IX. TIME DEPENDENT SCHRÖDINGER EQUATION

So far we have focused on one instant in time and learnt how the particle is described by a $\psi(x)$ and how to extract information from it regarding position, momentum, energy etc. This is what we call kinematics. Now for the dynamics, i.e., how ψ changes with time. So first we have to start referring to it as $\psi(x,t)$. This is like saying classically that for kinematics at any time you need an x and a p to describe it fully and that dynamically $x(t)$ and $p(t)$ vary with time and describe the particle's evolution in time. There we had $F = ma$ and here we have the time-dependent Schrödinger equation (SE):

$$i\hbar\frac{\partial\psi(x,t)}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2\psi(x,t)}{\partial x^2} + V(x)\psi(x,t) \tag{118}$$

At a mathematical level, this is a partial differential equation for a function of two variables (x,t). Since it specifies the first time- derivative of ψ, it follows that given the initial $\psi(x,0)$, its future value $\psi(x,t)$ is determined as above.

Let us not try to solve it for every possible initial $\psi(x,0)$. As a modest goal let us try to find a very limited class of solutions of the form

$$\psi(x,t) = F(t)\psi(x) \tag{119}$$

This is not generic, generically x and t will all be mixed up together. Let us plug this into Eq. 118 and see if it admit such a solution.

Bear in mind that the function in question is a product of two functions, one that depends on just t and one that depends on just x. In the LHS of Eq. 118 we have a partial time derivative which will act only on the $F(t)$ (while $\psi(x)$ just stands there). On the right hand side we have only partial derivatives with respect to x. These will act on just $\psi(x)$ (while $F(t)$ is idling) and on this function they act as total derivatives.

Thus we end up with

$$\psi(x)i\hbar\frac{dF(t)}{dt} = F(t)\left[-\frac{\hbar^2}{2m}\frac{d^2\psi(x,t)}{dx^2} + V(x)\psi(x)\right] \equiv H\psi(x) \tag{120}$$

where we have defined $H\psi$ to be that combination that occurs frequently. Dividing both sides by $F(t)\psi(x)$ we find

$$\frac{1}{F(t)}i\hbar\frac{dF(t)}{dt} = \frac{1}{\psi(x)}H\psi(x) \tag{121}$$

We now see a function of just t being equal to a function of x for all t and x. *This means both functions have to be constants since the function of t alone cannot have any x-dependence and the function of x alone cannot have any t-dependence.* Calling this constant E, we find

$$\frac{1}{F(t)} i\hbar \frac{dF(t)}{dt} = \frac{1}{\psi(x)} H\psi(x) = E \tag{122}$$

which means two equations:

$$i\hbar \frac{dF(t)}{dt} = EF(t) \tag{123}$$

$$\left[-\frac{\hbar^2}{2m} \frac{d^2\psi(x,t)}{dx^2} + V(x)\psi(x) \right] = E\psi(x) \tag{124}$$

Clearly the solution to the first equation is

$$F(t) = F(0)e^{-iEt/\hbar} \tag{125}$$

The second equation we recognize to be one that is obeyed by functions of definite energy E: $\psi(x) = \psi_E(x)$. Thus we find that the factorized solutions of the form $\psi(x,t) = F(t)\psi(x)$ do exist and are given by

$$\psi_E(x,t) = e^{-iEt/\hbar}\psi_E(x). \tag{126}$$

The factorized solution is telling us that of the many possible ways we could start out the system, if we start it out in a state of definite energy, $\psi(x,0) = \psi_E(x)$, all that happens with time is that it picks up a phase factor $e^{-iEt/\hbar}$.

Such a mode of vibration, in which ψ factors into a function of t times a function of x is called a *normal mode* and is familiar in classical mechanics. Consider a string clamped at $x = 0$ and $x = L$. If you pluck it and release it from some arbitrary initial shape $\psi(x,0)$, it will wiggle and jiggle in a complicated way, with ripples running back and forth. Such behavior does not have the factorized form. If however you start it off in any one of the following special initial states

$$\psi_n(x,0) = A \sin \frac{n\pi x}{L} \tag{127}$$

then at future times, every point on the string will rise and fall together as follows:

$$\psi_n(x,t) = A \sin \frac{n\pi x}{L} \cos \frac{n\pi vt}{L} \tag{128}$$

where v is the velocity of waves in a string. (Plot this at a few times within a full cycle of period $T = 2L/nv$ to visualize the motion.)

However, in the quantum case, despite the time-dependence $e^{-iEt/\hbar}$, all physical observables will be time-independent.

For example the probability density of finding the particle at x,

$$P(x,t) = |\psi(x,t)|^2 = |e^{-iEt/\hbar}\psi_E(x)|^2 = |e^{-iEt/\hbar}|^2|\psi_E(x)|^2 = |\psi_E(x)|^2 \tag{129}$$

is time-independent and stuck at the value it had at $t = 0$.

You must have seen pictures of *electronic probability clouds* in atoms. These are just plots of $|\psi_E(x,y,z)|^2$ for the electron in the electrostatic potential $V(r) = -Ze^2/r$ of the static nucleus, $-e$ and Ze being the electronic and nuclear charges.

Suppose we ask for the odds of finding the particle in a state of definite momentum. As per the postulate we would write at each time t,

$$\psi_E(x,t) = \sum_p A_p(t)\frac{e^{ipx/\hbar}}{\sqrt{L}} \tag{130}$$

where

$$A_p(t) = \int \frac{e^{-ipx/\hbar}}{\sqrt{L}}\psi_E(x,0)e^{-iEt/\hbar}dx = A_p(0)e^{-iEt/\hbar} \tag{131}$$

so that the probability of finding a momentum p at time t is

$$P(p,t) \propto |A_p(t)|^2 = |A_p(0)|^2. \tag{132}$$

The same goes for the probability for any other variable. For this reason the states $\psi_E(x,t)$ are called *stationary states.*

Note that this time-independence of probabilities holds only for single state of definite energy thanks to the fact that $|e^{-iEt/\hbar}|^2 = 1$. Consider the following superposition of two such states which, by linearity of the the Schrö dinger equation, is also a solution :

$$\psi(x,t) = A_1\psi_{E_1}(x)e^{-iE_1t/\hbar} + A_2\psi_{E_2}(x)e^{-iE_2t/\hbar} \tag{133}$$

It is clear that $|\psi(x,t)|^2$ has time dependence coming from cross terms. We shall return to a more detailed study of this point shortly.

Now it turns out that we have unwittingly also solved the general problem of computing the time evolution of *any* initial state. Here is how it goes.

Consider then the following sum of such solutions with constant coefficients A_E:

$$\psi(x,t) = \sum_E A_E e^{-iEt/\hbar}\psi_E(x). \tag{134}$$

Thanks to the linearity of the Scrödinger equation, this sum is also a solution.

At $t = 0$ this function becomes

$$\psi(x,0) = \sum_E A_E \psi_E(x). \tag{135}$$

Thus in any problem where the initial state takes the form of the sum above, we have the solution for future times.

But *any* function $\psi(x,0)$ can be written in this form since the functions $\psi_E(x)$ form a basis like $\mathbf{i}, \mathbf{j}, \mathbf{k}$ do in three dimensions for any vector $\mathbf{V}$.

That means that Eqn. 134 gives the evolution of any arbitrary initial state.

To make sure you are all on board, here is the procedure for solving the Schrödinger equation in three parts.

Step 1: Find A_E from $\psi(x,0)$ by doing the requisite integral

$$A_E = \int \psi_E^*(x)\psi(x,0)dx.$$

Step 2: Attach to each A_E the phase factor $e^{-iEt/\hbar}$ to get $A_E(t) = A_E e^{-iEt/\hbar}$.

Step 3: Write $\psi(x,t)$ as a sum over $\psi_E(x)$ with coefficients $A_E(t)$.

A. Back inside the box

Now for some illustrative examples from " particle in a box".

1. *Example I: A single energy state*

First let us say we have at $t = 0$ an initial state

$$\psi(x,0) = A \sin\left[\frac{n\pi x}{L}\right] \tag{136}$$

We can normalize it first and get

$$\psi(x,0) = \sqrt{\frac{2}{L}} \sin\left[\frac{n\pi x}{L}\right]. \tag{137}$$

What is the state at later times? Answer: because it is a state of definite energy, we assert

$$\psi(x,t) = \sqrt{\frac{2}{L}} \sin\left[\frac{n\pi x}{L}\right] e^{-iE_n t/\hbar} \tag{138}$$

where

$$E_n = \frac{n^2\hbar^2\pi^2}{2mL^2}. \tag{139}$$

Note that

$$P(x,t) = \frac{2}{L}\sin^2\left[\frac{n\pi x}{L}\right] \tag{140}$$

is time-independent.

2. *Example II": Superposition of two energy states.*

Now let

$$\psi(x,0) = 3\sqrt{\frac{2}{L}}\sin\left[\frac{2\pi x}{L}\right] + 4\sqrt{\frac{2}{L}}\sin\left[\frac{3\pi x}{L}\right] \tag{141}$$

Thus it is state with $A_2 = 3$, $A_3 = 4$ and all other $A_E's = 0$. The $A_E's$ were given and we did not have to calculate them.

This unnormalized represents a state which has a probability $P(2) = 3^2/(3^2+4^2)$ to be have energy E_2, probability $P(3) = 4^2/(3^2+4^2)$ to have energy E_3 and zero chance for any other value of energy. If, say, E_2 is obtained in the energy measurement, the wave function will collapse to $\psi_2(x)$.

If you redo this part of the problem by first normalizing ψ, then the $|A_E|^2$ should directly give the absolute probabilities. This will just replace 3 by 3/5 and 4 by 4/5. It will all work out because $(3/5)^2 + (4/5)^2 = 1$.

At any future time the *normalized* state will be

$$\psi(x,t) = \frac{3}{5}\sqrt{\frac{2}{L}}\sin\frac{2\pi x}{L}e^{-iE_2t/\hbar} + \frac{4}{5}\sqrt{\frac{2}{L}}\sin\frac{3\pi x}{L}e^{-iE_3t/\hbar}. \tag{142}$$

The probabilities for energies is unchanged, since each coefficient A_E was simply multiplied by a phase.

However probabilities for other variables can change with time. For example

$$\begin{aligned}
P(x,t) &= |\psi(x,t)|^2 = \left|\frac{3}{5}\sqrt{\frac{2}{L}}\sin\left[\frac{2\pi x}{L}\right]e^{-iE_2t/\hbar} + \frac{4}{5}\sqrt{\frac{2}{L}}\sin\left[\frac{3\pi x}{L}\right]e^{-iE_3t/\hbar}\right|^2 && (143)\\
&= \frac{18}{25L}\sin^2\frac{2\pi x}{L} + \frac{32}{25L}\sin^2\frac{3\pi x}{L} && (144)\\
&+ \frac{24}{25L}e^{-i(E_2-E_3)t/\hbar}\sin\frac{2\pi x}{L}\ \sin\frac{3\pi x}{L} + \frac{24}{25L}e^{-i(E_3-E_2)t/\hbar}\sin\frac{2\pi x}{L}\ \sin\frac{3\pi x}{L} && (145)\\
&= \frac{18}{25L}\sin^2\frac{2\pi x}{L} + \frac{32}{25L}\sin^2\frac{3\pi x}{L} && (146)\\
&+ \frac{48}{25L}\cos\left[(E_2-E_3)t/\hbar\right]\sin\frac{2\pi x}{L}\ \sin\frac{3\pi x}{L} && (147)
\end{aligned}$$

You can see that there are oscillations in the probability density as a function of time with a frequency $\omega = (E_3 - E_2)/\hbar$.

3. *Case III: A $\psi(x, 0)$ with A_E not given.*

The previous examples were trivial in that A_E was given and we just appended the phase $e^{\frac{-iE_n t}{\hbar}}$ to each coefficient coming from time evolution.

In general you have to work for the $A_E^{\prime}s$. Here is an example. We are given a particle in a box of length $L = 1$ in a state:

$$\psi(x, 0) = N\ x(1 - x) \tag{148}$$

where N is to be determined by normalization if we want. Note that ψ vanishes at both ends as it should.

Your mission: Normalize this, and tell me what $\psi(x, t)$ is.

Answer: I leave it to you to show that $N = \sqrt{30}$.

Next, the coefficients of expansion are (remember $L = 1$ in this example)

$$A_n = \int_0^1 \sqrt{\frac{2}{1}} \sin n\pi x \sqrt{30} x(1 - x)dx = \sqrt{240}\frac{1 - \cos n\pi}{n^3\pi^3} \tag{149}$$

You can use a table of integrals and use integration by parts to get this result. (If this comes in an an exam the integrals will be easier.)

If you draw some pictures you can see that whenever n is even you should get 0 since you will be integrating a function odd with respect to the point $x = \frac{1}{2}$ between $x = 0$ and $x = 1$. Our result agrees with this since $\cos n\pi = (-1)^n$.

So for $t > 0$ the state is

$$\psi(x, t) = \sum_{n=1,2,,,} \sqrt{240}\frac{1 - \cos n\pi}{n^3\pi^3} e^{-iE_n t/\hbar}\sqrt{2} \sin n\pi x. \tag{150}$$

It will be instructive for you to plot this as a function of time on a desktop computer, keeping more and more terms.

X. POSTULATES

Postulate 1 The *complete* information on the state of the particle is encoded in a complex function $\psi(x)$ called the wave function.

Postulate 2 The probability of finding the particle between x and $x + dx$ is given by

$$P(x)dx = |\psi(x)|^2 \, dx. \tag{151}$$

(To *normalize* the function is to choose its overall scale such that $\int_{\text{all space}} P(x)dx = 1.$)

Postulate 3 A state in which the particle has momentum p, denoted by $\psi_p(x)$, obeys

$$-i\hbar \frac{d\psi_p(x)}{dx} = p\psi_p(x).$$

The solution is given by

$$\psi_p(x) = \frac{1}{\sqrt{L}} e^{ipx/\hbar} \tag{152}$$

where L is the size of the one-dimensional world in which the particle lives, assumed to be closed on itself into a circle. (It is possible to let $L \to \infty$, with considerable mathematical effort, but not worth the trouble here.)

Mathematical result The only allowed values of momentum for a particle living on a circle are given by

$$p = \frac{2\pi m\hbar}{L} \qquad m = 0, \pm 1, \pm 2... \tag{153}$$

which comes from the requirement that

$$\psi(x) = \psi(x + L) \tag{154}$$

i.e., if we go around the circle and come back to the same point ψ must return to the same value. We say ψ is periodic or single valued on the circle.

Postulate 4 To find the probability of obtaining one of the above mentioned allowed values of p when momentum is measured on a particle in any state $\psi(x)$, first expand it as follows:

$$\psi(x) = \sum_{m=0,\pm 1,\pm 2..} A_m \frac{1}{\sqrt{L}} e^{2\pi imx/L} \tag{155}$$

where I have used m in place of p in the sum over states and in the wave function. Then

$$P(m) = |A_m|^2 \tag{156}$$

is the probability that the value m will be obtained in a momentum measurement. (By this I mean the momentum $p = 2\pi m\hbar/L$ will be obtained).

(Three mathematical points which are not postulates. First, any periodic function ψ can be expanded as a sum of exponentials with the precisely the allowed values of m listed above.

For these values of m each exponential function is periodic with period L. Second, to find the coefficients A_m in Eq. (155), we can either get the answer by inspection if ψ is a sum of trigonometric functions, or in every case, turn to

$$A_m = \int_0^L \frac{1}{\sqrt{L}} e^{-2\pi imx/L} \psi(x) dx. \tag{157}$$

Third, if we first normalize $\psi(x)$ or it is already normalized,

$$P(m) = |A_m|^2 \tag{158}$$

is the absolute probability. That is $\sum_m |A_m|^2 = 1$ and there is no need to divide by it.

Postulate 5 If x is measured, ψ will collapse to a spike at the measured value of x and if p is measured ψ will collapse to the one term in the sum Eq. (155) corresponding to the measured value.

Postulate 6 A particle in a state of definite energy E obeys the time-independent Schrödinger Equation

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

As with momentum any $\psi(x)$ can be written as

$$\psi(x) = \sum_E A_E \psi_E(x)$$

where the coefficients are

$$A_E = \int \psi_E^*(x)\psi(x) dx$$

provided $\psi_E(x)$ is normalized).

Again, if energy is measured, $\frac{|A_E|^2}{\sum_E A_E|^2}$ gives the probability of getting the value E, if ψ is not normalized. (There is no need to divide by the denominator if ψ is normalized.)

With a lot more machinery we can reduce the number of postulates by one, but it is not worth it. This was discussed in the optional Section VI.

Postulate 7 The evolution of ψ with time is given by the Schrodinger equation

$$i\hbar\frac{\partial\psi(x,t)}{\partial t} = \left[-\frac{h^2}{2m}\frac{\partial\psi(x,t)}{\partial x^2} + V(x)\psi(x,t)\right] \tag{159}$$

where $V(x)$ is the potential at point x.

A corollary is that if at $t = 0$

$$\psi(x,0) = \sum_E A_E(0)\psi_E(x),$$

then at any future time t,

$$\psi(x,t) = \sum_E A_E(0)e^{-iEt/\hbar}\psi_E(x)$$