_a(1)\psi_b(3)\psi_c(2) \longrightarrow \text{unnormalized}$$

Normalization of ψ' and the fact that one electron functions are orthonormal gives: ~~$|A|^2$~~

$$|A|^2(1+1+1+1+1+1) = 1$$

$$A = \frac{1}{\sqrt{6}} = \frac{1}{\sqrt{3!}}.$$

The normalized function for a three electron system is;

$$\psi' = \frac{1}{\sqrt{3!}}\Big[\psi_a(1)\psi_b(2)\psi_c(3) - \psi_a(2)\psi_b(1)\psi_c(3) + \psi_a(2)\psi_b(3)\psi_c(1) - \psi_a(3)\psi_b(2)\psi_c(1) + \psi_a(3)\psi_b(1)\psi_c(2) - \psi_a(1)\psi_b(3)\psi_c(2)\Big]$$

Which can be put into a 3×3 slater system determinant

$$\psi' = \frac{1}{\sqrt{3!}}\begin{vmatrix} \psi_a(1) & \psi_b(1) & \psi_c(1) \\ \psi_a(2) & \psi_b(2) & \psi_c(2) \\ \psi_a(3) & \psi_b(3) & \psi_c(3) \end{vmatrix}$$

Generally for a N- electron system, the slater determinant that gives the normalized antisymmetric wave function is

~~$\psi' = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_a(1) \\ \psi_a(2) \\ \psi_a(3) \end{vmatrix}$~~

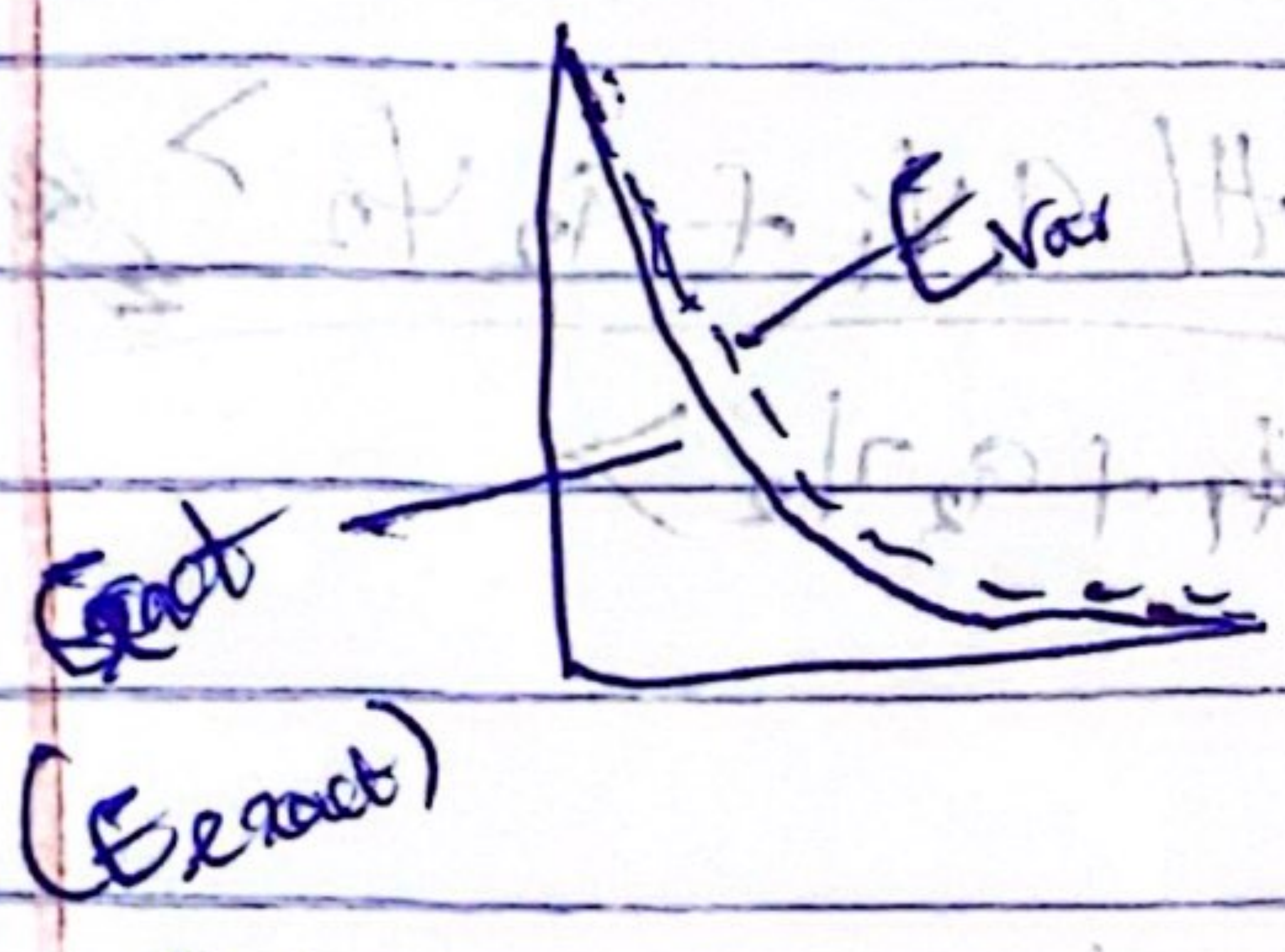
$$\psi' = \frac{1}{\sqrt{N!}}\begin{vmatrix} \psi_a(1) & \psi_b(1) & \cdots & \psi_z(1) \\ \psi_a(2) & \psi_b(2) & & \psi_z(2) \\ \vdots & \vdots & & \vdots \\ \psi_a(N) & \psi_b(N) & & \psi_z(N) \end{vmatrix}$$ where $z \geq N$

~~The Hydrogen Atom~~

Variational Method

Solving the scrodinger wave equation for atoms and molecules with more than one electron, requires the use of approximate methods. A commonly used method of approximation is based on the Variational Theorem

Variational principle can be used to get an upper bound for the ground state energy which can be very close to the exact value if determined carefully.



(E_{exact})

Consider a system with a Hamiltonian, whose lowest energy eigen value is ε_0 and having a well behaved function ϕ that satisfies the boundary conditions of the System

Variational theorem postulates that,

$$E_{var} = \left(\frac{\int \phi^* \hat{H} \phi \, d\tau}{\int \phi^* \phi \, d\tau} \right) \geq E_0$$

→ Variational integral

The eigen functions ~~size of~~ ψ_k of the Hamiltonian must satisfy the eigen value equations

$$\hat{H}\psi_k = E_k\psi_k$$

And form a complete set of orthonormal set of functions that can be used to expand Φ, i.e

$$\Phi = \sum_k c_k\psi_k$$

e.g $\Phi = a_1\psi_1 + a_2\psi_2$

Substitution for Φ in the variational integral gives

$$E = \frac{\langle\phi^* \hat{H}\phi\rangle}{\langle\phi^*\phi\rangle}, \quad E = \frac{\langle a_1\psi_1 + a_2\psi_2 | H | a_1\psi_1 + a_2\psi_2\rangle}{\langle a_1\psi_1 + a_2\psi_2 | a_1\psi_1 + a_2\psi_2\rangle}$$

Upon rearrangement

~~$E = (\langle a_1\psi_1 + a_2\psi_2 | a_1\psi_1 + a_2\psi_2\rangle)$~~

$$E\langle a_1\psi_1 + a_2\psi_2 | a_1\psi_1 + a_2\psi_2\rangle = \langle a_1\psi_1 + a_2\psi_2 | \hat{H} | a_1\psi_1 + a_2\psi_2\rangle$$

Let $H_{ii} = \langle\psi_i|\hat{H}|\psi_i\rangle$ e.g $\langle\psi_1|\hat{H}|\psi_1\rangle = H_{11}$

$H_{ij} = \langle\psi_i|\hat{H}|\psi_j\rangle$ e.g $\langle\psi_1|\hat{H}|\psi_2\rangle = H_{12}$ if $i \neq j$

and $S_{ij} = \langle\psi_i|\psi_j\rangle = S \ (i \neq j)$

According to variational principle, E must be minimized with respect to the variational parameters a_1

That is,

$\frac{dE}{da_1} = 0$ at the minimum port

Expansion of an equation gives.

$E[a_1^2 + a_1 a_2 S + a_2 a_1 S + a_2^2] = [a_1^2 H_{11} + a_1 a_2 H_{12}$
$+ a_2 a_1 H_{21} + a_2^2 H_{22}]$

Since $a_1 a_2 = a_2 a_1$

$E(a_1^2 + 2a_1 a_2 S + a_2^2) = (a_1^2 H_{11} + a_1 a_2 H_{12} + a_2 a_1 H_{21} + a_2^2 H_{22})$

By taking the partial derivatives of both side wrt a_1, we have;

$E(2a_1 + 2a_2 S + 0) + (a_1^2 + 2a_1 a_2 S + a_2^2) \frac{\partial E}{\partial a_1} = 2a_1 H_{11}$

$+ a_2 H_{12} + a_2 H_{21} + 0$

Since $\frac{\partial E}{\partial a_1} = \frac{\partial E}{\partial a_2} = 0$

Also, let us assume that

$H_{21} = H_{12}$, then

$E(2a_1 + 2a_2 S) = 2a_1 H_{11} + 2a_2 H_{12}$

$\Rightarrow a_1(H_{11} - E) + a_2(H_{12} - ES) = 0$
$\searrow$
1st secular equation

Minimization wrt a_2 $\nearrow$ 2nd Secular equation

$$a_1(H_{21} - ES) + a_2(H_{22} - E) = 0$$

By solving 1st and 2nd Secular equation Simultaneously

The trival Solution is that

$$a_1 \; \& \; a_2 = 0$$

But a non-trival solution requires a vanishing determinant of the form whose coefficient is.

$$\begin{vmatrix} H_{11} - E & H_{12} - ES \\ H_{21} - Es & H_{22} - E \end{vmatrix} = 0$$

$$(H_{11} - E)(H_{22} - E) - (H_{12} - Es)(H_{21} - Es) = 0$$

Assuming $H_{11} = H_{22}$ & $H_{12} = H_{21}$, we have;

$$(H_{11} - E)^2 = (H_{12} - Es)^2$$

$$\Rightarrow H_{11} - E = \pm (H_{12} - ES)$$

For

$$H_{11} - E = H_{12} - ES$$

$$E(S-1) = H_{12} - H_{11}$$

$$E = \frac{H_{12} - H_{11}}{S - 1} = \frac{H_{11} - H_{12}}{1 - S}$$

For $H_{11} - E = -(H_{12} - ES)$

$$E_+ = \frac{H_{11} + H_{12}}{1+S}$$

$$\therefore E_\pm = \frac{H_{11} \pm H_{12}}{1 \pm S}$$

For example, the Hamiltonian for the 1D harmonic oscillator is given as

$$\hat{H} = \frac{-\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}m\omega^2 x^2$$

Starting with Guassian $\phi(x) = Ae^{-bx^2}$ as a trival wave function where b is constant.

(i) Determine value of b for tightest bound

(ii). Hence, determine the minimum energy $\langle H\rangle_{min}$ and comment on the trival wave function and comparing the minimum energy with the exact ground state energy $E_{gs}\left(\frac{1}{2}\hbar\omega\right)$

Solution

$$E = \frac{\int \phi^* |\hat{H}| \phi \, d\tau}{\int \phi^* / \phi \, d\tau} \geq E_{gs}$$

Numerator $\displaystyle\int_{-\infty}^{+\infty} Ae^{-bx^2} \left| \frac{-\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}m\omega^2 x^2 \right| Ae^{-bx^2} dx$

$$= \int_{-\infty}^{+\infty} \phi^* |\hat{T}| \phi \, d\tau + \int_{-\infty}^{+\infty} \phi^* |\hat{V}| \phi \, d\tau$$

$$\langle \phi^* \hat{T} \phi \rangle = \frac{-\hbar^2}{2m} |A|^2 \int_{-\infty}^{+\infty} e^{-bx^2} \frac{d}{dx}\left(e^{-bx^2}\right) dx = \frac{\hbar^2 b}{2m}$$

$$\langle \phi^* \hat{V} \phi \rangle = \frac{1}{2} m w^2 |A|^2 \int_{-\infty}^{+\infty} e^{-bx^2} x^2 e^{-bx^2} dx = \frac{m w^2}{8b}$$

Denominator: $|A|^2 \int_{-\infty}^{+\infty} e^{-2bx^2} dx = 1$

$$\langle H \rangle = \frac{\hbar^2 b}{2m} + \frac{m w^2}{8b}$$

Minimization wrt b

$$\frac{d\langle H \rangle}{db} = \frac{\hbar^2}{2m} - \frac{m w^2}{8b^2} = 0$$

$$\Rightarrow b = \frac{m w}{2\hbar}$$

$$|A|^2 \int_{-\infty}^{+\infty} e^{-2bx} dx = |A|^2 \sqrt{\frac{\pi}{2b}}$$

$$A = \left(\frac{2b}{\pi}\right)^{1/4}$$

(VI) Putting $b = \frac{m\omega}{2\hbar}$ into $\langle H \rangle$

$$\langle H \rangle_{min} = \frac{\hbar^2}{2m} \cdot \frac{(m\omega)}{2\hbar} + \frac{m\omega^2}{8\left(\frac{m\omega}{2\hbar}\right)} = \frac{1}{2}\hbar\omega$$

Hence, the trial function ϕ is appropriate for the Harmonic Oscillator since what we obtain
$\langle H \rangle_{min} = E_{gs}$

Practice Question

Find the tightest band on the ground state Energy E_{gs} for the 1D harmonic oscillator using the trial wave function of ~~the~~ the form

$$\phi(x) = \frac{A}{x^2+b}$$

where A is determined by normalization and b is adjustable parameter.

20|01|2024

~~First Order Perturbation~~

~~Real life oscillator are not harmonic~~

$2\ \frac{b,x^2}{4}$

$\psi(x) = \varepsilon e^{-b/4\, x^2}$

Where ε ~~is~~ normalization constant

Find ε, Hint: $\int_0^\infty e^{-\alpha x^2} dx = \frac{1}{2}\left(\frac{\pi}{\alpha}\right)^{1/2}$

$$\int_{-\infty}^{\infty} \psi \cdot \psi^* = 1$$

$$\Rightarrow \int_{-\infty}^{\infty} \varepsilon e^{-b/4\, x^2} \cdot \varepsilon e^{-b/4\, x^2} = 1$$

$$\Rightarrow \int_{-\infty}^{\infty} \varepsilon^2 e^{-\frac{b}{2}x^2}$$

$$\Rightarrow \varepsilon^2 \int_{-\infty}^{\infty} e^{-\frac{b}{2}x^2} = 1$$

$$\text{from } \int_{-\infty}^{\infty} e^{-\frac{bx^2}{2}} = \int_{-\infty}^{0} e^{-\frac{bx^2}{2}} + \int_0^\infty e^{-\frac{bx^2}{2}}$$

for even functions

$$\int_{-\infty}^{0} e^{-ax^2} = \int_0^\infty e^{-ax^2}$$

$$\Rightarrow \int_{-\infty}^{\infty} e^{-\frac{bx^2}{2}} = 2\int_0^\infty e^{-\frac{bx^2}{2}}$$

$$\Rightarrow 2\,\xi^2 \int_0^\infty e^{-b/2\,x^2} = 1$$

from Hint

$$\int_0^\infty e^{-b/2\,x^2} = \frac{1}{2}\left(\frac{\pi}{b/2}\right)^{1/2}$$

$$\Rightarrow \cancel{2}\,\xi^2 \cdot \frac{1}{\cancel{2}}\left(\frac{2\pi}{b}\right)^{1/2} = 1$$

$$\xi^2 \left(\frac{2\pi}{b}\right)^{1/2} = 1$$

$$\xi^2 = \left(\frac{b}{2\pi}\right)^{1/2} \Rightarrow \xi = \left(\frac{b}{2\pi}\right)^{1/4}$$

(2) $\psi(x) = \xi x e^{-b/3\,x^2}$ Hint: $\int_0^\infty x^2 e^{-ax^2} = \frac{1}{4}\left(\frac{\pi}{a^3}\right)^{1/2}$

$$\int_{-\infty}^{\infty} \psi\psi^* \, dI = 1$$

$$\int_{-\infty}^{\infty} \xi x e^{-b/3\,x^2} \cdot \xi x e^{-b/3\,x^2} \, dI = 1$$

$$\int_{-\infty}^{\infty} \xi^2 x^2 e^{-\frac{2b}{3}x^2} \, dI = 1$$

$$\xi^2 \int_{-\infty}^{\infty} x^2 e^{-\frac{2b}{3}x^2} \, dI = 1$$

valid for even functions

From $\int_{-\infty}^{\infty} f(x) = \int_{-\infty}^{0} f(x) + \int_{0}^{\infty} f(x)$ $\Rightarrow$ $\left(\int_{-\infty}^{0} f(x) = \int_{0}^{\infty} f(x)\right)$

$\Rightarrow \int_{-\infty}^{\infty} f(x) = 2\int_{\text{[illegible]}}^{\infty} f(x)$

$\therefore \quad \varepsilon^2 2\int_0^{\infty} x^2 e^{-\frac{2bx^2}{3}}\, d I = 1$

From the hint; $\int_0^{\infty} x^2 e^{-\frac{2b}{3}x^2} = \frac{1}{4}\left(\frac{\pi}{\left(\frac{2b}{3}\right)^3}\right)^{1/2}$

$\therefore \quad \varepsilon^2 \cdot \cancel{2} \cdot \frac{1}{\cancel{4}_{2}} \left(\frac{\pi}{\frac{8b^3}{27}}\right)^{1/2} = 1$

$\varepsilon^2 \cdot \frac{1}{2}\left(\frac{27\pi}{8b^3}\right)^{1/2} = 1$

$\varepsilon^2 = \cancel{2\left(\frac{27\pi}{8b^3}\right)} \quad 2 \cdot \left(\frac{8b^3}{27\pi}\right)^{1/2}$

$\varepsilon^2 = 4^{1/2} \cdot \left(\frac{8b^3}{27\pi}\right)^{1/2}$

$\varepsilon = \left(\frac{32b^3}{27\pi}\right)^{1/4}$

3a $\psi(x) = Ae^{-a/2\, x^2}$ ~~and $\hat{H}\psi$~~

and $\hat{H} = \frac{-\hbar^2}{2m}\frac{d^2}{dx^2}$. Express $\hat{H}\psi$ in terms of a, x, ψ

$$H\psi = \frac{-\hbar^2}{2m}\frac{d^2}{dx^2}\psi$$

$$H\psi = \frac{\hbar}{2m}\frac{d^2}{dx^2} Ae^{-a/2\, x^2}$$

$$\frac{d}{dx} Ae^{-a/2\, x^2} = -\frac{\cancel{2a}}{\cancel{2}} x Ae^{-a/2\, x^2}$$

~~$\frac{d^2}{dx^2} Ae^{-a/2\, x^2} = 4x^2 Ae^{-a/2\, x^2}$~~

~~$H\psi = \frac{\hbar}{2m} 4x^2 Ae^{-a/2\, x^2}$~~

$$\frac{d}{dx} Ae^{-a/2\, x^2} = -axAe^{-a/2\, x^2}$$

$$\frac{d^2}{dx^2} Ae^{-a/2\, x^2} = -aAe^{-a/2\, x^2} \cancel{+} \frac{-2a}{\cancel{2}} Ae^{-a/2\, x^2} \cdot ax$$

$$= -aAe^{-a/2\, x^2} + a^2x^2 Ae^{-a/2\, x^2}$$

$$= Ae^{-a/2\, x^2}(a^2x - a)$$

$$= a^2x\psi - a\psi$$

$$H\psi = -\frac{\hbar^2}{2m}\left(a^2x\psi - a\psi\right)$$

$$H\psi = \frac{\hbar^2}{2m}a\psi(x) - \frac{\hbar^2}{2m}a^2x^2\psi(x)$$

(3b) Suppose the system has some potential function V(x) such that the total energy E = a

Find the expression for V(x), Evaluate V(0)

$$H\psi = E\psi \Rightarrow ~~H\psi + V(x) = a\psi~~$$

$$H = KE + V(x)$$

$$\hat{H} = \frac{-\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)$$

$$H\psi = E\psi$$

$$\Rightarrow \left(\frac{-\hbar}{2m}\frac{d^2}{dx^2} + V(x)\right)\psi = E\psi$$

$$= \frac{-\hbar^2}{2m}\frac{d^2}{dx^2}\psi + V(x)\psi = E\psi$$

$$\Rightarrow \frac{\hbar^2}{2m}a\psi(x) - \frac{\hbar^2}{2m}a^2x^2\psi(x) + V(x)\psi = a\psi$$

$$V(x)\psi = a\psi(x) - \frac{a\hbar^2}{2m}\psi(x) + \frac{a^2\hbar^2}{2m}x^2\psi$$

$$V(x)\psi = a - \frac{a\hbar^2}{2m} + \frac{a^2\hbar^2}{2m}x^2$$

$$V_{(0)} = a - \frac{a\hbar^2}{2m} \phi\ 0$$

$$V_{(0)} = a - \frac{a\hbar^2}{2m}$$

27/01/2025 — 1st Order Perturbation Theory

The first-order perturbation theory treats small perturbation to a system.

Let the wave eqn to the actual system be

$$H\psi - E\psi = 0 \quad \text{— ①}$$

Suppose the Hamiltonian $\hat{H}$ of the perturbed system in eq ① is only slightly different from the hamiltonian H^0 of the unperturbed system such that :

$$H^0\psi^0 - E^0\psi^0 = 0 \quad \text{— ②}$$

~~Define~~ the Schrödinger wave eqn for the unperturbed system.

Such that eq ② has known solution.

If the set of solutions to eq ② and corresponding energy state are : $\psi_0^0, \psi_1^0, \psi_2^0 \ldots \psi_k^0$ and the corresponding eigen energy ;

$E_0^0, E_1^0, E_2^0, \ldots, E_k^0$.

Since the perturbation is small, we can assume that hamiltonian of the real system (perturbed system) is :

$$H = H^0 + \alpha H' \quad \text{— ③}$$

extra term that defines the perturbation.

α.

α = measure of perturbation

H' = perturbation hamiltonian

A very common situation is that in which H' equals some additional or perturbing term in the P.E function H°

For example; if a SHO, is defined as $H^\circ = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}kx^2$. If the oscillator is not quite harmonic, the P.E fxn can be in form of $V(x) = \frac{1}{2}kx^2 + bx^4$. Which implies that H' as in eq ③ is simply

$H' = bx^4$ and the extent of perturbation will depend on the magnitude of b. Since the assumption is that the perturbation is small, which implies that the solution to eq (1) involves only a small correction to those of the unperturbed case

for the k^{th} state; $\psi_k = \psi_k^\circ + \alpha\psi_k'$;

$$E_k = E_k^\circ + \alpha E_k'$$

By substitution into eq ①, we've

$$(H_k^\circ + \alpha H_k')(\psi_k^\circ + \alpha\psi_k') - (E_k^\circ + \alpha E_k')(\psi_k^\circ + \alpha\psi_k'$$
$$= 0$$

Expanding the eqn;

$$\overset{\alpha^2 E_k'\psi_k'}{}$$

$$E_k^\circ\psi_k^\circ - \cancel{H_k^\circ\psi_k^\circ} + H_k^\circ\alpha\psi_k' + \alpha H_k'\psi_k^\circ + \cancel{\alpha^2 H_k'}\psi_k' - \cancel{E_k^\circ\psi_k^\circ} - E_k^\circ\alpha\psi_k'$$
$$E_k^\circ \; - \alpha E_k'\psi_k^\circ - \alpha^2 \cancel{E_k'\psi_k'} = 0$$

~~$E_k^0\psi_k^0 = H_k^0$~~.

$$H_k^0\alpha\psi_k' - E_k^0\alpha\psi_k' = E_k'\alpha\psi_k^0 - H_k'\alpha\psi_k^0$$

$$\cancel{\alpha}(H_k^0\psi_k' - E_k^0\psi_k') = \cancel{\alpha}(E_k' - H_k')\psi_k^0$$

$$(H_k^0 - E_k^0)\psi_k' = (E_k' - H_k')\psi_k^0 \quad — ④$$

Suppose the correction wavefxn / perturbation wavefxn ψ_k' can be expressed as some linear combination of the solution

$$\psi_k' = \sum_i a_i\psi_i^0$$

i.e $H^0\psi_k' = \sum a_i H^0\psi_i^0 = \sum a_i E_i\psi_i^0$

Substitution into eq ④

$$\sum_i a_i(E_i^0 - E_k^0)\psi_i^0 = (E_k' - H_k')\psi_k^0$$

Multiplication by complex conjugate of ψ_k^0 at both sides, i.e ψ_k^{0*}

$$\sum_i a_i(E_i^0 - E_k^0)\int\psi_k^{0*}\psi_i^0\,d\tau = \int\psi_k^{0*}(E_k' - H')\psi_k^0\,d\tau$$

— ⑤

The L.H.S of eq ⑤ equals zero since the wave ftn
are orthogonal, i.e

$$\int \psi_k^{o*} \psi_i^{o} \, d\tau = 0 \; ; \; k \neq i$$

The R.H.S can be separated into 2 integral & solve, for

$$\int \psi_k^{o*} E_k' \psi_k^{o} \, d\tau - \int \psi_k^{o*} H' \psi_k^{o} \, d\tau = 0$$

$$E_k' \int \psi_k^{o*} \psi_k^{o} \, d\tau = \int \psi_k^{o*} H' \psi_k^{o} \, d\tau$$

$$E_k' = \int \psi_k^{o*} H' \psi_k^{o} \, d\tau \quad — ⑥$$

Eq ⑥ gives E_k' and hence $\alpha E_k'$, the first order perturbation theory correction to the energy E_0 from the unperturbed. The constant, α, can be incorporated into E_k' and H' or it can be treated as equal to unity for the kth energy state. E' is obtained by averaging the perturbation ~~Cons~~ fxn H' over the unperturbed state of the system.

Thus, for example, for n=1 state of a harmonic oscillator for which $H' = bx^4$. Det. the Correction to the energy

Use: $$\int_0^\infty x^{2n} e^{-px^2} dx = \frac{1.3\,(2n-1)}{2^{n+1}} \left[\frac{\pi}{p^{2n+1}}\right]^{1/2}$$

for $p > 0$, $n = 1, 2, 3$

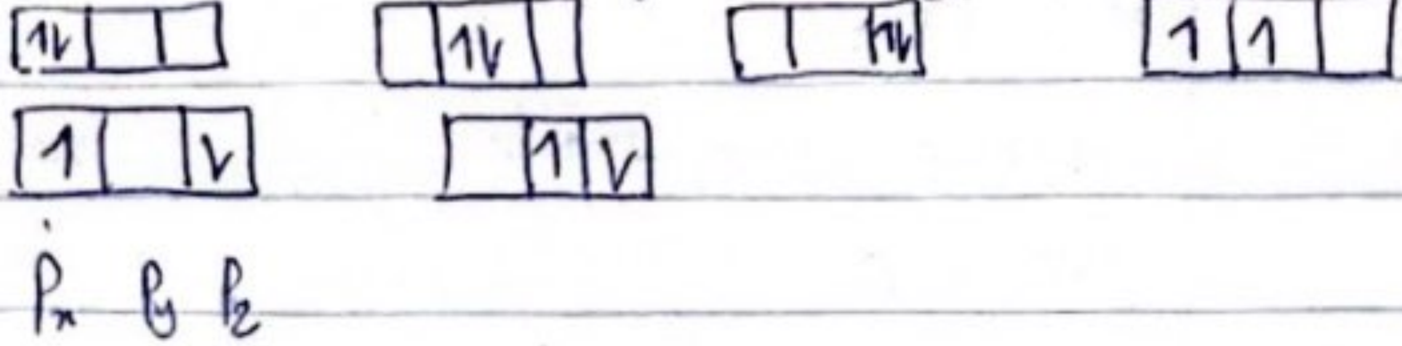
$^{16b}/_{4\alpha^2}$

Electronic States: Term Symbols

~~Electronic~~ Spectroscopic Term Symbols

A term symbol provides a more detailed description of an electron configuration. This is because basic electronic configuration lack information about the exact orbital being occupied by an electron as well as the overall spin of the electron. For example: a Carbon atom electron configuration $C: 1s^2 2s^2 2p^2$ might imply that the 2p electron are in orbital p_x, p_y or p_z or any two of the three, as long as it is consistent with the Pauli Exclusion principle.

However, the energies of each of the state corresponding to the orbital occupied may differ-



The term symbol is derived based on total orbital angular momentum, L, and total spin angular momentum S and also the vectorial addition of L & S ($\vec{L} + \vec{S}$) which gives the total angular momentum $\vec{J}$, resulting from Russell-Saunder Coupling and atomic term symbol is expressed in the form

$^{2S+1}L_J$ where $2S+1 \rightarrow$ multiplicity

$\vec{J} = \vec{L} + \vec{S}$

and L = 0, 1, 2 3 4 5 ...

Symbols = S P D F G H

The total orbital angular momentum, L, and the total spin angular momentum, S, are given by the vectorial sum

$$\hat{L} = \sum_i \vec{l_i} \quad \& \quad \hat{S} = \sum_i \vec{S_i}$$

Where the summation are over the electron in the atom or orbital.

① For example: The ground state of hydrogen atom has electronic config $1s^1$, $l = 0$; $m_s = \pm\frac{1}{2}$

$H: 1s^1$

$l = 0$, $m_s = \pm\frac{1}{2}$

$m_l = 0$

$L = 0 \quad S = \frac{1}{2}$

$J = L + S = 0 + \frac{1}{2} = \frac{1}{2}$

for $L = 0$, state symbol: S

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

$\therefore \; {}^{2}S_{1/2}$ (doublet, $S_{1/2}$ state

Two or more atoms can have the same term symbol. The term-symbol may also change when the electronic config changes for example; when there's an excitation of electron in an atom.

② Consider the electronic config, ns^2,

$l = 0$, $m_l = 0$

m_{l_1}	m_{s_1}	m_{l_2}	m_{s_2}	M_L	M_S
0	$\frac{1}{2}$	0	$-\frac{1}{2}$	0	0

Therefore, $M_L = 0$, $L = 0 \Rightarrow$ S state

$M_S = 0 \Rightarrow S = 0 \Rightarrow 2S + 1 = 1 \Rightarrow$ singlet

$J = L + S = 0 + 0 = 0$

∴ The term symbol is $^1S_0$

③ Let's consider for Na atom; $1s^2 2s^2 2p^6 \underline{3s^1}$

for the $3s^1$ electron;

$m_s = \pm \frac{1}{2}$; $m_l = 0 \Rightarrow L = 0$ S_{state}

$S = \cancel{2(\frac{1}{2})+1}\ \frac{1}{2}$; multiplicity $= 2(\frac{1}{2}) + 1 = 2$ (doublet)

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

∴ The term symbol is $^2S_{1/2}$

④ Consider np^6

The 6-electron in np^6 would've d fllg set of quantum

(n, l, m_l, m_s) $\{p_x, p_y, p_z\}$

$(n, 1, 1, \pm\frac{1}{2})$ $(n, 1, 0, \pm\frac{1}{2})$ $(n, 1, -1, \pm\frac{1}{2})$

2 electron 2 electron 2 electron

p_x p_y p_z

$M_L = \sum m_{l_i} = (1+1) + (0+0) + (-1-1) = 0, L = 0$

$M_S = \sum_i m_{s_i} = (+\frac{1}{2} - \frac{1}{2}) + (+\frac{1}{2} - \frac{1}{2}) + (+\frac{1}{2} - \frac{1}{2})$ $\overset{\Uparrow}{S}_{\text{state}}$

$= 0$

$S = 0$, $2S + 1 = 1 \Rightarrow$ Singlet

∴ $J = L + S = 0 + 0 = 0$

∴ The term symbol is $^1S_0$

⑤ Consider nd^{10}

This implies that M_L & M_S will be equal to 0, for completely filled sub-shell because, for every electron with a -ve value of m_{l_i}, there's another electron with a corresponding +ve value, same goes for m_{s_i}

Na: $1s^2 2s^2 2p^6 3s^1$
Na* (1st excited state) $1s^2 2s^2 2p^6 3s^0 3p^1$
$L = l$, $m_l = -1, 0, 1$, $m_s = \pm \frac{1}{2}$
$L = 1 \Rightarrow P_{\text{state}}$
$S = \frac{1}{2}$, multiplicity $= 2S+1 = 2$
$J = 1 + \frac{1}{2} = \frac{3}{2}$
$\therefore {}^2P_{3/2}$

Selection Rules

This states that $\Delta S = 0$, $\Delta L = 0, \pm 1$ & $\Delta J =$

& transition for $m_J = 0 \leftrightarrow m_J = 0$ is forbid

$^2S \to {}^1S$ (is forbidden)

$^1S \to {}^1S$ (is allowed)

$^2P \leftrightarrow {}^2S$ (is allowed)