Chapter 13

The Schrödinger Equation

13.1 Where we are so far

We have focused primarily on electron spin so far because it's a simple quantum system (there are only two basis states!), and yet it still shows much of the peculiar nature of reality on the quantum level. In particular, we've seen the following things in the theory of quantum mechanics:

- A "system" (e.g. the angular momentum vector of an electron) may be an an *indefinite* state, also sometimes called a "mixture" of states, where an observable doesn't have a set value. Rather, the state of the system is such that if the observable were measured, there is a probability of different values being observed. The mathematical theory represents this by allowing states to be sums of coefficients times orthogonal basis states. For example, with angular momentum of a spin-1/2 particle such as an electron, the basis states are $|{+z}\rangle$ and $|{-z}\rangle$.
- Observables may take on *quantized* values. For example, every time you measure the z component of angular momentum of an electron, you get either $+\hbar/2$ or $-\hbar/2$. This is in sharp contrast to what you'd see in classical physics.
- What propagates in quantum mechanics is *amplitudes*. For example, if an electron is in state $|\psi\rangle$, the amplitude to measure it to have z angular momentum $+\hbar/2$ is $\langle{+z}\,|\,\psi\rangle$. The *probability*, which is what we can really find in experiments, is the absolute square of the amplitude; in this example, that would be $|\langle{+z}\,|\,\psi\rangle|^2$.
- Different observables may be *orthogonal* (the second use of this term). If they are, then a system can not be in a definite state for those two observables at

the same time. The projections of angular momentum along different axes are orthogonal; position and momentum along the same direction are orthogonal.

- Observables in quantum mechanics are paired with *operators*. A quantum mechanical operator operates on a quantum state (represented by a ket vector), and the result of that operation is another (non-normalized) quantum states (i.e. another ket vector). For example, if we call the z component of angular momentum spin-z or just s_z, the operator that goes with it is $\hat{S}_z$, the spin-z operator. Operators are quite abstract, and form a mathematical part of the theory that is useful, but is difficult to interpret and associate directly with something that you could observe.

- A state that is a definite state for a given observable is an *eigenstate* of that operator. (We would also say that the ket vector that represents that state is an *eigenvector* of the operator; if we're representing operators as matrices, then the column vector that represents the state is an *eigenvector* of the operator.) An operator working on one of its eigenstate returns a constant times the same state. That constant is called the *eigenvalue* associated with the eigenstate. If this operator corresponds to an observable, that eigenvalue must be a real number, and corresponds to the physical measurement you'd make of that observable. For example:

  $$\hat{S}_z \left|+z\right\rangle \;=\; \frac{\hbar}{2} \left|+z\right\rangle .$$

  This equation is the *eigenvalue equation*, in this case specifically for the z-spin operator and the $|+z\rangle$ state. The state $|+z\rangle$ is a state of definite z-spin, so it is an eigenstate of the z-spin operator $\hat{S}_z$. The eigenvalue equation for this state and this operator includes the constant $\hbar/2$, which is the actual value of the z component of spin angular momentum that an electron in state $|+z\rangle$ has.

- You can find the *expectation value* for a system in state $|\psi\rangle$ for a given observable by sandwiching the observable's operator between $\langle\psi|$ and $|\psi\rangle$. For example, the expectation value for z-spin for a given electron is $\left\langle \psi \,\middle|\, \hat{S}_z \,\middle|\, \psi \right\rangle$. The expectation value is the *average* value you'd get if you measured the observable for that state. That is, if you took a large number of systems in that state and measured the observable for all of those systems, you'd get different results, with probabilities for each result predicted by the mathematics of quantum mechanics. The average of all those results would be the expectation values.

Although the eigenvalue equation is fairly abstract, it's a very important part of the mathematical theory of quantum mechanics. The only direct connection it has to what we might observe in the lab is that it extracts (in the form of the eigenvalue) the measured quantity for the observable that you'd get for a given eigenstate (i.e.

definite state) of that observable's operator. However, the operator itself doesn't represent any particular *physical* operation you might perform in the lab.

From a broader point of view, the eigenvalue equation is the equation you can use to *figure out* what states are possible definite states for a given operator, and therefore what values you might measure for the observable associated with that operator.

13.2 Stating the Equation

As was briefly mentioned in Section 8.5, the energy operator is an operator so important to quantum mechanics that it gets its own proper name, the Hamiltonian, and the eigenvalue equation for it also gets its own name, the Schrödinger equation. It is this equation that allows us to figure out the energy states of a system, and it could be argued that energy states are the most important states in quantum mechanics. It is energy levels in atoms that provides all of the structure that gives us the Periodic Table of the Elements, and it is transitions between those energy levels that we observe in a number of both terrestrial and astrophysical contexts.

At the most base level, the Schrödinger equation is just the energy operator eigenvalue equation:

$$\hat{H}\,|\psi\rangle \;=\; E\;|\psi\rangle$$

$\hat{H}$ is the Hamiltonian; it's the operator that corresponds to energy as an observable. Solutions $|\psi\rangle$ to this equation are the eigenstates of energy. The value E that goes with a given solution $|\psi\rangle$ is the energy associated with that state. Technically, this equation is called the *Time-Independent Schrödinger Equation.* (There is also a full Schrödinger equation that describes how quantum states evolve in time.)

A full investigation of the Hamiltonian requires differential calculus, so we won't fully present it here. However, you can break the Hamiltonian into two parts. In doing so, we're going to go to a *wave function* representation of the state vector $|\psi\rangle$. Whereas we have used column vectors to represent spin states, it is more traditional (and more useful) to represent energy states as functions of position $\psi(x, y, z)$. As with a regular function, $\psi(x, y, z)$ is just something into which you can plug a position (i.e. values of x, y, and z) and get a number— although in this case that number can be a complex number. Dividing the Hamiltonian into two parts and writing the state as a wave function yields this form of the Schrödinger equation:

$$\hat{K}\psi(x,y,z) \;+\; V(x,y,z)\psi(x,y,z) \;=\; E\,\psi(x,y,z)$$

The Hamiltonian here has been divided into the kinetic energy operator $\hat{K}$, and the potential energy $V(x, y, z)$. Note that the action of the potential energy operator is just multiplying the wave function by the potential energy! The aforementioned differential calculus is buried inside $\hat{K}$. In fact, there isn't a *single* Schrödinger equation. Rather, there's a different one for each form of the potential $V(x, y, z)$. This also means that the solutions $\psi(x, y, z)$ will be different for each potential.

Although the full time-independent Schrödinger equation is in fact a function in the full 3-D space that we live in, for much of what we do below we will simplify it and consider only one dimensional systems. This makes dealing with it conceptually simple, but does not obscure any of the essential physical results. Such systems can in fact be realistic. For example, if you consider a mass moving on a spring attached to a wall, that is essentially a one-dimensional system, as the mass moves only forwards and backwards along the direction the spring is oriented.

13.3 Free Particles & the de Broglie Wavelength

A particle is called a "free particle" if its potential is constant. That is, there are no potential energy wells or barriers anywhere. It's simplest to choose that constant potential energy to be zero, as that reduces the Schrödinger equation to:

$$\hat{K}\psi(x) \;=\; E\,\psi(x)$$

(in the one-dimensional case). Solutions to this equation are called "plane-wave" solutions. They are states with definite momentum $p = E^2/2m$ (which is exactly what you'd expect if you compare momentum and kinetic energy in classical physics). However, their position is completely undetermined; there is equal probability for *any* x, which is what you'd expect for a state of definite momentum given the Heisenberg Uncertainty Principle. The functional form of $\psi(x)$ is just a standard wave:

$$\psi(x) \;=\; A\,\cos(2\pi\, x/\lambda) \;\pm\; iA\,\sin(2\pi\, x/\lambda)$$

where A is a constant (a complex number) that normalizes the wave. The ± depends on whether the wave is moving to the right (i.e. momentum is in the $+x$ direction) or to the left (i.e. momentum is in the $-x$ direction). The normalization condition will only put a constraint on the absolute square of A, meaning that there will be many complex numbers that satisfy it. As such, there isn't one single solution to this equation; however, all of the solutions do give the same predictions for *measurable* things such as the probability of finding the electron at a given spot. The value λ that shows up in these equations is the *wavelength*; that is it's the range of x over which it takes the sine or the cosine to go through one complete cycle. Note that although $\psi(x)$ varies with space, the probability of finding x at any given position, $|\langle x\,|\,\psi\rangle|^2$, does not! See Section 13.7 for more details about this.

In this case, the energy levels are *not* quantized. E can be anything in the equation above. A different energy E does correspond to a different wavelength in the plane wave represented by ψ. In these solutions, the energy E of the particle is related to the wavelength λ of the wave function by:

$$E = \frac{h^2}{2\,m\,\lambda^2}$$

It's more traditional to express this wavelength, called the *de Broglie wavelength*, in terms of the momentum of the particle:

$$\lambda = \frac{h}{p}$$

You can get this equation directly from the previous equation by using the relationship $E = p^2/2m$, that results from the combination of kinetic energy $E = \frac{1}{2}mv^2$ and momentum $p = mv$. The constant h here is a version of Plank's Constant, related to $\hbar$ by $h = 2\pi\,\hbar$.

For example, what is the de Broglie wavelength of an electron moving at 1×10^6 m/s (a "typical" speed for an atomic electron)? We would plug the right numbers into this equation:

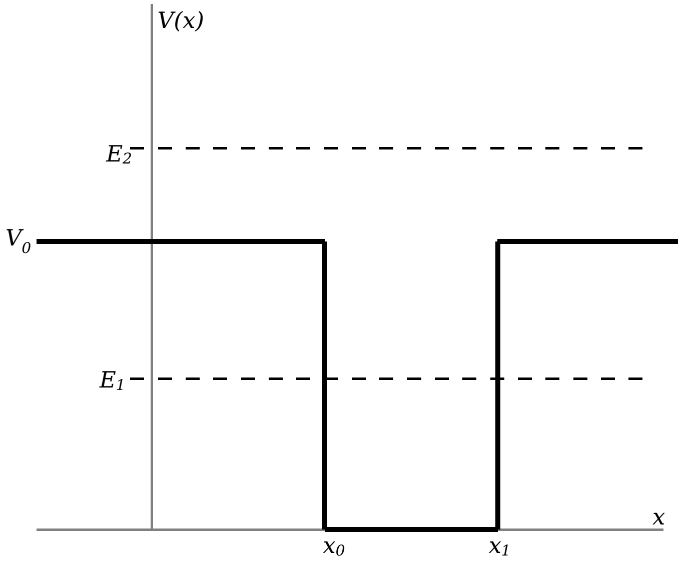
$$\begin{aligned} \lambda &= \frac{h}{p} = \frac{h}{mv} \\ &= \frac{6.626\times10^{-34}\,\mathrm{kg\,m^2\,s^{-1}}}{(9.109\times10^{-31}\,\mathrm{kg})(1\times10^{6}\,\mathrm{m\,s^{-1}})} \\ &= 7\times10^{-10}\,\mathrm{m} = 0.7\,\mathrm{nm} \end{aligned}$$

For comparison, this is about 1/1000 the wavelength of visible red light.

Many of the physical effects peculiar to quantum mechanics show up as wave interference between different components of a wave function $\psi(x)$. All waves, including those that derive from classical physics (such as waves on a string, sound waves, or electromagnetic (i.e. light) waves), show interference effects. The fact that the wave function, this abstract mathematical object which is used to figure out things about the state of a particle, also shows interference effects is what we mean when we say that sometimes particles behave like waves. In general, the longer the wavelength of a wave (i.e. the larger λ is), the easier it is to see interference effects. The de Broglie wavelength indicates that wavelength is inversely proportional to momentum. For a non-relativistic particle (which is implied here, as the Schrödinger equation assumes non-relativistic particles), $p = mv$. Thus, for particles moving at a given velocity, the larger m is, the smaller λ is. This is why it is so difficult to observe quantum interference effects for larger objects; the effective wavelength, and thus the typical separations that you'd need to see those effects, becomes tiny.

13.4 Quantized Energy Levels in Bound Systems

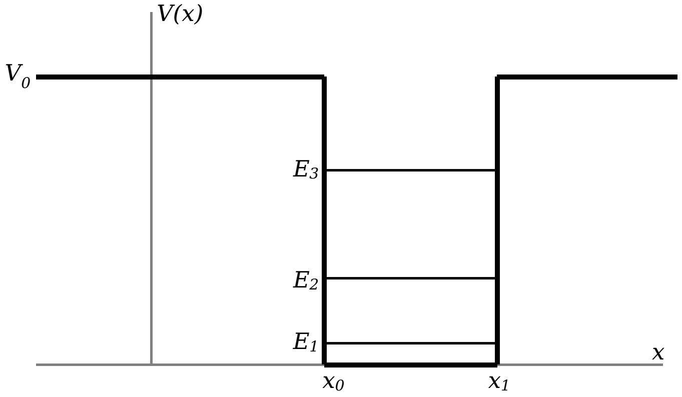
Whereas a free particle has a continuum of energy states available to it, if the particle is bound in a potential its available energy states are quantized. For a particle to be bound in a potential, the potential must limit a region of space that the particle could access classically. That is, if there is an energy well of some depth, the particle's energy over the bottom of the well must be *less* than the depth of the well:



A finite square potential well, with potential energy 0 chosen to be the bottom of the well. (Sometimes, one chooses the top of the well to be potential energy 0.) If a particle's total energy is less than the depth of the well V_0, as is the case for energy E_1 in the figure, that particle is bound in the well. If the particle's total energy is greater than the depth of the well, as is the case for energy E_2 in the figure, that particle is free, although its wave function is still influenced by the presence of the well.

In this example, a particle would be classically limited to the range of position $x_0 < x < x_1$ (see Section 2.2.2). Quantum mechanically, the particle is *most likely* to be found in that range, but it turns out there is a finite non-zero probability that the particle is found outside the classically allowed volume!

In this square well, there are a finite number of energy states available to a particle. Classically, a bound particle could have *any* energy $0 \leq E < V_0$. However, quantum mechanically, the particle *must* be in one of specific separated states. This is analogous to what we've seen with angular momentum of a spin-1/2 particle, where the projection of angular momentum along one axis must take on one of two specific separated values. For the square well, the allowed energy levels qualitatively looks something like:



In this example, there are only three allowed energy states, and the energies of those states are E_1, E_2, and E_3. Notice that the lowest allowed energy level is *not* 0! That is, you can't have a particle that's got no kinetic energy. This fits with the Heisenberg Uncertainty Principle. By binding the particle into the potential well, you've set constraints on the particle's position: it's most likely to be between x_0 and x_1. The particle isn't equally probable to be anywhere, so the uncertainty on the particle's position Δx is finite (and indeed will be something close to $x_1 - x_0$). As such, there must be a corresponding uncertainty in the particle's momentum Δp, so it's impossible for the particle to be in a zero-momentum state.

13.5 The Simple Harmonic Oscillator

One important potential energy function is the Simple Harmonic Oscillator, or SHO. This is the potential energy of a spring (so long as you don't stretch of squish the spring too much). It also turns out to be a decent approximation, at least for lower energy levels, for a number of quantum systems. One such system is the vibrational energy states of a Hydrogen molecule H_2. The form of this potential, in one dimension, is:

$$V(x) = \frac{1}{2} m \omega^2 x^2$$

Here, m is the mass of the particle moving in the potential. ω is the "natural frequency of oscillation" for the potential; for a *classical* spring, it would correspond to $2\pi/T$, where T is the period of oscillations. (Of course, for a classical spring, the system could also have any energy!)

The solution to the one dimensional Schrödinger equation for this potential gives the following energies for the energy eigenstates:

$$E_n \;=\; (n + \frac{1}{2})\,\hbar\,\omega$$

where n is an integer $0, 1, 2, \ldots$. As written, this potential is an infinitely high potential ($V(x)$ just keeps going up as x gets farther and farther from 0.) As such, there are an infinite number of allowed energy levels. Of course, as an approximation to a real physical system, usually the approximation will get worse and worse as x gets farther and farther from 0, which means that the solutions less and less of a good approximation to the real energy system for higher and higher energy levels.

13.6 The Hydrogen Atom

The potential that an electron in a Hydrogen atom experiences results from the electrostatic interaction between the electron (which is negatively charged) and the proton (which is positively charged). (A Hydrogen nucleus is composed of a single proton.) It is traditional (and convenient) to choose the zero level of the potential to be when the electron is extremely far away from the proton. This means that the potential energy gets more and more negative as the electron gets closer and closer to the proton. The form of this potential is:

$$V(r) \;=\; -\frac{1}{4\pi\epsilon_0}\,\frac{e^2}{r}$$

In this equation, ϵ_0 is a fundamental constant related to the effective strength of the electromagnetic force; it's value is $8.854 \times 10^{-12}\,\mathrm{C}^2\,\mathrm{m}^{-1}\,\mathrm{J}$. The letter e indicates the elementary charge; it is the charge on the proton, and the absolute value of the charge on the electron. It's value is 1.602×10^{-19} C, where C is "Coulombs", the SI unit of charge. Finally, r indicates the distance between the electron and the proton. If we consider the proton to be at the origin, then $r = \sqrt{x^2 + y^2 + z^2}$, with (x, y, z) indicating the position of the electron. The Schrödinger equation for an electron in a Hydrogen atom is then:

$$\hat{K}\psi(\vec{r}) \;-\; \frac{1}{4\pi\epsilon_0}\,\frac{e^2}{r}\,\psi(\vec{r}) \;=\; E\,\psi(\vec{r})$$

Here, we've written $\psi(\vec{r})$ as a shorthand for $\psi(x, y, z)$; the vector form of r, $\vec{r}$, indicates that the wave function depends on the electron's displacement from the origin. In fact, it's more common and more practical to express the wave function in terms of spherical coordinates $(r\,\theta, \phi)$, where r is the distance from the origin, θ is the angle off of the z axis, and ϕ is the angle off of the x axis in a projection on to the x-y

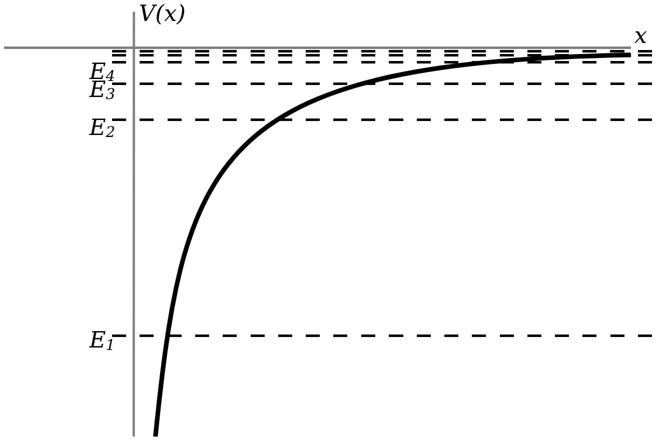
plane. (Even though the *potential* is spherically symmetric, in that it only depends on the distance from the origin, it turns out that the wave function solution is *not* always spherically symmetric. The reason for this is angular momentum, and that will be discussed in the next section.)

As with the other potentials discussed above, the allowed energy levels are quantized. In the Hydrogen atom, that energy level is specified by a *principle quantum number n*. The energy levels in a Hydrogen atom are:

$$E_n = \frac{-13.6\,\mathrm{eV}}{n^2}$$

The ground state of Hydrogen has an energy of −13.6 eV. That is, if you want to tear the electron off of the Hydrogen atom (a process known as *ionization*), you need to somehow provide at least 13.6 eV of energy in order to give the electron enough energy to make it out to extremely large distances away from the proton.

The figure below slows the Hydrogen atom potential and the first few energy levels. Higher and higher energy levels are less tightly bound (it takes less energy to ionize the atom, freeing the electron). They also get closer and closer together.



In fact, there are *three* quantum numbers associated with the solution to the Hydrogen atom. In addition to the principle quantum number n, there is also the total *orbital* angular momentum quantum number l, and the orbital z-angular momentum quantum number m. You could notate the energy eigenstates in a Hydrogen atom, corresponding to a state that the electron could actually be in, by $|n, l, m\rangle$. The ground state for a Hydrogen atom, in this notation, would be $|1, 0, 0\rangle$. For actual electrons, there's a fourth quantum number you have to specify: s, the z-spin of the electron. For every state n, l, m in a Hydrogen atom, there are in fact *two* different electron states, one where the electron has z-spin $+\hbar/2$, one where the electron has z-spin $-\hbar/2$. We'll call this quantum number s, and it will have either the value $+1/2$ or $-1/2$.

In Hydrogen, to very good approximation the energy of an eigenstate $|n, l, m\rangle$ only depends on the principal quantum number n, regardless of l and m. That is, the eigenvalue associated with states $|2, 1, 0\rangle$ and $|2, 0, 0\rangle$ are exactly the same (and are equal to $E = (-13.6\text{eV})/n^2 = -3.4\,\text{eV}$). In atoms with more than one electron, things get more complicated, and the energy of a given state may depend on the other quantum numbers.

13.7 Interpretation of the Wave Function $\psi(x)$

In general, it is best to view $\psi(x)$ the same way that you view $|\psi\rangle$. It's an abstract mathematical object that represents the state of the system. Quantum mechanics is then a theory, a mathematical model of reality that includes rules for manipulating $\psi(x)$ (or other representations of $|\psi\rangle$) in order to make predictions about the results of experiments, such as probabilities for observing particles in certain states, or expectation values for certain values.

It turns out that there is one particularly simple rule that can be applied to $\psi(x)$ in order to learn something about the state of the system. if $\psi(x)$ is a properly normalized single-particle wave function, then the construction $\psi^*(x)\psi(x)dx$ is the probability of finding that particle between position x and position $x + dx$, where dx is a small range of x. (By "small", we mean small enough that $\psi(x)$ does not appreciably change over the range.) As an example, consider the free particle wave function:

$$\psi(x) \;=\; A\;\left[\cos(2\pi\, x/\lambda) \;\pm\; i\sin(2\pi\, x/\lambda)\right]$$

If we want to find the probability for finding a particle at a given position, we multiply this function by its complex conjugate:

$$\begin{aligned}
\psi^*(x)\psi(x)dx &= A^*A\;\left[\cos\left(\tfrac{2\pi\, x}{\lambda}\right) \;\mp\; i\sin\left(\tfrac{2\pi\, x}{\lambda}\right)\right)\;\left(\cos\left(\tfrac{2\pi\, x}{\lambda}\right) \;\pm\; i\sin\left(\tfrac{2\pi\, x}{\lambda}\right)\right]\;dx \\
&= A^*A\;\Big[\cos^2\left(\tfrac{2\pi\, x}{\lambda}\right) \;+\; \sin^2\left(\tfrac{2\pi\, x}{\lambda}\right) \\
&\qquad\quad \pm i\cos\left(\tfrac{2\pi\, x}{\lambda}\right)\sin\left(\tfrac{2\pi\, x}{\lambda}\right) \;\mp\; i\cos\left(\tfrac{2\pi\, x}{\lambda}\right)\sin\left(\tfrac{2\pi\, x}{\lambda}\right)\Big]\;dx \\
&= A^*A\;\left[\cos^2\left(\tfrac{2\pi\, x}{\lambda}\right) \;+\; \sin^2\left(\tfrac{2\pi\, x}{\lambda}\right)\right]\;dx
\end{aligned}$$

To simplify this further, we can use the trigonometric identity $\sin^2\phi + \cos^2\phi = 1$ (this applies for all ϕ). Thus, we are left with:

$$\psi^*(x)\psi(x)dx \;=\; |A|^2\;dx$$

That is, the probability of finding a free particle at *any* x within a given range dx is always the same. This corresponds to an infinite uncertainty in position x, which is what we need given that this state has a definite momentum $p = h/\lambda$.

The construction $\psi^*(x)\psi(x)dx$ works for *any* one-dimensional wave function for calculating the probability of finding the particle at a given position. Using the three dimensional version of this construction on the solutions to the Hydrogen atom is what gives us the "electron cloud" diagrams you may have seen for electron orbitals. More about that in the next chapter.