

## Notes on wavefunctions IV: the Schrödinger equation in a potential and energy eigenstates.

We have now seen that the wavefunction for a free electron changes with time according to the Schrödinger Equation

$$i\hbar \frac{d\psi}{dt} = -\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} \quad (1)$$

where we have written the previous equation in a somewhat more conventional form by defining  $\hbar$  (pronounced “h-bar”) to be  $h/(2\pi)$ .

The solutions to this equation include time-dependent pure waves that describe momentum eigenstates, and various other time-dependent wavefunctions that describe superpositions of momentum eigenstates. Because these general wavefunctions are superpositions of electrons with a range of possible velocities, they will all tend to spread out with time. So the position uncertainty always goes to infinity as  $t$  goes to infinity. Examples include wavepackets for traveling electrons which become more and more spread out, or highly localized wavefunctions (e.g. that we obtain after a measurement of position) that quickly spread out in all directions.<sup>1</sup>

In nature, it is clearly not true that all electron wavefunctions spread out more and more as time passes. If we have an electron in an atom, the electron stays in the atom unless disturbed by some outside influence. Similarly, for an electron in a metal, the wavefunction might spread out through the metal, but the electron will not escape without some outside influence. The physical difference in these situations from the case of free electrons is that electrons in an atom or in a metal have forces acting on them. Equivalently, the electrons have a potential energy  $U(x)$  that is different for different locations (this leads to forces  $F(x) = -U'(x)$ ). To learn how wavefunctions evolve in the presence of these forces or potentials, we need to understand how to modify the Schrödinger equation when they are present. As a specific example, we might keep in mind the case of a hydrogen atom, where the potential energy that an electron feels is the Coulomb potential from the proton:

$$U(x) = -\frac{ke^2}{|x|} . \quad (2)$$

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<sup>1</sup>A good way to develop intuition for these time-dependent wavefunctions is by playing with the PHET “quantum tunneling” simulation, choosing a constant potential.

## Momentum eigenstates in a constant potential.

To understand how the potential  $U(x)$  should come into the Schrödinger equation, let's start by thinking about the simple situation where we have an electron with a definite momentum  $p$  traveling a region where the potential energy is constant but non-zero. In this case, the total energy of the electron is now

$$E = \frac{p^2}{2m} + U .$$

Since the electron still has momentum  $p$ , it should still be described as a pure wave with wavelength  $h/p$ . But according to the relation between energy and frequency, we expect that the frequency should now be

$$f = \frac{E}{h} = \frac{1}{h} \left( \frac{p^2}{2m} + U \right) .$$

Thus, the momentum eigenstate wavefunctions in a region of constant potential energy should be

$$\psi_p(x, t) = e^{i \frac{2\pi}{h} (px - (\frac{p^2}{2m} + U)t)} . \quad (3)$$

which reduces to our previous result when  $U = 0$ .

## The Schrödinger equation with a potential

We now want to know how to change the Schrödinger equation so that all of these waves are solutions. Looking at (1) above, we find that the left side now brings down a factor of  $p^2/(2m) + U$ , while the right side still only gives  $p^2/(2m)$  times the original wavefunction. To make make the functions (3) solve the equation we need to add  $U$  times the wavefunction to the right hand side. This gives:

$$i\hbar \frac{d\psi}{dt} = -\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + U\psi \quad (4)$$

By this simple modification, we now have an equation that correctly gives the time dependence of momentum eigenstates in the region of constant potential. But because any state can be written as a superposition of momentum

eigenstates, this equation also predicts the evolution of general wavefunctions in a constant potential.

What if we have a potential that is not constant? Remarkably, this equation gives the correct time-dependence even when the potential is a function of  $x$ . Equation (4) is in fact the general Schrödinger equation for quantum mechanics in one dimension. It is the exact quantum mechanical analog of  $\vec{F} = m\vec{a}$ .

For three dimensions, the wavefunction can depend on  $x$ ,  $y$ , and  $z$ , so the equation includes  $y$  and  $z$  derivatives also:

$$i\hbar \frac{d\psi}{dt} = -\frac{\hbar^2}{2m} \left( \frac{d^2\psi}{dx^2} + \frac{d^2\psi}{dy^2} + \frac{d^2\psi}{dz^2} \right) + U\psi \quad (5)$$

## Wavefunctions in a potential

Now that we have the general Schrödinger equation, we can begin to investigate the physics of electrons in atoms, molecules, wires, and other situations, as long as we can figure out the potential energy function (or a good approximation to it). The potential energy function is an input; it determines what physical system we are trying to describe. The other input is the initial wavefunction  $\psi(x, t = 0)$ . From these, we can determine the wavefunction  $\psi(x, t)$  at any later time  $t$ .

For starters, we can let a computer do the work and investigate the behavior of wavefunctions for particles in various kinds of potentials (e.g. using the PHET “Quantum Tunneling and Wave Packets” simulation where we can select various potentials and initial wavefunctions). A very important class of potentials is one where the potential energy goes to a constant  $U_\infty$  at infinity, and is less than this value in some localized region. This is the case for the Coulomb potential (2) in a Hydrogen atom, or the potential for an electron in a wire (which is approximately constant in the wire and then some larger constant outside the wire, with  $U_{out} - U_{in}$  equal to the work function  $W$  that we discussed in the photoelectric effect). For potentials like this in classical physics, particles are either trapped by the potential if their total energy is less than  $U_\infty$ , or can escape the potential if their total energy is greater than  $U_\infty$ .

What happens in the quantum mechanical simulation? If we start with a wavepacket that overlaps the region of the potential well (i.e. where the potential is lower), we often find that part of the wavefunction becomes

“trapped” by the potential, while part of the wavefunction spreads out to infinity. The interpretation is that if we make a measurement of the electron’s position at some later time, there is some probability that the electron will be found in the potential well, but some probability that it will have escaped.

This is quite different from the classical story, where the electron either has enough energy to escape or it does not. How can it be that both outcomes are possible in quantum mechanics?

## Energy eigenstates

You may have already guessed that, like position and momentum, energy is a quantity that doesn’t always have a definite value in quantum mechanical systems. Just as for those other quantities, there are special states (the ENERGY EIGENSTATES) which have a definite energy, but general states are quantum superpositions of these energy eigenstates, so there is no definite energy before a measurement is made. The wavefunction we discussed in the previous section was presumably a superposition of states with energies less than  $U_\infty$  and states with energies greater than  $U_\infty$ ; in this way, the electron had some probability to escape the potential but also some probability of being trapped.

We have already understood how to recognize position eigenstates (their wavefunctions are localized to a single location) and momentum eigenstates (their wavefunctions are pure waves with a definite wavelength  $h/\lambda$ ). But what are the properties of an energy eigenstate? Here, we need to remember the connection between energy and frequency. According to this connection, we would expect that *a state with some definite energy  $E$  is described by a wavefunction that oscillates with frequency  $f = E/h$* . We already saw this for the case of a constant potential. Here, the wavefunction for state with energy  $E = p^2/(2m) + U$  was described by the wavefunction (3), whose time dependence is just

$$\psi(x, t) = \psi(x, t = 0)e^{-i\frac{2\pi}{h}Et} . \quad (6)$$

For that special case, the energy eigenstates are the same as the momentum eigenstates since  $E = p^2/(2m) + U$ . So we can say that any initial wavefunction that is a pure wave

$$\psi(x, t = 0) = e^{i\frac{2\pi}{h}px}$$

will oscillate with a definite frequency and thus describe an energy eigenstate.

What about when the potential depends on  $x$ ? In this case, a state with definite momentum will not be an energy eigenstate. Since  $E = p^2/(2m) + U(x)$ , and we know that there is no definite value for  $x$  for a momentum eigenstate, there will be no definite value for  $U(x)$  and thus for  $E$ . So the energy eigenstates will have wavefunctions with some other shape. To figure out what they look like, we need to go back to our Schrödinger equation and ask what shape for the initial wavefunction will lead to a simple oscillating time dependence as in (6). If we plug in

$$\psi(x, t) = \psi_E(x)e^{-i\frac{E}{\hbar}t} \quad (7)$$

to the Schrödinger equation (4), we find that this is a solution only if the initial wavefunction  $\psi_E(x)$  obeys the equation

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

This is known as the TIME INDEPENDENT SCHRÖDINGER EQUATION, and it is an equation that only involves space and not time. For any potential  $U(x)$ , it determines which initial wavefunction shape  $\psi_E(x)$  will have energy  $E$ .

In three dimensions, the correct equation is

$$-\frac{\hbar^2}{2m} \left( \frac{d^2\psi_E}{dx^2} + \frac{d^2\psi_E}{dy^2} + \frac{d^2\psi_E}{dz^2} \right) + U(x)\psi_E = E\psi_E .$$

## Discrete energies for bound states

We're now ready to learn one of the most important lessons in all of quantum mechanics. In fact, it is the property that puts the “quantum” in “quantum mechanics”: if we try to solve the time independent Schrödinger equation for an energy  $E$  that is less than  $U_\infty$  (corresponding to a particle that doesn't have enough energy to escape to infinity), normalizable solutions exist only for certain specific energies. If we try to solve the equation at some other value, we find that the solution is a wavefunction that can't be normalized, and therefore doesn't correspond to a physical state. The conclusion is that *bound particles can only exist at certain specific energies*. For example, if we solve the time-independent Schrödinger equation (the three-dimensional

version) for the Coulomb potential of a hydrogen atom, we find that the allowed solutions have energies  $E = -13.6eV/n^2$  for any integer  $n$ .

The number and energies of these solutions, and the corresponding wavefunctions, are different for different potentials. These bound state energies are important (as you can read in great detail in chapter 41 and 42 of Knight), since they determine many of the observable properties of a the system (e.g. the emission and absorption spectra for gases).

Note that the discreteness of energy values is only true for  $E < U_\infty$ . For  $E > U_\infty$ , any energy is allowed. In this case, the wavefunctions aren't strictly normalizable, but we can combine the eigenstates to form normalizable wavepackets as we did for the free electrons (with  $U = 0$ ).

## Energy eigenstates as stationary states

To conclude our brief discussion of energy eigenstates, let us point out one more crucial property. If we calculate the probability density for any energy eigenstate wavefunction of the form (7), we find that

$$P(x, t) = |\psi(x, t)|^2 = |\psi_E(x)e^{-i\frac{E}{\hbar}t}|^2 = |\psi_E(x)|^2 |e^{-i\frac{E}{\hbar}t}|^2 = |\psi_E(x)|^2 ,$$

since

$$|e^{-i\frac{E}{\hbar}t}|^2 = \cos^2(-i\frac{E}{\hbar}t) + \sin^2(-i\frac{E}{\hbar}t) = 1 .$$

Thus, *for an energy eigenstate, the probability density for an energy eigenstate is completely independent of time.* For this reason, energy eigenstates are also known as STATIONARY STATES; even though the real and imaginary parts of the wavefunction oscillate with frequency  $E/h$ , the magnitude squared is constant in time.

In contrast, if we consider a superposition of energy eigenstates, the probability density will generally change with time. Knowledge of the energy eigenstates actually gives us a direct way to determine the time-dependence of general wavefunctions without using the (time-dependent) Schrödinger equation. Like other types of eigenstates, energy eigenstates form a basis for the set of all possible states. This means that any wavefunction can be written as a combination of energy eigenstate wavefunctions. Thus, if we have some initial wavefunction  $\psi(x, t = 0)$ , we can write it as

$$\psi(x, t = 0) = \sum_n c_n \psi_{E_n}(x) .$$

for some complex numbers  $c_n$ .<sup>2</sup>

Then the wavefunction at any later time is determined to be

$$\psi(x, t) = \sum_n c_n \psi_{E_n}(x) e^{-i \frac{E_n}{\hbar} t},$$

since we know how the individual energy eigenstates evolve with time. The numbers  $c_n$  tell us how much of the eigenstate with energy  $E_n$  is in the quantum superposition, so as usual, the numbers  $|c_n|^2$  determine the probability that we will find the value  $E_n$  if we make a measurement of the energy. Since the  $|c_n|^2$ s do not change, these probabilities are constant in time: this is the quantum mechanical version of energy conservation. On the other hand, the probability density  $|\psi(x, t)|$  does change with time, unless only one of the  $c_n$ s is nonzero (which is the case of an energy eigenstate).

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<sup>2</sup>This formula holds when all of the energies are discrete, which occurs when  $U_\infty = \infty$ . If  $U_\infty$  is finite, there will also be a set of energy eigenstate wavefunctions for any  $E > U_\infty$ , and in this case, we need to represent this part of the superposition by an integral  $\int_{U_\infty}^{\infty} c(E) \psi_E(x) dE$ .