CHM 305 - Lecture 3 - Schrödinger's Quantum Wave Equation

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In this lecture, we will discuss how quantum particles are described by "wavefunctions," and how we can find these wavefunctions by solving the Schrödinger equation, which acts like a quantum mechanical wave equation. At the level of this class, we really can't "derive" the Schrödinger equation, but we will try to motivate where it comes from. Note that we did not derive the classical wave equation in the last class, either! We just took it for granted, solved it and considered the form of its solutions.

The material in today's lecture is covered in Chapter 3 of McQuarrie, and to even better effect (I think) in Chapter 2 of Griffiths.

1 Quantum Waves

At the start of the last lecture, we considered classical traveling waves, which have the form

$$\Psi(x,t) = A\sin(kx - \omega t) \tag{1}$$

where $k = 2\pi/\lambda$ is the wave vector, a sort of spatial frequency (radians of oscillation per unit length), and $\omega = 2\pi\nu$ is the angular frequency (radians of oscillation per unit time). Using the Euler relation, we know that we can also equivalently express this traveling wave as:

$$\Psi(x,t) = Ce^{i(kx-\omega t)} \tag{2}$$

Let's think about how we can tweak this classical expression to describe the motion of a traveling quantum particle. In particular, we want to describe a particle traveling along with energy E and momentum p. In the first lecture, we touched on expressions for these quantities that are valid for quantum particles.

From deBroglie we learned that the momentum of a quantum particle is related to its wavelength by $\lambda = h/p$. We can therefore write that:

$$k = \frac{2\pi}{\lambda} = \frac{2\pi p}{h} = \frac{p}{\hbar} \tag{3}$$

where we've used $\hbar = h/2\pi$ for convenience.

From Planck and Einstein we learned that the relationship between the energy and frequency of a quantum particle is $E = h\nu = \hbar\omega$, and therefore

$$\omega = \frac{E}{\hbar} \tag{4}$$

We can plug Eqns. 3 and 4 back into Eqn. 2 to obtain:

$$\Psi(x,t) = Ce^{i(kx-\omega t)} = Ce^{i(px-Et)/\hbar} \tag{5}$$

We might think of this as a "quantum matter wave," which appears to describe the motion of a quantum particle with momentum p and energy E.

This quantum particle might already look a little strange. We are used to particles having well-defined trajectories described by their position and momentum as functions of time. Here, we seem to have well-defined momentum and energy, but the particle's position is indefinite, violating the idea of a trajectory. We will come back to this idea!

2 Motivating A Quantum Wave Equation

Our next step is to work backwards and think about what wave equation our quantum wave would be a solution to. Let's take some derivatives of the wavefunction and see what patterns appear.

For the first derivative with respect to t we find:

$$\frac{\partial}{\partial t}\Psi(x,t) = \frac{\partial}{\partial t}Ce^{i(px-Et)/\hbar} \tag{6}$$

$$= C\frac{-i}{\hbar}Ee^{i(px-Et)/\hbar} = \frac{-i}{\hbar}E\Psi(x,t) \tag{7}$$

$$\rightarrow i\hbar\frac{\partial}{\partial t}\Psi(x,t) = E\Psi(x,t) \tag{8}$$

This is a promising start! For the first two derivatives with respect to x we find:

$$\frac{\partial}{\partial x}\Psi(x,t) = \frac{\partial}{\partial x}Ce^{i(px-Et)/\hbar} \tag{9}$$

$$= \left(\frac{ip}{\hbar}\right)Ce^{i(px-Et)/\hbar} = \left(\frac{ip}{\hbar}\right)\Psi(x,t) \tag{10}$$

$$\frac{\partial^2}{\partial x^2}\Psi(x,t) = \frac{\partial}{\partial x}\left(\frac{ip}{\hbar}\right)\Psi(x,t) = \left(\frac{ip}{\hbar}\right)^2\Psi(x,t) = -\frac{p^2}{\hbar^2}\Psi(x,t) \tag{11}$$

$$\rightarrow -\hbar^2\frac{\partial^2}{\partial x^2}\Psi(x,t) = p^2\Psi(x,t) \tag{12}$$

Now we want to connect our results in Eqns. 8 and 12. Let's assume that our particle is traveling through free space, meaning that it has no potential energy and that E represents entirely kinetic energy. From classical physics we know that kinetic energy $KE = \frac{1}{2}mv^2$ and that momentum $p = mv$, where m is mass. Therefore:

$$E = \frac{1}{2}mv^2 = \frac{p^2}{2m} \tag{13}$$

$$\rightarrow p^2 = 2mE \tag{14}$$

And now we can put the pieces together using Eqns. 8 and 12:

$$-\hbar^2\frac{\partial^2}{\partial x^2}\Psi(x,t) = 2mE\Psi(x,t) \tag{15}$$

$$\rightarrow -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\Psi(x,t) = E\Psi(x,t) = i\hbar\frac{\partial}{\partial t}\Psi(x,t) \tag{16}$$

This is the one-dimensional Schrödinger equation for a free particle where all energy is kinetic energy.

Note something familiar here from our work with the classical wave equation: everything on the left-hand side of Eqn. 16 is a function of x while everything on the right-hand side is a function of t. This is a differential equation where the two independent variables have been separated using the energy E as a separation constant, just like we did in the classical wave equation to find standing waves. It might be nice to look for solutions to these equations that will factor into x and t terms!

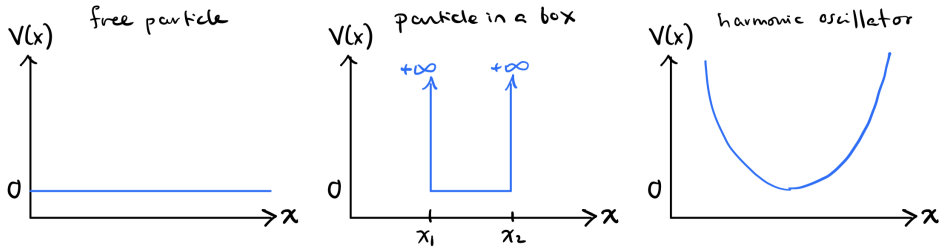
3 The 1D Schrödinger Equation

We have not quite reached the Schrödinger equation in its most general form. In particular Eqn. 16 is only valid for a particle in free space. We want to write down a more general expression that captures when the particle is exploring a potential energy landscape described with spatial dependence given by $V(x)$. We won't derive this expression, you will have to trust that we can simply add a $V(x)$ potential energy term to arrive at our final formulation of the **1D time-dependent Schrödinger equation (TDSE)**:

$$\boxed{\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}+V(x)\right]\Psi(x,t)=i\hbar\frac{\partial}{\partial t}\Psi(x,t)} \tag{17}$$

All valid 1D wavefunctions obey the differential equation in Eqn. 17. **However**, it's very important to note that we have intentionally not equated Eqn. 17 with $E\Psi(x,t)$. This will not be true in general, only for very special "stationary state" (quantum standing wave) solutions that factor neatly into spatial and temporal components which let us separate the 1D-SE and deal with its tidy x and t halves separately.

The general forms and time-dependence of the solutions to the 1D-SE may be very complicated, depending on the form of $V(x)$. What might $V(x)$ look like? Over the coming lectures, we will examine the behavior of particles in simple potentials $V(x)$, including the free particle (e.g. an electron in free space), the particle-in-a-box (e.g. an electron trapped in a π bond or a quantum dot), and the harmonic oscillator (e.g. a molecular vibration).



Our approach to solve Eqn. 17 will be to first search only for the stationary state solutions. We will then be able to use these stationary states as a convenient "basis" from which to construct general solutions – much like how we can build chords from combinations of standing wave guitar-string solutions for the classical wave equation.

So let's begin our search for these stationary states, which will allow us to break up the Schrödinger equation into two parts, and derive the *time-independent SE*. We'll assume that these

special solutions $\Psi(x,t)$ take the form of standing waves that are separable in x and t:

$$\Psi(x,t) = \psi(x) \cdot \phi(t) \tag{18}$$

Plugging this guess into the TDSE in Eqn. 17 we find:

$$\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)\right]\psi(x)\phi(t) = i\hbar\frac{\partial}{\partial t}\psi(x)\phi(t) \tag{19}$$

$$\rightarrow \quad \frac{1}{\psi(x)}\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi(x) + V(x)\psi(x)\right] = \frac{1}{\phi(t)}\left[i\hbar\frac{\partial\phi(t)}{\partial t}\right] \equiv E \tag{20}$$

In the last step, we again introduced the separation constant E. From here, we can re-express the Schrödinger equation as two separate differential equations:

$$\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)\right]\psi(x) = E\psi(x) \tag{21}$$

$$i\hbar\frac{\partial}{\partial t}\phi(t) = E\phi(t) \tag{22}$$

Eqn. 21 is the *time-independent Schrödinger equation*, which depends only on spatial coordinates. Solving this differential equation will give us the spatial envelopes of our quantum standing waves.

We will also often see the time-independent Schrödinger equation written in an alternative, compact form:

$$\hat{H}\psi(x) = E\psi(x) \tag{23}$$

where $\hat{H}$ is the *Hamiltonian operator*:

$$\hat{H} \equiv \frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x) \tag{24}$$

We can think of applying the $\hat{H}$ operator to our standing wave wavefunction in order to pull out its associated energy E. The $\hat{H}$ operator is composed of two terms. The first term, $\frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2}$, represents kinetic energy, while $V(x)$ represents potential energy.

It might seem like solving Eqns. 21 and 22 to find only the separable standing wave solutions would lead us to miss out on all kinds of possible solutions. But as we discussed for the classical wave equation, we will find that we can construct all possible valid solutions using linear combinations of our *basis set* of stationary state wavefunctions.

Solving the *time-dependent* part of the Schrödinger equation in Eqn. 22 will give us the temporal part of the wavefunction $\phi(t)$. This will prove to be the easy part. Solving the *time-independent* part of the Schrödinger equation in 21 for the spatial part of the wavefunction, $\psi(x)$, will typically be more challenging, depending on the form of $V(x)$.

4 Solving the Time-Dependent Part of the Schrödinger Equation

Let's go ahead and solve the differential equation in Eqn. 22 for the time-dependence of our stationary state wavefunctions. This is very straightforward, and we will only have to do it once.

We need only slightly rearrange this equation

$$\frac{d\phi(t)}{dt} = -\frac{iE}{\hbar}\phi(t) \tag{25}$$

to recognize that its solution is a function whose first derivative with respect to time is proportional to itself. And we should be familiar enough with this situation that we can write down the answer right away:

$$\phi(t) = Ce^{-iEt/\hbar} \tag{26}$$

And we therefore find that we can write the total stationary state wavefunction as:

$$\Psi(x,t) = \psi(x)\phi(t) = \psi(x)e^{-iEt/\hbar} \tag{27}$$

This is a general result for the time-dependence of standing wave solutions to the Schrödinger equation. Our standing wave solutions are so convenient precisely because their time dependence is so simple. The allowed values of energy E are yet to be determined. It will turn out that these fall out of solving the spatial part of the Schrödinger equation for $\psi(x)$.

Practice Problem: We will learn that $|\Psi(x,t)|^2 = \Psi^*(x,t) \cdot \Psi(x,t)$ represents the probability density for where we expect to find a quantum particle along the x axis at time t. What is the time-dependence of this quantity for the stationary state wavefunction given in Eqn. 27?

5 Solving the Time-Independent Schrödinger Equation

Our separable $\Psi(x,t) = \psi(x)\phi(t)$ wavefunctions can be thought of as quantum standing waves. We have now seen that standing waves have a very simple oscillatory time dependence, which leads to a spatial probability distribution that does not change with time. The critical feature of these standing waves is that they have well-defined energy E.

We will find the spatial patterns of these quantum standing waves by solving the time-independent Schrödinger equation. The next several lectures will involve solving this equation for various potentials $V(x)$. Let's examine it once again:

$$\hat{H}\psi(x) = \left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)\right]\psi(x) = E\psi(x) \tag{28}$$

- $\hat{H}$ is the Hamiltonian operator. This is the energy operator. When we apply it to a wavefunction $\psi(x)$, it spits out the expected energy of the system. The Hamiltonian consists of kinetic energy and potential energy components. While the KE term will always take a similar form, the potential energy $V(x)$ depends on the specific problem at hand.

- $\psi(x)$, as we already know, is the spatial part of the wavefunction. The valid solutions for $\psi(x)$ are functions that, when operated on by $\hat{H}$, produce themselves again, multiplied by a constant E. E is exactly the energy of $\psi(x)$, and goes on to determine the rate with which the temporal part of the wavefunction, $\phi(t)$, oscillates, as seen in Eqn. 27.

- When we solve the time-independent Schrödinger equation, we will retrieve an infinite collection of spatial solutions $\psi_1(x), \psi_2(x), \ldots \psi_n(x), \ldots$ just like we saw for the standing waves of a guitar string. These solutions will have corresponding energies $E_1, E_2, \ldots E_n, \ldots$ We will therefore be able to write down a series of stationary state wavefunctions:

$$\Psi_n(x,t) = \psi_n(x)\, e^{-iE_n t/\hbar} \tag{29}$$

- We can build *any* general solution to the original TSDE in Eqn. 17 by making linear combinations (or "chords") of stationary states:

$$\Phi(x,t) = \sum_{n=1}^{\infty} c_n\, \psi_n(x)\, e^{-iE_n t/\hbar} \tag{30}$$

  Any valid solution can be expressed this way, provided you find the correct coefficients c_n.

- Note that there is some subtlety here: If we have a non-stationary wavefunction $\Phi(x,t)$ that we express as a linear combination of stationary states, it will always be a solution to the time-dependent Schrödinger equation in Eqn. 17. However, $\Phi(x,t)$ will not satisfy the time-independent and time-dependent Schrödinger equations separately, as written in Eqns. 21 and 22. This is the distinction between being a general solution to the Schrödinger equation versus a stationary state.

Note that we have assumed here that the potential landscape $V(x)$ is purely a function of x and does not vary with time. In fact, it is this assumption that allows us to separate the time-dependent and time-independent parts of the Schrödinger equation. We will hold fast to this assumption throughout this course, though there are entire fields of research devoted to solving the Schrödinger equation for time-varying potentials.

The time-independent Schrödinger equation in Eqn. 28 is the basis of all quantum chemistry calculations of the structures and energies of atoms, molecules, and materials. It's not always easy to solve, especially when many electrons are involved. There is a huge field of active research striving to come up with more accurate and efficient computational methods to solve this equation when the Hamiltonian has a complicated form.

Practice Problem: We have learned that if $\psi_n(x)$ is a stationary state (e.g. a solution to the time-independent Schrödinger equation), then its full time-dependent form is:

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

1. Show that if $\psi_1(x)$ and $\psi_2(x)$ are both stationary states, then the state

$$\Phi(x,t) = c_1\, \psi_1(x)\, e^{-iE_1 t/\hbar} + c_2\, \psi_2(x)\, e^{-iE_2 t/\hbar}$$

   satisfies the full time-*dependent* Schrödinger equation ($\hat{H}\Phi = i\hbar\frac{\partial}{\partial t}\Phi$).

2. Does $\Phi(x,t)$ satisfy the time-*independent* Schrödinger equation ($\hat{H}\Phi = E\Phi$)? Show why or why not.