GENERAL PHYSICAL CHEMISTRY

CH1213

Quizzes : 30% Midsem : 30% Endsem : 40%

4 Quizzes - 25th Jan, 4th Feb, 21st march, 11th April

Textbooks - Atkins ; McQuarry & Simon

* Planck's constant was obtained by fitting. If Bohr or Einstein had done it for their theory, it would be named after them

	<u>Classical</u>	<u>Quantum</u>
1. State of the system	$x(t)$, $p(t)$	$\psi(\vec{r}, t)$
2. Observables	Function of state variables	Postulates 2, 3, 4
3. Dynamical equation	Newton's equation	Postulate 5

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Electrons govern Chemistry – all aspects of it.

Electrons are particles – it doesn't have size i.e. its a point particle

Postulates are statements that we observe to be true.
i.e. what axiom is to maths

There are 5 basic postulates which explain all ours observations.

Theoretical Chemistry is divided into two domains based on whether it explores the –

microscopic world : Quantum mechanics
Macroscopic world : Thermodynamics
Statistical mechanics

Rutherford's experiment proved that most of the space in an atom is empty. The mass is concentrated at the centre of the atom. So how is the atom stable?

Several expts in 20th century – Black body radiation, photoelectric effect, heat capacity, discrete atomic spectrum – couldnot be explained with classical physics.

This gave rise to Quantum Mechanics which governs the behaviour of electrons

* → Postulate 1

The state of a quantum system is given by a function of position and time
i.e. $\psi(\bar{r}, t)$

It is similar to the waves in classical mechanics where a wave also depends on position and time.

So this is called the Wave function.

The state of a quantum system is defined by ~~an~~ unique wave function i.e. $\psi = \phi e^{-i\theta}$

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In general, this wave function is a complex valued function (i.e. it takes a complex ~~value~~ number as a value) ×

Complex number : $z = a + ib$ where $a, b \in \mathbb{R}$ and $i = \sqrt{-1}$

$z = r(\cos\theta + i\sin\theta)$ & $\cos\theta + i\sin\theta = e^{i\theta}$

$|z|^2 = z.z^* = (a+ib)(a-ib) = a^2 + b^2$

z^* is called the complex conjugate and $z^* = e^{-i\theta}$

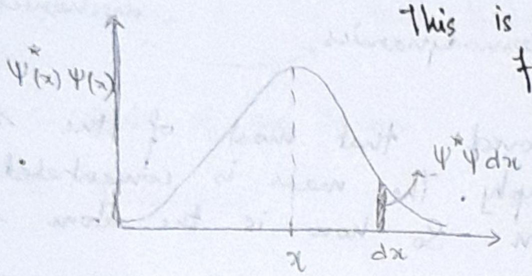
$\rho(x,t) = \psi^*\psi$ $\Rightarrow$ $\rho(x,t)\cdot dx$ – Probability of finding the parti-
Probability density at position x in interval dx

When we multiply $\psi(\bar{r},t)\,\psi^*(\bar{r},t)$ with a volume element, $dx\,dy\,dz$, then –

$\psi(\bar{r},t)\,\psi^*(\bar{r},t)\cdot dx\,dy\,dz$ → gives us the probability of finding the particle in the volume element $dx\,dy\,dz$ at $\bar{r}$.

As '$dx\,dy\,dz$' has dimensions of volume, that means $\psi\psi^*$ has the dimensions of probability density.

Eg: $\psi(x) = e^{-(x-x_0)^2}$ $\Rightarrow$ $\psi^*\psi = e^{-2(x-x_0)^2}$



This is an example for wave function in one dimension (?)

Here, the measurements are done on a snapshot of the system, so time component is not involved here.

Ensemble of systems : Multiple identical replicas of a system

In principle, a particle can be found in any place in any one of the systems

⇒ There is uncertainity which means that its not reproduible

But after <u>many</u> tials, we can find that we get a distibution over a curve of some shape.

Thus, Quantum mech is a statistical theory – fore one measurement is a probability.

But just knowing the probability density is not enough i.e just the distibution of positions ; we need to know the wave function to be able to say things about the system.

The wave function itself has no physical meaning but when we manipulate it, we get to know things about the system.

Σ Probability $= 1$

If it's finite, we can reduce it to 1 by normalisation.

$$\rightarrow \int_{-\infty}^{\infty} \psi^*(x,t)\,\psi(x,t)\cdot dx = 1$$ or it should be finite.

The wave function needs to be a <u>square integrable</u> function i.e. its integral over $-\infty$ to $+\infty$ should be finite.

<u>property</u>

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Another property of function is that $\psi(r, t)$ and $\frac{d\psi(r,t)}{dr}$ has to be continuous and finite. (bounded)
Its enough that ψ^* is continuous.

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TUTORIAL 01

1) Find real & imaginary parts

i) $(2-i)^3 = \cancel{(2-i)(2-i)^2} \cancel{(2-i)(4+1)} =$

$\Rightarrow 8 - i^3 - 3(2)(i)(2-i) = 8 + i - 6i(2-i) = 8 + i - 12i + 6i^2$

$\Rightarrow 2 - 11i$ Re : 2 Im : −11

ii) $e^{\pi i/2}$ $e^{i\theta} = \cos\theta + i\sin\theta$

$\Rightarrow \cos(\pi/2) + i\sin(\pi/2) = i$

2.) $z = 2 - 3i \Rightarrow z^* = 2 + 3i$ $z^2 = 4 + (3i)^2 - 2(2)(3i)$
$= 4 + 9(-1) - 12i = -5 - 12i$

$Re(z^*) = 2$

$Im(z^*) = 3$ $zz^* = (2-3i)(2+3i)$
$= (2)^2 - (3i)^2 = 4 - 9(-1) = 13$

$Re(z^2) = -5$

$Im(z^2) = -12$

$Re(zz^*) = 13$

$Im(zz^*) = 0$

3) Express as $re^{i\theta}$

a) $6i$ Here $a = 0$ $b = 6$ $\Rightarrow r = \sqrt{a^2 + b^2} = 6$

$\tan\theta = \frac{b}{a} \Rightarrow \theta = \tan^{-1}(\infty) = \pi/2$

$z = r[\cos\theta + i\sin\theta] = re^{i\theta}$

$z = 6e^{i\pi/2}$

b) $4 - \sqrt{2}i$ $a = 4$ $b = -\sqrt{2}$ $r = \sqrt{16+2} = 3\sqrt{2}$

$\theta = \tan^{-1}\left(\frac{\sqrt{2}}{2\times 2}\right) = \tan^{-1}\left(\frac{1}{2\sqrt{2}}\right)$

$z = re^{i\theta}$

4) express as $x + yi$

a) $e^{\pi/4i} = e^{-\frac{\pi}{4}i} \Rightarrow r = 1$ i.e. $x^2 + y^2 = 1$ $\Rightarrow x = y\frac{1}{\sqrt{2}}$

$\tan\left(-\frac{\pi}{4}\right) = -\tan\left(\frac{\pi}{4}\right) = -1 = \frac{y}{x} \Rightarrow -x = y$ $\because x^2 = y^2$

$\Rightarrow z = \frac{1}{\sqrt{2}} - \frac{1}{\sqrt{2}}i$

b) $6e^{\frac{2\pi}{3}i}$ $\Rightarrow$ $r = 6$ $\Rightarrow$ $x^2 + y^2 = 36$

$\tan\theta\left(\frac{2\pi}{3}\right) = \frac{y}{x} = -\sqrt{3}$ $\Rightarrow$ $x(-\sqrt{3}) = y$ $\Rightarrow$ $3x^2 = y^2$

$\Rightarrow$ $4x^2 = 36$ $\Rightarrow$ $x = \pm 3$

$z = 3 - \sqrt{3}\,i$

6) For a function to be acceptable as wave function $\Psi(r,t)$ and $\frac{d\Psi(r,t)}{dr}$ should be finite and continuous. It should also be square integrable.

Square integrable : the product of the function and its conjugate should be finite and non-zero.

But here, there is no imaginary part, so we just square it and integrate.

i) e^{-x} $(0, \infty)$

$$\int_0^\infty e^{-2x} = -\frac{e^{-2x}}{2}\Big|_0^\infty = \frac{1}{2}$$

$\Rightarrow$ e^{-x} is square integrable & it is continuous and differentiable in $(0, \infty)$

So, its acceptable as wave function

ii) e^{-x} $(-\infty, \infty)$

$$\int_{-\infty}^\infty e^{-2x} = \frac{e^{-2x}}{2}\Big|_{-\infty}^\infty = -\frac{1}{2}\left(e^{-\infty} - e^{\infty}\right)$$: Doesnot exist

So its not square integrable

Hence, its not acceptable as wave function.

iii) $\sin^{-}(x)$ in $(-1, 1)$

If $x = 0$ $\sin^{-}(x)$ can be $0, \pi, 2\pi \ldots n\pi$

As its not a single valued function, its not acceptable as wave function.

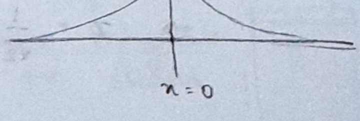
If we only consider it for principal values i.e from $-\pi/2$ to $\pi/2$, then its acceptable.

iv) $e^{-|x|}$ $(-\infty, \infty)$

At $x = 0$, $e^{-|x|}$ is not differentiable

i.e there are two slopes at $x = 0$

So its not acceptable



7) $\psi = ce^{-5x}$ from $(0,\infty)$

$\int \psi\psi^* = 1$ i.e. the total probability is 1

$\int_0^\infty ce^{-5x}\, ce^{-5x} .\, dx = 1 \Rightarrow c^2 \int_0^\infty e^{-10x} .\, dx = 1$

$\frac{c^2}{10} \int_0^\infty e^{-t} dt = 1 \Rightarrow c^2 = 10$

$\therefore c = \sqrt{10}$

This is the normalisation constant c.

5) Show that $|e^{i\theta}| = 1$

$e^{i\theta} = \cos\theta + i\sin\theta$

$|e^{i\theta}| = \sqrt{\cos^2\theta + \sin^2\theta} = \sqrt{1} = 1$

8) What is the probability that the particle in Q.7 will be found at x values greater than 1?

To find this, you integrate the square integrable form from 1 to ∞

$\Rightarrow \int_1^\infty 10e^{-10x} .\, dx = \frac{10}{10} \int_1^\infty e^{-t \cdot 10} .\, dt$

$\Rightarrow e^{-t}\Big|_1^\infty = e^{-\infty} - e^{-10} = e^{-10}$

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Postulates 2, 3 and 4 deal with observables or measurable properties. In Classical Mech, • observables are dynamic (time dependant) variable, • any value of an observable can be obtained without any restrictions, • for a given system, at a particular time, only a particular value of the observable is obtained.

→ Postulate 2

Corresponding to every measurable quantity in Classical mechanics, there is an operator# in Quantum mechanics.

An operator is something that acts on a function to give a new function: $\hat{O} f(x) = g(x)$

\# Linear & Hermitian

$$\hbar = \frac{h}{2\pi}$$

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- Position operator : $\hat{x}$ — Multiply by x i.e. $\hat{x} f(x) = x . f(x)$
- Momentum operator: $\hat{p}$ — $-i\hbar \frac{\partial}{\partial x}$ i.e. $\hat{p}\,\Psi(x,t) = -i\hbar \frac{\partial \Psi(x,t)}{\partial x}$
- Kinetic energy operator: $\hat{K}_x = \frac{\hat{P}^2}{2m} = \frac{\hat{P}\hat{P}}{2m} = +\frac{(-1)\hbar^2}{2m}\frac{\partial^2}{\partial x^2} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}$

$$\hat{K}_x \Psi(x,t) = -\frac{\hbar^2}{2m}\frac{\partial^2 \Psi(x,t)}{\partial x^2}$$

- Potential energy operator: $\hat{V}_x$ — Multiply by $V_x(x)$ i.e.

$$\hat{V}_x f(x) = V_x(x) . f(x) \quad \text{where } V_x(x) = \frac{1}{2}kx^2$$

- Total energy operator (Hamiltonian) : $\hat{H} = \hat{K}_x + \hat{V}_x = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V_x$

Later, the time evolution (dynamics) of the system will be dependant on the Hamiltonian.

- Angular momentum operator: $\vec{l} = \vec{r} \times \vec{p} = \begin{vmatrix} \hat{i} & \hat{j} & \hat{k} \\ x & y & z \\ P_x & P_y & P_z \end{vmatrix}$

$$\hat{l} = \begin{vmatrix} \hat{i} & \hat{j} & \hat{k} \\ \hat{x} & \hat{y} & \hat{z} \\ \hat{P_x} & \hat{P_y} & \hat{P_z} \end{vmatrix}$$

#If $v(x,p) = \vec{r}.\vec{p} = \vec{p}.\vec{r}$ is the quantity in classical mech

$$\hat{v} = \frac{1}{2}\left(\hat{r}.\hat{p} + \hat{p}.\hat{r}\right)$$

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Spin : It's a measurable quantity that doesn't have a classical equivalent — but its very important in quantum. This operator must be built up because its not dependant on position or momentum.

In 3 dimensions, the operators remain same inherently —

	Classical	Quantum
Position:	$\vec{r} = x\hat{i} + y\hat{j} + z\hat{k}$	Multiply by $\vec{r}$ i.e. $x\hat{i} + y\hat{j} + z\hat{k}$ — vectorized function
Momentum:	$\vec{p} = P_x\hat{i} + P_y\hat{j} + P_z\hat{k}$	$\hat{p} \Rightarrow -i\hbar\frac{\partial}{\partial x}\hat{i} - i\hbar\frac{\partial}{\partial y}\hat{j} - i\hbar\frac{\partial}{\partial z}\hat{k}$

#For 2 particles, more than 1 variable comes in — $x_1, x_2;\ y_1, y_2$ & z_1, z_2

→ Postulate 3

The only values one can obtain when one measures the property corresponding to the operator $\hat{A}$ are the eigenvalues of $\hat{A}$.

Generally, $\hat{A}f \rightarrow g$

But there are some functions called (eigenfunctions of operator $\hat{A}$, that satisfies this equation –

$$\hat{A}f = cf \qquad \text{i.e} \qquad \hat{A}f_i = a_i f_i$$

Here, the eqⁿ is called eigen-value eqⁿ and 'c' is called eigenvalue.

Some examples are –

$$e^{\lambda x} \qquad \frac{d}{dx} e^{\lambda x} = \lambda e^{\lambda x}$$

$$\sin(\lambda x) \qquad \frac{d^2}{dx^2} \sin(\lambda x) = (-\lambda^2) \sin(\lambda x)$$

If $f(x)$ is an eigenfunction, then, $c \cdot f(x)$ is also an eigenfunction.

Addition to Postulate 2 – For every observable in CM, ∃ a linear Hermitian operator in QM

Linear operator: $\hat{A}(f+g) = \hat{A}f + \hat{A}g$

$$\hat{A}(cf) = c\hat{A}f$$

Hermitian matrix: A symmetric matrix with complex numbers is called a hermitial matrix.

$$\begin{bmatrix} a_{11} & a_{12} & a_{13} & a_{14} \\ a_{12}^* & a_{22} & a_{23} & a_{24} \\ a_{13}^* & a_{23}^* & a_{33} & a_{34} \\ a_{14}^* & a_{24}^* & a_{34}^* & a_{44} \end{bmatrix}$$

Hermitian operator: $\int f^* \hat{A} g \, dt = \left[\int g^* \hat{A} f \, dt \right]^*$

A Hermitian operator has eigenvalues are all real (not imaginary), and all its eigenfunctions are orthonormal.

Eigenvalues are real – i.e. what we measure in the end is a real value and not an imaginary number.

⇒ importance – we can define ~~the~~ a functⁿ by basis functions

$\hat{O}f = \hat{O}(\Sigma c_i b_i(x))$. So if we know how $\hat{O}$ acts on basis functions we can get it to solve any function because its linear.

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Problem Set 02

1. For an operator to be linear —

$$\hat{A}(f+g) = \hat{A}f + \hat{A}g \quad \& \quad \hat{A}(cf) = c\hat{A}f.$$

a) $\hat{A}f = x^2 f$ — LINEAR

$$\Rightarrow \hat{A}(f+g) = x^2(f+g) = x^2 f + x^2 g = \hat{A}f + \hat{A}g$$

$$\hat{A}(cf) = x^2(c.f) = c\,x^2 f = c.\hat{A}f$$

b) $\hat{A}f = f^2$ — Not linear

$$\hat{A}(f+g) = (f+g)^2 \neq f^2 + g^2 = \hat{A}f + \hat{A}g$$

c) $\hat{A}f = f^*$ — Not linear

$$\hat{A}(f+g) = (f+g)^* \qquad \hat{A}f + \hat{A}g = f^* + g^* \neq (f+g)^*$$

d) $\hat{A}f = 0$ — Linear

$$\hat{A}(f+g) = 0 = \hat{A}f + \hat{A}g \; ; \quad \hat{A}(cf) = c\hat{A}f = 0.$$

2. Find any 3 eigenfunctions & corresponding eigenvalues

a) $\hat{A} = \frac{\partial}{dx}$: * $e^{\lambda x}$: $\frac{d}{dx}(e^{\lambda x}) = \lambda . e^{\lambda x}$ where $\lambda \in \mathbb{Q}$.

$\lambda \rightarrow$ eigenfunction.

* $\hat{A}f(x) = k\,f(x) \Rightarrow \frac{d}{dx}(f(x)) = k(f(x)) \Rightarrow \int \frac{d(f(x))}{f(x)} = \int k\,dx$

$$\Rightarrow \ln f = kx + c \quad \Rightarrow \quad f = e^{kx+c}$$

$$\therefore f = Pe^{kx} \qquad P = e^c$$

There are ∞ functions of this form, for which eigenvalues would be — $= Pk$

b) $\hat{A}f(x) = 3.f(x)$ ① $f(x) = x \Rightarrow \hat{A}f(x) = 3x = 3f(x)$

$\Rightarrow$ Eigenvalue is 3

② $f(x) = x^2 + x \Rightarrow \hat{A}f = 3(x^2+x) \Rightarrow$ Eigenvalue is 3.

③ $f(x) = \sin x \Rightarrow \hat{A}f = 3\sin x \Rightarrow$ ———— " ————

3) Show that $x^2 e^{6y}$ is an eigenfunction of operator $\frac{\partial}{\partial y}$. Find e-value

$\frac{d}{dx}(e^{kx}) = ke^{kx}$

$$\hat{A}f(y) = \frac{\partial}{\partial y} f(y) \; ; \Rightarrow \hat{A}(x^2 e^{6y}) = \frac{\partial}{\partial y}(x^2 e^{6y}) = x^2 . 6 . e^{6y}$$

$$\Rightarrow \hat{A}f = 6f \quad \Rightarrow \text{Eigenvalue is } 6$$

4) Show that e^{ikx} is an eigenvalue of linear momentum operator for a particle restricted to move in 1-D in x-axis

$f(x) = e^{ikx}$ $\quad\quad \hat{p}f = -i\hbar \frac{\partial}{\partial x} f$

$\hat{p}f = -i\hbar \frac{\partial}{\partial x}(e^{ikx}) = -i\hbar(ik)\, e^{ikx} = \hbar k\,(e^{ikx})$

Eigenvalue : $\hbar k$

5) $\hat{A} = \frac{\partial^2}{\partial x^2}$. Show that $\phi_m(x) = e^{imx}$ & $\phi_{-m}(x) = e^{-imx}$ are e-functions with same e-value. Show that linear combination of ϕ_m & ϕ_{-m} is also an e-funct^n

$\hat{A}\phi_m = \frac{\partial^2}{\partial x^2}(e^{imx}) = (im)^2 (e^{imx}) = -m^2 \phi_m$ $\quad$ Both have same eigenvalue

$\hat{A}\phi_{-m} = \frac{\partial^2}{\partial x^2}(e^{-imx}) = (-im)(-im)(e^{-imx}) = -m^2 \phi_{-m}$

$\phi = a\phi_m + b\phi_{-m} \Rightarrow \hat{A}\phi = a\frac{\delta^2}{\delta x^2}(e^{imx}) + b\frac{\delta^2}{\delta x^2}(e^{-imx})$

$\hat{A}\phi = a(-m^2)\phi_m + b(-m^2)\phi_{-m} = (-m^2)\phi$

So, ϕ is an eigenfunction.

6) Show that 1D QM positiond and linear momentum operators don't commute. Determine $\hat{x}\hat{p}_x - \hat{p}_x\hat{x}$

$\hat{x}f = xf$ $\quad\quad \hat{p}_x f = -i\hbar\frac{\partial}{\partial x}(f)$

$\hat{x}\hat{p}_x f = \hat{x}(\hat{p}_x f) = \hat{x}\left(-i\hbar\frac{\partial}{\partial x}[f]\right) = -i\hbar x\frac{\partial}{\partial x}[f]$

$\hat{p}_x\hat{x}f = \hat{p}_x(\hat{x}f) = \hat{p}_x(f.x) = -i\hbar\frac{\partial}{\partial x}(f.x)$ $\quad\quad \frac{\partial}{\partial x}(f(x)\cdot x) = \frac{\partial}{\partial x}(f) + f(x)$

$= -i\hbar\left[x.\frac{\partial}{\partial x}(f) + f.1\right]$

$\hat{p}_x\hat{x} \neq \hat{x}\hat{p}_x$ i.e. they don't commute.

$\hat{x}\hat{p}_x - \hat{p}_x\hat{x} = +i\hbar\, f(x)$

7) Write expression for y-component of angular momentum in terms of position & linear momentum. Write the expression of corresponding Q.M operator.

$$\vec{L} = \vec{r}\times\vec{p} = \begin{vmatrix} i & j & k \\ x & y & z \\ p_x & p_y & p_z \end{vmatrix} = \hat{i}(yp_z - zp_y) - \hat{j}(xp_z - zp_x) + \hat{k}(xp_y - yp_x)$$

$\Rightarrow (zp_x - xp_z)$: y-component of angular momentum

To normalise : $\langle A \rangle = \dfrac{\int \psi^* \hat{A} \psi \, dx}{\int \psi^* \psi \, dx} = \dfrac{\langle \psi | \hat{A} | \psi \rangle}{\langle \psi | \psi \rangle}$ — : probability is 1

$$\hat{L} = \hat{r} \times \hat{p} = \begin{vmatrix} \hat{i} & \hat{j} & \hat{k} \\ \hat{x} & \hat{y} & \hat{z} \\ \hat{p}_x & \hat{p}_y & \hat{p}_z \end{vmatrix}$$

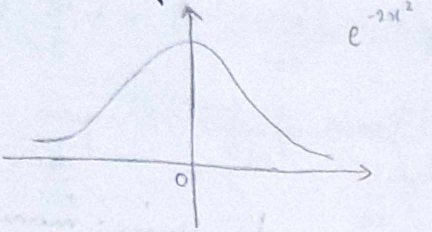
8) Write the $\hat{H}$ for free particle moving along x-direction

$\hat{H} = \hat{V}_x + \hat{K}$ Here, $\hat{V}_x = 0$ ∵ free particle

$\hat{K} = -\dfrac{\hbar^2}{2m} \dfrac{\partial^2}{\partial x^2} (f(x))$ where $f(x)$ is the function giving the eq^n of motion of particle

$\Rightarrow \hat{H} = \hat{K} = -\dfrac{\hbar^2}{2m} \dfrac{\partial^2}{\partial x^2} (f(x))$

9) Plot the function e^{-2x^2}, the Gaussian function.



$f(x) = a e^{-\frac{(x-b)^2}{2c^2}}$

a : height of peak

b : position of center of the peak

c : "width of the bell"

From Postulate 3 2

Hermitian operator ⇒ eigenvalues are all –

- real : $\hat{A} f_i = a_i f_i$ where $a_i \in \mathbb{R}$

eigenfunct^n are → orthonormal (?) : $\int_{\text{all space}} f_i^*(x) \, f_j(x) \, dx = \delta_{ij} = \begin{cases} 1 & \text{if } i = j \\ 0 & \text{if } i \neq j \end{cases}$

or orthonormalised

→ Postulate 4

This talks about the probability of obtaining an eigenvalue a_i i.e. $P(a_i)$

The average value of a property A is given by the following integral i.e. if a system is described by the NORMALISED wave function $\Psi(x,t)$, the avg value of A is given by –

$$\langle A \rangle = \int_{-\infty}^{\infty} \Psi^*(x,t) \, \hat{A} \Psi(x,t) \, dx$$

$\langle \Psi | \hat{A} | \Psi \rangle$: DIRAC NOTATION

Also known as expectation value (not accurate).

All eigenfunctions are wave functions i.e. subset of that

If $\psi(x,t) = f_i(x,t)$ where $\hat{A}\, f_i(x,t) = a_i\, f_i(x,t)$, then —

$$\langle A \rangle = \int_{-\infty}^{\infty} \psi^*(x,t)\, \hat{A}\, \psi(x,t) \cdot dx = \int_{-\infty}^{\infty} f_i^*(x,t) \cdot a_i \cdot f_i(x,t)\, dx$$

$\langle A \rangle = a_i\,(1)$ [Because the operator is orthonormal]

$\langle A \rangle = a_i$

→ Postulate 5

A quantum system evolves with time according to the Schrödinger's Equation

$$i\hbar \frac{\partial \psi}{\partial t} = \hat{H}\psi$$

~ to radioactivity equation

And we know that, $\hat{H} = \hat{K} + \hat{V}$

The KE operator is similar for all systems, but its the PE operator that tells us about the system and its the most important aspect

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Special Case of Conservative System [$\hat{H}$ is beig conserved]

$\hat{H}$ is time independant $\Rightarrow$ $\hat{V}$ is time independant

$\hat{K}$ is always time independant.

Lets try a solution of the form —

$$\psi(x,t) = \phi(x) \cdot \chi(t)$$

$$i\hbar \frac{\partial\,(\phi(x) \cdot \chi(t))}{\partial t} = \hat{H}\,[\phi(x) \cdot \chi(t)]$$

$$\cancel{i\hbar\, \chi(t) \cdot \frac{\partial}{\partial t}[\phi(x)] \neq \chi(t)\,[\phi(x)]}$$

$\because \hat{H}$ is time independant

$$i\hbar\, \phi(x) \cdot \frac{\partial}{\partial t}[\chi(t)] = \chi(t) \cdot \hat{H}\,[\phi(x)]$$

LHS is $f(t)$ and RHS is $g(x)$; and this says that $f(t) = g(x)$ for all values of x, t. This is only possible if $f(t) = g(x) = E$

$$E = i\hbar \frac{1}{\chi(t)} \frac{\partial}{\partial t}[\chi(t)] = \frac{1}{\phi(x)} \cdot \hat{H}\,[\phi(x)]$$

$$\Rightarrow \frac{\partial}{\partial t}[\chi(t)] = \frac{-iE}{\hbar} \cdot \chi(t) \Rightarrow \chi(t) = e^{-\frac{iEt}{\hbar}}$$

$\hat{H}\,\phi(x) = E \cdot \phi(x) \Rightarrow$ eigenfunction of $\hat{H}$

As the Hamiltonian doesn't depend on time —

$$i\hbar \frac{\partial \psi}{\partial t} = \hat{H}\psi \longrightarrow \boxed{\hat{H}\phi(x) = E.\phi(x)}$$ Time independant Schrodinger's equat

Also, the solution for such a function —

$$\psi(x,t) = \phi(x)\underbrace{e^{\frac{-iEt}{\hbar}}}_{\text{Phase factor}} \quad \text{where} \quad \hat{H}\phi_i(x) = E_i\phi_i(x). \quad i = 1,2,3\ldots$$

Phase factor — at given time t, this is consta

$$\Rightarrow \psi(x,t) = c_1\phi_1(x).e^{\frac{-iE_1t}{\hbar}} + c_2\phi_2(x).e^{-\frac{iE_2t}{\hbar}} + \cdots$$

$$f(x, t-t') = \sum_k c_k \phi_k(x) e^{\frac{-iE_k(t-t')}{\hbar}}$$

Let $\psi(x,t) = \phi_1 e^{\frac{-iE_1t}{\hbar}}$ → Stationary State

Probability density $\rho(x,t) = \phi_1 \cdot \phi_1^*$ — time independant

$$\psi(x,t) = c_1\phi_1 e^{\frac{-iE_1t}{\hbar}} + c_2\phi_2 e^{-iE_2t/\hbar}$$

$\rho(x,t)$ of this function is not time independant

Tutorial 03

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1) Time independant Hamiltonian. Suppose ϕ_i, $i = 1, 2\ldots$ are ~~eigenvalues~~ of eigenfunctions of $\hat{H}$

$$\hat{H}\phi_i(x) = E_i\phi_i(x)$$

Show that:

a) $\psi(x,t) = \phi_1(x) e^{\frac{-iE_1t}{\hbar}}$ is a solution.

$i\hbar \frac{\partial \psi}{\partial t} = \hat{H}\psi$: We've to show this

$$\Rightarrow \text{LHS}: \; i\hbar \frac{\partial}{\partial t}\left(\phi_1(x) e^{-iE_1t/\hbar}\right) = i\cancel{\hbar}.\phi_1(x)\left(\frac{-iE_1}{\cancel{\hbar}}\right).e^{-iE_1t/\hbar}$$

$$= E_1.\psi(x,t)$$

$$\text{RHS}: \; \hat{H}\phi_1(x)e^{-iE_1t/\hbar} = e^{-iE_1t/\hbar}\hat{H}\phi_1 x = e^{-iE_1t/\hbar} E_1\phi_1(x)$$

$$= E_1\psi(x,t)$$

RHS = LHS

b) $\psi(x,t) = c_1\phi_1(x)e^{-iE_1t/\hbar} + c_2\phi_2(x)e^{-iE_2t/\hbar}$

Again, we show $i\hbar \frac{\partial \psi}{\partial t} = \hat{H}\psi$

$$\text{LHS} = i\hbar\frac{\partial \psi}{\partial t} = i\hbar\left[c_1\phi_1(x).\frac{-iE_1}{\hbar}e^{-iE_1t/\hbar} + c_2\phi_2(x)\frac{-iE_2}{\hbar}e^{-iE_2t/\hbar}\right]$$

$$\text{LHS} = c_1\phi_1(x).E_1 e^{-iE_1t/\hbar} + c_2\phi_2(x).E_2 e^{-iE_2t/\hbar}$$

$(z_1 + z_2)^* = z_1^* + z_2^*$

$(z_1 z_2)^* = z_1^* z_2^*$

RHS $= \hat{H}\psi(x,t) = c_1 e^{-iE_1t/\hbar} E_1 \phi_1(x) + c_2 e^{-iE_2t/\hbar} E_2 \phi_2(x)$

∴ LHS = RHS

If 2 equations are solutions, then their linear combination is also a solution.

2) Consider a system with time independant Hamiltonian. If $\phi_i = 1, 2, \ldots$ are eigenfunctions of $\hat{H}$, ie.

$$\hat{H}\phi_i(x) = E_i \phi_i(x)$$

Show that prob. density corresponds to

a) $\psi(x,t) = \phi_1(x) e^{-iE_1t/\hbar}$ is time independant :

$\rho = \psi^* \psi = \left(\phi_1^*(x) e^{iE_1t/\hbar}\right)\left(\phi_1(x) e^{-iE_1t/\hbar}\right)$

$\rho = \phi_1^*(x) \cdot \phi_1(x)$ — time independant.

b) $\psi(x,t) = c_1 \phi_1(x) e^{-iE_1t/\hbar} + c_2 \phi_2(x) e^{-iE_2t/\hbar}$ is time dependent

$\rho = \psi^* \psi = \left(c_1 \phi_1^*(x) e^{iE_1t/\hbar} + c_2 \phi_2^*(x) e^{iE_2t/\hbar}\right)\left(c_1 \phi_1(x) e^{-iE_1t/\hbar} + c_2 \phi_2(x) e^{-iE_2t/\hbar}\right)$

$\rho = \phi_1^* \phi_1 c_1^2 + c_2^2 \phi_2^* \phi_2 + c_1 c_2 \left(\phi_1^* \phi_2 e^{\frac{it}{\hbar}(E_1 - E_2)} + \phi_2^* \phi_1 e^{\frac{it}{\hbar}(E_2 - E_1)}\right)$

Single time independant wave functions — always stationary state

linear combination of equations and time independant — then 2 types — 1) Degenerate state i.e $\hat{H}\psi_1 = E\psi_1$

$\hat{H}\psi_2 = E\psi_2$

2) Non degenerate

3) System where $\hat{H}\phi_i(x) = E_i \phi_i(x)$. the wavefunction at $t = 0$ is $\psi(x, t=0) = (1+2i)\phi_1(x) + \phi_3(x)$. Then —

a) What is the average energy at $t = 0$?

$$\langle E \rangle = \frac{\int_{-\infty}^{\infty} \psi^* \hat{H} \psi \, dx}{\int_{-\infty}^{\infty} \psi^* \psi \, dx} = \frac{\int \left[(1-2i)\phi_1^* x + \phi_3^*(x)\right] \hat{H} \left[(1+2i)\phi_1(x) + \phi_3(x)\right] dx}{\int \left[(1-2i)\phi_1^*(x) + \phi_3^*(x)\right]\left[(1+2i)\phi_1(x) + \phi_3(x)\right] dx}$$

$$\langle E \rangle = \frac{\int \left[(1-2i)\phi_1^*(x) + \phi_3^* x\right]\left[(1+2i)E_1\phi_1(x) + E_3\phi_3(x)\right] dx}{\int \left[(1-2i)\phi_1^*(x) + \phi_3^*(x)\right]\left[(1+2i)\phi_1(x) + \phi_3(x)\right] dx}$$

$$\langle E \rangle = \frac{\int 5E_1 |\phi_1(x)|^2 + E_3 |\phi_3(x)|^2 + (1-2i)\phi_1^*(x) . E_3 \phi_3(x) + (1+2i) E_1 \phi_3^*(x) . \phi_1(x)}{\int 5|\phi_1(x)|^2 + |\phi_3(x)|^2 + (1-2i)\phi_1^*(x)\phi_3(x) + (1+2i)\phi_1(x)\phi_3^*(x)}$$

If a function is an eigenfunction of $\hat{H}$, then it is a orthonormal function $\int \psi_m^* \psi_n = \delta_{mn}$ $\begin{cases} m = n : \delta = 1 \\ m \neq n : \delta = 0 \end{cases}$

$$\langle E \rangle = \frac{5E_1 + E_3}{5+1} = \frac{5E_1 + E_3}{6}$$

b) What will be the wave function of system at $t_{=2}$

$$\psi(x,t) = \phi(x)\, e^{-iEt/\hbar}$$

$$\psi(x, t=2) = (1+2i)\,\phi_1\, e^{\frac{-iE_1 2}{\hbar}} + \phi_3\, e^{\frac{-iE_3 2}{\hbar}}$$

4) For a normalised wave function $\psi(x)$, at a given time, WKT, $\psi(x)\,\psi^*(x)$ is probability density of finding the particle at x. Using this derive that average position of particle is $\int_{-\infty}^{\infty} \psi^*(x) \cdot x\, (\psi(x) \cdot dx$ without using Postulate 4.

$\psi^*\psi$ gives the probability density. If we multiply it by x, we get the average /expected value of position of particle

i.e. $\int_{-\infty}^{\infty} \psi^*\psi\, dx$: Probability density

$$\int_{-\infty}^{\infty} \psi^*\psi\, dx \cdot x = \langle x \rangle \rightarrow \text{Avg value}$$

$$\Rightarrow \langle x \rangle = \int_{-\infty}^{\infty} \psi^* \hat{x}\, \psi \cdot dx \quad (\text{because } \hat{x}\psi = x\psi)$$

5) Show that the functions are orthonormal -

$$f(x) = \begin{cases} \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right), & 0 < x < a \\ 0, & x > a,\ x < 0. \end{cases}$$

Box function

※

$\cos 2x = 1 - 2\sin^2 x$

$\sin^2 x = \frac{1-\cos 2x}{2}$

$$\int_0^a \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right) \cdot \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right) \cdot dx$$

$$\Rightarrow \frac{2}{a} \int_0^a \sin^2\left(\frac{n\pi x}{a}\right) \cdot dx = \frac{\cancel{2}}{a} \cdot \frac{1}{\cancel{2}} \int_0^a 1 - \cos\left(\frac{2n\pi x}{a}\right) \cdot dx$$

$$\Rightarrow \frac{1}{a}\left[\int_0^a dx - \int_0^a \cos\frac{2n\pi x}{a}\, dx\right] = \frac{1}{\cancel{a}}\left[\cancel{a} - \sin\left(\frac{2n\pi x}{a}\right) \cdot \frac{\cancel{a}}{2n\pi}\right]_0^a$$

$$\Rightarrow 1 - \left[\sin\left(\frac{2n\pi \cancel{a}}{\cancel{a}}\right) - \sin(0)\right] = 1 - 0 = 1$$

i.e. function is normal

$$\int_0^a \sqrt{\frac{2}{a}} \operatorname{Sin}\left(\frac{1\pi x}{a}\right) \sqrt{\frac{2}{a}} \operatorname{Sin}\left(\frac{2\pi x}{a}\right)$$

$$\Rightarrow \frac{\cancel{2}}{a} \int_0^a \frac{1}{\cancel{2}} \left(\operatorname{Cos}\left[\frac{\pi x}{a} - \frac{2\pi x}{a}\right] - \operatorname{Cos}\left[\frac{\pi x}{a} + \frac{2\pi x}{a}\right]\right) dx = \frac{1}{a} \int_0^a \left(\operatorname{Cos}\frac{\pi x}{a} - \operatorname{Cos}\frac{3\pi x}{a}\right) dx$$

$$\frac{1}{a}\left[\frac{\pi}{a}\left(\operatorname{Sin}\frac{\pi x}{a}\right)_0^a - \frac{3\pi}{a}\left(\operatorname{Sin}\frac{3\pi x}{a}\right)_0^a \right] = \frac{\pi}{a \cdot a}\left[(\operatorname{Sin}\pi - \operatorname{Sin}0) - 3(\operatorname{Sin}3\pi - \operatorname{Sin}0)\right]$$

$$= \frac{\pi}{a^2}(0) = 0$$

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Recap:

Schrodinger's equation, $i\hbar \frac{\partial \psi}{\partial t} = \hat{H}\psi$

If $\hat{H}$ ~~it~~ is time independant, then, ψ can be written as $\psi(x,t) = \phi(x) . e^{-iEt/\hbar}$ when $\hat{H}\phi(x) = E . \phi(x)$.

If $\hat{H}$ is time independant, then it doesn't mean that the wave function is time independant.

#"Stationary state is an eigenfunction of the Hamiltonian"

~~When~~ For such a $\psi(x,t)$, the probability density i.e. $P(x,t) = \psi^*\psi$ is also time independant

Such states are called Stationary States.

$\Rightarrow \int \psi^* \psi \, d\tau$ is also time independant.

But for $\psi(x,t) = c_1 \phi_1(x) e^{-iE_1 t/\hbar} + c_2 \phi_2 e^{-iE_2 t/\hbar}$

there, $P(x,t) = \psi^*\psi$ is time dependant

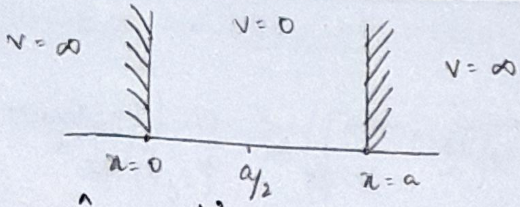
But the value $\int \psi^* \psi \, d\tau$ is time independant because the terms with 't' will go to 0 because the functions are orthonormal.

Particle in a Box System

This is also called the infinite square well

The problem is described as a quantum particle moving back and forth in a tube like structure

We'll solve this using postulates



$V = 0 , \quad 0 < x < a$

$V = \infty \quad x \leq 0 , \; x \geq a$

The Hamiltonian of this system.

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} \quad \text{for} \quad 0 < x < a$$

Its a given that if $V = \infty$, particle won't be found there $\Rightarrow \psi^*\psi = 0 \Rightarrow \psi(x) = 0 \;\; \forall \; x \leq 0 \; \& \; x \geq a$

(BOUNDARY CONDITION)

As ψ needs to be continuous $\Rightarrow \psi(0) = \psi(a) = 0$

So, we solve the Schrödinger's equation for this

But since $\hat{H}$ is time independant, its good enough to solve : $\hat{H}\phi = E\phi$

$$\Rightarrow -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}(\phi(x)) = E . \phi(x) \Rightarrow \frac{d^2}{dx^2}(\phi(x)) = -\frac{2mE}{\hbar^2}\phi(x) = -k^2\phi(x)$$

We can show that a general solution of this is : $\phi(x) = A\,\mathrm{Sin}(xk) + B\,\mathrm{Cos}(xk)$

where $k = \frac{\sqrt{2mE}}{\hbar}$

WKT, $\psi(0) = 0 \Rightarrow \phi(0) = 0$

$\Rightarrow \phi(0) = 0 + B = 0$

$\therefore B = 0 \quad \Rightarrow \phi(x) = A\sin(kx)$

$\phi(a) = 0 \quad \Rightarrow A\,\mathrm{Sin}(ka) = 0$

$\Rightarrow ka = n\pi$ where $n = 0, 1, 2, \ldots$

$\Rightarrow \frac{\sqrt{2mE}}{\hbar} a = n\pi \quad \Rightarrow E = \frac{n^2\pi^2\hbar^2}{2ma^2}$ where $n = 1, 2 \ldots$

This tells us that energy has discrete values i.e. quantised values

$$\therefore \boxed{E_n = \frac{n^2 h^2}{8ma^2}} \quad \text{where } n = \ldots -1, 0, 1, \ldots$$

$$\phi(x) = A\,\mathrm{Sin}\left(\frac{\sqrt{2mE}}{\hbar}x\right) = A\,\mathrm{Sin}\left(\frac{\sqrt{2m} \cdot \frac{n\pi\hbar}{\sqrt{2m}\cdot a}x}{\hbar}\right) = A\sin\left(\frac{n\pi x}{a}\right)$$

$\int_{-\infty}^{\infty} \psi^* \psi \, dx =$

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$\Rightarrow \phi_n(x) = A \sin\left(\frac{n\pi x}{a}\right)$

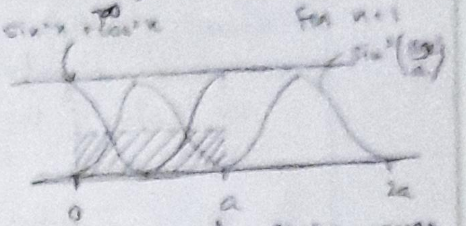
As $\psi^*\psi$ is a probabilistic function, $n=0$ is not allowed, because that would mean that probability of finding it anywhere is zero. (which is not possible)

$E_{n=1} = E_{n=-1}$ but $\psi_{n=1} = -\psi_{n=-1}$

Negative values of n give linearly dependent wavefunctions.

To get A, we utilise the fact that sum of probabilities of all events is 1 — $\int_{-\infty}^{\infty} \psi^* \psi \, dx = 1$

$\Rightarrow A^2 \int_0^a \sin^2\left(\frac{n\pi x}{a}\right) . dx = 1$

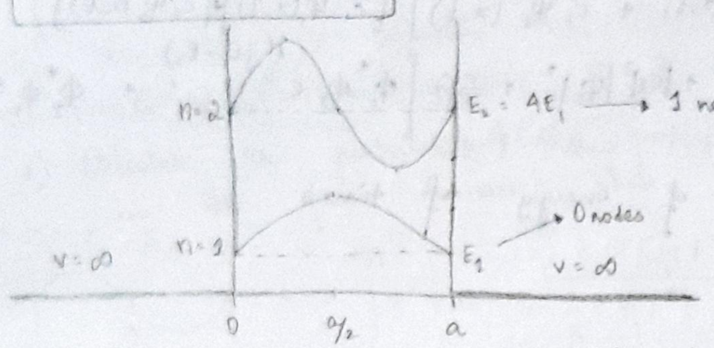


$\Rightarrow A^2 . \left(\frac{a}{2}\right) = 1$

$\therefore A = \sqrt{\frac{2}{a}}$

The integration of $\sin^2 x$ over the interval of a cycle is $1/2$

$\therefore \boxed{\phi_n(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right)} \Rightarrow \psi(x,t) = \phi_n(x) . e^{-iE_n t/\hbar}$



For a 2-D box, $\phi(x,y) = \sin\left(\frac{n_x \pi x}{a}\right) \sin\left(\frac{n_y \pi y}{a}\right)$

$E_{n_x, n_y} = \frac{(n_x^2 + n_y^2) h^2}{8ma^2}$

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Tutorial 4

1) Normalise the eigenfunction of PIB

$\psi = N \sin\left(\frac{n\pi x}{a}\right)$

$\int \psi^* \psi \, dx = 1 \Rightarrow N^2 \int_0^a \sin^2\left(\frac{n\pi x}{a}\right) . dx = N^2 \int_0^a \frac{1 - \cos\left(\frac{2n\pi x}{a}\right)}{2} . dx$

$\frac{N^2}{2} \int_0^a dx = 1 \Rightarrow N^2 = \frac{2}{a} \quad N = \sqrt{\frac{2}{a}}$

2) $\phi_i(x)$ is normalised eigenfunction of PIB hamiltonian with eigenvalue E_i

i) $\hat{H}\phi_i = E_i\phi_i \Rightarrow \psi(x,t) = \phi_i(x) \cdot e^{-iE_it/\hbar}$

ii) $f(x,t) = \psi^*\psi = \phi^*(x) e^{+iEt/\hbar} \phi(x) e^{-iEt/\hbar}$

$= \phi^*\phi$

iii) Average value of energy of system

$$\langle E \rangle = \frac{\langle \psi^* | \hat{H} | \psi \rangle}{\langle \psi^* | \psi \rangle} = \frac{E \langle \psi^* | \psi \rangle}{\langle \psi^* | \psi \rangle} = E$$

Since there's only one observed value (∵ theres only one eigenfunction ⇒ only one eigenvalue), the average is also the same

It doesn't change with time (?)

3) a. At a future time –

$$\psi(x,t) = c_1 \phi_1(x) e^{-iE_1t/\hbar} + c_2 \phi_2(x) e^{-iE_2t/\hbar}$$

b. Probability density at t=1 & t=2.

$$\psi^*\psi = \left[c_1 \psi_1^*(x,t) + c_2 \psi_2^*(x,t)\right]\left(\left[c_1 \psi_1(x,t)\right] + \left[c_2 \psi_2(x,t)\right]\right)$$

$$\psi^*\psi = |c_1|^2 |\phi_1|^2 + |c_2|^2 |\phi_2|^2 + \left[\phi_1^* \phi_2 e^{\frac{it}{\hbar}(E_1 - E_2)} (c_1^* c_2) + \phi_2^* \phi_1 e^{\frac{it}{\hbar}(E_2 - E_1)} (c_2^* c_1)\right]$$

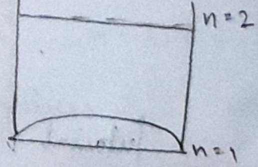
Substitute t=1 and t=2

c. Avg value of energy of time?

$$\langle E \rangle = \frac{\langle \psi^* | \hat{H} | \psi \rangle}{\langle \psi^* | \psi \rangle} =$$

4) $m_e = 9.1 \times 10^{-31}$ g. 1D box of size 1Å. What wavelength of light will be resonant with energy difference?

$$\Delta E = h\nu = \frac{hc}{\lambda} \qquad E_1 = \frac{h^2}{8ma^2} \qquad E_2 = \frac{4h^2}{8ma^2}$$



$$\Delta E = \frac{3h^2}{8ma^2} = \frac{hc}{\lambda} \Rightarrow \frac{\cancel{3} \times 6.634 \times 10^{-34}}{8 \times 9.1 \times 10^{-31} \times 10^{-20}} = \frac{\cancel{3} \times 10^8}{\lambda}$$

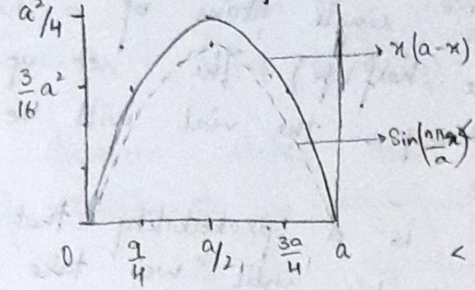
$$\Rightarrow \lambda = \frac{8 \times 9.1}{6.63} \times 10^{-9}$$

$$\therefore \underline{\underline{\lambda \sim 11 \text{ nm}}}$$

5) Wavefunction for a PIB — $\psi(x) = x(a-x),\ 0 \le x \le a$

$= 0,\ x \le 0,\ x \ge a$

a) Sketch the wave function



b) Avg value of energy?

$$\hat{H}\psi(x) = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}(ax - x^2) = 2\cdot\frac{\hbar^2}{2m}$$

$$\langle E\rangle = \frac{\langle\psi^*|\hat{H}|\psi\rangle}{\langle\psi^*|\psi\rangle} = \frac{\int_{-\infty}^{\infty}(xa - x^2)\cdot\frac{2\hbar^2}{2m}\cdot dx}{\int_{-\infty}^{\infty}x^2(a-x)^2\cdot dx}$$

$$\langle E\rangle = \frac{\frac{\hbar^2}{m}\int_0^a ax\,dx - \int_0^a x^2\,dx}{a^2\int_0^a x^2\,dx + \int_0^a x^4\,dx - 2a\int_0^a x^3\,dx}$$

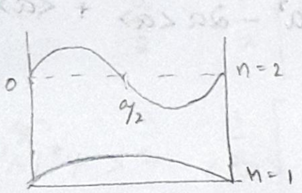
$$\langle E\rangle = \frac{\frac{\hbar^2}{m}\left[\frac{a^3}{2} - \frac{a^3}{3}\right]}{\frac{a^5}{3} + \frac{a^5}{5} - \frac{2a^5}{4}} = \frac{\frac{\hbar^2}{m}\left[\frac{a^3}{6}\right]}{\frac{a^5}{30}} = \frac{\hbar^2}{m}\times\frac{a^3\times 30}{a^5\times 6}$$

$$\langle E\rangle = \frac{5\hbar^2}{ma^2} = \underset{\to 0.126}{\frac{5h^2}{4\pi^2 ma^2}} \approx \underset{\to 0.125}{\frac{h^2}{8ma^2}} = E_1$$

This is quite similar to ground state wave function, but its not the same.

So, this $\psi(x)$ is actually the linear combination of two eigenfunctions — but its ~~gr~~ closest to the ground state

~~b)~~ 6) Calculate the probability that particle is found b/w 0 to $\frac{a}{2}$ in its first excited state.



$$\psi = \sqrt{\frac{2}{a}}\sin\left(\frac{2\pi x}{a}\right)$$

$$\int_0^{a/2}\psi^*\psi\,dx = \frac{2}{a}\int_0^{a/2}\sin^2\left(\frac{2\pi x}{a}\right)\cdot dx = \frac{\cancel{2}}{a}\cdot\frac{1}{\cancel{2}}\int_0^{a/2} 1 - \cos\left(\frac{4\pi x}{a}\right)$$

$$\Rightarrow \int\psi^*\psi\,dx = \frac{1}{\cancel{a}}\left[\left(\frac{\cancel{a}}{2}\right) - \sin\left(\frac{\overset{2}{\cancel{4}}\pi\cancel{a}}{\cancel{a}\cancel{2}}\right)\right] = \frac{1}{2}$$

Probability $= 1/2$

Quantum particles have no trajectory — they only have wave functions which evolve with time.

Hence, nodes can exist i.e. the particle doesn't have to 'travel through' anything

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Schrodinger's Cat

Imagine you place a cat in the box and a vial of poison which is connected to a controller in which there is a single atom of a radioactive element (with reasonable half life). The set up is such that if the atom decays, the vial will be broken and cat will die.

After some time, there is a probability that the cat is dead or alive - i.e until we take a measurement, the cat is in a superposed position between dead and live

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The wave function gives the probability density, which is only a distribution of the particle's position at some time - this can be continuous or discrete

The uncertainity is quantified by standard deviation of the distribution.

Let a be any property and let $\langle a \rangle$ be its averge and let ... wave function.

$\langle a \rangle = \langle \psi^* | \hat{a} | \psi \rangle$ where ψ is wave function.

The variance is given by -

$$\sigma^2 = \langle (a - \langle a \rangle)^2 \rangle = \langle a^2 - 2a\langle a \rangle + \langle a \rangle^2 \rangle$$

$$\sigma^2 = \langle a^2 \rangle - 2\langle a \rangle^2 + \langle a \rangle^2$$

$$\sigma^2 = \langle a^2 \rangle - \langle a \rangle^2$$

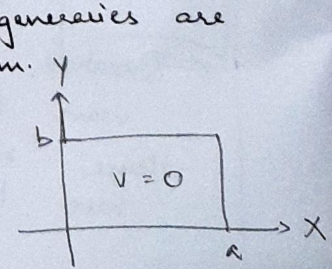
$\langle a^2 \rangle = \langle \psi^* | A^2 | \psi \rangle$

$\langle a \rangle^2 = \langle \psi^* | A | \psi \rangle^2$

2-Dimensional System

A degeneracy is when multiple eigenfunctions have a single eigenvalue - and these degeneracies are <u>not possible</u> in 1-Dimensional system.

$$V = \begin{cases} 0 & \text{if } 0 \le x \le a \ \& \ 0 \le y \le b \\ \infty & \text{everywhere else} \end{cases}$$



This is how a box in 2-D system is described.

$$\int uv\,dx = u\int v\,dx - \int \frac{du}{dx}\int v\,dx$$

$$\psi(x,y)\Big|_{\text{boundaries}} = 0$$

$$\hat{H} = \hat{K} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} - \frac{\hbar^2}{2m}\frac{\partial^2}{\partial y^2}$$

Hamiltonian

$\hat{H}(x,y) = \hat{H}_1(x) + \hat{H}_2(y)$ — i.e final eigenfunction can be written as sum of two Hamiltonian

The theorem states that —

if ~~$\phi(i)$~~ ϕ_i are eigenfunctions of $\hat{H}_1$: $\hat{H}_1\phi_i(x) = E_i^x\phi_i(x)$

χ_j are eigenfunctions of $\hat{H}_2$: $\hat{H}_2\chi_j(y) = E_j^y\chi_j(y)$

Then, $\psi(x,y) = \phi_i(x)\cdot\chi_j(y)$ is an eigenfunction of $\hat{H}$

i.e. $\hat{H}\psi(x,y) = (E_i^x + E_j^y)\,\phi_i(x)\,\chi_j(y)$

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Tutorial 05

$\psi = \sqrt{\frac{2}{a}}\,\sin\left(\frac{n\pi x}{a}\right)$

1) $\langle x\rangle = \langle\psi^*|\hat{x}|\psi\rangle$

$$\langle x\rangle = \frac{2}{a}\int_0^a \sin\left(\frac{n\pi x}{a}\right)\cdot\hat{x}\,\sin\left(\frac{n\pi x}{a}\right)\cdot dx = \frac{2}{a}\int_0^a x\,\sin^2\left(\frac{n\pi x}{a}\right)\cdot dx$$

$$\langle x\rangle = \frac{2}{a}\cdot\frac{1}{2}\int_0^a x\,dx - x\cos\left(\frac{2n\pi x}{a}\right)\cdot dx = \frac{1}{a}\left[\frac{x^2}{2}\Big|_0^a - \int_0^a x\cos\left(\frac{2n\pi x}{a}\right)\cdot dx\right]$$

$$\langle x\rangle = \frac{a}{2} - \frac{1}{a}\left[x\int_0^a \cos\left(\frac{2n\pi x}{a}\right) - \int_0^a 1\int\cos\frac{2n\pi x}{a}\right]$$

$$\langle x\rangle = \frac{a}{2} - \frac{1}{a}\left[\underbrace{x\,\sin\left(\frac{2n\pi x}{a}\right)\left(\frac{a}{2n\pi}\right)\Big|_0^a}_{0} - \int_0^a \sin\left(\frac{2n\pi x}{a}\right)\left(\frac{a}{2n\pi}\right)\right]$$

$$\langle x\rangle = \frac{a}{2} - \frac{1}{a}\left[\cos\left(\frac{2n\pi x}{a}\right)\cdot\left(\frac{a}{2n\pi}\right)^2\right]_0^a = \frac{a}{2} - \frac{1}{a}\left[\left(\frac{a}{2n\pi}\right)^2 - \left(\frac{a}{2n\pi}\right)^2\right]$$

$$\therefore \langle x\rangle = a/2$$

2) $\langle x^2\rangle = \langle\psi^*|x^2|\psi\rangle$

$$\langle x^2\rangle = \frac{a^2}{3} - \frac{a^2}{2n^2\pi^2}$$

3) $\sigma^2 = \langle x^2\rangle - \langle x\rangle^2$

$$= \frac{a^2}{3} - \frac{a^2}{2n^2\pi^2} - \frac{a^2}{4}$$

$$\therefore \sigma_x = \sqrt{\frac{a^2}{12} - \frac{a^2}{2n^2\pi^2}}$$

4) $\langle p \rangle = |\psi^* | \hat{p} | \psi \rangle$

$$\langle p \rangle = \frac{2}{a}\int_0^a \sin\left(\frac{n\pi x}{a}\right) . -i\hbar \frac{\partial}{\partial x}\left(\sin\frac{n\pi x}{a}\right) = -\frac{i\hbar \cancel{2}}{a}\cdot\frac{2}{\cancel{2}}\int_0^a + \sin\left(\frac{n\pi x}{a}\right)\cos\left(\frac{n\pi x}{a}\right)$$

$$\langle p \rangle = -\frac{i\hbar}{a}\left(\frac{n\pi}{a}\right)\int_0^a \sin\left(\frac{2n\pi x}{a}\right).dx = \cancel{+}\frac{i n\pi\hbar}{a^{\cancel{2}}}\cancel{+}\cos\left(\frac{2n\pi x}{a}\right)\Bigg|_0^a\left(\frac{\cancel{a}}{2\cancel{n\pi}}\right)$$

$$\langle p \rangle = \frac{i\hbar}{a}\left[\cos(2n\pi) - \cos 0\right] = 0$$

⇒ The probability of particle going in either direction is equal, so avg = 0

5) $\langle p^2 \rangle = \langle \psi^* | \hat{p}^2 | \psi \rangle$

$$\langle p^2 \rangle = \frac{2}{a}(-\hbar^2)\int_0^a \sin\left(\frac{n\pi x}{a}\right)\cdot\frac{\partial^2}{\partial x^2}\left(\sin\frac{n\pi x}{a}\right) . dx$$

$$\langle p^2 \rangle = \frac{\cancel{2}}{a}(-\hbar^2)\left(-\frac{n^2\pi^2}{a^2}\right).\frac{1}{\cancel{2}}\int_0^a \sin^2\left(\frac{2n\pi x}{a}\right).dx$$

$$\langle p^2 \rangle = \frac{n^2\pi^2\hbar^2}{a^3}\left[\int_0^a dx - \int_0^a \cos\left(\frac{2n\pi x}{a}\right).dx\right] \qquad \rightarrow \sin\left(\frac{2n\pi x}{a}\right) = 0$$

$$\langle p^2 \rangle = \frac{n^2\pi^2\hbar^2}{a^2} = \frac{n^2\cancel{\pi^2}h^2}{4\cancel{\pi^2}a^2} \Rightarrow \langle p^2 \rangle = \frac{n^2h^2}{4a^2}$$

6) $\sigma_p^2 = \langle p^2 \rangle - \langle p \rangle^2 = \frac{n^2\pi^2\hbar^2}{a^2} - 0$

$$\sigma_p = \frac{n\pi\hbar}{a}$$

7) $(\sigma_x \sigma_p)^2 = \left(\frac{a^2}{12} - \frac{a^2}{2n^2\pi^2}\right)\left(\frac{n^2\pi^2\hbar^2}{a^2}\right) = \frac{n^2\pi^2\hbar^2}{12} - \frac{\hbar^2}{2}$

$$(\sigma_x \sigma_p)^2 = \frac{\hbar^2}{2}\left[\frac{n^2\pi^2}{6} - 1\right] \Rightarrow \sigma_x\sigma_p = \frac{\hbar}{\sqrt{2}}\sqrt{\frac{n^2\pi^2}{6} - 1}$$

For $n = 1$

$$\sigma_x\sigma_p = \frac{h}{2\sqrt{2}\pi}\sqrt{\frac{\pi^2}{6} - 1} = \frac{0.2828\ h}{\pi} > \frac{h}{4\pi}$$

This talks of Heisenberg's Uncertainity Principle

Degeneracy is not seen in 1-D - Proof?

#

To prove : $\hat{H}_x \phi_n(x) = E_n^x \phi_n(x)$
$\hat{H}_y \chi_n(y) = E_n^y \chi_n(y)$
Then, $\phi_m(x)\cdot\chi_n(y)$ is an eigenfunction of $\hat{H}$.

i.e. $\hat{H}\phi_m(x)\chi_n(y) = E\,\phi_m(x).\chi_n(y)$

LHS : $[\hat{H}_x + \hat{H}_y]\,\phi_m(x)\cdot\chi_n(y) = E_m^x\,\phi_m(x)\,\chi_n(y) + E_n^y\,\phi_m(x)\,\chi_n(y)$

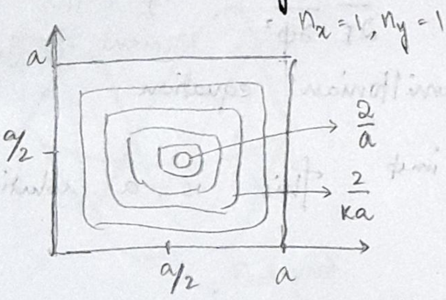
$\Rightarrow (E_m^x + E_n^y)\,\phi_m(x)\cdot\chi_n(y)$ = RHS where $E = E_m^x + E_n^y$

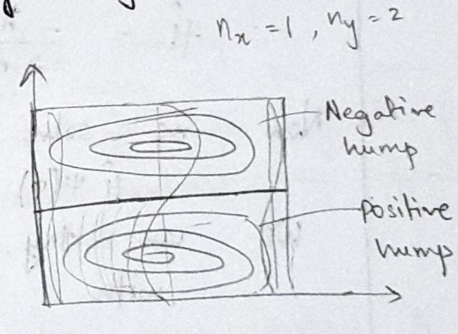
Here, m, n are quantum numbers
For a 2-D box, we will have 2 quantum nos. - (m, n)

For a 2-D square box — (i.e. x, y range from 0 to a)

$E_{m,n}$	n_x	n_y		
$2\cdot\frac{h^2}{8ma^2}$	1	1	$\sin\left(\frac{\pi x}{a}\right)\sin\left(\frac{\pi y}{a}\right)$	
$5\frac{h^2}{8ma^2}$	1	2	$\sin\left(\frac{\pi x}{a}\right)\sin\left(\frac{2\pi y}{a}\right)$	Degenerate eigenfunction
	2	1	$\sin\left(\frac{2\pi x}{a}\right)\sin\left(\frac{\pi y}{a}\right)$	

Degeneracies are only seen in higher dimensions.
Two linearly independant eigenfunctions are said to be degenerate if they have the same eigenvalues.
Symmetry is correlated with degeneracy. When we break symmetry, the existing degeneracy is lost.





Contour plot to visualise 2-D eigen functions
For $n_x = 2$, $n_y = 2$ (ϕ) we'll have a quadrant of contours.

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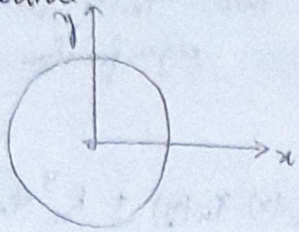
Particle on a Ring System



This system is defined as —

$$V(x,y) = \begin{cases} 0 & \text{. if } x^2+y^2 = r \\ \infty & \text{. otherwise} \end{cases}$$

Here, we use polar coordinates

$$x = r\cos\phi \qquad r = \sqrt{x^2+y^2}$$

$$y = r\sin\phi \qquad \phi = \tan^{-1}\left(\frac{y}{x}\right)$$

Also : $$\frac{\partial f}{\partial x} = \frac{\partial r}{\partial x}\frac{\partial f}{\partial r} + \frac{\partial \phi}{\partial x}\frac{\partial f}{\partial \phi}$$

$$\frac{\partial f}{\partial y} = \frac{\partial r}{\partial y}\frac{\partial f}{\partial r} + \frac{\partial \phi}{\partial y}\frac{\partial f}{\partial \phi}$$

The Hamiltonian of the system is —

$$\hat{H} = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right) \qquad [\text{when } x^2+y^2 = r^2]$$

$$\hat{H} = -\frac{\hbar^2}{2m}\left(\cancel{\frac{\partial^2}{\partial r^2}}^{\,0} + \frac{1}{r}\cancel{\frac{\partial}{\partial r}}^{\,0} + \frac{1}{r^2}\frac{\partial^2}{\partial \phi^2}\right)$$

For a constant r, any term with ∂r is 0, because the radius is not changing. → by defn of problem

$$\therefore \hat{H} = -\frac{\hbar^2}{2 \cdot mr^2}\frac{\partial^2}{\partial \phi^2} = -\frac{\hbar^2}{2I}\frac{\partial^2}{\partial \phi^2} \qquad I = mr^2$$

Moment of Inertia.

Now we solve the Hamiltonian equation :

$$\hat{H}\Psi(\phi) = E\Psi(\phi)$$

We can try. $\Psi_m(\phi) = e^{im\phi}$. This is a solution with $E_m = \frac{m^2h^2}{2I}$

The boundary / continuity condition for this is —

$$\Psi_m(\phi + 2\pi) = \Psi_m(\phi)$$

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$$\Rightarrow e^{im(\phi+2\pi)} = e^{im\phi} = e^{im\phi} \cdot e^{im2\pi}$$

$$\Rightarrow e^{im2\pi} = 1$$ → Integral values of m satisfy this equation.

$$\cos(2\pi m) + i\sin(2\pi m) = 1 \Rightarrow m = 0, \pm1, \pm2 \ldots..$$

$$\Rightarrow E_m = \frac{m^2h^2}{2I} \quad \text{where } m = 0, \pm1, \pm2 \ldots$$

Note: Here, m = 0 is an acceptable solution. Because –
$\psi(\phi) = e^{i0\cdot\phi} = 1$ which is fine.

Also, here negative values of m are allowed
For m = ±1, we get $\psi(\phi) = e^{i\phi}$ & $\psi(\phi) = e^{-i\phi}$
They have the same energy ⇒ degenerate functions.

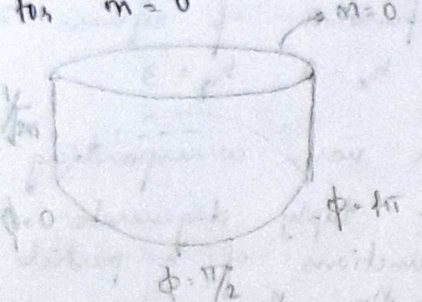
∵ In particle in a box system, -ve numbers of n were not allowed ∵ they'd just result in linearly dependant eigenfunctions.

So, in this system, all functions except for lowest energy one are doubly degenerate.

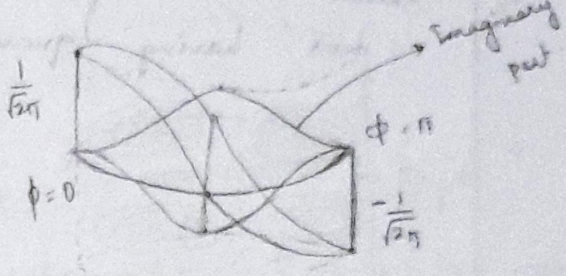
Normalised wave function : $\psi_m(\phi) = \frac{1}{\sqrt{2\pi}} e^{im\phi}$

Visualising this function : –

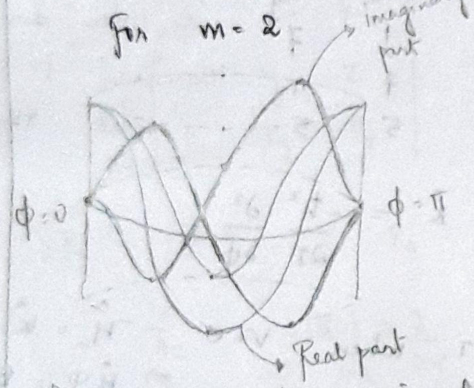
For m = 0



For m = 1, Real part (cos)



For m = 2



The probability density in all these cases is the same i.e. $\psi^*\psi = \frac{1}{2\pi}$ for any value of m
So, we can't extract any informat^n from that.

The degenerate eigenfunctions have the same energy & same $\psi^*\psi$ at a point. The one property in which they're different is – angular momentum.
So, the angular momentum operator is used to label the eigenfunctions i.e. to differentiate two similar energy eigenfunctions.

$e^{i\phi}$ $e^{-i\phi}$
Angular momentum: $\hbar$ $-\hbar$

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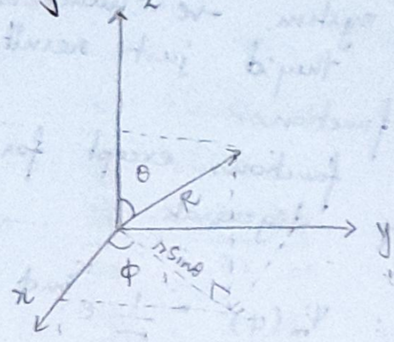
Particle on a Sphere

Real constants

This is defined by, $V(x,y,z) = 0$ when $x^2+y^2+z^2 = R^2$
$= \infty$ otherwise

Here, to solve this, we use the spherical coordinate system.



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

r is constant.

Here, the Hamiltonian is given by-
$\hat{H}\psi_{lm}(\theta,\phi) = E_l\psi_{l,m}(\theta,\phi)$

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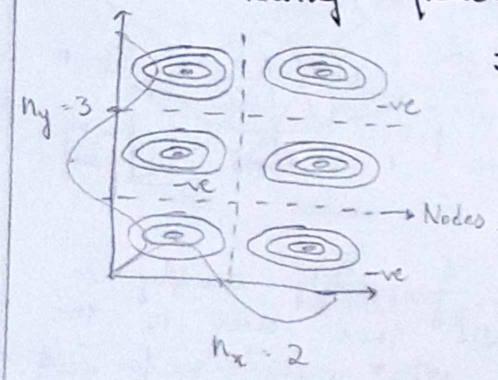
Tutorial - Problem set 6

1) Sketch contour plot of eigenfunction of square 2D box having quantum nos $n_x = 2$ $n_y = 3$



2) Quantum nos. corresponding to lowest triply degenerate eigenfunctions of a particle

Ans:

n_x	n_y
1	7
7	1
5	5

$E = 50E_0$

Try the double of squares to find out this

3) Particle on a ring: $\hat{H} = \hat{K} = \frac{-\hbar^2}{2I}\frac{\partial^2}{\partial\phi}$

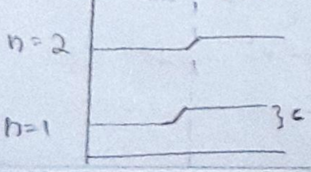
4) $\hat{V}\psi = c\psi$. $\hat{H}' = \hat{K} + \hat{V}$

WKT, when $V = 0$, $\hat{H} = \hat{K}$
$\Rightarrow \hat{H}\psi = E\psi$

$\Rightarrow$ ~~$\hat{H}' \neq -\frac{\hbar^2}{2I}$~~ $\hat{H}' = \hat{H} + \hat{V}$

$\Rightarrow \hat{H}'\psi = (\hat{H}+\hat{V})\psi = \hat{H}\psi + \hat{V}\psi = E\psi + c\psi$

$\therefore \hat{H}'\psi = (E+c)\psi$ Here, $E+c$ is the eigenvalue



5) Derive expression for $\frac{\partial}{\partial x}$ and $\frac{\partial}{\partial y}$ in terms of polar coordinates.

$$\frac{\partial f}{\partial x} = \frac{\partial r}{\partial x} \cdot \frac{\partial f}{\partial r} + \frac{\partial \phi}{\partial x}\frac{\partial f}{\partial \phi}$$

WKT, $r = \sqrt{x^2+y^2} \Rightarrow \frac{\partial r}{\partial x} = \frac{x}{\sqrt{x^2+y^2}} = \frac{r\cos\phi}{\sqrt{r^2\cos^2\phi + r^2\sin^2\phi}} = \cos\phi$

$$x = r\cos\phi \Rightarrow \frac{\partial x}{\partial x} = 1 = -r\sin\phi\frac{d\phi}{dx} + \cos\phi\frac{\partial r}{\partial x}$$

$$\Rightarrow r\cancel{\sin\phi}\frac{\partial\phi}{\partial x} = \cos^2\phi - 1 = -\sin^{\cancel{2}}\phi \Rightarrow \boxed{\frac{\partial\phi}{\partial x} = -\frac{\sin\phi}{r}}$$

Similarly, $\frac{\partial f}{\partial y} = \frac{\partial r}{\partial y}\frac{\partial f}{\partial r} + \frac{\partial\phi}{\partial y} \cdot \frac{\partial f}{\partial\phi}$ where $\frac{\partial r}{\partial y} = \sin\phi$

$$y = r\sin\phi \Rightarrow 1 = r\cos\phi\frac{\partial\phi}{\partial y} + \sin\phi\frac{\partial r}{\partial y} \Rightarrow \frac{\partial\phi}{\partial y} = \frac{\cos\phi}{r}$$

$$\therefore \frac{\partial}{\partial x} = \cos\phi\frac{\partial}{\partial r} - \frac{\sin\phi}{r}\frac{\partial}{\partial\phi}$$

$$\frac{\partial}{\partial y} = \sin\phi\frac{\partial}{\partial r} + \frac{\cos\phi}{r}\frac{\partial}{\partial\phi}$$

6. a) $\vec{l} = \vec{r}\times\vec{p} \Rightarrow \hat{l} = \hat{r}\times\hat{p}$ $\quad \cancel{\hat{p} - \vec{p}\psi^2} \quad \hat{r} = \vec{r}\psi$

$$\hat{l} = \begin{vmatrix} \hat{i} & \hat{j} & \hat{k} \\ x & y & z \\ p_x & p_y & p_z \end{vmatrix} = \hat{i}(yp_z - zp_y) - \hat{j}(xp_z - zp_x) + \hat{k}(xp_y - yp_x)$$

$$\therefore l_z = xp_y - yp_x$$

b) $\hat{p}_x = -i\hbar\frac{\partial}{\partial x} \qquad \hat{p}_y = -i\hbar\frac{\partial}{\partial y}$

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

Substitute carefully

c) $\hat{l}_z = -i\hbar\left[\cos^2\phi\frac{\partial}{\partial\phi} + \cancel{r\cos\phi\sin\phi\frac{\partial}{\partial}} + \sin^2\phi\frac{\partial}{\partial\phi} - \cancel{r\cos\phi\sin\phi\frac{\partial}{\partial r}}\right]$

$$\therefore \hat{l}_z = -i\hbar\frac{\partial}{\partial\phi}$$

d) $\psi_m(\phi) = \frac{e^{im\phi}}{\sqrt{2\pi}}$ $\quad \hat{H}\psi = -\frac{\hbar^2}{2I}\frac{\partial^2}{\partial\phi^2}\left(\frac{e^{im\phi}}{\sqrt{2\pi}}\right) = -\frac{\hbar^2}{2I} \cdot \frac{1}{\sqrt{2\pi}} i^2m^2\left(e^{im\phi}\right) = \frac{m^2\hbar^2\psi}{2I}$

$$l_z\psi = -i\hbar\frac{\partial}{\partial\phi}\left(\frac{e^{im\phi}}{\sqrt{2\pi}}\right) = m\hbar\psi \Rightarrow \boxed{\text{eigenvalue} = m\hbar}$$

c) When 2 functions are degenerate, their energies are the same

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Particle on a Sphere

$$V = \begin{cases} 0 & \text{when } x^2+y^2+z^2 = R = \text{constant} \\ \infty & \text{otherwise} \end{cases}$$

On solving $\hat{H}\Psi = E\Psi(\theta, \phi)$ for this system,

1. E is quantised : $E_l = \frac{l(l+1)\hbar^2}{2I}$ where $I = mR^2$, $l = 0, 1, 2 \ldots$

Taking -ve values of l will only give linearly dependant values — ?

2. Energies are degenerate for a particular l $(2l+1)$ no. of degeneracies.

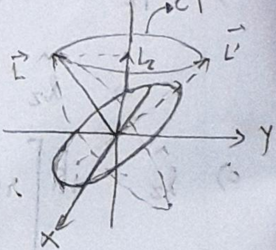
Energy : $E_l = \frac{l(l+1)\hbar^2}{2I}$, $\boxed{\text{Total}}$ angular momentum $= \sqrt{l(l+1)}\,\hbar$

In quantum mech, you cannot measure all 3 components of angular momentum. You can measure the total value and any one component

So, we only get some idea.

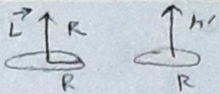
Length of angular momentum vector gives a measure of how fast the particle is moving

All the particles whose angular momentum vector $\vec{L}$ lie on circle c fit the measurements that we make and there could be infinite vectors that fit the description.



3. Additional to length, the direction of angular momentum is also quantised.

Because, $\vec{L}$ is a vector while energy was scalar.



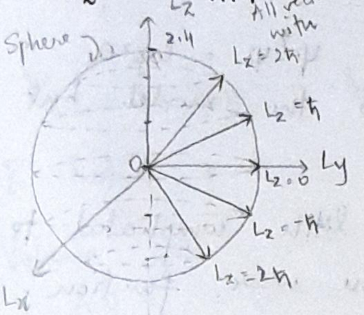
One of the components of angular momentum (z-component by ~~consider~~ convention) is quantised.

L_z for a particular l : $-l, -l+1 \ldots 0, 1, \ldots l-1, l$.

this quantum number is called m.

$l \rightarrow \sqrt{l(l+1)}\hbar$ – speeds satisfy this condition.

$l_z \rightarrow m\hbar$ where $m = -l \ldots 0 \ldots l$



Eg: Let $l = 2$

Radius of sphere $= \sqrt{l(l+1)}\hbar = \sqrt{6}\hbar$

$= 2.4\hbar$

L_z eigenvalue : $-2\hbar, -\hbar, 0, \hbar, 2\hbar$

The particle would be moving on a great circle that's $\perp^r$ to the $\vec{L}$ vector.

l – gives a measure of speed

m – gives some idea of direction

m, l are two quantum numbers which determine the eigenfunction.

There is uncertainity in two directions. The certain direction is labelled as z-axis. The motion of particle is symmetric along the other two directions.

$\hat{H}\Psi = E_l \Psi$ $\quad E_l = \dfrac{l(l+1)\hbar^2}{2I}$ l is $(2l+1)$ fold degenerate

These degenerate eigenfunctions can be distinguished by $L_z = m\hbar$ where $m = -l$ to l

$\Psi(\theta, \phi)$ are eigenfunctions called spherical harmonics.

$\Rightarrow Y_l^m(\theta, \phi) = A_l^m(\theta)\,\chi(\phi)$ where $\chi(\phi) = e^{im\phi}$

particle on a ring.

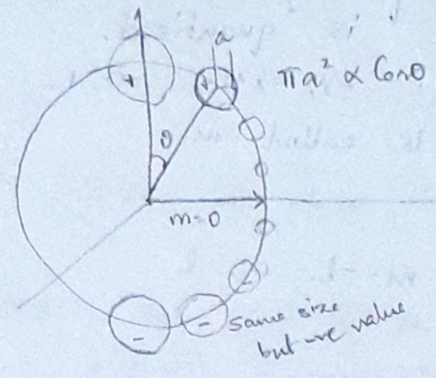
For $l = 0$ $\quad m = 0$ $\quad A_l^m(\theta) = 1$ $\quad \Psi(\theta, \phi) = 1$

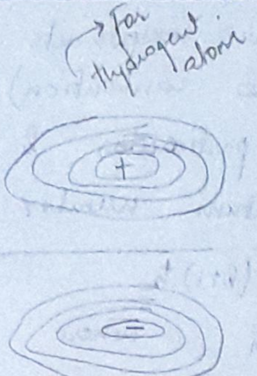
$l = 1$ $\quad m = 0$ $\quad A_l^m(\theta) = \cos\theta$ $\quad \Psi(\theta, \phi) = \cos\theta$

$m = 1, -1$ $\quad A_l^m(\theta) = \sin\theta$

Contours plot is more like latitudes of earth, each one containing diff values of probability density.

For $l = 1$, $m = 0$





For, this $\vec{L}$ is in horizontal plane

⇒ No particle can be found there

Greater density at the poles.

Here, $\psi^*\psi = \cos^2\theta$

Similar to the model but no signs

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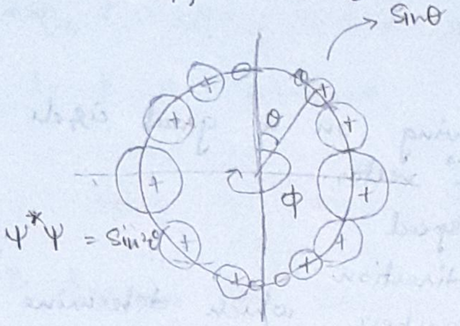
For $l = 1$ $m = 1$

$$\psi(\theta,\phi) = \sin\theta\, e^{i\phi}$$



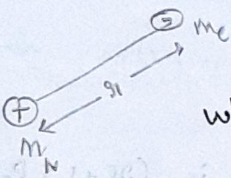
It's a little complicated to draw the wave function.

$$\psi^*\psi = \sin^2\theta$$

Model - like a taurus.

Hydrogen Atom

$$V(r) = -\frac{Ze^2}{4\pi\varepsilon_0 r}$$



Theorem: The two particle system where potential depends on r can be reduced to - (single particle system)

i) Translation of centre of Mass

ii) A motion of reduced mass $\mu = \frac{m_e m_N}{m_e + m_N} \sim m_e$ around a fixed point with

$V(r) = \frac{-Ze^2}{4\pi\varepsilon_0 r}$ - doesn't depend on time.

We solve the Hamiltonian : $\hat{H}\psi = E\psi$ ↪ $\psi(r,\theta,\varphi)$

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

The solution after we've solved the Hamiltonian will be -

$$E_n = -\frac{m_e e^4}{8\varepsilon_0^2 h^2 n^2} \qquad n = 1, 2, 3, 4 \ldots$$

$$E_1 = \frac{E_0}{n^2}$$

$$E_0 = -13.6\text{ eV}$$

−ve sign because the electron is bound.

First major success of Q.M. to be able to explain the expts.

The energy is quantised It is n^2 fold degenerate.
It's dependant of 3 quantum nos. – n, l, m

$0 < l < n-1$ and $-l < m < l$.

By convention, $l = 0$ s-orbital
$l = 1$ p-orbital
$l = 2$ d-orbital
$l = 3$ f orbital.

$$\psi_{n,l,m}(r,\theta,\phi) = R_{n,l}(r)\, Y_{l,m}(\theta,\phi).$$

R: Radial part Y: Angular part – spherical harmonic

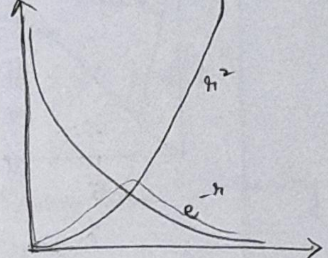
Volume is increasing quadratically i.e.

$$\Delta V = V(r+\Delta r) - V(r)$$

$$\Rightarrow \Delta V \propto r^2 \Delta r$$

The probability decreases exponentially –

$$P(r) = e^{-r}$$



Radial probability density = Probability density × Volume of shell

⇒ Probability of finding a particle varies radially & the maximum probability ~~at~~ is at some distance from the center, not at origin or at infinity.

⇒ Radial prob. density $= [R_{n,l}(r)]^2\, 4\pi r^2$

$$R_{n,l}(r) = \underset{\text{factor}}{\text{Normalization}} \times r^{l} \times e^{-r/na_0} \times L^{2l+1}_{n+1}\left(\frac{2r}{na_0}\right)$$

Associated Laguerre Polynomial whose roots are +ve & real

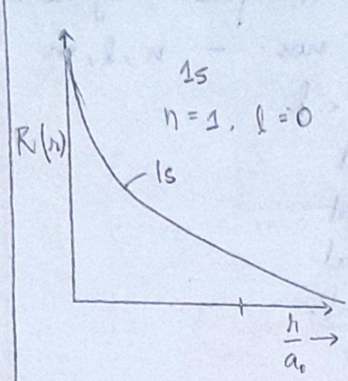
degree : $n-l-1$

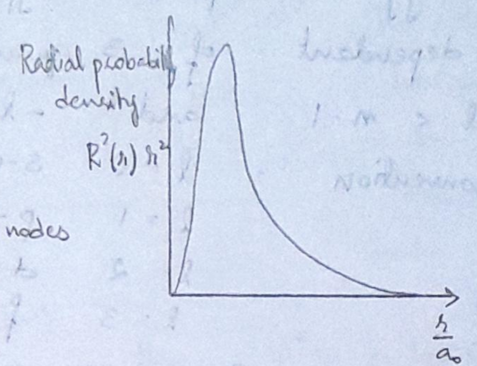
$$a_0 = \frac{\varepsilon_0 h^2}{\pi m_e e^2}$$

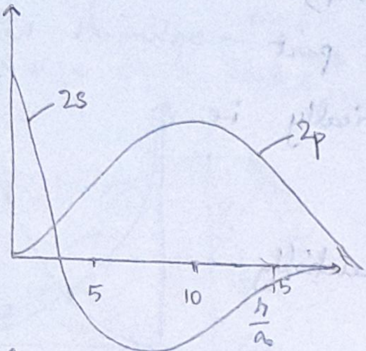
$R_{n,l}(r)\Big|_{r\to\infty} = 0$; e^{-r/na_0} term becomes 0.

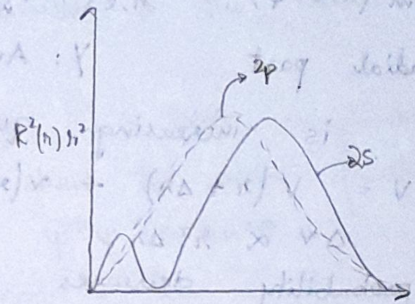
$R_{n,l}(r)\Big|_{r\to 0}$ → $l = 0$ ⇒ Constant, Not defined for $r = 0$.
→ $l \neq 0$ ⇒ Zero

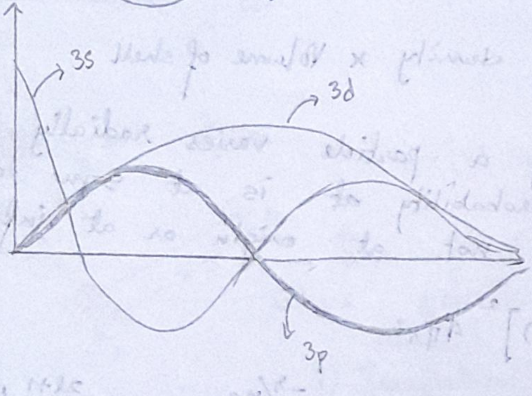
There are $(n-l-1)$ radial nodes in $R_{n,l}(r)$ besides 0 & ∞

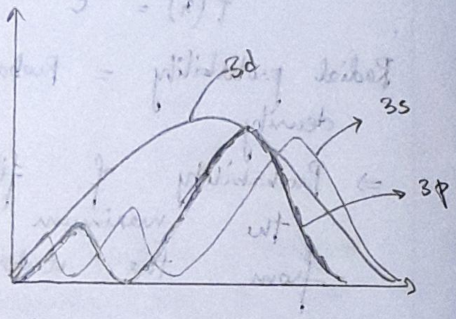












2|3|2020

We consider Hydrogen atom as single particle system with reduced mass.

$$\hat{H} = \frac{h^2}{2m_e} \nabla^2 + V(r) \quad \text{where} \quad V(r) = \frac{Ze^2}{4\pi\varepsilon_0 r}$$

$$\hat{H}\psi = E\psi \quad \text{where} \quad E_n = \frac{m_e e^4}{8\varepsilon_0^2 h^2 n^2} \quad \text{where } n = 1, 2 \ldots$$

$$\psi_{n,l,m}(r, \theta, \phi) = R_{n,l}(r)\, Y_{l,m}(\theta, \phi)$$

$$R_{n,l}(r) = \underset{\text{factor}}{\text{Normalisation}} \times r^{l} \times e^{-r/na_0} \times L^{2l+1}_{n+1}\left(\frac{r2}{na_0}\right)$$

$Y_{l,m}(\theta,\phi)$ = Normalisation factor × $P_l^{|m|}(\cos\theta) \times e^{im\phi}$

P : Associated Legendre functions

$P_{l=0}^{m=0} = 1$

$P_{l=1}^{m=0} = \cos\theta$ $\quad$ $P_{l=1}^{m=\pm1} = \sin\theta$

Shapes of Orbitals

→ 1s orbital : $\psi_{1s} = \psi_{n=1,l=0,m=0}(1,\theta,\phi)$

$= R_{n=01,l=0}(r) \times Y_{m=0,l=0}(\theta,\phi)$

$\propto r^0 \times e^{-r/a_0} \times$ Polynomial of degree 0 $\times 1 \times e^0$

$\psi_{1s} \propto e^{-r/a_0}$ ⇒

⇒ function is exponentially decreasing i.e. maximum density is at the centre and the decreases

→ 2s orbital : $\psi_{2s} = \psi_{n=2,l=0,m=0}(r,\theta,\phi)$

$\psi_{2s} = R_{n=2,l=0}(r) \times Y_{m=0,l=0}(\theta,\phi)$

$\psi_{2s} \propto r^0 \times e^{-r/a_0} \times$ Polynomial of degree 1 $\times 1 \times e^0$

$\psi_{2s} \propto e^{-r/a_0} \times$ Polynomial of degree 1

Because of the polynomial, there's a shell where probability density is 0 i.e. a node.

→ 2p orbital : $\psi_{2p} = \psi_{n=2,l=1,m=0}(r,\theta,\phi)$

$\psi_{2p} \propto r^1 \times e^{-r/2a_0} \times$ Polynomial of degree 0 $\times \cos\theta \times e^0$

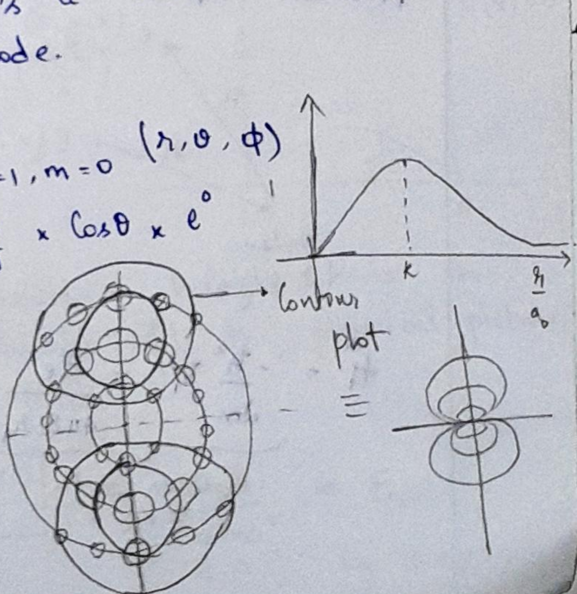
no ϕ dependance

$\psi_{2p} \propto \underbrace{r\cdot e^{-r/2a_0}}_{\text{Radial}} \; \underbrace{\cos\theta}_{\text{Angular}}$

$\propto z\, e^{-r/2a_0}$

$\downarrow$

axis



Now, for $m = \pm 1$

$$\psi_{2p,m=1} = \psi_{n=2,l=1,m=1}(r,\theta,\phi)$$

$$\propto r \times e^{-r/2a_0} \times \sin\theta \times e^{i\phi} \qquad l_z = m\hbar$$

$$\psi_{2p,m=-1} \propto r \times e^{-r/2a_0} \times \sin\theta \times e^{-i\phi} \qquad l_z = -m\hbar$$

$$f = (\psi_{2p,m=1} + \psi_{2p,m=-1}) \propto r \times e^{-r/2a_0} \times \sin\theta \times 2\cos\phi$$

$$g = (\psi_{2p,m=1} - \psi_{2p,m=-1}) \propto r \cdot e^{-r/a_0} \times \sin\theta \times 2i\sin\phi$$

$$\therefore f \propto x e^{-r/2a_0} \qquad g \propto y e^{-r/2a_0}$$

Comparing this to $\psi_{2p,m=0}$, we see that they're very similar, i.e, by symmetry, we can say that f and g will look like the first function but along X and Y axes.

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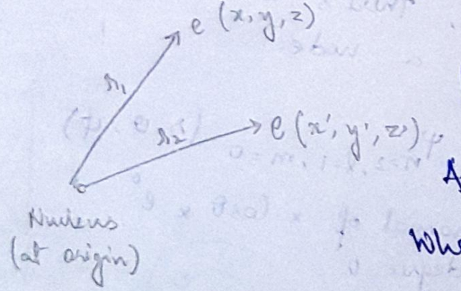
To make it convenient for calculations, we consider m_e, e, $\hbar$, $4\pi\varepsilon_0$ as 1 atomic unit for the respective measures.

So, $$E = -\frac{m_e e^4}{32\pi^2\varepsilon_0^2\hbar^2} = 1 \text{ a.u}$$

Helium atom



Nucleus is considered to be one particle because protons and nuetrons are packed closely together

Assumption: Reduced mass - $\mu = m_e$

When we write the Hamiltonian for this -

$$\hat{H} = \underbrace{-\frac{\hbar^2}{2m}\nabla_1^2 - \frac{Ze^2}{4\pi\varepsilon_0 r_1}}_{\text{H-atom with } Z=2} \underbrace{-\frac{\hbar^2}{2m}\nabla_2^2 - \frac{Ze^2}{4\pi\varepsilon_0 r_2}}_{\text{H-atom with } Z=2} + \frac{e^2}{4\pi\varepsilon_0 r_{12}}$$

This Hamiltonian, in atomic unit can be written as—

$$\hat{H} = \frac{-\nabla_1^2}{2} - \frac{\nabla_2^2}{2} - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}}$$

To explain the movement of one electron, you've to consider the movement of the other electron i.e. they are correlated electrons.

The equation : $\hat{H}\psi(r_1, r_2) = E\psi(r_1, r_2)$ hasn't been solved. One cannot solve a multielectron system using Schrodinger's equation, i.e we can't get an exact solution, but we have some approximatn

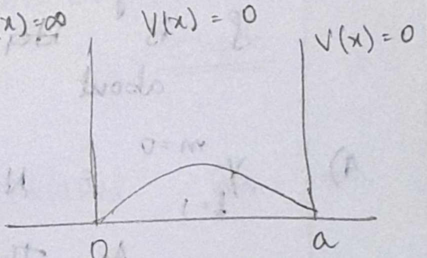
Variation Method — $\Rightarrow \int d\tau\, \psi^* \hat{H} \psi = \int d\tau\, \psi^* E \psi$

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

$$\therefore E = \frac{\int d\tau\, \psi^* \hat{H} \psi}{\int d\tau\, \psi^* \psi}$$

ψ is the real unknown wave function. We make a guess — let the trial wave function be ϕ where $\phi \approx \psi$. Let ε be the energy

$$\varepsilon = \frac{\int d\tau\, \phi^* \hat{H} \phi}{\int d\tau\, \phi^* \phi} \approx E \quad , \quad \varepsilon \geq E_0 \rightarrow \text{Ground state energy}$$



Example: Particle in a box

Exact solution : $\psi = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right)$

$$E_1 = \frac{\pi^2 \hbar^2}{2ma^2}$$

Let's forget we know this.

By Variation theorem, ϕ shouldn't have a node in ground state and it should fit the physical picture.

Let $\phi = a(a-x)$ ⟶ Our guess

$$\varepsilon = \frac{\int_0^a dx \cdot x(a-x)\left[\frac{-\hbar^2}{2m}\frac{d^2}{dx^2}(xa-x^2)\right]}{\int_0^a dx\, x^2(a-x)^2} = \frac{10\hbar^2}{2ma^2} \approx E_1$$

$\varepsilon > E_1$ by 1.4%.

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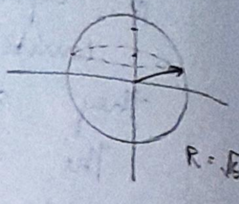
Tutorial - Problem Set 7

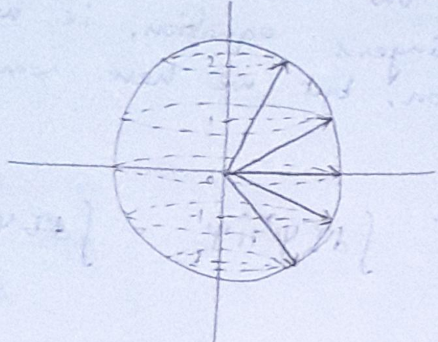
1) $l = 2 \qquad m = 1$

$$E_l = \frac{l(l+1)\hbar^2}{2I} = \frac{3\hbar^2}{I} \qquad l = \sqrt{l(l+1)}\,\hbar = \sqrt{6}\,\hbar$$



$$l_z = m\hbar = 1\hbar$$

2) For $l = 2$, $m = -2, -1, 0, 1, 2$



$$R = \sqrt{l(l+1)}\,\hbar = \sqrt{6}\,\hbar \sim 2.5\hbar$$

$$l_z = m\hbar$$

3) Show that probability densities corresponding to $Y^{l=1}_{m=1}$ and $Y^{m=-1}_{l=1}$ are identical & symmetric about z axis.

$$Y^{m=1}_{l=1} = N \sin\theta\, e^{i\phi} \qquad Y^{m=-1}_{l=1} = N \sin\theta\, e^{-i\phi}$$

Probability density : $Y^*Y = N^2 \sin^2\theta$ for both functions

ρ is ~~iteq~~ independant of ϕ. So its symmetric about z-axis.

4) $Y^{m=0}_{l=1} = N\cos\theta \Rightarrow \rho = Y^*Y = N^2\cos^2\theta$

As This is also independant of ϕ, for any ϕ, ρ will be the same for a given θ. So its symmetric about z-axis.

5) $Y_{l=0}^{m=0} = N_1$ → constant i.e. can't be 0. No node

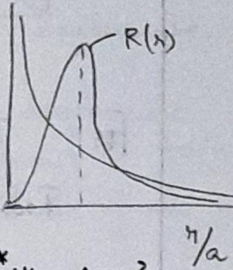
$Y_{l=1}^{m=0} = N_2 \cos\theta = 0$ at $\theta = \pi/2$ when $\theta \in [0, \pi]$

$Y_{l=1}^{m=1} = N_3 \sin\theta \, e^{i\theta} = 0$ at $\theta = 0, \pi$; ϕ can be anything

$Y_{l=1}^{m=-1} = N_3 \sin\theta \, e^{-i\theta} = 0$ at $\theta = 0, \pi$; ϕ can be anything

6) $$\Psi_{1s} = \overbrace{\frac{1}{\sqrt{2}}\left(\frac{1}{a_0}\right)^{3/2}}^{\text{Normalisat}^n \text{ factor}} e^{-r/a_0} \qquad \psi^*\psi = \frac{1}{2a_0^3} e^{-2r/a_0}$$

Differentiate $\psi^*\psi$ wrt r to find maxima & then double differentiate to confirm



$$\frac{dP}{dr} = \frac{c}{2a_0^3}\left[2r e^{-2r/a_0} - r^2 \cdot \frac{2}{a_0} e^{-2r/a_0}\right]$$

$$P = \psi^*\psi \cdot 4\pi r^2$$

$$P = \frac{c}{2a^3} r^2 e^{-2r/a_0}$$

$$= \frac{c}{2a_0^3} 2r e^{-2r/a_0}\left(1 - \frac{r}{a_0}\right) = 0$$

$\Rightarrow$ $r = 0$, $r = \infty$ or $\boxed{r = a_0}$ Required answer

7) $$\Psi_{1s} = \frac{1}{\sqrt{2}}\left(\frac{1}{a_0}\right)^{3/2} e^{-r/a_0}$$

Prob. density for all radial & angular case $= \int_{\theta=0}^{\pi}\int_{\phi=0}^{2\pi}\int_{r=0}^{a_0} \psi^*\psi \cdot r^2 \sin\theta \, dr \, d\theta \, d\phi = 0.323$

Check

to find radial probability at 1km —

$r = 1\text{km}$ $\quad \Delta r = 1\text{mm}$

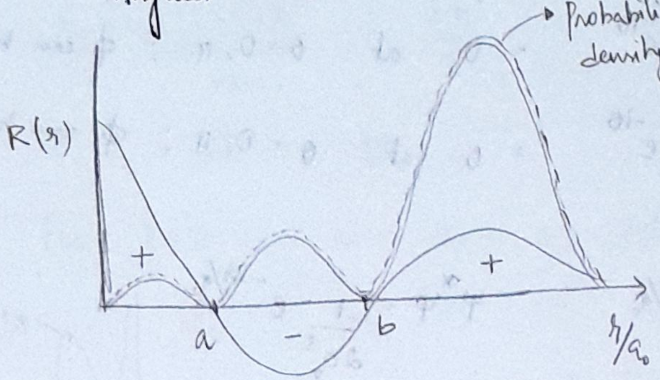
$$\rho = \psi^*\psi \cdot 4\pi r^2 \cdot \Delta r$$

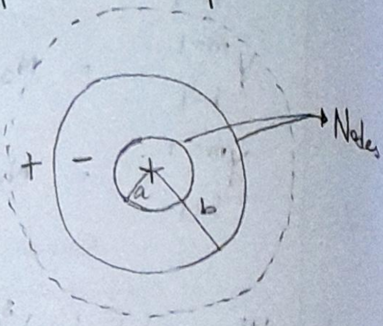
$$\rho = \frac{1}{2a_0^3} e^{-2r/a_0} \cdot 4\pi r^2 \cdot \Delta r =$$

8) For 3s : $n = 3$ $l = 0$ $m = 0$

Radial nodes = $(n-l-1) = 2$ - independant of θ & ϕ

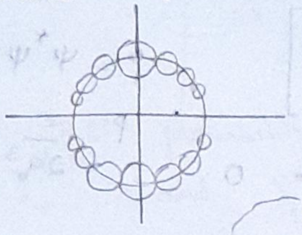
Angular nodes = $l = 0$ - independant of r

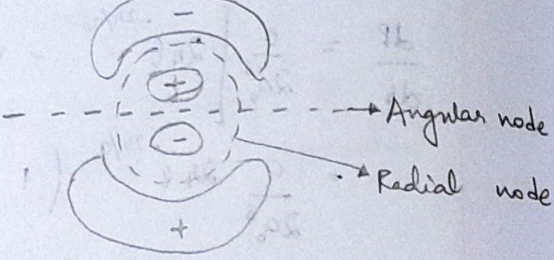


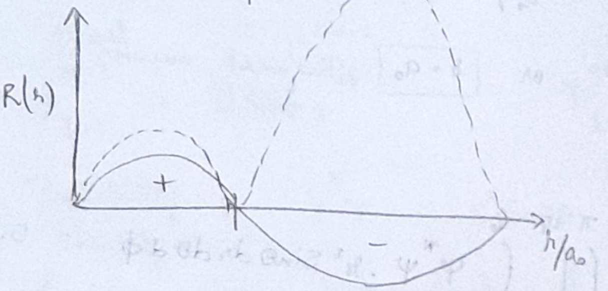


For $3p_z$: $n = 3$ $l = 1$ $m = 0$ $\Rightarrow$ $\cos\theta$ (no ϕ term)

Radial = 1 Angular = 1







9) $R_{n,l}(r) = c \cdot r^{l} e^{-r/a_0} L_{n-l-1}$ → Polynomial of degree $n-l-1$

$Y_{m,l}(\theta, \phi) = c_1 \cdot P_l^{|m|}(\cos\theta) \cdot e^{im\phi}$

↳ Polynomial of degree l.

The polynomial in the radial part of equation is of degree $n-l-1$ $\Rightarrow$ it has $n-l-1$ solutions i.e the no. of places where function goes to zero & thus creates a node.

Similarly, the angular part has a polynomial of degree $l \Rightarrow l$ nodes. In total, $(n-1)$ nodes

10) ★ $n = 1$ ⇒ $l = 0$ $m = 0$ 1 degenerate orbital

★ $n = 2$ ⇒ $l = 0$ $m = 0$
$l = 1$ $m = 0, +1, -1$ 4 degenerate

★ $n = 3$ ⇒ $l = 0$ $m = 0$
$l = 1$ $m = -1, 0, +1$
$l = 2$ $m = -2, -1, 0, 1, 2$ 9 degenerate

★ $n = 4$ ⇒ $l = 0$ $m = 0$
$l = 1$ $m = \pm 1, 0$
$l = 2$ $m = 0, \pm 1, \pm 2$
$l = 3$ $m = 0, \pm 1, \pm 2, \pm 3$ 16 degenerate.

For each value of l, it has $(2l+1)$ degenerate states. For n, the value of l ranges from 0 to $(n-1)$. For any n, the no. of degenerate states will be given by –

$S = [2(0)+1] + [2(1)+1] + \cdots\cdots [2(n-1)+1]$

$S = \underset{n \to 1}{1} + \underset{2}{3} + \underset{3}{5} \cdots\cdots + \underset{n}{(2n+1)}$ → Sum of first n odd natural numbers is given by n^2.

$S = n^2$

Therefore its n^2 degenerate.

Problem Set - 8

1) $$1E_h = \frac{m_e e^4}{16\pi^2 \varepsilon_0^2 \hbar^2}$$: Express this in J and eV

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$$1E_h = \frac{9.1 \times 10^{-31} \times (1.6 \times 10^{-19})^4 \times \cancel{4} \times \cancel{(3.14)^2}}{\times \underset{4}{\cancel{16}} \times \cancel{(3.14)^2} \times (8.854 \times 10^{-12})^2 \times (6.634 \times 10^{-34})^2} = \frac{2.275}{10^{15}} \times \left(\frac{1.6 \times 1.6}{8.854 \times 6.634}\right)^2$$

$1E_h = 2.275 \times (0.0435)^2 \times 10^{-15} = 4.35 \times 10^{-18}$ J

$1E_h = 27.211$ eV

2.) Find the ground state energy of –

$$E_n = -\frac{Z^2 me^4}{32 \varepsilon_0^2 \pi^2 \hbar^2 n^2} = \frac{-Z^2}{2n^2} E_h$$ where $n = 1$ (for ground state)
Z : Atomic numbers

Hydrogen atom: $Z = 1$ ⇒ $E_1 = -\frac{E_h}{2} = -13.6$ eV

Helium atom $Z = 2$ ⇒ $E_1 = \frac{-(2)^2 E_h}{2} = -27.2$ eV

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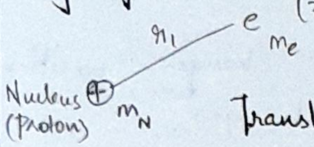
NOTE 01

Hydrogen Atom : technically a two particle system



$V(r) = \frac{-Ze^2}{4\pi\varepsilon_0 r}$

Translation of centre of mass ≈ Translation of nucleus

Relative motion of electron wrt. nucleus is motion of reduced mass: $\mu = \frac{m_e m_N}{m_e + m_N} \approx m_e$

This can be described by considering motion of electron -

$$\hat{H} = \frac{-\hbar^2}{2m}\nabla^2 - \frac{Ze^2}{4\pi\varepsilon_0 r} \quad ; \quad E_n = \frac{-m_e e^4}{32\pi^2\varepsilon_0^2\hbar^2 n^2}$$

Atomic Units

Mass of electron : $m_e = 9.1094 \times 10^{-31}$ kg $= 1$ a.u mass

Charge of electron : $e = 1.6022 \times 10^{-19}$ C $= 1$ a.u charge

Angular momentum : $h/2\pi = \hbar = 1.0546 \times 10^{-34}$ Js $= 1$ a.u

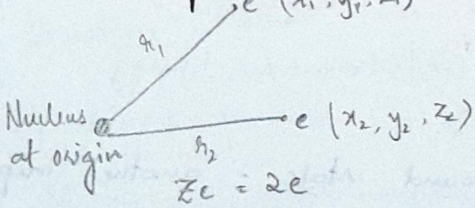
Permitivity , $4\pi\varepsilon = 1.1127 \times 10^{-10}\ C^2 J^{-1} m^{-1} = 1$ a.u

Distance (Bohr radius) $a_0 = \frac{4\pi\varepsilon\hbar^2}{m_e e^2} = 5.2918 \times 10^{-11}$ m $= 1$ au

Energy : $\frac{m_e e^2}{16\pi^2\varepsilon^2\hbar^2} = 4.3597 \times 10^{-8}$ J $= 1$ au $\approx 1 E_h$

For H-atom $E_n = -\frac{1}{2}\left[\frac{m_e e^4}{16\pi^2\varepsilon_0^2\hbar^2}\right] = -\frac{1}{2}E_h$

Helium atom : Three particle system
1 nucleus & 2 electrons ∵ the protons & nuetrons are very closely packed together.



$$\hat{H} = \frac{-\hbar^2}{2m_e}\nabla_1^2 - \frac{\hbar^2}{2m_e}\nabla_2^2 - \frac{Ze^2}{4\pi\varepsilon_0 r_1} - \frac{Ze^2}{4\pi\varepsilon_0 r_2} + \frac{1}{r_{12} 4\pi\varepsilon_0}$$

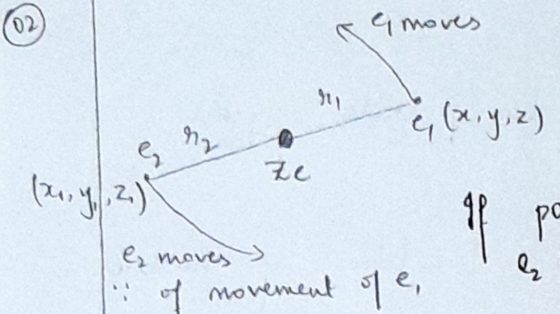
} New term arising from interaction of two electrons

$Ze = 2e$

In atomic units where $Z = 2$ (for He) —

$$\hat{H} = -\frac{\nabla_1^2}{2} - \frac{\nabla_2^2}{2} - \frac{Z}{r_1} - \frac{Z}{r_2} + \boxed{\frac{1}{r_{12}}}$$

→ Corresponds to electronic repulsion in the presence of the nucleus.



Both the electrons try to maintain largest distance b/w themselves but tries to remain close to the boy

If position of $e_1 (x, y, z)$ changes, position of $e_2 (x', y', z')$ also changes

As the motion of each electron cannot be treated seperately, this makes the Schrödinger's Eqⁿ unsolvable.

Only approximate solution of any multielectron system can be obtained.

Actual wavefunction of the atom would depend on coordinates of both electrons ; $\Psi(r_1, r_2)$

For multielectron system : $\Psi(r_1, r_2 \cdots r_i)$

Orbital Approximation : Think each electron is occupying its own orbital and write –

$$\Psi(r_1, r_2) = \phi(r_1)\,\phi(r_2) \quad ; \text{ an approximation.}$$

For eg, $\phi(r_1)$ & $\phi(r_2)$ can be considered as 1s orbital of H-atom. So, we can rewrite the eqⁿ as –

$$\hat{H} = \left[-\frac{\nabla_1^2}{2} - \frac{Z}{r_1}\right] + \left[-\frac{\nabla_2^2}{2} - \frac{Z}{r_2}\right] + \frac{1}{r_{12}} = \hat{H}_1 + \hat{H}_2 + \frac{1}{r_{12}}$$

$\hat{H}_1$ and $\hat{H}_2$ are Hamiltonian for H-atom but with $Z = 2$.

$$\hat{H}\Psi(r_1, r_2) = (\hat{H}_1 + \hat{H}_2)\,\phi(r_1)\,\phi(r_2) = \hat{H}_1(\phi(r_1)\,\phi(r_2)) + \phi(r_1)\,\hat{H}_2\,\phi(r_2)$$
$$= E_1\,\phi(r_1)\,\phi(r_2) + \phi(r_1)\,E_2\,\phi(r_2)$$
$$E\Psi(r_1, r_2) = (E_1 + E_2)\,\phi(r_1)\,\phi(r_2) = (E_1 + E_2)\,\Psi(r_1, r_2)$$

$\therefore\ E = E_1 + E_2$ where E_1, E_2 are hydrogen ground state energy with $Z = 2$.

$$\hat{H} = \underbrace{\hat{H}_1 + \hat{H}_2}_{\text{Can be solved unperturbed by Hamiltonian}} + \boxed{\frac{1}{r_{12}}} \rightarrow \text{Perturbation Term}$$

⇒ Apply the Perturbation term then correct the energy obtained from perturbation.

Total energy : $E = E_1 + E_2 + \boxed{\lambda E'}$ Perturbation Energy

Variation Method.

It deals with electronic ground state ; another important approximation method.

Almost all software packages used to compute electronic structures ~~like~~ of molecules are based on this method

$$\hat{H}\Psi(r_1, r_2) = E_0\Psi(r_1, r_2) \quad \text{– cannot be solved}$$

$$\int \psi^* \hat{H} \psi(r_1, r_2)\, d\tau = \int \psi^* E_0 \psi(r_1, r_2)\, d\tau$$

$$\therefore E_0 = \frac{\int \psi^* \hat{H} \psi\, d\tau}{\int \psi^* \psi\, d\tau}$$: Ground state energy.

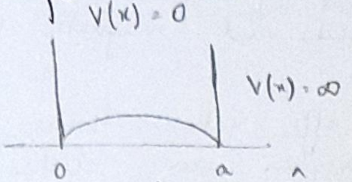
We don't know ψ. But based on physical concept, we assume a trial wavefunction ϕ for ground state (i.e. no nodes) of ψ.
$\Rightarrow \psi \approx \phi$ $\Rightarrow$ $\varepsilon = \dfrac{\int \phi^* \hat{H} \phi\, d\tau}{\int \phi^* \phi\, d\tau}$ Energy of trial wavefunct

If ϕ is close to ψ, then $\varepsilon \sim E_0$

Variation method says that $\varepsilon = \dfrac{\int \phi^* \hat{H} \phi\, d\tau}{\int \phi^* \phi\, d\tau} \geq E_0$

The choice of ϕ that gives the lowest energy (closest to E_0) is considered the choice.

Example: Particle in a box.



$\psi = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right) \Rightarrow E_0 = \dfrac{\pi^2 \hbar^2}{2ma^2}$

Ground state (n = 1) wavefunction & energy.

Let $\phi = x(a - x)$ — this satisfies the physical picture.

Physical picture $\hat{H} = -\dfrac{\hbar^2}{2m} \dfrac{d^2}{dx^2}$

$$\Rightarrow \varepsilon = \frac{\int \phi^* \left(-\frac{\hbar^2}{2m} \frac{d^2}{dx^2}\right) \phi\, dx}{\int \phi^* \phi\, dx} = \frac{\frac{\hbar^2 a^3}{6m}}{\frac{a^5}{30}} = \frac{5\hbar^2}{ma^2}$$

$\varepsilon = \dfrac{10\hbar^2}{2ma^2}$ [variation method] $E_0 = \dfrac{9.86\hbar^2}{2ma^2}$ [Exact solution]

$\varepsilon > E_0$ by 1.4%.

NOTE 02

In multi-electron systems, movement of one electron is correlated to other electrons & the repulsion term in the Hamiltonian makes it very difficult to solve. Hence, we use the Variation Method or Perturbation Theory to get approximate solution for the system.

Variation method for He-atom → Orbital approximation

$$\psi(r_1, r_2) = \phi(r_1)\, \phi(r_2)$$

Actual wave function of He-atom

Hydrogen-like 1-electron wave functions

Multi-electron wavefunction is represented as product of single-electron wave functions.

These single-electron wave functions are called orbitals.

Hartree-Fock Limit Using Variation Method with trial functions $\phi(r_1)$ & $\phi(r_2)$, if they're allowed to be flexible & completely general, then the solutions reach a limit that is both theoretical & practical

If we consider a trial function that doesnot employ single-electron wave function, then the <u>concept of orbitals</u>, which is critical in chemistry is lost.

Eg. $\psi(r_1, r_2) = e^{-Zr_1} e^{-Zr_2} [1 + cr_{12}]$

This can be used under variation method to achive very good agreement of theoretical energies with experimental values.

A more preferred model is the one that -

i) Explains experimental observations

ii) Provides simple physical/chemical insight

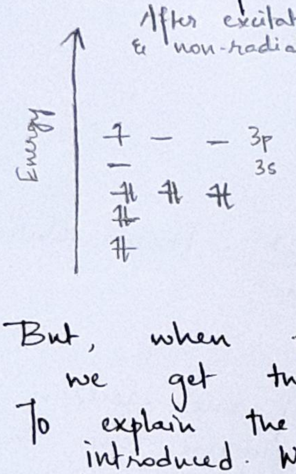
Hartree-Fock approximation is preferred because it fulfils both criteria optimally.

NOTE 03

Spin of electrons

Electron Spin is a quantum property of electrons - a form of angular momentum. Optical and magnetic properties are strongly dependant on spin.

In a flame test, sodium gives off yellow flame. First, some of Na^+ ions in flame regain an electron.

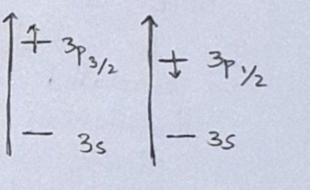


In excited state of Na, the valence electron jumps to 3p orbital ~~instead of~~ from 3s. When the excited electron comes back to 3s orbital, excess energy is emitted in form of yellow light.

From theory, the energy difference b/w 3p & 3s is calculated to be 590 nm which agrees with the emmission of yellow light.

But, when the emission is observed using a spectrometer, we get two emission lines - 589.59 nm & 588.99 nm

To explain the discrepancy, concept of spin is introduced. We can have two kinds of excited state - one with up-spin electron and the other with down spin.



Total Angular Momentum, J is introduced -

$J = (L+S), (L+S-1), \ldots\ldots (L-S)$

L: Total orbital angular momentum S: Total spin angular momentum

For the excited state $3P_{3/2}$ For $3P_{1/2}$

$L = 1$ $S = 1/2 \Rightarrow 588.99\,nm$ $L = 1$ $S = -1/2 \Rightarrow 589.59\,nm$

Spin of an electron was introduced in the theory to explain the atomic spectra of Na and other experimental observations.

There is no classical mechanics counterpart we bring an anology with angular momentum operators.

Orbital Angular Momentum of H-atom

As discussed in H-atom, eigenvalue equations are -

$$\hat{L}^2 Y_l^m(\theta,\phi) = \hbar^2 l(l+1) Y_l^m(\theta,\phi)$$

where $l \in [0,\infty)$

Square of orbital L -

$$L^2 = \hbar^2 (l+1) l$$

$$\hat{L}_z Y_l^m(\theta,\phi) = m\hbar\, Y_l^m(\theta,\phi)$$

$$\int \alpha^* \alpha \, d\sigma = \int \beta^* \beta \, d\sigma = 1$$

$$\int \alpha^* \beta \, d\sigma = \int \alpha \beta^* \, d\sigma = 0$$

σ : spin variable.

Not a continuous variable. Has only 2 z-components : $\pm\frac{\hbar}{2}$

Spin of an electron

We define : Spin operators - $\hat{S}^2$ & $\hat{S}_z$, & their eigenfunctions - α and β

$$\hat{S}^2 \alpha = \hbar^2 (s+1) s \alpha \quad ; \quad \hat{S}^2 \beta = \hbar^2 (s+1) s \beta$$

$$\hat{S}_z \alpha = m_s \alpha \hbar \overset{*}{=} \frac{1}{2}\hbar\alpha \quad ; \quad \hat{S}_z \beta = m_s \beta \hbar \overset{*}{=} -\frac{1}{2}\hbar\beta$$

Square of spin angular momentum -

$S^2 = \hbar^2 (s+1) s$ where $s = 1/2$

s is not allowed to assume large values & hence spin angular momentum can never assume classical behaviour.

$m_s = \pm\frac{1}{2}$ → only 2 values allowed.

\# α & β are ~~orthogonal~~ orthonormal functions

* According to Mc.Quarrie pg. 347

∴ m_s is the spin quantum number that represents the z-component of electron spin angular momentum

Complete Wave function of Hydrogen-like atom

For H-like atoms, groundstate corresponds to -

$n=1, \; l=0, \; m=0$ i.e 1s atomic orbital

$$\psi_{100}(r) = \left(\frac{Z^3}{\pi a_0^3}\right)^{1/2} e^{-Zr/a_0}$$

a_0 : Bohr radius

Z : Atomic number

This is the spatial part of the wavefunction

α and β are the spin part of the wavefunction that determines the value of m_s ($1/2$ or $-1/2$).

So, the complete wave function (time independent) is given by -

$$\Psi(r,\sigma) = \psi(r)\alpha(\sigma) \quad \text{or} \quad \psi(r)\beta(\sigma)$$

$$\therefore \Psi_{100\frac{1}{2}} = \left(\frac{Z^3}{\pi a_0^3}\right)^{1/2} e^{-Zr/a_0} \alpha(\sigma) \qquad \Psi_{100-\frac{1}{2}} = \left(\frac{Z^3}{\pi a_0^3}\right)^{1/2} e^{-Zr/a_0} \beta(\sigma)$$

Likewise, we can build entire series of 2s, 2p, 3s ---- orbital with spin information

NOTE 04

Pauli Exclusion Principle : No two electrons in an atom can have the same four values of quantum numbers.

This comes from Postulate 06 -

"All electronic wavefunctions must be antisymmetric under the interchange of any two electrons."

Electrons are indistinguishable as the trajectory or movement of electrons cannot be tracked

So, when we write wavefunctions, we write $\psi(\vec{r}_1,\vec{r}_2)$ indicating positions of two electrons. As they're indistinguishable, $\psi(\vec{r}_2,\vec{r}_1)$ is just as probable. So, $|\psi(\vec{r}_1,\vec{r}_2)|^2 = |\psi(\vec{r}_2,\vec{r}_1)|$

$$\Rightarrow \psi(r_1,r_2) = \pm\psi(r_2,r_1)$$

By Postulate 6, $\psi(\vec{r}_1,\vec{r}_2) = -\psi(\vec{r}_2,\vec{r}_1)$.

⑥ # Symmetric & Antisymmetric Wavefunctions

If the interchange of electrons changes the sign of wavefuncti then the function is antisymmetric.

1st e^- : $\vec{r}_1$ ψ_A

2nd e^- : $\vec{r}_2$ ψ_B

Position & Wavefunction are different from each other. ↳ Just tells us about the energy of electron.

Combined wave function : $\psi(\vec{r}_1, \vec{r}_2) = \psi_A(r_1)\,\psi_B(r_2)$ — ①

After exchange — $\psi(\vec{r}_2, \vec{r}_1) = \psi_A(r_2)\,\psi_B(r_1)$ — ②

But the probability distribution remains the same

i.e. $|\psi(\vec{r}_1, \vec{r}_2)|^2 = |\psi(\vec{r}_2, \vec{r}_1)|^2$

Symmetric	Antisymmetric
$\psi(\vec{r}_1, \vec{r}_2) = +\psi(\vec{r}_2, \vec{r}_1)$	$\psi(\vec{r}_1, \vec{r}_2) = -\psi(\vec{r}_2, \vec{r}_1)$
Bosons	fermions

General solution :- Linear combination of ① & ②

$\psi_{sym} = \frac{1}{\sqrt{2}}\left[\psi(\vec{r}_1, \vec{r}_2) \boxed{+} \psi(\vec{r}_2, \vec{r}_1)\right]$ # $\psi_{asym} = \frac{1}{\sqrt{2}}\left[\psi(\vec{r}_1, \vec{r}_2) \boxed{-} \psi(\vec{r}_2, \vec{r}_1)\right]$

Special case : Say, both the electrons are existing the same quantum state — ψ_A.

Then, $\psi(\vec{r}_1, \vec{r}_2) = \psi_A(r_1)\,\psi_A(r_2)$ After exchange:-

$\psi(\vec{r}_2, \vec{r}_1) = \psi_A(r_2)\,\psi_A(r_1)$ i.e they remain the same

Then, the general solution for symmetric wavefunction would give us some value, but it would vanish in case of antisymmetric wavefunction — which is not possible (because it would mean there are no electrons).

This tells us that two electrons cannot have the same exact quantum state — this is what Pauli's Exclusion Principle states.

For bosons, there is no change in the wavefunction after exchange, so the general solution has a positive sign. Conversely, when fermions exchange, their wavefunction changes, hence there's a negative sign.

NOTE 05

Chemical Bonding — Molecular Orbital Theory

Consider two Hydrogen atoms — H_A and H_B with one electron each in $1s_A$ and $1s_B$ orbital respectively.

WKT, $\psi_{n\ell m}(r, \theta, \phi) = R_n^{\ell}(r)\, Y_{\ell}^{m}(\theta, \phi)$

For the 1s orbital : $\psi_{100} = \left(\frac{Z^3}{\pi a_0^3}\right)^{1/2} e^{-Zr/a_0}$

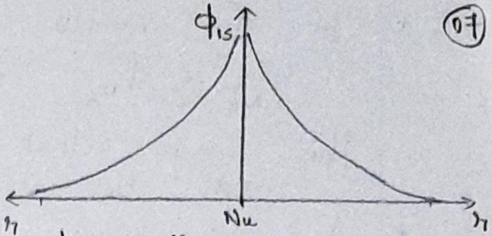
$Z = 1$ for H atom

$a_0 = 0.53$ Å

r : distance from nucleus.

We will use ϕ_{1s_A} and ϕ_{1s_B} to indicate 1s orbitals of isolated H_A and H_B

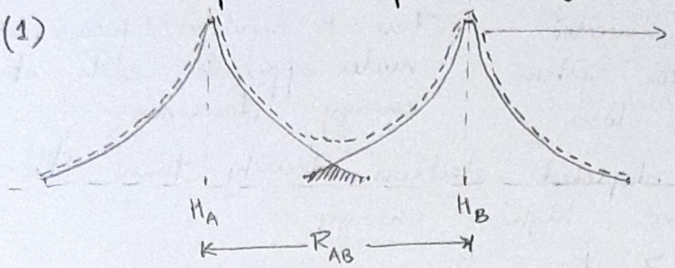
From the equation $\phi_{1s} \propto e^{-r/a_0}$
As the nucleus is at the center, ϕ_{1s} decreases exponentially, both on the right and left side of nucleus.



H_A and H_B are two such isolated systems. If the interaction between them reduces the total energy of the system, then they stay together – we call this a chemical bond.

Total wave function of the system –

(1)

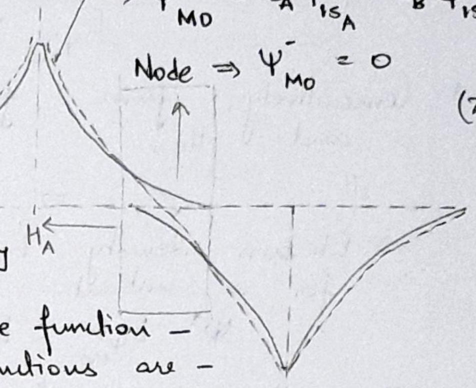


$\rightarrow \Psi^+_{MO} = c_A\phi_{1s_A} + c_B\phi_{1s_B}$

R_{AB} : distance between H_A & H_B nuclei

When the Hydrogen atoms come close to one another, ϕ_{1s_A} & ϕ_{1s_B} interact with each other.

The interaction can be positive or negative, as shown pictographically in diagrams (1) and (2)



$\rightarrow \Psi^-_{MO} = c_A\phi_{1s_A} - c_B\phi_{1s_B}$

Node $\Rightarrow \Psi^-_{MO} = 0$

(2)

We don't know the resultant wave function – so the proposed trial wave functions are –

$\Psi^+_{MO} = c_A\phi_{1s_A} + c_B\phi_{1s_B}$ and $\Psi^-_{MO} = c_A\phi_{1s_A} - c_B\phi_{1s_B}$

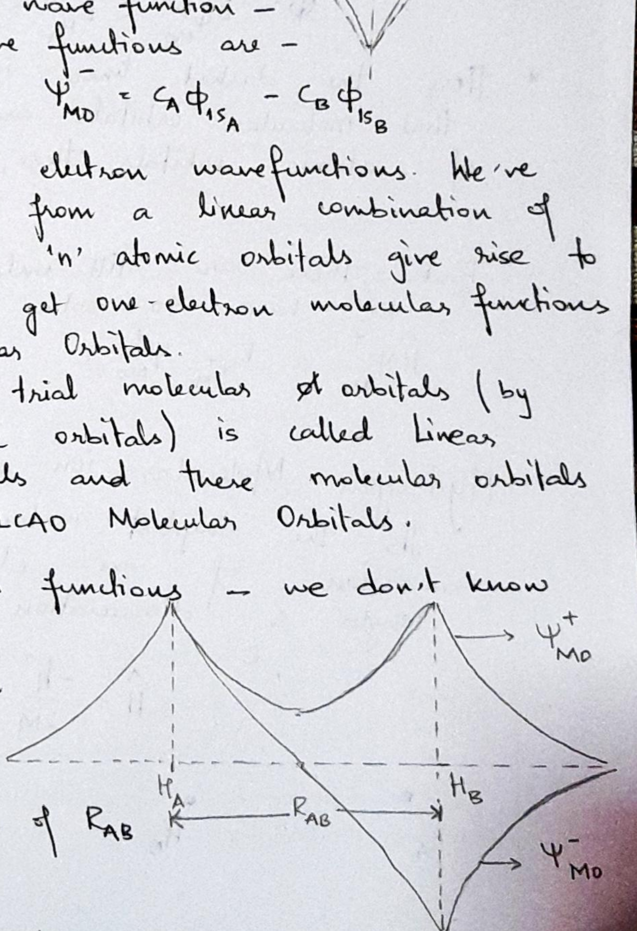
Recall, ϕ_{1s_A} & ϕ_{1s_B} are single electron wavefunctions. We've generated Ψ^+_{MO} and Ψ^-_{MO} from a linear combination of atomic orbitals. In general, 'n' atomic orbitals give rise to 'n' molecular functions. So, we get one-electron molecular functions that are termed as Molecular Orbitals.

This method of generating trial molecular ~~ot~~ orbitals (by linear combinat^n of atomic orbitals) is called Linear Combination of Atomic Orbitals and these molecular orbitals (Ψ^+_{MO} & Ψ^-_{MO}) are called LCAO Molecular Orbitals.

Remember they are only trial functions – we don't know their validity yet.

We can see that, $\Psi^-_{MO} = 0$ in the middle of H_A & H_B.

$\Rightarrow |\Psi^-_{MO}|^2 = 0$ i.e. electron density is zero in the middle of R_{AB}



- ★ In the middle region of figure (2), we see that –

$$\psi^-_{MO} < \phi_{1s_A} \Rightarrow |\psi^-_{MO}|^2 < |\phi_{1sA}|^2 \text{ & |||ly, } |\psi^-_{MO}|^2 < |\phi_{1s_B}|^2$$

This says that electron density, for ψ^-_{MO}, in between H_A and H_B is less than that of ϕ_{1s_A} or ϕ_{1s_B}

- ★ As we know, nuclei repel each other, but they're attracted to an electron – so, if the electron is in between, the nuclei come closer.

$$H^+_A \longrightarrow e^- \longleftarrow H^+_B \qquad\qquad H^+_A \longleftrightarrow H^+_B$$

Attractive force b/w e^- & nuclei brings the energy of the system lower & bring nuclei closer

Due to repulsive forces, as the nuclei approach each other, total energy decreases

Hence, ψ^-_{MO} with depleted electron density than ϕ_{1s} is expected to have higher energy –

$$E_{\psi^-_{MO}} > E_{H_A} = E_{H_B}$$

- ★ Consecutively, from figure (1) we see that, in between H_A and H_B,

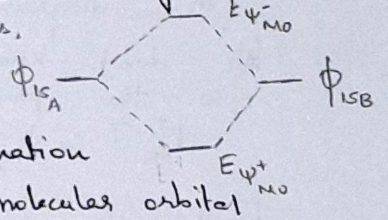
$$\psi^+_{MO} > \phi_{1s_A} = \phi_{1s_B}$$

$$\Rightarrow |\psi^+_{MO}|^2 > |\phi_{1s_A}|^2 = |\phi_{1sB}|^2$$

$\Rightarrow$ Electron density between H_A and H_B is higher. Hence for a constant R_{AB},

~~*~~ $$E_{\psi^+_{MO}} < E_{H_A} = E_{H_B}$$

Represented as,



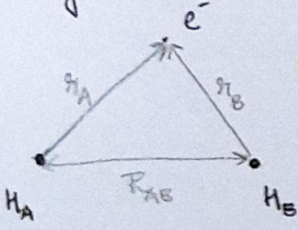
- ★ Here, the dashed lines indicate LCAO – that molecular orbitals are a linear combination of atomic orbitals. Here, ψ^+_{MO} : Bonding molecular orbital
  ψ^-_{MO} : Anti-bonding molecular orbital

But these are still only trial functions. To validate them, we have to solve the Schrödinger Equation –

$$\hat{H}\psi^+_{MO} = E_{\psi^+_{MO}}\psi^+_{MO} \quad \text{and} \quad \hat{H}\psi^-_{MO} = E_{\psi^-_{MO}}\psi^-_{MO}$$

Hydrogen Molekular ion : H_2^+

Its the simplest molekular system – H_2 molecule after ionisation of an electron. [~~It~~ It's experimental bond length & dissociation energies are known]



$$\hat{H} = \underbrace{\frac{-\hbar^2}{2M}(\nabla_A^2 + \nabla_B^2)}_{\text{Kinetic energy of the nucleus}} - \frac{\hbar^2}{2m_e}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0 r_A} - \frac{e^2}{4\pi\varepsilon_0 r_B} + \underbrace{\frac{e^2}{4\pi\varepsilon_0 R_{AB}}}_{\text{Repulsion due to 2 nuclei}}$$

M: Mass of Nucleus

Atomic orbitals have only one nucleus; but there are at least two in molecular orbitals, hence there's an R_{AB} term. As the masses of nuclei are much heavier than that of electron, their kinetic energy terms can be treated seperately. So the Hamiltonian becomes –

$$\hat{H} = -\frac{\hbar^2}{2m_e}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0 r_A} - \frac{e^2}{4\pi\varepsilon_0 r_B} + \frac{e^2}{4\pi\varepsilon_0 R_{AB}}$$

$$\hat{H} = \frac{1}{2}\nabla^2 - \frac{1}{r_A} - \frac{1}{r_B} + \frac{1}{R_{AB}}$$ — in atomic unit

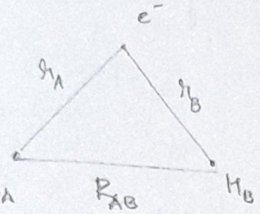
This approximation after neglecting nuclear motion is called Born-Oppenheimer approximation. It works very well for estimating energies & properties of molecules.

To calculate energies at different values of R_{AB}, $\hat{H}\Psi = E\Psi$ has to be solved for each value of R_{AB}

By applying variation method, we can calculate energy and then compare it with experimental data.

NOTE 06

Lecture – H_2^+ ion.



From LCAO, $\psi_{MO} = c_1\phi_{1s_A} + c_2\phi_{1s_B}$

As the probabilities of ϕ_{1s_A} & ϕ_{1s_B} are the same, & they are dependent on square of coefficients $\Rightarrow c_1^2 = c_2^2$

$\therefore c_1 = c_2 = c.$

$\therefore \psi_{MO} = c\left[\phi_{1s_A} \pm \phi_{1s_B}\right]$ With this, we could solve the Hamiltonian.

Find c by – $\int |\psi_{MO}|^2 d\tau = 1$: for c to have the probability interpretation

But if we insist that the coefficients be different, then we solve $\hat{H}\psi_{MO} = E\psi_{MO}$ to obtain c_1 and c_2. And we would get them to be the same : $c_1 = \pm c_2$

So, we continue with the practical choice. –

$$\int |\psi_{MO}|^2 d\tau = 1 \Rightarrow c^2 \int (\phi_{1s_A} + \phi_{1s_B})(\phi_{1s_A} + \phi_{1s_B})\, d\tau = 1$$

$$\Rightarrow c^2\left[\underbrace{\int \phi_{1s_A}\phi_{1s_A}\, d\tau}_{=1} + \underbrace{\int \phi_{1s_{AB}}\phi_{1s_B}\, d\tau}_{=1} + 2\int \phi_{1s_A}\phi_{1s_B}\, d\tau\right] = 1$$

ϕ_{1s_A} and ϕ_{1s_B} are two orbitals centered around two different nuclei. The last term cannot go to zero. Its called the Two-centre, one-electron integral or the overlap integral ; S_{AB}

Calculated usually with an elliptical coordinate system.

Obviously, $S_{AA} = S_{ABB} = 1$

From the previous equation –

$$c^2\left[2 + 2S_{AB}\right] = 1 \Rightarrow \therefore c_1^+ = \frac{1}{\sqrt{2(1+S_{AB})}}$$

For the wavefunction : $\psi_{MO}^- = c_1^-\left[\phi_{1s_A} - \phi_{1sB}\right]$

Then, $c_1^- = \dfrac{1}{\sqrt{2(1-S_{AB})}}$

We'll do the rest of calculation for ψ_{MO}^+ given by –

$$\psi_{MO}^+ = \frac{1}{\sqrt{2(1+S_{AB})}}\left[\phi_{1sA} + \phi_{1sB}\right]$$

$$\langle E\rangle_{\psi_{MO}^+} = \int \psi_{MO}^+ \hat{H} \psi_{MO}^+ \, d\tau \quad \text{where } \hat{H} = \frac{-\hbar^2}{2m_e}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0}\left[\frac{1}{r_A} + \frac{1}{r_B} - \frac{1}{R_{AB}}\right]$$

$$\therefore \langle E\rangle_{\psi_{MO}^+} = \frac{1}{2(1+S_{AB})}\int\left[\phi_{1sA} + \phi_{1sB}\right] \times \left(\frac{-\hbar^2}{2m_e}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0}\left\{\frac{1}{r_A} + \frac{1}{r_B} - \frac{1}{R_{AB}}\right\}\right)(\phi_{1sA} + \phi_{1sB})\, d\tau$$

We will ~~to~~ look at the terms seperately –

- $\displaystyle\int \phi_{1s_A}\left[\frac{-\hbar^2}{2m_e}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0 r_A}\right]\phi_{1sA}\, d\tau = E_{1s}$ → KE & PE of electron wrt nucleus A. This is the ground state energy for electron in 1s orbital of atom A.
- $\displaystyle\int \phi_{1sA}\left(\frac{-e^2}{4\pi\varepsilon_0 r_B}\right)\phi_{1sA}\, d\tau = J$: Coulumb integral
- $\displaystyle\int \phi_{1s_A}\left(\frac{e^2}{4\pi\varepsilon_0 R_{AB}}\right)\phi_{1s_A}\, d\tau = \frac{e^2}{4\pi\varepsilon_0 R_{AB}}$
- $\displaystyle\int \phi_{1s_A}\left(\frac{-\hbar^2}{2m_e}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0 r_A}\right)\phi_{1s_B}\, d\tau = E_{1s}\cdot S$
- $\displaystyle\int \phi_{1s_A}\left(\frac{-e^2}{4\pi\varepsilon_0 r_B}\right)\phi_{1s_B}\, d\tau = K$: Exchange integral.
- $\displaystyle\int \phi_{1s_A}\left(\frac{e^2}{4\pi\varepsilon_0 R_{AB}}\right)\phi_{1s_B}\, d\tau = \frac{e^2}{4\pi\varepsilon_0 R_{AB}}\cdot S$

This is when we start with ϕ_{1s_A} ; we will get identical terms when we repeat this with ϕ_{1s_B}.

Hence, the simplified expression is –

$$\langle E\rangle_{\psi_{MO}^+} = \frac{1}{\cancel{2}(1+S)}\,\cancel{2}\left\{\left(E_{1s} + \frac{e^2}{4\pi\varepsilon_0 R_{AB}}\right)(1+S) + J + K\right\}$$

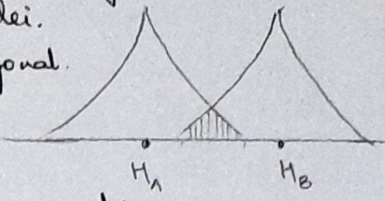
$$\therefore E_{\pm} = \underbrace{E_{1s}}_{\text{H-atom energy}} + \underbrace{\frac{e^2}{4\pi\varepsilon_0 R_{AB}}}_{\text{Proton - proton repulsion}} + \underbrace{\frac{J \pm K}{1 \pm S}}_{\text{Bonding energy}}$$

Explanations and Implications —

From Chem Libre texts → S, J, K used in other places
Dont get confused with

01. Overlap Integral : $S = \int \phi_{1S_A} \phi_{1S_B} \, d\tau$

- * We get a reasonable value of S only where ϕ_{1S_A} and ϕ_{1S_B} have considerable values i.e only in the regions where they overlap — middle part b/w nuclei.
- * If $S = 0$, then the functions are orthogonal.
- * The value of S ranges from 0 to 1 as the distance between nuclei varies from $R = \infty$ to $R = 0$., because when nuclei come closer, the overlap increases —



$$S(R_{AB}) = e^{-R_{AB}}\left(1 + R_{AB} + \frac{R_{AB}^2}{3}\right)$$: Positive quantity

02. Coulumb Integral : $J = \int \phi_{1S_A} \left(\frac{-e^2}{4\pi\varepsilon_0 r_B}\right) \phi_{1S_A} \, d\tau$

It gives the potential energy of charge density around proton A — essentially, it accounts for the attraction of proton B to the electron density of A. (hence, its a negative quantity). At infinite seperation ($R = \infty$), the value of J tends to 0.

$$J(R_{AB}) = e^{-2R_{AB}}\left(1 + 1/R_{AB}\right) - 1/R_{AB}$$ ⇒ Negative term

03. Exchange Integral : $K = \int \phi_{1S_A} \left(\frac{-e^2}{4\pi\varepsilon_0 r_B}\right) \phi_{1S_B} \, d\tau$

It is the potential energy due to interaction of overlap charge density with one of the protons. It accounts for the added attraction of proton due to the build up of electron charge density between the two protons

$$K(R_{AB}) = -e^{-R_{AB}}\left(1 + R_{AB}\right)$$ ⇒ Negative term

---

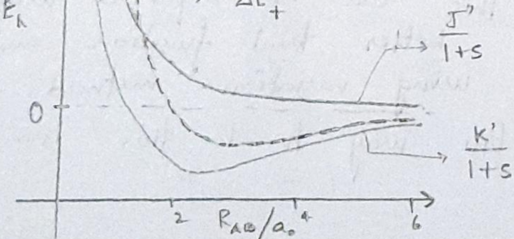
Difference in two-energy states —

$$\Delta E_\pm = E_\pm - E_H = \overset{ⓐ}{\frac{e^2}{4\pi\varepsilon_0 R_{AB}}} + \overset{ⓑ}{\frac{J \pm K}{1 \pm S}}$$

To get a chemical bond, & a stable H_2^+, $\Delta E_\pm$ must be less than zero & have a minimum ⓑ term to overcome the positive repulsive energy given by ⓐ term.

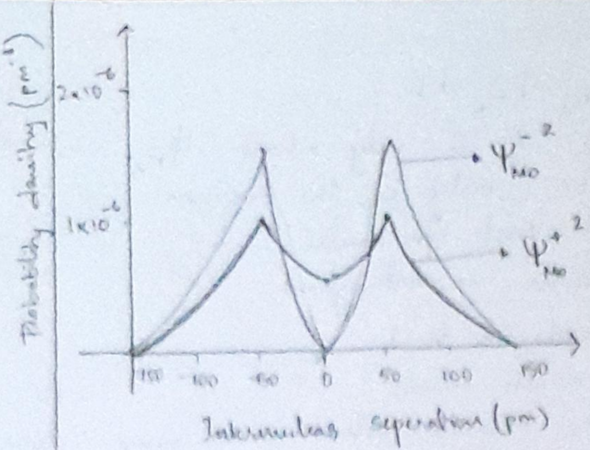
Say, $K' = K + \frac{S}{R_{AB}}\left(\frac{e^2}{4\pi\varepsilon_0}\right)$ $J' = J + \frac{1}{R_{AB}}\left(\frac{e^2}{4\pi\varepsilon_0}\right)$ ⇒ $\Delta E_\pm = \frac{J' \pm K'}{1 \pm S}$

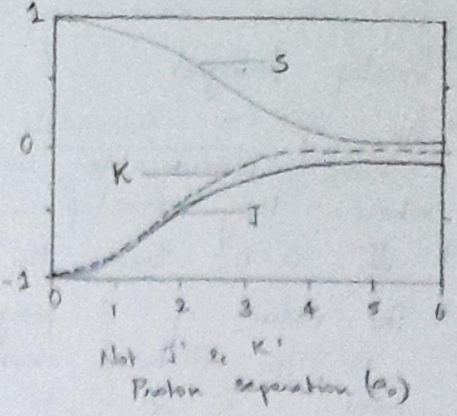
$$\Delta E_+ = \frac{J'}{1+S} + \frac{K'}{1+S}$$



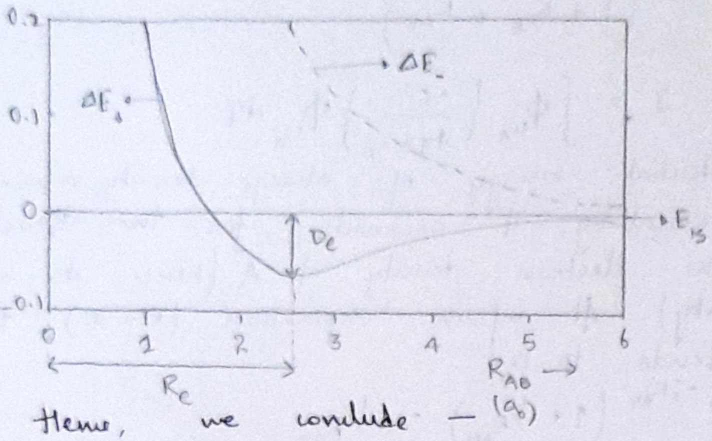
The plot shows that K' is responsible for the bond in H_2^+. Since K' is a quantum mechanical phenomena, results highlight that chemical bond is quantum mechanical in nature

⑫





Potential Energy Surface



$\Delta E_- > 0$ $\Delta E_+ < 0$

$\Rightarrow E_{\psi^-_{MO}} > E_{1s}$ & $E_{\psi^+_{MO}} < E_{1s}$

D_e : Bond dissociation energy

R_e : Bond length.

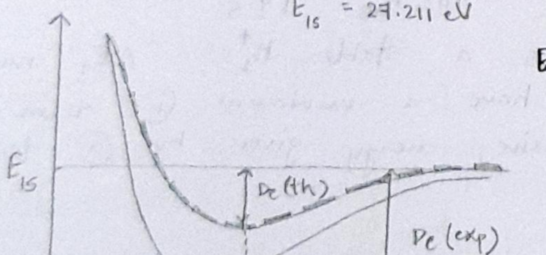
Hence, we conclude —

Bonding orbital	Antibonding orbital
$\psi^+_{MO} = \frac{1}{\sqrt{2(1+S)}}\left[\phi_{1s_A} + \phi_{1s_B}\right]$	$\psi^-_{MO} = \frac{1}{\sqrt{2(1-S)}}\left[\phi_{1s_A} - \phi_{1s_B}\right]$
$E_{\psi^+_{MO}} = E_{1s} + \frac{J' + K'}{1+S}$	$E_{\psi^-_{MO}} = E_{1s} + \frac{J' - K'}{1-S}$

D_e is the energy required to dissociate the bond.
R_e is the distance R_{AB} at which energy of ψ^+_{MO} is minimum — called the bond length.

Comparing Values.

$E_{1s} = 27.211$ eV



	D_e	R_e
Theory	$0.0648 E_{1s}$	$2.5 a_0 = 1.32$ Å
Experiment	$0.102 E_{1s}$	$2.0 a_0 = 1.06$ Å

This is using the trial function we've used and we get a significant difference in values. This can be improved using a better trial function and using variation method.

One way to do this is —

In our selection of $\psi^{\pm}_{MO}$ and ϕ_{1s}, we have assumed that $Z = 1$. But this need not be true. We've learnt that : $E_{exp} < E_{\psi^+_{MO}}$.

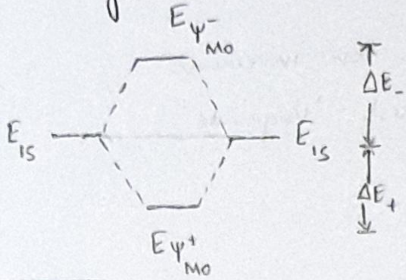
So, keeping Z as a variable, we can minimise $E_{\psi^+_{MO}}$ till we get acceptable values i.e. mathematically,

$$\frac{d\left(E_{\psi^+_{MO}}\right)}{dZ} = 0$$

This will improve the agreement b/w experimental and theoretical value of R_e & D_e

Eventually, the best possible trial function, LCAO Molecular Orbitals give R_e & D_e very close to exptl values.

Thus, MOT and Experimental results are in very close agreement with one another.



$\Delta E_- = E_{\psi^-_{MO}} - E_{1s}$

$\Delta E_+ = E_{\psi^+_{MO}} - E_{1s} = D_e$ (at $R_{AB} = R_e$)

NOTE 07

Shapes of orbitals

1s orbital of H-atom is spherical in shape ∵ all positive values of ϕ_{1s_A}.

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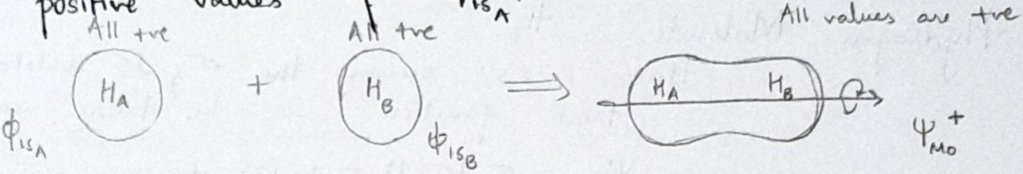

1s orbitals of isolated H-atoms

Bonding molecular orbital

Internuclear axis : connects the two nuclei by a straight line. If we rotate ψ^+_{MO} wrt it, then it doesn't change.

σ Orbital : It is symmetric about the internuclear axis and the chemical bond is termed σ bond.

So, $\psi^+_{MO} = \psi_b = \sigma 1s$

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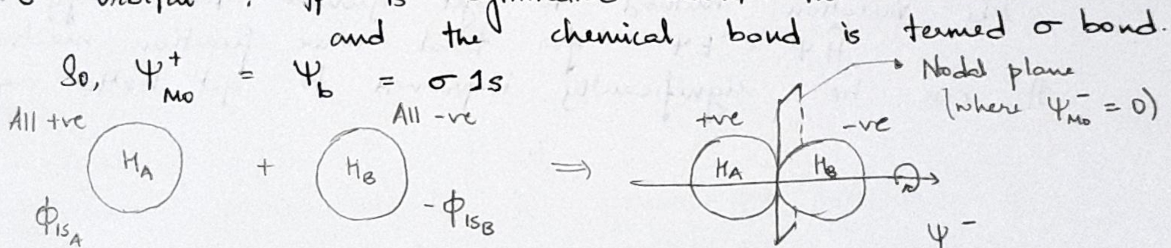


The antibonding orbital is also symmetric about the interdnuclear axis.

$\Rightarrow \psi^-_{MO} = \psi_a = \sigma 1s$

One way to distinguish between them –

$\psi_b = \sigma 1s$ $\qquad \psi_a = \sigma^* 1s$

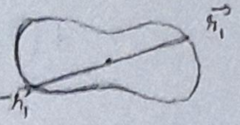
A more scientific method of classification is to use the symmetry of two orbitals –

→ For ψ_b

Here, all values are positive, which means –

$$\psi_b(r_1) = +\psi_b(-r_1) \quad \text{or} \quad \psi_b(x, y, z) = \psi_b(-x, -y, -z)$$

This is called Inversion Symmetry

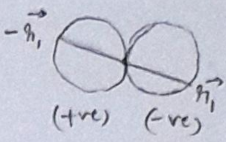


So, ψ_b has an inversion point midway between the two nuclei. Molecular orbitals that have inversion symmetry are called 'Gerade' [German: even] and are denoted by 'g'.

$$\therefore \psi_b = \sigma_g 1s.$$

→ For ψ_a

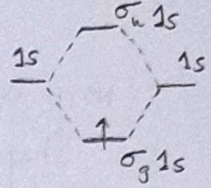
Here, the function changes sign on inversion. Such molecular orbitals are called 'Ungerade' [German: odd] & denoted as 'u'



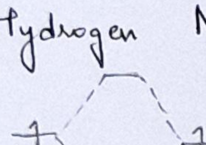
i.e. $\psi_a(r_1) = -\psi_a(-r_1)$

$$\therefore \psi_a = \sigma_u 1s$$

Therefore, the representation for H_2^+ ion is :



Hydrogen Molecule : H_2



Here 2 e^-s occupy the $\sigma_g 1s$ orbital. So, trial function can be taken as –

$$\psi_b = \sigma_g 1s\,\overset{\text{electron 1}}{(1)}\;\sigma_u 1s\,\overset{\text{electron 2 ?}}{(2)} \cdot \phi_s$$

ϕ_s is the spin part of total wavefunction

Here, $\sigma_g 1s = \psi^+_{MO}$ and $\sigma_u 1s = \psi^-_{MO}$

Since there are 2 electrons, we use approximation methods like Variation method to get ground state energy for $\hat{H}\psi = E\psi$ for trial wave function mentioned.

It can be significantly improved to get better agreement.