Why study quantum mechanics?

QM pervades all of chemistry. The basis for

- the Periodic Table
- atomic and molecular spectra
- chemical bonding (structure and reactivity)
- chemical kinetics
- energies (zero-point, ionization, activation, bond energies)

Even mass spectroscopy which on its face appears to be strictly classical physics: charged particles moving in circular paths in a magnetic field, yet fragmentation patterns, ionization energies (thresholds for production of particular ions) all have basis in QM.

QM can be used at various levels: Some calculations are so big, that approximations still have to be used even in this age of computers. Some consequences and examples are very simple and transparent.

As in all other areas of science, we sometimes will use model systems which are simple and exactly solvable, and which illustrate the principles of QM more clearly (since we can do the math with pencil and paper) than real systems do. Examples of these are the particle in a one-dimensional box (or the particle that lives on a straight line), the particle that lives on a ring, the rigid rotor, the harmonic oscillator, the non-relativistic hydrogen atom. Your first problem set uses two model systems: the electron that lives on a ring and the electron that lives on a straight line in order to provide a simple physical understanding and predictions of the trends in the UV-Vis spectra observed for catacondensed aromatic hydrocarbons and conjugated “linear” hydrocarbons. An electron that lives on a helical line has been used to derive the fundamental characteristics and consequences of handedness on spectra, and in fact provides, in the 1 August 2003 issue of the Journal of Chemical Physics, a very good model system that is solvable in closed form for the determination of the fundamental relationship between chirality and the NMR chemical shift tensor.

1. INTRODUCTION TO QUANTUM MECHANICS

1.1 The Postulates of Quantum Mechanics

1.1.1 Operators

1.1.2 Eigenvalues

1.1.3 Example: Application to Particle on a Ring

1.1.4 Example: Application to Particle on a Line

1.1.5 Separability of a Problem: Method of Separation of Variables

1.1.6 Expectation Values

POSTULATES of QUANTUM MECHANICS

Postulate zero: Definition

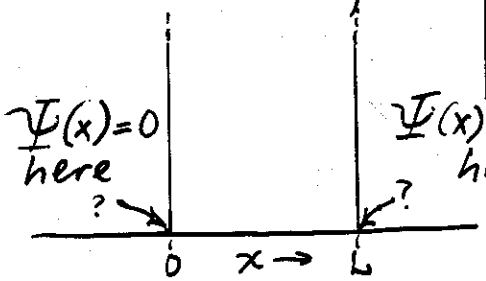
The state of a physical system is a function Ψ of variables such as coordinates, momenta, time, a function from which, by the rules of quantum theory, significant information about the physical system can be obtained.

Ψ is defined to be "well-behaved", i.e.

- a) Ψ (and its first derivative) must be single-valued, continuous, and finite.

For example: $\Psi(\alpha) = \Psi(\alpha + 2n\pi)$ for all integers

"single-valued"



$\Psi(0) = 0$, $\Psi(L) = 0$ } "continuous"

e^{+x} is not acceptable "finite" where x is a Cartesian coordinate

- b) Ψ must be "quadratically integrable"

i.e., $\left| \int \Psi^* \Psi \, d\tau \right| < \infty$

* means COMPLEX CONJUGATE

Ψ is said to be normalized if,

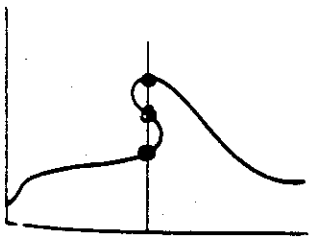
$$\int_{\tau} \Psi^* \Psi \, d\tau = 1$$

FOR THIS TO HOLD BOTH Ψ and its FIRST DERIVATIVE MUST VANISH AT INFINITY

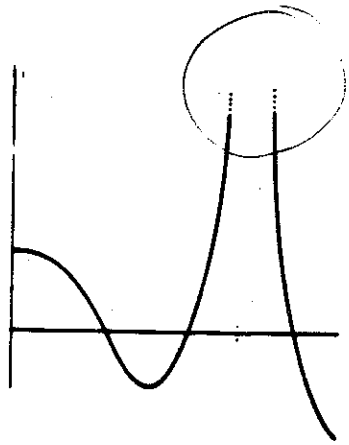
$d\tau$ volume element in configuration space

$d\tau = dx\,dy\,dz$ for one particle

$d\tau = dx_1\,dy_1\,dz_1\,dx_2\,dy_2\,dz_2$ for two particles

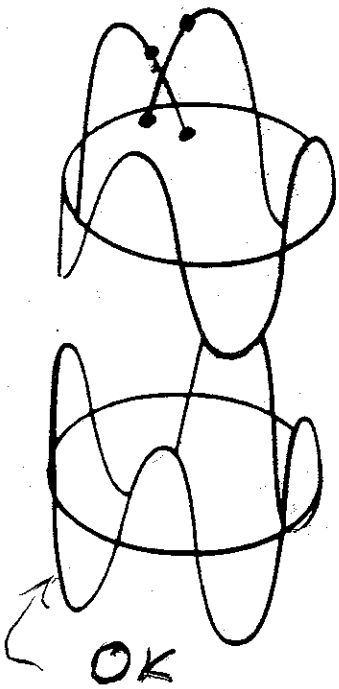


NOT SINGLE-VALUED

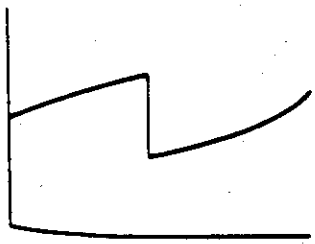


NOT FINITE

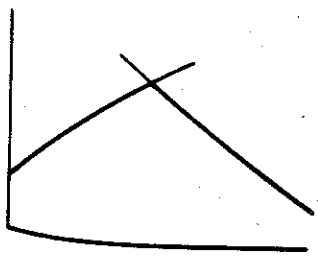
NOT SINGLE-VALUED



OK
WELL-BEHAVED



DISCONTINUOUS



DISCONTINUOUS DERIVATIVE

Postulate one: OPERATORS

To every OBSERVABLE there corresponds an OPERATOR.

An OBSERVABLE is a physically measurable quantity.

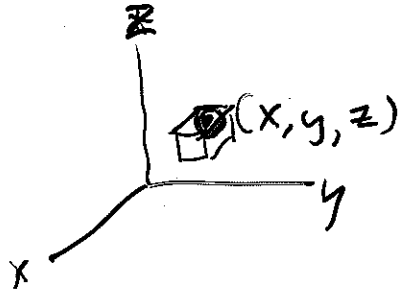
The RULES for generating the correct mathematical OPERATORS from the CLASSICAL MECHANICAL ANALOG are:

OBSERVABLE	CLASSICAL-MECHANICAL DYNAMICAL VARIABLE	QUANTUM MECHANICAL OPERATOR
Cartesian coordinate of ith particle	x_i	x_i
LINEAR MOMENTUM x component of for ith particle	$(P_x)_i = m_i \dot{x}_i$	$\frac{\hbar}{i}\frac{\partial}{\partial x_i}$
vector	$\vec{P}$	$\frac{\hbar}{i}\vec{\nabla}_i$ GRADIENT
KINETIC ENERGY	$T = \sum_i \frac{P_i^2}{2m_i}$	$\sum_i \frac{-\hbar^2}{2m_i}\nabla_i^2$ LAPLACIAN
		$\nabla_i^2 \equiv \frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2}$
TOTAL ENERGY E of a single mass point in a potential V	$H = \frac{P^2}{2m} + V$	$H = \frac{-\hbar^2}{2m}\nabla^2 + V$ HAMILTONIAN
TOTAL ENERGY, EXPLICITLY time-DEPENDENT SYSTEM	H	$i\hbar\frac{\partial}{\partial t}$

Above examples refer to systems which are classically described as groups of mass points having $3N$ degrees of freedom, subject to NO EXTERNAL FORCES and not requiring RELATIVISTIC TREATMENT.

The Laplacian in various coordinate systems

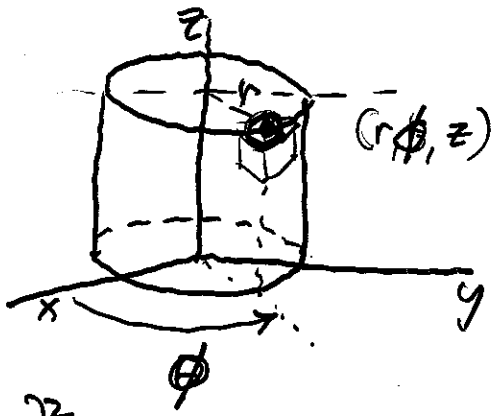
CARTESIAN



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

$$d\tau = dx\,dy\,dz \qquad x = -\infty \text{ to } +\infty, \quad y = -\infty \text{ to } +\infty, \quad z = -\infty \text{ to } +\infty$$

CYLINDRICAL



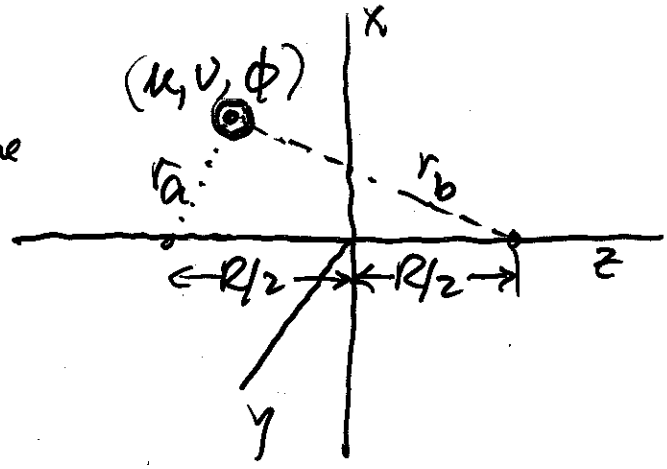
$r = 0$ to ∞
$\phi = 0$ to 2π
$z = -\infty$ to $+\infty$

$x = r\cos\phi$
$y = r\sin\phi$
z

$$d\tau = r\,dr\,d\phi\,dz$$

$$\nabla^2 = \frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial}{\partial r}\right) + \frac{1}{r^2}\frac{\partial^2}{\partial \phi^2} + \frac{\partial^2}{\partial z^2}$$

ELLIPTICAL



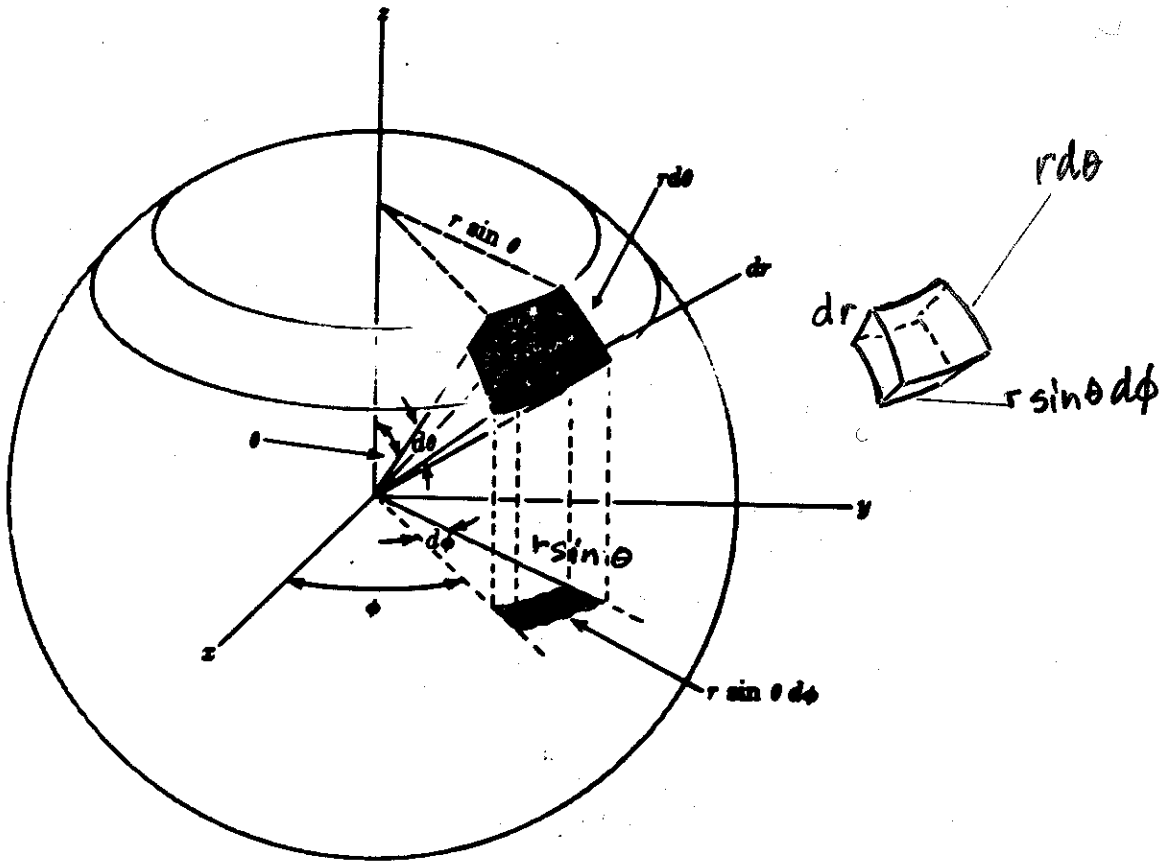
ϕ measured from x z plane

$$u = \frac{r_a + r_b}{R}, \quad v = \frac{r_a - r_b}{R}, \quad \phi$$

$$d\tau = \frac{R^2}{8}(u^2 - v^2)\,du\,dv\,d\phi$$

$u = 1$ to ∞
$v = -1$ to $+1$
$\phi = 0$ to 2π

$$\nabla^2 = \frac{4}{R(u^2 - v^2)}\left[\frac{\partial}{\partial u}\left\{(u^2-1)\frac{\partial}{\partial u}\right\} + \frac{\partial}{\partial v}\left\{(1-v^2)\frac{\partial}{\partial v}\right\} + \frac{u^2 - v^2}{(u^2-1)(1-v^2)}\frac{\partial^2}{\partial \phi^2}\right]$$



$$r = 0 \text{ to } \infty$$
$$\phi = 0 \text{ to } 2\pi$$
$$\theta = 0 \text{ to } \pi$$

$$d\tau = dx\,dy\,dz$$
$$= r^2\,dr\,\sin\theta\,d\theta\,d\phi$$

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

SPHERICAL POLAR

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}$$

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Postulate two: EIGENVALUES

The **ONLY** possible values which a **SINGLE MEASUREMENT** of an observable associated with an OPERATOR S_{op} can yield, are the EIGENVALUES s of the equation:

$$S_{op}\psi = s\psi$$

In general, the operator equation can be satisfied by a number (often, an infinite number) of different solutions:

$$S_{op}\psi_\lambda = s_\lambda \psi_\lambda$$

OPERATOR — EIGENFUNCTION — EIGENVALUE

A particularly important eigenvalue equation is that for the ENERGY, which is called the **SCHRÖDINGER EQUATION.**
For a single mass point:

CLASSICAL ENERGY $H = T + V = \frac{1}{2m}(p_x^2 + p_y^2 + p_z^2) + V(x,y,z)$

SCHRÖDINGER EQUATION:

$$H_{op}\psi_\lambda(x,y,z) = \left\{\frac{-\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) + V(x,y,z)\right\}\psi_\lambda(x,y,z) = E_\lambda \psi_\lambda(x,y,z)$$

in VECTOR NOTATION:

$$\left\{\frac{-\hbar^2}{2m}\nabla^2 + V(\vec{r})\right\}\psi_\lambda(\vec{r}) = E_\lambda \psi_\lambda(\vec{r})$$

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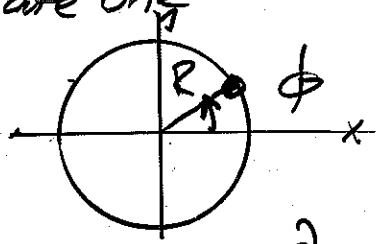
EXAMPLE: Application of Postulates zero, one, and two to A PARTICLE on a RING (CIRCLE)

$$H = -\frac{\hbar^2}{2M}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right)$$ Postulate one



Can adopt polar coordinates

$x = R\cos\phi \qquad y = R\sin\phi$

Since R = constant for a circle, drop $\frac{\partial}{\partial R}$ in

$$\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} = \frac{\partial^2}{\partial R^2} + \frac{1}{R}\frac{\partial}{\partial R} + \underline{\frac{1}{R^2}\frac{\partial^2}{\partial \phi^2}}$$

leaving $$H = \frac{-\hbar^2}{2M}\underline{\frac{1}{R^2}\frac{d^2}{d\phi^2}}$$

The observable energies are the EIGENVALUES of the Schrödinger equation:

$$H\Psi(\phi) = E\Psi(\phi)$$

Postulate two

$$\frac{-\hbar^2}{2MR^2}\frac{d^2}{d\phi^2}\Psi(\phi) = E\Psi(\phi)$$

Solutions are: $\Psi(\phi) = Ae^{im\phi}$ where A and m are unknown constants (independent of ϕ)

$\Psi(\phi) = \Psi(\phi + 2\pi)$ SINGLE-VALUED Postulate zero

That is, $Ae^{im\phi} \overset{\text{MUST}}{=} Ae^{im(\phi+2\pi)} = Ae^{im\phi}\cdot e^{im2\pi}$

$e^{im2\pi} \equiv \cos m2\pi + i\sin m2\pi$ ← MUST BE 1

CAN ONLY BE 1 if m is ZERO or ± INTEGER

Normalization: Postulate zero

$$\int_0^{2\pi} \Psi^*_{(\phi)}\, \Psi(\phi)\, d\phi = 1$$

$$\int_0^{2\pi} A^* e^{-im\phi} \cdot A e^{im\phi}\, d\phi = 1$$

$$|A^2| \int_0^{2\pi} d\phi = 1 \qquad \therefore A = \frac{1}{\sqrt{2\pi}}$$

$$\Psi_m(\phi) = \frac{1}{\sqrt{2\pi}} e^{im\phi} \qquad m = 0, \pm 1, \pm 2, \pm 3, \ldots$$

Then: Substitute the function $\Psi(\phi)$ into the Schrödinger equation to find **EIGENVALUES** for ENERGY:

$$-\frac{\hbar^2}{2MR^2} \underbrace{\frac{d^2}{d\phi^2}\left(\frac{1}{\sqrt{2\pi}} e^{im\phi}\right)}_{\frac{1}{\sqrt{2\pi}}(im)^2 e^{im\phi}} = E\left(\frac{1}{\sqrt{2\pi}} e^{im\phi}\right)$$

$$E = \frac{m^2\hbar^2}{2MR^2}$$

$E = \frac{3^2\hbar^2}{2MR^2}$ $m = +3$ ——— ——— -3 . . . and so on

$\Psi_{+2}(\phi) = \frac{e^{i2\phi}}{\sqrt{2\pi}}$ $\Psi_{-2}(\phi) = \frac{e^{-i2\phi}}{\sqrt{2\pi}}$

$E = \frac{2^2\hbar^2}{2MR^2}$ $m = +2$ ——— ——— -2

$E = \frac{1^2\hbar^2}{2MR^2}$ $m = +1$ ——— ——— -1

$\Psi_0(\phi) = \frac{1}{\sqrt{2\pi}}$ $E = 0$ $m = 0$ ———

Two states are said to be **DEGENERATE** if **same eigenvalue, different states** i.e. **different EIGENFUNCTIONS**

Example:

$$E_{m=1} = \text{eigenvalue} = \frac{l^2\hbar^2}{2MR^2} \qquad \Psi_{m=+1}(\phi) = \frac{e^{i\phi}}{\sqrt{2\pi}}$$

$$E_{m=-1} = \frac{l^2\hbar^2}{2MR^2} \qquad \Psi_{m=-1}(\phi) = \frac{e^{-i\phi}}{\sqrt{2\pi}}$$

same eigenvalue — different eigenfunctions

Both eigenfunctions satisfy the Schrödinger equation

$$-\frac{\hbar^2}{2M}\frac{1}{R^2}\frac{d^2}{d\phi^2}\Psi(\phi) = E\Psi(\phi)$$

$$\Psi_{+1}(\phi) = \frac{e^{i\phi}}{\sqrt{2\pi}}$$

or $$\Psi_{-1}(\phi) = \frac{e^{-i\phi}}{\sqrt{2\pi}}$$

$\hat{O}\psi_a = E_1\psi_a \qquad \hat{O}\psi_b = E_1\psi_b$

$\hat{O}(c'\psi_a + c''\psi_b) = ?$

(c', c'': any numbers)

$= c'\underbrace{\hat{O}\psi_a}_{E_1\psi_a} + c''\underbrace{\hat{O}\psi_b}_{E_1\psi_b}$

$= c'E_1\psi_a + c''E_1\psi_b$

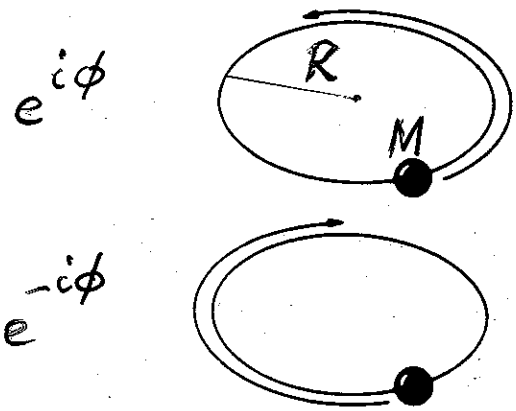
$\hat{O}(c'\psi_a + c''\psi_b) = E_1\{c'\psi_a + c''\psi_b\}$

$(c'\psi_a + c''\psi_b)$: also an eigenfunction of $\hat{O}$ with eigenvalue E_1

Happens because E_1 can be factored out

WAVE FUNCTIONS FOR A PARTICLE ON A RING

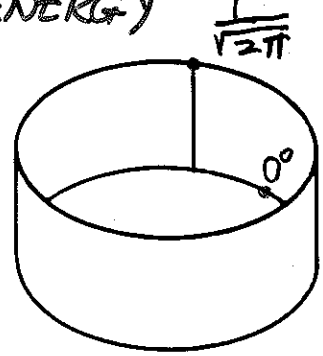
EIGENFUNCTIONS of ENERGY



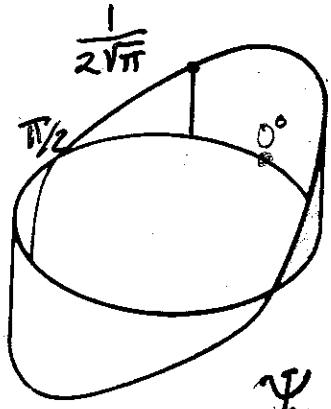
$$\Psi_m(\phi) = \frac{1}{\sqrt{2\pi}} e^{im\phi}$$ COMPLEX FORM

$$E_m = \frac{m^2\hbar^2}{2MR^2}$$

$$m = 0, \pm 1, \pm 2, \ldots$$



$\Psi_0(\phi)$



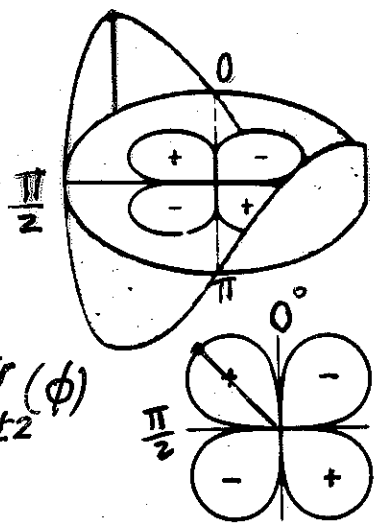
$\Psi_{\pm 1}(\phi)$

$$\Psi_{REAL} = \frac{\Psi_{+1}(\phi) + \Psi_{-1}(\phi)}{\sqrt{2}} = \frac{1}{\sqrt{\pi}}\cos(\phi)$$

REAL FUNCTIONS

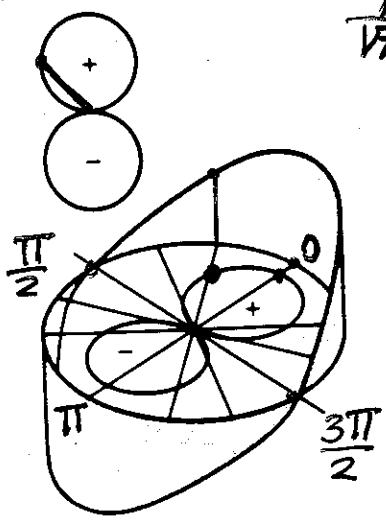
OR

$$= \frac{\Psi_{+1}(\phi) - \Psi_{-1}(\phi)}{\sqrt{2}} = \frac{1}{\sqrt{\pi}}\sin(\phi)$$



$\Psi_{\pm 2}(\phi)$

$$\frac{1}{\sqrt{\pi}}\sin 2\phi$$



$\Psi_{\pm 1}(\phi)$

$$\frac{1}{\sqrt{\pi}}\cos\phi$$

Note $\Psi(\phi = 45°)$ value in each case

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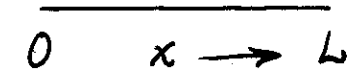
EXAMPLE: PARTICLE on a LINE

$V(x) = 0$ for $0 \le x \le L$

$V(x) = \infty$ for $x < 0$ and $x > L$



Kinetic energy $= \frac{P_x^2}{2M}$

$H_{op} = -\frac{\hbar^2}{2M}\frac{\partial^2}{\partial x^2}$ Postulate 1 (OPERATORS)

$H\Psi(x) = E\Psi(x)$ Postulate 2 Schrödinger eq.

The observable energies are the EIGENVALUES of the equation.

$-\frac{\hbar^2}{2M}\frac{\partial^2}{\partial x^2}\Psi(x) = E\Psi(x)$ or $\frac{d^2}{dx^2}\Psi(x) = -\frac{E2M}{\hbar^2}\Psi(x)$

Solutions are:

$$\Psi(x) = A\sin(kx) + B\cos(kx)$$

where k A and B are unknown constants (independent of x)

$\Psi(x<0) = 0$ $\Psi(x>L) = 0$

Impose the conditions that

$\Psi(x=0) = 0$

$\Psi(x=L) = 0$

Postulate zero (continuous, single-valued)

that is,

at $x=0$ $\quad 0 = A\underbrace{\sin(k\cdot 0)}_{\text{zero}} + B\underbrace{\cos(k\cdot 0)}_{1}$ THEREFORE B must be zero

at $x=L$ $\quad 0 = A\sin(kL) + \cancel{B}^{\text{zero}}\cos(kL)$ can be satisfied by $A=0$, or by $\sin(kL)=0$

$A=0$: NOT POSSIBLE since this will make $\Psi(x)=0$ EVERYWHERE!

$\sin(kL)=0$: HOLDS ONLY for $kL = 0, \pi, 2\pi, \ldots$ or $kL = n\pi$

$n=0$? NOT ALLOWED, makes $\Psi(x)=0$ EVERYWHERE

n negative? DOES NOT LEAD TO A DIFFERENT $\Psi(x)$ SINCE $\sin(-\alpha) = -\sin(\alpha)$

n AN INTEGER!

THUS we find the value of k:

$k = n\pi/L$

Thus, using Postulate ZERO we find

$$\Psi(x) = A\sin\left(\frac{n\pi}{L}x\right) \quad \text{where } n = 1, 2, 3, \ldots$$

Let us substitute this into the Schrödinger equation to find E

$$\frac{d^2}{dx^2}\left(A\sin\left(\frac{n\pi}{L}x\right)\right) = -\frac{E2M}{\hbar^2}\left(A\sin\left(\frac{n\pi}{L}x\right)\right)$$

$$\frac{d}{dx}\, A\frac{n\pi}{L}\cos\left(\frac{n\pi}{L}x\right)$$

$$-A\left(\frac{n\pi}{L}\right)^2\sin\left(\frac{n\pi}{L}x\right) = -\frac{E2M}{\hbar^2}\left(A\sin\left(\frac{n\pi}{L}x\right)\right)$$

Solving for E, $\quad E = \frac{\hbar^2}{2M}\frac{n^2\pi^2}{L^2}$

where $\hbar \equiv \frac{h}{2\pi}$ $\qquad E = \frac{n^2h^2}{8ML^2} \quad n = 1, 2, 3, \ldots$

Normalization of $\Psi(x)$ to find A:

$$\int_0^L \Psi^*(x)\,\Psi(x)\,dx = 1$$

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

$$A^2\left[\frac{1}{2}x - \frac{1}{4\left(\frac{n\pi}{L}\right)}\sin\left(2\,\frac{n\pi}{L}x\right)\right]_0^L = 1$$

$$A^2\frac{L}{2} = 1 \quad \text{or} \quad A = \sqrt{\frac{2}{L}}$$

Therefore, we have

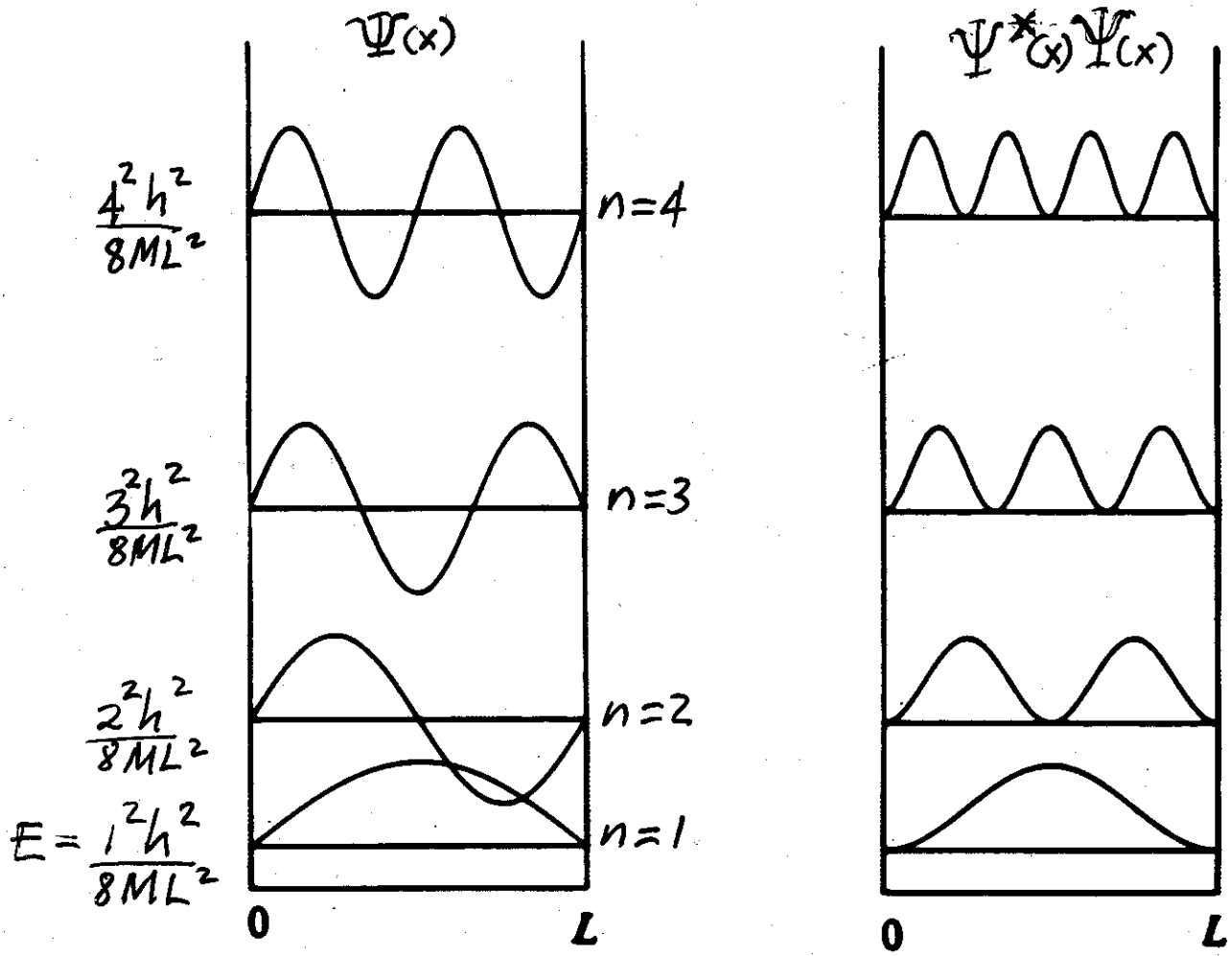
EIGENFUNCTIONS of ENERGY: $\Psi(x) = \left(\frac{2}{L}\right)^{1/2}\sin\left(\frac{n\pi}{L}x\right)$

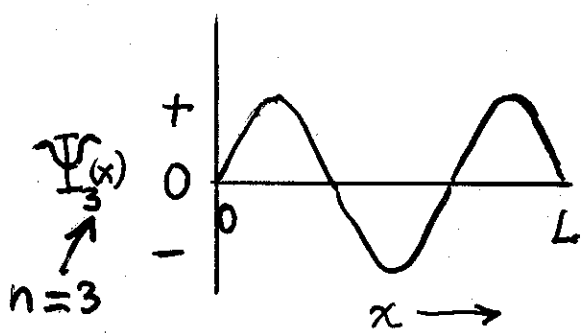
EIGENVALUES of ENERGY: $E = \frac{n^2h^2}{8ML^2} \quad n = 1, 2, 3, \ldots$

For a PARTICLE of mass M on a line of length L (also called a ONE-DIMENSIONAL BOX)

"A PARTICLE in a ONE-DIMENSIONAL BOX"

A PARTICLE CONSTRAINED TO MOVE ON A LINE





$$\Psi_n(x) = \left(\frac{2}{L}\right)^{1/2} \sin\left(\frac{n\pi}{L}x\right)$$

1. INTRODUCTION TO QUANTUM MECHANICS

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SEPARABILITY of a PROBLEM

Method of SEPARATION of VARIABLES

Suppose an operator is separable into two independent parts, for example,

$$H = H(x) + H(y)$$

where x and y are the Cartesian positions of the particle, Then the differential eqn.

$$H\Psi(x,y) = E\Psi(x,y) \text{ where } H = \frac{-\hbar^2}{2M}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right)$$

can be solved by the method of separation of variables:

Let $\Psi(x,y) = F(x)\cdot G(y)$ a function which is a simple PRODUCT

See if it satisfies the eqn:

$$H\Psi(x,y) = [H(x) + H(y)]\,F(x)\cdot G(y) = E\,F(x)\cdot G(y)$$

$$G(y)H(x)\,F(x) + F(x)\cdot H(y)\,G(y) = E\,F(x)\cdot G(y)$$

Divide the equation by $F(x)\cdot G(y)$

$$\frac{G(y)\cdot H(x)\,F(x)}{F(x)\cdot G(y)} + \frac{F(x)\cdot H(y)\,G(y)}{F(x)\cdot G(y)} = E\,\frac{F(x)\cdot G(y)}{F(x)\cdot G(y)}$$

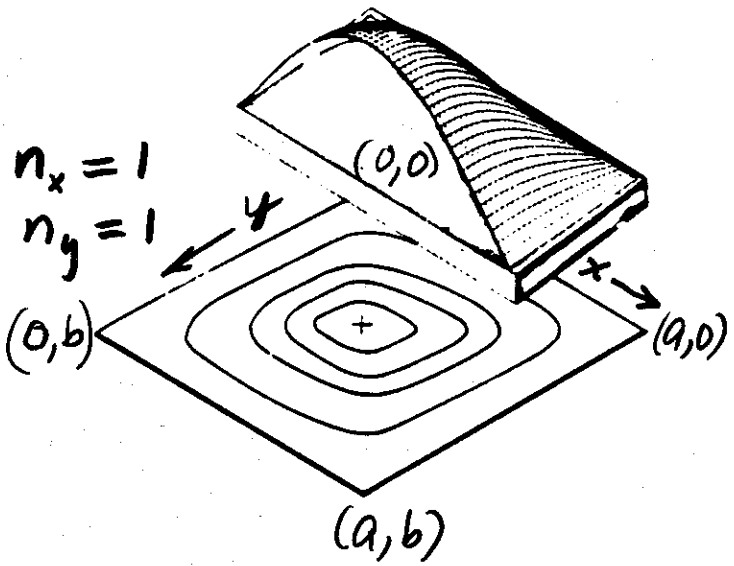
$$\underbrace{\frac{H(x)F(x)}{F(x)}}_{\text{a function only of } x} + \underbrace{\frac{H(y)G(y)}{G(y)}}_{\text{a function only of } y} = E \quad \text{a constant!}$$

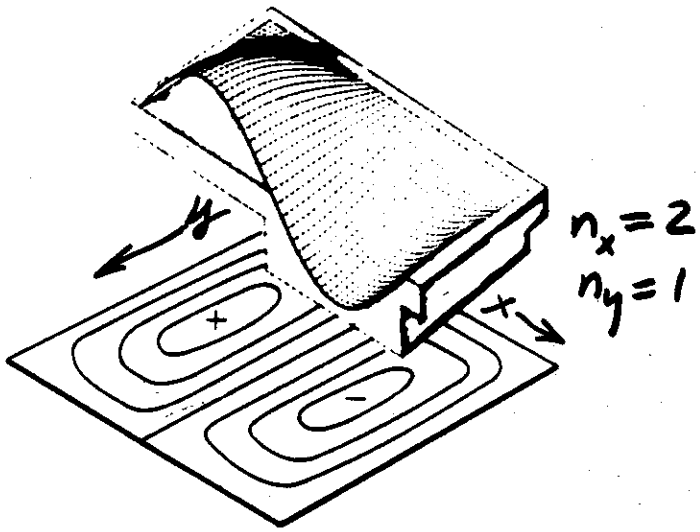
Can only be true for arbitrary x and y if

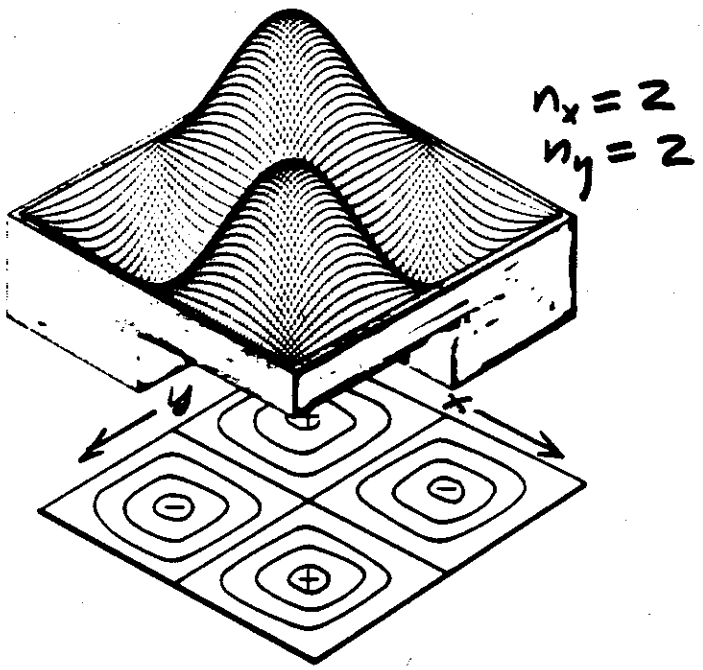
$$\frac{H(x)F(x)}{F(x)} = \text{a constant} \qquad \frac{H(y)G(y)}{G(y)} = \text{a constant}$$

such that $E =$ (constant) + (constant)

A PARTICLE constrained to move on a PLANE or "A PARTICLE in a TWO-DIMENSIONAL BOX"







$$H_{op} = \frac{-\hbar^2}{2M}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right)$$

$$\Psi(x,y) = \left(\frac{2}{a}\right)^{1/2} \sin\left(\frac{n_x \pi}{a} x\right) \cdot \left(\frac{2}{b}\right)^{1/2} \sin\left(\frac{n_y \pi}{b} y\right)$$

$$E = \frac{\hbar^2 n_x^2}{8Ma^2} + \frac{\hbar^2 n_y^2}{8Mb^2}$$

$n_x = 1, 2, 3, \cdots$ $\qquad$ $n_y = 1, 2, 3, \cdots$

This is exactly the same as the problem

$$H = H(x_1) + H(x_2) = \frac{-\hbar^2}{2M}\frac{\partial^2}{\partial x_1^2} \quad \frac{-\hbar^2}{2M}\frac{\partial^2}{\partial x_2^2}$$

where x_1 and x_2 are the positions of particles 1 and 2 respectively. Only the names of variables have been changed.

$$H\Psi(x_1, x_2) = E\Psi(x_1, x_2)$$

The solutions are:

$$\Psi(x_1, x_2) = F(x_1) \cdot G(x_2)$$

which lead to:

$$\underbrace{\frac{H(x_1)F(x_1)}{F(x_1)}}_{\text{a function only of } x_1} + \underbrace{\frac{H(x_2)G(x_2)}{G(x_2)}}_{\text{a function only of } x_2} = E \quad \text{a constant}$$

This is a constant which can be found by solving

$$\frac{H(x_1)F(x_1)}{F(x_1)} = \text{a constant (call it } E_1)$$

$$\frac{-\hbar^2}{2M}\frac{d^2}{dx_1^2}F(x_1) = E_1 F(x_1)$$

$$F(x_1) = \sqrt{\frac{2}{L}}\sin\left(\frac{n_1\pi x_1}{L}\right)$$

$$E_1 = \frac{n_1^2\hbar^2}{8ML^2}$$

$n_1 = 1, 2, 3, \cdots$

$$\frac{-\hbar^2}{2M}\frac{d^2}{dx_2^2}G(x_2) = E_2 G(x_2)$$

$$G(x_2) = \sqrt{\frac{2}{L}}\sin\left(\frac{n_2\pi}{L}x_2\right)$$

$$E_2 = \frac{n_2^2\hbar^2}{8ML^2}$$

$n_2 = 1, 2, 3, \cdots$

IN OTHER WORDS it is EXACTLY THE SAME MATHEMATICAL PROBLEM, only the NAMES have been changed.

1. INTRODUCTION TO QUANTUM MECHANICS

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1.1.6 Expectation Values

Postulate three: EXPECTATION VALUES

If a system is in a state represented by the wavefunction Ψ, then the **AVERAGE** of **A SEQUENCE OF MEASUREMENTS** of an OBSERVABLE S which is associated with the OPERATOR S_{op} is

$$\langle S \rangle = \frac{\int \Psi^* S_{op} \Psi \, d\tau}{\int \Psi^* \Psi \, d\tau}$$

"EXPECTATION VALUE" or "EXPECTED MEAN"

angular brackets signify AVERAGE

where Ψ is **NOT NECESSARILY** an EIGENFUNCTION of S_{op}

EXAMPLE:

one die

EIGENVALUES of S are

$s = 1, 2, 3, 4, 5, 6$

Any **SINGLE MEASUREMENT** of S can yield only these values

A sequence of measurements will give an AVERAGE VALUE $\langle S \rangle = 3.5$ if a fair die (not "loaded") is used.

"loading" ~ how much of each EIGENFUNCTION of S is in Ψ

EXAMPLE:

Consider the expected mean of a series of measurements of x, the EXPECTATION VALUE of x_{op} is, by Postulate three,

$$\langle x \rangle = \frac{\int \Psi^*(x)\, x_{op}\, \Psi(x)\, dx}{\int \Psi^*(x)\, \Psi(x)\, dx}$$

If we let $f(x) \equiv \Psi^*(x)\,\Psi(x)$ we can write the average value as

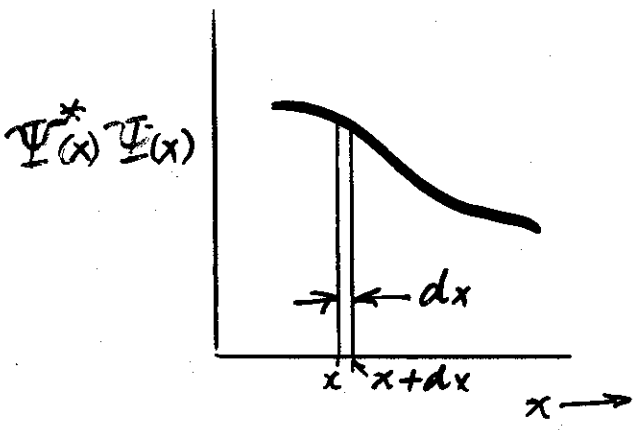
$$\langle x \rangle = \frac{\int x\, f(x)\, dx}{\int f(x)\, dx}$$

THIS is THE USUAL FORMULA OF AN AVERAGE VALUE of x if the PROBABILITY of finding the system in the interval x and $x+dx$ is given by

$$\frac{f(x)\,dx}{\int f(x)\,dx} = 1$$

NORMALIZED PROBABILITY

Thus, we associate $\Psi^*(x)\,\Psi(x)\,dx$ with the PROBABILITY of finding the system in the interval x and $x+dx$



$$\int_{-\infty}^{+\infty} \Psi^*(x)\,\Psi(x)\,dx = 1$$

NORMALIZATION OF PROBABILITY

TOTAL PROBABILITY = 1

The probability of finding the system in the interval x and $x+dx$:

$$\Psi^*(x)\,\Psi(x)\,dx = \frac{2}{L}\sin^2\left(\frac{n\pi}{L}x\right)dx$$

The probability of finding the system in the central third of the "box":

$$\int_{L/3}^{2L/3} \Psi^*(x)\;\Psi(x)\,dx = \frac{2}{L}\left[\frac{x}{2} - \frac{1}{4n\pi/L}\sin\frac{2n\pi}{L}x\right]_{\frac{L}{3}}^{\frac{2L}{3}}$$

The EXPECTATION VALUE of x, that is, the average position of the particle:

$$\langle x\rangle = \frac{\int_0^L \Psi^*(x)\,x\,\Psi(x)\,dx}{\left[\int_0^L \Psi^*(x)\overset{(1)}{}\Psi(x)\,dx\right]_{\text{IF NORMALIZED}}} = \frac{2}{L}\left[\frac{x^2}{4} - \frac{x\sin 2\frac{n\pi}{L}x}{4n\pi/L} - \frac{\cos 2\frac{n\pi}{L}x}{8(n\pi/L)^2}\right]_0^L$$

$$= \frac{2}{L}\left(\frac{L^2}{4}\right) = \frac{L}{2}$$

The average velocity of the particle

$$Mv_x = p_x \xrightarrow[\text{one}]{\text{Postulate}} \text{OPERATOR}$$

$$\text{for } p_x = \frac{\hbar}{i}\frac{\partial}{\partial x}$$

$$\text{for } v_x = \frac{\hbar}{iM}\frac{\partial}{\partial x}$$

$$\langle v_x\rangle = \frac{\int_0^L \Psi^*(x)\,\hat{\frac{\hbar}{iM}\frac{d}{dx}}\,\Psi(x)\,dx}{1}$$

$$\frac{d}{dx}\sin\left(\frac{n\pi}{L}x\right) = \frac{n\pi}{L}\cos\left(\frac{n\pi}{L}x\right)$$

$$\langle v_x\rangle = \int_0^L \frac{2}{L}\frac{\hbar}{iM}\sin\left(\frac{n\pi}{L}x\right)\frac{n\pi}{L}\cos\left(\frac{n\pi}{L}x\right)dx = 0$$

THE EIGENFUNCTIONS OF AN OPERATOR FORM A COMPLETE SET OF FUNCTIONS

A complete set in the sense that they can be used to build another function.

THE EIGENFUNCTIONS WHICH CORRESPOND to DIFFERENT EIGENVALUES ARE ORTHOGONAL. This means that if $\hat{S}_{op}\Psi_\lambda = s_\lambda \Psi_\lambda$

then $\int \Psi_\lambda^* \Psi_{\lambda'} d\tau = \delta_{\lambda\lambda'}$ (Kronecker delta) $\begin{cases} = 1 & \text{if } \lambda = \lambda' \\ = 0 & \text{if } \lambda \neq \lambda' \end{cases}$

EXAMPLE: $\Psi(\phi) = \frac{1}{\sqrt{2\pi}} e^{im\phi}$ are EIGENFUNCTIONS of the operator $\frac{-\hbar^2}{2MR^2}\frac{d^2}{d\phi^2}$ with eigenvalues $\frac{m^2\hbar^2}{2MR^2}$

[They are also eigenfunctions of the operator $\frac{\hbar}{i}\frac{d}{d\phi}$ with eigenvalues $m\hbar$]

ORTHOGONALITY REQUIREMENT is

$$\int_0^{2\pi} \Psi_m^*(\phi)\,\Psi_{m'}(\phi)\,d\phi = 0 \quad \text{when } m \neq m'$$

Show this is true:

$$\frac{1}{2\pi}\int_0^{2\pi} e^{-im\phi} e^{im'\phi} d\phi = \frac{1}{2\pi}\int_0^{2\pi} e^{i(m'-m)\phi} d\phi$$

$$= \frac{1}{2\pi}\left[\frac{e^{i(m'-m)\phi}}{i(m'-m)}\right]_0^{2\pi} = \frac{1}{2\pi}\left[\frac{e^{i(m'-m)2\pi} - e^{i0}}{i(m'-m)}\right]$$

But since m' and m are INTEGERS

$m'-m$ = INTEGER

$$= \frac{1}{2\pi}\left[\frac{1-1}{i(m'-m)}\right] = 0 \text{ provided } m' \neq m$$

IF TWO FUNCTIONS CORRESPOND TO THE SAME EIGENVALUE THEN ANY LINEAR COMBINATION of these FUNCTIONS SATISFY the OPERATOR EQUATION:

Example: $\hat{S}_{op}\Psi_\lambda = a\Psi_\lambda$, $\hat{S}_{op}\Psi_{\lambda'} = a\Psi_{\lambda'}$ } Two different functions one and the same EIGENVALUE

Then any linear combination $(c_1\Psi_\lambda + c_2\Psi_{\lambda'})$ gives

$$\hat{S}_{op}(c_1\Psi_\lambda + c_2\Psi_{\lambda'}) = c_1 a\Psi_\lambda + c_2 a\Psi_{\lambda'}$$
$$= a(c_1\Psi_\lambda + c_2\Psi_{\lambda'})$$

This says that any linear combination of the DEGENERATE eigenfunctions Ψ_λ and $\Psi_{\lambda'}$ are also EIGENFUNCTIONS of $\hat{S}_{op}$ for the EIGENVALUE a.

Therefore, can choose two linear combinations such that they are ORTHOGONAL to one another. For example, starting with ORTHOGONAL Ψ_λ $\Psi_{\lambda'}$

CHOOSE THIS SET $\frac{1}{\sqrt{2}}(\Psi_\lambda + \Psi_{\lambda'})$ and $\frac{1}{\sqrt{2}}(\Psi_\lambda - \Psi_{\lambda'})$ are ORTHOGONAL

$$\int \frac{1}{\sqrt{2}}(\Psi_\lambda^* + \Psi_{\lambda'}^*)\cdot\frac{1}{\sqrt{2}}(\Psi_\lambda - \Psi_{\lambda'})\,d\tau = \frac{1}{2}\int \Psi_\lambda^*\Psi_\lambda\,d\tau - \frac{1}{2}\int \Psi_{\lambda'}^*\Psi_{\lambda'}\,d\tau$$

(the two integrals in brackets) zero

$$+\frac{1}{\sqrt{2}}\int \Psi_{\lambda'}^*\Psi_\lambda\,d\tau \text{ zero}$$
$$-\frac{1}{\sqrt{2}}\int \Psi_\lambda^*\Psi_{\lambda'}\,d\tau \text{ zero}$$
$$= 0$$

Therefore the functions $\frac{1}{\sqrt{2}}(\Psi_\lambda + \Psi_{\lambda'})$ and $\frac{1}{\sqrt{2}}(\Psi_\lambda - \Psi_{\lambda'})$ are ORTHOGONAL to each other.

They will also be found to be ORTHOGONAL to all the other Ψ_i corresponding to other EIGENVALUES of operator $\hat{S}_{op}$.

1. INTRODUCTION TO QUANTUM MECHANICS

IT IS POSSIBLE TO EXPRESS another function G in terms of the COMPLETE SET of EIGENFUNCTIONS of an OPERATOR.

Let $\{f_n\}$ be a complete set of eigenfunctions of operator S_{op}

Write function G in terms of this set

$$G = \sum_n c_n f_n$$ where c_n are numbers which can be found

Operate with $\int f_m^* d\tau$ on both sides to get

$$\boxed{\int f_m^* G \, d\tau} = \underbrace{\sum_n c_n \int f_m^* f_n \, d\tau}_{\text{of all the integrals in this sum only the } m^{th} \text{ one survives!}} = \boxed{c_m}$$

"OVERLAP INTEGRAL"

ORTHOGONALITY of EIGENFUNCTIONS

EXPECTATION VALUE of S if the system is in a state G, a function known in terms of c_n

$$\langle S \rangle = \frac{\int G^* S_{op} G \, d\tau}{\int G^* G \, d\tau} = \frac{\int \sum_n c_n^* f_n^* \left(\sum_m c_m S_{op} f_m \right) d\tau}{\int \sum_n c_n^* f_n^* \left(\sum_m c_m f_m \right) d\tau}$$

$$= \frac{\int \sum_n c_n^* f_n^* \left(\sum_m c_m s_m f_m \right) d\tau}{\int \sum_n c_n^* f_n^* \left(\sum_m c_m f_m \right) d\tau}$$

IN BOTH NUMERATOR and DENOMINATOR ONLY $m = n$ terms survive (ORTHOGONALITY)

$$\langle S \rangle = \frac{\sum_n c_n^* c_n s_n}{\underbrace{\sum_n c_n^* c_n}_{1}} = \sum_n \underbrace{(c_n^* c_n)}_{\text{weighting factors: HOW MUCH OF EACH EIGENFUNCTION of } S_{op} \text{ is contained in state } G} s_n$$

s_n ↑ EIGENVALUES of S_{op}

Analogy:

EIGENVALUES of S_{op} $\quad s_n = 1, 2, 3, 4, 5, 6$

Consider a loaded die, loaded such that the one-spot has 10% probability, 2-spot 10% 3-spot 10%, 4-spot - 20%, 5-spot - 20% and the 6-spot 30%.

$c_1^* c_1 = |c_1^2| = 0.10$
$c_2^* c_2 = 0.10$
$c_3^* c_3 = 0.10$
$c_4^* c_4 = 0.20$
$c_5^* c_5 = 0.20$
$c_6^* c_6 = 0.30$

These are NORMALIZED probabilities so sum equals 1.

$$\sum_n c_n^* c_n = 1$$

The "EXPECTATION VALUE" or the EXPECTED MEAN or the EXPECTED AVERAGE is

$$\langle S \rangle = \sum_n \underbrace{c_n^* c_n}_{\text{weighting factors: HOW MUCH OF EACH EIGENFUNCTION of } S_{op} \text{ is contained in state } \Psi} \underbrace{s_n}_{\text{EIGENVALUES of } S_{op}}$$

SUMMARY:

$$\langle S \rangle = \frac{\int \Psi^* S_{op} \Psi \, d\tau}{\int \Psi^* \Psi \, d\tau}$$

Suppose the EIGENVALUES of S_{op} are

$s_n = 1, 2, 3, 4, 5, 6$

with corresponding EIGENFUNCTIONS

$F_1 \quad F_2 \quad F_3 \quad F_4 \quad F_5 \quad F_6$

Case one: System is in state $\Psi = F_3$

Measure S in the laboratory: 3 3 3 3 3 3 3 3 3 3 ...

$\langle S \rangle = 3$

Case two: System is in state $\Psi = \sqrt{0.1}F_1 + \sqrt{0.1}F_2 + \sqrt{0.1}F_3 + \sqrt{0.2}F_4 + \sqrt{0.2}F_5 + \sqrt{0.3}F_6$

Measure S in the laboratory: 6 4 1 6 5 3 5 2 6 4 ...

$\langle S \rangle = 4.2$

1. INTRODUCTION TO QUANTUM MECHANICS

More on OPERATORS

① The OPERATORS of QUANTUM MECHANICS are LINEAR OPERATORS, that is

$$S_{op}(a\psi) = a S_{op}\psi$$

$$(S_{op} + T_{op})\psi = S_{op}\psi + T_{op}\psi$$

$$S_{op} T_{op} \psi = S_{op}(T_{op}\psi)$$

② The OPERATORS corresponding to OBSERVABLES are HERMITIAN OPERATORS

Since all measurable quantities are ultimately related to the measurements obtained by meter sticks, clocks, and balances, it is necessary that all the corresponding operators have REAL EIGENVALUES. This requirement is met by a CLASS of OPERATORS known as HERMITIAN OPERATORS. Not all operators encountered in QUANTUM MECHANICS are HERMITIAN, but ONLY HERMITIAN OPERATORS CAN CORRESPOND to OBSERVABLES.

For any two functions f and g, O_p is HERMITIAN if

$$\int f^* O_p g \, d\tau = \left[\int g^* O_p f \, d\tau\right]^* = \int (O_p^* f^*) g \, d\tau$$

"COMPLEX CONJUGATE TRANSPOSE"

Properties of HERMITIAN OPERATORS:

1. THE EIGENVALUES OF HERMITIAN OPERATORS ARE REAL
2. THE EIGENFUNCTIONS CORRESPONDING TO DIFFERENT EIGENVALUES OF HERMITIAN OPERATORS ARE ORTHOGONAL

Let ψ_n and ψ_m be EIGENFUNCTIONS of operator S_{op} with EIGENVALUES s_n and s_m

Postulate 2 $S_{op}\psi_n = s_n\psi_n$ $S_{op}\psi_m = s_m\psi_m$

Operate with $\int \psi_m^* d\tau$ Operate with $\psi_n^* d\tau$

$\int \psi_m^* S_{op}\psi_n d\tau = s_n \int \psi_m^*\psi_n d\tau$ $\int \psi_n^* S_{op}\psi_m d\tau = s_m \int \psi_n^*\psi_m d\tau$

S_{op} is a Hermitian operator Take complex conjugate

$\left[\int \psi_n^* S_{op}\psi_m d\tau\right]^* = s_n \int \psi_m^*\psi_n d\tau$ $\left(\int \psi_m^* S_{op}\psi_n d\tau\right)^* = s_m^* \int \psi_m^*\psi_n d\tau$

Subtract 2nd eqn from the first (left)

$$0 = (s_n - s_m^*)\int \psi_m^*\psi_n d\tau$$

For special case where $n = m$

$$0 = (s_m - s_m^*)\underbrace{\int \psi_m^*\psi_m d\tau}_{\text{normalized}}$$

$\int \psi_m^*\psi_m d\tau = 1$

Therefore $s_m = s_m^*$

$\therefore$ EIGENVALUES are REAL

For the case where $n \neq m$

$$0 = (s_n - s_m^*)\int \psi_m^*\psi_n d\tau$$

eigenvalues are real

$$0 = (s_n - s_m)\int \psi_m^*\psi_n d\tau$$

if these are different eigenvalues then

This must be zero

(3) Some OPERATORS COMMUTE, that is

$$S_{op} T_{op} \Psi = T_{op} S_{op} \Psi$$

or $$[S_{op}, T_{op}]\Psi \equiv (S_{op} T_{op} - T_{op} S_{op})\Psi = 0$$

Some OPERATORS DO NOT COMMUTE, that is

$$\underbrace{[S_{op}, T_{op}]} \neq 0 \quad \text{or} \quad S_{op} T_{op} \Psi \neq T_{op} S_{op} \Psi$$

This is called the COMMUTATOR

④ COMMUTING OPERATORS

Suppose that two operators S_{op} and T_{op} COMMUTE, that is, $S_{op}T_{op}\psi = T_{op}S_{op}\psi$ or $[S_{op}, T_{op}] = 0$

Each of the operators S_{op} and T_{op} will have its own set of EIGENFUNCTIONS and EIGENVALUES

Postulate two:

$S_{op}\psi_i = s_i\psi_i$ $\quad \psi_1\ s_1,\ \psi_2\ s_2,\ \psi_3\ s_3,\ \ldots$ $\qquad$ $T_{op}\chi_n = t_n\chi_n$ $\quad \chi_1\ t_1,\ \chi_2\ t_2,\ \chi_3\ t_3,\ \chi_4\ t_4,\ \ldots$

Now consider the combination $S_{op}T_{op}$ operating on the eigenfunctions of S_{op}

$$\underbrace{S_{op}T_{op}}_{\text{COMMUTE}}\psi_i = \underbrace{T_{op}S_{op}}_{\text{LINEAR OPERATORS}}\psi_i = T_{op}\underbrace{(S_{op}\psi_i)}_{\text{Postulate two}} = T_{op}\underbrace{s_i\psi_i}_{\text{LINEAR OPERATOR}} = s_i T_{op}\psi_i$$

That is, we have found

$$S_{op}\underbrace{(T_{op}\psi_i)} = s_i\underbrace{(T_{op}\psi_i)}$$

This says that $(T_{op}\psi_i)$ must be an EIGENFUNCTION of S_{op} with EIGENVALUE s_i !!!

If the EIGENFUNCTIONS are NON-DEGENERATE, that is, if there is only one EIGENFUNCTION corresponding to the EIGENVALUE s_i, then $(T_{op}\psi_i)$ must be the same as ψ_i except possibly by a constant factor, that is

$$(T_{op}\psi_i) = (\text{constant})\psi_i$$

But NOTE! This says that ψ_i is an EIGENFUNCTION of T_{op} !! Since we already know the eigenfunctions of T_{op} are the set $\chi_1, \chi_2, \chi_3, \ldots$ then, IF S_{op} and T_{op} ARE OPERATING IN THE SAME SPACE, then the functions $\{\psi\}$ and $\{\chi\}$ ARE IDENTICAL FUNCTIONS. COMMUTING OPERATORS may be said to have SIMULTANEOUS EIGENFUNCTIONS.

If the EIGENFUNCTIONS are DEGENERATE it is possible to choose some LINEAR COMBINATION of ψ_i to get χ_n. That is, we can construct from the m-FOLD DEGENERATE EIGENFUNCTIONS of S_{op} to get a new set of m FUNCTIONS which are LINEARLY INDEPENDENT EIGENFUNCTIONS of S_{op} that are ALSO EIGENFUNCTIONS of T_{op}.

If the operators S_{op} and T_{op} are not in the same space then we have incomplete information. Example,

$L_z(\phi)$ commutes with $H_{op}(r,\theta,\phi)$

$\frac{\hbar}{i}\frac{\partial}{\partial\phi}$ eigenfunctions are $\frac{1}{\sqrt{2\pi}}e^{im\phi}$

$H_{op}(r,\theta,\phi)$ eigenfunctions are $f(r,\theta)\cdot\frac{1}{\sqrt{2\pi}}e^{im\phi}$

WHEN THE OPERATORS COMMUTE, a measurement of first ONE OF THE OBSERVABLES and then THE OTHER can lead to results with a STANDARD DEVIATION of ZERO since it is possible for the SYSTEM to be SIMULTANEOUSLY in an EIGENSTATE of S_{op} and in an EIGENSTATE of T_{op}. THIS IS NEVER POSSIBLE WITH OPERATORS THAT DO NOT COMMUTE.

1. INTRODUCTION TO QUANTUM MECHANICS

3.14. Schwarz' Inequality.—Let f and g be any two functions of x such that the integrals

$$A = \int f^* f dx, \quad B = \int f^* g dx, \quad C = \int g^* g dx \tag{3-111}$$

exist. The integrations extend over any definite range of the variable x. Certainly the integral

$$\int [\lambda f^*(x) + g^*(x)]\,[\lambda f(x) + g(x)]\,dx = A\lambda^2 + (B^* + B)\lambda + C$$

in which λ is to be considered as a *real* variable, independent of x, is always positive or zero (zero only when g is directly proportional to f) and hence has no real roots in λ. But the roots of $A\lambda^2 + (B^* + B)\lambda + C$ are given by

$$\lambda = -\frac{B^* + B}{2A} \pm \frac{1}{2A}\sqrt{(B^* + B)^2 - 4AC}$$

They are real unless

$$4AC \geq (B^* + B)^2 \tag{3-112}$$

The equality sign here holds only when $g = const. \times f$.

The right-hand side of (112) is twice the real part of B. Hence, if f and g are real functions, the inequality becomes

$$\int f^2 dx \cdot \int g^2 dx \geq \left(\int fg dx\right)^2 \tag{3-113}$$

which is one form of Schwarz' inequality.

For complex functions f and g, (112) may be modified. Write f and g in polar form:

$$f(x) = \rho_1(x)e^{i\theta_1(x)}\ ;\ g(x) = \rho_2(x)e^{i\theta_2(x)}$$

Then $B = \int \rho_1\rho_2 e^{i(\theta_2 - \theta_1)}dx$. Since (112) holds for every pair of functions f and g (which have integrable squares), it must also be true when g is replaced by $g' = ge^{i(\theta_1 - \theta_2)}$. But the substitution of g' for g leaves the values of A and C unchanged while it converts both B^* and B into $\int \rho_1\rho_2 dx = |\,B\,|$, which is the modulus of B. Hence

$$\boxed{\int f^* f dx \int g^* g dx \geq \left|\int f^* g dx\right|^2} \tag{3-114}$$

This is the more general form of the Schwarz inequality. Further generalization to functions of more than one real variable is obvious.

STANDARD DEVIATION OF A SERIES OF MEASUREMENTS. THE UNCERTAINTY PRINCIPLE

STANDARD DEVIATION or ROOT MEAN SQUARE DEVIATION σ_S

$$\sigma_S^2 = \int \psi^* (S_{op} - \langle S \rangle)^2 \psi \, d\tau \quad \text{if } \psi \text{ is normalized}$$

MEAN SQUARE DEVIATION

Question: How is σ_S^2 for one observable related to σ_T^2 for another observable measured on the SAME SYSTEM ?

Derive answer by using Schwarz' inequality:

$$\int u^* u \, d\tau \cdot \int v^* v \, d\tau \geq \left\{ \int \frac{u^* v + v^* u}{2} d\tau \right\}^2$$

Let $\begin{cases} u = (S_{op} - \langle S \rangle)\psi \\ v = i(T_{op} - \langle T \rangle)\psi \end{cases}$

Substitute these into Schwarz' inequality

ψ meets the usual conditions for a function describing the state of a system

S_{op} and T_{op} are HERMITIAN operators since they correspond to observables

$\langle S \rangle$ and $\langle T \rangle$ are REAL numbers

$(S_{op} - \langle S \rangle)$ are also
$(T_{op} - \langle T \rangle)$ HERMITIAN

$$\int (S_{op} - \langle S \rangle)^* \psi^* (S_{op} - \langle S \rangle)\psi \, d\tau \cdot \int i^* (T_{op} - \langle T \rangle)^* \psi^* i (T_{op} - \langle T \rangle)\psi \, d\tau$$

$$\geq \frac{1}{4} \left\{ \int (S_{op} - \langle S \rangle)^* \psi^* \, i (T_{op} - \langle T \rangle)\psi \, d\tau + \int i^* (T_{op} - \langle T \rangle)^* \psi^* (S_{op} - \langle S \rangle)\psi \, d\tau \right\}^2$$

Left hand side $\overset{\text{HERMITIAN OPS.}}{=\!=} \int \psi^* (S_{op} - \langle S \rangle)(S_{op} - \langle S \rangle)\psi \, d\tau \cdot \int \psi^* (T_{op} - \langle T \rangle)(T_{op} - \langle T \rangle)\psi \, d\tau$

$$= \int \psi^* (S_{op} - \langle S \rangle)^2 \psi \, d\tau \cdot \int \psi^* (T_{op} - \langle T \rangle)^2 \psi \, d\tau$$

$$= \sigma_S^2 \cdot \sigma_T^2$$

Right hand side $\overset{\text{HERMITIAN OPS.}}{=}$ $\frac{1}{4}\left\{ i\int \psi^*(S_{op} - \langle S\rangle)(T_{op} - \langle T\rangle)\psi\, d\tau \right.$ (NUMBERS)

$\left. -i\int \psi^*(T_{op} - \langle T\rangle)(S_{op} - \langle S\rangle)\psi\, d\tau \right\}^2$

$= \frac{1}{4}\left\{ i\int \psi^*(S_{op}T_{op} - T_{op}S_{op})\psi\, d\tau \right\}^2$

$= \left\{ \frac{1}{2}\int \psi^* \frac{[S_{op}, T_{op}]}{i}\psi\, d\tau \right\}^2 = \left\{ \frac{1}{2}\left\langle \frac{[S_{op}, T_{op}]}{i} \right\rangle \right\}^2$

Finally, we have

$$\sigma_S \cdot \sigma_T \geq \frac{1}{2}\left\langle \frac{[S_{op}, T_{op}]}{i} \right\rangle$$

THE UNCERTAINTY PRINCIPLE
PRECISE FORM

σ_S, σ_T: STANDARD DEVIATIONS in MEASUREMENTS of OBSERVABLES S and T

This says that

1. If S_{op} and T_{op} COMMUTE, then the MINIMUM POSSIBLE STANDARD DEVIATIONS in SIMULTANEOUS MEASUREMENT of S and T is ZERO.
$$\sigma_S \cdot \sigma_T \geq 0$$

2. If S_{op} and T_{op} DO NOT COMMUTE, then the MINIMUM PRODUCT OF STANDARD DEVIATIONS IS NOT ZERO BUT DEPENDS ON the AVERAGE VALUE OF THE COMMUTATOR

Example:

$$S_{op} = x \qquad T_{op} = p_x = \frac{\hbar}{i}\frac{\partial}{\partial x}$$

$$\left[x, \frac{\hbar}{i}\frac{\partial}{\partial x}\right]\psi = x\frac{\hbar}{i}\frac{\partial\psi}{\partial x} - \frac{\hbar}{i}\frac{\partial(x\psi)}{\partial x}$$

$$= x\frac{\hbar}{i}\frac{\partial\psi}{\partial x} - \frac{\hbar}{i}x\frac{\partial\psi}{\partial x} - \frac{\hbar}{i}\psi = \left(\frac{-\hbar}{i}\right)\psi$$

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

1. INTRODUCTION TO QUANTUM MECHANICS

TIME DEPENDENCE

TIME-DEPENDENT SCHRÖDINGER EQUATION:

$$i\hbar \frac{\partial}{\partial t}\Psi(x,y,z,t) = H(x,y,z,t)\Psi(x,y,z,t)$$

IF H DOES NOT EXPLICITLY DEPEND ON t
try substituting a product function:

$$\Psi(x,y,z,t) = \underbrace{\psi(x,y,z)}_{\text{space only}} \cdot \underbrace{F(t)}_{\text{time only}}$$

$$i\hbar \frac{\partial}{\partial t}\psi(x,y,z)\cdot F(t) = H(x,y,z)\,\psi(x,y,z)\cdot F(t)$$

(H: NO TIME)

$$\psi(x,y,z)\cdot i\hbar \frac{\partial F(t)}{\partial t} = F(t)\cdot H(x,y,z)\psi(x,y,z)$$

Divide equation by $\psi(x,y,z)\cdot F(t)$

$$\frac{\cancel{\psi(x,y,z)}\cdot i\hbar \frac{\partial F(t)}{\partial t}}{\cancel{\psi(x,y,z)}\cdot F(t)} = \frac{\cancel{F(t)}\cdot H(x,y,z)\psi(x,y,z)}{\cancel{F(t)}\cdot\psi(x,y,z)}$$

$$\underbrace{\frac{i\hbar\, \partial F(t)/\partial t}{F(t)}}_{\text{depends on } t \text{ only}} = \underbrace{\frac{H(x,y,z)\psi(x,y,z)}{\psi(x,y,z)}}_{\text{depends on space coordinates only}}$$

yet always equal

Can happen only if each side is equal to a constant, the same constant (call it E).

$$i\hbar \frac{\partial F(t)}{\partial t} = E\,F(t)$$

$$H(x,y,z)\psi(x,y,z) = E\,\psi(x,y,z)$$

TIME-INDEPENDENT SCHRÖDINGER EQUATION

$$\frac{dF(t)}{F(t)} = E\frac{dt}{i\hbar} \quad \text{integrates to}$$

$$F(t) = Ce^{-iEt/\hbar}$$

$$\Psi_\lambda(x,y,z,t) = \underbrace{\psi_\lambda(x,y,z)}_{\text{STATIONARY STATE}}\, e^{-iE_\lambda t/\hbar}$$

(E_λ: characteristic)

1. INTRODUCTION TO QUANTUM MECHANICS

For an OPERATOR S_{op} NOT EXPLICITLY DEPENDENT ON TIME:

a. For a STATIONARY STATE:

$$\langle S \rangle = \int \Psi_\lambda^*(x,y,z,t)\, S_{op}\, \Psi_\lambda(x,y,z,t)\, d\tau$$

$$= \int \psi_\lambda^*(x,y,z) e^{iE_\lambda t/\hbar}\, S_{op}\, \psi_\lambda(x,y,z) e^{-iE_\lambda t/\hbar}\, d\tau$$

$$\langle S \rangle = \int \psi_\lambda^*(x,y,z)\, S_{op}\, \psi_\lambda(x,y,z)\, d\tau \quad \text{INDEPENDENT OF TIME}$$

"STATIONARY STATE" in the sense that its properties are independent of time.

b. For Ψ NOT necessarily a stationary state, it is still possible for S to be a "**CONSTANT OF THE MOTION**", i.e., INVARIANT with time, provided only that S_{op} **COMMUTES with H.**

Proof: $$\frac{d}{dt}\langle S \rangle = \frac{d}{dt}\int \Psi^*(x,y,z,t) S_{op} \Psi(x,y,z,t) d\tau$$

$$= \int \frac{\partial}{\partial t}\Psi^*(x,y,z,t)\, S_{op}\, \Psi(x,y,z,t)\, d\tau + \int \Psi^*(x,y,z,t) S_{op} \frac{\partial \Psi}{\partial t}(x,y,z,t) d\tau$$

But $i\hbar \frac{\partial \Psi}{\partial t} = H\Psi$ or $-i\hbar \frac{\partial \Psi^*}{\partial t} = H^*\Psi^*$

$$\frac{d}{dt}\langle S \rangle = \int \frac{H^*\Psi^*}{-i\hbar} S_{op} \Psi\, d\tau + \int \Psi^* S_{op} \frac{H\Psi}{i\hbar} d\tau$$

$$= \int \frac{\Psi^* H S_{op} \Psi}{-i\hbar} d\tau + \int \Psi^* S_{op} \frac{H\Psi}{i\hbar} d\tau$$

$$\frac{d}{dt}\langle S\rangle = \frac{i}{\hbar}\left\langle [H, S_{op}] \right\rangle$$

S is a CONSTANT OF THE MOTION IF S_{op} COMMUTES WITH H

(THE EXPECTATION VALUE of S is CONSERVED)

Note that Ψ is NOT NECESSARILY an EIGENFUNCTION of S_{op}.

EXAMPLE:

Is linear momentum a constant of the motion in a one-dimensional system?

$$\frac{d}{dt}\langle P_x\rangle = \frac{i}{\hbar}\left\langle [H, P_x] \right\rangle$$

$$H = -\frac{\hbar^2}{2M}\frac{d^2}{dx^2} + V(x)$$

$$P_x = \frac{\hbar}{i}\frac{d}{dx}$$

$$[H, P_x]\Psi = \underbrace{\left[-\frac{\hbar^2}{2M}\frac{d^2}{dx^2}, \frac{\hbar}{i}\frac{d}{dx}\right]}_{\text{zero}}\Psi + \left[V(x), \frac{\hbar}{i}\frac{d}{dx}\right]\Psi$$

$$V(x)\frac{\hbar}{i}\frac{d\Psi}{dx} - \frac{\hbar}{i}\frac{d}{dx}V(x)\Psi = V(x)\frac{\hbar}{i}\frac{d\Psi}{dx} - V(x)\frac{\hbar}{i}\frac{d\Psi}{dx} - \frac{\hbar}{i}\Psi\frac{dV(x)}{dx}$$

$$[H, P_x] = -\frac{\hbar}{i}\frac{d}{dx}V(x)$$

$$\frac{d}{dt}\langle P_x\rangle = -\left\langle \frac{dV(x)}{dx} \right\rangle$$

In words: THE LINEAR MOMENTUM IS A CONSTANT OF THE MOTION WHEN THE EXPECTATION VALUE OF THE FORCE = ZERO

ISAAC NEWTON Law #1

THE TIME DERIVATIVE OF THE EXPECTATION VALUE OF THE LINEAR MOMENTUM IS EQUAL TO THE EXPECTATION VALUE OF THE FORCE.

ISAAC NEWTON Law #2

Classical mechanics is only a SPECIAL CASE OF Quantum Mechanics

For an OPERATOR S_{op} THAT HAS AN EXPLICIT DEPENDENCE ON TIME:

$$\frac{d}{dt}\langle S\rangle = \frac{i}{\hbar}\langle [H, S_{op}]\rangle + \left\langle \frac{\partial S}{\partial t}\right\rangle$$

The time-energy uncertainty relation:

Consider
- H not explicitly dependent on time
- S not explicitly dependent on time

$$\frac{d}{dt}\langle S\rangle = \frac{i}{\hbar}\langle [H, S_{op}]\rangle = \frac{1}{\hbar}\left\langle \frac{[S_{op}, H]}{i}\right\rangle$$

Heisenberg

$$\sigma_S \cdot \sigma_E \geq \frac{1}{2}\left\langle \frac{[S_{op}, H]}{i}\right\rangle$$

substituting,

$$\sigma_S \cdot \sigma_E \geq \frac{1}{2}\,\hbar\,\frac{d}{dt}\langle S\rangle$$

$$\frac{\sigma_S}{\frac{d}{dt}\langle S\rangle}\,\sigma_E \geq \frac{\hbar}{2}$$

define τ_S a time characteristic of the evolution of the statistical distribution of S

Let τ be the shortest one of all τ_s

τ may be considered as a characteristic time of evolution of the system itself

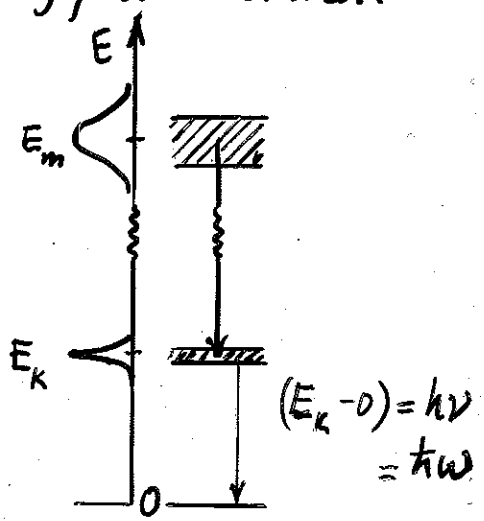
$$\tau \cdot \sigma_E \geq \frac{\hbar}{2}$$

The time - energy uncertainty relation

$$\sigma_E \cdot \sigma_t \geq \frac{\hbar}{2}$$

associate this with the LIFETIME of a state

Interpretation: Lifetime of a state and uncertainty in its energy are related.



$$4\pi\sigma_\nu \cdot \sigma_t \geq 1$$

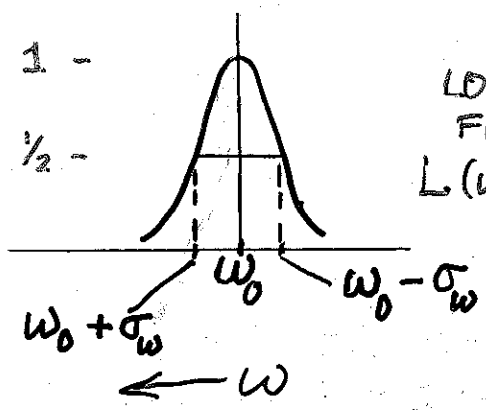
or

$$2\sigma_\omega \cdot \sigma_t \geq 1$$

("NATURAL LINEWIDTH") · (LIFETIME) = 1

full width at half maximum

smallest σ_t



LORENTZIAN FUNCTION

$$L(\omega - \omega_0) \approx \frac{\sigma_\omega^2}{(\omega - \omega_0)^2 + \sigma_\omega^2}$$

ω radians/sec

ν cycles/sec (Hertz)

Time-energy uncertainty relation

$$\sigma_E \cdot \Delta t \geq \frac{\hbar}{2}$$

is analogous to position-momentum uncertainty relation. However, its physical interpretation is quite different. In the position-momentum uncertainty relation the position and momentum variables play exactly symmetrical roles; they can both be measured at a given time t. The statistical distributions of the results of measurement and consequently the rms are all derivable from the value of the wavefunction at that time.

In $\sigma_E \cdot \Delta t \geq \hbar/2$ on the other hand, energy and time play fundamentally different roles.
E is a dynamical variable of the system
t is a parameter
σ_E is the uncertainty in the value taken by this dynamical variable
Δt is a time interval characteristic of the rate of change of the system.

Consequences:

(a) The precision σ_E of the energy measurement is connected with the time Δt required for the measurement.

(b) Lifetime-linewidth relation

σ_E spread of energy spectrum or width of the energy level

Δt mean lifetime

$E = h\nu$

$\sigma_E \cdot \Delta t \geq \frac{\hbar}{2}$

$h\sigma_\nu \cdot \Delta t \geq \frac{\hbar}{2}$

$2\pi\nu = \omega$

↑ Hertz, cycles s^{-1} ; ↑ rads s^{-1}

$\sigma_\nu \cdot \Delta t \geq \frac{1}{4\pi}$

$2\pi\sigma_\nu \cdot \Delta t \geq \frac{1}{2}$

$\sigma_\omega \cdot \Delta t \geq \frac{1}{2}$

$2\sigma_\omega \cdot \Delta t \geq 1$

$2\sigma_\omega$: Full Width at Half Maximum

Δt: lifetime

$$\left(\begin{array}{c}\text{natural linewidth} \\ \text{in rad } s^{-1}\end{array}\right) \cdot \left(\begin{array}{c}\text{lifetime} \\ s\end{array}\right) \geq 1$$

A Lorentzian function

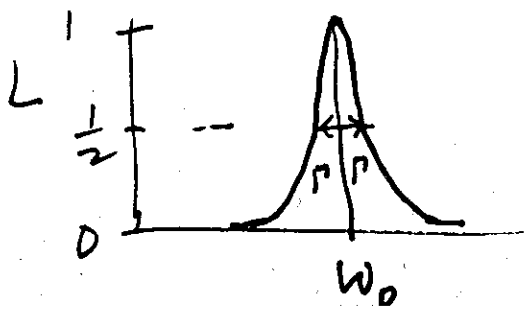
$$L(\omega - \omega_0) = \frac{\Gamma^2}{(\omega-\omega_0)^2 + \Gamma^2}$$

normalized such that $L(\omega_0) = 1$

at half maximum

$$L = \frac{1}{2} = \frac{\Gamma^2}{(\omega-\omega_0)^2 + \Gamma^2} \quad \therefore \Gamma^2 = (\omega-\omega_0)^2$$

literally $\omega - \omega_0$ is the root mean square deviation



FWHM $= 2\Gamma$

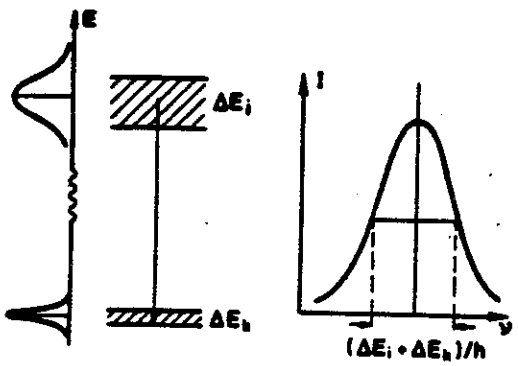


Fig.3.3. Illustration of the uncertainty principle which relates the natural linewidth to the energy uncertainties of upper and lower level

$\omega_{ik} = (E_i - E_k)/\hbar$ of a transition terminating in the stable ground state E_k has therefore an uncertainty

$$\delta\omega = \Delta E_i/\hbar = 1/\tau_i \quad . \tag{3.22}$$

If the lower level E_k is not the ground state but also an excited state with a lifetime τ_k, the uncertainties ΔE_i and ΔE_k of the two levels both contribute to the linewidth. This yields for the total uncertainty

$$\Delta E = \Delta E_i + \Delta E_k \Rightarrow \delta\omega_n = (1/\tau_i + 1/\tau_k) \quad . \tag{3.23}$$