

Thus far we have not mentioned time. It has been assumed that when we make successive measurements they are done with negligible time delay. In this section we will consider how states should change with time.

It is important to realize that in non-relativistic quantum mechanics we do not treat time as an operator - it is not an observable in the same way that position is. Time is treated as a parameter in much the same way as it is in classical non-relativistic mechanics.

Let's suppose at some time t_0 we prepare a state $|\alpha\rangle$. In general, we should allow this state to change over time according to some, as yet unspecified, dynamics

$$|\alpha, t_0\rangle \xrightarrow[\text{evolution}]{\text{time}} |\alpha, t_1\rangle$$

We can represent the effect of a 'translation in time' by an operator, just like we did for a translation in space

$$|\alpha, t_1\rangle = \hat{U}(t_1, t_0) |\alpha, t_0\rangle$$

We can try to determine $\hat{U}(t_1, t_0)$ by proposing properties that it must have

1. probability conservation: $\langle \alpha, t_0 | \alpha, t_0 \rangle = 1 \rightarrow \langle \alpha, t_1 | \alpha, t_1 \rangle = 1$
 $\Rightarrow \hat{U}^\dagger(t_1, t_0) \hat{U}(t_1, t_0) = 1 \Rightarrow \hat{U} \text{ is unitary}$

2. a translation from t_0 to t_2 should be the same as a translation from t_0 to t_1 followed by a translation from t_1 to t_2 :

$$\hat{U}(t_2, t_0) = \hat{U}(t_2, t_1) \hat{U}(t_1, t_0)$$

3. if the translation is reduced to nothing the operator should do nothing:

$$\lim_{dt \rightarrow 0} \hat{U}(t_0 + dt, t_0) = 1$$

A solution satisfying all these postulates in the case of an infinitesimal translation is

$$\hat{U}(t_0 + dt, t_0) = 1 - \frac{i}{\hbar} \hat{H} dt \quad \text{where } \hat{H} \text{ is a Hermitian operator and } dt \text{ is a convenient normalization.}$$

The units of \hat{H} are [energy] and correspondence with classical mechanics suggests that the generator of time translation should be the Hamiltonian

We can derive a differential equation that $\hat{U}(t, t_0)$ must satisfy:

$$\hat{U}(t+dt, t_0) = \hat{U}(t+dt, t) \hat{U}(t, t_0) = \left(1 - \frac{i}{\hbar} \hat{H} dt\right) \hat{U}(t, t_0)$$

$$\text{Hence } \hat{U}(t+dt, t_0) = \hat{U}(t, t_0) - \frac{i}{\hbar} \hat{H} dt \hat{U}(t, t_0)$$

$$\text{or } \frac{\hat{U}(t+dt, t_0) - \hat{U}(t, t_0)}{dt} = -\frac{i}{\hbar} \hat{H} \hat{U}(t, t_0)$$

$$\Rightarrow i\hbar \frac{d}{dt} \hat{U}(t, t_0) = \hat{H} \hat{U}(t, t_0)$$

"Schrödinger eqn for the time evolution operator"

$$\Rightarrow i\hbar \frac{d}{dt} \hat{U}(t, t_0) |\alpha, t_0\rangle = \hat{H} \hat{U}(t, t_0) |\alpha, t_0\rangle$$

$$\Rightarrow i\hbar \frac{d}{dt} |\alpha, t_0; t\rangle = \hat{H} |\alpha, t_0; t\rangle$$

In fact solving for the time-evolution operator is all we need to do since we can apply it to any state to obtain the time-evolved state.

In the case that the Hamiltonian operator \hat{H} is independent of time a simple formal solution can easily be found (we'll deal with the case that \hat{H} depends upon t later in the course):

$$\hat{U}(t, t_0) = e^{-\frac{i}{\hbar} \hat{H} (t-t_0)} = 1 - \frac{i}{\hbar} \hat{H} (t-t_0) + \left(\frac{-i}{\hbar}\right)^2 \frac{(t-t_0)^2}{2} \hat{H} \hat{H} + \dots$$

$$\frac{d}{dt} \hat{U}(t, t_0) = -\frac{i}{\hbar} \hat{H} + \left(\frac{-i}{\hbar}\right)^2 \cdot \frac{2}{2} (t-t_0) \hat{H} \hat{H} + \dots = -\frac{i}{\hbar} \hat{H} \left(1 - \frac{i}{\hbar} \hat{H} (t-t_0) + \dots\right)$$

$$\Rightarrow i\hbar \frac{d}{dt} \hat{U}(t, t_0) = \hat{H} \hat{U}(t, t_0) \quad \checkmark$$

Recall that if two operators commute they have simultaneous eigenstates -
 suppose we can find an operator \hat{A} that commutes with the Hamiltonian \hat{H} ,

$$[\hat{A}, \hat{H}] = 0 \quad \text{then} \quad \hat{A}|a_i\rangle = a_i|a_i\rangle \\
 \& \hat{H}|a_i\rangle = E_i|a_i\rangle \quad \text{where } E_i \text{ is the energy of state } |a_i\rangle$$

$|a_i\rangle$ is an energy eigenket or a "stationary" state (for reasons that will become clear)

Consider expressing the time evolution operator in the \hat{A} eigenbasis:

$$e^{-i/\hbar \hat{H}t} = \sum_{ij} |a_j\rangle \langle a_j| e^{-i/\hbar \hat{H}t} |a_i\rangle \langle a_i| = \sum_i e^{-i/\hbar E_i t} |a_i\rangle \langle a_i|$$

now solving for the time evolution of an arbitrary state is easy:

$$|\alpha, t_0=0\rangle = \sum_i |a_i\rangle \langle a_i|\alpha\rangle \equiv \sum_i c_i |a_i\rangle \quad (\text{ie. we express } |\alpha\rangle \text{ as a superposition of all } |a_i\rangle)$$

then

$$|\alpha, t_0=0; t\rangle = e^{-i/\hbar \hat{H}t} |\alpha, t_0=0\rangle = \sum_i e^{-i/\hbar E_i t} |a_i\rangle \langle a_i|\alpha, t_0=0\rangle \\
 = \sum_i e^{-i/\hbar E_i t} c_i |a_i\rangle$$

so the net effect of time evolution is to change the amount of each eigenstate in the superposition

$$c_i(t) = e^{-i/\hbar E_i t} c_i(0)$$

Note that if the initial state $|\alpha\rangle$ happens to be an energy eigenket we have

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

that is to say only the phase of the normalization varies with time.

A very useful way to characterise states in quantum dynamics is to find a set of operators which all commute with the Hamiltonian. The simultaneous eigenstates of these operators form a handy basis - the eigenvalues are often referred to as "good quantum numbers".

The value of a "good quantum number" will not change with time

$$\langle a_i, t_0 | \hat{A} |a_i, t_0\rangle = a_i \quad ; \quad \langle a_i, t | \hat{A} |a_i, t\rangle = a_i |e^{-i/\hbar E_i t}|^2 = a_i$$

in the state $|a_i, t\rangle$, a_i will be measured by \hat{A} with probability $|e^{-i/\hbar E_i t}|^2 = 1$

We might wonder what happens to the expectation value of an operator that doesn't commute with the Hamiltonian in such a state $[\hat{H}, \hat{B}] \neq 0$

$$\langle \hat{B} \rangle = \langle a_i | \hat{U}^\dagger(t, 0) \hat{B} \hat{U}(t, 0) | a_i \rangle = \langle a_i | e^{i\frac{E_i}{\hbar}t} \hat{B} e^{-i\frac{E_i}{\hbar}t} | a_i \rangle = \langle a_i | \hat{B} | a_i \rangle$$

The expectation value does not change with time, even though \hat{B} does not commute with \hat{H} . This is one reason we refer to $|a_i\rangle$ as a "stationary state".

Suppose rather than a single energy eigenket, we have a superposition

$$|\alpha, t=0\rangle = \sum_i c_i |a_i\rangle$$

$$\text{then } \langle \alpha, t | \hat{B} | \alpha, t \rangle = \sum_{ij} c_i^*(0) e^{i\frac{E_i}{\hbar}t} \langle a_i | \hat{B} | a_j \rangle c_j(0) e^{-i\frac{E_j}{\hbar}t}$$

$$= \sum_{ij} c_i^*(0) c_j(0) \langle a_i | \hat{B} | a_j \rangle \exp\left[-\frac{i}{\hbar}(E_j - E_i)t\right]$$

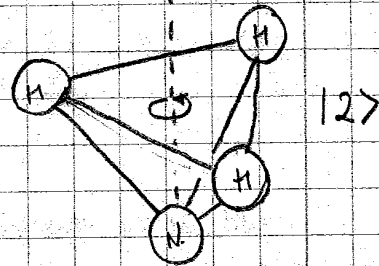
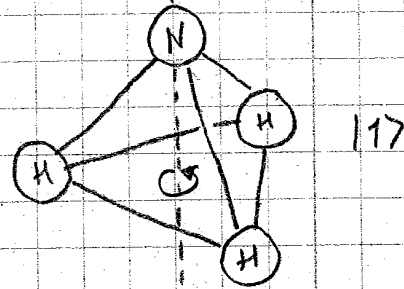
so that the expectation value has a time dependence which is a weighted sum of oscillating terms (a Fourier series)

- THE AMMONIA MOLECULE

Consider the tetrahedral ammonia molecule (NH_3). The system is assumed to be rotating with a fixed angular momentum about the axis shown, and we neglect vibrational modes.

There are two possible positions for the nitrogen atom: above or below the H_3 plane. We assume that we can do an experiment to determine this.

The 'above' orientation we will call state $|1\rangle$ & the 'below' state $|2\rangle$.



The simplest model of this system would assume that a molecule prepared in state $|1\rangle$ would always remain in state $|1\rangle$. Similarly for state $|2\rangle$.

In this case $|1\rangle$ & $|2\rangle$ are stationary states of the system & we know that

$$c_1(t) = c_1(0)e^{-iE_1 t} \quad \& \quad c_2(t) = c_2(0)e^{-iE_2 t}$$

$$\hat{H}|1\rangle = E_1|1\rangle \quad \& \quad \hat{H}|2\rangle = E_2|2\rangle$$

$$\begin{cases} \hat{H} = E_1|1\rangle\langle 1| + E_2|2\rangle\langle 2| \\ \hat{H} \sim \begin{bmatrix} E_1 & 0 \\ 0 & E_2 \end{bmatrix} \end{cases} \begin{matrix} |1\rangle \sim \begin{bmatrix} 1 \\ 0 \end{bmatrix} \\ |2\rangle \sim \begin{bmatrix} 0 \\ 1 \end{bmatrix} \end{matrix}$$

Since the system is symmetrical we'd expect $E_1 = E_2 \equiv E_0$. Then any initial superposition $A|1\rangle + B|2\rangle$ would remain the same over time:

$$|\alpha\rangle = |1\rangle\langle 1|\alpha\rangle + |2\rangle\langle 2|\alpha\rangle = c_1(0)|1\rangle + c_2(0)|2\rangle$$

$$\rightarrow |\alpha; t\rangle = c_1(t)|1\rangle + c_2(t)|2\rangle = e^{-iE_0 t} (c_1(0)|1\rangle + c_2(0)|2\rangle)$$

So the probability of finding the state in either $|1\rangle$ or $|2\rangle$ does not change with time

$$P_1(t) = |c_1(t)|^2 = |c_1(0)e^{-iE_0 t}|^2 = |c_1(0)|^2$$

$$P_2(t) = |c_2(t)|^2 = |c_2(0)e^{-iE_0 t}|^2 = |c_2(0)|^2$$

In fact, quantum mechanically there is a small probability for the nitrogen atom to push its way through the H_3 plane and hence for a $|1\rangle$ state to become a $|2\rangle$ state or vice-versa. In order to build this into our model we should add an extra piece to the Hamiltonian:

$$\hat{H} = E_0(|1\rangle\langle 1| + |2\rangle\langle 2|) - \epsilon(|1\rangle\langle 2| + |2\rangle\langle 1|) \quad \text{or in matrix representation} \quad \hat{H} \sim \begin{bmatrix} E_0 & -\epsilon \\ -\epsilon & E_0 \end{bmatrix}$$

With this enhanced Hamiltonian we can try to solve the Schrödinger eqn:

$$i\hbar \frac{\partial}{\partial t} |\alpha; t\rangle = \hat{H} |\alpha; t\rangle$$

We'll do this in the $|1\rangle, |2\rangle$ basis:

$$i\hbar \frac{d}{dt} |\alpha; t\rangle = \hat{H} |\alpha; t\rangle = \sum_{i=1,2} \langle \hat{H} | i \rangle \langle i | \alpha; t \rangle$$

$$\Rightarrow i\hbar \frac{d}{dt} \underbrace{\langle j | \alpha; t \rangle}_{c_j(t)} = \sum_{i=1,2} \underbrace{\langle j | \hat{H} | i \rangle}_{H_{ji}} \underbrace{\langle i | \alpha; t \rangle}_{c_i(t)}$$

$$\text{explicitly } i\hbar \frac{dc_1}{dt} = H_{11}c_1 + H_{12}c_2 \quad \& \quad i\hbar \frac{dc_2}{dt} = H_{21}c_1 + H_{22}c_2$$

$$= E_0 c_1 - \epsilon c_2 \quad \quad \quad = -\epsilon c_1 + E_0 c_2$$

$$\text{add the equations: } i\hbar \frac{d}{dt} (c_1 + c_2) = (E_0 - \epsilon)(c_1 + c_2) \Rightarrow c_1 + c_2 = a e^{-\frac{i}{\hbar}(E_0 - \epsilon)t}$$

$$\text{subtract the equations: } i\hbar \frac{d}{dt} (c_1 - c_2) = (E_0 + \epsilon)(c_1 - c_2) \Rightarrow c_1 - c_2 = b e^{-\frac{i}{\hbar}(E_0 + \epsilon)t}$$

$$\Rightarrow c_1(t) = \frac{a}{2} e^{-\frac{i}{\hbar}(E_0 - \epsilon)t} + \frac{b}{2} e^{-\frac{i}{\hbar}(E_0 + \epsilon)t} \quad c_1(0) = \frac{1}{2}(a+b)$$

$$c_2(t) = \frac{a}{2} e^{-\frac{i}{\hbar}(E_0 - \epsilon)t} - \frac{b}{2} e^{-\frac{i}{\hbar}(E_0 + \epsilon)t} \quad c_2(0) = \frac{1}{2}(a-b)$$

Suppose we prepare an initial state such that $b=0$, this is the state*
 $\frac{1}{\sqrt{2}}(|1\rangle + |2\rangle)$, at a later time this state becomes $e^{-\frac{i}{\hbar}(E_0 - \epsilon)t} \frac{1}{\sqrt{2}}(|1\rangle + |2\rangle)$

which we recognise as a stationary state of energy $E_0 - \epsilon$.

Similarly the state $\frac{1}{\sqrt{2}}(|1\rangle - |2\rangle)$ is a stationary state of energy $E_0 + \epsilon$.

The possibility of 'tunneling' from state $|1\rangle$ to $|2\rangle$ and vice versa has meant that rather than two degenerate energy eigenstates of energy E_0 there is a lower energy state, $E_0 - \epsilon$ & a higher energy state $E_0 + \epsilon$.

What about the time dependence of states other than $\frac{1}{\sqrt{2}}(|1\rangle \pm |2\rangle)$?

Suppose we begin with the ammonia molecule definitely in the 'above' position, state $|1\rangle$ - we can ask what is the probability that at a later time, the nitrogen is found to be either above or below the N_3 plane?

$$t=0 \quad |\alpha\rangle = |1\rangle \Rightarrow c_1(0) = 1 \quad ; \quad c_2(0) = 0 \Rightarrow \left. \begin{array}{l} \frac{1}{2}(a+b) = 1 \\ \frac{1}{2}(a-b) = 0 \end{array} \right\} a=b=1$$

* if we normalise it

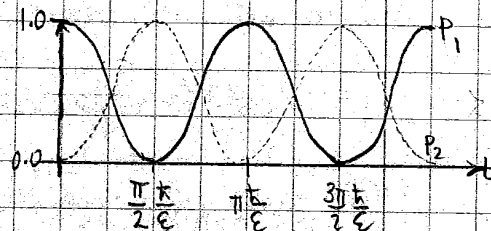
$$\text{then } C_1(t) = e^{-iE_0 t/\hbar} \left(\frac{e^{iEt/\hbar} + e^{-iEt/\hbar}}{2} \right) = \cos\left(\frac{E}{\hbar}t\right) e^{-iE_0 t/\hbar}$$

$$C_2(t) = e^{-iE_0 t/\hbar} \left(\frac{e^{iEt/\hbar} - e^{-iEt/\hbar}}{2} \right) = i \sin\left(\frac{E}{\hbar}t\right) e^{-iE_0 t/\hbar}$$

Then the probability of finding the system in state $|1\rangle$ at a time t is

$$P_1(t) = |\langle 1|\alpha;t\rangle|^2 = |C_1(t)|^2 = \cos^2\left(\frac{E}{\hbar}t\right)$$

$$\text{and } P_2(t) = |\langle 2|\alpha;t\rangle|^2 = |C_2(t)|^2 = \sin^2\left(\frac{E}{\hbar}t\right)$$



Now you'll notice that the math wasn't very difficult there and we solved the Schrödinger eqn using a trick. We'd better learn a general technique that we can use in more complicated situations.

We need to realize that the stationary states are the eigenstates of the Hamiltonian, and that in the matrix representation this corresponds to solving a matrix eigenvalue equation

$$\underline{H}\underline{C} = E\underline{C}$$

The eigenvalues follow as the roots of $\det(\underline{H} - E\underline{1}) = 0$. For this problem

$$\underline{H} = \begin{bmatrix} E_0 - E & -E \\ -E & E_0 \end{bmatrix} \Rightarrow \det(\underline{H} - E\underline{1}) = \begin{vmatrix} E_0 - E & -E \\ -E & E_0 - E \end{vmatrix} = (E_0 - E)^2 - (-E)^2 = 0$$

$$(E_0^2 - E^2) - 2E_0 \cdot E + E^2 = 0 = (E - (E_0 - E))(E - (E_0 + E)) \Rightarrow E = \begin{cases} E_0 + E \\ E_0 - E \end{cases}$$

& for the eigenvectors

$$\begin{bmatrix} E_0 - E & -E \\ -E & E_0 \end{bmatrix} \begin{bmatrix} C_1^{(+)} \\ C_2^{(+)} \end{bmatrix} = (E_0 + E) \begin{bmatrix} C_1^{(+)} \\ C_2^{(+)} \end{bmatrix} \Rightarrow \begin{bmatrix} -E & -E \\ -E & -E \end{bmatrix} \begin{bmatrix} C_1^{(+)} \\ C_2^{(+)} \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \end{bmatrix} \Rightarrow \begin{cases} C_1^{(+)} + C_2^{(+)} = 0 \\ C_1^{(+)} = -C_2^{(+)} \end{cases}$$

\Rightarrow with the eigenvalue $E_0 + E$ we have the eigenvector $\frac{1}{\sqrt{2}} \begin{bmatrix} +1 \\ -1 \end{bmatrix} \rightsquigarrow \frac{1}{\sqrt{2}}(|1\rangle - |2\rangle)$

$$\begin{bmatrix} E_0 - E & -E \\ -E & E_0 \end{bmatrix} \begin{bmatrix} C_1^{(-)} \\ C_2^{(-)} \end{bmatrix} = (E_0 - E) \begin{bmatrix} C_1^{(-)} \\ C_2^{(-)} \end{bmatrix} \Rightarrow \begin{bmatrix} E & -E \\ -E & E \end{bmatrix} \begin{bmatrix} C_1^{(-)} \\ C_2^{(-)} \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \end{bmatrix} \Rightarrow \begin{cases} C_1^{(-)} - C_2^{(-)} = 0 \\ C_1^{(-)} = C_2^{(-)} \end{cases}$$

\Rightarrow with the eigenvalue $E_0 - E$ we have the eigenvector $\frac{1}{\sqrt{2}} \begin{bmatrix} +1 \\ +1 \end{bmatrix} \rightsquigarrow \frac{1}{\sqrt{2}}(|1\rangle + |2\rangle)$

TIME EVOLUTION OF STATES IN A CONTINUOUS BASIS

We now have a general technique for finding the stationary states of a quantum system of finite dimension. Earlier we considered cases like position & momentum where the space is continuous, and here we don't have matrix representations (at least not finite-sized matrices) but rather we found, differential operators, e.g.

$$\langle x' | \hat{p} | x \rangle = -i\hbar \frac{\partial}{\partial x'} \delta(x'-x).$$

This gives us a clue as to the type of mathematics we're likely to use in solving for the stationary states of a continuous quantum system.

Let's return to our definition of the spatial wavefunction of a state $|\alpha\rangle$

$$\psi_\alpha(x) = \langle x | \alpha \rangle$$

or, more generally, for a time-varying state $|\alpha; t\rangle$:

$$\psi_\alpha(x; t) = \langle x | \alpha; t \rangle.$$

We've come to expect that the Hamiltonian is an operator version of the energy of a system, so for a single particle moving non-relativistically in a static potential we might propose

$$\hat{H} = \frac{\hat{p}^2}{2m} + \hat{V}$$

which we can express in the position basis as

$$\langle x' | \hat{H} | x \rangle = \frac{1}{2m} \langle x' | \hat{p}^2 | x \rangle + \langle x' | \hat{V} | x \rangle.$$

We'll assume that the potential is 'local' in the following sense

$$\langle x' | \hat{V} | x \rangle = V(x) \delta(x'-x) \quad \text{where to make the Hamiltonian Hermitian, } V(x) \text{ must be real.}$$

$$\begin{aligned} \langle x' | \hat{p}^2 | x \rangle &= \int dx'' \langle x' | \hat{p} | x'' \rangle \langle x'' | \hat{p} | x \rangle = \int dx'' \left(-i\hbar \frac{\partial}{\partial x'} \delta(x'-x'') \right) \left(-i\hbar \frac{\partial}{\partial x''} \delta(x''-x) \right) \\ &= -\hbar^2 \frac{\partial^2}{\partial x^2} \delta(x'-x) \end{aligned}$$

Recall that the Schrödinger eqn for the time evolution of a state $|\alpha\rangle$ is

$$i\hbar \frac{\partial}{\partial t} |\alpha; t\rangle = \hat{H} |\alpha; t\rangle$$

hence, in the position basis $i\hbar \frac{\partial}{\partial t} \langle x | \alpha; t \rangle = \int dx' \langle x | \hat{H} | x' \rangle \langle x' | \alpha; t \rangle$

$$\Rightarrow i\hbar \frac{\partial}{\partial t} \psi_\alpha(x, t) = \int dx' \left(-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x'^2} + V(x') \right) \delta(x'-x) \psi_\alpha(x', t)$$

$$\Rightarrow \boxed{i\hbar \frac{\partial}{\partial t} \psi_\alpha(x, t) = \left(-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x) \right) \psi_\alpha(x, t)} \quad \text{"Schrödinger's wave equation"}$$

In seeking stationary-state solutions to this equation we can supply the desired time-dependence

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

which yields the "time-independent Schrödinger wave equation"

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

We shall demand that the solutions be normalised to 1, that is

$$\int dx \phi_E^*(x) \phi_E(x) = 1, \quad \text{this is the condition that the wavefunction be "square-integrable"}$$

For integration from $-\infty$ to $+\infty$ then we require that $\phi_E(x \rightarrow \pm\infty) \rightarrow 0$, which acts as a boundary condition on the differential equation.

It can be shown that the wave equation subject to the boundary condition has solutions only for certain values of $E = E_n$.

We can check certain general properties we proved earlier in the specific case of wavefunctions in position space:

$$\left. \begin{aligned} \int dx \phi_m^*(x) \hat{H} \phi_n(x) &= E_n \int dx \phi_m^*(x) \phi_n(x) \\ &= \int dx (\hat{H} \phi_m(x))^* \phi_n(x) = E_m^* \int dx \phi_m^*(x) \phi_n(x) \end{aligned} \right\} (E_m^* - E_n) \int dx \phi_m^*(x) \phi_n(x) = 0$$

if $n=m$: $(E_n^* - E_n) = 0 \Rightarrow E_n$ is real

if $n \neq m$ & $E_n \neq E_m$ $\int dx \phi_m^*(x) \phi_n(x) = 0 \Rightarrow \phi_m(x), \phi_n(x)$ are "orthogonal functions"

In the abstract bra-ket notation we happily expanded an arbitrary state as a linear superposition of some basis states $|\alpha\rangle = \sum_i |a_i\rangle \langle a_i|\alpha\rangle$

With wavefunctions we just consider this in the continuous position basis:
 $\langle x|\alpha\rangle = \int \langle x|a_i\rangle \langle a_i|\alpha\rangle$

or, in our new notation $\psi(x) = \sum_i C_i \phi_i(x)$

For a complete set of eigenkets we have a completeness relation:

$$\sum_n |E_n\rangle \langle E_n| = 1 \Rightarrow \sum_n \langle x|E_n\rangle \langle E_n|x'\rangle = \langle x|x'\rangle = \delta(x-x')$$
$$\Rightarrow \sum_n \phi_n(x) \phi_n^*(x') = \delta(x-x')$$

A totally general solution to the time-dependent Schrödinger wave equation can be written

$$\psi(x,t) = \sum_n C_n e^{-iE_n t/\hbar} \phi_n(x)$$