Using Quantum Mechanics in Simple Systems
Chapter 15

Quantization arises when the location of a particle (here an electron) is confined to a dimensionally small region of space – *quantum confinement*.

The simplest system that can be considered to study the *effect of confinement* is to consider a single electron system restricted to a space in a single dimension.

To understand the characteristics of a particle in a one dimensional box system it is necessary to solve the SE.

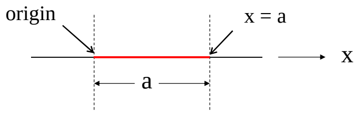
Solving Schrodinger equation (SE) yields ψ's which can be used to obtain values for measurable quantities like energy.

The particle in a 1D box

Understanding of the solution to the particle in a 1-D box case, would allow us to gain some insights into the nature of quantum systems.

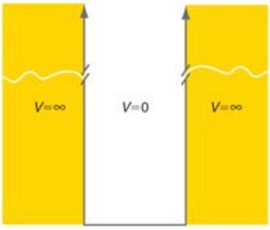
That is, the idea of quantum behavior and the appearance of discrete states with specific energies.

1D box system: A conceptually simple system where electron confined to a space in x direction of length 'a' and *completely free (of zero potential energy) to move* in that space of length 'a' but not allowed to move outside the space of length 'a'.



The particle cannot leave the box, in energy terms, the particle is incapable of overcoming an enormously large energy barrier for $0 > x > a$. That is, for $0 > x > a$ the potential energy $V = \infty$, and for $0 < x < a$, $V = 0$.

Solving for ψ s of starting with SE



Using SE;

$$\hat{H}\psi(x)=E\psi(x)$$

$$\underbrace{\left(\frac{-\hbar^2}{2m}\frac{d^2}{dx^2}+V(x)\right)}\psi(x)=E\psi(x)$$

$$\frac{-\hbar^2}{2m}\frac{d^2}{dx^2}\psi(x)=(E-V(x))\psi(x)$$

$$\frac{d^2}{dx^2}\psi(x)=\frac{2m}{\hbar^2}(V(x)-E)\psi(x)$$

$V(x)=0$, for $a \ge x \ge 0$

$V(x)=\infty$, for $x > a, x < 0$

The potential energy outside the 'line' is ∞ making the particle *totally confined* within the line, cannot penetrate the potential barrier. (V inside = 0 – for convenience, can be any constant.)

$$\left(\frac{-\hbar^2}{2m}\frac{d^2}{dx^2}+V(x)\right)\psi(x)=E\psi(x)$$

Inside the box, V(x) = 0

$$\underbrace{\frac{-\hbar^2}{2m}\frac{d^2}{dx^2}}_{\widehat{H}}\psi(x)=E\psi(x)$$

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

$$\frac{d^2\psi(x)}{dx^2}=-k^2\psi(x)$$

Solving the SE would yield ψ's as a solutions for allowed states.

Solutions to this differential equation are of the above form:

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

Solving the SE would yield ψ's, *wavefunctions* as solutions for allowed states. SE is linear, then of ψ is a solution then $b\psi$ is a solution, b = constant.

The linearity of the SE is important and the consequence is not trivial.

This linearity is in quantum mechanical amplitude.

A general solution of SE is not a normalized function.

Linearity allows normalization of the wave function.

Determining *k*, A and B

For ψ to be a *well behaved function*, for 0 > x >a. At x = 0 and x = a; the wave function is not allowed to acquire a value and also cannot become infinite.

Thus $\psi(0) = 0$ and $\psi(a) = 0$ (boundary conditions).

Apply BC; $\psi(x) = A\sin kx + B\cos kx$

$\psi(0) = 0 + B = 0 \quad \Rightarrow A \neq 0$

$\psi(a) = A\sin ka = 0 \quad \Rightarrow \sin ka = 0$

which makes, $\psi(x) = A\sin kx$

Also; $\psi(a) = A \sin ka = 0$

$A \neq 0$, if not there is no function at all; which makes,

$$\sin(ka) = 0$$
$$ka = n\pi$$
$$k = \frac{n\pi}{a}$$

Where n = 1,2,… and $n \neq 0$.

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

n = quantum number

Each n defines a state.

A wavefunction ψ_n is associated with a state – **bound state**, meaning the particle's existence is confined/bound into the box.

Quantum numbers are the outcome of the application of boundary conditions in the solution of the differential equations.

For the particle in a 1D box, a state is associated with a single quantum number, n. A *single quantum number* is generated because there is only *one set of boundary conditions* involved here.

Generally each set of boundary conditions lead to a quantum number.

A general solution of SE is not a normalized function.

Normalization to find the Amplitude A.

A = ? $\qquad \psi_n(x) = A\sin\left(\frac{n\pi x}{a}\right) \qquad \int_0^a \psi^2(x)dx = 1$

n = 1,2,… and $n \neq 0$.

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

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

$$A^2\frac{a}{2} = 1 \Rightarrow A = \sqrt{\frac{2}{a}}$$

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

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

Complete set of wavefunctions:

$$\psi_n(x) = A\sin\left(\frac{n\pi x}{a}\right), \quad \text{for } n = 1, 2, 3, 4, \ldots \infty$$

n defines a state with the associated state function ψ_n.

For a particle in an infinitely deep potential well there are an infinite number of – **bound states.** Particle in never 'free' i.e. always confined into the box.

Full wave function is of the form: 'space' * 'time'

$$\Psi(x,t) = \psi(x)e^{-i(E/\hbar)t}$$

$$\psi_n(x) = A\sin\left(\frac{n\pi x}{a}\right), \quad \text{for } n = 1, 2, 3, 4, \ldots\infty$$

The **solutions** of the particle in a box **(SE)** forms a **complete set** of functions.

$$\Psi(x,t) = \psi(x)e^{-i(E/\hbar)t}$$

Note; the wave functions (*solutions of SE equation*) above are *eigen functions of the total energy operator*.

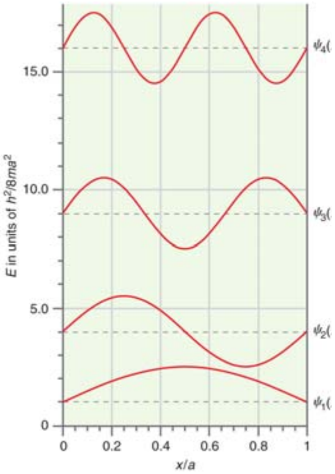
Wave functions that are eigen functions of a certain operator *<u>are not necessarily be eigen functions of another operator</u>; they may be eigen functions of the another operator or may be not.*

Well behaved ψ_n s.

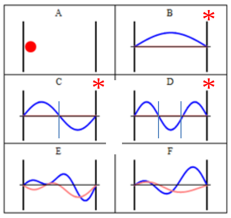
Standing waves

Note within 'a' ;
#nodes = n-1

The time evolving wave function, - standing waves.



The time evolving wave function, - standing waves.



Some trajectories of a particle in a box according to Newton's laws of classical mechanics (A), and according to the Schrödinger equation of quantum mechanics (B-F). In (B-F), the horizontal axis is position, and the vertical axis is the real part (blue) and imaginary part (red) of the wavefunction.

The states (B,C,D) are energy eigenstates, but (E,F) are not.

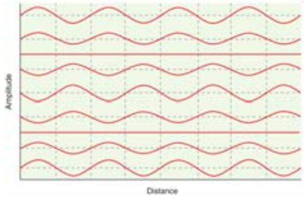
http://en.wikipedia.org/wiki/Particle_in_a_box

<u>Full wave function</u> - form: space * time

$$\Psi(x,t) = \psi(x)e^{-i(E/\hbar)t}$$

The time variation of the wave functions will be exactly as previously seen.

n = 8



One part shown.

Time independent Schrodinger Equation ⇨ ψ **Key to calculation of observables**

Calculation of energy of states 1D Box:

Energy operator = $\widehat{H}$

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

$$\widehat{H}\psi(x) = E\psi(x)$$

$$\widehat{H}\psi_n(x) = E_n\psi_n(x)$$

$$\widehat{H}\psi_n(x) = E_n\psi_n(x)$$

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

$$\underbrace{-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}}_{\widehat{H}}\underbrace{\psi_n}_{} = \underbrace{\frac{\hbar^2}{2m}\left(\frac{n\pi}{a}\right)^2}_{E_n}\underbrace{\sqrt{\frac{2}{a}}\sin\frac{n\pi x}{a}}_{\psi_n}$$

$$-\frac{\hbar^2}{2m}\frac{d^2\psi_n(x)}{dx^2} = \underbrace{\frac{\hbar^2}{2m}\left(\frac{n\pi}{a}\right)^2}\sqrt{\frac{2}{a}}\sin\left(\frac{n\pi x}{a}\right)$$

$$E_n = \underbrace{\frac{\hbar^2}{2m}\left(\frac{n\pi}{a}\right)^2} = \underbrace{\frac{h^2n^2}{8ma^2}}, \quad \text{for } n = 1, 2, 3, \ldots \underbrace{\infty}$$

Note eigenenergies are of precise values. Measuring the energy of an *eigenstate always produce the same value*.

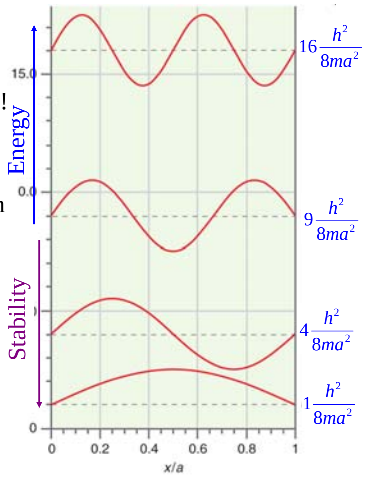
Energy quantized and increases with n.

Lowest energy non-zero! ***Zero point energy***.

BC dictates the number of wave lengths between two consecutive states is λ/2.

Wave vector:

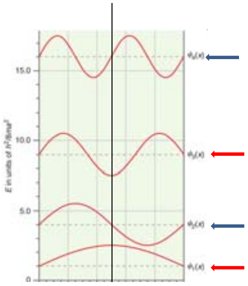
$$k = \frac{2\pi}{\lambda} = \frac{\sqrt{2mE}}{\hbar}$$



Parity of functions

The eigenfunctions are symmetrical.
n = 1, 3 mirror image relationship, even parity, even function
n = 2, 4   inverted relationship, odd parity, odd function

Mathematically useful



Functions with different parities are always orthogonal.

So integrals involving products of functions with different parities are zero.

$$\frac{1}{\lambda^2} = \frac{2m(E - V(x))}{h^2}$$

$$\frac{1}{\lambda^2} = \frac{2mE}{h^2}$$

$$\Rightarrow \frac{1}{\lambda} = \sqrt{\frac{2mE}{h^2}} = \frac{\sqrt{2mE}}{h}$$

$$k = \frac{2\pi}{\lambda} = \frac{\sqrt{2mE}}{\hbar}$$

For ψ to be a well behaved function, at 0 > x > a, and at x = 0 and x = a the wave function is not allowed to become infinite.

Thus $\psi(0) = 0$ and $\psi(a) = 0$ (boundary conditions).

The boundary condition turned the eigenfunctions of SE from travelling waves to standing waves associate with discrete values for energy;

$$E_n = \frac{n^2 h^2}{8ma^2}$$

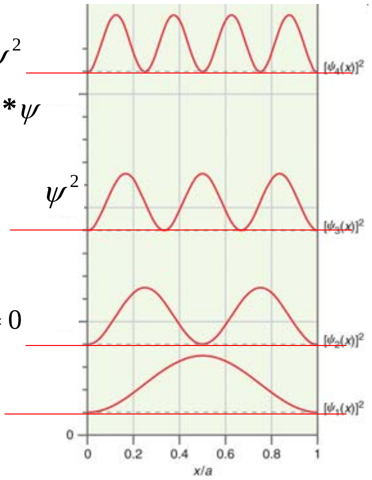
Probability density = ψ^2

$= \psi^* \psi$

Probability in a space dτ $= \psi^* \psi \, d\tau$

$d\tau = dx$

$$\int_{x}^{x+\Delta x} \psi^*(x)\psi(x)dx \neq 0$$



The *quantization of energy levels* arises as a natural outcome of the solution of SE, as opposed to an arbitrary assumption (Bohr model).

The *wavefunctions associated with the energy levels* are a natural consequence of the mathematical solution of the SE.

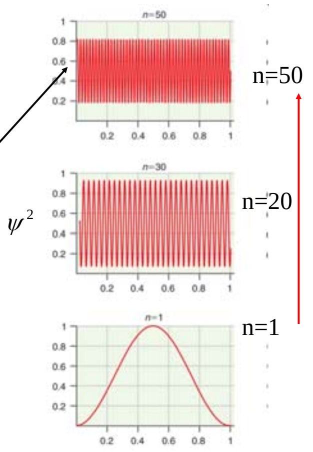
SE of any system, more complicated than the 1D particle in a box would have the same general properties and characteristics.

It is the confinement of the particle by way of trapping the particle in a 'potential well' that leads to quantization!

As n increases quantum system morphs into a classical system.

Particle found with ~same probability every where.

Correspondence Principle.



Further lifting the confinement (a >> 0) makes a quantum system reach it's classical limit - correspondence principle.

$$\psi_n(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right) \longrightarrow 0$$

$$E_n = \frac{\hbar^2}{2m}\left(\frac{n\pi}{a}\right)^2 \longrightarrow 0$$

Ramification of completeness of the set of wave functions

The solutions of the particle in a box (eigenfunctions) forms a **complete set** (of functions).

$$\psi_n(x) = A\sin\left(\frac{n\pi x}{a}\right) \qquad \text{for all } n.$$

Any wave function *f(x)* that satisfies the requirements of an acceptable well behaved wave function can be ‘constructed’ from the ‘members’ of the complete set of functions.

The ‘constructed’ wave function would be a sum with each term in the sum is associated with a coefficient (i.e. weight/amplitude) that is a measure of the contribution by that ‘member’.

Any f(x) is expanded in terms of the normalized eigenfunctions.

$$\psi_n = \sqrt{\frac{2}{a}}\,\mathbf{sin}\,\frac{n\pi x}{a}$$

normalized set of eigenfunctions
(Basis set - basis)

$$f(x) = \sum_{n=1}^{\infty} b_n\psi_n = \sum_{n=1}^{\infty} b_n\sqrt{\frac{2}{a}}\,\mathbf{sin}\,\frac{n\pi x}{a}$$

The set of expansion coefficient b_n is the representation in *f(x)* from the base function ψ_n.

Determination of Expansion coefficients; b_m

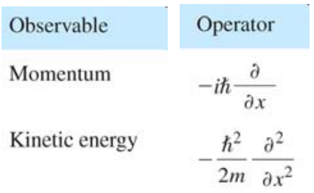
$$f(x) = \sum_{n=1}^{\infty} b_n\psi_n$$

pre-multiply by ψ_m^* and integrate;

$$\int \psi_m^* f(x)dx = \int \psi_m^*\left[\sum_n b_n\psi_n\right] dx$$

$$\sum_n b_m \int \psi_m^*\psi_n dx = \sum_n b_m\delta_{mn} = b_m$$

$$\int \psi_m^* f(x)dx \qquad \text{overlap integral}$$



Observable	Operator
Momentum	$-i\hbar\frac{\partial}{\partial x}$
Kinetic energy	$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}$

$$\hat{E}_{kinetic} = \frac{1}{2m}\left(\hat{p}_x\right)\left(\hat{p}_x\right)$$

Energy operator for particle in a 3D box:

$$E = KE + \cancel{PE} = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)$$

$$\widehat{H} = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)$$

2D and 3D 'boxes'

Extending the results from 1-D to 2-D/3-D is deceptively easy. For a box of size a × b × c with BCs,

$$V(x, y, z) = 0 \quad \text{for } 0 \le x \le a; \quad 0 \le y \le b; \quad 0 \le z \le c$$

$$= \infty \quad \text{otherwise}$$

the time independent SE;

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)\psi(x, y, z) = E\psi(x, y, z)$$

In SE:

$$-\frac{\hbar^2}{2m}\left(Y(y)Z(z)\frac{d^2X(x)}{dx^2}+X(x)Z(z)\frac{d^2Y(y)}{dy^2}+X(x)Y(y)\frac{d^2Z(z)}{dz^2}\right)$$

$$= EX(x)Y(y)Z(z)$$

Division by $\psi(x,y,z)$,

$$-\frac{\hbar^2}{2m}\left[\frac{1}{X(x)}\frac{d^2X(x)}{dx^2}+\frac{1}{Y(y)}\frac{d^2Y(y)}{dy^2}+\frac{1}{Z(z)}\frac{d^2Z(z)}{dz^2}\right] = E$$

Solutions are of form; $\psi(x, y, z) = X(x)Y(y)Z(z)$

Separation of variables

and $E = E_x+E_y+E_z$

The wave equation where $\hat{H}$ can be written as a sum of terms that do not share coordinates can be resolved into the set (DE with three variables transforms to three DEs, each with one variable);

$$-\frac{\hbar^2}{2m}\frac{d^2X(x)}{dx^2} = E_xX(x)$$

Solutions ~ 1D solutions !!

$$-\frac{\hbar^2}{2m}\frac{d^2Y(y)}{dy^2} = E_yY(y)$$

$$-\frac{\hbar^2}{2m}\frac{d^2Z(z)}{dz^2} = E_zZ(z)$$

$$X(x) = \sqrt{\frac{2}{a}}\sin\frac{n_x\pi x}{a} \qquad E_{n_x} = \frac{n_x^2h^2}{8ma^2}$$

$$Y(y) = \sqrt{\frac{2}{b}}\sin\frac{n_y\pi y}{b} \qquad E_{n_y} = \frac{n_y^2h^2}{8mb^2}$$

$$Z(z) = \sqrt{\frac{2}{c}}\sin\frac{n_z\pi z}{c} \qquad E_{n_z} = \frac{n_z^2h^2}{8mc^2}$$

$$\psi_{n_x,n_y,n_z}(x,y,z) = \sqrt{\frac{8}{abc}}\sin\frac{n_x\pi x}{a}\sin\frac{n_y\pi y}{b}\sin\frac{n_z\pi z}{c}$$

$$E_{n_x,n_y,n_z} = \frac{h^2}{8m}\left(\frac{n_x^2}{a^2}+\frac{n_y^2}{b^2}+\frac{n_z^2}{c^2}\right)$$

If the total energy can be written as a sum of independent variables corresponding to different degrees of freedom, the wave function is a product of individual terms, each corresponding to one of the degrees of freedom.

For a ***cube*** of side a;

$$\psi_{n_x,n_y,n_z}(x,y,z) = \sqrt{\frac{8}{a^3}} sin\frac{n_x \pi x}{a} sin\frac{n_y \pi y}{a} sin\frac{n_z \pi z}{a}$$

$$E_{n_x,n_y,n_z} = \frac{h^2}{8m}\left(\frac{n_x^2}{a^2}+\frac{n_y^2}{a^2}+\frac{n_z^2}{a^2}\right)$$

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

Several n_i combinations can yield the same $E_{j,k,l}$ - degenerate states

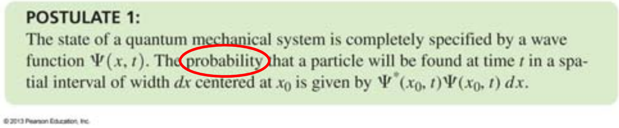
Leads to the concept of degeneracy.

Degeneracy is the number of ways a system can achieve a certain specified energy.

For the particle in a 3D box, a state is associated with a three quantum numbers. Three quantum numbers are generated because there are three sets of boundary conditions involved in 3D box.

More than one eigenfunction (state) would be associated with the same eigenvalue (energy) in degenerate states.

Consolidation of QM Postulates with solutions of Particle in a Box



POSTULATE 1:

The state of a quantum mechanical system is completely specified by a wave function $\Psi(x,t)$. The probability that a particle will be found at time t in a spatial interval of width dx centered at x_0 is given by $\Psi^*(x_0,t)\Psi(x_0,t)\,dx$.

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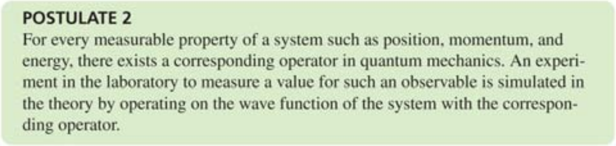
In general can Ψ be a complex function with terms carrying i = √(-1); $\Psi^*(x,t)\Psi(x,t)dx$

If Ψ is real then use; $\Psi^2(x,t)dx$



POSTULATE 2

For every measurable property of a system such as position, momentum, and energy, there exists a corresponding operator in quantum mechanics. An experiment in the laboratory to measure a value for such an observable is simulated in the theory by operating on the wave function of the system with the corresponding operator.

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Note: eigenvalues from an operator are of precise values. Measuring the value of a property associated with the operator of an *eigen state always produce the same value*.

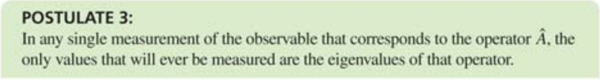
i.e. $\hat{H}\psi_n(x) = E_n\psi_n(x)$

What if the state is described by a function that is not an eigen function of the operator (yet a well behaved, and acceptable wave function)?

Then the energy associated with that wave function would *not* yield *a precise value* (like an eigenvalue) every time the property is measured.

What we would be able to calculate in such a case is the *average value* of the multiple single values that experiment would produce; and is also called the *expectation value*.

The single determinations are the eigen values that the operator would produce.



POSTULATE 3:

In any single measurement of the observable that corresponds to the operator $\hat{A}$, the only values that will ever be measured are the eigenvalues of that operator.

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Consider a normalized wave function constructed by adding two wave functions of particle in a box,
n =1 and n = 2 states as follows;

$$\psi_1 = c\sqrt{\frac{2}{a}}\,\mathbf{sin}\left(\frac{\pi x}{a}\right)+d\sqrt{\frac{2}{a}}\,\mathbf{sin}\left(\frac{2\pi x}{a}\right)$$

$$\psi_2 = \left(c'\,\mathbf{sin}\left(\frac{\pi x}{a}\right)+d'\,\mathbf{sin}\left(\frac{2\pi x}{a}\right)\right)$$

This is an *acceptable wave function*, well behaved first and second derivatives, BCs satisfied.

$$\underbrace{-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}}_{\widehat{H}}\underbrace{\left[\left(c'\,\mathbf{sin}\left(\frac{\pi x}{a}\right)+d'\,\mathbf{sin}\left(\frac{2\pi x}{a}\right)\right)\right]}_{}=\widehat{H}\psi$$

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\left[\left(c'\,\mathbf{sin}\left(\frac{\pi x}{a}\right)+d'\,\mathbf{sin}\left(\frac{2\pi x}{a}\right)\right)\right]$$

$$=\underbrace{\frac{\hbar^2\pi^2}{2ma^2}}_{\#}\underbrace{\left(c'\,\mathbf{sin}\left(\frac{\pi x}{a}\right)+4d'\,\mathbf{sin}\left(\frac{2\pi x}{a}\right)\right)}_{!?!}=E\psi'\neq E\psi$$

But ψ is *not* an eigenfunction of the energy operator.

$$c\cdot\sin\left(\frac{\pi\cdot x}{a}\right)+d\cdot\sin\left(\frac{2\cdot\pi\cdot x}{a}\right)$$

$$\frac{d}{dx}\qquad c\cdot\cos\left(\pi\cdot\frac{x}{a}\right)\cdot\frac{\pi}{a}+2\cdot d\cdot\cos\left(2\cdot\pi\cdot\frac{x}{a}\right)\cdot\frac{\pi}{a}$$

$$\frac{d^2}{dx^2}\qquad -c\cdot\sin\left(\pi\cdot\frac{x}{a}\right)\cdot\frac{\pi^2}{a^2}-4\cdot d\cdot\sin\left(2\cdot\pi\cdot\frac{x}{a}\right)\cdot\frac{\pi^2}{a^2}$$

Normalized function – however;

$$\int_0^a\left(c\sqrt{\frac{2}{a}}\,\mathbf{sin}\left(\frac{\pi x}{a}\right)+d\sqrt{\frac{2}{a}}\,\mathbf{sin}\left(\frac{2\pi x}{a}\right)\right)^2dx=1$$

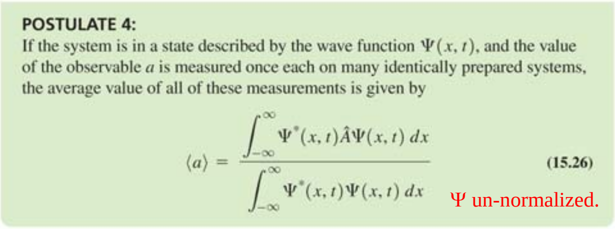
$$\int_0^a\left(c^2\overset{=1}{\left(\cancel{\sqrt{\frac{2}{a}}\,\mathbf{sin}\left(\frac{\pi x}{a}\right)}\right)^2}+2cd\,\overset{=0}{\cancel{\sqrt{\frac{2}{a}}\,\mathbf{sin}\left(\frac{\pi x}{a}\right)\sqrt{\frac{2}{a}}\,\mathbf{sin}\left(\frac{2\pi x}{a}\right)}}+d^2\overset{=1}{\left(\cancel{\sqrt{\frac{2}{a}}\,\mathbf{sin}\left(\frac{2\pi x}{a}\right)}\right)^2}\right)dx$$

$=c^2+d^2=1$ Normalization

Note the condition: $c^2+d^2=1$

$|c|<1$ and $|d|<1$

c^2 and d^2 are interpreted as the probability that the state *emulates* eigenstates n=1 and n=2 respectively



POSTULATE 4:

If the system is in a state described by the wave function $\Psi(x,t)$, and the value of the observable a is measured once each on many identically prepared systems, the average value of all of these measurements is given by

$$\langle a\rangle=\frac{\int_{-\infty}^{\infty}\Psi^*(x,t)\hat{A}\Psi(x,t)\,dx}{\int_{-\infty}^{\infty}\Psi^*(x,t)\Psi(x,t)\,dx}\qquad(15.26)$$

Ψ un-normalized.

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Because wave function is real and normalized

$$\int\Psi^*(x)\Psi(x)dx=\int\Psi(x)\Psi(x)dx=1$$

In general $<E>=\int\Psi^*(x)\widehat{H}\Psi(x)dx$

$$\langle E\rangle = \int_0^a \psi^*(x)\left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}+V(x)\right]\psi(x)\,dx$$

$$\langle E\rangle = \frac{2}{a}\int_0^a\left(c^*\sin\frac{\pi x}{a}+d^*\sin\frac{2\pi x}{a}\right)\left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\right]\left(c\sin\frac{\pi x}{a}+d\sin\frac{2\pi x}{a}\right)dx$$

$$\langle E\rangle = \overset{\downarrow}{\frac{2}{a}}\left[|c|^2E_1\overbrace{\int_0^a \sin^2\frac{\pi x}{a}\,dx} + |d|^2E_2\overbrace{\int_0^a\sin^2\frac{2\pi x}{a}\,dx}\right] + \frac{2}{a}\left[c^*\,d\,E_2\int_0^a \cancel{\sin\frac{\pi x}{a}\sin\frac{2\pi x}{a}}\,dx + d^*\,c\,E_1\int_0^a\cancel{\sin\frac{\pi x}{a}\sin\frac{2\pi x}{a}}\,dx\right]$$

$$\langle E\rangle = |c|^2E_1+|d|^2E_2$$

Calculating momentum:

Solutions of 1D box: $\psi_n(x) = \sqrt{\frac{2}{a}}\sin\left(\frac{n\pi x}{a}\right)$

ψ_n is an eigenfunction of the Hamiltonian not an eigenfunction of momentum operator.

The QM operator for momentum p is; $\hat{p} = -i\hbar\frac{d}{dx}$

So we calculate the average, <p> using postulate 4.

$$\langle p\rangle = \int_0^a \psi(x)\hat{p}\psi(x)dx$$

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

$$\langle p \rangle = \int_0^a \psi^*(x)\hat{p}\psi(x)dx$$

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

$$= \frac{-2i\hbar n\pi}{a^2}\int^a \sin\left(\frac{n\pi x}{a}\right)\cos\left(\frac{n\pi x}{a}\right)dx = \frac{-i\hbar}{a}\left[\sin^2 n\pi - \sin^2 0\right] = 0$$

Note:
Calculated <p> = 0; despite KE = $p^2/2m \neq 0$!!

Explain.

Calculating position:

Solutions of 1D box: $\psi_n(x) = \sqrt{\frac{2}{a}}\sin\left(\frac{n\pi x}{a}\right)$

Again it is a eigenfunction of the Hamiltonian not an eigenfunction of position operator.

The QM operator for position x is; $\hat{x} = x$

So we calculate <x>; mean x using postulate 4.

$$\langle x \rangle = \int_0^a \psi(x)\hat{x}\psi(x)dx = \int_0^a \psi(x)x\psi(x)dx$$

$$\langle x \rangle = \int_0^a \psi(x)\hat{x}\psi(x)dx$$

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

$$\langle x \rangle = \frac{a}{2}$$

Calculated <x> = a/2; the average value of the position is half way between the ends if 1D box.

Motion of particles in confined boundaries leads to quantization (discrete values for properties) and the quantized states are described by standing wave like wavefunctions.

Motion of particles in infinite space, i.e. unconfined space (free particles) leads to a range of values for the properties. The wavefunction in such situations resemble a propagating wave.