Schrödinger's Equation

Lecture 5

Physics 342
Quantum Mechanics I

Wednesday, February 6th, 2008

Today we discuss Schrödinger's equation and show that it supports the basic interpretation of the fundamental object of study in quantum mechanics: the wave function. The operational procedures of quantum mechanics begin with this PDE, and its associated boundary and initial conditions. So while it is easy to state the basic axioms, and even motivate the expressions, the shift in focus is dramatic.

In classical mechanics, our goal is always to find or describe the salient features of a curve $\mathbf{x}(t)$, the trajectory of a particle under some impressed force. The relation of force to curve is provided by Newton's second law: $\mathbf{F} = m\,\ddot{\mathbf{x}}(t)$, and the physically inspired initial (or boundary) conditions. The job is straightforward, if complicated at times. The interpretation is simple: The particle moves along the curve.

In quantum mechanics, our initial goal will be to find the probability density $|\Psi(x,t)|^2$ for a particular system, from which we can calculate expectation values (the outcomes of experiment). The relation of a classical potential to the density (or equivalently, $\Psi(x,t)$, the wave function) is provided by Schrödinger's equation.

There are a few obvious questions that come up as we exploit the probabilistic interpretation of the wave function. We know that if we have a probability density $\rho(x,t)$, we can compute the outcome of experiments that rely on position, since $\langle f(x)\rangle = \int_{-\infty}^{\infty} f(x)\,\rho(x,t)\,dx$. What, then, should we make of experiments that measure velocity (or momentum)? A related question is why, given that it is $\rho(x,t)$ that we want, does Schrödinger's equation govern $\Psi(x,t)$? Shouldn't we have a PDE that tells us about the evolution of $\rho(x,t)$ itself?

5.1 Without Further Ado

Here it is – for a complex field $\Psi(x,t)$, Schrödinger's equation says that the dynamical evolution of Ψ is given by (in one spatial dimension):

$$i\,\hbar\,\frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2\,m}\,\frac{\partial^2 \Psi}{\partial x^2} + V(x)\,\Psi \tag{5.1}$$

for a potential $V(x)$. This is the quantum mechanical analogue of the classical Newton's second law: the dynamical evolution of a particle is given by its trajectory $x(t)$ governed by $m\ddot{\mathbf{x}} = -\nabla V$.

Our statistical interpretation is provided by viewing $\Psi(x,t)^*\,\Psi(x,t)$ as a density: $\rho(x,t) = |\Psi(x,t)|^2$ so that

$$P(a,b) = \int_a^b \rho(x,t)\,dx = \int_a^b |\Psi(x,t)|^2\,dx \tag{5.2}$$

is the probability a particle is found between $x = a$ and $x = b$. We are talking about the probability density associated with a *particle*, that explains the m in Schrödinger's equation. The constant $\hbar$ tells us this is not a classical system. If we turn off $\hbar$, we get $\Psi = 0$, which seems reasonable – classically, the probability density would be given by: $\rho(x,t)_{CM} = \delta(x - x(t))$, so that with probability 1, the particle is on its classical trajectory $x(t)$. Without some notion of $x(t)$, there is no probability density at all, so $\Psi = 0$ is as good a solution as any. Of course, $\hbar$ is doing more than setting units, but we will see that later on.

No statistical interpretation exists in Schrödinger's equation alone – for example, the equation itself does not demand that $\int_{-\infty}^{\infty} |\Psi(x,t)|^2\,dx = 1$ for all time. But, it does *support* the statistical interpretation in the sense that if we solved the above, and required that, at time $t = 0$ (or any particular time), $\int_{-\infty}^{\infty} |\Psi(x,t)|^2\,dx = 1$, then the equation leaves the total probability constant in time – so once a probability density, always a probability density.

We can see this by taking the time derivative of $\int_{-\infty}^{\infty} |\Psi(x,t)|^2\,dx = 1$, and showing that, as long as $\Psi(x,t)$ satisfies (5.1), the normalization remains intact. It is, then, up to us to ensure that $\Psi(x,t)$ is appropriately normalized *at some time*. Take:

$$\frac{d}{dt}\int_{-\infty}^{\infty} |\Psi(x,t)|^2\,dx = \int_{-\infty}^{\infty} \frac{\partial}{\partial t}\left(\Psi^*(x,t)\,\Psi(x,t)\right)\,dx, \tag{5.3}$$

then we just need the temporal derivative of the norm (squared) of $\Psi(x,t)$:

$$\frac{\partial}{\partial t}\left(\Psi^*(x,t)\,\Psi(x,t)\right) = \frac{\partial \Psi^*}{\partial t}\,\Psi + \Psi^*\,\frac{\partial \Psi}{\partial t}, \tag{5.4}$$

which is fine, but this is under an integral w.r.t. x, so we'd like a mechanism for turning temporal derivatives into spatial ones (preparatory to integration by parts). Schrödinger's equation, and its complex conjugate provide precisely the desired connection:

$$\begin{aligned}\frac{\partial \Psi}{\partial t} &= \frac{i\,\hbar}{2\,m}\,\frac{\partial^2 \Psi}{\partial x^2} - \frac{i}{\hbar}\,V(x)\,\Psi \\ \frac{\partial \Psi^*}{\partial t} &= -\frac{i\,\hbar}{2\,m}\,\frac{\partial^2 \Psi^*}{\partial x^2} + \frac{i}{\hbar}\,V(x)\,\Psi^*,\end{aligned} \tag{5.5}$$

and we can write the above as:

$$\frac{\partial}{\partial t}\left(\Psi^*(x,t)\,\Psi(x,t)\right) = \frac{i\,\hbar}{2\,m}\left(-\frac{\partial^2 \Psi^*}{\partial x^2}\,\Psi + \Psi^*\,\frac{\partial^2 \Psi}{\partial x^2}\right). \tag{5.6}$$

Now, under the integral, we can use integration by parts[1] to simplify the above – consider the first term:

$$\int_{-\infty}^{\infty} \frac{\partial^2 \Psi^*}{\partial x^2}\,\Psi\,dx = \left(\frac{\partial \Psi^*}{\partial x}\,\Psi\right)\Bigg|_{-\infty}^{\infty} - \int_{-\infty}^{\infty} \frac{\partial \Psi^*}{\partial x}\,\frac{\partial \Psi}{\partial x}\,dx. \tag{5.9}$$

We can get rid of the boundary term by assuming (an additional requirement!) that $\Psi(x,t) \longrightarrow 0$ as $|x| \longrightarrow \infty$. This is a reasonable assumption, and a common one when dealing with densities (charge distributions do not extend to infinity except in artificial cases, for example). Then, going back to the original time derivative of the density:

$$\begin{aligned}\frac{d}{dt}\int_{-\infty}^{\infty}\left(\Psi^*(x,t)\,\Psi(x,t)\right) &= \frac{i\,\hbar}{2\,m}\int_{-\infty}^{\infty}\left[\left(-\frac{\partial^2 \Psi^*}{\partial x^2}\,\Psi + \Psi^*\,\frac{\partial^2 \Psi}{\partial x^2}\right)\right]dx \\ &= \frac{i\,\hbar}{2\,m}\int_{-\infty}^{\infty}\left[\frac{\partial \Psi^*}{\partial x}\,\frac{\partial \Psi}{\partial x} - \frac{\partial \Psi^*}{\partial x}\,\frac{\partial \Psi}{\partial x}\right]dx \\ &= 0,\end{aligned} \tag{5.10}$$

[1] For two functions $u(x)$ and $v(x)$, we have

$$\int_a^b \frac{d}{dx}\left(u(x)\,v(x)\right)dx = u(x)\,v(x)|_a^b, \tag{5.7}$$

and using the product rule on the left gives:

$$\int_a^b \left[\frac{du(x)}{dx}\,v(x) + u(x)\,\frac{dv(x)}{dx}\right]dx = u(x)\,v(x)|_a^b, \tag{5.8}$$

from which the "usual" form of integration by parts follows.

and we have the result: The time derivative of the probability that a particle exists somewhere spatially is zero, hence we can normalize $\Psi(x,t)$ so that the probability the particle exists somewhere is $= 1$, and it will remain 1 for all time.

Notice that the statement:

$$\frac{d}{dt}\int \rho(x,t)\,dx = 0 \tag{5.11}$$

is reminiscent of charge conservation. This is a "probability" conservation sentiment. By analogy with charge, though, we should be able to find a "probability current" associated with the conservation. This must be an object whose x-derivative is equal to the right-hand-side of (5.10) (the top line, before we integrate by parts) – easy to find in this case. We want:

$$\frac{d}{dx}\,J(x,t) = -\frac{i\,\hbar}{2\,m}\left[-\frac{\partial^2\Psi^*}{\partial x^2}\,\Psi + \Psi^*\,\frac{\partial^2\Psi}{\partial x^2}\right], \tag{5.12}$$

(the minus sign is convention, and we will use it in a moment to make contact with other conservation laws) and it is pretty clear that:

$$\boxed{J(x,t) = -\frac{i\,\hbar}{2\,m}\left[\Psi^*\,\frac{\partial\Psi}{\partial x} - \frac{\partial\Psi^*}{\partial x}\,\Psi\right]} \tag{5.13}$$

has the desired property.

Interesting – then we have another view of the conservation statement – we would write it, in one dimension, as

$$\frac{d}{dt}\int_{-\infty}^{\infty}\rho(x,t)\,dx = -\int_{-\infty}^{\infty}\frac{d}{dx}\,J(x,t)\,dx. \tag{5.14}$$

Here, the right-hand side is clearly zero by the fundamental theorem of calculus, and the requirement that Ψ vanish at spatial infinity. We have basically rewritten integration by parts, but this rewrite allows us to make a "differential" continuity statement:

$$\frac{\partial\rho}{\partial t} = -\frac{\partial J}{\partial x}. \tag{5.15}$$

In three dimensions, this would read;

$$\frac{\partial\rho}{\partial t} = -\nabla\cdot\mathbf{J} \qquad \mathbf{J} = -\frac{i\,\hbar}{2\,m}\left[\Psi^*\,\nabla\Psi - \Psi\,\nabla\Psi^*\right]. \tag{5.16}$$

Now we see the analogy: In E&M, the rate of change of charge in a volume is determined by the charge flowing in through a surface. We have $\int_V \rho \, d\tau$ as the charge in the volume, and $\oint \mathbf{J} \cdot d\mathbf{a}$ is the surface integral for the current – then the statement is

$$\frac{\partial \rho}{\partial t} = -\nabla \cdot \mathbf{J} \longrightarrow \frac{d}{dt} \int_V \rho \, d\tau = -\oint_{\partial V} \mathbf{J} \cdot d\mathbf{a}, \tag{5.17}$$

where we get the integral form by integrating both sides of the differential one and applying the divergence theorem. The same conservation law holds for mass flow in a fluid. Evidently, in quantum mechanics, the local probability of finding a particle in a volume can change over time according to a probability flux that can be used to account for probability "flowing" into and out of the volume through its boundary.

5.2 Expectation Values

Let's take stock: We have a PDE that governs the temporal evolution of a "wavefunction" $\Psi(x,t)$ given a classical potential $V(x)$, Schrödinger's equation. This PDE supports a probabilistic interpretation for the absolute value (squared) of $\Psi(x,t)$, i.e. "$|\Psi|^2$ is the probability density for finding the particle at location x at time t." provided $\Psi(x,t)$ vanishes at spatial infinity. That gives us a boundary condition for $\Psi(x,t)$, but we are missing the initial condition – what is the spatial function $\Psi(x, t = 0)$? We'll come back to this, but one thing is clear, it must have the property: $\int_{-\infty}^{\infty} |\Psi(x, t = 0)|^2 \, dx = 1$ for the probabilistic interpretation to hold. We have, so far, a complex $\Psi(x,t)$ to be found subject to:

$$\boxed{\begin{aligned} i\,\hbar \frac{\partial \Psi}{\partial t} &= -\frac{\hbar^2}{2\,m} \frac{\partial^2 \Psi}{\partial x^2} + V(x)\,\Psi \\ \Psi(x \to \pm\infty, t) &= 0 \\ \int_{-\infty}^{\infty} |\Psi(x,0)|^2 \, dx &= 1. \end{aligned}} \tag{5.18}$$

If we had the wavefunction, all manner of interesting physical properties could be calculated. We can start with the simplest – the expectation value of position: $\langle x \rangle$. From the density, we know that

$$\boxed{\langle x \rangle = \int_{-\infty}^{\infty} x\,\rho(x,t)\,dx = \int_{-\infty}^{\infty} \Psi^*\,x\,\Psi\,dx} \tag{5.19}$$

which is reasonable. We have put x in between Ψ and its complex conjugate, that doesn't matter here, just notation.

One can define the expectation of "velocity" to be the time-derivative of $\langle x \rangle$, i.e. if we know how the expected position changes in time, we might call that the "expected" velocity. Since expectation values proceed by integration over all positions, the notion of time-dependence for x itself is not particularly useful. The objects with time-dependence are expectation values, and these inherit their time-dependence directly from the wavefunction's, so we are sort of forced into viewing particle "velocity" as the time-dependence of the particle's expected position. At that point, we have

$$\begin{aligned} \frac{d\langle x \rangle}{dt} &= \int_{-\infty}^{\infty} \frac{\partial}{\partial t} \left(\rho(x,t)\, x \right) \, dx \\ &= \int_{-\infty}^{\infty} \frac{\partial \rho}{\partial t} \, x \, dx \\ &= -\int_{-\infty}^{\infty} \frac{\partial J}{\partial x} \, x \, dx \\ &= \int_{-\infty}^{\infty} J \, dx, \end{aligned} \tag{5.20}$$

where we have used the local form of conservation: $\frac{\partial \rho}{\partial t} = -\frac{\partial J}{\partial x}$, and integration by parts.

This makes some sense when we think of the current density from E&M, or the fluid flux density in hydrodynamics – in either case, with appropriate interpretation of ρ, we have $\mathbf{J} = \rho \, \mathbf{v}$ – in our present setting, the ρ is probability density, and the $\mathbf{v}$ then represents some sort of velocity with which the probability is flowing – the natural expectation value here would be $\langle v \rangle = \int_{-\infty}^{\infty} \rho \, v \, d\tau$ in one dimension. But that's what the above *is*. There is a sleight-of-hand going on here, we just associated v with probability flux, and yet, we'd like to understand the expectation value of v in terms of a particle's velocity – don't take the above argument as anything more than motivation at this point.

Pressing on, we can write the integral itself in a more illuminating form using the definition of J from (5.13):

$$\begin{aligned} \langle v \rangle &= \int_{-\infty}^{\infty} J \, dx = \int_{-\infty}^{\infty} \left[\Psi \left(\frac{i\hbar}{2m} \frac{\partial}{\partial x} \right) \Psi^* - \Psi^* \left(\frac{i\hbar}{2m} \frac{\partial}{\partial x} \right) \Psi \right] dx \\ &= -\int_{-\infty}^{\infty} \Psi^* \left(\frac{i\hbar}{m} \frac{\partial}{\partial x} \right) \Psi dx \end{aligned} \tag{5.21}$$

where we used integration by parts to combine the two terms. In the end, we can move the mass over to the right, and define the expectation value of momentum (of the particle, now):

$$\boxed{\langle p \rangle = \langle m\, v \rangle = \int_{-\infty}^{\infty} \Psi^* \left(\frac{\hbar}{i} \frac{\partial}{\partial x}\right) \Psi\, dx.} \tag{5.22}$$

Looking at the expectation value of position again,

$$\langle x \rangle = \int_{-\infty}^{\infty} \Psi^*\, x\, \Psi\, dx \tag{5.23}$$

we are tempted to define "operators" x and p (whose expectation values are given by the above) via:

$$\boxed{x \sim x \qquad p \sim \frac{\hbar}{i} \frac{\partial}{\partial x}.} \tag{5.24}$$

These are operators in the sense (obvious for p) that they act on the wave function.

This seems like a strange move, and it is a literal translation of what the expectation values are telling us, so there's no reason to believe any of it just yet – we will let the correctness of the predictions of this theory do the convincing. For now it is the case that with a sensible definition of expectation value, and the peculiar factoring of probability density provided by the wave function, we are led to the above association.

With this in hand, we can define any classical quantity's expectation value by replacing $x \sim x$ and $p \sim \frac{\hbar}{i} \frac{\partial}{\partial x}$, and sandwhiching it between the wave function and its complex conjugate. For a classical function $Q(x, p)$, we have

$$\langle Q \rangle = \int_{-\infty}^{\infty} \Psi^*\, Q\left(x, \frac{\hbar}{i} \frac{\partial}{\partial x}\right) \Psi\, dx. \tag{5.25}$$

Things are beginning to look suspiciously like $\langle \alpha |\, Q\, | \alpha \rangle$ with an inner product defined by integration, which is no accident. What is also no accident is the fact that for the classical Hamiltonian, a function of x and p: $H = \frac{p^2}{2\,m} + V(x)$, our prescription for the expectation value is:

$$\langle H \rangle = \int_{-\infty}^{\infty} \Psi^* \left(-\frac{\hbar^2}{2\,m} \frac{\partial^2}{\partial x^2} + V(x)\right) \Psi\, dx, \tag{5.26}$$

and if you cover up the integral and Ψ^*, what you have is one side of Schrödinger's equation.

Homework

Reading: Griffiths, pp. 12–20.

Problem 5.1

Griffiths 1.4. In part c., you are asked where the particle is most likely to be found – technically, what we want is the maximum of $\rho(x)$ here – that is, the location of the particle with the largest $\rho(x)\,dx$.

Problem 5.2

Griffiths 1.7. This problem is about (an example of) Ehrenfest's theorem – it provides good practice with integration by parts, in addition to the computational utility of the result.

Problem 5.3

Working from the separated form of Schrödinger's equation: For $\Psi(x,t) = \psi(x)\,\phi(t)$, we had

$$\begin{aligned} -\frac{\hbar^2}{2\,m}\,\frac{d^2\psi(x)}{dx^2} + V(x)\,\psi(x) &= E\,\psi(x) \\ \phi(t) &= e^{-\frac{i\,E\,t}{\hbar}}. \end{aligned} \tag{5.27}$$

Consider a physical configuration in which we have $V(x) = 0$ and require that $\psi(0) = \psi(d) = 0$. This represents a particle confined to a one-dimensional "box" of width d. The wavefunction (and hence the probability density) is zero outside the interval, and continuity requires that the wavefunction must then vanish at the endpoints of the interval.

a. Solve the upper equation for $\psi(x)$, with boundary conditions. This should look familiar by now, and there will be an integer n that indexes your solutions. Write the "energy" E as a function of n, and form the full wavefunction: $\Psi_n(x,t)$. This should have an undetermined overall constant in it.

b. Suppose we have a wavefunction $\Psi(x,t) = \Psi_n(x,t)$ – in order to interpret $\rho(x,t) = \Psi^*(x,t)\,\Psi(x,t)$ as a probability density, we must have $\int_{-\infty}^{\infty} \rho(x,t)\,dx = 1$. Fix your overall constant in $\Psi_n(x,t)$ by normalizing the wavefunction.

c. Again, using $\Psi(x,t) = \Psi_n(x,t)$, calculate:

$$\langle x \rangle \qquad \text{and} \qquad \langle p \rangle. \tag{5.28}$$