QUANTUM MECHANICS

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Chapter 1

Introduction:

- ✓ **Why Do We Need Quantum Mechanics?**

Just over 100 years ago, in the 1890's, physics looked in pretty good shape. The beautiful mathematical development of Newton's mechanics, coupled with increasingly sophisticated technology, predicted the movements of the solar system to incredible accuracy, apart from a tiny discrepancy in the orbit of Mercury. It had been less than a hundred years since it was realized that an electric current could exert a force on a magnet, but that discovery had led to power stations, electric trains, and a network of telegraph wires across land and under the oceans. It had also been only a hundred years since it had been established that light was a wave, and only forty years since Maxwell's realization that the waves in a light signal were electric and magnetic fields, satisfying a wave equation he was able to derive purely by considering electric and magnetic field phenomena. In particular, he was able to predict the speed of light by measuring the electrostatic attractive forces between charges and the magnetic forces between currents.

At about the same time, in the 1860's, Maxwell and Boltzmann gave a brilliant account of the properties of gases by assuming that they were made up of weakly interacting molecules flying about in a container, bouncing off the sides, with a statistical distribution of energies so that the probability of a molecule having energy EE was proportional to $exp(-E/kT)$, kk being a universal constant known as Boltzmann's constant. Boltzmann generalized this result from a box of gas to any system. For example, a solid can be envisioned classically as a lattice of balls (the atoms) connected by springs, which can sustain oscillations in many ways, each such mode can be thought of as a simple harmonic oscillator, with reasonable approximations concerning the properties of the springs, etc. Boltzmann's work leads to the conclusion that each such mode of oscillation, or degree of freedom, would at temperature T have average energy kT, made up of $12kT$ potential energy, $12kT$ kinetic energy. Notice that this average energy is independent of the strength of the springs, or the masses! *All* modes of vibration, which will vibrate at very different rates, contain the same energy at the same temperature. This equal sharing is called *the Equipartition of Energy*. It is not difficult to check this for a one-dimensional classical harmonic oscillator, averaging the energy by integrating over all displacements and momenta (independently) with the weighting factor $exp(-E/kT)$, (which of course needs to be normalized). The result doesn't depend on the spring constant or the mass. Boltzmann's result gave an excellent account of the specific heats of a wide range of materials over a wide temperature range, but there *were* some exceptions, for example hydrogen gas at low temperatures, and even solids at low enough temperatures. Still, it was generally felt these problems could be handled within the existing framework, just as the slightly odd behavior of Mercury was likely caused by a small planet, named Vulcan, closer to the sun, and so very hard to observe.

✓ What was Wrong with Classical Mechanics?

Basically, classical statistical mechanics wasn't making sense...

Maxwell and Boltzmann evolved the equipartition theorem: a physical system can have many states (gas with particles having different velocities, or springs in different states of compression).

At nonzero temperature, energy will flow around in the system, it will constantly move from one state to another. So, what is the probability that at any instant it is in a particular state with energy E?

M&B proves it was proportional to $exp(-E/kT)$. This proportionality factor is also correct for any subsystem of the system: for example, a single molecule.

Notice this means if a system is a set of oscillators, different masses on different strength springs, for example, then in thermal equilibrium each oscillator has on average the same energy as all the others. For three-dimensional oscillators in thermal equilibrium, the average energy of each oscillator is $3kT$, where k is Boltzmann's constant.

✓ Black Body Radiation

Now put this together with Maxwell's discovery that light is an electromagnetic wave: inside a hot oven, Maxwell's equations can be solved yielding standing wave solutions, and the set of different wavelengths allowed standing waves amount to an infinite series of oscillators, with no upper limit on the frequencies on going far into the ultraviolet. Therefore, from the classical equipartition theorem, an oven at thermal equilibrium at a definite temperature should contain an infinite amount of energy—of order kT in each of an infinite number of modes—and if you let radiation out through a tiny hole in the side, you should see radiation of all frequencies.

This is not, of course, what is observed: as an oven is warmed, it emits infrared, then red, then yellow light, etc. This means that the higher frequency oscillators (blue, etc.) are in fact not excited at low temperatures: equipartition is not true.

Planck showed that the experimentally observed intensity/frequency curve was exactly reproduced if it was assumed that the radiation was quantized: light of frequency f could only be emitted in quanta—now photons—having energy hf, h being Planck's constant. This was the beginning of quantum mechanics.

✓ The Photoelectric Effect

Einstein showed the same quantization of electromagnetic radiation explained the photoelectric effect: a photon of energy hf knocks an electron out of a metal, it takes a certain work W to get it out, the rest of the photon energy goes to the kinetic energy of the electron, for the fastest electrons emitted (those that come right from the surface, so encountering no further resistance). Plotting the maximum electron kinetic energy as a function of incident light frequency confirms the hypothesis, giving the same value for h as that needed to explain radiation from an oven. (It had previously been assumed that more intense light would increase the kinetic energy—this turned out not to be the case.)

✓ The Bohr Atom

Bohr put together this quantization of light energy with Rutherford's discovery that the atom had a nucleus, with electrons somehow orbiting around it: for the hydrogen atom, light emitted when the atom is thermally excited has a particular pattern, the observed emitted wavelengths are given by

$$1\lambda = RH(14 - 1n2)$$

with $n = 3,4,5$.. RHRH is now called the Rydberg constant.) Bohr realized these were photons having energy equal to the energy difference between two allowed orbits of the electron circling the nucleus (the proton), $En - Em = hf$, leading to the conclusion that the allowed levels must be:

$$En = -hcRHn2$$

How could the quantum hf restricting allowed radiation energies also restrict the allowed electron orbits? Bohr realized there must be a connection— because h has the dimensions of angular momentum! What if the electron were only allowed to be in circular orbits of angular momentum nKh, with n an integer? Bohr did the math for orbits under an inverse square law and found that the observed spectra were in fact correctly accounted for by taking $K = 1/2\pi$.

But then he realized he did not even need the experimental results to find KK: quantum mechanics must agree with classical mechanics in the regime where we know experimentally that classical mechanics (including Maxwell's equations) is correct, that is, for systems of macroscopic size. Consider a negative charge orbiting around a fixed positive charge at a radius of 10 cm., the charges being such that the speed is of order meters per second (we don't want relativistic effects making things more complicated). Then from classical E&M, the charge will radiate at the orbital frequency. Now imagine this is a hydrogen atom, in a perfect vacuum, in a high state of excitation. It must be radiating at this same frequency. But Bohr's theory can't just be right for small orbits, so the radiation must satisfy $En - Em = hf$. The spacing between adjacent levels will vary slowly for these large orbits, so h times the orbital frequency must be the energy difference between adjacent levels. Now, that energy difference depends on the allowed angular momentum step between the adjacent levels: that is, on K. Reconciling these two expressions for the radiation frequency gives $K = 1/2\pi$.

This classical limit argument, then, predicts the Rydberg constant in terms of already known quantities:

$$RH = (1/4\pi\varepsilon 0)2 \cdot 2\pi 2me4ch3$$

- ✓ **What’s right about the Bohr atom?**
- It gives the Balmer series spectra.
- The first orbit size is close to the observed size of the atom: and remember there are no adjustable parameters, the classical limit argument determines the spectra and the size.
- ✓ **What’s wrong with the Bohr atom?**

No explanation for why angular momentum should be quantized. (This was solved by de Broglie a little later.)

Why don’t the circling electrons radiate, as predicted classically? Well, the fact that radiation is quantized means the classical picture of an accelerating charge smoothly emitting radiation cannot work if the energies involved are of order h times the frequencies involved.

The lowest state has nonzero angular momentum. This is a defect of the model, corrected in the truly quantum model (Schrödinger’s equation).

In an inverse square field, orbits are in general elliptical.

This was at first a puzzle: why should there be only circular orbits allowed? In fact, the model does allow elliptical orbits, and they do not show up in the Balmer series because, as proved by Sommerfeld, if the allowed elliptical orbits have the same allowed angular momenta as Bohr’s orbits, they have the same set of energies. This is a special property of the inverse square force.

✓ De Broglie Waves

The first explanation of why only certain angular momenta is allowed for the circling electron was given by de Broglie: just as photons act like particles (definite energy and momentum), but undoubtedly are wave like, being light, so particles like electrons perhaps have wave like properties. For photons, the relationship between wavelength and momentum is $p = h/\lambda$. Assuming this is also true of electrons, and that the allowed circular orbits are standing waves, Bohr's angular momentum quantization follows.

✓ The Nature of Matter

By the 1890's and early 1900's, most scientists believed in the existence of atoms. Not all—the distinguished German chemist Ostwald did not, for example. But nobody had a clear picture of even a hydrogen atom. The electron had just been discovered, and it was believed that the hydrogen atom had a single electron. It was suggested that maybe the electron went in circles around a central charge, but nobody believed that because Maxwell had established that accelerating charges radiate, so it was assumed that a circling electron would rapidly loose energy, spiral into the center, and the atom would collapse. Instead, it was thought, the hydrogen atom (which was of course electrically neutral) was a ball of positively charged jelly with an electron inside, which would oscillate when heated, and emit radiation. Rough calculations, based on the accepted size of the atom, suggested that the radiation would be in the visible range, but no-one could remotely reproduce the known spectrum of hydrogen.

The big breakthrough came in 1909, when Rutherford tried to map the distribution of positive charge in a heavy atom (gold) by scattering alpha particles from it. To his amazement, he found the positive charge was all concentrated in a tiny nucleus, with a radius of order one ten-thousandth that of the atom. This meant that after all the electrons must be going in planetary orbits, and the Maxwell's equations prediction of radiation did not apply, just as it did not always apply in blackbody radiation.

Chapter 2

2.1: The One-Dimensional Wave Equation

✓ **Learning Objectives**

- To introduce the wave equation including time and position dependence

In the most general sense, waves are particles or other media with wavelike properties and structure (presence of crests and troughs).

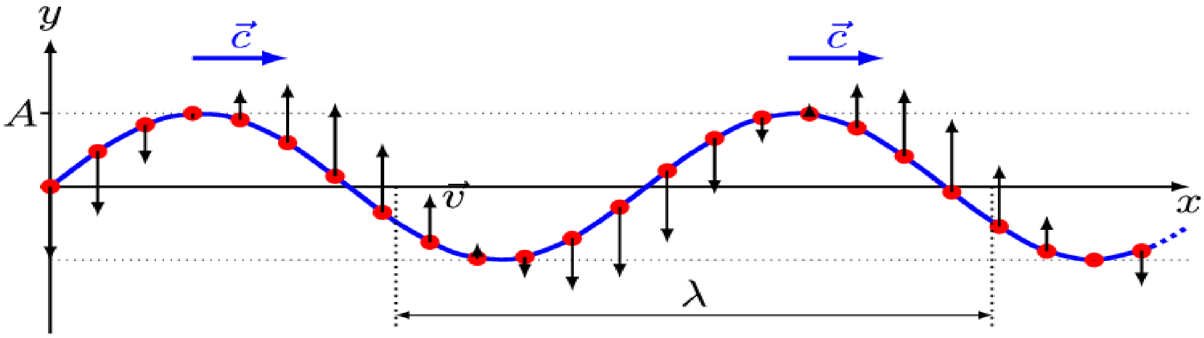


Figure 2.1.1: A simple translational (transverse) wave. (CC BY-SA 4.0 International; And 1mu via Wikimedia Commons)

The simplest wave is the (spatially) one-dimensional sine wave (Figure 2.1.1) with a varying amplitude AA described by the equation:

$$A(x,t) = A_o sin(kx - \omega t + \phi) \tag{2.1.1}$$

Where,

- Ao is the maximum amplitude of the wave, maximum distance from the highest point of the disturbance in the medium (the crest) to the equilibrium point during one wave cycle. In Figure 2.1.1, this is the maximum vertical distance between the baseline and the wave.
- x is the space coordinate
- t is the time coordinate
- k is the wavenumber
- ω is the angular frequency
- ϕ is the phase constant.

One can categorize "waves" into two different groups: *traveling waves* and *stationary waves*.

✓ Traveling Waves

Traveling waves, such as ocean waves or electromagnetic radiation, are waves that "move," meaning that they have a frequency and are propagated through time and space. Another way of describing this property of "wave movement" is in terms of energy transmission – a wave travels, or transmits energy, over a set distance. The most important kinds of traveling waves in everyday life are electromagnetic waves, sound waves, and perhaps water waves, depending on where you live. It is difficult to analyze waves spreading out in three dimensions, reflecting off objects, etc., so we begin with the simplest interesting examples of waves, those restricted to move along a line. Let's start with a rope, like a clothesline, stretched between two hooks. You take one end off the hook, holding the rope, and, keeping it stretched fairly tight, wave your hand up and back once. If you, do it fast enough, you'll see a single bump travel along the rope:

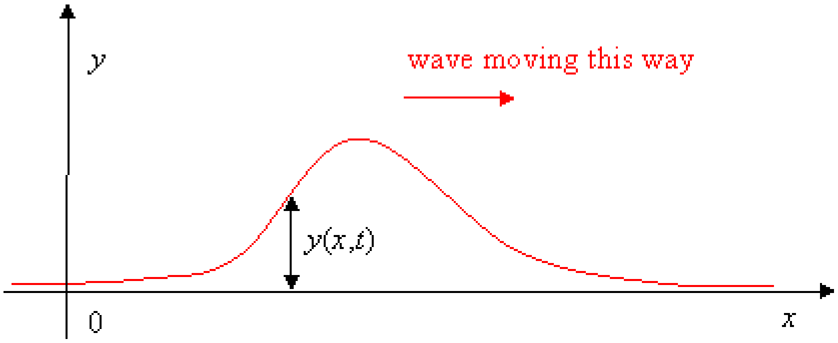


Figure 2.1.2: A one-dimensional traveling wave at one instance of time t.

This is the simplest example of a *traveling wave*. You can make waves of different shapes by moving your hand up and down in different patterns, for example an upward bump followed by a dip, or two bumps. You'll find that the traveling wave *keeps the same shape* as it moves down the rope. Taking the rope to be stretched tightly enough that we can take it to be horizontal, we'll use its rest position as our *x*-axis (Figure 2.1.1). The y-axis is taken vertically upwards, and we only wave the rope in an up-and-down way, so actually $y(x,t)$ will be how far from the rope is from its rest position at x at time t: that is, Figure 2.1.2 shows where the rope is at a single time t.

We can now express the observation that the wave “keeps the same shape” more precisely. Taking for convenience time t=0 to be the moment when the peak of the wave passes x=0, we graph here the rope’s position at $t = 0$ and some later times t as a movie (Figure 2.1.3). Denoting the first function by $y(x,0) = f(x)$, then the second $y(x,t) = f(x - vt)$: it is the same function with the “same shape,” but just moved over by vt, where v is the velocity of the wave.

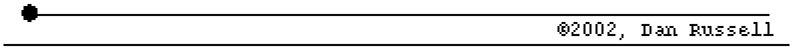


Figure 2.1.3: A one-dimensional traveling wave at as a function of time. Traveling waves propagate energy from one spot to another with a fixed velocity vv. (CC BY-NC-ND; Daniel A. Russell).

To summarize: on sending a traveling wave down a rope by jerking the end up and down, from observation the wave travels at constant speed and keeps its shape, so the displacement *y* of the rope at any horizontal position at x at time t has the form

$$y(x,t) = f(x - vt) \tag{2.1.2}$$

We are neglecting frictional effects—in a real rope, the bump gradually gets smaller as it moves along.

✓ Standing Waves

In contrast to traveling waves, *standing waves,* or stationary waves, remain in a constant position with crests and troughs in fixed intervals. One way of producing a variety of standing waves is by plucking a melody on a set of guitar or violin strings. When placing one’s finger on a part of the string and then plucking it with another, one has created a standing wave. The solutions to this problem involve the string oscillating in a sine-wave pattern (Figure 2.1.4) with no vibration at the ends. There is also no vibration at a series of equally spaced points between the ends; these "quiet" places are *nodes*. The places of maximum oscillation are *antinodes*.

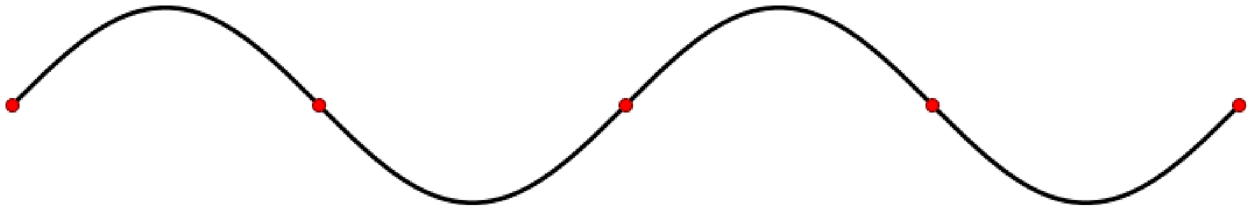


Figure 2.1.4: Animation of standing wave in the stationary medium with marked wave nodes (red circles). (Public domain; Lucas VB).

✓ Bound vs. Free particles and Traveling vs. Stationary Waves

Traveling waves exhibit movement and propagate through time and space and stationary wave have crests and troughs at fixed intervals separated by nodes. "Free" particles like the photoelectron discussed in the photoelectron effect, exhibit traveling wave like properties. In contrast, electrons that are "bound" waves will exhibit stationary wave like properties. The latter was invoked for the Bohr atom for quantizing angular moment of an electron bound within a hydrogen atom.

✓ The Wave Equation

The mathematical description of the one-dimensional waves (both traveling and standing) can be expressed as

$$\partial^2 u(x,t)/\partial x^2 = (1/v^2)\ \partial^2 u(x,t)/\partial t^2 \tag{2.1.3}$$

with u is the amplitude of the wave at position x and time t, and v is the velocity of the wave (Figure 2.1.2).

Equation 2.1.3 is called the classical wave equation in one dimension and is a *linear partial differential equation*. It tells us how the displacement u can change as a function of position and time and the function. The solutions to the wave equation ($u(x,t)$) are obtained by appropriate integration techniques. It may not be surprising that not all possible waves will satisfy Equation 2.1.3 and the waves that do must satisfy both **the initial conditions** and the **boundary conditions**, i.e. on how the wave is produced and what is happening on the ends of the string.

For example, for a standing wave of string with length L held taut at two ends (Figure 2.1.3), the boundary conditions are

$$u(0,t) = 0 \tag{2.1.4}$$

and

$$u(L,t) = 0 \tag{2.1.5}$$

for all values of t. As expected, different system will have different boundary conditions and hence different solutions.

✓ Summary

Waves which exhibit movement and are propagated through time and space. The two basic types of waves are traveling and stationary. Both exhibit wavelike properties and structure (presence of crests and troughs) which can be mathematically described by a wavefunction or amplitude function. Both wave types display movement (up and down displacement), but in different ways. Traveling waves have crests and troughs which are constantly moving from one point to another as they travel over a length or distance. In this way, energy is transmitted along the length of a traveling wave. In contrast, standing waves have nodes at fixed positions; this means that the wave's crests and troughs are also located at fixed intervals. Therefore, standing waves only experience vibrational movement (up and down displacement) on these set intervals - no movement or energy travels along the length of a standing wave.

1.4: Matter Has Wavelike Properties

✓ Learning Objectives

- To introduce the wave-particle duality of light extends to matter

The next real advance in understanding the atom came from an unlikely quarter - a student prince in Paris. Prince Louis de Broglie was a member of an illustrious family, prominent in politics and the military since the 1600's. Louis began his university studies with history, but his elder brother Maurice studied x-rays in his own laboratory, and Louis became interested in physics. After World War I, de Broglie focused his attention on Einstein's two major achievements, the theory of special relativity and the quantization of light waves. He wondered if there could be some connection between them. Perhaps the quantum of radiation really should be thought of as a particle. De Broglie suggested that if waves (photons) could behave as particles, as demonstrated by the photoelectric effect, then the converse, namely that particles could behave as waves, should be true. He associated a wavelength λ to a particle with momentum pp using Planck's constant as the constant of proportionality:

$$\lambda = h/p \tag{1.4.1}$$

which is called the de Broglie wavelength. The fact that particles can behave as waves but also as particles, depending on which experiment you perform on them, is known as the particle-wave duality.

✓ Deriving the de Broglie Wavelength

From the discussion of the photoelectric effect, we have the first part of the particle-wave duality, namely, that electromagnetic waves can behave like particles. These particles are known as photons, and they move at the speed of light. Any particle that moves at or near the speed of light has kinetic energy given by Einstein's special theory of relatively. In general, a particle of mass mm and momentum pp has an energy

$$E = \sqrt{p2c2 + m2c4} \tag{1.4.2}$$

Note that if $p = 0$, this reduces to the famous rest-energy expression $E = mc2$. However, photons are massless particles (technically rest-massless) that always have a finite momentum p. In this case, Equation 1.4.2 becomes

$$E = pc.$$

From Planck's hypothesis, one quantum of electromagnetic radiation has energy $E = h\nu$ Thus, equating these two expressions for the kinetic energy of a photon, we have

$$h\nu = hc/\lambda = pc$$

Solving for the wavelength λ gives Equation 1.6.1:

$$\lambda = h/p = h/mv \qquad (1.4.3)$$

Where, v is the velocity of the particle. Hence, de Broglie argued that if particles can behave as waves, then a relationship like this, which pertains particularly to waves, should also apply to particles.

Equation 1.4.3 allows us to associate a wavelength λ to a particle with momentum p. As the momentum increases, the wavelength decreases. In both cases, this means the energy becomes larger. i.e., short wavelengths and high momenta correspond to high energies.

It is a common feature of quantum mechanics that particles and waves with short wavelengths correspond to high energies and vice versa.

Having decided that the photon might well be a particle with a rest mass, even if very small, it dawned on de Broglie that in other respects it might not be too different from other particles, especially the very light electron. In particular, may be the electron also had an associated wave. The obvious objection was that if the electron was wavelike, why had no diffraction or interference effects been observed? But there was an answer. If de Broglie's relation between momentum and wavelength also held for electrons, the wavelength was sufficiently short that these effects would be easy to miss. As de Broglie himself pointed out, the wave nature of light is not very evident in everyday life. As the next section will demonstrate, the validity of de Broglie’s proposal was confirmed by electron diffraction experiments of G.P. Thomson in 1926 and of C. Davisson and L. H. Germer in 1927. In these experiments it was found that electrons were scattered from atoms in a crystal and that these scattered electrons produced an interference pattern. These diffraction patterns are characteristic of wave-like behavior and are exhibited by both electrons (i.e., matter) and electromagnetic radiation (i.e., light).

✓ **Example 1.4.1: Electron Waves**

Calculate the de Broglie wavelength for an electron with a kinetic energy of 1000 eV.

✓ **Solution**

To calculate the de Broglie wavelength (Equation 1.4.3), the momentum of the particle must be established and requires knowledge of both the mass and velocity of the particle. The mass of an electron is $9.109383\times10-^{28}$g and the velocity is obtained from the given kinetic energy of 1000 eV:

$$KE = mv2/2 = p2/2m = 1000eV$$

Solve for momentum

$$p = \sqrt{2mKE}$$

convert to SI units

$$p = \sqrt{(1000eV)(1.6 \times 10^{-19} J/1eV)(2)(9.109383 \times 10^{-31} kg)}$$

expanding definition of joule into base SI units and cancel

$$p = \sqrt{(3.1 \times 10 - 16 kg \cdot m2/s2)(9.109383 \times 10^{-31} kg)}$$

$$= \sqrt{2.9 \times 10^{-40} kg2m2/s2}$$

$$= 1.7 \times 10^{-23} kg \cdot m/s$$

Now substitute the momentum into the equation for de Broglie's wavelength (Equation 1.6.1) with Planck constant ($h = 6.626069 \times 10^{-34} \cdot s$). After expanding expanding unites in Planks constant

$$\lambda = h/p$$

$$= (6.626069 \times 10^{-34} kg \cdot m2/s \cdot s)/(1.7 \times 10^{-23} kg \cdot m/s)$$

$$= 3.87 \times 10^{-11}\ m\ or\ 38.9\ pm$$

✓ **Exercise 1.4.1: Baseball Waves**

Calculate the de Broglie wavelength for a fast ball thrown at 100 miles per hour and weighing 4 ounces. Comment on whether the wave properties of baseballs could be experimentally observed.

✓ **Answer**

Following the unit conversions below, a 4 oz baseball has a mass of 0.11 kg. The velocity of a fast ball thrown at 100 miles per hour in m/s is 44.7 m/s.

$$m = (4oz)(0.0283kg/1oz) = 0.11kg$$

$$v = (100mi/hr)(1609.34m/mi)(1hr/3600s) = 44.7m/s$$

The de Broglie wavelength of this fast ball is:

$$\lambda = h/mv = 6.626069 \times 10^{-34} kg \cdot m2/s/(0.11kg)(44.7m/s)$$

$$= 1.3 \times 10^{-34} m$$

1.5: de Broglie Waves can be Experimentally Observed

- ✓ **Learning Objectives**
- To present the experimental evidence behind the wave-particle duality of matter

The validity of de Broglie's proposal was confirmed by electron diffraction experiments of G.P. Thomson in 1926 and of C. Davisson and L. H. Germer in 1927. In these experiments it was found that electrons were scattered from atoms in a crystal and that these scattered electrons produced an interference pattern. The interference pattern was just like that produced when water waves pass through two holes in a barrier to generate separate wave fronts that combine and interfere with each other. These diffraction patterns are characteristic of wave-like behavior and are exhibited by both matter (e.g., electrons and neutrons) and electromagnetic radiation. Diffraction patterns are obtained if the wavelength is comparable to the spacing between scattering centers.

Diffraction occurs when waves encounter obstacles whose size is ***comparable*** *with its wavelength.*

Continuing with our analysis of experiments that lead to the new quantum theory, we now look at the phenomenon of electron diffraction.

✓ Diffraction of Light (Light as a Wave)

It is well-known that *light* has the ability to diffract around objects in its path, leading to an interference pattern that is particular to the object. This is, in fact, how holography works (the interference pattern is created by allowing the diffracted light to interfere with the original beam so that the hologram can be viewed by shining the original beam on the image). A simple illustration of light diffraction is the Young double slit experiment (Figure 1.5.1).

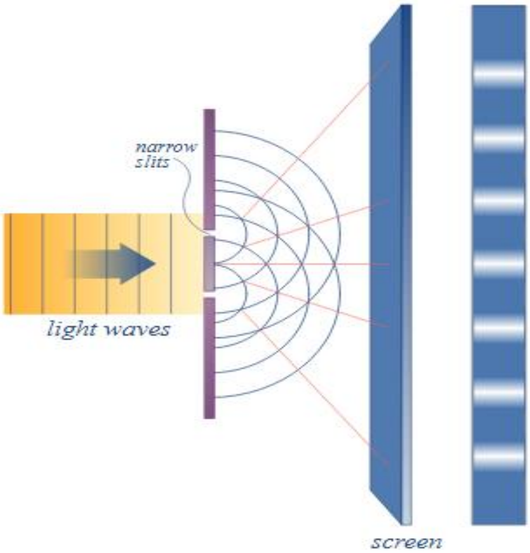


Figure 1.5.1: Young double slit experiment. Two slits are illuminated by a plane light waves. (CC BY-NC; Ümit Kaya)

Here, light as waves (pictured as waves in a plane parallel to the double slit apparatus) impinge on the two slits. Each slit then becomes a point source for spherical waves that subsequently interfere with each other, giving rise to the light and dark fringes on the screen at the right.

Interference is a wave phenomenon in which two waves superimpose to form a resultant wave of greater or lower amplitude. It is the primary property used to identify wave behavior.

✓ Diffraction of Electrons (Electrons as Waves)

According to classical physics, electrons should behave like particles - they travel in straight lines and do not curve in flight unless acted on by an external agent, like a magnetic field. In this model, if we fire a beam of electrons through a double slit onto a detector, we should get two bands of "hits", much as you would get if you fired a machine gun at the side of a house with two windows - you would get two areas of bullet-marked wall inside, and the rest would be intact Figure 1.5.2 (left).

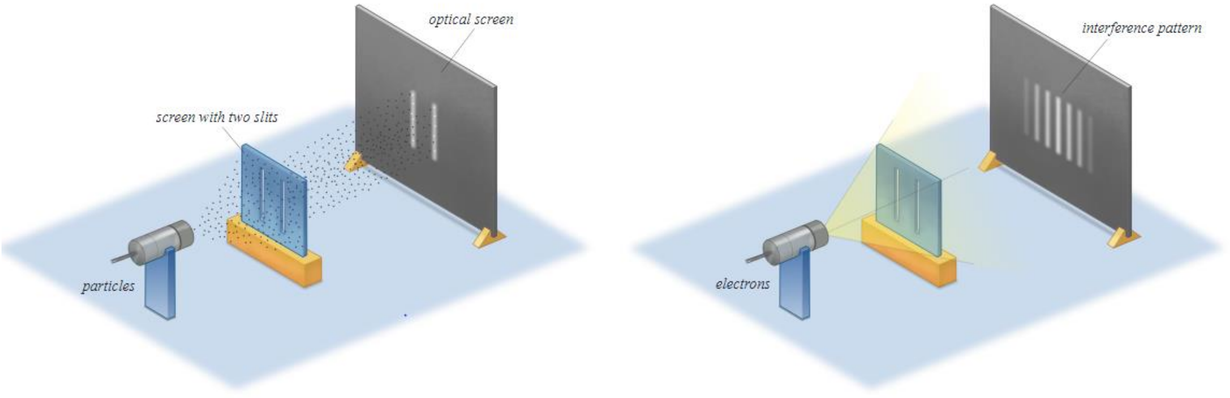


Figure 1.5.2: (left) classical model of electrons. (right) wave property of electrons. (CC BY-NC; Ümit Kaya)

However, if the slits are made small enough and close enough together, we actually observe the electrons are *diffracting* through the slits and *interfering* with each other just like waves. This means that the electrons have wave-particle duality, just like photons, in agreement with de Broglie's hypothesis discussed previously. In this case, they must have properties like wavelength and frequency. We can deduce the properties from the behavior of the electrons as they pass through our diffraction grating.

This was a pivotal result in the development of quantum mechanics. Just as the photoelectric effect demonstrated the particle nature of light, the Davisson–Germer experiment showed the wave-nature of matter and completed the theory of wave-particle duality. For physicists this idea was important because it meant that not only could any particle exhibit wave characteristics, but that one could use wave equations to describe phenomena in matter if one used the de Broglie wavelength.

Figure 1.5.3: An image of an ant in a scanning electron microscope based on the wave properties of electrons. (Public Domain; United States Geological Survey, an agency of the United States Department of the Interior)

An electron microscope uses a beam of accelerated electrons as a source of illumination. Since the wavelength of electrons can be up to 100,000 times shorter than that of visible light photons, electron microscopes have a higher resolving power than light microscopes and can reveal the structure of smaller objects. A transmission electron microscope can achieve better than 50 pm resolution and magnifications of up to about 10,000,000x whereas most light microscopes are limited by diffraction to about 200 nm resolution and useful magnifications below 2000x (Figure 1.5.3).

✓ Is Matter a Particle or a Wave?

An electron, indeed, any particle, is neither a particle nor a wave. Describing the electron as a particle is a mathematical model that works well in some circumstances while describing it as a wave is a different mathematical model that works well in other circumstances. When you choose to do some calculation of the electron's behavior that treats it either as a particle or as a wave, you're not saying the electron is a particle or is a wave: you're just choosing the mathematical model that makes it easiest to do the calculation.

✓ Neutrons Diffraction (Neutrons as Waves)

Like all quantum particles, neutrons can also exhibit wave phenomena and if that wavelength is short enough, atoms or their nuclei can serve as diffraction obstacles. When a beam of neutrons emanating from a reactor is slowed down and selected properly by their speed, their wavelength lies near one angstrom (0.1 nanometer), the typical separation between atoms in a solid material. Such a beam can then be used to perform a diffraction experiment. Neutrons interact directly with the nucleus of the atom, and the contribution to the diffracted intensity depends on each isotope; for example, regular hydrogen and deuterium contribute differently. It is also often the case that light (low Z) atoms contribute strongly to the diffracted intensity even in the presence of large Z atoms.

Example 1.7.1: Neutron Diffraction

Neutrons have no electric charge, so they do not interact with the atomic electrons. Hence, they are very penetrating (e.g., typically 10 cm in lead). Neutron diffraction was proposed in 1934, to exploit de Broglie's hypothesis about the wave nature of matter. Calculate the momentum and kinetic energy of a neutron whose wavelength is comparable to atomic spacing ($1.8 \times 10^{-10} m$).

- ✓ **Solution**

This is a simple use of de Broglie's equation

$$\lambda = h/p$$

where we recognize that the wavelength of the neutron must be comparable to atomic spacing (let's assumed equal for convenience, so $\lambda = 1.8 \times 10^{-10}$m). Rearranging the de Broglie wavelength relationship above to solve for momentum (p):

$$p = h/\lambda$$

$$= 6.6 \times 10^{-34} Js/1.8 \times 10^{-10} m$$

$$= 3.7 \times 10^{-24} kg\ m\ s^{-1}$$

The relationship for kinetic energy is

$$KE = (1/2)\, mv2 = p2/2m$$

where v is the velocity of the particle. From the reference table of physical constants, the mass of a neutron is $1.6749273 \times 10^{-27} kg$, so

$$KE = (3.7 \times 10^{-24} kg\, m\, s^{-1})2/(2(1.6749273 \times 10^{-27} kg))$$

$$= 4.0 \times 10^{-21} J$$

The neutrons released in nuclear fission are ‘fast’ neutrons, i.e., much more energetic than this. Their wavelengths be much smaller than atomic dimensions and will not be useful for neutron diffraction. We slow down these fast neutrons by introducing a "moderator", which is a material (e.g., graphite) that neutrons can penetrate, but will slow down appreciable.

1.6: The Heisenberg Uncertainty Principle

✓ **Learning Objectives**

- To understand that sometimes you cannot know everything about a quantum system as demonstrated by the Heisenberg uncertainly principle.

In classical physics, studying the behavior of a physical system is often a simple task since several physical qualities can be measured simultaneously. However, this possibility is absent in the quantum world. In 1927 the German physicist Werner Heisenberg described such limitations as the Heisenberg Uncertainty Principle, or simply the Uncertainty Principle, stating that it is not possible to measure both the momentum and position of a particle simultaneously.

The Heisenberg Uncertainty Principle is a fundamental theory in quantum mechanics that defines why a scientist cannot measure multiple quantum variables simultaneously. Until the dawn of quantum mechanics, it was held as a fact that all variables of an object could be known to exact precision simultaneously for a given moment. Newtonian physics placed no limits on how better procedures and techniques could reduce measurement uncertainty so that it was conceivable that with proper care and accuracy all information could be defined. Heisenberg made the bold proposition that there is a lower limit to this precision making our knowledge of a particle inherently uncertain.

✓ **Probability**

Matter and photons are waves, implying they are spread out over some distance. What is the position of a particle, such as an electron? Is it at the center of the wave? The answer lies in how you measure the position of an electron. Experiments show that you will find the electron at some definite location, unlike a wave. But if you set up exactly the same situation and measure it again, you will find the electron in a different location, often far outside any experimental uncertainty in your measurement. Repeated measurements will display a statistical distribution of locations that appears wavelike (Figure 1.6.1).

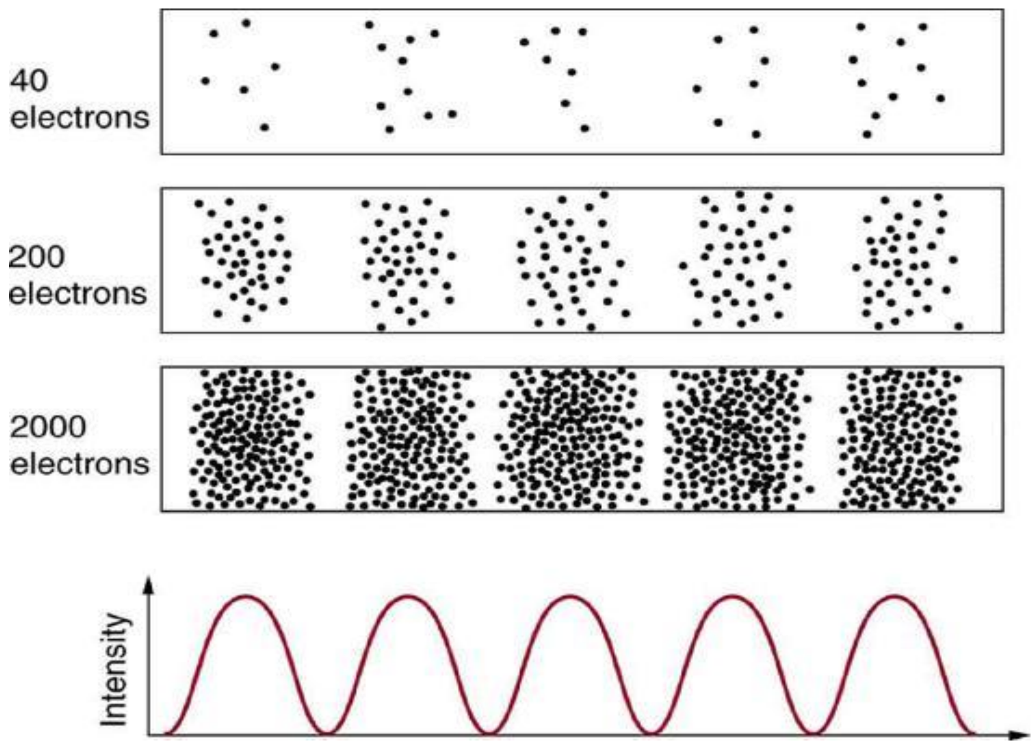


Figure 1.6.1: The building up of the diffraction pattern of electrons scattered from a crystal surface. Each electron arrives at a definite location, which cannot be precisely predicted. The overall distribution shown at the bottom can be predicted as the diffraction of waves having the de Broglie wavelength of the electrons. Image used with permission (CC BY; OpenStax).

After de Broglie proposed the wave nature of matter, many physicists, including Schrödinger and Heisenberg, explored the consequences. The idea quickly emerged that, *because of its wave character, a particle's trajectory and destination cannot be precisely predicted for each particle individually*. However, each particle goes to a definite place (Figure 1.6.1). After compiling enough data, you get a distribution related to the particle's wavelength and diffraction pattern. There is a certain *probability* of finding the particle at a given location, and the overall pattern is called a **probability distribution**. Those who developed quantum mechanics devised equations that predicted the probability distribution in various circumstances.

It is somewhat disquieting to think that you cannot predict exactly where an individual particle will go, or even follow it to its destination. Let us explore what happens if we try to follow a particle. Consider the double-slit patterns obtained for electrons and photons in Figure 1.6.2. The interference patterns build up statistically as individual particles fall on the detector. This can be observed for photons or electrons—for now, let us concentrate on electrons. You might imagine that the electrons are interfering with one another as any waves do. To test this, you can lower the intensity until there is never more than one electron between the slits and the screen. The same interference pattern builds up!

This implies that a particle’s probability distribution spans both slits, and the particles actually interfere with themselves. Does this also mean that the electron goes through both slits? An electron is a basic unit of matter that is not divisible. But it is a fair question, and so we should look to see if the electron traverses one slit or the other, or both. One possibility is to have coils around the slits that detect charges moving through them. What is observed is that an electron always goes through one slit or the other; it does not split to go through both.

But there is a catch. If you determine that the electron went through one of the slits, you no longer get a double slit pattern—instead, you get single slit interference. There is no escape by using another method of determining which slit the electron went through. Knowing the particle went through one slit force a single-slit pattern. If you do not observe which slit the electron goes through, you obtain a double-slit pattern. How does knowing which slit the electron passed through change the pattern? The answer is fundamentally important measurement *affects the system being observed*. Information can be lost, and in some cases, it is impossible to measure two physical quantities simultaneously to exact precision. For example, you can measure the position of a moving electron by scattering light or other electrons from it. Those probes have momentum themselves, and by scattering from the electron, they change its momentum *in a manner that loses information*. There is a limit to absolute knowledge, even in principle.

✓ Heisenberg’s Uncertainty Principle

It is mathematically possible to express the uncertainty that, Heisenberg concluded, always exists if one attempts to measure the momentum and position of particles. First, we must define the variable "x" as the position of the particle and define "p" as the momentum of the particle. The momentum of a photon of light is known to simply be its frequency, expressed by the ratio h/λ, where h represents Planck's constant and λ represents the wavelength of the photon. The position of a photon of light is simply its wavelength (λ). To represent finite change in quantities, the Greek uppercase letter delta, or Δ, is placed in front of the quantity. Therefore,

$$\Delta p = h/\lambda \tag{1.6.1}$$

$$\Delta x = \lambda \tag{1.6.2}$$

By substituting Δx for λ into Equation 1.6.1, we derive

$$\Delta p = h/\Delta x \tag{1.6.3}$$

or,

$$\Delta p \Delta x = h \tag{1.6.4}$$

early form of uncertainty principle

✓ A Common Trend in Quantum Systems

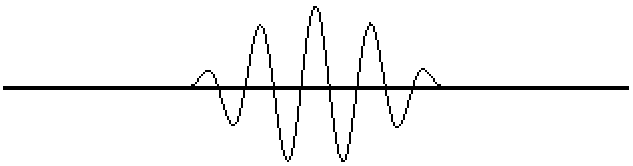
Equation 1.6.4 can be derived by assuming the particle of interest is behaving as a particle, and not as a wave. Simply let $\Delta p = mv, and\ \Delta x = h/(mv)$ (from De Broglie's expression for the wavelength of a particle). Substituting in Δp for mv in the second equation leads to Equation 1.6.4.

Equation 1.6.4 was further refined by Heisenberg and his colleague Niels Bohr, and was eventually rewritten as

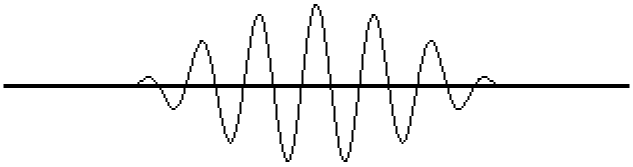
$$\Delta p_x \Delta x \geq h/4\pi = \hbar/2 \tag{1.6.5}$$

with $\hbar = h/2\pi = 1.0545718 \times 10^{-34}\, m_2 \cdot kg/s$.

Equation 1.6.5 reveals that the more accurately a particle's position is known (the smaller Δx is), the less accurately the momentum of the particle in the x direction (Δpx) is known. Mathematically, this occurs because the smaller Δx becomes, the larger Δpx must become in order to satisfy the inequality. However, the more accurately momentum is known the less accurately position is known (Figure 1.6.2).



Momentum (→ wavelength → colour)



Position

Figure 1.6.2: The animation shows the relevant spreads in the uncertainty for position and momentum of light/photons (light wave's corresponding photon particle). From the result of de Broglie, we know that for a particle with known momentum, pp will have a precise value for its de Broglie wavelength can be determined (and hence a specific color of the light).

✓ What is the Proper Definition of Uncertainty?

Equation 1.6.5 relates the uncertainty of momentum and position. An immediate question that arises is if Δx represents the full range of possible x values or if it is half (e.g., $\langle x \rangle \pm \Delta x$). Δx is the standard deviation and is a statistic measure of the spread of x values? The use of half the possible range is more accurate estimate of Δx. As we will demonstrated later, once we construct a wavefunction to describe the system, then both xx and Δx can be explicitly derived. However for now, Equation 1.6.5 will work.

For example: If a problem argues a particle is trapped in a box of length, L, then the uncertainly of it position is ±L/2. So the value of Δx used in Equation 1.6.5 should be L/2, not L.

✓ Example 1.6.1

An electron is confined to the size of a magnesium atom with a 150 pm radius. What is the minimum uncertainty in its velocity?

- ✓ **Solution**

The uncertainty principle (Equation 1.6.5):

$$\Delta p \Delta x \geq \hbar/2$$

can be written

$$\Delta p \geq \hbar/2\Delta x$$

and substituting $\Delta p = m\Delta v$ since the mass is not uncertain.

$$\Delta v \geq \hbar/2m\Delta x$$

the relevant parameters are mass of electron $m = me = 9.109383 \times 10^{-31} kg$

uncertainty in position: $\Delta x = 150 \times 10^{-12} m$

$$\Delta v \geq (1.0545718 \times 10^{-34} kgm2/s)/((2)(9.109383 \times 10^{-31}\ kg)(150 \times 10^{-12} m))$$

$$= 3.9 \times 10^{5}\ m/s$$

- ✓ **Exercise 1.6.1**

What is the maximum uncertainty of velocity the electron described in Example 1.9.1?

- ✓ **Answer**

Infinity. There is no limit in the maximum uncertainty, just the minimum uncertainty.

- ✓ **Example 1.6.2**

The speed of a 1.0 g projectile is known to within 10^{-5}m/s.

a. Calculate the minimum uncertainty in its position.
b. What is the maximum uncertainty of its position?

- ✓ **Solution**

a) From Equation 1.6.5, the $\Delta px = m\Delta vx$ with m=1.0 g. Solving for Δx to get

$$\Delta x = \hbar/2m\Delta v$$

$$= (1.0545718 \times 10^{-34} m2 \cdot kg/s)/(2)(0.001kg)(10^{-6} m/s)$$
$$= 5.3 \times 10^{-26} m$$

This negligible for all intents and purpose as expected for any macroscopic object.

b) Unlimited (or the size of the universe). The Heisenberg uncertainty principles does not quantify the maximum uncertainty.

- ✓ **Exercise 1.6.2**

Estimate the minimum uncertainty in the speed of an electron confined to a hydrogen atom within a diameter of $1\times10^{-10} m$?

- ✓ **Answer**

We need to quantify the uncertainty of the electron in position. We can estimate that as $\pm5\times10^{-10}$ m. Hence, substituting the relevant numbers into Equation 1.6.5 and solving for Δv we get

$$\Delta v = 1.15 \times 10^{6}\ km/s$$

Notice that the uncertainty is significantly greater for the electron in a hydrogen atom than in the magnesium atom (Example 1.6.1) as expected since the magnesium atom is appreciably bigger.

Heisenberg's Uncertainty Principle not only helped shape the new school of thought known today as quantum mechanics, but it also helped discredit older theories. Most importantly, the Heisenberg Uncertainty Principle made it obvious that there was a fundamental error in the Bohr model of the atom. Since the position and momentum of a particle cannot be known simultaneously, Bohr's theory that the electron traveled in a circular path of a fixed radius orbiting the nucleus was obsolete. Furthermore, Heisenberg's uncertainty principle, when combined with other revolutionary theories in quantum mechanics, helped shape wave mechanics and the current scientific understanding of the atom.

- ✓ **Humor: Heisenberg and the Police**

Heisenberg get pulled over for speeding by the police. The officer asks him "Do you know how fast you were going?"

Heisenberg replies, "No, but we know exactly where we are!"

The officer looks at him confused and says, "you were going 108 miles per hour!" Heisenberg throws his arms up and cries, "Great! Now we're lost!"

Chapter 3

The Schrödinger Equation and a Particle in a Box

The particle in a box model provides one of the very few problems in quantum mechanics which can be solved analytically, without approximations. This means that the observable properties of the particle (such as its energy and position) are related to the mass of the particle and the width of the well by simple mathematical expressions. Due to its simplicity, the model allows insight into quantum effects without the need for complicated mathematics

3.1: The Schrödinger Equation

✓ Learning Objectives

- To be introduced to the general properties of the Schrödinger equation and its solutions.

De Broglie’s doctoral thesis, defended at the end of 1924, created a lot of excitement in European physics circles. Shortly after it was published in the fall of 1925 Pieter Debye, Professor of Theoretical Physics at Zurich and Einstein's successor, suggested to Erwin Schrödinger that he give a seminar on de Broglie’s work. Schrödinger gave a polished presentation, but at the end Debye remarked that he considered the whole theory rather childish: why should a wave confine itself to a circle in space? It wasn’t as if the circle was a waving circular string, real waves in space diffracted and diffused, in fact they obeyed three-dimensional wave equations, and that was what was needed. This was a direct challenge to Schrödinger, who spent some weeks in the Swiss mountains working on the problem and constructing his equation. There is no rigorous derivation of Schrödinger’s equation from previously established theory, but it can be made very plausible by thinking about the connection between light waves and photons, and construction an analogous structure for de Broglie’s waves and electrons (and, later, other particles).

✓ The Schrödinger Equation: A Better Approach

While the Bohr model is able to predict the allowed energies of any single-electron atom or cation, it by no means, a general approach. Moreover, it relies heavily on classical ideas, clumsily grafting quantization onto an essentially classical picture, and therefore, provides no real insights into the true quantum nature of the atom. Any rule that might be capable of predicting the allowed energies of a quantum system must also account for the *wave-particle duality* and implicitly include a wave-like description for particles. Nonetheless, we will attempt a heuristic argument to make the result at least plausible. In classical electromagnetic theory, it follows from Maxwell's equations that each component of the electric and magnetic fields in vacuum is a solution of the 3-D wave equation for electromagnetic waves:

$$\nabla^2\Psi(x,y,z,t) - (1/c^2)\,\partial^2\Psi(x,y,z,t)/\partial t^2 = 0 \tag{3.1.1}$$

The wave equation in Equation 3.1.1 is the three-dimensional analog to the wave equation presented earlier (Equation 2.1.1) with the velocity fixed to the known speed of light: c. Instead of a partial derivative $\partial^2/\partial x^2$ in one dimension, the Laplacian (or "del-squared") operator is introduced:

$$\nabla^2 = \partial^2/\partial x^2 + \partial^2/\partial y^2 + \partial^2/\partial z^2 \tag{3.1.2}$$

Corresponding, the solution to this 3D equation wave equation is a function of *four* independent variables: x, y, z, and t and is generally called the **wavefunction** ψ.

We will attempt now to create an analogous equation for de Broglie's matter waves. Accordingly, let us consider an only 1-dimensional wave motion propagating in the *x*-direction. At a given instant of time, the form of a wave might be represented by a function such as

$$\Psi(x) = f(2\pi x/\lambda) \tag{3.1.3}$$

where $f(\theta)$ represents a sinusoidal function such as $sin\theta$, $cos\theta$, $e^{i\theta}$, $e^{-i\theta}$ or some linear combination of these. The most suggestive form will turn out to be the complex exponential, which is related to the sine and cosine by Euler's formula

$$exp(\pm i\theta) = cos\theta \pm isin\theta \tag{3.1.4}$$

Each of the above is a periodic function, its value repeating every time its argument increases by 2π. This happens whenever x increases by one wavelength λ. At a fixed point in space, the time-dependence of the wave has an analogous structure:

$$T(t) = f(2\pi\nu t) \tag{3.1.5}$$

where ν gives the number of cycles of the wave per unit time. Taking into account both x and t dependence, we consider a wavefunction of the form

$$\Psi(x,t) = exp[2\pi i(x/\lambda - \nu t)] \tag{3.1.6}$$

representing waves traveling from left to right. Now we make use of the Planck formula ($E = h\nu$) and de Broglie formulas ($p = h\lambda$) to replace ν and λ by their particle analogs. This gives

$$\Psi(x,t) = exp[i(px - Et)/\hbar] \tag{3.1.7}$$

Where,

$$\hbar \equiv h/2\pi \tag{3.1.8}$$

Since Planck's constant occurs in most formulas with the denominator 2π, the $\hbar$ symbol was introduced by Paul Dirac. Equation 3.1.5 represents in some way the wavelike nature of a particle with energy E and momentum p. The time derivative of Equation 3.1.7 gives

$$\partial\Psi/\partial t = -(iE/\hbar)exp[i(px - Et)/\hbar] \tag{3.1.9}$$

Thus from a simple comparison of Equations 3.1.7 and 3.1.9

$$i\hbar\, \partial\Psi/\partial t = E\Psi \tag{3.1.10}$$

or analogously differentiation of Equation 3.1.9 with respect to x

$$-i\hbar\, \partial\Psi/\partial x = p\Psi \qquad (3.1.11)$$

and then the second derivative

$$-\hbar^2\, \partial^2\Psi/\partial x^2 = p^2\Psi \qquad (3.1.12)$$

The energy and momentum for a *nonrelativistic* free particle (i.e., all energy is kinetic with no potential energy involved) are related by

$$E = (1/2)\, mv^2 = p^2/2m \qquad (3.1.13)$$

Substituting Equations 3.1.12 and 3.1.10 into Equation 3.1.13 shows that $\Psi(x,t)$ satisfies the following partial differential equation

$$i\hbar\, \partial\Psi/\partial t = (-\hbar^2/2m)\, \partial^2\Psi/\partial x^2 \qquad (3.1.14)$$

Equation 3.1.14 is the applicable differential equation describing the wavefunction of a *free particle* that is not bound by any external forces or equivalently not in a region where its potential energy $V(x,t)$ varies.

For a particle with a non-zero potential energy $V(x)$, the total energy E is then a sum of kinetics and potential energies

$$E = p^2/2m + V(x) \qquad (3.1.15)$$

we postulate that Equation 3.1.3 for matter waves can be generalized to

$$i\hbar\partial\, \Psi(x,t)/\partial t = [-(\hbar^2/2m)\, \partial^2/\partial x^2 + V(x)]\Psi(x,t) \qquad (3.1.16)$$

time-dependent Schrödinger equation in 1D

For matter waves in three dimensions, Equation 3.1.6 is then expanded

$$i\hbar\, \partial\Psi\left(\vec{r},t\right)/\partial t = \left[-(\hbar^2/2m)\, \nabla 2 + V\left(\vec{r}\right)\right]\Psi\left(\vec{r},t\right)$$

(3.1.17)

time-dependent Schrödinger equation in 3D

Here the potential energy and the wavefunctions Ψ depend on the three space coordinates x, y, z, which we write for brevity as $\vec{r}$. Notice that the potential energy is assumed to depend on position only and not time (i.e., particle motion). This is applicable for conservative forces that a potential energy function $V\left(\vec{r}\right)$ can be formulated.

✓ The Laplacian Operator

The three second derivatives in parentheses together are called the Laplacian

operator, or del-squared,

$$\nabla^2 = \nabla \cdot \nabla$$

$$= (\partial 2/\partial x2 + \partial 2/\partial y2 + \partial 2/\partial z2) \tag{3.1.18}$$

with the del operator,

$$\nabla = \left(\vec{x}\,\partial/\partial x + \vec{y}\,\partial/\partial y + \vec{z}\,\partial/\partial z\right) \tag{3.1.19}$$

Remember from basic calculus that when the del operator is directly operates on a field (e.g., $\nabla f(x, y, x)$, it denotes the gradient (i.e., the locally steepest slope) of the field. The symbols with arrows in Equation 3.1.19 are unit vectors.

Equation 3.1.17 is the *time-dependent Schrödinger* equation describing the wavefunction amplitude $\Psi\left(\vec{r}, t\right)$ of matter waves associated with the particle within a specified potential $V\left(\vec{r}\right)$. Its formulation in 1926 represents the start of modern quantum mechanics (Heisenberg in 1925 proposed another version known as matrix mechanics).

For *conservative* systems, the energy is a constant, and the time-dependent factor from Equation 3.1.7 can be separated from the space-only factor (via the *Separation of Variables* technique discussed in Section 2.2)

$$\Psi\left(\vec{r},t\right) = \psi\left(\vec{r}\right) exp(-iEt/\hbar) \qquad (3.1.20)$$

where $\psi(\vec{r})$ is a wavefunction dependent (or time-independent) wavefuction that only depends on space coordinates. Putting Equation 3.1.20 into Equation 3.1.17 and cancelling the exponential factors, we obtain the time-independent Schrödinger equation:

$$[(-\hbar_2/2m)\nabla_2 + V(\vec{r})]\psi(\vec{r}) = E\,\psi(\vec{r}) \qquad (3.1.21)$$

time-independent Schrödinger equation

The overall form of the Equation 3.1.21 is not unusual or unexpected as it uses the principle of the **conservation of energy**. Most of our applications of quantum mechanics to chemistry will be based on this equation (with the exception of spectroscopy). The terms of the time-independent Schrödinger equation can then be interpreted as total energy of the system, equal to the system kinetic energy plus the system potential energy. In this respect, it is just the same as in classical physics.

✓ Time Dependence to the Wavefunctions

Notice that the wavefunctions used with the time-independent Schrödinger equation (i.e., $\psi(\vec{r})$) do not have explicit t dependences like the wavefunctions of time-dependent analog in Equation 3.1.17 (i.e., $\Psi(\vec{r},t)$). That does not imply that there is no time dependence to the wavefunction. Equation 3.1.20 argues that the time-dependent (i.e., full spatial and temporal) wavefunction ($\Psi(\vec{r},t)$) differs from the time-independent (i.e., spatial only) wavefunction $\psi(\vec{r})$) by a "phase factor" of constant magnitude. Using the Euler relationship in Equation 3.1.4, the total wavefunction above can be expanded

$$\Psi(\vec{r},t) = \psi(\vec{r})(cos\,(Et/\hbar) - i\,sin\,(Et/\hbar)) \qquad (3.1.22)$$

This means the total wavefunction has a complex behavior with a real part and an imaginary part. Moreover, using the trigonometry identity $sin(\theta) = cos(\theta - \pi/2)$ Equation 3.1.22 can further simplified to

$$\Psi(\vec{r},t) = \psi(\vec{r})cos(Et/\hbar) - i\psi(\vec{r})cos(Et/\hbar - \pi/2) \tag{3.1.23}$$

This shows that both the real and the imaginary components of the total wavefunction oscillate the imaginary part of the total wavefunction oscillates out of phase by $\pi/2$ with respect to the real part.

Note that while all wavefunctions have a time-dependence, that dependence may not impact in simple quantum problems as the next sections discuss and can often be ignored.

Before we embark on this, however, let us pause to comment on the validity of quantum mechanics. Despite its weirdness, its abstractness, and its strange view of the universe as a place of randomness and unpredictability, quantum theory has been subject to intense experimental scrutiny. It has been found to agree with experiments to better than $10^{-10}\%$ for all cases studied so far. When the Schrödinger Equation is combined with a quantum description of the electromagnetic field, a theory known as *quantum electrodynamics*, the result is one of the most accurate theories of matter that has ever been put forth. Keeping this in mind, let us forge ahead in our discussion of the quantum universe and how to apply quantum theory to both model and real situations.

3.2: Linear Operators in Quantum Mechanics

✓ **Learning Objectives**

- Classical-Mechanical quantities are represented by linear operators in Quantum Mechanics
- Understand that "algebra" of scalars and functions do not always to operators (specifically the commutative property)

The bracketed object in the time-independent Schrödinger Equation (in 1D)

$$[-(\hbar 2/2m)\nabla 2+V(\vec{r})]\psi(\vec{r})=E\psi(\vec{r}) \tag{3.2.1}$$

is called an *operator*. An operator is a generalization of the concept of a function applied to a function. Whereas a function is a rule for turning one number into another, an operator is a rule for turning one function into another. For the time-independent Schrödinger Equation, the operator of relevance is the Hamiltonian operator (often just called the Hamiltonian) and is the most ubiquitous operator in quantum mechanics.

$$\hat{H}=-(\hbar 2/2m)\nabla 2+V(\vec{r}) \tag{3.2.2}$$

We often (but not always) indicate that an object is an operator by placing a 'hat' over it, e.g., $\hat{H}$. So time-independent Schrödinger Equation can then be simplified from Equation 3.2.1 to

$$\hat{H}\,\psi(\vec{r})=E\psi(\vec{r}) \tag{3.2.3}$$

Equation 3.2.3 says that the Hamiltonian operator operates on the wavefunction to produce the energy, which is a scalar (i.e., a number, a quantity and observable) times the wavefunction. Such an equation, where the operator, operating on a function, produces a constant times the function, is called an **eigenvalue equation**. The function is called an eigenfunction, and the resulting numerical value is called the eigenvalue. Eigen here is the German word meaning self or own. We will discuss this in detail in later Sections.

✓ Fundamental Properties of Operators

Most properties of operators are straightforward, but they are summarized below for completeness.

The sum and difference of two operators A^ and B^ are given by

$$(A\hat{}\pm B\hat{})f = A\hat{}f \pm B\hat{}f \qquad (3.2.4)$$

The product of two operators is defined by

$$A\hat{}B\hat{}f \equiv A\hat{}[B\hat{}f] \qquad (3.2.5)$$

Two operators are equal if

$$A\hat{}f = B\hat{}f \qquad (3.2.6)$$

for **all** functions ff. The identity operator 1^ does nothing (or multiplies by 1)

$$1\hat{}f = f \qquad (3.2.7)$$

The n-th power of an operator A^n is defined as n successive applications of the operator, e.g.

$$A\hat{}2f = A\hat{}A\hat{}f \qquad (3.2.8)$$

The *associative law* holds for operators

$$A\hat{}(B\hat{}C\hat{}) = (A\hat{}B\hat{})C\hat{} \qquad (3.2.9)$$

The *commutative law* does **not** generally hold for operators. In general, but not always,

$$A\hat{}B\hat{} \neq B\hat{}A\hat{} \qquad (3.2.10)$$

To help identify if the inequality in Equation 3.2.10 holds for any two specific operators, we define the commutator.

✓ Definition: The Commutator

It is convenient to define the commutator of A^ and B^

$$[A\hat{},B\hat{}] \equiv A\hat{}B\hat{} - B\hat{}A\hat{} \qquad (3.2.11)$$

$If\ A\hat{}\ and\ B\hat{}$ commute, then

$$[A\hat{},B\hat{}] = 0. \qquad (3.2.12)$$

If the commutator is not zero, the order of operating matters and the operators are said to "not commute." Moreover, this property applies

$$[A^{\wedge}, B^{\wedge}] = -[B^{\wedge}, A^{\wedge}]. \tag{3.2.13}$$

✓ Linear Operators

The action of an operator that turns the function $f(x)$ into the function g(x) is represented by

$$A^{\wedge} f(x) = g(x) \tag{3.2.14}$$

The most common kind of operator encountered are *linear operators* which satisfies the following two conditions:

$$O^{\wedge}(f(x) + g(x)) = O^{\wedge} f(x) + O^{\wedge} g(x) \tag{3.2.15}$$

Condition A

and

$$O^{\wedge} c f(x) = c O^{\wedge} f(x) \tag{3.2.16}$$

Condition B

where

- $O^{\wedge}$ is a linear operator,
- c is a constant that can be a complex number ($c = a + ib$), and
- $f(x)$ and $g(x)$ are functions of x

If an operator fails to satisfy either Equations 3.2.15 or 3.2.16 then it is not a linear operator.

✓ Example 3.2.1

Is this operator $O^{\wedge} = -i\hbar\, d/dx$ linear?

✓ Solution

To confirm is an operator is linear, both conditions in Equation 3.2.16 must be demonstrated.

Condition A (Equation 3.2.15):

$$O^{\wedge}(f(x) + g(x)) = -i\hbar\, d/dx(f(x) + g(x))$$

From basic calculus, we know that we can use the sum rule for differentiation

$$O\hat{}(f(x)+g(x)) = -i\hbar\, d/dx\, f(x) - i\hbar\, d/dx\, g(x)$$

$$= O\hat{}\ f(x) + O\hat{}\ g(x) \checkmark$$

Condition A is confirmed. Does Condition B (Equation 3.2.16) hold?

$$O\hat{}\ c\, f(x) = -i\hbar\, d/dx\, c\, f(x)$$

Also from basic calculus, this can be factored out of the derivative

$$O\hat{}\ cf(x) = -ci\hbar\, d/dx\, f(x) = cO\hat{}\ f(x) \checkmark$$

Yes. This operator is a linear operator (this is the linear momentum operator).

- ✓ **Exercise 3.2.1**

Confirm if the square root operator √f(x) linear or not?

- ✓ **Answer**

To confirm is an operator is linear, both conditions in
Equations 3.2.15 and 3.2.16 must be demonstrated. Let's look first at Condition B.
Does Condition B (Equation 3.2.16) hold?

$$O\hat{}cf(x) = cO\hat{}f(x)$$

$$\sqrt{cf(x)} \neq cf(x)$$

Condition B does not hold; therefore, the square root operator is not linear.

The most operators encountered in quantum mechanics are *linear operators*.

- ✓ **Hermitian Operators**

An important property of operators is suggested by considering the Hamiltonian

for the particle in a box:

$$H\hat{} = -(\hbar 2/2m)\ \ d2/dx2 \qquad (3.2.17)$$

Let f(x) and g(x) be arbitrary functions which obey the same boundary values as the eigenfunctions of H^ (e.g., they vanish at x=0 and x=a). Consider the integral

$$\int_0^a f(x)H^\wedge g(x)dx = -(\hbar 2/2m)\int_0^a f(x)g''(x)dx \tag{3.2.18}$$

Now, using integration by parts,

$$\int_0^a f(x)g''(x)dx \; = -\int_0^a f'(x)g'(x)dx \; + f(x)g'(x)\Big| \tag{3.2.19}$$

The boundary terms vanish by the assumed conditions on f and g. A second integration by parts transforms Equation 3.2.19 to

$$\int_0^a f''(x)g(x)dx - f'(x)g(x) \mid a0 \tag{3.2.20}$$

It follows therefore that

$$\int_0^a f(x)H^\wedge g(x)dx = \int_0^a g(x)H^\wedge f(x)dx \tag{3.2.21}$$

An obvious generalization for complex functions will read

$$\int_0^a f*(x)H^\wedge g(x)dx = (\int_0^a g*(x)H^\wedge f(x)dx)* \tag{3.2.22}$$

In mathematical terminology, an operator A^ for which

$$\int f * A^\wedge \; g \; d\tau = (\int g * A^\wedge \; f \; d\tau) * \tag{3.2.23}$$

for all functions f and g which obey specified boundary conditions is classified as *Hermitian* or *self-adjoint*. Evidently, the Hamiltonian is a Hermitian operator. It is postulated that *all* quantum-mechanical operators that represent dynamical variables are Hermitian. The term is also used for specific times of matrices in linear algebra courses.

All quantum-mechanical operators that represent dynamical variables are Hermitian.

3.3: The Schrödinger Equation is an Eigenvalue Problem

✓ **Learning Objectives**

- To recognize that each quantum mechanical observable is determined by solve by an eigenvalue problem with different operators for different observable
- Confirm if a specific wavefunction is an eigenfunction of a specific operation and extract the corresponding observable (the eigenvalue)
- To recognize that the Schrödinger equation, just like all measurable, is also an eigenvalue problem with the eigenvalue ascribed to total energy
- Identity and manipulate several common quantum mechanical operators

As per the definition, an operator acting on a function gives another function, however a special case occurs when the generated function is proportional to the original

$$A^{\wedge}\psi \propto \psi \tag{3.3.1}$$

This case can be expressed in terms of a equality by introducing a proportionality constant k

$$A^{\wedge}\psi = k\psi \tag{3.3.2}$$

Not all functions will solve an equation like in Equation 3.3.2 If a function does, then ψ is known as an **eigenfunction** and the constant k is called its **eigenvalue** (these terms are hybrids with German, the purely English equivalents being "characteristic function" and "characteristic value", respectively). Solving eigenvalue problems are discussed in most linear algebra courses.

In quantum mechanics, every experimental measurable aa is the eigenvalue of a specific operator (A^):

$$A^{\wedge}\psi = a\psi \tag{3.3.3}$$

The aa eigenvalues represent the possible measured values of the A^ operator. Classically, aa would be allowed to vary continuously, but in quantum mechanics, aa typically has only a sub-set of allowed values (hence the quantum aspect). Both time-dependent and time-independent Schrödinger equations are the best-known instances of an eigenvalue equations in quantum mechanics, with its eigenvalues corresponding to the allowed energy levels of the quantum system.

$$[-(\hbar 2/2m)\ \ \nabla 2+V(\vec{r}\,)]\psi(\vec{r}\,)=E\psi(\vec{r}\,) \tag{3.3.4}$$

The object on the left that acts on ψ(x)ψ(x) is an example of an **operator**

$$[-(\hbar 2/2m)\ \ \nabla 2+V(\vec{r}\,)] \tag{3.3.5}$$

In effect, what is says to do is "take the second derivative of $\psi(x)$, multiply the result by $-(\hbar 2/2m)$ and then add $V(x)\psi(x)$ to the result of that." Quantum mechanics involves many different types of operators. This one, however, plays a special role because it appears on the left side of the Schrödinger equation. It is called the **Hamiltonian** *operator* and is denoted as

$$H\hat{}=-(\hbar 2/2m)\ \ \nabla 2+V(\vec{r}\,) \tag{3.3.6}$$

Therefore, the time-dependent Schrödinger equation can be (and it more commonly) written as

$$H\hat{}\psi(x,t)=i\hbar\ (\partial/\partial t)\ \psi(x,t) \tag{3.3.7}$$

and the time-independent Schrödinger equation

$$H\hat{}\psi(x)=E\psi(x) \tag{3.3.8}$$

Note that the functional form of Equation 3.3.8 is the same as the general eigenvalue equation in Equation 3.3.2 where the eigenvalues are the (allowed) total energies (E).

The Hamiltonian, named after the Irish mathematician Hamilton, comes from the formulation of Classical Mechanics that is based on the total energy, $H=T+V$, rather than Newton's second law, $F=ma$. Equation 3.3.8 says that the Hamiltonian operator operates on the wavefunction to produce the energy E, which is a scalar (e.g., expressed in Joules) times the wavefunction.

✓ Correspondence Principle

Note that $H^\wedge$ is derived from the classical energy $p2/2m+V(x)$ simply by replacing $p \rightarrow -i\hbar(d/dx)$. This is an example of the Correspondence Principle initially proposed by Niels Bohr that states that the behavior of systems described by quantum theory reproduces classical physics in the limit of large quantum numbers.

It is a general principle of Quantum Mechanics that there is an operator for every physical observable. A physical observable is anything that can be measured. If the wavefunction that describes a system is an eigenfunction of an operator, then the value of the associated observable is extracted from the eigenfunction by operating on the eigenfunction with the appropriate operator. The value of the observable for the system is then the eigenvalue, and the system is said to be in an eigenstate. Equation 3.3.8 states this principle mathematically for the case of energy as the observable. If the wavefunction is not the eigenfunction of the operation, then the measurement will give an eigenvalue (by definition), but not necessarily the same one for each measurement (this will be discussed in more detail in later section).

✓ Common Operators

Although we could theoretically come up with an infinite number of operators, in practice there are a few which are much more important than any others.

- **Linear Momentum:**

  The linear momentum operator of a particle moving in one dimension (the x-direction) is

$$p^\wedge x = -i\hbar \ \partial/\partial x \tag{3.3.9}$$

  and can be generalized in three dimensions:

$$\vec{p}\ ^\wedge = -i\hbar\nabla \tag{3.3.10}$$

- **Position**

The position operator of a particle moving in one dimension (the x-direction) is

$$x\hat{} = x \qquad (3.3.11)$$

and can be generalized in three dimensions:

$$r^{\rightarrow}\hat{} = r^{\rightarrow} \qquad (3.3.12)$$

where $r^{\rightarrow} = (x, y, z)$.

- **Kinetic Energy**

Classically, the kinetic energy of a particle moving in one dimension (the x-direction), in terms of momentum, is

$$KEclassical = p2x/2m \qquad (3.3.13)$$

Quantum mechanically, the corresponding kinetic energy operator is

$$KE\hat{}quantum = -(\hbar 2/2m)\ \partial 2/\partial x2 \qquad (3.3.14)$$

and can be generalized in three dimensions:

$$KE\hat{}quantum = -(\hbar 2/2m)\ \nabla 2 \qquad (3.3.15)$$

- **Angular Momentum:**

Angular momentum requires a more complex discussion, but is the cross product of the position operator $r^{\rightarrow}\hat{}$ and the momentum operator $p\hat{}$

$$L^{\rightarrow}\hat{} = -i\hbar(r^{\rightarrow} \times \nabla) \qquad (3.3.16)$$

- **Hamiltonian:**

The Hamiltonian operator corresponds to the total energy of the system

$$H\hat{} = -(\hbar 2/2m)\ \ \partial 2/\partial x2 + V(x) \qquad (3.3.17)$$

and it represents the total energy of the particle of mass m in the potential $V(x)$. The Hamiltonian in three dimensions is

$$H^\wedge = -(\hbar 2/2m)\,\nabla 2 + V(\vec{r}\,) \tag{3.3.18}$$

- **Total Energy:**

The energy operator from the time-dependent Schrödinger equation

$$i\hbar\,(\partial/\partial t)\,\Psi(x,t) = H^\wedge\ \Psi(x,t) \tag{3.3.19}$$

The right hand side of Equation 3.3.6 is the Hamiltonian Operator. In addition, determining system energies, the Hamiltonian operator dictates the time evolution of the wavefunction

$$H^\wedge\Psi\,(x,t) = i\hbar\,\partial\Psi(x,t)/\partial t \tag{3.3.20}$$

This aspect will be discussed in more detail elsewhere.

✓ Eigenstate, Eigenvalues, Wavefunctions, Measurables and Observables

In general, the wavefunction gives the "state of the system" for the system under discussion. It stores all the information available to the observer about the system. Often in discussions of quantum mechanics, the terms eigenstate and wavefunction are used interchangeably. The term eigenvalue is used to designate the value of measurable quantity associated with the wavefunction.

- If you want to measure the energy of a particle, you have to operate on the wavefunction with the Hamiltonian operator (Equation 3.3.6).
- If you want to measure the momentum of a particle, you have to operate on wavefunction with the momentum operator (Equation 3.3.9).
- If you want to measure the position of a particle, you have to operate on wavefunction with the position operator (Equation 3.3.11).
- If you want to measure the kinetic energy of a particle, you have to operate on wavefunction with the kinetic energy operator (Equation 3.3.14).

When discussing the eigenstates of the Hamiltonian (H^), the associated eigenvalues represent energies and within the context of the momentum operators, the associated eigenvalues refer to the momentum of the particle. However, not all wavefunctions (ψ) are eigenstates of an operator (ϕ) − and if they are not, they can usually be written as superpositions of eigenstates.

$$\psi = \sum ci\phi i \tag{3.3.21}$$

This will be discussed in more detail in later sections.

While the wavefunction may not be the eigenstate of an observable, when that

operator operates on that wavefunction, the wavefunction becomes an eigenstate of that observable and only eigenvalues can be observed. Another way to say this is that the wavefunction "collapses" into an eigenstate of the

observable. Because quantum mechanical operators have different forms, their associated eigenstates are similarly often (i.e., most of the time) different. For example, when a wavefunction is an eigenstate of total energy, it will not be an eigenstate of momentum.

If a wavefunction is an eigenstate of one operator, (e.g., momentum), that state is not necessarily an eigenstate of a different operator (e.g., energy), although not always.

The wavefunction immediately after a measurement is an eigenstate of the operator associated with this measurement. What happens to the wavefunction after the measurement is a different topic.

- ✓ **Example 3.3.1**

Confirm that the following wavefunctions are eigenstates of linear momentum and kinetic energy (or neither or both):

a. $\psi = A\ sin(ax)$
b. $\psi = N\quad exp(-ix/\hbar)$

- ✓ **Strategy**

This question is asking if the eigenvalue equation holds for the operators and these wavefunctions. This is just asking if these wavefunctions are solutions to Equation 3.3.2 using the operators in Equations 3.3.9 and 3.3.14, i.e., are these equations true:

$$p\hat{}x\ \psi = px\ \psi \tag{3.3.22}$$

$$KE\hat{}\ \psi = KE\ \psi \tag{3.3.23}$$

where px and KE are the measurables (eigenvalues) for these operators.

✓ **Solution**

a. Let's evaluate the left side of the linear momentum eigenvalue problem (Equation 3.3.22)

$$-i\hbar\ (\partial/\partial x)\ Asin(ax) = -i\hbar\ Aa\ cos(ax)$$

and compare to the right side of Equation 3.3.22

$$px\ A\ sin(ax)$$

These are not the same so this wavefunction is not an eigenstate of momentum.

Let's look at the left side of the kinetic energy eigenvalue problem (Equation 3.3.23)

$$-(\hbar 2/2m)\ \ \partial 2/\partial x2\ A\ sin(ax) = -(\hbar 2/2m)\ \partial/\partial x\ Aa\ cos(ax)$$

$$= +(\hbar 2/2m)\ \ Aa2\ sin(ax)$$

and compare to the right side

$$KE\ A\ sin(ax)$$

These are same, so this specific wavefunction is an eigenstate of kinetic energy. Moreover, the measured kinetic energy will be

$$KE = +(\hbar 2/2m)\ a2$$

b. Let's look at the left side of Equation 3.3.22 for linear momentum

$$-i\hbar\ (\partial/\partial x)\ N\ exp(-ix/\hbar) = -N\ exp(-ix/\hbar)$$

and the right side of Equation 3.3.22

$$px\ N\ exp(-ix/\hbar)$$

These are the same so this wavefunction is an eigenstate of momentum with momentum $px = -N$.

Let's look at the left side of Equation 3.3.23 for kinetic energy

$$\begin{aligned} -(\hbar 2/2m)\ \ \partial 2/\partial x2\ N\ exp(-ix/\hbar) &= +i(\hbar/2m)\ \ \partial/\partial x\ N\ exp(-ix/\hbar) \\ &= +1/2m\ \ N\ exp(-ix/\hbar) \end{aligned}$$

and the right side

$$KE\ N\ exp(-ix/\hbar)$$

These are same so this wavefunction is an eigenstate of kinetic energy. And the measured kinetic energy will be

$$KE = 1/2m$$

This wavefunction is an eigenstate of both momentum and kinetic energy.

✓ **Exercise 3.3.1**

Are $\psi = M\ exp(-bx)$ functions eigenstates of linear momentum and kinetic energy (or neither or both)?

✓ **Answer**

Ψ is an eigenstate of linear momentum with an eigenvalue of $bi\hbar$ and also an eigenstate of kinetic energy with an eigenvalue of $b2$.

3.4: Wavefunctions Have a Probabilistic Interpretation

✓ **Learning Objectives**

- To understand that wavefunctions can have probabilistic interpretations.
- To calculate the probabilities directly from a wavefunctions

For a single-particle system, the wavefunction $\Psi(r^{\rightarrow}, t), or\ \psi(r^{\rightarrow})$ for the time-independent case, represents the amplitude of the still vaguely defined matter waves. Since wavefunctions can in general be complex functions, the physical significance cannot be found from the function itself because the √−1 is not a property of the physical world. Rather, the physical significance is found in the product of the wavefunction and its complex conjugate, i.e., the absolute square of the wavefunction, which also is called the square of the modulus (also called absolute value).

$$P(r^{\rightarrow}, t) = \Psi * (r^{\rightarrow}, t)\Psi(r^{\rightarrow}, t) \tag{3.4.1}$$

$$= |\Psi(r^{\rightarrow}, t)|2 \tag{3.4.2}$$

Where, $r^{\rightarrow}$ is a vector (x, y, z) specifying a point in three-dimensional space. The square is used, rather than the modulus itself, just like the intensity of a light wave depends on the square of the electric field.

Born proposed in 1926, the most commonly accepted interpretation of the wavefunction that the square of the modulus (Equation 3.4.2) is proportional to the probability density (probability per unit volume) that the electron is in the volume $d\tau$ located at ri. Since the wavefunction represents the wave properties of matter, the probability amplitude $P(x, t)$ will also exhibit wave-like behavior. Probability density is the three-dimensional analog of the diffraction pattern that appears on the two-dimensional screen in the double-slit diffraction experiment for electrons. The idea that we can understand the world of atoms and molecules only in terms of probabilities is disturbing to some, who are seeking more satisfying descriptions through ongoing research.

The Born interpretation therefore calls the wavefunction the probability amplitude, the absolute square of the wavefunction is called the probability density, and the probability density times a volume element in three-dimensional space ($d\tau$) is the probability P

The probability that a single quantum particle moving in one spatial dimension will be found in a region $x \in [a, b]$ if a measurement of its location is performed is

$$P(x \in [a,b]) = \int_{a}^{b} |\psi(x)|2dx \tag{3.4.3}$$

In three dimensions, Equation 3.4.3 is represented differently

$$P(x \in [a,b]) = \int V|\psi(\vec{\tau})|2\ \ d\tau \tag{3.4.4}$$

This integration extends over a specified volume (V) with the symbol $d\tau$ designating the appropriate volume element (including a Jacobian) of the coordinate system adopted:

- Cartesian:

$$d\tau = dx\ dy\ dz \tag{3.4.5}$$

- Spherical:

$$d\tau = r2\ sin\phi\ dr\ d\theta\ d\phi \tag{3.4.6}$$

- Cylindrical:

$$d\tau = r\ dr\ d\phi\ dz \tag{3.4.7}$$

For rectilinear Cartesian space, Equation 3.4.4 can be is expanded with dimension explicitly indicated

$$P(x \in [a,b]) = \int_{ax}^{bx} \int_{ay}^{by} \int_{az}^{bz}\ |\psi(x,y,z)|2\ dx\ dy\ dz \tag{3.4.8}$$

where the limits of integration are selected to encompass the volume V of consideration.

The Born interpretation (Equation 3.4.2) of relating the wavefunction to probability forces certain demands on its mathematical behavior of wavefunctions and not any mathematical function can be a valid wavefunction.

✓ **Required Properties of Wavefunction**

- The wavefunction must be a single-valued function of all its coordinates since the probability density ought to be uniquely determined at each point in space.

- The wavefunction should be both finite as an infinite probability has no meaning.
- The wavefunction should be continuous everywhere, as expected for a physically meaningful probability density.

The conditions that the wavefunction be single-valued, finite and continuous--in short, "well behaved"-- lead to restrictions on solutions of the Schrödinger equation such that only certain values of the energy and other dynamical variables are allowed. This is called *quantization* and is in the feature that gives *quantum* mechanics its name.

It is important to note that this interpretation implies the wavefunction does **not** mean the particle is distributed over a large region as a sort of "charge cloud". The wavefunction is used to describe the electron motion that behaves like waves and satisfies a wave equation. This is akin to how a grade distribution in a large class does not represent a smearing of grades for a single student, but only makes sense when taking into account that the distribution is the result of many measurables (e.g., student performances).

3.5: The Energy of a Particle in a Box is Quantized

✓ **Learning Objectives**

- Solve the particle-in-a-box model used to describing a trapped particle in 1 D well
- Characterize the particle-in-a-box eigenstates (i.e., wavefunctions) and the eigen energies as a function of the quantum number
- Demonstrate that the eigenstates are orthogonal

The *particle in the box* model system is the simplest non-trivial application of the Schrödinger equation, but one which illustrates many of the fundamental concepts of quantum mechanics. For a particle moving in one dimension (again along the x- axis), the Schrödinger equation can be written

$$-(\hbar 2/2m)\ \psi''(x) + V(x)\,\psi(x) = E\psi(x)$$

Assume that the particle can move freely between two endpoints $x = 0$ and $x = L$, but cannot penetrate past either end. This is equivalent to a potential energy dependent on xx with

$$V(x) = \begin{cases} 0 & 0 \leq x \leq L \\ \infty & x < 0 \; and \; x > L \end{cases}$$

This potential is represented in Figure 3.5.1 The infinite potential energy constitutes an impenetrable barrier since the particle would have an infinite potential energy if found there, which is clearly impossible.

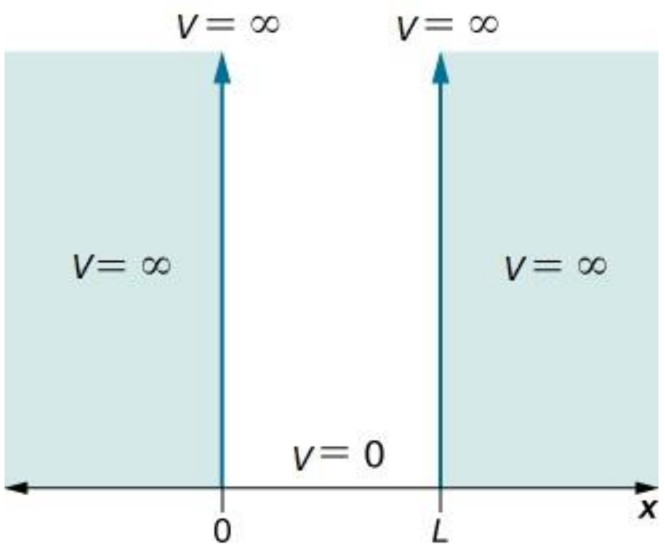


Figure 3.5.1: The barriers outside a one-dimensional box have infinitely large potential, while the interior of the box has a constant, zero potential. (CC-BY 4.0; OpenStax).

The particle is thus bound to a "*potential well*" since the particle cannot penetrate beyond $x = 0 \; or \; x = L$

$$\psi(x) = 0 \quad for \; x < 0 \; and \; x > L \tag{3.5.1}$$

By the requirement that the wavefunction be continuous, it must be true as well that

$$\psi(0) = 0 \qquad and \qquad \psi(L) = \; 0 \tag{3.5.2}$$

which constitutes a pair of boundary conditions on the wavefunction within the box. Inside the box, $V(x) = 0$, so the Schrödinger equation reduces to the free-particle form:

$$-(\hbar 2/2m)\, \psi''(x) = E\, \psi(x) \tag{3.5.3}$$

with $0 \leq x \leq L$.

We again have the differential equation

$$\psi''(x) + \; k2\, \psi(x) = 0 \tag{3.5.4}$$

with

$$k2 \ = 2mE/\hbar 2 \tag{3.5.5}$$

The general solution can be written

$$\psi(x) = A\ sinkx\ \ + B\ coskx \tag{3.5.6}$$

where A and B are constants to be determined by the boundary conditions in Equation 3.5.2 By the first condition, we find

$$\psi(0)\ \ = A\ sin0 + B\ cos0 = B = 0 \tag{3.5.7}$$

The second boundary condition at $x = L$ then implies

$$\psi(a) = A\ sin\ kL = 0 \tag{3.5.8}$$

It is assumed that $A \neq 0$, for otherwise $\psi(x)$ would be zero everywhere and the particle would disappear (i.e., the trivial solution). The condition that $sin\ kx = 0$ implies that

$$kL = n\pi \tag{3.5.9}$$

Where, n is a integer, positive, negative or zero. The case $n = 0$ must be excluded, for then $k = 0$ and again $\psi(x)$ would vanish everywhere. Eliminating k between Equation 3.5.4 and 3.5.9, we obtain

$$En = (\hbar 2\pi 2/2mL2)n2 = (h2/8mL2)n2 \tag{3.5.10}$$

with $n = 1,2,,3\ldots$.

These are the only values of the energy which allows solutions of the Schrödinger Equation 3.5.3 consistent with the boundary conditions in Equation 3.5.2. The integer n, called a *quantum number*, is appended as a subscript on E to label the allowed energy levels. Negative values of n add nothing new because the energies in Equation 3.5.10 depends on $n2$.

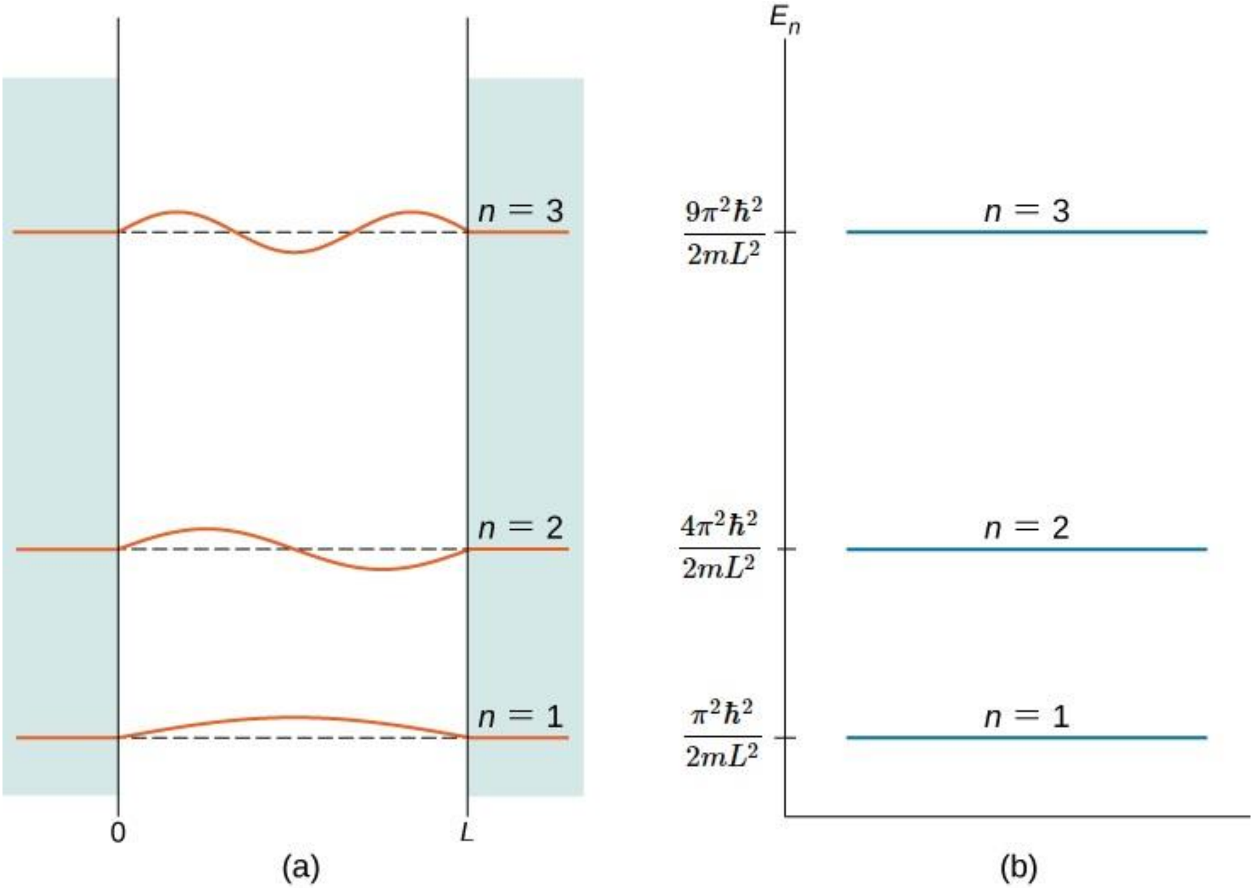


Figure 3.5.2: A plot of $\psi n(x)$ for the first four wavefunctions. (CC-BY 4.0; OpenStax).

Figure 3.5.2 shows part of the energy-level diagram for the particle in a box. The occurrence of discrete or quantized energy levels is characteristic of a bound system, that is, one confined to a finite region in space. For the free particle, the absence of confinement allowed an energy continuum. Note that, in both cases, the number of energy levels is infinite-denumerably infinite for the particle in a box, but nondenumerable infinite for the free particle.

The particle in a box assumes its lowest possible energy when $n = 1$, namely

$$E1 = h2/8mL2 \tag{3.5.11}$$

The state of lowest energy for a quantum system is termed its *ground state*.

✓ **Zero Point Energy**

An interesting point is that $E1 > 0$, whereas the corresponding classical system would have a minimum energy of zero. This is a recurrent phenomenon in quantum mechanics. The residual energy of the ground state, that is, the energy in excess of the classical minimum, is known as zero-point energy. In effect, the kinetic energy, hence the momentum, of a bound particle cannot be reduced to zero. The minimum value of momentum is found by equating $E1$ to $p2/2m$, giving $pmin = \ \pm h/2L$. This can be expressed as an uncertainty in momentum given by $\varDelta p \approx h/L$. Coupling this with the uncertainty in position, $\varDelta x \approx L$, from the size of the box, we can write

$$\varDelta x \varDelta p \approx h \tag{3.5.12}$$

This is in accord with the Heisenberg uncertainty principle.

The particle-in-a-box eigenfunctions are given by Equation 3.5.13, with $B = 0$ and $k = n\pi/L = a$, in accordance with Equation 3.5.9

$$\psi n(x) = Asin(n\pi x/L) \tag{3.5.13}$$

with $n = 1,2,3 \ldots$

These, like the energies, can be labeled by the quantum number n. The constant A, thus far arbitrary, can be adjusted so that $\psi n(x)$ is normalized. The normalization condition is, in this case,

$$\int_0^a [\psi n(x)]2 \, dx = 1 \tag{3.5.14}$$

the integration running over the domain of the particle $0 \leq x \leq L$. Substituting Equation 3.5.13 into Equation 3.5.14,

$$A^2 \int_0^L sin2 \ (n\pi x/L)dx = A^2 \ (L/n\pi) \int_0^{n\pi} sin2 \ \theta \ d\theta \tag{3.5.15}$$

$$= A^2 \ \ L/2 = 1 \tag{3.5.16}$$

We have made the substitution $\theta = n\pi x/L$ and used the fact that the average value of $sin2\,\theta$ over an integral number of half wavelengths equals 1/2 (alternatively, one could refer to standard integral tables). From Equation 3.5.16, we can identify the general normalization constant

$$A = \sqrt{2/L} \tag{3.5.17}$$

for all values of n. Finally, we can write the normalized eigenfunctions:

$$\psi n(x) = \sqrt{2/L}\ sin\ (n\pi x/L) \tag{3.5.18}$$

with $n = 1,2,3\ldots$

The first few eigenfunctions and the corresponding probability distributions are plotted in Figure 3.5.3. There is a close analogy between the states of this quantum system and the modes of vibration of a violin string. The patterns of standing waves on the string are, in fact, identical in form with the wavefunctions in Equation 3.5.18.

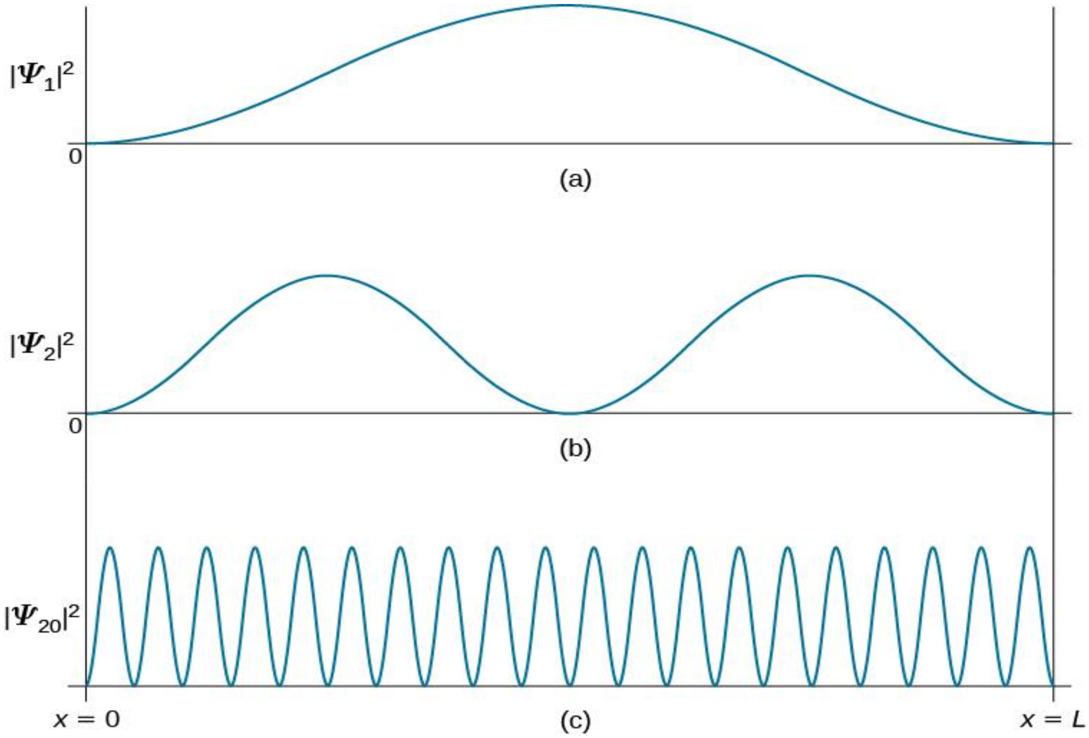


Figure 3.5.3: The probability density distribution $|\psi n(x)|2|$ for a quantum particle in a box for: (a) the ground state, n=1; (b) the first excited state, n=2; and (c) the nineteenth excited state, n=2. (CC-BY 4.0; OpenStax).

✓ Nodes and Curvature

A significant feature of the particle-in-a-box quantum states is the occurrence of nodes. These are points, other than the two end points (which are fixed by the boundary conditions), at which the wavefunction vanishes. At a node there is exactly zero probability of finding the particle. The nth quantum state has, in fact, n−1 nodes. It is generally true that the number of nodes increases with the energy of the quantum state, which can be rationalized by the following qualitative argument. As the number of nodes increases, so does the number and the steepness of the 'wiggles' in the wavefunction. It's like skiing down a slalom course. Accordingly, the average curvature, given by the second derivative, must increase. But the second derivative is proportional to the kinetic energy operator. Therefore, the more nodes, the higher the energy. This will prove to be an invaluable guide in more complex quantum systems.

✓ Example 3.5.1: Excited State Probabilities

For a particle in a one-dimensional box of length L, the second excited state wavefunction ($n = 3$) is

$$\psi 3 = \sqrt{2/L}\ \ sin\ (3\pi x/L)$$

- What is the probability that the particle is in the left half of the box?
- What is the probability that the particle is in the middle third of the box?

✓ Solution

Probability that the particle will be found between a and b is

$$P(a,b) = \int_a^b \psi 2 \quad dx$$

For this problem,

$$\psi 3 = \sqrt{2/L}\ \ sin\ (3\pi x/L)$$

therefore,

$$P(a,b) = (2/L)\int_{a}^{b} sin2\ (3\pi x/L)\ dx$$

$$= (2/L)(x/2 - Lsin(6\pi x/L)/12\pi)\ |\ ba$$

$$= ((b-a)/L) - (1/6\pi)\ [sin(6\pi b/L) - sin(6\pi a/L)]$$

(a) The probability that the particle is in the left half of the box is

$$P(0, L/2) = (L/2 - 0)/L - (1/6\pi)\ [sin(6\pi(L/2)/L) - sin(6\pi\ (0)/L)] = 1/2$$

(b) The probability that the particle is in the middle third of the box

$$P(L/3,2L/3) = (2L/3 - L/3)/L - (1/6\pi)[sin(6\pi(2L/3)/L) - sin(6\pi(L/3)/L)]$$

$$= 1/3$$

✓ **Exercise 3.5.1: Ground State Probability**

For a particle in a one-dimensional box, the ground state wavefunction is

$$\psi 1 = \sqrt{2/L}\, sin(x\pi/L)$$

What is the probability that the particle is in the left half of the box in the ground state?

✓ **Answer**

$$P(0, L/2) = 2/L\int_{0}^{L/2} sin2\ (x\pi/L)dx$$

$$= (2/L)\ L\pi/L +\ sin\ (0) +\ sin\ (L\pi/L)/(4\pi/L)$$

$$= 1/2$$

This is the same answer as for the $\psi 3$ state in Example 3.5.1. This is because the eigenstate squared (. e., probability density) for the particle in a 1D box will always be symmetric around the center of the box. So, there will be equal probability to be on either side (i.e., no side is favored).

✓ Time Dependence and Complex Nature of Wavefunctions

Recall that the time-dependence of the wavefunction with time-independent potential was discussed in Section 3.1 and is expressed as

$$\Psi(x,t) = \psi(x) exp - iEt/\hbar \tag{3.5.19}$$

so, for the particle in a box, these are

$$\psi n(x) = \sqrt{2/L}\, sin\ (n\pi x/L)\ exp - iEnt/\hbar \tag{3.5.20}$$

with En given by Equation 3.5.10.

The phase part of Equation 3.5.20 can be expanded into a real part and a complex components. So, the total wavefunction for a particle in a box is

$$\Psi(x,t) = (\sqrt{2/L}\, sin\ (n\pi x/L))(cos\ Ent/\hbar) - i(\sqrt{2/L}\, sin\ (n\pi x/L))(sin\ Ent/\hbar) \tag{3.5.21}$$

which can be simplified (slightly) to

$$\Psi(x,t) = \left(\sqrt{2/L} sin(n\pi x/L)\right)(cosEnt/\hbar) - i(\sqrt{2/L}\, sin\ (n\pi x/L))(cos\ Ent/\hbar - \pi/2) \tag{3.5.22}$$

As discussed previously, the imaginary part of the total wavefunction oscillates out of phase by π/2 with respect to the real part (we call this "out of phase"). This is demonstrated in the time-dependent behavior of the first three eigenfunctions in Figure 3.5.4.

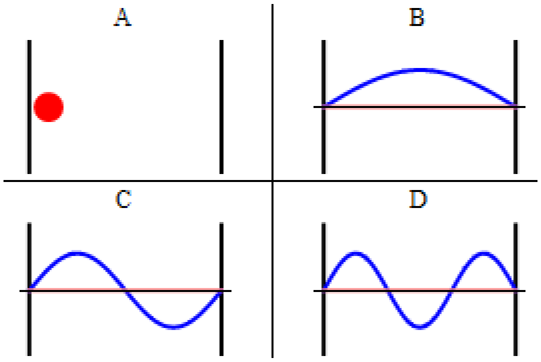


Figure 3.5.4: Some trajectories of a particle in a box according to Newton's laws of classical mechanics (A), and according to the Schrödinger equation of quantum mechanics (B-D). In (B-D), the horizontal axis is position, and the vertical axis is the real part (blue) and imaginary part (red) of the wavefunction. The states (B, C, D) are energy eigenstates. (Public Domain; Sbyrnes321 via Wikipedia).

Note that as n increased, the energy of the wavefunction increases (Equation 3.5.10) and both the number of nodes and antinodes increase and the frequency of oscillation of the wavefunction increases.

It is generally true in quantum systems (not just for particles in boxes) that the number of nodes in a wavefunction increases with the energy of the quantum state.

- ✓ **Orthonormality of the Eigenstates**

Another important property of the eigenfunctions in Equation 3.5.18 applies to the integral over a product of two *different* eigenfunctions (Equation 3.5.18). It is easy to see from Figure 3.5.5 that the integral

$$\int_0^L \psi_2(x)\, \psi_1(x) dx = 0 \tag{3.5.23}$$

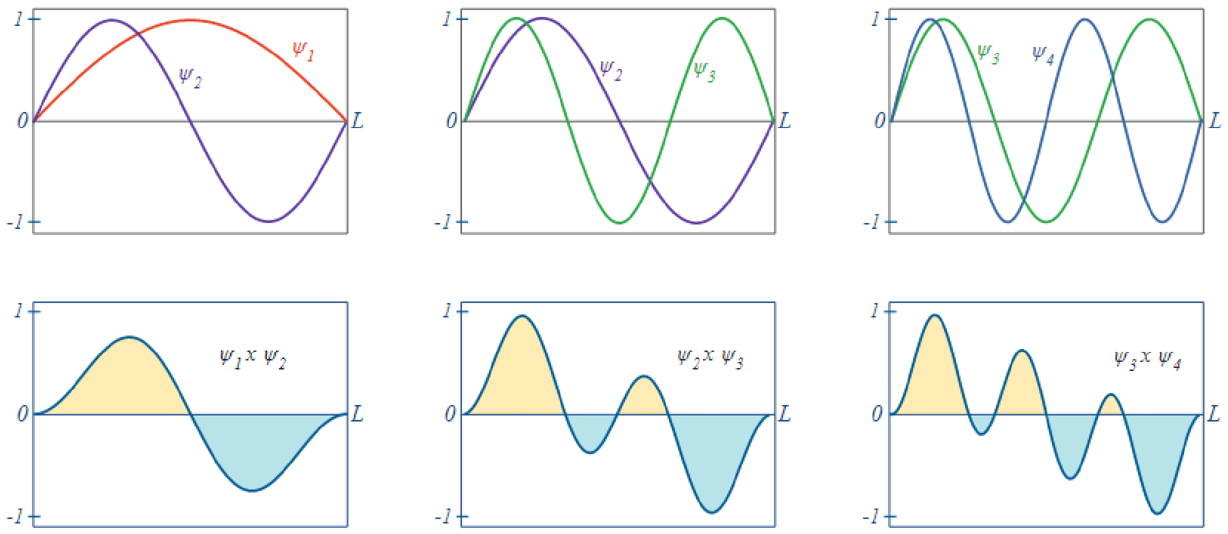


Figure 3.5.5: (Top Row): Select plots of the n=1 (red curves), n=2 (purple curves), n=3 (green curves), and n=4 (blue curves) eigenfunctions. (Bottom Row): Product of different eigenstates with positive (tan) and negative (cyan) areas emphasized. Note that the negative and positive areas perfectly cancel when added together. Created via fooplot (CC BY-NC; Ümit Kaya)

To prove this result in general, use the trigonometric identity

$$sin\alpha\ sin\beta = (1/2)[cos(\alpha-\beta) - cos(\alpha+\beta)] \tag{3.5.24}$$

to show that

$$\int_0^L \psi m(x)\ \psi n(x)dx\ = 0 \quad if\ \ m \neq n \tag{3.5.25}$$

This property is called **orthogonality**. We will show in the next Chapter, that this is a general result from quantum-mechanical eigenfunctions. The normalization (Equation 3.5.23) together with the orthogonality (Equation 3.5.25) can be combined into a single relationship

$$\int_0^L \psi m(x)\ \psi n(x)dx = \delta mn \tag{3.5.26}$$

In terms of the *Kronecker delta*

$$\delta mn = \begin{cases} 1 & if\quad m = n \\ 0 & if\quad m \neq n \end{cases} \tag{3.5.27}$$

A set of functions $\{\psi n\}$ which obeys Equation 3.5.26. is called *orthonormal*.

- ✓ **Example 3.5.2**

Evaluate $\langle\psi 3|\psi 3\rangle$

for the normalized wavefunctions:

$$|\psi 3\rangle = \sqrt{2/L}\, sin(3x\pi/L)$$

- ✓ **Strategy**

These are four different integrals and we can solve them directly or use orthonormality (Equation 3.5.27) to evaluate.

$$\langle\psi 3|\psi 3 = \int_{-\infty}^{\infty} (\sqrt{2/L}\, sin(3x\pi/L))\, (\sqrt{2/L}\, sin(3x\pi/L))dx$$

$$= 2/L \int_{-\infty}^{\infty} \big(sin2\ (3x\pi/L)\big)dx$$

This is an integration over an even function, so it cannot be tossed out via symmetry. We can use the Trigonometry relationship in Equation 3.5.24 to get

$$2/L \int_{-\infty}^{\infty} \big(sin2\ (3x\pi/L)\big)dx = 2/L \int_{-\infty}^{\infty} \frac{1}{2}\left(1 - cos\frac{6\pi x}{L}\right) dx$$

and we can continue the fun. However, there is no need. Since the we can recognize that $\langle\psi 3|\psi 3\rangle$ is 1 by the normalization criteria which is folded into the orthonormal criteria (Equation 3.5.27).

Therefore ⟨ψ3|ψ3⟩=1.

We can expand this integral and evaluate, but since the integrand is odd, this integral is zero. Alternatively, we can use the orthogonality criteria into the greater orthonormal criteria (Equation 3.5.27).

3.6: Wavefunctions Must Be Normalized

✓ **Learning Objectives**

- Calculate the probability of an event from the wavefunction
- Understand the utility and importance of normalizing wavefunctions
- Demonstrate how to normalize an arbitrary wavefunction

✓ **Extracting Probabilities**

Since wavefunctions can in general be complex functions, the physical significance of wavefunctions cannot be found from the functions themselves because the √−1 is not a property of the physical world. Rather, the physical significance is found in the product of the wavefunction and its complex conjugate, i.e., the absolute square of the wavefunction, which also is called the **square of the modulus**.

$$\Psi * (r,t)\, \Psi(r,t) = |\Psi(r,t)|2 \tag{3.6.1}$$

where r is a vector specifying a point in three-dimensional space. The square is used, rather than the modulus itself, just like the intensity of a light wave depends on the square of the electric field. Remember that the Born interpretation is that $\psi * (ri)\ \psi(ri) d\tau$ is the **probability** that the electron is in the volume $d\tau$ located at ri. The Born interpretation therefore calls the wavefunction the probability amplitude, the absolute square of the wavefunction is called the **probability density**, and the probability density times a volume element in three-dimensional space ($d\tau$) is the probability.

Since the squared magnitude $|\psi|2$ of the wavefunction of a particle can be interpreted as the probability density, then the probability for a one-dimensional wavefunction between the points x=a and x=b can be calculated by

$$P1D = \int_a^b |\psi(x)|2\, dx \tag{3.6.2}$$

This is just the area under the under the $|\psi|2$ curve (Figure 3.6.1).

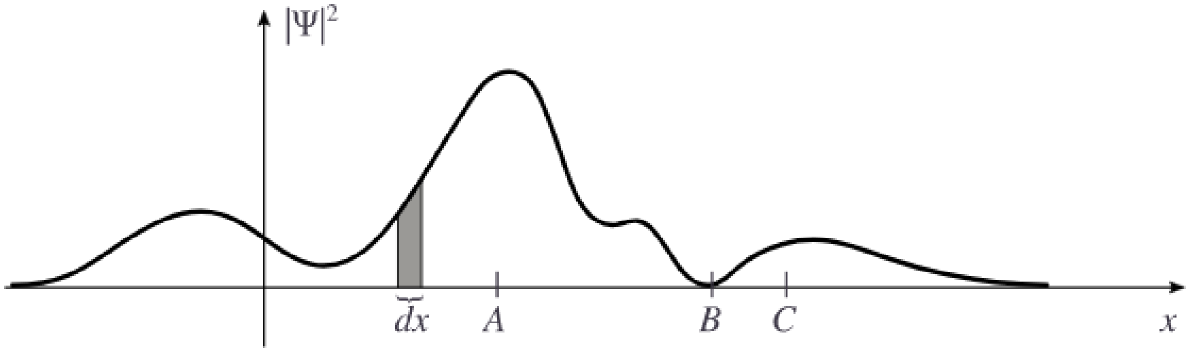


Figure 3.6.1: The probability can be interpreted as an area under the probability density |ψ|2. (CC BY-NC Copyright; Ümit Kaya)

If the probability of a two-dimensional wavefunction is being evaluated, then Equation 3.6.2 will be amended to include a double integral:

$$P_{2D} = \iint a_{1}, a_{2} b_{1}, b_{2} |\psi(x,y)|_{2}\, dx\, dy \qquad (3.6.3)$$

and similarly, a triple integral would be used for calculating probabilities of three-dimensional wavefunctions:

$$P_{3D} = \iiint a_{1}, a_{2}, a_{3} b_{1}, b_{2}, b_{3} |\psi(x,y,z)|_{2}\, dx\, dy\, dz \qquad (3.6.4)$$

✓ **Example 3.6.1: Probability of a Particle in a Box**

Calculate the probability of finding an electron at L/2 in a box of infinite height within an interval ranging from $L/2 - L/200\ to\ L/2 + L/200$ for the $n = 1$ and $n = 2$ states. Since the length of the interval, $L/100$, is small compared to L, you can get an approximate answer without explicitly integrating.

✓ **Solution**

The wavefunction for the particle in a box is

$$\psi(x) = \sqrt{2/L}\, sin(nx\pi/L)$$

and the wavefunction for the n=1 state is

$$\psi n = 1 = \sqrt{2/L}\, sin(x\pi/L)$$

From the interpretation that the wavefunction modulus squared is the probability density, we can establish the following integral to solve the problem (note the limits of integration)

$$|\psi n = 1|^2 = 2/L \int_{99L/200}^{101L/200} sin^2\,(x\pi/L)dx \tag{3.6.5}$$

We can solve this, but we can also recognize that Equation 3.6.5 is just calculating an area that can be approximated as the area of a rectangle with a height $((2/L)\ sin2(\pi x/L))$ at $x = L/2$ and width $\Delta x = L/100$ (Figure 3.6.2).

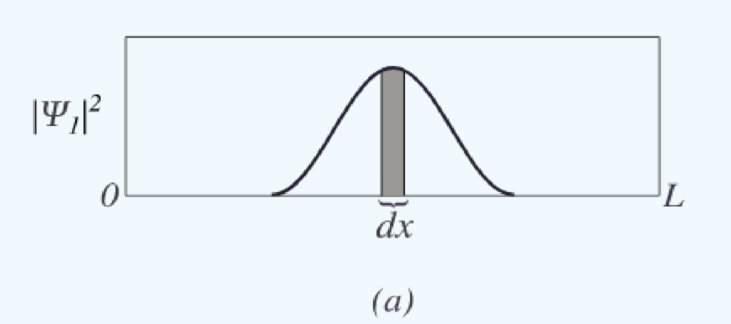


Figure 3.6.2: The probability can be interpreted as an area under the probability density $|\psi 1|2$. (CC BY-NC Copyright; Ümit Kaya)

This area can be computed:

$$|\psi n = 1|2 \approx (2/L)sin2(\pi(L/2)/L)\Delta x$$

$$\approx (2/L)(L/100)$$

$$\approx 1/50 = 0.02$$

Given that the wavefunction is sinusoidal, the actual probability of finding an electron within the given interval at $L2$ should be slightly less because of the behavior of the sinusoid at $L2$ is at its peak of the wavefunction (Figure 3.6.2).

The wavefunction for the $n = 2$ state

$$\psi n = 2 = \sqrt{2/L}\, sin(2x\pi/L)$$

so, the integral that we need to construct and solve is

$$|\psi n = 2|^2 = 2/L \int_{99L/200}^{101L/200} sin^2\,(2x\pi/L)dx$$

We can use the same graphical interpretation as above but using the probability density of the $\psi 2$ wavefunction (Figure 3.6.3).

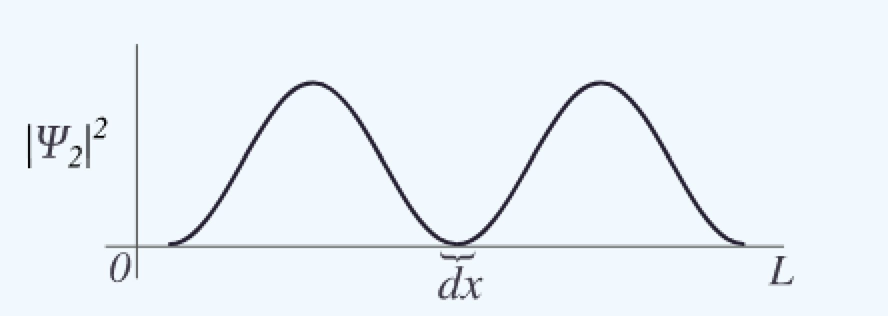


Figure 3.6.3: The probability can be interpreted as an area under the probability density $|\psi 2|2$. (CC BY-NC Copyright; Ümit Kaya)

$$|\psi n = 1|2 \approx 2/L\, sin2(2\pi(L/2)/L)\Delta x \approx 0$$

The probability of finding an electron in a box at $L2$ for $n = 2$ is approximately zero.

✓ Normalizing of the Wavefunction

A probability is a real number between 0 and 1, inclusive. An outcome of a measurement which has a probability 0 is an impossible outcome, whereas an outcome which has a probability 1 is a certain outcome. According to Equation 3.6.1, the probability of a measurement of x yielding a result between −∞− and +∞ is

$$P_{x\,\in\,-\infty:\,\infty}(t) = \int_{-\infty}^{\infty} |\psi(x,t)|_2\, dx. \tag{3.6.6}$$

However, a measurement of x *must* yield a value between −∞ and +∞ since the particle must be located somewhere. It follows that Px∈−∞:∞(t)=1 or

$$\int_{-\infty}^{\infty} |\psi(x,t)|^2 \, dx. = 1 \qquad (3.6.7),$$

which is generally known as the **normalization condition** for the wavefunction.

✓ Time Dependence to the Wavefunction

Now, it is important to demonstrate that if a wavefunction is initially normalized then it stays normalized as it evolves in time according to the time-dependent Schrödinger's equation. If this is not the case then the probability interpretation of the wavefunction is untenable, since it does not make sense for the probability that a measurement of x yields *any* possible outcome (which is, manifestly, unity) to change in time. Hence, we require that

$$d/dt \int_{-\infty}^{\infty} |\psi(x,t)|^2 \, dx. = 0 \qquad (3.6.8)$$

for wavefunctions satisfying the time-dependent Schrödinger's equation (this results from the time-dependent Schrödinger's equation and Equation 3.6.7). The above equation gives

$$d/dt \int_{-\infty}^{\infty} \psi^* \, \psi \, dx \, dx. = \int_{-\infty}^{\infty} (\partial\psi^*/\partial t) \, \psi \; + \; \psi^* (\partial\psi/\partial t))dx = 0 \qquad (3.6.9)$$

Now, multiplying Schrödinger's equation by $\psi^*/(i\hbar)$, we obtain

$$\psi^* \; \partial\psi/\partial t = (i/2m) \, \psi^* \; \partial^2\psi/\partial x^2 - (i/\hbar) \, V|\psi|^2 \qquad (3.6.10)$$

The complex conjugate of this expression yields

$$\psi \, \partial\psi^*/\partial t = (-i/2m) \, \psi \, \partial^2\psi^*/\partial x^2 + \; (i/\hbar) \, V \, |\psi|^2 \qquad (3.6.11)$$

since

- $(AB)^* = A^* B^*,$
- $A^{**} = A, and$
- $i^* = -i.$

Summing Equation 3.6.10 and 3.6.11 results in

$$\partial\psi*/\partial t\ \ \psi+\psi*\partial\psi/\partial t=i/2m\ (\psi*\partial 2\psi/\partial x2-\psi\,\partial 2\psi*/\partial x2)$$
$$=i/2m\ \ (\partial/\partial x)(\psi*\ \ \partial\psi/\partial x-\psi\,\partial\psi*/\partial x). \qquad (3.6.12)$$

Equations 3.6.9 and 3.6.12 can be combined to produce

$$d/dt\int_{-\infty}^{\infty}|\psi|_{2}\,dx.\ dx=i/2m\ [\psi*\ \ \partial\psi/\partial x-\psi\,\partial\psi*/\partial x]\infty-\infty=0. \qquad (3.6.13)$$

The above equation is satisfied provided the wavefunction converges

$$lim|x|\rightarrow\infty|\psi|=0 \qquad (3.6.14)$$

However, this is a necessary condition for the integral on the left-hand side of Equation 3.6.7 to converge. Hence, we conclude that all wavefunctions which are *square-integrable* [i.e., are such that the integral in equation 3.6.7 converges] have the property that if the normalization condition Equation 3.6.7 is satisfied at one instant in time then it is satisfied at all subsequent times.

✓ Not all Wavefunctions can be Normalized

Not all wavefunctions can be normalized according to the scheme set out in Equation 3.6.7 For instance, a planewave wavefunction for a quantum free particle

$$\Psi(x,t)=\psi 0\ exp(i(kx-\omega t))$$

is not square-integrable, and, thus, cannot be normalized. For such wavefunctions, the best we can say is that

$$Px\in a\!:b(t)\propto\int_{-\infty}^{\infty}|\psi(x,t)|_{2}\,dx.$$

In the following, all wavefunctions are assumed to be square-integrable

and normalized, unless otherwise stated.

3.7: The Average Momentum of a Particle in a Box is Zero

✓ Learning Objectives

- Calculate the expectation value for a measurement
- Apply the expectation value concept to calculate average properties of a participle in a box model
- Understand the origin of a zero-point energy/zero-point motion.
- Extend the concept of orthogonality from vectors to mathematical functions (and wavefunctions).

Now that we have mathematical expressions for the wavefunctions and energies for the particle-in-a-box, we can answer several interesting questions. The answers to these questions use quantum mechanics to predict some important and general properties for electrons, atoms, molecules, gases, liquids, and solids. Key to addressing these questions is the formulation and use of expectation values. This is demonstrated below and used in the context of evaluating average properties (momentum of the particle in a box for the case below).

✓ Classical Expectation Values

The expectation value is the probabilistic expected value of the result (measurement) of an experiment. It is not the most probable value of a measurement; indeed, the expectation value may even have zero probability of occurring. The expected value (or expectation, mathematical expectation, mean, or first moment) refers to the value of a variable one would "expect" to find if one could repeat the random variable process an infinite number of times and take the average of the values obtained. More formally, the expected value is a weighted average of all possible values.

✓ Example 3.7.1: Classical Expectation Value of Exam Scores (a discretized example)

A classical example is calculating the expectation value (i.e., average) of the exam grades in the class. For example, if the class scores for an exam were

65	67	94	43	67	76	94	67

The discrete way is to sum up all scores and divide by the number of students:

$$\langle s\rangle = \sum iNs(i)/N \tag{3.7.1}$$

which of this example of scores is

$$\langle s\rangle = 65 + 67 + 94 + 43 + 67 + 76 + 94 + 768 = 71.625$$

Notice that the average is not an allowable score on an individual exam. Equation 3.7.1 can be rewritten with "probability" or "probability weights"

$$\langle s\rangle = \sum iNs(i)Ps(i) \tag{3.7.2}$$

Where, $Ps(i)$ is the probability of observing a score of s. This is just the number of times it occurs in a dataset divided by the number of elements in that data set. Applying Equation 3.7.2 to the set of scores, we need to calculate these weights:

Score	**65**	**67**	**94**	**43**	**76**
Ps	1/8	3/8	2/8	1/8	1/8

As with all probabilities, the sum of all probabilities possible must be one. These confirm that for the weights here:

$$18 + 38 + 28 + 18 + 18 = 88 = 1 \tag{3.7.3}$$

This is the discretized "normalization" criterion (the same as why we normalize wavefunctions). So, now we can use Equation 3.7.2 properly

$$\langle s\rangle = 65 \times 18 + 67 \times 38 + 94 \times 28 + 43 \times 18 + 76 \times 18 = 71.625$$

Hence, Equation 3.7.2 gives the same result, as expected, from Equation 3.7.1.

✓ **Quantum Expectation Values**

The extension of the classical expectation (average) approach in Example 3.7.1 using Equation 3.7.2 to evaluating quantum mechanical expectation values requires three small changes:

1. Switch from discretized to continuous variables
2. Substitute the wavefunction squared for the probability weights (i.e., the probability distribution)
3. Use an operator instead of the scalar

Hence, the quantum mechanical expectation value $\langle o \rangle$ for an observable, o, associated with an operator, $O^\wedge$, is given by

$$\langle o \rangle = \int_{-\infty}^{\infty} \psi * \; O^\wedge \, \psi \, dx. \tag{3.7.4}$$

where x is the range of space that is integrated over (i.e., an integration over all possible probabilities). The expectation value changes as the wavefunction changes and the operator used (i.e., which observable you are averaging over).

In general, changing the wavefunction changes the expectation value for that operator for a state defined by that wavefunction.

- ✓ **Average Energy of a Particle in a Box**

If we generalize this conclusion, such integrals give the average value for any physical quantity by using the operator corresponding to that physical observable in the integral in Equation 3.7.4. In the equation below, the symbol $\langle H \rangle$ is used to denote the average value for the total energy.

$$\langle H \rangle = \int_{-\infty}^{\infty} \psi * (x) \; H^\wedge \, \psi(x) \, dx \tag{3.7.5}$$

$$= \int_{-\infty}^{\infty} \psi * (x) \; KE^\wedge \, \psi(x) dx \; + \int_{-\infty}^{\infty} \psi * (x) \; V^\wedge \, \psi(x) dx \tag{3.7.6}$$

$$= \int_{-\infty}^{\infty} \psi * (x)(-\hbar 2/2m)(\partial 2/\partial x2)\psi(x) dx + \int_{-\infty}^{\infty} \psi * (x) \; V^\wedge \, \psi(x) dx \tag{3.7.7}$$

The Hamiltonian operator consists of a kinetic energy term and a potential energy term. The kinetic energy operator involves differentiation of the wavefunction to the right of it. This step must be completed before multiplying by the complex conjugate of the wavefunction. The potential energy, however, usually depends only on position and not momentum (i.e., it involves conservative forces). The potential energy operator therefore only involves the coordinates of a particle and does not involve differentiation. For this reason we do not need to use a caret over V in Equation 3.7.7

Equation 3.7.7can be simplified

$$\langle H\rangle = \langle KE\rangle + \langle V\rangle \tag{3.7.8}$$

The potential energy integral then involves only products of functions, and the order of multiplication does not affect the result, e.g., 6×4 = 4×6 = 24. This property is called the **commutative property**. The average potential energy therefore can be written as

$$\langle V\rangle = \int_{-\infty}^{\infty} V(x)\,\psi*(x)\ \psi(x)dx \tag{3.7.9}$$

This integral is telling us to take the probability that the particle is in the interval dx at x, which is $\psi*(x)\psi(x)dx$, multiply this probability by the potential energy at x, and sum (i.e., integrate) over all possible values of x. This procedure is just the way to calculate the average potential energy $\langle V\rangle$ of the particle.

✓ Average Position of a Particle in a Box

We can calculate the most probable position of the particle from knowledge of probability distribution, $\psi*\psi$. For the ground-state particle in a box wavefunction with n=1 (Figure 3.7.1a)

$$\psi n=1 = (\sqrt{2}/L)sin(\pi x/L) \tag{3.7.10}$$

This state has the following probability distribution (Figure 3.7.1b):

$$\psi*n=1\psi n=1 = (2/L)\ sin2(\pi x/L) \tag{3.7.11}$$

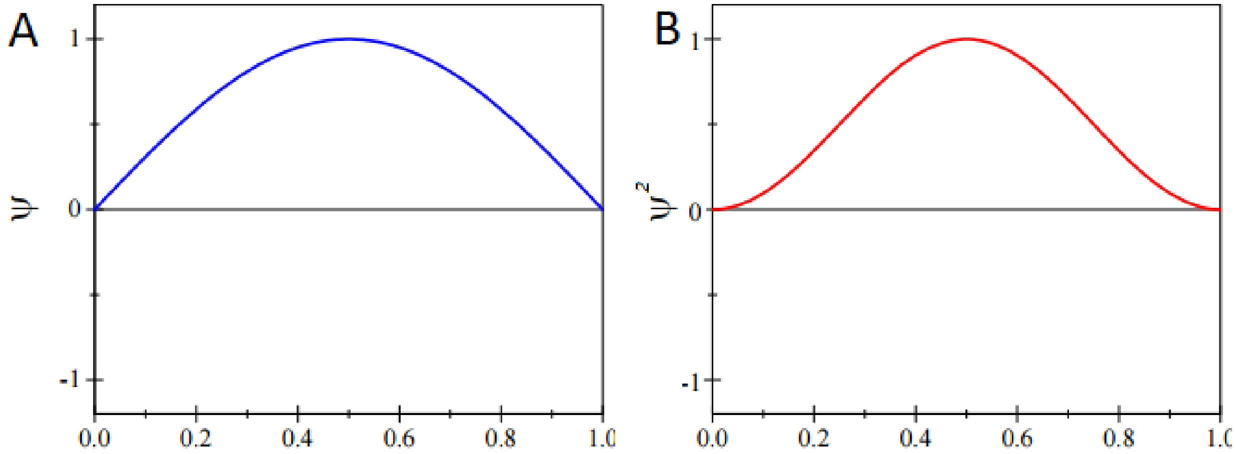


Figure 3.7.1: (left) The ground-state (n=1) wavefunction for a particle in a box. (right) The ground-state (n=1) probability for a particle in a box.

The expectation value for position with the $x^\wedge = x$ operation for any wavefunction (Equation 3.7.4) is

$$\langle x \rangle = \int_{-\infty}^{\infty} \psi * \, x \, \psi \, dx \tag{3.7.12}$$

which for the ground-state wavefunction (Equation 3.7.10) shown in Figure 3.7.1 is

$$\langle x \rangle = \int_{-\infty}^{\infty} \sqrt{2/L}\, sin(\pi x/L) x \;\sqrt{2/L}\; sin(\pi x/L) dx \tag{3.7.13}$$

$$= (2/L) \int_{-\infty}^{\infty} \; x \; sin2\, (\pi x/L) \tag{3.7.14}$$

✓ **Solution by Inspection**

Without even having to evaluate Equation 3.7.14, we can get the expectation value from simply inspecting $\psi * n = 1\ \psi n = 1\ in$ (Figure 3.7.1;right3.7.1;right). This is a symmetric distribution around the center of the box (L/2) so it is just as likely to be found in the left half than the right half. Moreover, specifically at any point a fixed distance away from the mean, i.e.

$$\psi * n = 1\ \psi n = 1(L/2 + \Delta x) = \psi * n = 1\ \psi n = 1(L/2 - \Delta x)$$

Therefore, the particle is most likely to be found at the center of the box. So

$$\langle x \rangle = L/2$$

✓ Average Momentum of a Particle in a Box

What is the average momentum of a particle in the box? We start with Equation 3.7.4 and use the momentum operator

$$p\hat{}_x = -i\hbar\, \partial/\partial x \tag{3.7.15}$$

✓ Example 3.7.3: The Average Momentum of a Particle in a Box is Zero

Even though the wavefunctions are not momentum eigenfunctions, we can calculate the expectation value for the momentum. Show that the expectation or average value for the momentum of an electron in the box is zero in every state (i.e., arbitrary values of n).

✓ Strategy

First write the expectation value integral (Equation 3.7.4) with the momentum operator. Then insert the expression for the wavefunction and evaluate the integral as shown here.

✓ Answer

$$\begin{aligned}\langle p\rangle &= \int_0^L \psi * n(x)(-i\hbar\, d/dx)\psi n(x)dx \\ &= \int_0^L (2/L)1/2\, sin(n\pi x/L)(-i\hbar\, d/dx)(2/L)1/2\, sin(n\pi x/L)dx \\ &= -i\hbar(2/L)\int_0^L sin(n\pi x/L)(d/dx)\, sin(n\pi x/L)dx \\ &= -i\hbar(2/L)(n\pi/L)\int_0^L sin(n\pi x/L)cos(n\pi x/L)dx = 0\end{aligned}$$

Note that this makes sense since the particles spends an equal amount of time traveling in the $+x$ and $-x$ direction.

✓ Interpretation

It may seem that this means the particle in a box does not have any momentum, which is incorrect because we know the energy is never zero. In fact, the energy that we obtained for the particle-in-a-box is entirely kinetic energy because we set the potential energy at 0. Since the kinetic energy is the momentum squared divided by twice the mass, it is easy to understand how the average momentum can be zero and the kinetic energy finite

✓ Did we just Violate the Uncertainty Principle?

Does the fact that the average momentum of an electron is zero and the average position is $L/2$ violate the Heisenberg Uncertainty Principle? No, because the Heisenberg Uncertainty Principle pertains to the uncertainty in the momentum and in the position, not to the average values. Quantitative values for these uncertainties can be obtained to compare with the limit set by the Heisenberg Uncertainty Principle for the product of the uncertainties in the momentum and position. However, to do this we need a quantitative definition of uncertainty, which is discussed in the following Section.

✓ Orthogonality

In vector calculus, orthogonality is the relation of two lines at right angles to one another (i.e., perpendicularity), but is generalized into n dimensions via zero amplitude "dot products" or "inner products." Hence, orthogonality is thought of as describing non-overlapping, uncorrelated, or independent objects of some kind. The concept of orthogonality extends to functions (wavefunctions or otherwise) too. Two functions ψA and ψB are said to be orthogonal if

$$\int_{allspace}^{L} \psi * A\, \psi B\, d\tau = 0 \tag{3.7.16}$$

In general, eigenfunctions of a quantum mechanical operator with different eigenvalues are orthogonal. Are the eigenfunctions of the particle-in-a-box Hamiltonian orthogonal?

3.8: A Particle in a Three-Dimensional Box

✓ **Learning Objectives**

- To demonstrate how the particle in 1-D box problem can extend to a particle in a 3D box
- Introduction to nodal surfaces (e.g., nodal planes)

The quantum particle in the 1D box problem can be expanded to consider a particle within a higher dimension as demonstrated elsewhere for a quantum particle in a 2D box. Here we continue the expansion into a particle trapped in a 3D box with three lengths Lx, Ly, and Lz. As with the other systems, there is NO FORCE (i.e., no potential) acting on the particles *inside* the box (Figure 3.8.1).

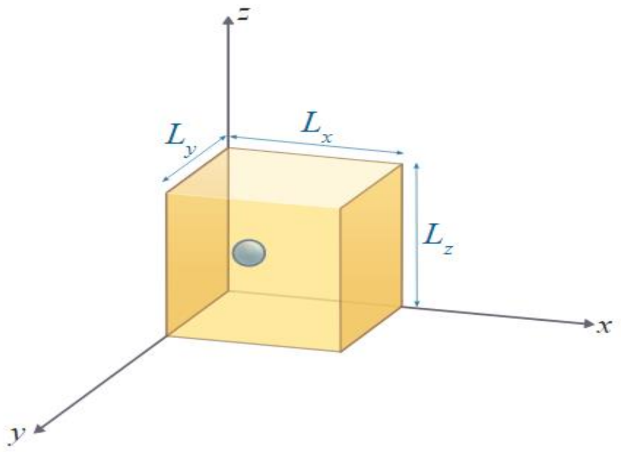


Figure 3.8.1: A particle in 3D box with three lengths Lx, Ly, and Lz. (CC BY-NC; Ümit Kaya)

The potential for the particle inside the box

$$V(\vec{r}) = 0 \tag{3.8.1}$$

- $0 \leq x \leq L_x$
- $0 \leq y \leq L_y$
- $0 \leq z \leq L_z$
- $L_x < x < 0$
- $L_y < y < 0$
- $L_z < z < 0$

$r^{\rightarrow}$ is the vector with all three components along the three axes of the 3-D box: $r^{\rightarrow} = Lx\ x^\wedge + Ly\ y^\wedge + Lz\ z^\wedge$. When the potential energy is infinite, then the wavefunction equals zero. When the potential energy is zero, then the wavefunction obeys the Time-Independent Schrödinger Equation

$$(-\hbar 2/2m)\ \nabla 2\psi(r) + V(r)\psi(r) = E\psi(r) \tag{3.8.2}$$

Since we are dealing with a 3-dimensional figure, we need to add the 3 different axes into the Schrödinger equation:

$$(-\hbar 2/2m)(d2\psi(r)/dx2 + d2\psi(r)/dy2 + d2\psi(r)/dz2) = E\psi(r) \tag{3.8.3}$$

The easiest way in solving this partial differential equation is by having the wavefunction equal to a **product** of individual function for each independent variable (e.g., the Separation of Variables technique):

$$\psi(x, y, z) = X(x)Y(y)Z(z) \tag{3.8.4}$$

Now each function has its own variable:

- $X(x)$ is a function of variable x only
- $Y(y)$ is a function of variable y only
- $Z(z)$ is a function of variable z only

Now substitute Equation 3.8.4 into Equation 3.8.3 and divide it by the xyz product:

$$d2\psi/dx2 = YZd2X/dx2 \Rightarrow (1/X)\ d2X/dx2 \tag{3.8.5}$$

$$d2\psi/dy2 = XZd2Y/dy2 \Rightarrow (1/Y)\ d2Y/dy2 \tag{3.8.6}$$

$$d2\psi/dz2 = XYd2Z/dz2 \Rightarrow (1/Z)\ d2Z/dz2 \tag{3.8.7}$$

$$((-\hbar 2/2mX)\ d2X/dx2)\ +\ (-\hbar 2/2mY)\ d2Y/dy2)$$

$$+\ (-\hbar 2/2mZ)\ d2Z/dz2) \quad = \ E \tag{3.8.8}$$

E is an energy constant and is the sum of x, y, and z. For this to work, each term must equal its own constant. For example,

$$d2X/dx2 + (2m/\hbar 2)\ \varepsilon x\ X = 0 \tag{3.8.9}$$

Now separate each term in Equation 3.8.8 to equal zero:

$$d2X/dx2 + (2m/\hbar 2)\ \varepsilon x\ X = 0$$

$$d2Y/dy2 + (2m/\hbar 2)\ \varepsilon y\ Y = 0$$

$$d2Z/dz2 + (2m/\hbar 2)\ \varepsilon z\ Z = 0$$

Now we can add all the energies together to get the total energy:

$$\varepsilon x + \varepsilon y + \varepsilon z = E \tag{3.8.10}$$

Do these equations look familiar? They should because we have now reduced the 3D box into three particles in a 1D box problems!

$$d2X/dx2 + (2m/\hbar 2)ExX = 0 \approx d2\psi/dx2 = -(4\pi 2/\lambda 2)\psi \tag{3.8.11}$$

Now the equations are very similar to a 1-D box and the boundary conditions are identical, i.e.,

$$n = 1,2,..\infty \tag{3.8.12}$$

Use the normalization wavefunction equation for each variable:

$$\psi(x) = \begin{cases} \sqrt{2/Lx}\ sin\ (n\pi x/Lx) & if\ 0 \leq x \leq L \\ 0 & if\ L < x < 0 \end{cases} \tag{3.8.13}$$

Normalization wavefunction equation for each variable (that substitute into Equation 3.8.4):

$$X(x) = \sqrt{2/Lx}\ sin\ (n\pi x/Lx) \tag{3.8.14}$$

$$Y(y) = \sqrt{2/Ly}\ sin\ (n\pi y/Ly) \tag{3.8.15}$$

$$Z(z) = \sqrt{2/Lz}\, sin\,(n\pi z/Lz) \tag{3.8.16}$$

The limits of the three quantum numbers

- $nx = 1,2,3, \ldots \infty$
- $ny = 1,2,3, \ldots \infty$
- $nz = 1,2,3, \ldots \infty$

For each constant use the de Broglie Energy equation:

$$\varepsilon x = n2xh2/8mL2x \tag{3.8.17}$$

with $nx = 1 \ldots \infty$

Do the same for variables ny and nz. Combine Equation 3.8.4 with Equations 3.8.14 -3.8.16 to find the wavefunctions inside a 3D box.

$$\psi(r) = \sqrt{8/V}\ \ sin(nx\pi x/Lx)\ sin(ny\pi y/Ly)\ sin(nz\pi z/Lz) \tag{3.8.18}$$

with

$$V = Lx \times Ly \times Lz\ \ \{volume\ of\ box\} \tag{3.8.19}$$

To find the Total Energy, add Equation 3.8.17 and Equation 3.8.103.

$$Enx, ny, nz = (h2/8m)(n2x/L2x + n2y/L2y + n2z/L2z) \tag{3.8.20}$$

Notice the similarity between the energies a particle in a 3D box (Equation 3.8.20) and a 1D box.

- ✓ **Degeneracy in a 3D Cube**

The energy of the particle in a 3-D cube (i.e., $Lx = Ly = L$) in the ground state is given by Equation 3.8.20 with $nx = 1$, $ny = 1$, and $nz = 1$. This energy (E1,1,1) is hence

$$E1{,}1{,}1 = 3h2/8mL2 \tag{3.8.21}$$

The ground state has only one wavefunction and no other state has this specific energy; the ground state and the energy level are said to be non-degenerate. However, in the 3-D cubical box potential the energy of a state depends upon the sum of the squares of the quantum numbers

(Equation 3.8.18). The particle having a particular value of energy in the excited state MAY has several different stationary states or wavefunctions. If so, these states and energy eigenvalues are said to be degenerate.

For the first excited state, three combinations of the quantum numbers

$(nx, ny, nz)\ are\ (2,1,1), (1,2,1), (1,1,2)$. The sum of squares of the quantum numbers in each combination is same (equal to 6). Each wavefunction has same energy:

$$E2,1,1 = E1,2,1 = E1,1,2 = 6h2/8mL2 \qquad (3.8.22)$$

Corresponding to these combinations three different wavefunctions and three different states are possible. Hence, the first excited state is said to be three-fold or triply degenerate. The number of independent wavefunctions for the stationary states of an energy level is called as the degree of degeneracy

of the energy level. The value of energy levels with the corresponding combinations and sum of squares of the quantum numbers

$$n2 = n2x + n2y + n2z \qquad (3.8.23)$$

as well as the degree of degeneracy

✓ **Example 3.8.1: Accidental Degeneracies**

When is there degeneracy in a 3-D box when none of the sides are of equal length (i.e., $Lx \neq Ly \neq Lz$)?

✓ **Solution**

From simple inspection of Equation 3.8.20, it is clear that degeneracy originates from different combinations of $n2x/L2x$, $n2y/L2y\ and\ n2z/L2z$ that give the same value. These will occur at common multiples of at least two of these quantities (the Least Common Multiple is one example). For example

if

$$n2x/L2x = n2y/L2y$$

there will be a degeneracy. Also, degeneracies will exist if

$$n2y/L2y = n2z/L2z$$

or if

$$n2x/L2x = n2z/L2z$$

and especially if

$$n2x/L2x = n2y/L2y = n2z/L2z.$$

There are two general kinds of degeneracies in quantum mechanics: degeneracies due to a symmetry ($i.e.,\ Lx = Ly$) and accidental degeneracies like those above.

✓ **Exercise 3.8.1**

The 6th energy level of a particle in a 3D Cube box is 6-fold degenerate.

a. What is the energy of the 7th energy level?
b. What is the degeneracy of the 7th energy level?

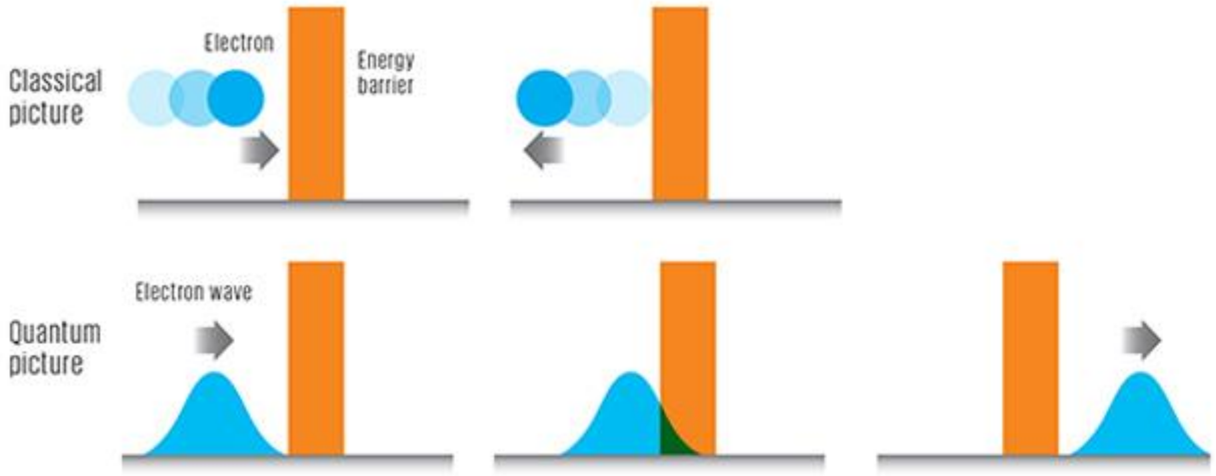
✓ **Answer a**

17h2/8mL2

✓ **Answer b**

three-fold (i.e., there are three wavefunctions that share the same energy.

Tunnel Effect



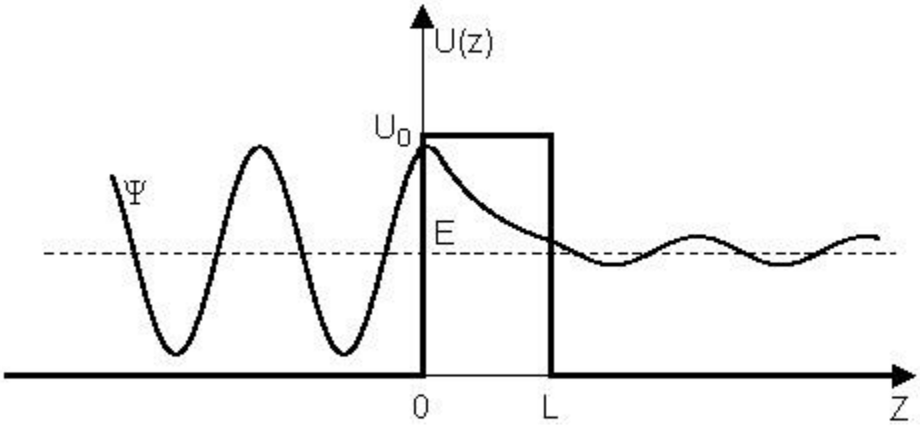
Quantum tunneling or **tunneling** refers to the quantum mechanical phenomenon where a particle tunnels through a barrier that it classically could not surmount. This plays an essential role in several physical phenomena, such as the **alpha decay** and the **nuclear fusion** that occurs in main sequence stars like the Sun. It has important applications to modern devices such as the **tunnel diode**, **quantum computing**, and the **scanning tunneling microscope**.

Tunneling is often explained using the Heisenberg uncertainty principle and the wave–particle duality of matter. Pure quantum mechanical concepts are central to the phenomenon, so quantum tunneling is one of the novel implications of quantum mechanics.

Quantum tunneling falls under the domain of **quantum mechanics**: the study of what happens at the quantum scale. This process cannot be directly perceived, but much of its understanding is shaped by the microscopic world, which classical mechanics cannot adequately explain. To understand the phenomenon, particles attempting to travel between potential barriers can be compared to a ball trying to roll over a hill; quantum mechanics and classical mechanics differ in their treatment of this scenario. Classical mechanics predicts that particles that do not have enough energy to classically surmount a barrier will not be able to reach the other side. Thus, a ball without sufficient energy to surmount the hill would roll back down. Or, lacking the energy to penetrate a wall, it would bounce back (reflection) or in the extreme case, bury itself inside the wall (absorption). In quantum mechanics, these particles can, with a very small probability, ***tunnel*** to the other side, thus crossing the barrier. Here, the “ball” could, in a sense, *borrow* energy from its surroundings to tunnel through the wall or “roll over the hill”, paying it back by making the reflected electrons more energetic than they otherwise would have been.

The reason for this difference comes from the treatment of matter in quantum mechanics as having properties of **waves and particles**. One interpretation of this duality involves the Heisenberg uncertainty principle, which defines a limit on how precisely the position and the momentum of a particle can be known at the same time. This implies that there are no solutions with a probability of **exactly zero** (or one), though a solution may approach infinity if, for example, the calculation for its position was taken as a probability of 1, the other, i.e. its speed, would have to be infinity. Hence, the probability of a given particle’s existence on the opposite side of an intervening barrier is **non-zero**, and such particles will appear on the ‘other’ (a semantically difficult word in this instance) side with a relative frequency proportional to this probability.

The image below shows the wave function of a particle after a potential barrier.



The Tunnel effect is involved in many physical phenomena and even in some common technological applications, we see some examples.

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