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).

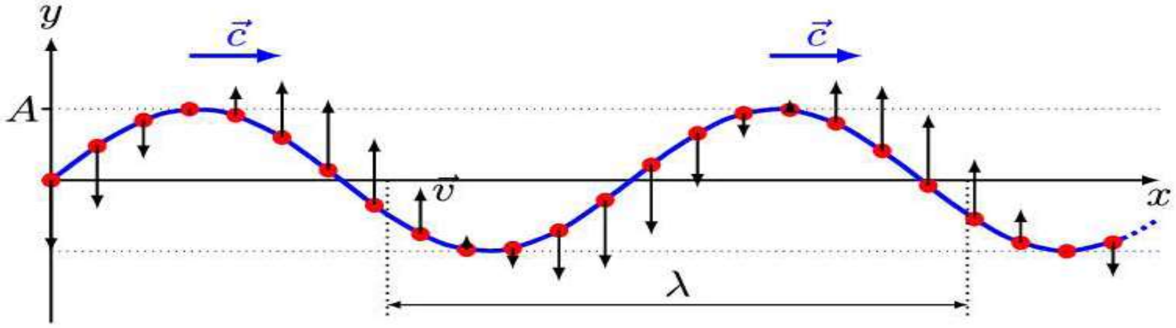

Figure 2.1.1: A simple translational (transverse) wave. (CC BY-SA 4.0 International; And 1mu via Wikimedia Commons)

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:

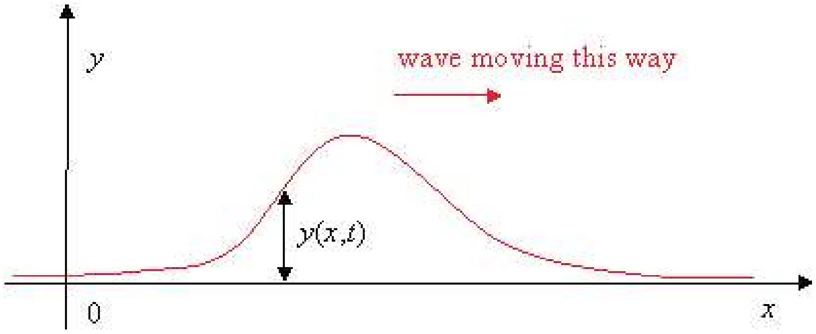

Figure 2.1.2: A one-dimensional traveling wave at one instance of time t.

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

$$\partial 2u(x,t)/\partial x2 = (1/v2)\ \partial 2u(x,t)/\partial t2 \qquad (2.1.3)$$

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.

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 ∂2/∂x2 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

$$-i\hbar\, \partial\Psi/\partial x = p\Psi \tag{3.1.11}$$

and then the second derivative

$$-\hbar^2\, \partial^2\Psi/\partial x^2 = p^2\Psi \tag{3.1.12}$$

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

$$E = (1/2)\, mv^2 = p^2/2m \tag{3.1.13}$$

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

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

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

$$E = p^2/2m + V(x) \tag{3.1.15}$$

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

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

time-dependent Schrödinger equation in 1D

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

$$i\hbar\, \partial\Psi(\vec{r},t)/\partial t = \left[-(\hbar^2/2m)\, \nabla 2 + V(\vec{r})\right]\Psi(\vec{r},t) \tag{3.1.17}$$

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 $V(\vec{r})$ can be formulated.

- ✓ **The Laplacian Operator**

The three second derivatives in parentheses together are called the Laplacian

operator, or del-squared,

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

$$= (\partial 2/\partial x2 + \partial 2/\partial y2 + \partial 2/\partial z2) \quad (3.1.18)$$

with the del operator,

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

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 $\Psi(\vec{r}, t)$ of matter waves associated with the particle within a specified potential $V(\vec{r})$. 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)

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

where $\psi(r^{\rightarrow})$ 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:

$$[(-\hbar 2/2m)\nabla 2+V(r^{\rightarrow})]\psi(r^{\rightarrow})=E\,\psi(r^{\rightarrow}) \qquad (3.1.21)$$

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., $\psi(r^{\rightarrow})$ do not have explicit t dependences like the wavefunctions of time-dependent analog in Equation 3.1.17 (i.e., $\Psi(r^{\rightarrow},t)$). 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 ($\Psi(r^{\rightarrow},t)$) differs from the time-independent (i.e., spatial only) wavefunction $\psi(r^{\rightarrow})$) by a "phase factor" of constant magnitude. Using the Euler relationship in Equation 3.1.4, the total wavefunction above can be expanded

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

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

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

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 $\mathrm{A}^{\wedge}$ and $\mathrm{B}^{\wedge}$ are given by

$$(A^{\wedge} \pm B^{\wedge})f = A^{\wedge}f \pm B^{\wedge}f \tag{3.2.4}$$

The product of two operators is defined by

$$A^{\wedge}B^{\wedge}f \equiv A^{\wedge}[B^{\wedge}f] \tag{3.2.5}$$

Two operators are equal if

$$A^{\wedge}f = B^{\wedge}f \tag{3.2.6}$$

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

$$1^{\wedge}f = f \tag{3.2.7}$$

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

$$A^{\wedge}2f = A^{\wedge}A^{\wedge}f \tag{3.2.8}$$

The *associative law* holds for operators

$$A^{\wedge}(B^{\wedge}C^{\wedge}) = (A^{\wedge}B^{\wedge})C^{\wedge} \tag{3.2.9}$$

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

$$A^{\wedge}B^{\wedge} \neq B^{\wedge}A^{\wedge} \tag{3.2.10}$$

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^

$$[A^{\wedge}, B^{\wedge}] \equiv A^{\wedge}B^{\wedge} - B^{\wedge}A^{\wedge} \tag{3.2.11}$$

$If\ A^{\wedge}\ and\ B^{\wedge}$ commute, then

$$[A^{\wedge}, B^{\wedge}] = 0. \tag{3.2.12}$$

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

$$[A^\wedge, B^\wedge] = -[B^\wedge, A^\wedge]. \qquad (3.2.13)$$

✓ Linear Operators

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

$$A^\wedge f(x) = g(x) \qquad (3.2.14)$$

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

$$O^\wedge(f(x) + g(x)) = O^\wedge f(x) + O^\wedge g(x) \qquad (3.2.15)$$

Condition A

and

$$O^\wedge cf(x) = cO^\wedge f(x) \qquad (3.2.16)$$

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

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

$$= O^\wedge\, f(x) + O^\wedge\, g(x)\checkmark$$

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

$$O^\wedge\, c\, f(x) = -i\hbar\, d/dx\, c\, f(x)$$

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

$$O^\wedge\, cf(x) = -ci\hbar\, d/dx\, f(x) = cO^\wedge\, f(x)\checkmark$$

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?

$$O^\wedge cf(x) = cO^\wedge f(x)$$
$$\sqrt{cf(x)} \neq cf(x)$$

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:

$$H^\wedge = -(\hbar 2/2m)\ \ d2/dx2 \qquad (3.2.17)$$

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

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

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

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

An obvious generalization for complex functions will read

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

In mathematical terminology, an operator A^ for which

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

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

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

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

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

and the time-independent Schrödinger equation

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

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

$$x\hat{} = x \tag{3.3.11}$$

and can be generalized in three dimensions:

$$\vec{r}\ \hat{} = \vec{r} \tag{3.3.12}$$

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

- **Kinetic Energy**

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

$$KEclassical = p2x/2m \tag{3.3.13}$$

Quantum mechanically, the corresponding kinetic energy operator is

$$KE\hat{}quantum = -(\hbar2/2m)\ \partial2/\partial x2 \tag{3.3.14}$$

and can be generalized in three dimensions:

$$KE\hat{}quantum = -(\hbar2/2m)\ \nabla2 \tag{3.3.15}$$

- **Angular Momentum:**

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

$$\vec{L}\ \hat{} = -i\hbar(\vec{r}\ \times \nabla) \tag{3.3.16}$$

- **Hamiltonian:**

The Hamiltonian operator corresponds to the total energy of the system

$$H\hat{} = -(\hbar2/2m)\ \ \partial2/\partial x2 + V(x) \tag{3.3.17}$$

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.

$$\psi = \sum ci\phi i \qquad (3.3.21)$$

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)

$$-i\hbar\,(\partial/\partial x)\,A sin(ax) = -i\hbar\,Aa\,cos(ax)$$

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

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