**Time Dependent Schrödinger Equation**

Up until now we have been talking about “stationary states” which don’t change with time, but recall that the state function $\Psi$ is also a function of time, $\Psi(q_1, \ldots, q_n, t)$ in general. When will we care about time dependence? Most of the time! For examples, spectroscopy $\Rightarrow$ molecule interacting with electromagnetic radiation and implies transitions between states. Chemical reactions imply transitions between at least two states.

The time evolution of a state function is given by **Postulate V**, which says that the state function $\Psi$ satisfies the simple appearing differential equation:

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

and $\hat{H}$ is the Hamiltonian operator. So we must solve this equation. We will do so by means of **Separation of Variables**. This is a very important technique, one that we shall use again and again. Essentially no problem is solvable unless we can separate variables. Note carefully the logic in what follows: First, **assume** that $\Psi(x, t)$ is a the product form $\Psi(x, t) = \varphi(x) f(t)$

We then try to solve the Schrödinger equation with such a separable form. If we succeed in finding a general solution with this restrictive assumption, then we have justified our separability assumption, and all is well.
So, making this assumption, the Schrödinger equation becomes

\[ \hat{H}(\varphi(x)f(t)) = i\hbar \frac{\partial \varphi(x)f(t)}{\partial t} = \varphi(x) i\hbar \frac{\partial f(t)}{\partial t} = \varphi(x) i\hbar \frac{d f(t)}{dt} \]

So, with this assumption, the right side of the above equation simplifies as above.

Now, if in addition, \( \hat{H} \) contains no explicit time dependence, then \( f(t) \) is also a constant with respect to the actions indicated by \( \hat{H} \) and \( f(t) \) can be brought through the \( \hat{H} \) operator.

(What does it mean for \( \hat{H} \) to have no time dependence?)

*In any event, we obtain*

\[ f(t)\hat{H}\varphi(x) = \varphi(x) i\hbar \frac{\partial f(t)}{\partial t} \]

an equation which we need to solve.
There are basically two standard things one should always think about (as before): "No. 1" Divide by $\Psi$ written in product form [Here it is $\phi(x)f(t)$]

"No. 2" Multiply by $\phi^*$ and integrate.
(We used both earlier in the proof of properties of Hermitian operators.)

**After applying No. 1, we have**

\[
\frac{f(t)}{f(t)\phi(x)} \hat{H}\phi(x) = \frac{\phi(x)}{f(t)\phi(x)} i\hbar \frac{\partial f(t)}{\partial t}
\]

or

\[
\frac{\hat{H}\phi(x)}{\phi(x)} = \frac{i\hbar}{f(t)} \frac{\partial f(t)}{\partial t}
\]

(as before, why can't I cancel out $\phi$ on the left side ??)

Notice that the left side is a function of $x$ only and the right side is a function of $t$ only. Thus we have that $b(x) = g(t)$ for all $x$ and all $t$. This can only be the case if

$b(x) = \text{constant} = g(t)$

Call the constant something convenient. Since units are energy, call it $E$. Then
\[
\frac{\hat{H}\varphi(x)}{\varphi(x)} = E \quad (a)
\]

and

\[
E = \frac{i\hbar}{f(t)} \frac{df(t)}{dt} \quad (b)
\]

Look at (b)

\[
\frac{df(t)}{dt} = \frac{-iE}{\hbar} f(t)
\]

Integrate this equation to obtain

\[
f(t) = e^{\frac{iEt}{\hbar}}
\]

for the time dependence of \(\Psi(x,t)\).
The spatial dependence comes from solving equation (a), rewritten as

\[ \hat{H} \phi(x) = E \phi(x) \]

a relation that we recognize as the total energy eigenvalue equation. This is exactly the equation that we solved earlier to obtain the energy states of the particle in a box! This total energy eigenvalue equation is best known as the

**Time Independent Schrödinger Equation**

The existence of a **product form** solution enabled the one differential equation in two variables to be written as two separate differential equations, each having only one variable. This is useful because we can kill any differential equation in one variable with only computing and no thinking.

This concept is very important and will occur again and again.
A final point for your consideration. Consider what the state function looks like if we are in an energy eigenstate, say $E_n$, with spatial dependence $\phi_n$.

The full state function is $\Psi(x, t) = \phi_n(x) e^{-iE_nt/\hbar}$, with a complex time dependence!

However, the probability density $P$ is given by $\Psi^*\Psi$,

$P = \Psi^*\Psi = \phi_n^*(x)e^{iE_nt/\hbar} \phi_n(x)e^{-iE_nt/\hbar} = \phi_n^*(x) \phi_n(x)$

There is no time dependence in the probability density.

This is a property of an **eigenstate** or a **stationary state**.

For an eigenstate $\Psi_m$, probability densities and average values are time-independent! But for a state function that is not an eigenfunction, $\Psi^*\Psi \, dx$ will depend on time.
After assuming a product form solution \( \psi(x,t) = \psi(x) \cdot \phi(t) \), the TDSE becomes

\[
\begin{align*}
\hbar \frac{1}{\varphi} \frac{\partial \varphi}{\partial t} &= -\frac{\hbar^2}{2m} \frac{1}{\psi} \frac{\partial^2 \psi}{\partial x^2} + V = E \nend{align*}
\]

If the potential energy function \( V \) in the Schrödinger Equation is a function of time, as well as \( x \), \( [V = V(x,t)] \) would separation of variables still work; that is, would there still be solutions to the SE of the form \( \Psi(x,t) = \psi(x) \cdot \phi(t) \)?

A) Yes, always  B) No, never
C) Depends on the functional dependence of \( V \) on \( x \) and \( t \)
TIME DEPENDENCE of $\Psi$

Now we have seen how to separate variables and obtain a solution to the above equation when the state function could be written as a product, $\Psi(q,t) = \psi(q)f(t)$. We saw that $\Psi^*(q,t)\Psi(q,t)$ was NOT a function of time when $\psi(q)$ was an eigenfunction of $\hat{H}$.

We demonstrate a more general solution, but one still restricted to the case that does not contain explicit time dependence. This restriction allows us to view the propagation of a wave packet and make additional connection with our intuitive understanding. We demonstrate a solution for a two term form, but the general result will be obvious.
TIME DEPENDENCE of $\Psi$

Let $\psi_1(x)$ and $\psi_2(x)$ be eigenfunctions of $\hat{H}$ with eigenvalues $E_1$ and $E_2$ respectively. Consider the following state function $\Psi_s(x, t)$

$$\Psi_s(x, t) = \psi_1(x) e^{-\frac{iE_1 t}{\hbar}} + \psi_2(x) e^{-\frac{iE_2 t}{\hbar}}$$

We will show that it is a solution to the time dependent Schrödinger equation.

$$\hat{H}\Psi_s(x, t) = i \hbar \frac{\partial \Psi_s(x, t)}{\partial t}$$

If $\hat{H}$ does not depend upon time, then the left side of the time-dependent Schrödinger equation can be expanded as

$$\hat{H}\Psi_s(x, t) = E_1 \psi_1(x) \exp\left(-\frac{iE_1 t}{\hbar}\right) + E_2 \psi_2(x) \exp\left(-\frac{iE_2 t}{\hbar}\right)$$
\[ \hat{H}\Psi_s(x,t) = E_1\psi_1(x)\exp^{\frac{-iE_1t}{\hbar}} + E_2\psi_2(x)\exp^{\frac{-iE_2t}{\hbar}} \]

and the right side as the following:

\[ i\hbar \frac{\partial\Psi_s(x,t)}{\partial t} = i\hbar \left[ \frac{-iE_1}{\hbar} \right] \psi_1(x)\exp^{\frac{-iE_1t}{\hbar}} + i\hbar \left[ \frac{-iE_2}{\hbar} \right] \psi_2(x)\exp^{\frac{-iE_2t}{\hbar}} \]

\[ = E_1\psi_1(x)\exp^{\frac{-iE_1t}{\hbar}} + E_2\psi_2(x)\exp^{\frac{-iE_2t}{\hbar}} \]

Since the two sides are identical, this sum of products form is a solution to the time dependent Schrödinger equation whenever \( \hat{H} \) has no time dependence. Note that now \( \Psi_s^*(x,t)\Psi_s(x,t) \) has time dependence.

\[ \Psi_s^*\Psi_s = \psi_1^2(x) + \psi_2^2(x) + \psi_1\psi_2 e^{\frac{i(E_1-E_2)t}{\hbar}} + \psi_1\psi_2 e^{\frac{i(E_1-E_2)t}{\hbar}} \]

\[ = \psi_1^2(x) + \psi_2^2(x) + \psi_1\psi_2 \cos \left( \frac{(E_1-E_2)t}{\hbar} \right) \]
Use Mathcad to see some other examples of acceptable state functions for the particle in a box. Let the box extend from 0 to $\pi$. Consider a state function which is the sum of the first 100 eigenfunctions.

Set ranges for $x$ and $n$.

$n = 1, 2, \ldots 100 \quad 0 < x < \pi$

Define the eigenfunctions.

$$f(x, n) := \sqrt{\frac{2}{\pi}} \cdot \sin(n \cdot x)$$

Are the $f(x,n)$ orthogonal? Normalized? Check one numerically!

$$\int_{0}^{\pi} f(x, 4) \cdot f(x, 16) \, dx = -3.654 \cdot 10^{-16} \quad \quad \int_{0}^{\pi} f(x, 4)^2 \, dx = 1$$

YES!

Now define our 100 term function, $g(x)$. Is it normalized?

$$g(x) := 0.1 \cdot \sum_{n = 1}^{100} f(x, n) \quad \quad \int_{0}^{\pi} g(x)^2 \, dx = 1$$
What does the state function look like? Is it an acceptable state function?
and what is the probability density?

\[ g(x)^2 \]

What is the average kinetic energy? How does it propagate in time? How does this relate to the so-called \( \delta \) function? Also, if we set \( E_1 = 1 \), then \( E_n = n^2 \), and we easily find \( \langle E \rangle \) as

\[
\langle E \rangle = 0.01 \sum_{n=1}^{100} E_n =
\]

How would this state function evolve in time?
Lets look at an example.

Consider the evolution of a localized particle on the left side of a box. First, we construct a state function localized on the left side of the box. We could put a Gaussian or some such function on the left side of the box, with whatever width we choose.

A simpler way to get a feeling for this is to employ the sum of the first 10 particle in a box eigenfunctions as our initial state. The box extends from \( x = 0 \) to \( x = 1 \). We construct the time dependent state function with the first 10 eigenfunctions having equal weight.

\[
\Psi_s(x, t) = \sum_{j=1}^{10} \sqrt{2} \sin(j\pi x) e^{\frac{iE_j t}{\hbar}}
\]

The individual components are all in phase at \( t = 0 \). This will give a peak near the left side of the box at \( t=0 \).

What do the individual components look like?

We then propagate the function in time, using the expression above.
Time Dependence of $\Psi$

The initial state is the sum of the first 10 particle in a box eigenfunctions.
The box extends from 0 to 1

- We construct the time dependent state function with all of the first 10 eigenfunctions having equal weight.
- They are all in phase at t = 0. This will give a peak near the left side of the box at t=0.
- What do the individual components look like?
- We then propagate the function in time, using the expression from notes.
Individual components of $\Psi$
\[ t = 0 \]
\[ t = 0.01 \]
t=0.02
\( t = 0.03 \)
\( t = 0.04 \)
$t = 0.05$
$t = 0.06$
$t = 0.07$
$t = 0.08$
$t = 0.09$
t=0.1
t=0.125
t=0.15
t=0.175
\( t = 0.2 \)
$t = 6.283 \quad \text{Note recurrence!}$