Lecture-XXVI

Time-Independent Schrodinger Equation

Time Independent Schrodinger Equation:

The time-dependent Schrodinger equation: $$i\hbar\frac{\partial\Psi}{\partial t}=-\frac{\hbar^2}{2m}\frac{\partial^2\Psi}{\partial x^2}+V\Psi.$$

Assume that V is independent of time t. In that case the Schrodinger equation can be solved by the method of separation of variables: $\Psi(x,t)=\psi(x)\,f(t)$

$$\frac{\partial\Psi}{\partial t}=\psi\frac{df}{dt},\quad \frac{\partial^2\Psi}{\partial x^2}=\frac{d^2\psi}{dx^2}f \qquad\qquad i\hbar\psi\frac{df}{dt}=-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2}f+V\psi f.$$

Then dividing through by ψf: $$i\hbar\frac{1}{f}\frac{df}{dt}=-\frac{\hbar^2}{2m}\frac{1}{\psi}\frac{d^2\psi}{dx^2}+V.$$

Now the left side is a function of t alone, and the right side is a function of x alone. The only way this can possibly be true is if both sides are constant (*say E, the exact meaning will be clear later*). Then

$$i\hbar\frac{1}{f}\frac{df}{dt}=E,\quad f(t)=e^{-iEt/\hbar}. \quad\Bigg|\quad -\frac{\hbar^2}{2m}\frac{1}{\psi}\frac{d^2\psi}{dx^2}+V=E,\ \text{or}\ \boxed{-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2}+V\psi=E\psi.}$$

The second is called the **time-independent Schrodinger equation**; it requires the knowledge of the potential *V*. Before solving the time-independent Schrodinger equation for certain potentials, let us understand the property of the solution.

I. Stationary states: Although the wave function itself,

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

does obviously depend on t, the probability density

$$|\Psi(x,t)|^2 = \Psi^*\Psi = \psi^* e^{+iEt/\hbar}\psi e^{-iEt/\hbar} = |\psi(x)|^2$$

does not--the time dependence cancels out. That is why they are called stationary states.

The same thing happens in calculating the expectation value of any dynamical variable reduces to

$$\langle Q(x,p)\rangle = \int \psi^* Q(x, \frac{\hbar}{i}\frac{d}{dx})\psi\, dx.$$

Every expectation value is constant in time. In particular, <*x*> is constant, and hence <*p*> = 0. Nothing ever happens in a stationary state.

Note: To become the expectation values real, finite, well-behaved physical quantities, the ψ(x) and dψ(x)/dx then must be finite, single valued and continuous.

II. States of definite total energy:

In classical mechanics, the total energy (kinetic plus potential) is called the Hamiltonian: $H(x, p) = \frac{p^2}{2m} + V(x).$

The corresponding Hamiltonian operator is : $\hat{H} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x).$

Thus the time-independent Schrodinger equation can be written as $\hat{H}\psi = E\psi,$

and the expectation value of the total energy is $\langle H\rangle = \int \psi^* \hat{H}\psi\, dx = E\int |\psi|^2\, dx = E.$

and hence $\langle H^2\rangle = \int \psi^* \hat{H}^2\psi\, dx = E^2\int |\psi|^2\, dx = E^2.$

So the standard deviation in *H* is given by $\sigma_H^2 = \langle H^2\rangle - \langle H\rangle^2 = E^2 - E^2 = 0.$

But remember, if σ=0, then every member of the sample must share the same value.

Conclusion: A separable solution has the property that every measurement of the total energy is certain to return the value *E*.

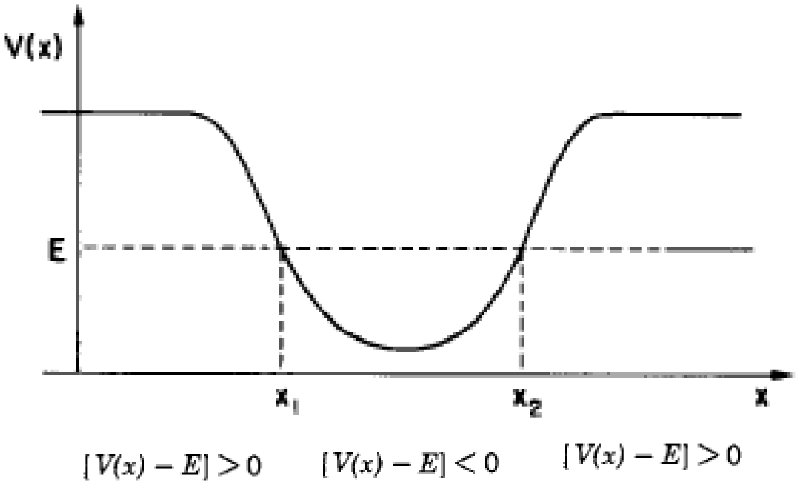
If the stationary state ψ is eigenfunction of any QM operator *A*, then there will be no uncertainty on the measured value *a* by operating *A* on ψ.

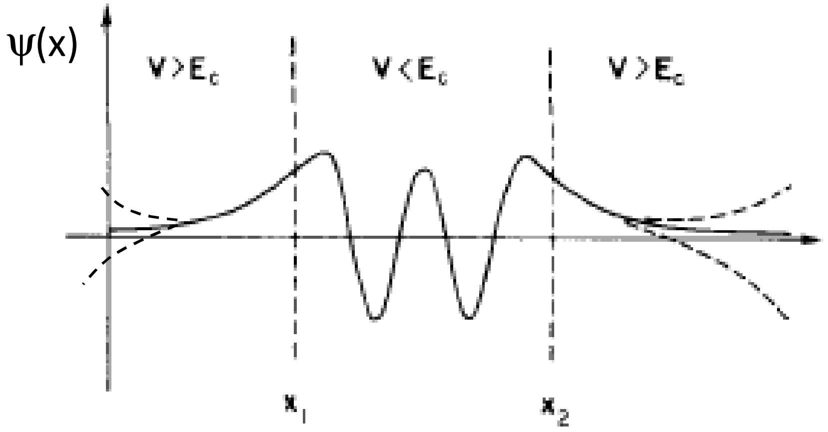
III. Discrete energy levels:

How a differential equation involving continuous functions and continuous variables give rise to discrete energy levels? Consider an electron confined in a region of space by some kind of a potential well. Now the electron must have well defined discrete energy levels.

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

$$k = \sqrt{\frac{2m}{\hbar^2}\left|V(x) - E\right|}$$





$$\frac{d^2\psi}{dx^2} - k^2\psi = 0$$

Exponential solution

$$\frac{d^2\psi}{dx^2} + k^2\psi = 0$$

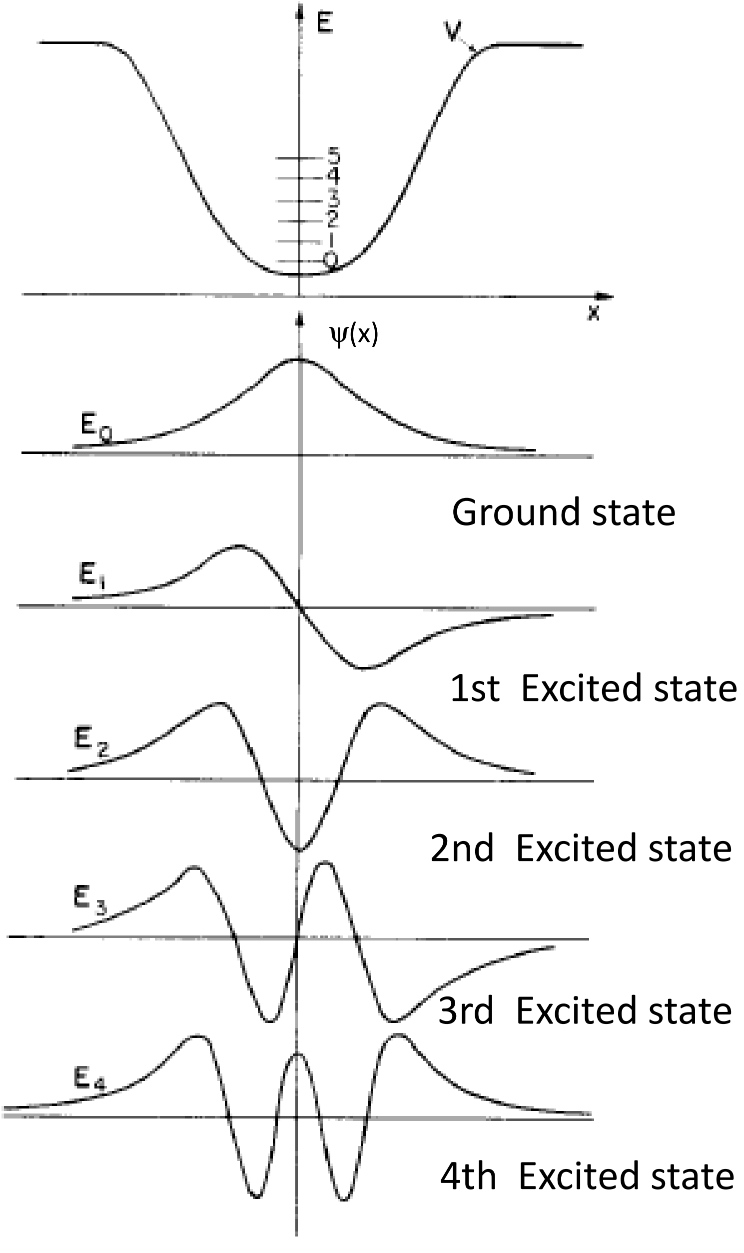
Oscillatory solution

$$\frac{d^2\psi}{dx^2} - k^2\psi = 0$$

Exponential solution

The solutions represented by dotted lines correspond to $E_c \pm \Delta E$. There exists a physically acceptable solution only for a particular value of E.

It does not mean that there is only one energy for a particle bound in a potential well.



Ground state

1st Excited state

2nd Excited state

3rd Excited state

4th Excited state

Other energies are possible but not energies arbitrarily close to E_c (or E).

Note that the solution we have plotted in the last slide, crosses the x-axis 4 times within the region $x_1<x<x_2$.

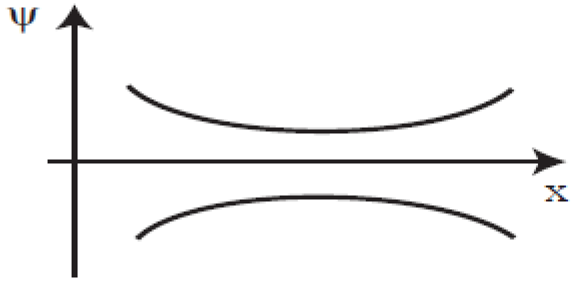
If there exists a solution corresponding to an energy less than E, then the solution must cross the x-axis only 3 times, only 2 times, only once or not at all within the region $x_1<x<x_2$.

There may also be other solutions corresponding to values of the energy higher than once shown.

Conclusion is that if a particle is bound in a potential well, its energy can take only the certain special values in a discrete energy spectrum.

IV. E_0 must be greater than V_{min}

if $E < V_{min}$, then ψ” and ψ always have the same sign: If ψ is positive (negative), then ψ” is also positive (negative). This means that ψ always curves away from the axis. However, it has got to go to zero as x→±∞ (else it would not be normalizable). At some point it’s got to depart from zero (if it doesn’t, it’s going to be identically zero everywhere), in (say) the positive direction. At this point its slope is positive, and increasing, so ψ gets bigger and bigger as x increases. It can’t ever “turn over” and head back toward the axis, because that would require a negative second derivative—it always has to bend away from the axis. By the same token, if it starts out heading negative, it just runs more and more negative. In neither case is there any way for it to come back to zero, as it must (at *x*→∞*) in order to be normalizable.*



V. Eigenvalues are real:

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

Since the Hamiltonian is a Harmitian operator, then

$$\int_{-\infty}^{+\infty} \psi^{*}(x)\,\hat{H}\psi(x)\,dx = \int_{-\infty}^{+\infty} \psi(x)\,\hat{H}^{\dagger}\psi^{*}(x)\,dx$$

$$E\int_{-\infty}^{+\infty} \psi^{*}(x)\psi(x)\,dx = E^{*}\int_{-\infty}^{+\infty} \psi(x)\psi^{*}(x)\,dx,\ E = E^{*},\ E\,\text{is real.}$$

VI. Eigenstates of different eigenvalues are orthogonal:

$$\hat{H}\psi_1 = E_1\psi_1;\quad \hat{H}\psi_2 = E_2\psi_2 \qquad \hat{H}^{\dagger}\psi_1^{*} = E_1^{*}\psi_1^{*};\ \hat{H}^{\dagger}\psi_2^{*} = E_2^{*}\psi_2^{*}$$

$$\int_{-\infty}^{+\infty} \psi_2^{*}(x)\,\hat{H}\psi_1(x)\,dx = \int_{-\infty}^{+\infty} \psi_1(x)\,\hat{H}^{\dagger}\psi_2^{*}(x)\,dx \qquad E_1^{*} = E_1,\ E_2^{*} = E_2$$

$$E_1\int_{-\infty}^{+\infty} \psi_2^{*}(x)\psi_1(x)\,dx = E_2^{*}\int_{-\infty}^{+\infty} \psi_1(x)\psi_2^{*}(x)\,dx = E_2\int_{-\infty}^{+\infty} \psi_1(x)\psi_2^{*}(x)\,dx$$

$$(E_2 - E_1)\int_{-\infty}^{+\infty} \psi_2^{*}(x)\psi_1(x)\,dx = 0;\ \text{Since}\ E_2 \neq E_1,\ \int_{-\infty}^{+\infty} \psi_2^{*}(x)\psi_1(x)\,dx = 0$$

$$\int_{-\infty}^{+\infty} \psi_m^{*}(x)\,\psi_n(x)\,dx = \delta_{mn},\ \ \delta_{mn} = \begin{cases} 1 & \text{for } n = m \\ 0 & \text{for } n \neq m \end{cases}$$

VII. Linear combination of separable solutions:

The general solution is a linear combination of separable solutions. As the time-independent Schrodinger equation yields an infinite collection of solutions $\psi_1(x)$, $\psi_2(x)$, $\psi_3(x)$, ... , each with its associated value of energy eigenvalues E_1, E_2, E_3 .... ; thus there is a different wave function for each allowed energy:

$$\Psi_1(x,t) = \psi_1(x)e^{-iE_1t/\hbar}, \quad \Psi_2(x,t) = \psi_2(x)e^{-iE_2t/\hbar}, \ldots .$$

Now the (time-dependent) Schrodinger equation has the property that any linear combinations of solutions is itself a solution. Once we have found the separable solutions, then, we can immediately construct a much more general solution, of the form

$$\Psi(x,t) = \sum_{n=1}^{\infty} c_n \psi_n(x) e^{-iE_nt/\hbar}.$$

It so happens that every solution to the (time-dependent) Schrodinger equation can be written in this form--it is simply a matter of finding the right constants (c_1, c_2, ...) so as to fit the initial conditions for the problem at hand.

VIII. Physical Interpretation of Expansion Coefficients:

The general solution can be written as a linear combinations of eigenfunctions as

$$\Psi(x,t) = \sum_{n=1}^{\infty} c_n \psi_n(x) e^{-iE_n t/\hbar}.$$

Now the orthonormality relation can be used to find c_n

$$\int \psi_n^*(x)\Psi(x,0)\,dx = \int dx\,\psi_n^*(x)\sum_{m=1}^{\infty} c_m \psi_m(x) = \sum_{m=1}^{\infty} c_m \int dx\,\psi_n^*(x)\psi_m(x) = \sum_{m=1}^{\infty} c_m \delta_{mn} = c_n$$

c_n tells us how much ψ_n is contained in $\psi(x,t)$, and a measurement has to return one of the eigenvalues of an operator Q.

$$1 = \int \Psi^*(x,0)\Psi(x,0)\,dx = \sum_{m=1}^{\infty}\sum_{n=1}^{\infty} c_m^* c_n \int \psi_m^*(x)\psi_n(x)\,dx = \sum_{m=1}^{\infty}\sum_{n=1}^{\infty} c_m^* c_n \delta_{mn} = \sum_{n=1}^{\infty} |c_n|^2$$

c_n^2 is the probability to find a particle in an eigenstate ψ_n in a generalized wavefunction $\psi(x,t)$.

$$\langle H \rangle = \int \Psi^* \hat{H} \Psi dx = \sum_{m=1}^{\infty}\sum_{n=1}^{\infty} c_m^* c_n E_n \int \psi_m^*(x)\psi_n(x)\,dx = \sum_{m=1}^{\infty}\sum_{n=1}^{\infty} c_m^* c_n E_n \delta_{mn} = \sum_{n=1}^{\infty} |c_n|^2 E_n$$

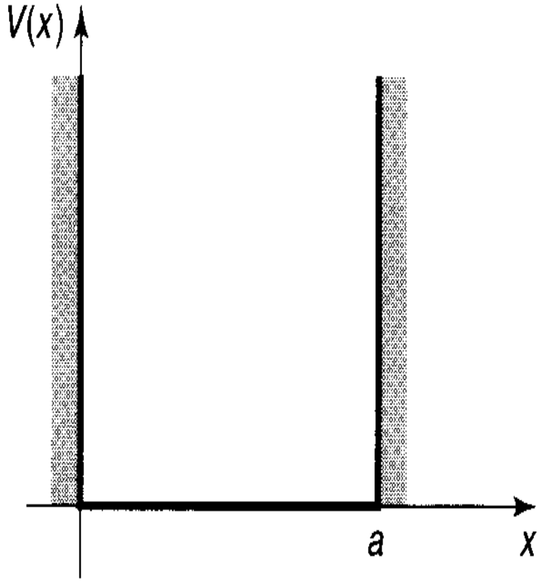
This is a manifestation of conservation of energy in quantum mechanics.

Analogy to Vector Analysis

QM	Vector
wavefunction: $\psi(x) = \sum_i c_i u_i(x)$	vector: $\mathbf{v} = \sum_i c_i \hat{e}_i$
energy eigenfunction: $u_i(x)$	basis vector: $\hat{e}_i$
# of independent $u_i(x)$	dimension of vector space
$\int_{-\infty}^{\infty} dx u_i^*(x)\psi(x)$	dot product: $\hat{e}_i \cdot \mathbf{v}$
$\int_{-\infty}^{\infty} dx u_i^*(x)u_j^*(x) = \delta_{ij}$	orthonormality: $\hat{e}_i \cdot \hat{e}_j = \delta_{ij}$

The wave functions $\psi(x)$ form a vector space, called the Hilbert space, the energy eigenfunctions $u_n(x)$ form a basis.

The Infinite Square Well Potential



The infinite square well potential is written as

$$V(x) = \begin{cases} 0, & \text{if } 0 \le x \le a, \\ \infty, & \text{otherwise} \end{cases}$$

For instance, take the potential for a conduction electron in a block of metal to be a finite square well. Infinite square well potentials can be used to discuss the quantum mechanical properties particles which are strictly confined within certain region of space.

In the region within the well V=0, hence the Schrodinger equation is given by

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = E\psi,$$ with $E > 0$. or $$\frac{d^2\psi}{dx^2} = -k^2\psi, \quad \text{where } k \equiv \frac{\sqrt{2mE}}{\hbar}.$$

The above equation is the (classical) simple harmonic oscillator equation; the general solution is

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

where A and B are arbitrary constants. Typically, these constants are fixed by the boundary conditions of the problem.

Both Ψ and dΨ/dx are continuous. But where the potential goes to infinity only the first of these applies.

Therefore $\psi(0) = \psi(a) = 0,$

At x = 0 $\psi(0) = A\sin 0 + B\cos 0 = B,$ so $B = 0,$ and hence $\psi(x) = A\sin kx.$

At x = a $\psi(a) = A\sin ka = 0,$ if *A* = 0, in which case we're left with the trivial nonnormalizable solution ψ(x) = 0.

then, $\sin ka = 0,$ which means that $ka = 0,\ \pm\pi,\ \pm 2\pi,\ \pm 3\pi, \ldots.$

But k = 0 is no good. Again, that would imply ψ(x) = 0. The negative solutions give nothing new, since sin(-θ) = - sin(θ) and the minus sign can be absorbed into A. So the distinct solutions are

$$\psi_n(x) = A\sin k_n x \quad \text{for} \quad k_n = \frac{n\pi}{a}, \quad \text{with } n = 1,\ 2,\ 3, \ldots.$$

Through normalization, *A* can be fixed.

$$\int_0^a |A|^2 \sin^2(kx)\,dx = |A|^2\frac{a}{2} = 1, \quad \text{so} \quad |A|^2 = \frac{2}{a}.$$

Inside the well, then, the solutions are

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

$$\int_0^{\pi} \sin ax \sin bx dx = \int_0^{\pi} \cos ax \cos bx dx = \begin{cases} 0 & \text{if } a \neq b \\ \pi/2 & \text{if } a = b \end{cases} \qquad \int_0^{\pi} \sin ax \cos ax dx = 0$$

Position and momentum expectations for the nth stationary state

$$\langle x\rangle = \int x|\psi|^2 dx = \frac{2}{a}\int_0^a x\sin^2\left(\frac{n\pi}{a}x\right)dx. \qquad \text{Let } y \equiv \frac{n\pi}{a}x, \text{ so } dx = \frac{a}{n\pi}dy; \quad y: 0 \to n\pi.$$

$$= \frac{2}{a}\left(\frac{a}{n\pi}\right)^2 \int_0^{n\pi} y\sin^2 y\, dy = \frac{2a}{n^2\pi^2}\left[\frac{y^2}{4} - \frac{y\sin 2y}{4} - \frac{\cos 2y}{8}\right]\Bigg|_0^{n\pi}$$

$$= \frac{2a}{n^2\pi^2}\left[\frac{n^2\pi^2}{4} - \frac{\cos 2n\pi}{8} + \frac{1}{8}\right] = \boxed{\frac{a}{2}.} \quad \text{(Independent of } n.\text{)}$$

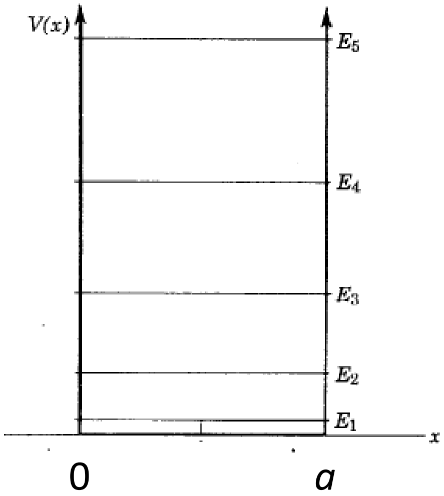
$$\langle p\rangle = m\frac{d\langle x\rangle}{dt} = \boxed{0.}$$

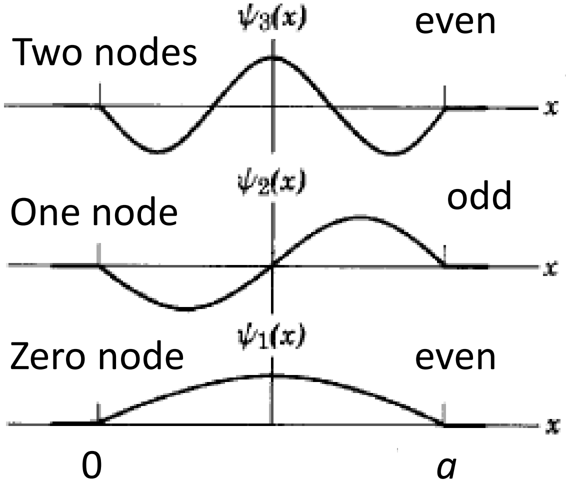
Note: it is true for stationary states of any potential.

Energy quantization:

Since $k_n = n\pi/a$ $\quad E_n = \frac{\hbar^2 k_n^2}{2m} = \frac{\pi^2 \hbar^2 n^2}{2ma^2} \quad n = 1, 2, 3, 4, 5, \ldots$

In sharp contrast to the classical case, **a quantum particle in the infinite square well can only have certain specific values. The total energy of the particle in the well is quantized.**





The first energy eigenvalue for the infinite square well it is $E_1 = \frac{\pi^2 \hbar^2}{2ma^2}$

This is called the *zero-point energy.* It is the lowest possible total energy the particle can have if it is bound by the infinite square well potential to the region 0<x<*a*. The particle cannot have zero total energy. The phenomenon is basically a result of the uncertainty principle.

Helium will not solidify even at the lowest attainable temperature (0.001°K), unless a very high pressure is applied.

Eigenstates are mutually orthogonal:

$$\int \psi_m(x)^* \psi_n(x)\, dx = \frac{2}{a} \int_0^a \sin\left(\frac{m\pi}{a}x\right) \sin\left(\frac{n\pi}{a}x\right) dx = 0. \qquad \text{since} \quad m \neq n.$$

Eigenstates form a complete set:

The stationary states are then $\Psi_n(x, t) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a}x\right) e^{-i(n^2\pi^2\hbar/2ma^2)t}.$

The general solution to the (time-dependent) Schrodinger equation is a linear combination of stationary states:

$$\Psi(x, t) = \sum_{n=1}^{\infty} c_n \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a}x\right) e^{-i(n^2\pi^2\hbar/2ma^2)t}.$$

The initial wave function then can be written as $\Psi(x, 0) = \sum_{n=1}^{\infty} c_n \psi_n(x).$

Now the orthonormality condition determines the actual coefficients:

$$c_n = \sqrt{\frac{2}{a}} \int_0^a \sin\left(\frac{n\pi}{a}x\right) \Psi(x, 0)\, dx. \qquad \text{and} \qquad \sum_{n=1}^{\infty} |c_n|^2 = 1$$

Therefore given the initial wave function, $\psi(x,0)$, compute the expansion coefficients c_n, and then one could obtain $\psi(x,t)$. Having the wave function, one can compute any dynamical quantities of interest.

Example: Consider the particle in the infinite square well has its initial wave function an even mixture of the first two stationary states:

$$\Psi(x,0) = A[\psi_1(x) + \psi_2(x)].$$

Find ψ(x, t), Compute <x>, <p> and <*H*>.

First, normalize the wave function:

$$|\Psi|^2 = \Psi^2\Psi = |A|^2(\psi_1^* + \psi_2^*)(\psi_1 + \psi_2) = |A|^2[\psi_1^*\psi_1 + \psi_1^*\psi_2 + \psi_2^*\psi_1 + \psi_2^*\psi_2].$$

$$1 = \int |\Psi|^2 dx = |A|^2 \int [|\psi_1|^2 + \psi_1^*\psi_2 + \psi_2^*\psi_1 + |\psi_2|^2] dx = 2|A|^2 \Rightarrow \boxed{A = 1/\sqrt{2}.}$$

Then ψ(x, t) is given by

$$\Psi(x,t) = \frac{1}{\sqrt{2}}\left[\psi_1 e^{-iE_1 t/\hbar} + \psi_2 e^{-iE_2 t/\hbar}\right]$$

Position expectation:

$$\langle x \rangle = \int x|\Psi(x,t)|^2 dx$$

$$= \frac{1}{a}\int_0^a x\left[\sin^2\left(\frac{\pi}{a}x\right) + \sin^2\left(\frac{2\pi}{a}x\right) + 2\sin\left(\frac{\pi}{a}x\right)\sin\left(\frac{2\pi}{a}x\right)\cos(3\omega t)\right] dx$$

$$= \frac{a}{2}\left[1 - \frac{32}{9\pi^2}\cos(3\omega t)\right]. \qquad \text{where} \qquad 3\omega = \frac{3\pi^2\hbar}{2ma^2}.$$

Momentum expectation:

$$\langle p \rangle = m\frac{d\langle x\rangle}{dt} = m\left(\frac{a}{2}\right)\left(-\frac{32}{9\pi^2}\right)(-3\omega)\sin(3\omega t) = \boxed{\frac{8\hbar}{3a}\sin(3\omega t).}$$

Energy expectation:

You could get either $\boxed{E_1 = \pi^2\hbar^2/2ma^2}$ or $\boxed{E_2 = 2\pi^2\hbar^2/ma^2,}$

with equal probability $\boxed{P_1 = P_2 = 1/2.}$

So $\langle H \rangle = \boxed{\frac{1}{2}(E_1 + E_2) = \frac{5\pi^2\hbar^2}{4ma^2};}$ it’s the *average of* E_1 *and* E_2.