Schrödinger Equation

The Dirac δ-Function

History

In development of quantum mechanics by P. Dirac, the following sequence of ideas occurred

(1) Observable = measurable quantity = Hermitian operator

(2) Physical states are linear combinations of the eigenvectors [requires complete orthonormal basis]

(3) Possible measurements are represented by the eigenvalues [must be real numbers]

$$\hat{O}\,|\lambda\rangle = \lambda\,|\lambda\rangle \quad , \quad |\lambda\rangle = eigenvector \quad , \quad \lambda = eigenvalue$$

(4) Some observables have a discrete spectrum [finite number or denumerably infinite number] —> eigenvectors satisfy

$$\langle \lambda' \mid \lambda \rangle = \delta_{\lambda'\lambda}$$

In this case, for different eigenvalues this is a well-defined statement.

(5) Other observables have a continuous spectrum [non-denumerably infinite number of eigenvalues].

For example, the position operator $\hat{X}$, which we have discussed and will discuss further shortly, is such that

$$\hat{X}\,|x\rangle = x\,|x\rangle \quad , \quad |x\rangle = eigenvector \quad , \quad x = eigenvalue$$

Now ask question, what is $\langle x' \mid x \rangle$? Dirac assumed

$$\langle x' \mid x\rangle \equiv \delta_{x'x} \equiv \delta(x-x')$$

where he proposed the definitions

$$\int_{-\infty}^{\infty} \delta(x-x')dx' = 1 \qquad \delta(x-x') = 0 \text{ if } x' \neq x \qquad \int_{-\infty}^{\infty} f(x')\delta(x-x')dx' = f(x)$$

Although, the new mathematical object assumed by Dirac did not fit in with any mathematics known at time (1929), the assumption gave the correct physical theory in sense that all its predictions agreed with experiments.

Eventually(1960), mathematicians, who initially vehemently disputed Dirac's assumption of new "function", caught up to physicists and proved all of its properties in the Theory of Distributions.

Introduction to the Schrödinger Equation in One Dimension

Time Evolution

One way of doing quantum calculations —> the Schrödinger Picture and involves Schrödinger equation for determining wavefunctions corresponding to energy eigenstates and for specifying time evolution of physical quantities. In this picture:

(a) states are represented by ket vectors that depend on t, $|\psi(t)\rangle$

(b) operators $\hat{Q}$ representing observables or measurable quantities are independent of t

We then get a time-dependent expectation value of the form $\left\langle \hat{Q}(t) \right\rangle = \langle \psi(t)| \hat{Q} |\psi(t)\rangle$

Let t be continuous parameter. Consider a family of unitary operators $\hat{U}(t)$, with following properties

$$\hat{U}(0) = \hat{I} \quad , \quad \hat{U}(t_1+t_2) = \hat{U}(t_1)\hat{U}(t_2)$$

Other transformations such as displacements, rotations and Lorentz boosts also satisfy these properties.

The operator $\hat{U}(t)$ is the time development operator whose existence was one of our postulates and whose form we specified earlier.

Now consider infinitesimal t.

We then write an infinitesimal version of unitary transformation (using Taylor series) as

$$\hat{U}(t) = \hat{I} + \left.\frac{d\hat{U}(t)}{dt}\right|_{t=0} t + O(t^2)$$

Since a unitary operator must satisfy unitarity condition $\hat{U}\hat{U}^+ = \hat{I}$ for all t, we have

$$\hat{U}\hat{U}^+ = \hat{I} = \left(\hat{I} + \left.\frac{d\hat{U}(t)}{dt}\right|_{t=0} t + ...\right)\left(\hat{I} + \left.\frac{d\hat{U}^+(t)}{dt}\right|_{t=0} t + ...\right) = \hat{I} + \left.\left[\frac{d\hat{U}(t)}{dt} + \frac{d\hat{U}^+(t)}{dt}\right]\right|_{t=0} t + ...$$

which implies that

$$\left.\left[\frac{d\hat{U}(t)}{dt} + \frac{d\hat{U}^+(t)}{dt}\right]\right|_{t=0} = 0$$

If we define $\left.\frac{d\hat{U}(t)}{dt}\right|_{t=0} = -i\hat{H}$ then condition becomes $-i\hat{H} = +(i\hat{H})^+ = -i\hat{H}^+$ or $\hat{H} = \hat{H}^+$

—> $\hat{H}$ is Hermitian operator —> generator of family of transformations $\hat{U}(t)$ because it determines operators uniquely. Now consider property $\hat{U}(t_1 + t_2) = \hat{U}(t_1)\hat{U}(t_2)$

A partial derivative is defined by $$\frac{\partial f(x,y,z)}{\partial x} = \left.\frac{df(x,y,z)}{dx}\right|_{y,z=\text{constants}}$$

For example, if f(x,y,z) = $x^3y + xy^7z + x^2\sin(z)$, then

$$\frac{\partial f}{\partial x} = 3x^2y + y^7z + 2x\sin(z)$$

$$\frac{\partial f}{\partial y} = x^3 + 7xy^6z$$

$$\frac{\partial f}{\partial x} = xy^7 + x^2\cos(z)$$

Using the partial derivative we have

$$\left.\frac{\partial}{\partial t_1}\hat{U}(t_1+t_2)\right|_{t_1=0} = \left.\frac{d}{dt}\hat{U}(t)\right|_{t=t_2} = \left.\left(\frac{d}{dt_1}\hat{U}(t_1)\right)\right|_{t_1=0}\hat{U}(t_2) = -i\hat{H}\hat{U}(t_2)$$

which is the equation for arbitrary t

$$i\frac{d\hat{U}(t)}{dt} = \hat{H}\hat{U}(t)$$

This equation is satisfied by the unique solution $$\hat{U}(t) = e^{-i\hat{H}t}$$

which gives an expression for time development operator in terms of Hamiltonian.

Formally —> Stone’s theorem.

Same form as we specified earlier for time-development operator.

Schrödinger picture follows directly from discussion of $\hat{U}(t)$ operator.

Suppose we have some physical system represented by state vector $|\psi(0)\rangle$ at t = 0 and represented by state vector $|\psi(t)\rangle$ at t.

We ask this question.

How are these state vectors related to each other?

We make the following assumptions:

(1) every vector $|\psi(0)\rangle$ such that $\langle\psi(0) \mid \psi(0)\rangle = 1$ represents a possible state at t=0

(2) every vector $|\psi(t)\rangle$ such that $\langle\psi(t)|\psi(t)\rangle = 1$ represents possible state at t

(3) every Hermitian operator represents an observable or measurable quantity

(4) properties of physical system determine state vectors to within phase factor since $|\phi\rangle = e^{i\alpha} |\psi\rangle$ implies that
$$\langle\varphi \mid \varphi\rangle = \langle\psi| e^{-i\alpha} e^{i\alpha} |\psi\rangle = \langle\psi \mid \psi\rangle = 1$$

(5) $|\psi(t)\rangle$ is determined by $|\psi(0)\rangle$

Now, if $|\psi(0)\rangle$ and $|\phi(0)\rangle$ represent two possible states at t = 0 and $|\psi(t)\rangle$ and $|\phi(t)\rangle$ represent corresponding states at t, then

$|\langle\phi(0) \mid \psi(0)\rangle|^2$ = probability of finding system in state represented by $|\phi(0)\rangle$ given that system is in state $|\psi(0)\rangle$ at t=0

$|\langle\phi(t) \mid \psi(t)\rangle|^2$ = probability of finding system in state represented by $|\phi(t)\rangle$ given that system is in state $|\psi(t)\rangle$ at t

(6) It makes physical sense to assume that these two probabilities should be same

$$|\langle\varphi(0) \mid \psi(0)\rangle|^2 = |\langle\varphi(t) \mid \psi(t)\rangle|^2$$

Wigner's theorem (linear algebra) —> exists unitary, linear operator $\hat{U}$ such that

$|\psi(t)\rangle = \hat{U}(t)\,|\psi(0)\rangle$ and an expression of the form

$$\left|\langle\alpha|\,\hat{U}(t)\,|\beta\rangle\right|^2$$

gives the probability that the system is in state $|\alpha\rangle$ at t given that it was in state $|\beta\rangle$ at t=0.

We assume this expression is continuous function of t. We already showed that $\hat{U}(t)$ satisfies the equation

$$i\frac{d\hat{U}(t)}{dt} = \hat{H}\hat{U}(t) \qquad \text{or} \qquad \hat{U}(t) = e^{-i\hat{H}t}$$

and thus,

$$|\psi(t)\rangle = \hat{U}(t)\,|\psi(0)\rangle = e^{-i\hat{H}t}\,|\psi(0)\rangle$$

which —> an equation of motion for state vector

$$i\frac{d\hat{U}(t)}{dt}\,|\psi(0)\rangle = \hat{H}\hat{U}(t)\,|\psi(0)\rangle \longrightarrow i\frac{d}{dt}\,|\psi(t)\rangle = \hat{H}\,|\psi(t)\rangle$$

which is the abstract form of the famous Schrödinger equation.

We will derive the standard form of the equation shortly.

As said earlier, operator $\hat{U}(t) = e^{-i\hat{H}t}$ —> time evolution operator.

Finally, we can write the time-dependent expectation value as

$$|\psi(t)\rangle = \hat{U}(t)\,|\psi(0)\rangle = e^{-i\hat{H}t}\,|\psi(0)\rangle \longrightarrow \left\langle \hat{Q}(t) \right\rangle = \langle\psi(t)|\,\hat{Q}\,|\psi(t)\rangle$$

—> Schrödinger picture where state vectors change with time and operators are constant in time.

Note that Schrödinger picture is not the same as Schrödinger equation.

The Schrödinger equation involves mathematical object called the wave function which is one particular representation of state vector, namely the position representation - will see later.

Thus, Schrödinger equation is applicable only to Hamiltonians that describe operators dependent on external degrees of freedom like position and momentum.

The Schrödinger picture, on other hand, works with both internal and external degrees of freedom and can handle much wider class of physical systems, as shall see.

Schrödinger Wave equation - Coordinate Representation - Wave functions: Approach #2

To form representation of an abstract linear vector space we must carry out these steps:

(1) Choose complete, orthonormal set of basis vectors $\{|\alpha_k\rangle\}$

(2) Construct identity operator $\hat{I}$ as sum over one-dimensional subspace projection operators $|\alpha_k\rangle\langle\alpha_k|$

$$\hat{I} = \sum_k |\alpha_k\rangle\,\langle\alpha_k|$$

(3) Write arbitrary vector $|\psi\rangle$ as linear combination or superposition of basis vectors using identity operator

$$|\psi\rangle = \hat{I}\,|\psi\rangle = (\sum_k |\alpha_k\rangle \langle\alpha_k|)\,|\psi\rangle = \sum_k \langle\alpha_k \mid \psi\rangle\,|\alpha_k\rangle$$

It is clear from equation, that knowledge about behavior(say in time) of the expansion coefficients $\langle\alpha_k \mid \psi\rangle$ —> behavior of state vector $|\psi\rangle$ and allow us to make predictions.

Remember also, that the expansion coefficient is the probability amplitude for particle in state $|\psi\rangle$ to behave like it is in state $|\alpha_k\rangle$.

A particular representation, very important in study of many systems using Quantum Mechanics, is formed using the eigenstates of the position operator as a basis —> coordinate or position representation.

We restrict our attention to one dimension for simplicity.

Eigenstates $\{|x\rangle\}$ of the position operator $\hat{x}$ satisfy $\hat{x}\,|x\rangle = x\,|x\rangle$

where eigenvalues x are continuous variables in range $[-\infty,\infty]$ —> basis of coordinate representation.

Expanding earlier discussions, in this case, the summations become integrals and we have

$$\hat{I} = \int |x\rangle \langle x|\,dx \longrightarrow |\psi\rangle = \hat{I}\,|\psi\rangle = \int (|x\rangle \langle x|)\,|\psi\rangle\,dx = \int \langle x \mid \psi\rangle\,|x\rangle\,dx$$

The expansion coefficient in the coordinate representation is given by $\psi(x) = \langle x \mid \psi\rangle$

Since the inner product defined for all states |x⟩, the new object is clearly function of eigenvalues x —> probability amplitude for finding particle at point x in 1-dimensional space if in (abstract)state vector |ψ⟩ —> wave function.

Bra vector corresponding to |ψ⟩ is $\langle\psi| = \langle\psi|\,\hat{I} = \int \langle\psi \mid x\rangle \langle x|\,dx = \int \langle x \mid \psi\rangle^* \langle x|\,dx$

The normalization condition takes the form

$$\langle\psi \mid \psi\rangle = 1 = \langle\psi|\,\hat{I}\,|\psi\rangle = \int \langle\psi \mid x\rangle \langle x \mid \psi\rangle\,dx = \int |\langle x \mid \psi\rangle|^2 dx = \int |\psi(x)|^2 dx = \int \psi^*(x)\psi(x)dx$$

The probability amplitude for a particle in state |ψ⟩ to behave like it is in state |ϕ⟩ is

$$\langle\phi \mid \psi\rangle = (\int \langle x \mid \phi\rangle^* \langle x|\,dx)(\int \langle x' \mid \psi\rangle\,|x'\rangle\,dx') \quad = \int dx \int dx' \langle x \mid \phi\rangle^* \langle x' \mid \psi\rangle \langle x \mid x'\rangle$$

In order to evaluate this, need the normalization condition $\langle x \mid x'\rangle$.

We have

$$|\psi\rangle = \int \langle x' \mid \psi\rangle\,|x'\rangle\,dx' \qquad \langle x \mid \psi\rangle = \int \langle x' \mid \psi\rangle \langle x \mid x'\rangle\,dx' \qquad \psi(x) = \int \psi(x') \langle x \mid x'\rangle\,dx'$$

which implies that $\langle x \mid x'\rangle = \delta(x - x')$

where $\delta(x-a) = \begin{cases} \text{undefined} & x \neq a \\ 0 & \text{otherwise} \end{cases}$ and $\int\limits_{-\infty}^{\infty} f(x)\delta(x-a)dx = f(a)$

for any function f(x) —> Dirac delta function as mentioned earlier.

Putting into above equation for ψ(x), we have

$$\psi(x) = \int \psi(x') \langle x \mid x' \rangle \, dx' = \int \psi(x')\delta(x - x')dx'$$ —> defining integral.

Thus, delta function normalization follows from completeness property of projection operators.

Using this result we get

$$\langle \varphi \mid \psi \rangle = \int dx \int dx' \, \langle x \mid \varphi \rangle^* \langle x' \mid \psi \rangle \, \delta(x - x') \quad = \int \langle x \mid \varphi \rangle^* \langle x \mid \psi \rangle \, dx = \int \varphi^*(x)\psi(x)dx$$

We formally write $\hat{x}$ operator using expansion in eigenvalues and projection operators as

$$\hat{x} = \int x \, |x\rangle \langle x| \, dx$$

Will also need properties of linear momentum operator. Eigenstates {|p⟩} of momentum operator $\hat{p}$ satisfy $\hat{p}\,|p\rangle = p\,|p\rangle$

where eigenvalues p are continuous variables in range [–∞,∞] —> basis of momentum representation. Repeating the mathematical step used with x-representation we have

$$\hat{I} = \frac{1}{2\pi\hbar} \int |p\rangle \langle p| \, dp \, |\psi\rangle = \hat{I} \, |\psi\rangle = \frac{1}{2\pi\hbar} \int (|p\rangle \langle p|) \, |\psi\rangle \, dp = \frac{1}{2\pi\hbar} \int \langle p \mid \psi \rangle \, |p\rangle \, dp \quad \Psi(p) = \langle p \mid \psi \rangle$$

$$\langle \psi | = \langle \psi | \, \hat{I} = \frac{1}{2\pi\hbar} \int \langle \psi \mid p \rangle \langle p| \, dp = \frac{1}{2\pi\hbar} \int \langle p \mid \psi \rangle^* \langle p| \, dp$$

$$\frac{1}{2\pi\hbar} \langle p \mid p' \rangle = \delta(p - p')$$

$$\hat{p} = \frac{1}{2\pi\hbar} \int p \, |p\rangle \langle p| \, dp$$

Now we derive connections between two representations.

Need to determine quantity ⟨x | p⟩ —> $\langle x \mid p \rangle = e^{ipx/\hbar}$ —> key result.

It will enable us to derive the Schrödinger equation.

Derivation: A representation of Dirac delta function is

$$\frac{1}{2\pi\hbar}\int_{-\infty}^{\infty} e^{ip(x-x')}dp = \delta(x-x')$$

By representation —> can show that

$$\int_{-\infty}^{\infty} f(x)\left[\frac{1}{2\pi\hbar}\int_{-\infty}^{\infty} e^{ip(x-a)}dp\right]dx = f(a)$$

for any function f(x).

Result follows from Fourier transform theory.

Now can rewrite equation in another way

$$\frac{1}{2\pi\hbar}\int_{-\infty}^{\infty} e^{ip(x-x')}dp = \delta(x-x') = \langle x \mid x' \rangle = \langle x|\,\hat{I}\,|x'\rangle$$

$$= \langle x|\left[\int_{-\infty}^{\infty} |p\rangle\langle p|\,dp\right]|x'\rangle = \int_{-\infty}^{\infty} \langle x \mid p\rangle\langle p \mid x'\rangle\,dp \;=\; \int_{-\infty}^{\infty} \langle x \mid p\rangle\langle x' \mid p\rangle^{*}\,dp$$

which is clearly satisfied by $\langle x \mid p \rangle = e^{ipx/\hbar}$

It is not unique choice, however.

It is choice, however, that allows Quantum Mechanics to make predictions that agree with experiment.

We might even say that this choice is another postulate!

Now, we can use these results to determine the expectation values of operators involving position and momentum operators.

Since we are interested in coordinate representation need only determine these relationships.

Position operator calculations are straightforward

$$\langle x|\,\hat{x}\,|\psi\rangle = x\,\langle x \mid \psi\rangle \quad , \quad \langle x|\,f(\hat{x})\,|\psi\rangle = f(x)\,\langle x \mid \psi\rangle$$

For the momentum operator write

$$\langle x|\,\hat{p}\,|\psi\rangle = \frac{1}{2\pi\hbar}\int dp\,\langle x|\hat{p}\,|p\rangle\,\langle p \mid \psi\rangle = \frac{1}{2\pi\hbar}\int dp\,\langle x|p\,|p\rangle\,\langle p \mid \psi\rangle = \frac{1}{2\pi\hbar}\int pdp\,\langle x \mid p\rangle\,\langle p \mid \psi\rangle$$

Using $\langle x \mid p\rangle = e^{ipx/\hbar}$ we have $p\,\langle x \mid p\rangle = -i\hbar\frac{d}{dx}\,\langle x \mid p\rangle = \langle x|\,\hat{p}\,|p\rangle$

and

$$\begin{aligned}\langle x|\,\hat{p}\,|\psi\rangle &= \frac{1}{2\pi\hbar}\int dp\,\langle x|\hat{p}\,|p\rangle\,\langle p \mid \psi\rangle \\ &= \frac{1}{2\pi\hbar}\int dp\,\langle x|p\,|p\rangle\,\langle p \mid \psi\rangle = \frac{1}{2\pi\hbar}\int dp\left[-i\hbar\frac{d}{dx}\,\langle x \mid p\rangle\right]\langle p \mid \psi\rangle \\ &= \frac{-i}{2\pi}\frac{d}{dx}\int dp\,\langle x \mid p\rangle\,\langle p \mid \psi\rangle = -i\hbar\frac{d}{dx}\,\langle x \mid \psi\rangle\end{aligned}$$

Can also show that $$\langle \vec{x} | \hat{p}^2 | \psi \rangle = -\left(-i\hbar \frac{d}{dx}\right)^2 \langle \vec{x} \mid \psi \rangle = -\hbar^2 \frac{d^2}{dx^2} \langle \vec{x} \mid \psi \rangle$$

Using these results, we can now derive Schrödinger wave equation.

Schrödinger wave equation in one dimension is a differential equation that corresponds to eigenvector/eigenvalue equation for Hamiltonian operator or energy operator.

The resulting states are energy eigenstates.

We already saw that energy eigenstates are stationary states and thus have simple time dependence.

This property allows us to find time dependence of amplitudes for very complex systems in straightforward way.

We have $\hat{H} |\psi_E\rangle = E |\psi_E\rangle$ where E is a number and

$$\hat{H} = \text{energy operator} = (\text{kinetic energy} + \text{potential energy}) \text{ operators} = \frac{\hat{p}^2}{2m} + V(\hat{x})$$

Then have

$$\langle x | \frac{\hat{p}^2}{2m} + V(\hat{x}) |\psi_E\rangle = E \langle x \mid \psi_E \rangle \longrightarrow \langle x | \frac{\hat{p}^2}{2m} |\psi_E\rangle + \langle x | V(\hat{x}) |\psi_E\rangle = E \langle x \mid \psi_E \rangle$$

$$-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \langle x \mid \psi_E \rangle + V(x) \langle x \mid \psi_E \rangle = E \langle x \mid \psi_E \rangle \longrightarrow -\frac{\hbar^2}{2m} \frac{d^2 \psi_E(x)}{dx^2} + V(x)\psi_E(x) = E\psi_E(x)$$

—> time-independent Schrödinger wave equation in 1 dimension.

Quantity $\psi_E(x) = \langle x \mid \psi_E \rangle$ is the wave function or energy eigenfunction in the position representation corresponding to energy E.

Quantity $|\psi_E(x)|^2 = |\langle x \mid \psi_E\rangle|^2$ represents probability density to find particle at coordinate x if in state represented by vector $|\psi_E\rangle$.

Since

$$\hat{U}(t)\,|\psi_E\rangle = e^{-i\frac{\hat{H}}{\hbar}t}\,|\psi_E\rangle = e^{-i\frac{E}{\hbar}t}\,|\psi_E\rangle \quad \text{have} \quad \langle x|\,\hat{U}(t)\,|\psi_E\rangle = \psi_E(x,t) = e^{-i\frac{E}{\hbar}t}\,\langle x \mid \psi_E\rangle$$

$$\longrightarrow \qquad \psi_E(x,t) = e^{-i\frac{E}{\hbar}t}\psi_E(x,0)$$

Therefore,

$$-\frac{\hbar^2}{2m}\frac{d^2\psi_E(x,t)}{dx^2} + V(x)\psi_E(x,t) = E\psi_E(x,t)$$

$$-\frac{\hbar^2}{2m}\frac{d^2\psi_E(x,t)}{dx^2} + V(\vec{x})\psi_E(x,t) = i\hbar\frac{\partial}{\partial t}\psi_E(x,t)$$

which is time-dependent Schrödinger wave equation.

Clearly, systems change in time.

One change is collapse process, discontinuous (and non-unitary).

We have also developed (from postulate #4) a deterministic (unitary) time evolution between measurements.

Between measurements states evolve according to equation

$$|\psi(t)\rangle = \hat{U}(t)\,|\psi(0)\rangle = e^{-i\hat{H}t/\hbar}\,|\psi(0)\rangle$$

For energy eigenstates we find that

$$|\psi_E(t)\rangle = \hat{U}(t)\,|\psi_E(0)\rangle = e^{-i\frac{\hat{H}}{\hbar}t}\,|\psi_E(0)\rangle = e^{-i\frac{E}{\hbar}t}\,|\psi_E(0)\rangle$$

that is, they only change by a phase factor.

Look at simple example to illustrate process.

Consider particle with hardness property but now place it in an external force that makes the system have a higher energy when particle in hard state $|h\rangle$ than when in soft state $|s\rangle$.

Define two energies $+E_0$ for $|h\rangle$ and $-E_0$ for $|s\rangle$.

These energies —> corresponding energy eigenvalues for two states.

Therefore, energy operator (in hard-soft basis) given by

$$\hat{H} = \begin{pmatrix} +E_0 & 0 \\ 0 & -E_0 \end{pmatrix}$$

Thus, have

Case #1 $\quad |\psi(0)\rangle = |h\rangle \qquad |\psi(t)\rangle = e^{-i\hat{H}t/\hbar}|h\rangle = e^{-iE_0 t/\hbar}|h\rangle$ and

Case #2 $\quad |\psi(0)\rangle = |s\rangle \qquad |\psi(t)\rangle = e^{-i\hat{H}t/\hbar}|s\rangle = e^{iE_0 t/\hbar}|s\rangle$

In either case, if measure hardness of this particle at t, still has same value as at t = 0, that is, for case #1

$$|\langle h \mid \psi(t)\rangle|^2 = \left|\langle h| e^{-iE_0 t/\hbar}|h\rangle\right|^2 = |\langle h \mid h\rangle|^2 = 1$$

$$|\langle s \mid \psi(t)\rangle|^2 = \left|\langle s| e^{-iE_0 t/\hbar}|h\rangle\right|^2 = |\langle s \mid h\rangle|^2 = 0$$

or hardness of particle does not change in time if starts out in state of definite hardness (—> energy eigenstates)

When initial state is not an energy eigenstate, that is, when it is superposition of hard and soft states, then it will change with time.

The change will be in relative phase between the components.

$$|\psi(0)\rangle = \frac{1}{\sqrt{2}}\left(|h\rangle + |s\rangle\right) \rightarrow |g\rangle$$

$$|\psi(t)\rangle = e^{-i\hat{H}t/\hbar}\,|\psi(0)\rangle = \frac{1}{\sqrt{2}}e^{-i\hat{H}t/\hbar}\left(|h\rangle + |s\rangle\right) = \frac{1}{\sqrt{2}}\left(e^{-i\hat{H}t/\hbar}\,|h\rangle + e^{-i\hat{H}t/\hbar}\,|s\rangle\right)$$

$$= \frac{1}{\sqrt{2}}\left(e^{-iE_0t/\hbar}\,|h\rangle + e^{iE_0t/\hbar}\,|s\rangle\right)$$

so relative phase is $e^{2iE_0t/\hbar}$.

This state is not eigenstate of hardness or color! What is probability of measuring various results?

Initially:

$$|\langle h \mid \psi(0)\rangle|^2 = \frac{1}{2} = |\langle s \mid \psi(0)\rangle|^2 \qquad\qquad |\langle g \mid \psi(0)\rangle|^2 = 1 \quad , \quad |\langle m \mid \psi(0)\rangle|^2 = 0$$

At time t:

$$|\langle h \mid \psi(t)\rangle|^2 = \left|\langle h|\left(\frac{1}{\sqrt{2}}\left(e^{-iE_0t/\hbar}\,|h\rangle + e^{iE_0t/\hbar}\,|s\rangle\right)\right)\right|^2 = \left|\frac{1}{\sqrt{2}}e^{-iE_0t/\hbar}\right|^2 = \frac{1}{2}$$

$$|\langle s \mid \psi(t)\rangle|^2 = \left|\langle s|\left(\frac{1}{\sqrt{2}}\left(e^{-iE_0t/\hbar}\,|h\rangle + e^{iE_0t/\hbar}\,|s\rangle\right)\right)\right|^2 = \left|\frac{1}{\sqrt{2}}e^{iE_0t/\hbar}\right|^2 = \frac{1}{2}$$

$$|\langle g \mid \psi(t)\rangle|^2 = \left|\langle g|\left(\frac{1}{\sqrt{2}}\left(e^{-iE_0t/\hbar}\,|h\rangle + e^{iE_0t/\hbar}\,|s\rangle\right)\right)\right|^2$$

$$= \left|\frac{1}{\sqrt{2}}e^{-iE_0t/\hbar}\,\langle g \mid h\rangle + \frac{1}{\sqrt{2}}e^{iE_0t/\hbar}\,\langle g \mid s\rangle\right|^2 = \left|\frac{1}{2}e^{-iE_0t/\hbar} + \frac{1}{2}e^{iE_0t/\hbar}\right|^2 = \cos^2\frac{2E_0t}{\hbar}$$

$$|\langle m \mid \psi(t)\rangle|^2 = \left|\langle m| \left(\frac{1}{\sqrt{2}} \left(e^{-iE_0 t/\hbar} |h\rangle + e^{iE_0 t/\hbar} |s\rangle \right) \right) \right|^2$$

$$= \left| \frac{1}{\sqrt{2}} e^{-iE_0 t/\hbar} \langle m \mid h\rangle + \frac{1}{\sqrt{2}} e^{iE_0 t/\hbar} \langle m \mid s\rangle \right|^2 = \left| \frac{1}{2} e^{-iE_0 t/\hbar} - \frac{1}{2} e^{iE_0 t/\hbar} \right|^2 = \sin^2 \frac{2E_0 t}{\hbar}$$

So the probability of measuring the hardness of a particle that was originally in green state remains 1/2 (as was at t = 0) since they are energy eigenstates or stationary states.

But much more interesting is the fact that probability for measurements of color oscillates between probability =1 for green and probability = 1 for magenta.

So the procedure is as follows:

(1) Find the energy operator for the physical system.

(2) Express the initial state as a superposition of energy eigenstates.

(3) Insert the simple time dependence of the energy eigenstate to obtain the time dependence of the state of the system.

(4) Determine probability for final measurements by taking appropriate inner products.

One-Dimensional Quantum Systems

Schrodinger equation in 1-dimension is

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

Solutions $\psi_E(x)$ are energy eigenstates (eigenfunctions). Time dependence given by

$$\psi_E(x,t) = e^{-i\frac{E}{\hbar}t}\psi_E(x,0) \qquad \text{where} \qquad \psi_E(x,0) = \langle x \mid E\rangle$$

and $\hat{H}\,|E\rangle = E\,|E\rangle$ where $\hat{H} = \frac{\hat{p}^2}{2m} + V(\hat{x})$

Thus we are faced with solving an ordinary differential equation with boundary conditions.

Since $\psi_E(x)$ is physically related to the probability amplitude and hence to the measurable probability, we assume that $\psi_E(x)$ is continuous.

Using this fact, we can determine the general continuity properties of $d\psi_E(x)/dx$.

The continuity property at a particular point, say $x = x_0$, is derived as follows:

$$\int_{x_0-\varepsilon}^{x_0+\varepsilon} \frac{d^2\psi_E(x)}{dx^2}dx = \int_{x_0-\varepsilon}^{x_0+\varepsilon} d\left(\frac{d\psi_E(x)}{dx}\right) = -\frac{2m}{\hbar^2}\left[E\int_{x_0-\varepsilon}^{x_0+\varepsilon}\psi_E(x)dx - \int_{x_0-\varepsilon}^{x_0+\varepsilon}V(x)\psi_E(x)dx\right]$$

Taking limit as $\varepsilon \to 0$

$$\lim_{\varepsilon\to 0}\left(\left.\frac{d\psi_E(x)}{dx}\right|_{x=x_0+\varepsilon} - \left.\frac{d\psi_E(x)}{dx}\right|_{x=x_0-\varepsilon}\right) = -\frac{2m}{\hbar^2}\left[E\lim_{\varepsilon\to 0}\int_{x_0-\varepsilon}^{x_0+\varepsilon}\psi_E(x)dx - \lim_{\varepsilon\to 0}\int_{x_0-\varepsilon}^{x_0+\varepsilon}V(x)\psi_E(x)dx\right]$$

or

$$\Delta\left(\frac{d\psi_E(x)}{dx}\right) = \frac{2m}{\hbar^2}\lim_{\varepsilon\to 0}\int\limits_{x_0-\varepsilon}^{x_0+\varepsilon} V(x)\psi_E(x)dx$$

where have used continuity of $\psi_E(x)$ to set

$$\lim_{\varepsilon\to 0}\int\limits_{x_0-\varepsilon}^{x_0+\varepsilon} \psi_E(x)dx = 0$$

—> that whether or not $d\psi_E(x)/dx$ has a discontinuity depends directly on the potential energy function.

If V(x) continuous at x = x_0, i.e., if $\lim_{\varepsilon\to 0}[V(x_0+\varepsilon) - V(x_0-\varepsilon)] = 0$ then

$$\Delta\left(\frac{d\psi_E(x)}{dx}\right) = \frac{2m}{\hbar^2}\lim_{\varepsilon\to 0}\int\limits_{x_0-\varepsilon}^{x_0+\varepsilon} V(x)\psi_E(x)dx = 0$$

and $d\psi_E(x)/dx$ is continuous.

If V(x) has finite discontinuity (jump) at x = x_0, i.e., $\lim_{\varepsilon\to 0}[V(x_0+\varepsilon) - V(x_0-\varepsilon)] = finite$ then

$$\Delta\left(\frac{d\psi_E(x)}{dx}\right) = \frac{2m}{\hbar^2}\lim_{\varepsilon\to 0}\int\limits_{x_0-\varepsilon}^{x_0+\varepsilon} V(x)\psi_E(x)dx = 0$$

and $d\psi_E(x)/dx$ is continuous.

Finally, if V(x) has an **infinite** jump at x = x_0, then we have two choices

(1) if potential is infinite over an extended region of x, then we must force $\psi_E(x) = 0$ in that region and use only the continuity of $\psi_E(x)$ as boundary condition at the edge of region.

(2) if potential is infinite at single point, i.e., $V(x) = \delta(x - x_0)$, then would have

$$\Delta\left(\frac{d\psi_E(x)}{dx}\right) = \frac{2m}{\hbar^2}\lim_{\varepsilon\to 0}\int_{x_0-\varepsilon}^{x_0+\varepsilon} V(x)\psi_E(x)dx = \frac{2m}{\hbar^2}\lim_{\varepsilon\to 0}\int_{x_0-\varepsilon}^{x_0+\varepsilon} \delta(x-x_0)\psi_E(x)dx$$

$$= \frac{2m}{\hbar^2}\lim_{\varepsilon\to 0}\psi_E(x_0) = \frac{2m}{\hbar^2}\psi_E(x_0)$$

and thus $d\psi_E(x)/dx$ is discontinuous.

Last thing we must worry about is the validity of probability interpretation of $\psi_E(x)$, i.e., $\psi_E(x) = \langle x|\psi_E\rangle$ = probability amplitude for particle in state $|\psi_E\rangle$ to be found at x —> must also have

$$\langle\psi_E \mid \psi_E\rangle = \int_{-\infty}^{\infty} |\psi_E(x)|^2\, dx < \infty$$

This means that we must be able to normalize the wave functions and make total probability that particle is somewhere on x–axis equal to one.

A wide range of interesting physical systems can be studied using 1-dimensional potential energy functions.

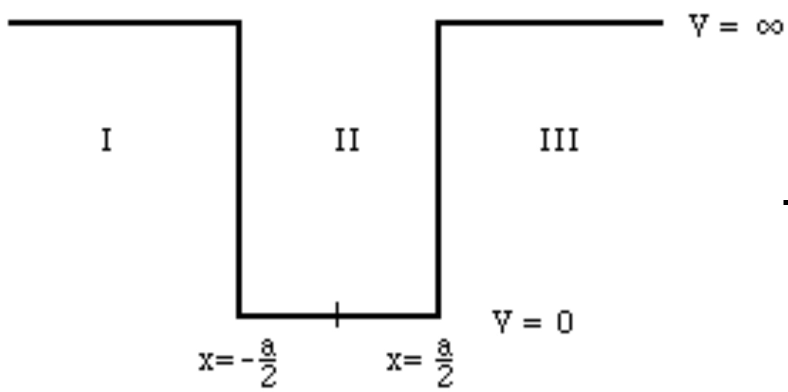
Quantized Energy Levels in the Infinite Square Well Potential

This is standard first problem in any quantum mechanics class!

Now consider potential energy function

$$V(x) = \begin{cases} 0 & -a/2 \le x \le a/2 \\ \infty & |x| \ge a/2 \end{cases}$$

This is the so-called infinite square well shown in the figure.



We consider the three regions labeled I, II, III.

—> example of potential that is infinite in an extended region.

Therefore, must require that wave function ψ(x) = 0 in these regions or the Schrodinger equation makes no sense mathematically. In this case have

$$\psi_I(x) = 0 \quad , \quad \psi_{III}(x) = 0$$

Digression: Solving Second-Order ODEs

The solution technique use in most cases is called **exponential substitution**.

Exponential Substitution = Method applicable to all ordinary differential equations of form

$$A\frac{d^2y}{dt^2} + B\frac{dy}{dt} + Cy = 0$$

where A, B and C are constants.

Definitions:

2nd-order = order of highest derivative
linear = no squares or worse
homogeneous = right-hand side = 0
constant coefficients = A, B, C

Therefore this equation is a 2nd-order, homogeneous, linear differential equation with constant coefficients.

Method: Consider a typical equation of form

$$\frac{d^2y}{dt^2} + 3\frac{dy}{dt} + 2y = 0$$

Make the exponential substitution

$$y = e^{\alpha t}$$

into ODE. This will convert diffEQ into an algebraic equation for α. We thus have

$$\frac{d^2y}{dt^2} = \frac{d^2e^{\alpha t}}{dt^2} = \alpha^2 e^{\alpha t} \qquad \frac{dy}{dt} = \frac{de^{\alpha t}}{dt} = \alpha e^{\alpha t}$$

which gives result

$$\left(\alpha^2 + 3\alpha + 2\right) e^{\alpha t} = 0 \Rightarrow \alpha^2 + 3\alpha + 2 = 0 \qquad \text{since } e^{\alpha t} \neq 0.$$

Solutions of algebraic equation tell us allowed values of α that give valid solutions to ODE.

In particular, in this case we get

$$\alpha = -1, -2$$

as solutions to quadratic equation.

This result means that $y = e^{-t}$ and $y = e^{-2t}$ satisfy the original ODE as can be seen by direct substitution.

If there is more than one allowed value of (as in this case), then the most general solution will be a linear combination of all possible solutions(because this is a linear diffEQ).

Since, in this case, allowed values of α are α = –1, –2, the most general solution of ODE is

$$y(t) = ae^{-t} + be^{-2t}$$

where a and b are constants to be determined by the initial conditions.

Number of arbitrary constants that need to be determined by initial conditions is equal to order(highest derivative → 2 in this case) of this ODE.

Suppose the initial conditions are

$$y = 0 \quad , \quad \frac{dy}{dt} = 1 \qquad \text{at } t = 0.$$

Then have

$$y(t) = ae^{-t} + be^{-2t} \qquad y(0) = 0 = a + b$$

$$\frac{dy}{dt} = -ae^{-t} - 2be^{-2t} \qquad \frac{dy}{dt}(0) = -a - 2b = 1$$

which gives a = –b = 1 and thus the solution is

$$y(t) = e^{-t} - e^{-2t}$$

One can easily substitute this solution into original equation and see that it works and has the correct initial conditions!!

Now **Simple Harmonic Motion**. The equation(spring) of motion has the form

$$M\frac{dv}{dt} = -kx \Rightarrow M\frac{d}{dt}\left(\frac{dx}{dt}\right) = -kx \Rightarrow M\frac{d^2x}{dt^2} + kx = 0$$

so that A=M, C=k and B=0

Although the exponential substitution method is very powerful as described, we can make it even more powerful by using a mathematical quantity called the complex exponential.

The change allows us to use this method for the SHM case.

Complex Exponentials - Alternative Very Powerful Method

Earlier found

$$e^{\pm i\alpha t} = \cos\alpha t \pm i\sin\alpha t \quad \text{or} \quad \sin\omega t = \frac{e^{i\omega t} - e^{-i\omega t}}{2i} \quad , \quad \cos\omega t = \frac{e^{i\omega t} + e^{-i\omega t}}{2}$$

Can use these results to solve SHM equation

$$M\frac{d^2y}{dt^2} + ky = 0 \rightarrow \frac{d^2y}{dt^2} + \omega^2 y = 0 \quad , \quad \omega^2 = \frac{k}{M}$$

Substituting y = $e^{\alpha t}$ get algebraic equation

$$\alpha^2 + \omega^2 = 0$$

—> solutions (allowed values of α) α = ±iω —> most general solution

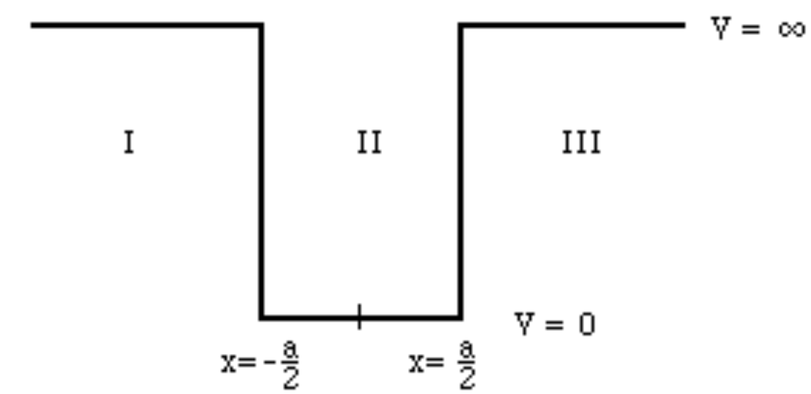
$$y(t) = Ae^{i\omega t} + Be^{-i\omega t}$$

Suppose initial conditions are $y = y_0 \quad , \quad \frac{dy}{dt} = 0$ at t = 0.

Then have

$$y(0) = y_0 = A + B \longrightarrow A = B = \frac{y_0}{2} \longrightarrow y(t) = y_0 \frac{e^{i\omega t} + e^{-i\omega t}}{2} = y_0 \cos \omega t$$

Returning to infinite square well Schrodinger equation:



Now in region II, Schrodinger equation becomes

$$-\frac{\hbar^2}{2m}\frac{d^2\psi_{II}}{dx^2} = E\psi_{II} \quad , \quad E = \frac{p^2}{2m} = \frac{\hbar^2 k^2}{2m}$$

which has general solution(using above method) given by

$$\psi_{II}(x) = Ae^{ikx} + Be^{-ikx}$$

where k is some parameter to be determined.

Continuity of wavefunction at x = ±a/2 says —>

$$\psi_{II}(-\frac{a}{2}) = Ae^{-i\frac{ka}{2}} + Be^{i\frac{ka}{2}} = 0 \text{ and } \psi_{II}(\frac{a}{2}) = Ae^{i\frac{ka}{2}} + Be^{-i\frac{ka}{2}} = 0$$

which imply that

$\frac{B}{A} = -e^{-ika} = -e^{ika}$ —> equation for allowed values (values corresponding to a valid solution) of parameter k.

Equation is $e^{2ika} = 1$ —> allowed values of k form a discrete spectrum of energy eigenvalues (**quantized** energies) given by

$$2k_n a = 2n\pi \rightarrow k_n = \frac{n\pi}{a} \rightarrow E_n = \frac{\hbar^2 k_n^2}{2m} = \frac{n^2\pi^2\hbar^2}{2ma^2} \, , \, n = 1, 2, 3, 4, ...$$

The corresponding wave functions are

$$\psi_{II}^{(n)}(x) = A_n(e^{ik_n x} - e^{-ik_n a}e^{-ik_n x}) = A_n e^{-i\frac{k_n a}{2}}\left(e^{ik_n\left(x+\frac{a}{2}\right)} - e^{-ik_n\left(x+\frac{a}{2}\right)}\right) = \tilde{A}_n \sin k_n\left(x+\frac{a}{2}\right)$$

and so on…..

We have mathematically solved ODE problem. Now what is the physical meaning of results?

We find a discrete spectrum of allowed energies corresponding to bound states of Hamiltonian.

Energy is quantized.

Bound states designate states localized in space, i.e., probability large only over restricted regions of space and goes to zero far from potential region.

Lowest energy value or lowest energy level or ground state energy is $E_1 = \frac{\pi^2\hbar^2}{2ma^2} > 0$

with

$$\psi_1(x) = \begin{cases} A\cos\left(\frac{\pi x}{a}\right) & |x| \leq a/2 \\ 0 & |x| \geq a/2 \end{cases}$$

This minimum energy is not zero because of the Heisenberg uncertainty principle(next lecture). Since particle has nonzero amplitude for being in well, we say that it is localized such that $\Delta x \approx a$ and thus

$$\Delta p \geq \frac{\hbar}{\Delta x} \approx \frac{\hbar}{a}$$

This says kinetic energy (or energy in this case because potential energy equals zero in region II) must have **minimum** value given approximately by

$$E_{\min} = K_{\min} \approx \frac{(\Delta p)^2}{2m} \approx \frac{\hbar^2}{2ma^2}$$

The solutions also have the property

$$\psi(-x) = \psi(x) \qquad n \text{ odd} \qquad\qquad \psi(-x) = -\psi(x) \qquad n \text{ even}$$

A discrete transformation of wave function corresponds to parity operator $\hat{\wp}$ where we have

$$\hat{\wp}\psi(x) = \psi(-x) = \psi(x) \rightarrow \textit{ even parity} \qquad\qquad \hat{\wp}\psi(x) = \psi(-x) = -\psi(x) \rightarrow \textit{ odd parity}$$

Now look more generally at the parity operation.

Suppose that the potential energy function obeys the rule $V(\vec{x}) = V(-\vec{x})$ and let $\psi(\vec{x})$ be solution of Schrodinger equation with energy E. Then

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

Now let $\vec{x} \rightarrow \vec{x}$ to get the equation

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + V(-\vec{x})\right)\psi(-\vec{x}) = E\psi(-\vec{x}) \qquad \text{or} \qquad \left(-\frac{\hbar^2}{2m}\nabla^2 + V(\vec{x})\right)\psi(-\vec{x}) = E\psi(-\vec{x})$$

—> that, if $\psi(\vec{x})$ is solution of Schrodinger equation with energy E, then $\psi(-\vec{x})$ is also solution of same Schrodinger equation and hence with same energy E —> $\psi(\vec{x}) \pm \psi(-\vec{x})$ are also solutions of same Schrodinger equation with same energy E (by linearity).

Now

$$\psi(\vec{x}) + \psi(-\vec{x}) \rightarrow \textit{ even parity solution} \qquad\qquad \psi(\vec{x}) - \psi(-\vec{x}) \rightarrow \textit{ odd parity solution}$$

This says that if $V(\vec{x}) = V(-\vec{x})$, then we can always choose solutions that have definite parity (even or odd).

Formally, we define the parity operator by the relation

$$\langle\vec{x}|\,\hat{\wp}\,|\psi\rangle = \langle -\vec{x} \mid \psi\rangle$$

Since

$$\langle\vec{x}|\,\hat{\wp}^2\,|\psi\rangle = \langle -\vec{x}|\,\hat{\wp}\,|\psi\rangle = \langle\vec{x} \mid \psi\rangle$$

—> must have $\hat{\wp}^2 = \hat{I}$, which means eigenvalues of $\hat{\wp}$ are ±1 as indicated earlier.

Now can show $\left[\hat{H},\hat{\wp}\right] = 0$ for symmetric potentials, i.e.,

$$\begin{aligned}
&\hat{\wp}\hat{H}\,|E\rangle = \hat{\wp}E\,|E\rangle = E\hat{\wp}\,|E\rangle = \pm E\,|E\rangle \\
&\hat{H}\hat{\wp}\,|E\rangle = \pm\hat{H}\,|E\rangle = \pm E\,|E\rangle \\
&\Rightarrow \left(\hat{\wp}\hat{H} - \hat{H}\hat{\wp}\right)|E\rangle = 0 \\
&\Rightarrow \left[\hat{H},\hat{\wp}\right] = 0
\end{aligned}$$

since $|E\rangle$ is an arbitrary state.

This commutator relationship says that $\hat{H}$ and $\hat{\wp}$ share a common set of eigenfunctions and that

$$\begin{aligned}
&\hat{H}\hat{\wp} = \hat{\wp}\hat{H} \\
&\hat{\wp}\hat{H}\hat{\wp} = \hat{\wp}^2\hat{H} = \hat{H} \\
&\hat{\wp}^{-1}\hat{H}\hat{\wp} = \hat{H}
\end{aligned}$$

This means that $\hat{H}$ is invariant under $\hat{\wp}$ transformation.

where we have used $\hat{\wp}^2 = \hat{I}$ in the derivation. It also says that

$$\hat{H}\left(\hat{\wp}\,|E\rangle\right) = \hat{\wp}\left(\hat{H}\,|E\rangle\right) = E\left(\hat{\wp}\,|E\rangle\right)$$

or $\hat{\wp}$ |E⟩ is an eigenstate of $\hat{H}$ with energy E as we stated.

The concept of parity invariance and the fact that $\hat{H}$ and $\hat{\wp}$ share a common set of eigenfunctions can greatly simplify the solution of the Schrodinger equation in many cases.