Unit 8: Energy of quantum particles

To summarize the last few section*s, in the quantum mechanics description of physics, the primary description of the state is the wave function, Ψ. For a particle moving in one dimension, the wave function is $\Psi(x, t)$. The wave function determines the **probability** of a measurement, which is given by the absolute square of the wave function. So far, we discussed how wave functions give the probability of measuring a particle at a given position and momentum.

In this section*, we consider how to compute the result of an energy measurement. We will find out that in many situations, the energy we can measure in a quantum system will only be one of several discrete amounts, or quanta. This is the origin of the name of quantum mechanics!

After this unit, you should be able to

- Check whether wave functions satisfy the time-independent Schrödinger equation.

- Explain how the Schrödinger equation is consistent with experimental observations of the relationship between wavelength, momentum, and energy for a free particle.

- For a particle in an infinite square well of length L, compute the allowed energies that could be measured.

- If the particle is in an energy eigenstate of the infinite square well with quantum number n, compute the probability of it being found between $x = a$ and $x = b$.

Energy of a free particle

- The energy of a free particle with wave function Ae^{ikx} is $\frac{\hbar^2 k^2}{2m}$

From the last section*, recall that if a particle has a definite momentum, then its wave function is given by

$$\Psi(x) = Ae^{ikx}. \tag{1}$$

If we measure the momentum of this particle, say by observing how it bends in a magnetic field, then with probability 1 the momentum will come out to $\hbar k$. We will write this as $p_k = \hbar k$, where the k subscript represents that the wave function of the particl is from Eqn 1.

What is the energy of a free particle with the wave function of Eqn 1? You may recall from classical mechanics that it is $\frac{1}{2}mv^2$. Since our formula is in terms of $p_k = mv = \hbar k$, we write the energy as

$$E_k = \frac{p_k^2}{2m} = \frac{\hbar^2 k^2}{2m}. \tag{2}$$

The momentum equation

To review the logic of the previous section*s, we know empirically that we describe the state of a particle using a wave function, and the wave function of a particle with momentum p is Ae^{ikx}, with $k = p/\hbar$. We find the possible values of momentum by expanding any wave function as a superposition of momentum eigenstates, and then reading the probabilities off the expansion.

If we want to know what energies can be measured, we need a way to find **energy eigenstates** when there is a potential energy. For that we will need to generalize our principle beyond just empirically measuring the wave function using diffraction. The principle of quantum mechanics is that you find eigenstates by performing an operation on the wave function, and if the wave function does not change other than a total factor, then the wave function is an eigenstate. This is the 'same' of eigenstate, from German.

For momentum, the operation is the derivative $-i\hbar\frac{\partial}{\partial x}$. Applying that to our momentum eigenstate, we get

$$-i\hbar\frac{\partial Ae^{ikx}}{\partial x} = \hbar k Ae^{ikx} = pAe^{ikx}. \tag{3}$$

So we see that we get back the original wave function with a constant factor of the momentum applied. Note that this equation means that it holds for **all** values of x; this is an equality of functions.

The Schrödinger equation: the energy operation

- The time-independent Schrödinger equation tells us which wave functions are energy eigenstates.

For this section* (and this course), we will just consider a wave function at a given time, which we will write $\Psi(x)$. Time propagation in quantum mechanics is a surprisingly advanced topic that you will learn about in your next class. For a particle of mass m in one dimension, the Schrödinger equation is

$$-\frac{\hbar^2}{2m}\frac{d^2\Psi(x)}{dx^2} + U(x)\Psi(x) = E\Psi(x). \tag{4}$$

In this equation, $U(x)$ is the external potential energy, and $-\frac{\hbar^2}{2m}\frac{d^2\Psi(x)}{dx^2}$ is our momentum operation squared, divided by $2m$. This is analogous to the energy being written as $p^2/2m + U$ in classical mechanics.

There are several important things to note about this equation:

- Only certain wave functions satisfy Eqn 4. These special wave functions are called **energy eigenstates**

- E is a number that gives the energy of the wave function.

- If a particle is in an energy eigenstate, any measurement of its energy will result in E. For many systems, only certain values of E have a wave function that satifies Eqn 4.

- Energy eigenstates are also called **stationary states**. Their probabilities don't change in time.

- For the wave function to be an energy eigenstate, it must be true for **all** values of x, for the same value of E. You don't get to change E for different values of x.

Example: free particle

Let's describe a free particle using the Schrödinger equation. In that case, the external potential is zero (that's what "free" means!), and the equation is:

$$-\frac{\hbar^2}{2m}\frac{d^2\Psi(x)}{dx^2} = E\Psi(x). \tag{5}$$

The most common solution method is to guess a wave function and check whether it satisfies Eqn 5. Let's guess $\Psi_k(x) = Ae^{ikx}$ as the wave function. Then

$$-\frac{\hbar^2}{2m}\frac{d^2 Ae^{ikx}}{dx^2} = -\frac{\hbar^2}{2m}(ik)^2 Ae^{ikx} = \frac{\hbar^2 k^2}{2m}\Psi_k(x). \tag{6}$$

So this wave function satisfies the Schrödinger equation if the energy $E = \frac{\hbar^2 k^2}{2m}$, and any wave function of this form is an energy eigenfunction. In this case, k can be any real number, so the energy can take on any positive value. In quantum mechanics, k is an example of a **quantum number**, which is a label for the energy eigenstates.

This makes some sense; we said earlier that a particle with wave function e^{ikx} has momentum $p = \hbar k$. For a free particle, all energy is kinetic energy, so we would expect the energy to be

$$\frac{1}{2}mv^2 = \frac{p^2}{2m} = \frac{\hbar^2 k^2}{2m}. \tag{7}$$

So the derivative term is associated with kinetic energy, which matches the $U(x)$ term that is associated with potential energy.

Example II: a non-energy eigenstate for a free particle

Now consider the wave function $\Psi(x) = ae^{ik_1 x} + be^{ik_2 x}$. Then

$$-\frac{\hbar^2}{2m}\frac{d^2 ae^{ik_1 x} + be^{ik_2 x}}{dx^2} = \frac{\hbar^2 k_1^2}{2m}ae^{ik_1 x} + \frac{\hbar^2 k_2^2}{2m}be^{ik_2 x}. \tag{8}$$

No matter what we do, we cannot get back a constant times Ψ on the right hand side, since $k_1 \neq k_2$. So this wave function is **not** an energy eigenstate. In fact, if we measure the energy of such a particle using a magnetic field, for example, then we will measure:

Energy	Probability
$\frac{\hbar^2 k_1^2}{2m}$	$\frac{a^2}{a^2+b^2}$
$\frac{\hbar^2 k_2^2}{2m}$	$\frac{b^2}{a^2+b^2}$

We can compute this because we have expanded Ψ in terms of energy eigenstates $e^{ik_1 x}$ and $e^{ik_2 x}$.

Quantized energy levels: infinite square well

Now we consider a case where U is not just zero. Imagine creating a well (a 1D box) in which the particle is allowed to move freely from $x = 0$ to $x = L$, but encounters an infinite potential barrier at either side. In this case,

$$U(x) = \begin{cases} 0 & \text{if } 0 < x < L \\ \infty & \text{otherwise} \end{cases} \tag{9}$$

Given this, let's look back at Eqn 4 to see what kind of wave function can satisfy the equality. The first thing we can notice is that since U is ∞ outside the box, the only way for the equality to be satisfied is for either $\Psi(x)$ to be zero, or have infinite energy. The more physically possible case is for the wave function to be zero outside the box. This makes some sense classically; if a particle is inside a box with infinitely hard walls, there is zero probability to find it outside the box.

Inside the box, $U = 0$, so the Schrödinger equation looks a lot like the free particle case. However, we have an additional constraint–the wave function goes to zero at the edges. This has to happen in order for the Schrödinger equation to be satisfied, since the potential energy is infinite there. A guess wave function that works is

$$\Psi(x) = \begin{cases} A \sin(\frac{n\pi x}{L}) & \text{if } 0 < x < L \\ 0 & \text{otherwise,} \end{cases} \tag{10}$$

where n is an integer.

We can find A by enforcing normalization:

$$\int_0^L A^2 \sin^2\left(\frac{n\pi x}{L}\right) dx = 1. \tag{11}$$

You can verify that if $A = \sqrt{\frac{2}{L}}$, then this integral is equal to 1. By plugging our guess Ψ into the Schrödinger equation, we can get the energy:

$$E_n = \frac{\hbar^2 n^2 \pi^2}{2mL^2} \tag{12}$$

Important things to note about this:

- Because of the boundary conditions (Ψ must be zero at 0 and L), only integer values of n are allowed.

- The more oscillations in the wave function, the higher the energy.

- Since only certain values of n are allowed, only certain values of the energy are allowed.

What it means to have only certain energies allowed

In the previous section*, we saw that sometimes a quantum system can only be observed to have certain values of the energy. Let's investigate what that means practically. Let's suppose that we have a quantum system (an atom) with two allowed energy levels, E_1 and E_2, with corresponding energy eigenstates Ψ_1 and Ψ_2. There may be more energy eigenstates but we will just consider those two for simplicity.

Imagine that the atom has wave function equal to the ground state (lowest energy state), Ψ_1. As we will find later, if the atom is not disturbed, it will remain in the ground state forever. Suppose now that we disturb the system by allowing a photon to come near it. There is a chance that the photon will interact with the atom. Let's consider the possibilities:

1. At the end of the process, a photon comes out with energy $\hbar\omega$ and the atom is left with energy E_1.

2. The photon is absorbed by the atom. No photon comes out and the atom is left with energy E_2.

While possibility 1 can always happen, possibility 2 can only happen if $E_2 - E_1 = \hbar\omega$. This is because energy is still conserved in quantum mechanics; so if we started with $E_1 + \hbar\omega$ energy, we must end with that much energy when everything is settled. Similarly, if the atom started in Ψ_2, then it might emit a photon with energy $\hbar\omega = E_2 - E_1$.

Atoms, liquids, solids, etc can only absorb photons with energy equal to the difference between their energy levels. This is why glass is transparent, why we can see through air and water. It is why rose-tinted glasses remove all colors but rose. Similarly, quantum systems can only emit photons with energy equal to a difference between their energy levels. This is what gives neon lights their particular color, and in general is what gives objects their color. The list of energies that a given quantum system can obtain is called the **spectrum**. In Latin, spectrum meant 'image' and indeed the spectrum of a quantum system determines what type of light it interacts with.

Application: quantum dot technology

At the time of this writing, new displays are emerging that use quantum dot technology to emit light of very pure frequencies. Here is some data that Samsung[1] published:
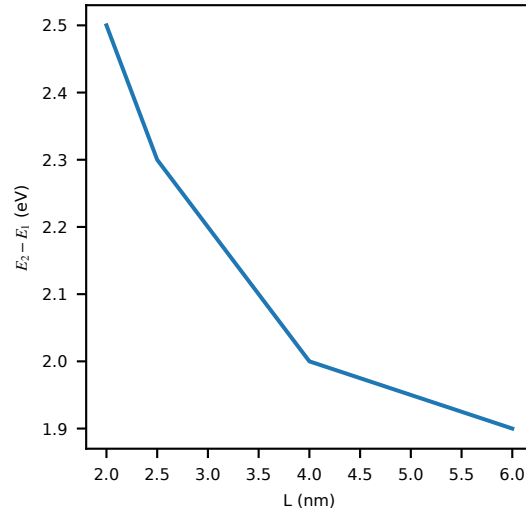
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[1]https://news.samsung.com/global/why-are-quantum-dot-displays-so-good

Figure 1: Photon energies emitted by a quantum dot versus the size. It is a reciprocal relationship, as we derived in Eqn 12

Size of the dot (nm)	Wavelength of light emitted (nm)	$E_2 - E_1$ (eV)[2]	Color
2	500	2.5	Blue
2.5	530	2.3	Green
3	570	2.2	Green-yellow
5	610	2.0	Orange
6	640	1.9	Red

Fig 1

shows this same data, where we can see that it matches our model from Eqn 12 pretty well, since we would predict that the energy difference between the lowest energy eigenstate and the next higher energy eigenstate is

$$E_2 - E_1 = \frac{\hbar^2 3\pi^2}{2mL^2}. \tag{13}$$

The fact that the energies are quantized means that the quantum dot *physically cannot* emit light which is not equal to an energy difference between energy eigenstates. This makes the light very highly peaked around a single wavelength, which allows these displays to be very beautiful.