Schrödinger’s wave equation

We now have a set of individual operators that can extract dynamical quantities of interest from the wave function, but how do we find the wave function in the first place? The free particle wave function was easy, but what about for a particle under the influence of a potential \( V(x, t) \)? Let us use the correspondence principle and classical physics to lead us to a general equation that dictates the form of the wave function, and thus tells us about the dynamics of the system. We know that the total energy for a (non-relativistic) particle is given by \( E = T + V \). We now turn to the operators that we just discovered and replace the quantities in the energy equation by their respective operators:

\[
E = T + V \Rightarrow 
\]

\[
\frac{i\hbar}{\partial t} \psi = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V 
\]

This is an operator equation, and doesn’t really make much sense until we take it and operate on a wave function:

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

Of course, we really only get our expectation values of the quantities when we multiply (from the left) by \( \psi^* \) and integrate over all space. But, in order for that to give us reasonable quantities that describe the (quantum mechanical) motion of a particle, the wave function must obey this differential equation. This is Schrödinger’s Equation, and you will spend much of the rest of this semester finding solution to it, assuming different potentials.

We now have several constraints on the wave function \( \psi \):

1) It must obey Schrödinger’s equation.
2) It must be normalizable such that the integral of \( \psi^*\psi \) from minus infinity to infinity equals one. This means that \( \psi \) must go to zero faster than one over root \( x \) as \( x \) approaches infinity.

Let’s now make some self-consistency checks:

**Time Dependence of Normalization**

When we normalize the wave function at some time \( t \), how are we to know for sure that it stays normalized? We can check:
\[ \frac{d}{dt} \int_{-\infty}^{\infty} (\Psi^* \Psi) dx = \int_{-\infty}^{\infty} \frac{\partial}{\partial t} (\Psi^* \Psi) dx \]

\[ = \int_{-\infty}^{\infty} \left( \frac{\partial \Psi^*}{\partial t} \Psi + \Psi^* \frac{\partial \Psi}{\partial t} \right) dx \]

but,

\[ \frac{\partial \Psi}{\partial t} = \frac{i \hbar}{2m} \frac{\partial^2 \Psi}{\partial x^2} - \frac{i}{\hbar} \nabla \Psi \]

\[ \frac{\partial \Psi^*}{\partial t} = -\frac{i \hbar}{2m} \frac{\partial^2 \Psi^*}{\partial x^2} + \frac{i}{\hbar} \nabla \Psi^* \]

from Schrödinger’s equation, so

\[ \frac{d}{dt} \int_{-\infty}^{\infty} (\Psi^* \Psi) dx = \frac{i \hbar}{2m} \int_{-\infty}^{\infty} \left( \Psi^* \frac{\partial^2 \Psi}{\partial x^2} - \frac{\partial^2 \Psi^*}{\partial x^2} \Psi \right) dx \]

\[ = \left[ \frac{i \hbar}{2m} \int_{-\infty}^{\infty} \frac{\partial}{\partial x} \left( \Psi^* \frac{\partial \Psi}{\partial x} - \frac{\partial \Psi^*}{\partial x} \Psi \right) dx \right] \]

\[ = \frac{i \hbar}{2m} \left( \Psi^* \frac{\partial \Psi}{\partial x} - \frac{\partial \Psi^*}{\partial x} \Psi \right)_{-\infty}^{\infty} \]

But, since the wave function is square-integrable, it must go to zero at infinity and thus the time derivative of the total probability is zero. Therefore, if we normalize at some time \( t \), the wavefunction stays normalized.

**Continuity Equation**

It is interesting to ask about the integral above if we don’t integrate over the whole space, in other words what is: \( \frac{d}{dt} \int_{a}^{b} (\Psi^* \Psi) dx \)?

\[ \frac{d}{dt} \int_{a}^{b} (\Psi^* \Psi) dx = \frac{i \hbar}{2m} \int_{a}^{b} \left( \Psi^* \frac{\partial^2 \Psi}{\partial x^2} - \frac{\partial^2 \Psi^*}{\partial x^2} \Psi \right) dx \]

\[ = \int_{a}^{b} \frac{\partial}{\partial x} \left[ \frac{i \hbar}{2m} \left( \Psi^* \frac{\partial \Psi}{\partial x} - \frac{\partial \Psi^*}{\partial x} \Psi \right) \right] dx \]

\[ = \left[ \frac{i \hbar}{2m} \left( \Psi^* \frac{\partial \Psi}{\partial x} - \frac{\partial \Psi^*}{\partial x} \Psi \right) \right]_{a}^{b} \]

We associate the term in the square brackets with the current density \( J(x,t) \). The equation reads: The change in the probability of finding a particle between points \( a \) and \( b \) is difference in the current going into the region and the current leaving the region.
Perhaps it may be clearer in three dimensions:

\[
\frac{d}{dt} \int \langle \Psi^* \Psi \rangle dV = \frac{i\hbar}{2m} \int \langle \Psi^* (\nabla^2 \Psi) - (\nabla^2 \Psi^*) \Psi \rangle dV \\
= \int \nabla \left[ \frac{i\hbar}{2m} \langle \Psi^* (\nabla \ Psi) - (\nabla \Psi^*) \Psi \rangle \right] dV \\
= \int \vec{\nabla} \cdot \vec{J} dV \\
= \int \vec{J} \cdot d\vec{A}
\]

where the last step uses the divergence theorem and again reads: The change in the probability of finding the particle in a volume V, is equal to the net current through the surface bounding the volume.

**Homework**

**Problem 1.14** Let \( P_{ab}(t) \) be the probability of finding a particle in the range \( (a < x < b) \), at time \( t \).

(a) Show that

\[
\frac{dP_{ab}}{dt} = J(a, t) - J(b, t),
\]

where

\[
J(x, t) = \frac{i\hbar}{2m} \left( \Psi \frac{\partial \Psi^*}{\partial x} - \Psi^* \frac{\partial \Psi}{\partial x} \right).
\]

What are the units of \( J(x, t) \)? **Comment:** \( J \) is called the **probability current**, because it tells you the rate at which probability is “flowing” past the point \( x \). If \( P_{ab}(t) \) is increasing, then more probability is flowing into the region at one end than flows out at the other.

(b) Find the probability current for the wave function below. (This is not a very pithy example, I’m afraid; we’ll encounter more substantial ones in due course.)

\[
\Psi(x, t) = Ae^{-\alpha[(mx^2/\hbar) + it]},
\]

**Momentum Operator from Velocity of \( \langle x \rangle \)**

We can now also check our operators for consistency.
Instead of asking what the expectation value of momentum is, let’s ask what is the time dependency of the expectation value of the position, (or the velocity of the expectation value):

\[
\frac{d}{dt} \langle x \rangle = \frac{d}{dt} \int_{-\infty}^{\infty} \Psi^*(x, t)x\Psi(x, t)dx
\]

\[
= \frac{d}{dt} \int_{-\infty}^{\infty} x\Psi^*(x, t)\Psi(x, t)dx
\]

\[
= \int_{-\infty}^{\infty} \frac{\partial}{\partial t} \left[x\Psi^*(x, t)\Psi(x, t)\right]dx
\]

\[
= \int_{-\infty}^{\infty} \left[\frac{\partial x}{\partial t} \Psi^*(x, t)\Psi(x, t) + x \frac{\partial}{\partial t} \left[\Psi^*(x, t)\Psi(x, t)\right]\right]dx
\]

\[
= \int_{-\infty}^{\infty} x \frac{\partial}{\partial t} \left[\Psi^*(x, t)\Psi(x, t)\right] dx
\]

\[
= \frac{ih}{2m} \int_{-\infty}^{\infty} x \frac{\partial}{\partial x} \left(\Psi^* \frac{\partial \Psi}{\partial x} - \frac{\partial \Psi^*}{\partial x} \Psi\right)dx
\]

I now use a very useful integration technique known as integration by parts. Since you will use it often in this class, I diverge for a moment to explain it:

The product rule for differentiation says:

\[
\frac{d}{dx} (fg) = f \frac{dg}{dx} + \frac{df}{dx} g \Rightarrow
\]

\[
f \frac{dg}{dx} = -\frac{df}{dx} g + \frac{d}{dx} (fg)
\]

Integrating both sides:

\[
\int_{a}^{b} f \frac{dg}{dx} dx = -\int_{a}^{b} \frac{df}{dx} g dx + \int_{a}^{b} \frac{d}{dx} (fg) dx
\]

\[
= -\int_{a}^{b} \frac{df}{dx} g dx + (fg)_{a}^{b}
\]

I like the way Griffiths phrases it: “…you can peel a derivative off one factor in a product, slap it on the other one – it’ll cost you a minus sign and you’ll pick up a boundary term.”

OK, back to our problem. If we let f = x, and g = (…) then df/dx = 1 and we have:
\[
\frac{d}{dt} \langle x \rangle = \frac{i \hbar}{2m} \int_{-\infty}^{\infty} x \frac{\partial}{\partial x} \left( \Psi^* \frac{\partial \Psi}{\partial x} - \frac{\partial \Psi^*}{\partial x} \Psi \right) dx \\
= -\frac{i \hbar}{2m} \int_{-\infty}^{\infty} \left( \Psi^* \frac{\partial \Psi}{\partial x} - \frac{\partial \Psi^*}{\partial x} \Psi \right) dx + \left( x\Psi^* \frac{\partial \Psi}{\partial x} - x \frac{\partial \Psi^*}{\partial x} \Psi \right)_{-\infty}^{\infty}
\]

but again, since \( \Psi \) goes to zero at infinity, the boundary term vanishes and we have

\[
\frac{d}{dt} \langle x \rangle = -\frac{i \hbar}{2m} \int_{-\infty}^{\infty} \left( \Psi^* \frac{\partial \Psi}{\partial x} - \frac{\partial \Psi^*}{\partial x} \Psi \right) dx
\]

We can perform another integration by parts on the second term:

\[
\frac{d}{dt} \langle x \rangle = -\frac{i \hbar}{2m} \int_{-\infty}^{\infty} \left( \Psi^* \frac{\partial \Psi}{\partial x} - \frac{\partial \Psi^*}{\partial x} \Psi \right) dx \\
= -\frac{i \hbar}{2m} \left[ \int_{-\infty}^{\infty} \Psi^* \frac{\partial \Psi}{\partial x} dx - \int_{-\infty}^{\infty} \frac{\partial \Psi^*}{\partial x} \Psi dx \right] \\
= -\frac{i \hbar}{2m} \left[ \int_{-\infty}^{\infty} \Psi^* \frac{\partial \Psi}{\partial x} dx + \int_{-\infty}^{\infty} \Psi^* \frac{\partial \Psi}{\partial x} dx - \left( \Psi^* \Psi \right)_{-\infty}^{\infty} \right] \\
= -\frac{i \hbar}{m} \int_{-\infty}^{\infty} \Psi^* \frac{\partial \Psi}{\partial x} dx
\]

where again the boundary term goes to zero. We now notice that the velocity of the expectation value has the same operator as the momentum operator that we developed earlier (divided by the mass \( m \)). Again, we should feel reassured that we have a consistent theory.