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Introduction to Wave Mechanics

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1. Beginning of Quantum Physics

1.1 Around the turn of the last century it was noticed that certain experiments on atomic systems could not be understood using classical physics. Instead, new theories were required. This led to the creation of *quantum theory*. There are really *two* quantum theories. **"Old quantum theory"** (pre-1925) was a hodgepodge of guesses, vague ideas, semiclassical techniques, and *ad hoc* theories. **"New quantum theory"** (post-1925), the theory which we know today, was based on fundamental work of Schrödinger, Heisenberg, Dirac, and others.

1.2 It is not a good idea to try to follow the tortuous chronological development of the theory, nor is it the best way to learn the subject. Nevertheless, we will discuss some of the key historical experiments that convinced physicists that something was not quite right with classical physics. We begin with the phenomenon of blackbody radiation.

2. The Conundrum of Blackbody Radiation

2.1 If you have ever looked into a toaster, you will have seen that the filaments glow red when they are hot. It is a fact that all bodies emit electromagnetic radiation when heated. The amazing thing is that the spectral distribution of the radiation (crudely, the amount of power emitted at each frequency) has the same characteristic shape for most objects in the universe. The spectral distribution of radiation emitted by various bodies was the subject of intensive investigation in the late 1880s and 1890s. The problem was that no classical model based on Maxwell's equations and thermodynamics could explain the precise shape of the curve representing this radiation.

2.2 To understand the problem more fully, we introduce the **spectral radiance (function)** $R(\lambda, T)$ of a body:

$R(\lambda, T)\, d\lambda =$ the power per unit area emitted by the body at temperature T between λ and $\lambda + d\lambda$.

The **total emissive power flux** $R(T)$ is the power per unit surface area emitted by the body at all wavelengths:

$$R(T) = \int_0^\infty R(\lambda, T)\, d\lambda. \tag{2.1}$$

Some typical curves are shown in Figure 1.

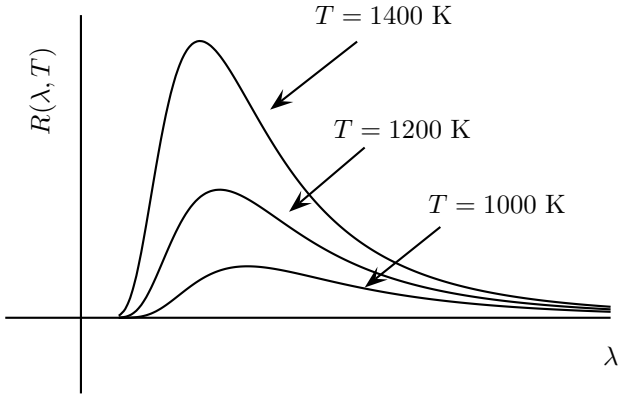

Figure 1: Some typical spectral radiance functions

2.3 At low temperatures (around 300 K), most of the radiation is emitted in the infrared region of the electromagnetic spectrum. At medium temperatures (around 5000 K), a large fraction of the radiation is emitted in the visible region, which we see as a glow. (It is no accident that our sun has a surface temperature of approximately 5800 K.) At high temperatures (around 25,000 K), most of the radiation is emitted in the ultraviolet region and beyond.

2.4 In addition to emitting radiation, all bodies absorb radiation as well. We define the **absorptivity** (or **absorption coefficient**) a as the fraction of incident radiation absorbed by the body at a given wavelength and temperature. That is

$$\boxed{a(\lambda, T) := \frac{\text{absorbed power at } \lambda \text{ and } T}{\text{incident power at } \lambda \text{ and } T}}.$$

The **reflectivity** (or **reflection coefficient**) $r(\lambda, T)$ is defined by $r(\lambda, T) = 1 - a(\lambda, T)$. To avoid cumbersome terminology we often suppress the dependence on λ and T and simply speak of the absorptivity or reflectivity of the body. A highly reflective body has a low absorptivity (near zero), while a dark body has a high absorptivity (near unity). This motivates the following important definition:

$$\boxed{\text{A } \textbf{blackbody} \text{ is a body for which } a = 1 \text{ (at all } \lambda \text{ and } T)}.$$

2.5 A common confusion is to say that, since a blackbody absorbs everything, it cannot emit anything. But this is not true. A blackbody *emits* lots of radiation (indeed, it may not appear black!); it simply does not *reflect* any radiation. Clearly, this is an idealization. As far as we know, the only perfect blackbody in nature is a black hole.

2.6 In **thermal equilibrium** a body maintains a constant temperature. In that case the power radiated by the body must equal the power absorbed by the body. This radiation is called **thermal radiation**. The thermal radiation emitted by a blackbody is called **blackbody radiation**.

2.7 It turns out that the power spectrum of blackbody radiation is independent of the composition of the blackbody. This is a famous result of Kirchhoff from 1859. The argument goes as follows. A **cavity radiator** is a large hollow box whose walls are coated with some very dark substance and with a tiny hole cut in the side, in thermal equilibrium at some temperature T. Any radiation incident on the hole goes into the box, hits the walls, and is either absorbed or reflected. But the reflected ray is either absorbed or reflected, and so on. Because the hole is small, the chances are negligible that the original incident ray is reflected back out of the hole, which means that all the incident radiation must eventually be absorbed by the walls of the cavity; the hole in the side of the cavity radiator acts like a blackbody. Of course, the atoms in the walls also emit their own radiation, some of which escapes from the hole. We call the radiation emerging from the hole **cavity radiation**.

2.8 Now suppose we block the hole with the blackbody surface (also in thermal equilibrium at temperature T) directed into the cavity. Place a filter between the cavity and the blackbody that passes only radiation in a narrow band of wavelengths between λ and $\lambda + d\lambda$. All the power emitted by the cavity is absorbed by the black body, and conversely. In thermal equilibrium, as much power must go into the cavity as out of it, so we must have $R_{\text{cavity}}(\lambda, T) = R_{\text{bb}}(\lambda, T)$, where $R_{\text{cavity}}(\lambda, T)$ is the spectral radiance function of the hole and $R_{\text{bb}}(\lambda, T)$ is the spectral radiance function of a black body at that same temperature. By using blackbodies of different compositions, we see that the spectral radiance function of the blackbody must be independent of its composition. That is, $R_{\text{bb}}(\lambda, T)$ is a *universal function*.

2.9 Kirchhoff's result is often reformulated as follows. Define the **emissivity** $e(\lambda, T)$ of an object at wavelength λ and temperature T to be the ratio of the spectral radiance

$R(\lambda, T)$ of the object to the spectral radiance of a blackbody at that same wavelength and temperature:

$$\boxed{e(\lambda, T) := \frac{R(\lambda, T)}{R_{\text{bb}}(\lambda, T)}}. \tag{2.2}$$

Then **Kirchhoff's Law of Thermal Radiation** states that, for any body in thermal equilibrium at temperature T,

$$\boxed{\text{emissivity } e(\lambda, T) = \text{absorptivity } a(\lambda, T)}. \tag{2.3}$$

2.10 The proof is similar to that given above. Begin with a cavity radiator at temperature T and a filter passing only wavelengths between λ and $\lambda + d\lambda$, but instead of blocking the hole with a blackbody, put any body there. Again, in thermal equilibrium, the body must emit as much power as it absorbs, but this time the body does not absorb all of the incident radiation, because some is reflected back into the cavity. Hence

$$R_{\text{cavity}}(\lambda, T) = R(\lambda, T) + r(\lambda, T) R_{\text{cavity}}(\lambda, T). \tag{2.4}$$

As $R_{\text{cavity}}(\lambda, T) = R_{\text{bb}}(\lambda, T)$, it follows that

$$(1 - r(\lambda, T)) R_{\text{bb}}(\lambda, T) = R(\lambda, T) = e(\lambda, T) R_{\text{bb}}(\lambda, T),$$

and so dividing by $R_{\text{bb}}(\lambda, T)$ gives

$$a(\lambda, T) = 1 - r(\lambda, T) = e(\lambda, T).$$

2.11 Yet another equivalent formulation of Kirchhoff's law is that, for any two bodies 1 and 2 in thermal equilibrium at the same temperature,

$$\frac{R_1(\lambda, T)}{a_1(\lambda, T)} = \frac{R_2(\lambda, T)}{a_2(\lambda, T)}, \tag{2.5}$$

which follows from (2.2) and (2.3).

2.12 Some experimental, as well as theoretical, support in favor of the universality of blackbody radiation was provided by Jozef Stefan and Ludwig Boltzmann. Stefan measured the total emissive power flux from various bodies and observed the following empirical law for blackbodies:

$$\boxed{R(T) = \sigma T^4}, \tag{2.6}$$

where

$$\boxed{\sigma = 5.67 \times 10^{-8} \frac{\mathrm{W}}{\mathrm{m}^2 \cdot \mathrm{K}^4}}, \tag{2.7}$$

is called **Stefan's constant**. Boltzmann deduced this law in 1884 from the laws of thermodynamics, so that today (2.6) is known as the **Stefan-Boltzmann Law**. As the total emissive power flux from a blackbody depends only on the temperature of the body and a universal constant, it is clearly independent of the composition and shape of the body.

2.13 Although this result is encouraging, we still want to be able to predict the spectral radiance functions of various bodies. Kirchhoff's law tells us that $R(\lambda, T) = a(\lambda, T) R_{\mathrm{bb}}(\lambda, T)$. It is easy to measure the absorptivity (or equivalently, the reflectivity) of a body, so the key is to determine $R_{\mathrm{bb}}(\lambda, T)$, which, by the above discussion, is the same thing as $R_{\mathrm{cavity}}(\lambda, T)$. The power flux emerging from the hole of a cavity radiator must depend on the energy density of radiation inside the cavity (which, by another argument of Kirchhoff, is homogeneous, isotropic, and independent of the shape of the cavity). A short computation reveals that

$$R_{\mathrm{cavity}}(\lambda, T) = \frac{c}{4} u(\lambda, T), \tag{2.8}$$

where $u(\lambda, T)$ is the **spectral density**, namely the energy of the radiation inside the cavity per unit volume per unit wavelength. The problem therefore reduces to computing the spectral density function.

2.14 The first successful attempt was made by Wilhelm Wien in 1894, who showed from general thermodynamic principles that the functional dependence of the spectral density on λ and T must be of the form

$$u(\lambda, T) = \lambda^{-5} g(\lambda T), \tag{2.9}$$

for some unknown function g. Based on the shape of the curve, he guessed that $g(\lambda T) = Ce^{-\alpha/\lambda T}$, for some constants C and α, so that

$$u(\lambda, T) = \frac{C}{\lambda^5} e^{-\alpha/\lambda T}. \tag{2.10}$$

But although this was a good fit at small wavelengths, it did not seem to work at large wavelengths. Wien could not determine the precise form of g, but his argument was powerful enough to yield the **Wein Displacement Law**, namely that the wavelength $\lambda_{\max}$ where the spectral radiance function achieves its maximum is given by

$$\boxed{\lambda_{\max} = \frac{b}{T}}, \tag{2.11}$$

for some constant b, now called **Wien's displacement constant**. [1]

2.15 Exercise. Starting from (2.9), prove the Wien displacement law (2.11).

2.16 Exercise. Wien's law can be used to determine the temperature of distant objects. Given that the predominant wavelength of light emitted by the Sun is around 550 nm, what is the exterior temperature of the Sun? Use $b = 2.898 \times 10^{-3}$ m·K and assume the Sun is approximately a blackbody.

2.17 The next serious attempt was made around 1900 by Lord Rayleigh and Sir James Jeans. Their basic idea was to treat the atoms in the walls of the cavity as if they were vibrating on springs (so-called **cavity oscillators**), and to assume that they absorbed and reemitted electromagnetic standing waves, or **radiative modes**, inside the cavity. (By classical electromagnetic theory, the wavelength of the waves emitted by a cavity oscillator oscillating with a frequency ν is just $\lambda = c/\nu$.) A counting argument gave the number of independent modes per unit volume between λ and $\lambda + d\lambda$ as

$$f(\lambda)\, d\lambda = \frac{8\pi}{\lambda^4}\, d\lambda. \tag{2.12}$$

From the classical equipartition theorem and statistical mechanics, a system in thermal equilibrium at temperature T has an energy of $kT/2$ per degree of freedom, where $k = 1.38 \times 10^{-23}$ J/K is Boltzmann's constant. As a linear harmonic oscillator has two degrees of freedom, the average thermal energy per mode must be $\langle \epsilon \rangle = kT$. [2] Multiplying the two quantities gives the famous **Rayleigh-Jeans Law**:

$$u(\lambda, T) = f(\lambda)\langle \epsilon \rangle = \frac{8\pi kT}{\lambda^4}. \tag{2.13}$$

(Note that the right hand side is indeed of the form predicted by Wien.)

2.18 The Rayleigh-Jeans law works well enough at long wavelengths, but fails spectacularly at short wavelengths. The total energy density in the cavity, obtained by integrating (2.13) over all wavelengths, is infinite. As this may be attributed to the unbounded contribution of the short wavelength modes, and as the short wavelengths lie in the ultraviolet

[1] It is called the 'displacement' law because it governs how the radiation peak is moved or displaced as the temperature is changed. Wien won the Nobel Prize in 1911 for his work on thermal radiation.

[2] We may think of a cavity oscillator as two masses connected by a spring. In one dimension each particle has one degree of freedom (its position), so the system has two degrees of freedom. Alternatively, one can think of a degree of freedom as a place to store energy. As an oscillator can have both vibrational and translational energy, it has two degrees of freedom.

region of the spectrum and beyond, this failure came to be known as the **ultraviolet catastrophe**.

2.19 In 1900 Max Planck, based on classical thermodynamical considerations and inspired guesswork, proposed a formula that interpolated between the Wein law and the long wavelength Rayleigh-Jeans result. His formula was

$$\boxed{u(\lambda, T) = \frac{8\pi hc}{\lambda^5} \frac{1}{e^{hc/\lambda kT} - 1}}, \tag{2.14}$$

where k is Boltzmann's constant, c is the speed of light, T is the temperature, and h is a new constant of nature, now called **Planck's constant**.

2.20 Planck's formula met with resounding success: (i) it correctly predicts the observed spectral radiance curves of bodies emitting thermal radiation; (ii) it reduces to the Wien formula (2.10) at short wavelengths and the Rayleigh-Jeans formula (2.13) at long wavelengths; (iii) it gives a finite energy in the cavity instead of an infinite energy; (iv) it implies the Stefan-Boltzmann law and provides a formula for Stefan's constant, and (v) it implies Wien's displacement law and gives a formula for Wien's constant.

2.21 EXERCISE. Show that Planck's law (2.14) reduces to Wien's formula (2.10) at short wavelengths, and the Rayleigh-Jeans formula (2.13) at long wavelengths.

2.22 EXERCISE. Derive the Stefan-Boltzmann law (2.6) from Planck's formula (2.14), and thereby obtain an expression for the Stefan constant in terms of c, h, and k. [Hint: $\int_0^\infty \frac{x^3\,dx}{e^x - 1} = \frac{\pi^4}{15}$.]

2.23 EXERCISE. Derive Wien's displacement law (2.11) from Planck's formula (2.14), and thereby obtain an expression for Wien's constant in terms of c, h, and k. [Hint: You will have to perform a numerical approximation.]

2.24 If we write Planck's result as $u(\lambda, T) = f(\lambda)\langle\epsilon\rangle$ where $\langle\epsilon\rangle$ is the average energy of a cavity oscillator, then using (2.12) we find

$$\langle\epsilon\rangle = kT \left[\frac{hc/\lambda kT}{e^{hc/\lambda kT} - 1}\right], \tag{2.15}$$

rather than the classical result kT. In effect, the quantity in brackets is a correction factor to the classical equipartition theorem. There was no precedent for it in all of physics,

and it gave one of the first indications that there was a world beyond classical physics. Planck himself struggled to find a reason why this might be true. Finally, in "an act of desperation", he realized that if for some reason the possible energies of the cavity oscillators were not arbitrary (as required by classical physics), but rather were restricted to be integral multiples of a fundamental unit of energy

$$\boxed{\epsilon_0 = \frac{hc}{\lambda} = h\nu}\,, \tag{2.16}$$

then his formula (2.14) would follow. [3]

2.25 By comparing the known value of Stefan's constant with the expression for it in terms of the fundamental constants c, h, and k (see Exercise **2.22**), Planck was able to estimate the value of his constant. A more modern value is

$$\boxed{h = 6.626 \times 10^{-34}\ \mathrm{J \cdot s}} \qquad \text{(Planck's constant)}.$$

2.26 The reason why no one had ever noticed this discreteness of energy levels prior to Planck was now apparent: *it is because Planck's constant is so small.* For example, consider a particle of mass $m = 300$ g attached to a spring of constant $k = 3$ N/m, oscillating with an amplitude $A = 10$ cm. The natural frequency of oscillation of this system is

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{m}} = 0.50\ \mathrm{Hz},$$

and the energy is

$$E = \frac{1}{2}kA^2 = 0.015\ \mathrm{J}.$$

Suppose there is some friction and the oscillator loses energy. The smallest amount of energy is can lose, according to Planck, is

$$\Delta E = \epsilon_0 = h\nu = (6.6 \times 10^{-34}\ \mathrm{J \cdot s})(0.50\ \mathrm{Hz}) = 3.3 \times 10^{-34}\ \mathrm{J}.$$

This corresponds to a fractional energy loss of

$$\frac{\Delta E}{E} = 2.2 \times 10^{-32},$$

which is much too small to be observed directly.

[3] In 1918 Planck won the Nobel Prize for his work.

3. The Photoelectric Effect

3.1 Thanks to technological breakthroughs in the production of evacuated glass tubes in the late 1800s, physicists were able to perform experiments that culminated in the discovery of the electron by J. J. Thomson in 1896. Thomson observed that when a metal plate inside a vacuum tube was struck by ultraviolet light, the plate emitted electrons, today known as **photoelectrons**.

3.2 More careful measurements were made by Philipp Lenard in 1902. Lenard placed two metal plates in an evacuated glass tube and connected them outside the tube to a voltage source, as shown in Figure 2a. When ultraviolet light hit the cathode [4], electrons were emitted. When the voltage source was such that the cathode was at a lower potential than the anode [5], the electrons flowed across the gap between the plates, thereby giving rise to a **photocurrent** through the circuit.

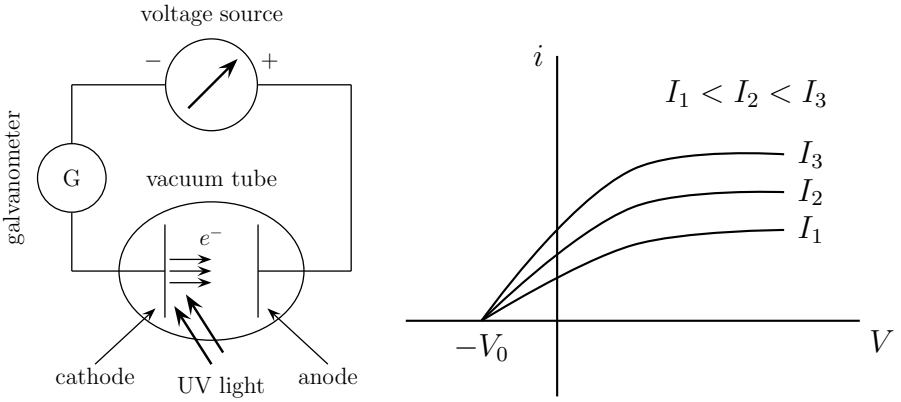

Figure 2a: Lenard's photoelectric apparatus. Figure 2b: Photocurrent versus voltage for three different intensities of light at constant frequency.

3.3 Two features stand out immediately from the data in Figure 2b:

1. The higher the intensity of the incident light, the higher the photocurrent.

[4] The *cathode* of an electrical device (from the Greek $\kappa\alpha\theta o\delta o\varsigma$ (kathodos), meaning 'descent') is the port through which electric current flows out of the device.

[5] The *anode* of an electrical device (from the Greek $\alpha\nu o\delta o\varsigma$ (anodos), meaning 'ascent') is the port through which electric current flows into the device.

2. The photocurrent vanishes when $V = -V_0$, independent of the intensity of the incident light. V_0 is called the **stopping potential**.

Additional experiments reveal that

3. The stopping potential varies *linearly* with frequency.

4. For each metal surface there is a **threshold frequency** ν_t for the incident radiation, below which there is no photocurrent no matter what the intensity, and no matter how long the surface is irradiated.

5. As soon as the light is turned on, the photocurrent appears—there is no delay.

3.4 Let us see if we can explain any of these facts within classical physics. In the classical physics model, incident electromagnetic waves force electrons in the metallic surface to oscillate back and forth in forced, damped harmonic oscillation. The idea is that the electron absorbs energy from the wave until it oscillates so wildly it is ripped from the surface. Increasing the intensity of the wave means increasing the amplitude of the electric field, and hence the amplitude of oscillation of the electron. One might expect that it would come off the surface with more kinetic energy, and therefore greater velocity. This would increase the photocurrent, which is what is consistent with observation (1). So far so good.

3.5 The problem is that we cannot account for any of the other observations. By classical electromagnetic theory, the work done by the electric field on the electron as it crosses the gap is $e\Delta V$. If the voltage polarity is reversed so that the anode is at a lower potential than the cathode, then by energy conservation we must have

$$\frac{1}{2}mv_{\max}^2 = eV_0, \tag{3.1}$$

where $v_{\max}$ is the maximum velocity of the emitted electrons. (Electrons emitted with lower velocities never cross the gap.) Hence, if we increase the intensity of the light, the classical physics model would predict that V_0 should increase, but this contradicts observation (2). Moreover, there is no frequency dependence at all in (3.1), so observation (3) is inexplicable. Also, according to classical physics, as long as we put in enough energy, *something* should come out, no matter what frequency we use, but this contradicts observation (4). Finally, according to classical physics it should take a bit of time for enough energy to build up

that an electron can be ejected from the surface, but by observation (5) there is essentially no delay between the time the surface is illuminated and the time the electron is emitted.

3.6 At this point if you were a classical physicist you might be tempted to change careers. But in 1905 Einstein proposed a simple, elegant explanation that accounted for every observation listed above and then some. [6] He suggested that light is carried by little corpuscles or **quanta**. We now call these quanta **photons**, and although this terminology was not invented until 1921, we will use it anyway. Einstein said that a light wave of frequency ν was really a stream consisting of a very large number of these photons, each of which carried an energy

$$\boxed{E = h\nu = \frac{hc}{\lambda}}, \tag{3.2}$$

where h is Planck's constant. The energy of the electromagnetic field is said to be **quantized**.

3.7 Exercise. Red light has a wavelength around 700 nm, while blue light has a wavelength around 400 nm. What is the energy of each type of photon (in eV)? Which type of photon is more energetic?

3.8 Exercise. Compute the frequency (in Hz) and wavelength (in fm) of a 100 MeV photon. (1 fm, which stands for 1 femtometer or 1 fermi, is 10^{-15} m.)

3.9 Exercise. The energy required to break a chemical bond is typically a few eV. Should you be worried about radiation damage from cell phones that operate in the 1 to 2 gigahertz range?

3.10 Exercise. A 10 kW radio transmitter operates at a frequency of 880 kHz. (a) How many photons per second does it emit? (b) What is the concentration of photons (number density) at a distance of 50 km away from the transmitter, assuming the antenna radiates isotropically above ground.

3.11 Although (3.2) looks just like Planck's formula (2.16), it is subtly different, as Einstein himself emphasized. Planck's formula (2.16) referred to the minimum energy of a cavity oscillator; Planck still thought that the electromagnetic waves in the cavity could have any energy. Einstein, on the other hand, asserted that the electromagnetic waves

[6] In 1921 Einstein received the Nobel Prize for this work.

themselves were quantized. Einstein viewed his hypothesis as an *independent* confirmation of Planck's idea concerning the existence of quantized energy levels, and indeed it was.

3.12 Let's see how Einstein's simple hypothesis of the quantum masterfully accounts for every aspect of the photoelectric effect. Photons hitting a metal surface are either scattered or absorbed. If they are absorbed by an atom they give up all their energy, which can cause the atom to eject a photoelectron. But the reason why electrons do not simply slough off surfaces is that they are held by electromagnetic forces. A certain minimum energy W is required to remove an electron from any surface. W is called the **work function**. It depends only on the type of metal from which the surface is composed. By conservation of energy, then, the maximum kinetic energy of an ejected photoelectron is

$$\boxed{\frac{1}{2}mv_{\max}^2 = h\nu - W}\,. \tag{3.3}$$

3.13 According to this picture, the *intensity* of a light wave is proportional to the *number of photons per unit time per unit area*. But, the greater the number of photons striking the surface per unit time, the greater the number of photoelectrons ejected per unit time, and hence the greater the photocurrent. This explains observation (1).

3.14 Combining (3.1) and (3.3) gives

$$eV_0 = h\nu - W. \tag{3.4}$$

This is independent of the intensity of the incident light, which is observation (2). Obviously, V_0 varies linearly with ν, which yields observation (3).

3.15 By (3.3), if a photon has a frequency below

$$\boxed{\nu_t = \frac{W}{h}}\,, \tag{3.5}$$

it will not have enough energy to overcome the work function. In that case, no photoelectron will be ejected, so there will be no photocurrent, no matter how many photons are hitting the surface per unit time. This takes care of observation (4).

3.16 Lastly, we assume that the process of absorption of the photon and emission of the photoelectron is essentially instantaneous, which explains (5).

3.17 Between the years of 1914 and 1916, Robert Millikan made careful measurements of the stopping potential V_0 as a function of frequency ν for various metal surfaces. By fitting the slopes of the resulting lines he obtained a value for Planck's constant, namely $h = 6.56 \times 10^{-34}$ J·s, which (more or less) agreed with the value obtained earlier by Planck himself, thereby reaffirming Einstein's hypothesis. [7]

3.18 EXERCISE. The threshold frequency for magnesium is 8.88×10^8 MHz. What is the work function of magnesium (in eV)?

3.19 EXERCISE. The threshold frequency for photoelectric emission in copper is 1.08×10^{15} Hz. Find the maximum energy of photoelectrons (in eV) when light of frequency 1.50×10^{15} Hz falls on a copper surface.

4. The Compton Effect

4.1 Further evidence for the particulate nature of light was afforded by x-ray scattering experiments. In the early 1900s many physicists were studying the newly discovered x-rays, or **Röntgen rays** as they were known. Charles Barkla, a student of J.J. Thomson, performed scattering experiments and observed anomalous peaks at short wavelengths (so-called *hard* x-rays). The peaks were considered anomalous, because classical theory predicts that a charged particle exposed to an electromagnetic wave will reradiate the wave at the same frequency (*Thomson scattering*), but in Barkla's experiments some of the x-rays produced secondary waves at higher wavelengths. Barkla was not able to make more precise observations, however, because he was unable to determine the exact wavelength of the x-rays in his apparatus. It was only with the x-ray diffraction work of Max von Laue in 1912 and William Bragg a few years later that such measurements became more reliable.

4.2 In 1922 Arthur Holly Compton carried out more precise x-ray scattering experiments and was able to quantitively determine the anomalous shift that Barkla had observed. A schematic of his experimental apparatus is shown in Figure 3, while some of the data are presented in Figure 4.

[7] To find h from the slope of the V_0 versus ν lines Millikan had to know e, the charge on the electron. Fortunately, he had already measured this as well in his famous oil drop experiment! Millikan was awarded the Nobel Prize in 1923 for his experimental accomplishments.

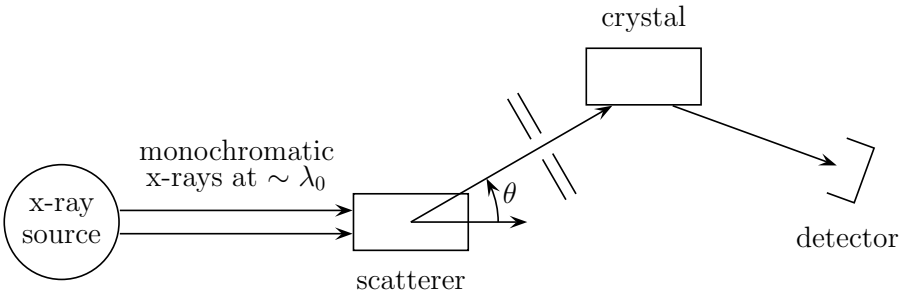

Figure 3: Compton's x-ray scattering apparatus

4.3 The **Compton shift** $\Delta\lambda := \lambda_1 - \lambda_0$ is the wavelength difference between the usual Thomson peak at λ_0 and the anomalous peak at λ_1. Compton observed experimentally that

$$\Delta\lambda = A \sin^2 \frac{\theta}{2}, \tag{4.1}$$

where the constant was determined to be $A = 0.048 \times 10^{-10}$ m, independent of λ_0 and independent of the scattering material.

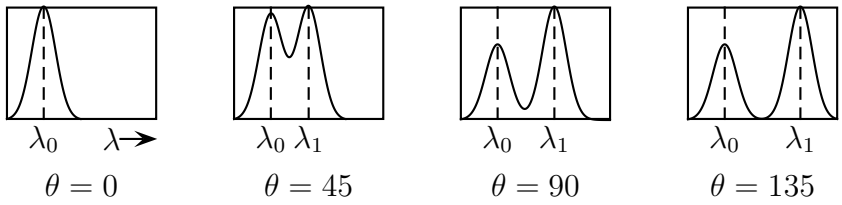

Figure 4: Scattered intensity versus wavelength at different scattering angles

4.4 Compton suggested that the anomalous peak could be explained if, following Einstein, one supposed that x-rays were highly energetic photons, and that they scattered off loosely bound electrons in the target. Because x-ray photons are so energetic, one could treat the target electrons as being essentially free (unbound). This would explain why the Compton shift was independent of the target material.

4.5 Using Einstein's newly discovered (1905) laws of special relativity, Compton was able to confirm his guess and derive an expression for the Compton shift as follows (see Figure 5).

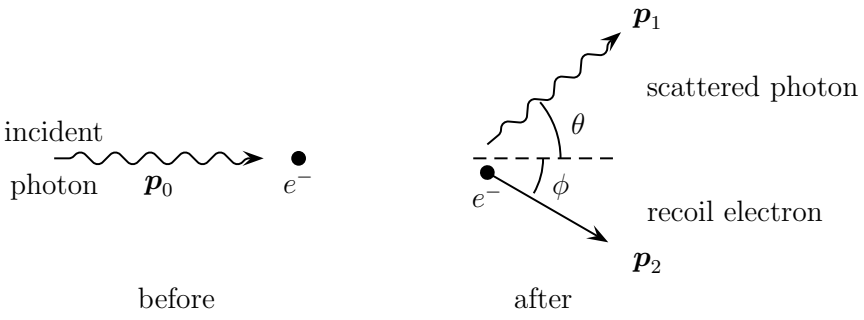

Figure 5: Compton scattering

By conservation of momentum we have

$$\mathbf{p}_2 = \mathbf{p}_0 - \mathbf{p}_1. \tag{4.2}$$

Squaring both sides gives

$$p_2^2 = p_0^2 - 2p_0p_1\cos\theta + p_1^2. \tag{4.3}$$

Conservation of energy reads

$$E_0 + m = E_1 + E_2, \tag{4.4}$$

where we adopt the convention $c = 1$. If T_2 is the kinetic energy of the recoil electron, (4.4) gives

$$E_0 + m = E_1 + T_2 + m \Longrightarrow T_2 = E_0 - E_1 = p_0 - p_1, \tag{4.5}$$

where we used the fact that the photon has no rest mass, so $E = p$. The invariant mass equation applied to the electron gives

$$(T_2 + m)^2 = E_2^2 = p_2^2 + m^2 \Rightarrow T_2^2 + 2T_2m = p_2^2. \tag{4.6}$$

Combining (4.3), (4.5), and (4.6) yields

$$\begin{aligned} &(p_0 - p_1)^2 + 2(p_0 - p_1)m = p_0^2 - 2p_0p_1\cos\theta + p_1^2 \\ \Rightarrow \quad &m(p_0 - p_1) = p_0p_1(1 - \cos\theta) \\ \Rightarrow \quad &\frac{1}{p_1} - \frac{1}{p_0} = \frac{1}{m}(1 - \cos\theta) = \frac{2}{m}\sin^2\left(\frac{\theta}{2}\right). \end{aligned} \tag{4.7}$$

According to Einstein's hypothesis, the energy of a photon corresponding to light of wavelength λ is (with $c = 1$) $\lambda = h/E = h/p$, so multiplying both sides of (4.7) by h gives **Compton's formula**

$$\boxed{\Delta\lambda = \lambda_1 - \lambda_0 = 2\lambda_c\sin^2\left(\frac{\theta}{2}\right)}, \tag{4.8}$$

where

$$\boxed{\lambda_c = \frac{h}{mc}} \tag{4.9}$$

is the **Compton wavelength** of the electron. Plugging in the known values of h, m, and c gives $2\lambda_C = 0.04852$ Å, which gives excellent agreement with the data. (Recall that one angstrom (Å) is 10^{-8} m.)

4.6 Note that this derivation also explains the classical Thomson scattering peak. Energetic x-ray photons that strike a very tightly bound electron effectively encounter a particle whose mass M is that of the entire atom. The Compton wavelength of the atom is much smaller than that of the electron, so the corresponding Compton shift is negligible.

4.7 The recoil electrons were observed by W. Bothe and C.T.R. Wilson in 1923. In 1925 W. Bothe and H. Geiger demonstrated that the scattered photon and electron appear at the same time, and in 1927 A.A. Bless measured the energy of the ejected electrons and found that they agreed with the predictions of Compton's theory. Compton was awarded the Nobel prize in 1927.

4.8 Exercise. A 10 keV x-ray photon collides with an electron and is scattered through an angle of 90°. Find its new energy.

4.9 Exercise. There are three primary ways in which photons lose energy as they go through matter. At relatively low energies (a few eV) the photons are absorbed by the electrons surrounding the atoms, and the electrons are then ejected from the material (photoelectric effect). At higher energies (up to about an MeV) the photon energy is attenuated by Compton scattering from the electrons. At very high energies (over an MeV) and in the presence of a heavy nucleus the photon can be annihilated and produce an electron-positron pair. (The positron is the antiparticle of the electron.) This is called *pair production.*

a) Verify that the minimum energy a photon must have to create an electron-positron pair in the presence of a stationary particle of mass M is

$$E = 2mc^2(1 + m/M),$$

where m is the mass of the electron.

b) What is the minimum energy for pair production in the presence of a proton?

5. The de Broglie Hypothesis

5.1 Motivated by the results of Einstein and others, Prince Louis de Broglie proposed (around 1923) that, just as light is both a particle and a wave, so is matter. For a light wave we have $E = h\nu$ and $p = E/c = h\nu/c = h/\lambda$, so de Broglie proposed that somehow one could associate a *matter wave* with a particle satisfying the same relations:

$$\boxed{\nu = \frac{E}{h}} \qquad \text{and} \qquad \boxed{\lambda = \frac{h}{p}}. \tag{5.1}$$

Although there was no experimental evidence for these formulae at the time, his bold guess turned out to be correct. Moreover, the de Broglie relations are *relativistically correct*, in the sense that the 'E' and 'p' appearing in (5.1) are the relativistic energy and momentum, respectively, of the particle. de Broglie received the Nobel prize in 1929, after his relations were spectacularly confirmed by Davisson and Germer in 1927.

5.2 To get an idea of the numbers involved, let's estimate the de Broglie wavelength of a particle. Consider a macroscopic particle (such as a ping-pong ball) with a mass of 1 g moving at a speed of 1 m/s. Its de Broglie wavelength would be

$$\lambda = \frac{6.626 \times 10^{-34}\ \text{J}\cdot\text{s}}{(10^{-3}\ \text{kg})(1\ \text{m/s})} = 6.6 \times 10^{-31}\ \text{m} = 6.6 \times 10^{-21}\ \text{Å}. \tag{5.2}$$

5.3 This is *much too small* to be observed. Recall from classical optics that, in order for a disturbance to exhibit wave behavior, such as diffraction, the wavelength of the wave must be comparable to the size of the object that is scattering the wave. We still cannot probe distance scales this small with the devices available to us.

5.4 But now consider the de Broglie wavelength of a non-relativistic electron of mass $m = 9.1 \times 10^{-31}$ kg accelerated through a potential difference of V_0 volts. It gains a kinetic energy $\frac{1}{2}mv^2 = eV_0$, and so would have a wavelength of

$$\lambda = \frac{h}{\sqrt{2meV_0}}. \tag{5.3}$$

The de Broglie wavelengths corresponding to some small accelerating potentials are given in Table 1.

V_0 (volts)	1	10	100	1000
λ(Å)	12.3	3.89	1.23	0.39

Table 1: de Broglie wavelengths of electrons
accelerated through various potentials

These wavelengths are comparable to those of x-rays, so one ought to be able to observe the wave nature of particles by employing a crystal as a diffraction grating, just as von Laue and the Braggs (father William and son Lawrence) had done about ten years earlier for x-rays.

5.5 Around 1927 C. J. Davisson and L. H. Germer (and, independently, G. P. Thomson) performed just such an experiment. [8] A schematic of their apparatus appears in Figure 6.

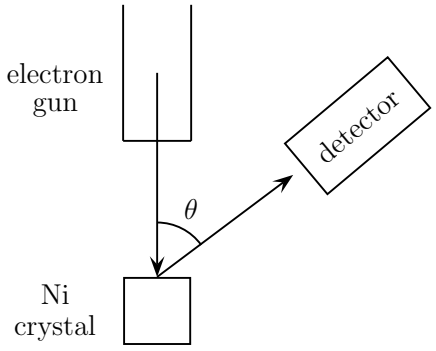

Figure 6: Davisson-Germer Experiment

Electrons from an electron gun (cathode ray tube) were scattered from a nickel crystal and measured by a detector. The result was a pronounced intensity peak at 50° for 54 eV electrons, as shown in Figure 7.

[8] Davisson and Thomson shared the Nobel prize in 1937 for their verification of the de Broglie hypothesis. Incidentally, G. P. Thomson was the son of J. J. Thomson, who won the Nobel in 1906 for his discovery of the electron and his measurement of the electron charge to mass ratio. The famous historian of science, Max Jammer, has written that "...Thomson, the father, was awarded the Nobel prize for having shown that the electron is a particle, and Thomson, the son, for having shown that the electron is a wave".

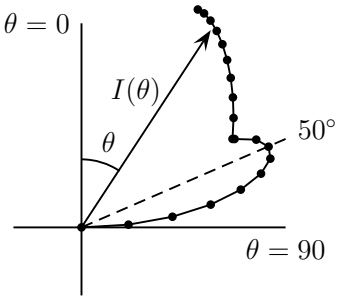

Figure 7: Polar plot of electron scattering intensity

5.6 Davisson and Germer realized that the only natural explanation was that the electrons were undergoing Bragg scattering from the nickel crystal. W. Bragg had shown that one could understand the diffraction of light from a crystal by assuming that the atomic planes act as a kind of mirror, and that intensity peaks in the scattered radiation are due to constructive interference from parallel atomic planes (now called Bragg planes). The situation is illustrated in Figures 8 and 9.

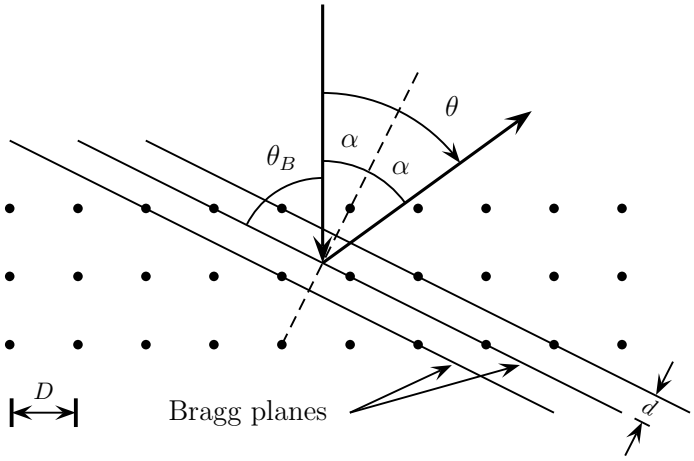

Figure 8: Scattering from Bragg planes

5.7 Parallel incoming rays reflect off parallel Bragg planes and add constructively in the detector if the path length difference between them is an integral multiple of the wavelength. This occurs when

$$2\ell = n\lambda \quad \Rightarrow \quad 2d\cos\alpha = 2d\sin\theta_B = n\lambda \qquad n = 0, 1, 2, \ldots, \tag{5.4}$$

where θ_B is the Bragg scattering angle (the angle between the incoming radiation and the surface), and d is the distance between adjacent Bragg planes. This is related to the

distance D between the atoms by the relation

$$d = D \sin \alpha, \tag{5.5}$$

where α is the incidence angle of the radiation.

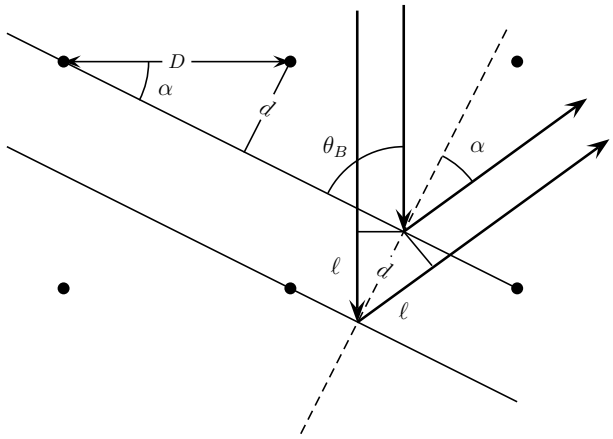

Figure 9: A closeup of the geometry for adjacent electron rays

It follows that we may write the Bragg condition for constructive interference as

$$n\lambda = 2d \cos \alpha = 2D \sin \alpha \cos \alpha = D \sin 2\alpha = D \sin \theta, \tag{5.6}$$

where $\theta = 2\alpha$ is the measured scattering angle. Hence we conclude that constructive interference occurs when

$$\boxed{n\lambda = D \sin \theta}\,. \tag{5.7}$$

5.8 X-ray diffraction experiments revealed that $D = 2.15$ Å for nickel, so assuming that the observed intensity peak at 50° occurred in the first order ($n = 1$), the experimental wavelength of the incoming electrons should have been

$$\lambda = 2.15 \sin 50 = 1.65 \text{ Å}. \tag{5.8}$$

For 54 eV electrons de Broglie's relation gives

$$\lambda = 1.67 \text{ Å}. \tag{5.9}$$

The agreement between these two numbers is remarkable. Furthermore, all the other higher order maxima occurred as predicted. Particles indeed act like waves!

5.9 In 1961 C. Jönsson performed the classic double slit experiment with electrons instead of photons. He bombarded a copper foil with 50 keV electrons corresponding to a de Broglie wavelength of 0.05 Å. The slits were $a = 0.5\mu$m wide and $d = 2\mu$m apart, and the screen was $D = 0.35$ m away from the foil. The expected spacing of fringes was $s \approx D\lambda/d \approx 1\mu$m, in excellent agreement with the data.

5.10 Lest one think that the wave properties of particles have no relevance to the real world, it is worth observing that this phenomenon underlies the operation of the **electron microscope**. Because the wavelength of the electrons is about 5000 times shorter than that of visible light, one can image much smaller objects with an electron microscope than with an ordinary light microscope. In order to see objects this small with a light microscope would require the use of x-rays. But x-rays are very difficult to focus (because they tend to go right through things) whereas electrons are easily focused using electric and magnetic fields. [9]

5.11 All material particles have wave properties. In 1929 Esterman and Stern showed that helium atoms and hydrogen molecules are diffracted according to de Broglie's theory. In 1988 Keith et. al. showed that sodium atoms (A=34) are diffracted. As E. Wichmann puts it "under suitable experimental conditions, a grand piano is a wave".

5.12 Planck's constant sets the scale for quantum mechanical phenomena. The reason we do not observe quantum phenomena at the macroscopic scale is because Planck's constant is so small. Put another way, the de Broglie wavelength of a particle is $\lambda = h/p$, so in the artificial limit $h \to 0$ we have $\lambda \to 0$, and the wavelike behavior of matter disappears, leaving only particle-like behavior. Just as geometric optics is the short wavelength limit of wave optics, so classical mechanics is the short wavelength limit of wave (quantum) mechanics.

5.13 EXERCISE. A certain electron microscope uses 40 eV electrons. Compute the de Broglie wavelength of the electrons to three significant figures in two ways, nonrelativistically and relativistically, and compare your answers. What do you conclude?

5.14 EXERCISE. Show that, if the energy of a particle is much greater than its rest energy, its de Broglie wavelength is the same as that of a photon with the same energy.

[9] On the other hand, one needs a huge vacuum system for an electron microscope to work, otherwise the electrons are scattered by the air molecules.

5.15 Exercise. The average kinetic energy of thermalized nonrelativistic classical particles is $E = 3kT/2$ where $k = 1.38 \times 10^{-23}$ J/K is Boltzmann's constant. Estimate the de Broglie wavelength of a nitrogen molecule at room temperature (300 K). How does this compare to the average spacing between the molecules at STP?

5.16 Exercise. Repeat the previous calculation for a 'gas' of electrons inside a piece of copper metal. Assume roughly one free (conduction) electron per copper atom, so that the average spacing between electrons is approximately equal to the average spacing between copper atoms. The density of copper is 8.94 g/cc. Use a periodic table to find the atomic weight of copper. [Remark: One expects that quantum mechanical effects will be important for particles that are packed within a few de Broglie wavelengths of one another.]

5.17 Exercise. The smallest angle of Bragg scattering in potassium chloride (KCl) is $\theta_B = 28.4^\circ$ for 0.30 nm xrays. What is the distance between atoms in KCl? If KCl is bombarded with 40 eV electrons, at what angle θ would you expect the first scattering peak?

6. Wave or Particle?

6.1 How do we reconcile these apparently irreconcilable facts of the wave and particle nature of matter? Let's consider again the double slit experiment, which, according to Richard Feynman, "contains all of the mystery of quantum mechanics". A schematic representation of the apparatus is in Figure 10. We bombard the double slit target with monoenergetic particles corresponding to monochromatic waves, and measure the number arriving at the screen ('intensity') using a detector of some sort that counts particles at each location.

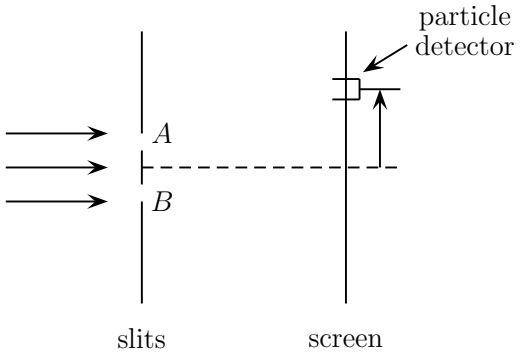

Figure 10: The double slit experiment apparatus

6.2 If quantum mechanical particles behaved the way you expect classical particles to behave, most of them would end up opposite the slits, but some would perhaps hit the edges of the slits and end up somewhere else. In other words, you might expect two well defined intensity peaks sort of spread out along the screen, as shown in Figure 11.

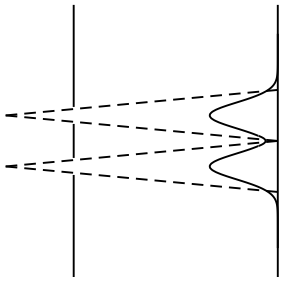

Figure 11: Expected intensity pattern if quantum mechanical particles acted like classical particles

Yet instead we observe the usual double slit pattern shown in Figure 12. [10]

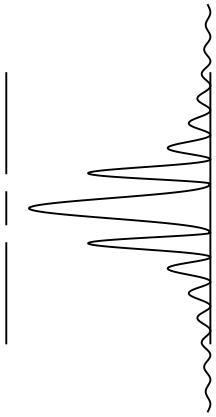

Figure 12: Observed intensity pattern

It is especially noteworthy that **there are some places on the screen where particles never land**! This is difficult to explain using a particle interpretation but perfectly understandable using the idea of total destructive interference of waves. We appear forced to conclude that particles act like diffuse waves when they propagate, but like packets of energy when they are detected.

6.3 Trying to explain this, you might argue that perhaps the wavelike nature of particles is some complex effect due to the interaction of so many particles together, and that if you

[10] Recall that, in the usual double slit interference experiement, we see a combined effect of interference from the two slits and diffraction from each slit by itself. The result is an ideal two slit interference pattern modulated by a diffraction envelope, which explains the amplitude attenuation of the fringes.

just sent one particle through at a time, you would observe familiar particle behavior. But this contradicts the facts. The experiments show that **the interference pattern builds up one particle at a time** (whether it be photons or electrons or whatnot). Somehow we are forced to conclude that the particle **interferes with itself**, and not with other particles.

6.4 Next, you might propose that somehow the particle splits up into pieces, and that somehow these pieces interfere with one another. But this, too, does not accord with the facts. First of all, we never detect particle fragments in our detector. If particles were to somehow split up, we would expect to sometimes measure half of a particle. But then it would have a lower energy or momentum (and hence a different wavelength, by the de Broglie relation) than expected, and this is never observed. Second, if particles were to split up in flight but then mysteriously recombine at the detector, one piece might have to move faster than light, contradicting Einstein's theory of special relativity.

6.5 Well, if the particles do not split up, then surely any given particle must go either through slit A or slit B, right? No, this too contradicts experiment. Suppose we were to close slit B, so that we know that the particle goes through A. Then we do not find, say, a double slit pattern but with half the intensity of the original experiment. Instead we find a washed out blob on the screen corresponding to a single particle, and the interference pattern disappears! The same happens if we close A. But the weird thing is that when we open A and B at the same time, we do not just get the sum of two blobs, but instead recover the original interference pattern!

6.6 The physicist Niels Bohr (who first postulated many of the properties of atomic systems, including quantization of energy) proposed his famous idea of **complementarity**, namely that the wave and particle properties of matter are somehow mutually exclusive. The more you know about one the less you know about the other.

6.7 Put yet another way, it is impossible to predict where the particle will land on the screen, because if you could, you would be able to trace back its path and tell which slit it went through (by, say, moving the screen closer to the source). But this would cause the interference pattern to disappear. [11]

[11] Wooters and Zurek have demonstrated theoretically (*Phys. Rev.*, **D19** (1979) 473-484) how measuring the trajectory of the particles and observing the interference pattern are complimentary. The more precisely you try to determine the trajectory of the particles, the more washed out the interference pattern becomes. This idea has been confirmed in many different experiments.

6.8 But if we cannot predict where a given particle will land, what can we predict? The answer comes from the experiment itself. It is the interference pattern itself which is reproducible (and hence predictable). But the information contained in the pattern is the **relative frequency** of hits on the screen, namely the **probability distribution** of particle hits. Hence we can only predict the **probability** that the particle will land at a certain spot. **Quantum mechanics is inherently probabilistic.** [12]

7. What is Waving?

7.1 By analogy with the wave phenomena of interference and diffraction observed for light, the physicist Erwin Schrödinger postulated the existence of something called a **wave function**, analogous to the electric field and usually written $\psi(x, y, z, t)$, that somehow describes the location of a particle. Exactly how it represents the particle and how it should be interpreted took a while to work out.

7.2 In classical wave theory the intensity of light on the screen is proportional to the electric field amplitude *squared*. Indeed, we showed that, if we use a complex representation for the electric field, the intensity is proportional to the *modulus squared* of the electric field amplitude. So if ψ is complex valued, which turns out to be the case (see below), we must take its modulus squared to get the intensity.

7.3 Reasoning along these lines, we tentatively say that the probability to find the particle at the point (x, y, z) at time t is proportional to $|\psi(x, y, z, t)|^2$. Although this is not quite correct, we can work with it until we come up with something better. Again by analogy with electric fields, we call ψ a **probability amplitude**, because it must be squared to get a probability.

7.4 To recover the double slit interference pattern, ψ must obey the **principle of superposition**. Given two matter waves ψ_1 and ψ_2, they must add together to get the resultant

[12] Over the years many people have tried to construct theories, called *hidden variable theories*, that basically assert that quantum theory is really deterministic, and that if we knew more about the world (if we knew those 'hidden variables' governing the behavior of quantum systems), we could predict where each particle would land. For many years people believed that they had proved mathematically or physically that hidden variable theories were not possible. These 'proofs' turned out to be wrong, and a hidden variable theory *is* possible, but such theories require that we accept that nature is *non-local*, meaning that there is some mysterious connection between widely separated objects. This spooky connection (which is compatible with special relativity) is called *entanglement*. See the literature for more about these ideas.

wave ψ:

$$\psi = \psi_1 + \psi_2. \tag{7.1}$$

In this case, the probability to find the particle at a particular point should be proportional to

$$|\psi|^2 = |\psi_1 + \psi_2|^2 = |\psi_1|^2 + |\psi_2|^2 + 2\mathrm{Re}\psi_1^*\psi_2. \tag{7.2}$$

It is this last term that is responsible for the interference phenomenon of matter waves. If it were not present, we would have instead

$$|\psi|^2 = |\psi_1|^2 + |\psi_2|^2, \tag{7.3}$$

and the particle intensities from the two slits would just add together, resulting in two blobs on the screen.

7.5 To learn more about these probability amplitudes, we seek the law governing their behaviour. Based upon our experience with classical physics, we know that the motion of waves is governed by a wave equation of some kind. For example, light waves are governed by Maxwell's equations, shallow water waves are governed by the Kortweeg-de Vries equation, and so forth. What sort of equation governs the motion of matter waves? Whatever it is, we expect it to be some sort of wave equation. We also expect it to be *linear* in order to accommodate the principle of linear superposition.

8. The Wave Equation

8.1 In order to discover the equation governing matter waves, let spend a few moments reviewing the ordinary wave equation. For simplicity, we will restrict ourselves to one dimension, but everything generalizes easily to three dimensions.

8.2 First, recall the idea of a partial derivative. Suppose we have a function of two variables, say $f(x, y)$, and say we are interested in how this function varies as we vary x but keep y fixed. This is what the partial derivative is designed to do. It works just like the ordinary derivative, only it treats as constant all the variables that we do not vary. For example, suppose $f(x, y) = x^2y^3$. Then $\frac{\partial f}{\partial x} = 2xy^3$ and $\frac{\partial f}{\partial y} = 3x^2y^2$. Higher dimensional examples work similarly.

8.3 Next, consider the equation

$$\frac{\partial^2 y(x,t)}{\partial x^2} = \frac{1}{v^2}\frac{\partial^2 y(x,t)}{\partial t^2}. \tag{8.1}$$

This is a second order, linear, homogeneous partial differential equation with constant coefficients. It is second order, because the highest order derivative is two. It is linear, because a sum of solutions is again a solution. It is homogeneous, because there is no term in the equation that does not depend on y. The coefficients are constant because v is a constant (*i.e.,* not a function of x or t). It is one of the simplest partial differential equations, and is called a **wave equation** because its solutions are waves. The most general solution to Equation (8.1) is

$$y(x,t) = f(x - vt) + g(x + vt), \tag{8.2}$$

where f and g are **completely arbitrary functions**. [13] What sort of solution is this? That is, what does it represent physically?

8.4 Exercise. Show that (8.2) is a solution to (8.1).

8.5 To investigate this, let us consider the solution $y(x,t) = f(x - vt)$ where $f(z)$ is a simple bump function, as shown.

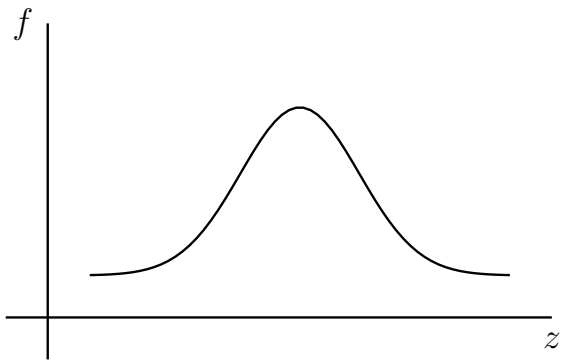

Figure 13. A bump function.

Now, we cannot graph $y(x,t)$ in two dimensions. [14] So instead we look at snapshots of $y(x,t)$ at the times $t = 0$ and $t = t$.

[13] Of course, they must be twice differentiable.

[14] We could do so in three dimensions, but that might be a little confusing.

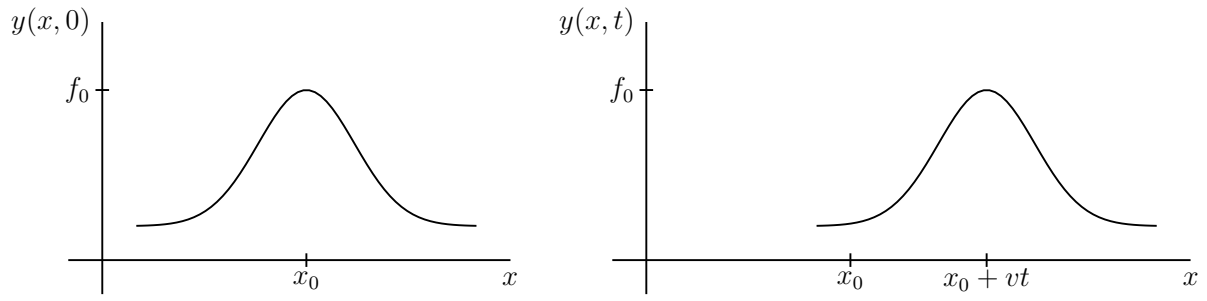

Figure 14. Two snapshots of the same wave.

Clearly, a graph of $y(x,0) = f(x)$ versus x looks identical to the previous picture. Suppose that the maximum of $f(x)$ occurs at the point $x = x_0$, and suppose that $f(x_0) = f_0$. Now, some time t later we have $y(x,t) = f(x - vt)$. Where is the maximum point now? We simply set $y(x,t) = f_0$ and solve for x. That is, we set $f(x - vt) = f_0 = f(x_0)$. Clearly for this equation to hold we must have $x - vt = x_0$ or $x = x_0 + vt$. In other words, after a time t, the maximum has moved to the right a distance vt, that is, it moved to the right with velocity v. Similarly, if we were to follow any other point on the curve, we would find that it moved similarly, so that the entire curve maintains its shape as time passes; when this happens we say the motion is **non-dispersive**.

8.6 The upshot of this analysis is that the solution $y(x,t) = f(x - vt)$ represents a disturbance traveling to the right with speed v. We call this disturbance a wave, hence the name 'wave equation'. Similarly, the other solution $y(x,t) = g(x + vt)$ represents a wave traveling to the left with speed v; the general solution is a superposition of the two.

8.7 One type of wave with which you are familiar is a **harmonic** wave, namely a wave in which $f(x) = \sin x$ or $f(x) = \cos x$. As you will learn later, **any** wave disturbance can be written as a superposition of these harmonic waves. [15] Hence there is no loss of generality in restricting ourselves for the time being to harmonic waves.

8.8 For example, one harmonic wave moving in the positive x-direction is the wave

$$y(x,t) = \cos(kx - \omega t) = \cos[k(x - vt)]. \tag{8.3}$$

Clearly, this is of the required type, being a function of the form $f(x - vt)$. The quantity k is called the **wave number** while the quantity ω is the **angular frequency** of the wave.

[15] This is called Fourier analysis—see below.

By recalling that the **wavelength** λ of a wave is the distance over which it repeats, we can see from (8.3) that $k = 2\pi/\lambda$. Similarly, as the **period** T is the time before the wave repeats itself, we have $\omega = 2\pi/T$, whence $\omega = 2\pi\nu$, where ν is the **frequency** of the wave.

8.9 It is clear from (8.3) that we must have

$$\omega = kv, \tag{8.4}$$

which is called **the (non-relativistic) dispersion relation** for a harmonic wave. As we discussed in Section **8.5**, any function of the form $f(x - vt)$ satisfying the wave equation (8.1) is actually non-dispersive, so if the relation (8.4) holds between ω and k, the wave retains its shape as it propagates.

9. Schrödinger's Equation for a Free Particle

9.1 We now attempt to reason by analogy with the above discussion in order to construct an equation governing the motion of de Broglie matter waves. For a particle moving to the right we expect that

$$\psi(x,t) = A\sin(kx - \omega t) + B\cos(kx - \omega t). \tag{9.1}$$

As the particle is free (no forces) and non-relativistic, its energy must simply equal its kinetic energy

$$E = \frac{p^2}{2m}. \tag{9.2}$$

Introducing the **reduced Planck constant** [16]

$$\boxed{\hbar := \frac{h}{2\pi}}, \tag{9.3}$$

we can write the de Broglie relations (5.1) in the form

$$\boxed{E = \hbar\omega} \qquad \text{and} \qquad \boxed{p = \hbar k}. \tag{9.4}$$

Substituting (9.4) into (9.2) we arrive at the **(non-relativistic) dispersion relation for a free particle**:

$$\boxed{\hbar\omega = \frac{(\hbar k)^2}{2m}}. \tag{9.5}$$

[16] The symbol $\hbar$ is pronounced "h-bar".

9.2 One of the first things you notice about this equation is that it is *not* of the form of Equation (8.4). This means *we expect de Broglie waves to be dispersive*, that is, to change shape as they propagate. This is indeed true, although we will not develop the necessary mathematical machinery to prove it here.

9.3 More importantly for our purposes, Equation (9.5) provides us with a clue as to what sort of differential equation our de Broglie wave will satisfy, as (9.5) must be a consequence of the wave equation. From (9.1) we see that we must differentiate ψ *once* with respect to t in order to get one factor of ω and *twice* with respect to x in order to bring out two factors of k. The only function that retains its form when differentiated once **or** twice is the exponential. But ψ must be of the form (9.1). So we are led to the tentative expression

$$\psi(x,t) = Ae^{i(kx-\omega t)} = A\cos(kx-\omega t) + iA\sin(kx-\omega t) \tag{9.6}$$

for the wave function representing a free, non-relativistic particle traveling to the right with energy and momentum

9.4 In your study of electrodynamics you may have learned that we could represent a real electromagnetic wave by a complex exponential of the form (9.6). But this was just a mathematical convenience, and could be avoided. One of the unusual features of quantum theory is that complex waves appear to be required. This introduction of complex numbers into physics was quite disturbing for some people. Many felt that physical theories ought to be expressible solely in terms of real numbers, because the results of any measurement are always real numbers.

9.5 In any event, taking Equation (9.6) to be the wave function corresponding to a free particle, we may now reason backwards and try to find the equation for which it is a solution. The simplest equation which does the job that also satisfies the dispersion relation (9.5) is **Schrödinger's wave equation for a free particle in one dimension (1926)**:

$$\boxed{i\hbar\frac{\partial\psi(x,t)}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2\psi(x,t)}{\partial x^2}}\,. \tag{9.7}$$

9.6 Although we have made this equation plausible (I hope!) we cannot say that we have *derived* it, any more than we can say that we have *derived* Newton's law. The test of any theory is whether it agrees with experiment, and the amazing thing is that this one does. Schrödinger was awarded the Nobel prize in 1933 for his discovery of the equation that bears his name.

10. Probabilities and Expectation Values

10.1 Thus far our success has been rather modest. We have succeeded in discovering a wave equation for free, non-relativistic particles. We also have some understanding of the probabilistic nature of the wave function. But free particles are uninteresting. We really want to know how particles interact with other particles. For this we need to generalize (9.7) to include forces (or interactions). But to do this, we must take a rather long detour first.

10.2 We begin by reviewing the basic notions of probability theory that we will need in order to achieve a fuller understanding of quantum theory. Perhaps you remember a little toy called a Pachinko machine. It consisted of a wooden board on which pegs were placed in an interlaced pattern, and a ball which you dropped into a hole at the top of the board. As the ball descended, it hit a peg, and it had essentially a 50-50 chance of bouncing off to the right or to the left on its way down. The resulting path was a random zig-zag to the bottom.

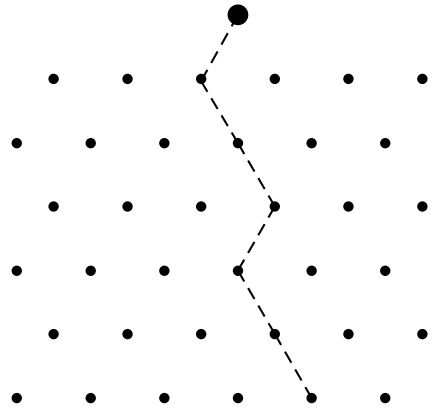

Figure 15. A Pachinko machine.

The laws of probability predict that the balls will fall mostly into the center of the bottom, with fewer balls as one gets farther away from the center line. This behavior is borne out by repeatedly dropping balls through the Pachinko machine.

10.3 To make the discussion quantitative, let us suppose that the balls could end up in one of 5 slots, with slot 3 right below the opening at the top of the machine. And let us

suppose that we drop $N = 18$ balls into the machine and that we record the following final positions for the balls: $3, 3, 2, 4, 2, 3, 3, 4, 3, 1, 3, 3, 3, 2, 3, 2, 4, 5$.

10.4 The first question we want to answer is: what is the expected final position of the ball? Intuitively we expect this to be the **average** or **mean** value of all the trials

$$\bar{x} = \frac{1}{N} \sum x_i, \tag{10.1}$$

which in this case is $\bar{x} = 2.94$. Here x_i represents a single measurement. The number $\bar{x}$ tells us that we might expect the final position of the ball to be the third slot. [17] But we can do better than this.

10.5 Let us draw a histogram representing the data. You recall that a histogram gives the number of times a certain data point appears. So let us change notation slightly. Let us denote the **possible values** of the experiment by the variables x_k, so that now $x_1 = 1$, $x_2 = 2$, $x_3 = 3$, $x_4 = 4$ and $x_5 = 5$. Also, let n_k denote the **frequency** of occurrence of the variable x_k, that is, the number of times it shows up. Then we may draw the following histogram to represent our experiment:

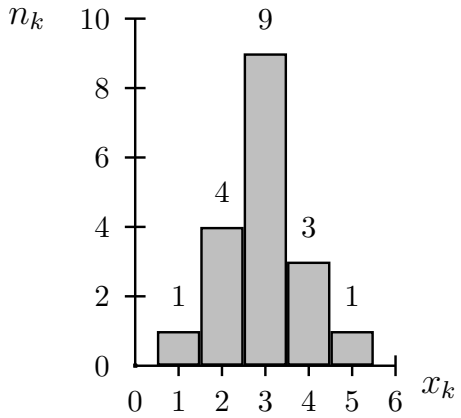

Figure 16. A histogram.

As N, the number of trials, gets larger, the histogram will, of course, get much bigger. But if there is some underlying cause for the pattern, the **shape** of the histogram, will remain the same. So, to get a good sample, we use a large number N of measurements,

[17] It is worth remarking that the *average value* is not always the same as the *most probable* value. For our example the average is 2.94, but the most probable value is 3, because 3 is the number that shows up most often. Yet people often use the two concepts interchangeably, because the average and most probable values tend to agree in many instances. You should remember, though, that these two concepts are not the same.

but we scale everything by N, so that now the histogram is a histogram of **relative frequencies** or **probabilities**. For our data set we get

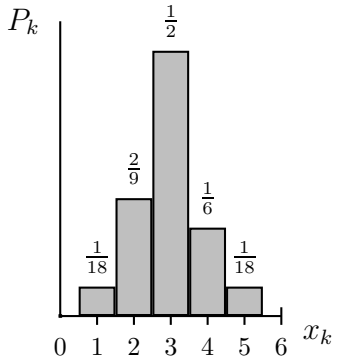

Figure 17. A relative frequency histogram.

where $P_k = n_k/N$ is the relative frequency of occurrence of x_k, or the probability of finding x_k.

According to this new way of looking at things, the average $\bar{x}$ now becomes the **expectation value** of x:

$$\langle x \rangle = \bar{x} = \frac{1}{N} \sum_k x_k n_k = \sum_k x_k P_k, \tag{10.2}$$

where

$$\sum_k P_k = 1. \tag{10.3}$$

10.6 Now suppose we perform more and more measurements at finer and finer resolution. Then we get a limiting distribution, called the **probability distribution** for the measurements.

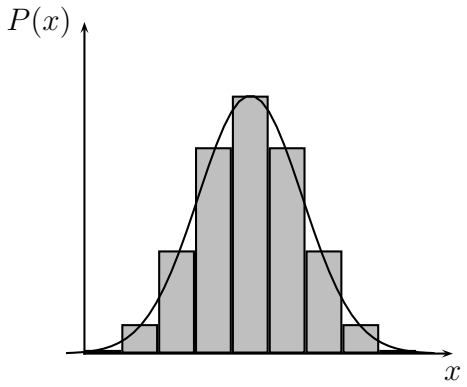

Figure 18. A probability distribution.

At this point we run into a minor problem. Previously, P_3, for example, represented the probability that the final position of the particle was at $x = 3$. What this really meant was that P_3 was the probability that the final position of the particle was, say, between $x = 2.5$ and $x = 3.5$. As we make finer and finer distinctions, we must replace the discrete set P_k by the continuous set $P(x)$, but the interval to which this applies is infinitessimal in size. In the limit, the interval becomes zero, and there is no probability to find the particle there at all!

10.7 To avoid this unpleasantness we define

$$P(x)\,dx$$

to be the probability to find the particle between x and $x + dx$. In other words, we let $P(x)$ be a **probability density** or probability per unit interval. In this way we retain the idea inherited from the discrete histogram, namely that the area under the curve between two points a and b

$$\int_a^b P(x)\,dx$$

gives the probability to find the particle between those two points.

10.8 It is now clear how to write the continuum analogues of (10.2) and (10.3). The expectation value of the variable x for the process governed by the probability distribution given by $P(x)$ is [18]

$$\langle x\rangle := \int x\,P(x)\,dx, \tag{10.4}$$

where the **normalization condition** is

$$\int P(x)\,dx = 1. \tag{10.5}$$

This latter condition guarantees that the probability to find the particle somewhere is equal to 1. In the event of an unnormalized probability distribution we define the expectation value of x as follows

$$\boxed{\langle x\rangle := \frac{\int x\,P(x)\,dx}{\int P(x)\,dx}}, \tag{10.6}$$

which is equivalent to (10.4) for the normalized probability distribution:

$$P(x) \longrightarrow \frac{P(x)}{\int P(x)\,dx}. \tag{10.7}$$

[18] When the limits on the integral are omitted it is understood that they are $-\infty$ and $+\infty$.

10.9 The form of the expression (10.4) should be familiar to you from mechanics. It is the same expression that allows you to compute the x-component of the **center of mass** of a mass distribution, provided we identify $P(x)$ with the mass density. In the case at hand, $P(x)$ represents the probability density, and (10.4) gives the center of mass of the probability distribution.

10.10 Exercise. The *exponential probability distribution*, defined on the interval $[0, \infty]$, is given by

$$f(x) = \lambda e^{-\lambda x}. \tag{10.8}$$

Show that the distribution is normalized to unity. What is the expectation value of x?

11. The Born Interpretation and Matter Waves

11.1 With these definitions in hand, we can now give a more precise statement of quantum mechanical probabilities. Previously we said that the probability to find the particle at the point (x, y, z) at a time t was proportional to $|\psi(x, y, z, t)|^2$. But now we see that this cannot be quite correct, because for any continuous probability distribution the probability to find the particle at any particular location must be zero. Instead, following the work of the great physicist Max Born, [19] we assert that **the probability to find the particle within a volume $dx\,dy\,dz$ at a time t is proportional to**

$$\boxed{|\psi(x, y, z, t)|^2\, dx\, dy\, dz}\,. \tag{11.1}$$

According to this hypothesis, $|\psi|^2$ is a **probability density** (probability per unit volume). As noted previously, one refers to the wavefunction ψ as a **probability amplitude**, by analogy with the electric field amplitude of an electromagnetic wave. Observe that we *must* use the modulus squared in this formula, because wave functions are generally complex, whereas probabilities are real.

11.2 Let's see what this interpretation tells us about the one dimensional matter wave (9.6):

$$\psi = Ae^{i(kx-\omega t)}.$$

[19] Born proposed this idea in 1926 and won the Nobel prize in 1954 for this work.

The points of constant phase satisfy

$$kx - \omega t = \text{constant}, \tag{11.2}$$

or

$$x = \text{constant} + \frac{\omega}{k}t, \tag{11.3}$$

so (9.6) represents a disturbance traveling to the right with **wave speed** or **phase velocity**

$$\boxed{v_p = \frac{\omega}{k}}. \tag{11.4}$$

11.3 Using the de Broglie relations (9.4) we can write

$$\psi(x,t) = Ae^{i(px-Et)/\hbar}. \tag{11.5}$$

What does this mean? Well, it appears to represent a wave traveling to the right with momentum p and energy E. That is, the momentum and energy of this particle are perfectly well defined.

11.4 But ... where is the particle? According to the Born interpretation (11.1), the probability to find the particle between x and $x + dx$ is

$$|\psi(x,t)|^2\,dx = |A|^2\,dx. \tag{11.6}$$

In other words, **it is equally likely to find the particle anywhere along the x axis**–every position is equiprobable. Another way to say this is that the position of the particle is **completely uncertain**—it could be anywhere.

11.5 This is peculiar, but it gets worse. First, observe that, according to (11.4), the phase velocity of the wave is

$$v_p = \frac{\omega}{k} = \frac{E}{p}. \tag{11.7}$$

But for a nonrelativistic particle, $E = p^2/2m$, so the phase velocity of this matter wave is

$$v_p = \frac{p}{2m} = \frac{v}{2}, \tag{11.8}$$

which is half the speed of the particle. What are we to make of this?

11.6 Yet another problem is that the probability to find the particle anywhere is

$$\int_{-\infty}^{\infty} |\psi|^2\,dx = |A|^2 \int_{-\infty}^{\infty} dx = \infty. \tag{11.9}$$

In other words, the probability to find the particle anywhere is *infinite* when it should be *unity* (because probabilities are numbers between 0 and 1).

12.1 The resolution of all these problems lies in the idea of wave packets. By the principle of superposition, we can add two waves to get another wave. So let's say we have two waves of the same amplitude that are close in frequency:

$$\psi_1 = Ae^{i(kx-\omega t)} \qquad \text{and} \qquad \psi_2 = Ae^{i((k+\delta k)x-(\omega+\delta\omega)t)}. \tag{12.1}$$

Adding them together using the identity

$$1 + e^{ix} = e^{ix/2}(e^{-ix/2} + e^{ix/2}) = 2e^{ix/2}\cos(x/2) \tag{12.2}$$

we get

$$\begin{aligned}\psi = \psi_1 + \psi_2 &= Ae^{i(kx-\omega t)}\left(1 + e^{i((\delta k)x-(\delta\omega)t)}\right) \\ &= 2Ae^{i(kx-\omega t)}e^{i((\delta k/2)x-(\delta\omega/2)t)}\cos((\delta k/2)x - (\delta\omega/2)t) \\ &\approx 2A\cos((\delta k/2)x - (\delta\omega/2)t)e^{i(kx-\omega t)}.\end{aligned} \tag{12.3}$$

In the last step we used the fact that $\delta k \ll k$ and $\delta\omega \ll \omega$. We see that ψ represents a harmonic wave traveling to the right with phase velocity $v_p = \omega/k$ but with a **modulated amplitude**. This is the familiar phenomenon of **beats**, in which two sounds with nearby frequencies add to give a sound with essentially the same frequency but with a slowly varying intensity. From (12.3) we observe that the speed of the envelope (amplitude modulation) is $v_g = \delta\omega/\delta k$. (See Figure 19.)

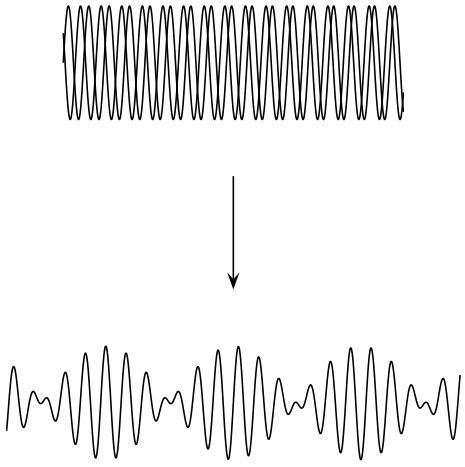

Figure 19: The sum of two waves with the same amplitude and nearby frequencies gives an amplitude modulated wave

12.2 This idea admits a vast generalization. Instead of just adding two harmonic waves with nearby frequencies and the same amplitude, we can add any number of harmonic waves with different amplitudes and different frequencies to get a new wave. A (one-dimensional) harmonic wave is of the form

$$e^{i(kx-\omega_k t)}, \tag{12.4}$$

where we have written ω_k to emphasize that it depends on k via the dispersion relation (9.5). From these harmonic waves we can construct a general wave by superposition:

$$\psi(x,t) = \sum_k A_k e^{i(kx-\omega_k t)}. \tag{12.5}$$

In the limit of an infinite number of waves the sum becomes an integral, and we write [20]

$$\psi(x,t) = \int A(k) e^{i(kx-\omega_k t)}\, dk. \tag{12.6}$$

The resulting wave is called a **wave packet**, because it is precisely that, namely a packet of waves. The $A(k)$ is a **weighting function**, which tells you how much of each pure frequency you must add to get the wave packet $\psi(x,t)$. Given $A(k)$ you can construct $\psi(x,t)$ via (12.6).

12.3 Using the idea of wave packets we can resolve some of the problems we encountered previously. By choosing the weighting function $A(k)$ appropriately, as illustrated on the left side of Figure 20, one can construct any wave disturbance one wishes, such as the localized wave packet illustrated on the right side of Figure 20.

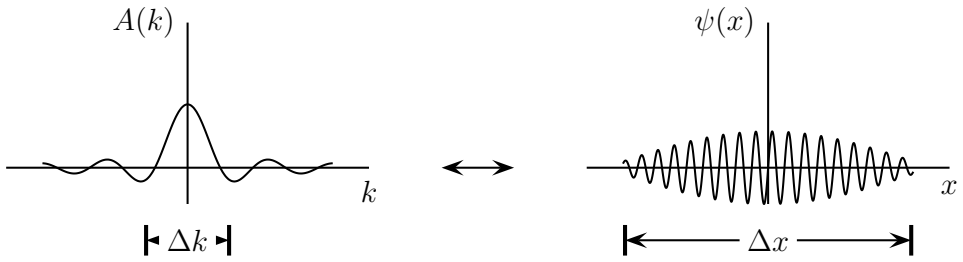

Figure 20: Constructing a localized wave packet by superposition

This wave packet corresponds to a particle localized to within a distance Δx, because that is where the wavefunction is nonzero. Hence, realistic particles are not described by pure harmonic waves of the form (9.6) but rather by localized wave packets.

[20] If this rings a bell for some of you, it is because this is indeed related to the subject of **Fourier analysis**. One small difference here is that we have both space and time dependence, whereas usually we consider only one or the other.

12.4 Moreover, it is clear by inspection of Figure 20 that integrating the probability density over the whole line will give a finite answer, because the waves have finite amplitude and are confined to a finite range.

12.5 Lastly, we can resolve the conundrum of the strange phase velocity. Because a localized particle is described by a localized wave packet consisting of waves of different frequencies, it does not travel at the phase velocity v_p of its constituent waves, but instead it moves at the velocity of the packet. This velocity v_g is called the **group velocity** of the packet, and it is akin to the velocity of the modulated envelope in the example of beats given above. Just as the beat velocity was $v_g = \delta\omega/\delta k$, we find that the group velocity is well approximated by the expression

$$\boxed{v_g = \frac{d\omega}{dk}}. \tag{12.7}$$

12.6 Let's see why this is so. Choose the weighting function $A(k)$ to be peaked around some central wavenumber k_0. Then the integral (12.6) will be dominated by wavenumbers near k_0. Assuming a general dispersion relation $\omega = \omega(k)$, we can expand the frequency ω in a Taylor series around k_0 to get

$$\omega(k) \approx \omega_0 + \left.\frac{d\omega}{dk}\right|_{k_0} (k - k_0), \tag{12.8}$$

where $\omega_0 = \omega(k_0)$. Plugging this into (12.6) gives

$$\psi(x,t) \approx \int A(k) e^{i(kx - \omega_0 t - \omega'(k_0)(k-k_0)t)} dk. \tag{12.9}$$

Using (12.6) again we can rewrite (12.9) as

$$\psi(x,t) \approx e^{i(k_0\omega'(k_0) - \omega_0)t} \psi(x - \omega'(k_0)t, 0). \tag{12.10}$$

The exponential prefactor is irrelevant to the dynamics of the system, because it disappears when we compute the probability density: [21]

$$|\psi(x,t)|^2 = |\psi(x - \omega'(k_0)t, 0)|^2. \tag{12.11}$$

Equation (12.11) shows that the wavepacket travels to the right with speed $\omega'(k_0)$, as promised. [22]

[21] Prefactors of this form are called *phase factors* because they shift the wavefunction by an overall phase.

[22] Note that this analysis is only valid if the weighting function is strongly peaked around some value. If not, the notion of group velocity becomes undefined, because we can no longer identify where the wave packet is.

12.7 Recalling the dispersion relation (9.5) for the free particle, namely $\omega = \hbar k^2/2m$, we find

$$v_g = \frac{d\omega}{dk} = \frac{\hbar k}{m} = \frac{p}{m} = v. \tag{12.12}$$

In other words, the wave packet travels with the speed of the particle, a reassuring result.

12.8 Exercise. Compute the shape of the wavepacket $\psi(x, 0)$ for a Gaussian weighting function

$$A(k) = De^{-ak^2}, \tag{12.13}$$

where D is some constant. [Hint: Consult Appendix A.]

12.9 Exercise. The **Dirac delta function** $\delta(x)$, although not really a function *per se*, can be thought of as representing the limit of a sequence of functions with unit area that are more and more sharply peaked around $x = 0$. It is defined by the so-called *sifting property*, which says that, for any sufficiently well-behaved test function $f(x)$,

$$\int f(x)\delta(x)\,dx = f(0). \tag{12.14}$$

(The nomenclature is appropriate, because, from all the possible values of the function $f(x)$, the Dirac delta function 'sifts' out the single value $f(0)$.) Compute the shape of the wavepacket $\psi(x, t)$ for the Dirac delta weighting function $A(k) = \delta(k - k_0)$.

12.10 Exercise. The frequency of an ocean wave is related to its wavelength by

$$\nu = \left(\frac{g}{2\pi\lambda}\right)^{1/2}, \tag{12.15}$$

where g is the acceleration of gravity. Show that the group velocity is half the phase velocity.

13. The Heisenberg Uncertainty Principle

13.1 Unfortunately, in the process of constructing a particle with well defined position, we have lost information about its momentum. The point is that the wave packet consists of waves of different wavenumbers and hence different momenta. This means that **the momentum of the particle is not well defined**. Imagine a series of increasingly localized

wavepackets obtained by adding together more and more waves of different momenta, as illustrated in Figure 21.

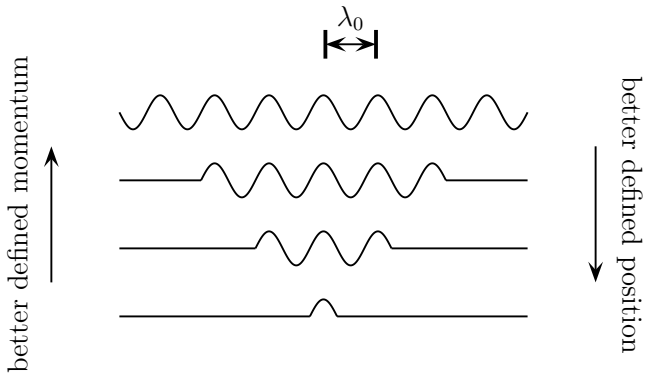

Figure 21: The essence of the Heisenberg uncertainty principle

As the wavepacket becomes more and more localized, the momentum becomes less well defined. **This is the essential idea of Heisenberg's Uncertainty Principle**, which basically says that there is a kind of tradeoff between knowing where the particle is and knowing its momentum.

13.2 We denote the uncertainty in the x position of the particle by Δx, and the uncertainty in the x direction momentum by Δp_x. We can get a heuristic estimate for the uncertainty in these quantities as follows. Suppose that the peak-to-peak distance of each of these waves is λ_0. Then the uncertainty in the x position of the particle is

$$\Delta x \sim n\lambda_0, \tag{13.1}$$

where n counts the number of oscillations in the wave packet. But, if the wave packet is finite in extent, it becomes more and more difficult to actually measure the wavelength. Suppose we wanted to count the peaks that pass by. If the peaks are very widely separated it is difficult to measure accurately the distance between them, and if there are fewer of them we have fewer chances to average our result to get a decent estimate. So our uncertainty $\Delta\lambda$ in the wavelength should go up if λ_0 goes up and n goes down. This can be expressed by saying that the fractional uncertainty in the wavelength should vary inversely with n:

$$\frac{\Delta\lambda}{\lambda_0} \sim \frac{1}{n}. \tag{13.2}$$

Hence

$$\left(\frac{\Delta\lambda}{\lambda_0}\right)\left(\frac{\Delta x}{\lambda_0}\right) \sim 1. \tag{13.3}$$

But

$$k_0 = \frac{2\pi}{\lambda_0} \quad \Rightarrow \quad \Delta k \approx -\frac{2\pi}{\lambda_0^2}\Delta\lambda, \tag{13.4}$$

so (ignoring the irrelevant sign, because uncertainties are always taken to be positive) we can write (13.3) as

$$\Delta x\, \Delta k \sim 2\pi, \tag{13.5}$$

or

$$\Delta x\, \Delta p_x \sim h. \tag{13.6}$$

If we had a wavepacket that did not look as nice as the ones in Figure 21 the uncertainty in the momentum would only be greater, in which case we would have

$$\Delta x\, \Delta p_x \gtrsim h. \tag{13.7}$$

In actual fact, the correct (rigorous) result is [23]

$$\boxed{\Delta x\, \Delta p_x \geq \frac{\hbar}{2}}. \tag{13.8}$$

Observe that, among other things, (13.8) implies that Δx and Δp_x cannot vanish simultaneously. There are many different interpretations of the uncertainty principle, some of which we will discuss below. In the meantime, let's play with a few of the numbers.

13.3 Example. An electron is confined to a box of size 1 Å. What is the smallest uncertainty in its velocity? We have

$$\Delta p_x = \frac{h}{4\pi\Delta x} = \frac{6.63\times10^{-34}\ \mathrm{J\cdot s}}{(4\pi)(10^{-10}\ \mathrm{m})} = 5.3\times10^{-25}\ \mathrm{kg\cdot m/s}$$

so the minimum uncertainty in its velocity is

$$\Delta v_x = \frac{\Delta p_x}{m} = \frac{5.3\times10^{-25}\ \mathrm{kg\cdot m/s}}{9.1\times10^{-31}\ \mathrm{kg}} = 5.8\times10^{5}\ \mathrm{m/s} = 0.002\,\mathrm{c}$$

This is a sizeable fraction of the speed of light!

13.4 Example. A man of mass $m = 100$ kg is sitting still in a chair of size 0.5 m. What is the minimum uncertainty in his velocity? Now we have

$$\Delta p_x = \frac{h}{4\pi\Delta x} = \frac{6.63\times10^{-34}\ \mathrm{J\cdot s}}{(4\pi)(0.5\ \mathrm{m})} = 1.1\times10^{-34}\ \mathrm{kg\cdot m/s}$$

[23] See Appendix B for a proof based on ideas discussed below.

so the minimum uncertainty in his velocity is

$$\Delta v_x = \frac{\Delta p_x}{m} = \frac{1.1 \times 10^{-34} \text{ kg} \cdot \text{m/s}}{100 \text{ kg}} = 1.1 \times 10^{-36} \text{ m/s}$$

This is immeasurably small. Obviously, the uncertainty principle only plays a role for microscopic objects.

13.5 EXERCISE. As we have seen, if a particle's position is initially uncertain by an amount Δx_0, then the smallest uncertainty in its velocity is $\Delta v = h/4\pi m(\Delta x_0)$. After a time t has elapsed, this uncertainty in velocity leads to an increased uncertainty of $\Delta x = t\Delta v$ in the particle's position. Find the time t that must elapse so that $\Delta x = \Delta x_0$. This is a measure of how much time it takes for us to lose track of the particle. Evaluate this time for the two examples above. Comment.

13.6 EXERCISE. A harmonic oscillator of mass m and spring constant k has an energy $E = mv^2/2 + kx^2/2$ and oscillates with a frequency $\omega = \sqrt{k/m}$. Classically, there is no Heisenberg principle, so the oscillator can be at rest at $x = 0$. But quantum mechanically the position and momentum cannot simultaneously vanish. By assuming that x and p are of the same order of magnitude as their uncertainties, show by extremizing E that the minimum energy of the oscillator is $\frac{1}{2}\hbar\omega$. This is called the **zero point energy** of the oscillator, and it plays a very important role in such diverse phenomena as the behavior of materials at low temperatures and the interactions of fundamental particles.

13.7 In the above discussion there was nothing special about the x direction. A similar derivation in three dimensions therefore yields the uncertainty relations

$$\boxed{\Delta y \, \Delta p_y \geq \frac{\hbar}{2}} \qquad \text{and} \qquad \boxed{\Delta z \, \Delta p_z \geq \frac{\hbar}{2}}. \tag{13.9}$$

But, for example,

$$\Delta x \, \Delta p_y = 0, \tag{13.10}$$

because we can easily construct a three dimensional wavepacket that is localized in the x direction (so $\Delta x = 0$) but extends sinusoidally for an infinite distance in the y direction (so $\Delta p_y = 0$), as illustrated in Figure 22.

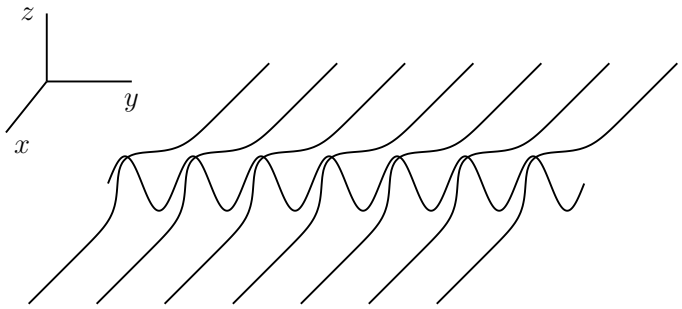

Figure 22: A wave packet in three dimensions that falls off in the x direction but oscillates sinusoidally in the y direction

Pairs of variables such as (x, p_x) that obey the Heisenberg uncertainty relation (13.8) are called **complementary variables** or **incompatible observables**.

13.8 When Heisenberg first stated his principle there was some confusion as to whether it was an epistemological claim or an ontological one. **Epistemology** is the science of knowledge, namely the study of what we know and how we know it. **Ontology** is the science of being, namely the study of what is, independent of our knowlege of it.

13.9 The epistemological interpretation of the Heisenberg uncertainty principle is as a **measurement** problem. This is illustrated by the notorious Heisenberg microscope, which Heisenberg used to motivate his principle. As we have discussed previously, in order for diffraction of a particle to occur, its wavelength must be comparable to the size of the obstruction. Put another way, in order for light scattering to occur from an object, the illuminating light must have a wavelength comparable to the size of the object, otherwise the light passes by the object without deviation and we cannot see it. To see a microscopic particle such as an atom we would have to illuminate it with light of a very small wavelength. The smaller the object the smaller the required wavelength. But $p = h/\lambda$, so this corresponds to very energetic photons. These photons are so energetic that they give a huge kick to the particle being observed, thereby making it impossible to measure accurately the particle's momentum. Put another way, the more we *know* about the particle's position, the *less* we know about its momentum. This is an epistemological problem, because it is a limitation on our ability to *know* a phenomenon. It leaves open the possibility that the particle simultaneously has a well defined position and momentum, but that we are unable to measure them at the same time.

13.10 On the other hand, as we can see from the way in which we first motivated the Heisenberg principle, we can interpret it as an ontological statement about the nature of particles, namely that **particles do not simultaneously possess a well-defined position and momentum**. This is not a limitation on our ability to know something about particles, but rather a limitation on the very idea of a particle. According to this interpretation of the Heisenberg uncertainty principle, we are forced to conclude that particles simply do not have the properties that we normally ascribe to them, such as position and momentum. Yet we continue to speak about them as if they do. This kind of 'doublethink' is required if one is to understand the quantum world.

13.11 Incidentally, you could ask which interpretation is correct. The answer is that both are correct, and that, furthermore, there is a third way to interpret the Heisenberg uncertainty principle as a *statistical statement* (see Section **20.5**) that is also correct. (So perhaps we must engage in 'triplethink'!)

13.12 It turns out that there is another pair of complementary variables in quantum theory, namely energy and time, although the metaphysical status of the corresponding uncertainty principle is even less clear than that of position and momentum. Imagine a wave going by. To measure its frequency we count the number of peaks that pass in a time Δt. The shorter the time the less certain we are about the number of peaks, so we expect that

$$\Delta\nu \gtrsim \frac{1}{\Delta t}, \tag{13.11}$$

or, since $E = h\nu$,

$$\Delta E\, \Delta t \gtrsim h. \tag{13.12}$$

As before, a more careful analysis yields

$$\boxed{\Delta E\, \Delta t \geq \frac{\hbar}{2}}. \tag{13.13}$$

13.13 Once again, we can interpret this epistemologically or ontologically. According to the former interpretation, if we try to measure a system for a time Δt, we are uncertain about its energy by a corresponding amount ΔE, and *vice versa*. According to the latter interpretation, objects with finite lifetimes simply do not possess well defined energies. This turns out to be true, and manifests itself crucially in at least two places. First, most subatomic particles have finite lifetimes. Indeed, some of them live for only a very

short time. Their energies are correspondingly uncertain. But since $E = mc^2$, their masses are also uncertain. This sometimes makes it difficult to tell whether or not one has actually seen a particle! Second, atoms in excited states have finite lifetimes, so their corresponding energy levels are uncertain. This helps resolve a minor paradox in the emission and absorption of radiation from atoms.

13.14 Example. A free neutron has a half-life of about 10 minutes. What is the uncertainty in its rest energy? We have

$$\Delta E = \frac{h}{4\pi\Delta t} = \frac{6.63 \times 10^{-34}\ \text{J}\cdot\text{s}}{(4\pi)(600\ \text{s})(1.6 \times 10^{-13}\ \text{J/MeV})} = 5.5 \times 10^{-25}\ \text{MeV}.$$

The rest energy of a neutron is around 1 GeV, so this is completely negligible.

13.15 Example. The baryon Δ has a rest energy of 1236 MeV and a lifetime of approximately 10^{-23} s. What is the fractional uncertainty in its rest energy? We have

$$\frac{\Delta E}{E} = \frac{h}{4\pi E\Delta t} = \frac{6.63 \times 10^{-34}\ \text{J}\cdot\text{s}}{(4\pi)(10^{-23}\ \text{s})(1.6 \times 10^{-13}\ \text{J/MeV})(1236\ \text{MeV})} = 0.03 = 3\%,$$

a non-negligible fraction.

13.16 One consequence of the energy-time uncertainty relation is that empty space is not empty, but is instead filled with what are called *virtual particles*. Suppose we try to measure the energy of a small region of space. If we measure for a time Δt, then we will be uncertain about the energy in that region by an amount $\Delta E \approx \hbar/2\Delta t$. This means that there could be this much energy in that region. As energy is mass, the region could be filled with particles having this much energy. These particles are called 'virtual', as opposed to 'real', because they cannot be measured directly. It turns out, however, that their effects can be measured *indirectly*, so in some sense at least they would seem to exist. According to the time-energy uncertainty relation, the shorter the lifetimes of these particles, the higher their energies can be. Another way to say this is that conservation of energy is violated for short times, although it is restored in the long run, because the particles must disappear before they contravene the Heisenberg principle.

13.17 Exercise. A single virtual electron cannot appear in space without violating the principle of charge conservation (which as far as we know, is still respected in quantum theory), but nothing prevents the spontaneous appearance of an electron-positron pair, which has zero net charge. This *virtual pair production* causes something called *vacuum polarization*, which is important in the theory of quantum electrodynamics. What is the maximum duration for the existence of a virtual electron-positron pair?

14. Expectation Values in Quantum Theory

14.1 As we have seen, to obtain a realistic wavefunction for a particle we must construct a wave packet $\psi(x,t)$ which contains all the information about the particle's position and momentum. But, in general, $\psi(x,t)$ is too complicated to understand in its entirety, so we would like to extract some basic information from it. One of the most basic features of a probability distribution is its average, so as a first step we can try to determine the average position of the particle.

14.2 In one dimension, the probability to find the particle between the points x and $x+dx$ at time t is proportional to

$$|\psi(x,t)|^2\,dx. \tag{14.1}$$

It follows from our understanding of probabilities (*cf.* Equation (10.4)) that the expectation value for the position of the particle in the state $\psi(x,t)$ as a function of time is given by

$$\langle x\rangle = \int x\psi^*(x,t)\psi(x,t)\,dx, \tag{14.2}$$

provided we choose $\psi(x,t)$ so that

$$\int \psi^*(x,t)\psi(x,t)\,dx = 1. \tag{14.3}$$

Remark. We are being a little sloppy here. Technically, we should write $\langle x\rangle_\psi$ for $\langle x\rangle$ to emphasize that we are computing the expectation value of the position of the particle when the particle is described by the wavefunction ψ. But more often than not the state is clear from context, and we drop the subscript.

14.3 When (14.3) holds, we say the wavefunction is **normalized** (in which case the corresponding probability distribution is normalized). As before, if the wavefunction is not normalized, we must instead write

$$\boxed{\langle x\rangle = \frac{\int x\psi^*(x,t)\psi(x,t)\,dx}{\int \psi^*(x,t)\psi(x,t)\,dx}}. \tag{14.4}$$

14.4 We may generalize this to any arbitrary function $G(x)$ of x, such as the potential energy $V(x)$ of the system. The expectation value of the quantity $G(x)$ is thus given by

$$\langle G(x)\rangle = \frac{\int G(x)\psi^*(x,t)\psi(x,t)\,dx}{\int \psi^*(x,t)\psi(x,t)\,dx}. \tag{14.5}$$

14.5 Exercise. Suppose we have a particle whose wavefunction at $t = 0$ is given by

$$\psi(x, 0) = Ce^{-\alpha x^2/2}.$$

Find the constant C which normalizes $\psi(x, 0)$. [Hint: Consult Appendix A.]

14.6 Exercise. Using the normalized wavefunction you computed in the previous exercise, compute $\langle x \rangle$ and $\langle x^2 \rangle$.

14.7 Now, suppose we wish to compute the expectation value of the particle's momentum. The obvious thing to try is

$$\langle p \rangle = \int p(x)\psi^*(x, t)\psi(x, t)\, dx, \tag{14.6}$$

but this is impossible, because **there can be no such function** $p(x)$. A function of the form $p(x)$ would violate the uncertainty principle, because it assigns a precise momentum to a particle given its position.

15. Fourier Analysis and the Momentum Operator

15.1 To find a way out of this problem, we must press on further into the nether reaches of quantum land. As we argued above, in order to construct a particle with a reasonably well-defined position, we had to construct a wave packet as a superposition of harmonic waves. Let us introduce a new quantity, called the **momentum space wavefunction** $\phi(k, t)$ by defining

$$\phi(k, t) = \sqrt{2\pi}A(k)e^{-i\omega_k t}. \tag{15.1}$$

Then equation (12.6) can be written

$$\boxed{\psi(x, t) = \frac{1}{\sqrt{2\pi}} \int \phi(k, t)e^{ikx}\, dk}. \tag{15.2}$$

It follows from the theory of Fourier transforms that

$$\boxed{\phi(k, t) = \frac{1}{\sqrt{2\pi}} \int \psi(x, t)e^{-ikx}\, dx}. \tag{15.3}$$

The essential point is that we may specify the state of a particle by specifying either $\psi(x,t)$ or $\phi(k,t)$, but not both. $\psi(x,t)$ is more suitable for answering questions about the particle's position, while $\phi(k,t)$ is more suitable for answering questions about the particle's momentum (recall $p = \hbar k$). Which one we choose to use is solely a matter of taste. [24]

15.2 Yet another result from the theory of Fourier analysis is that, for two functions related according to (15.2) and (15.3), we have **Parseval's theorem**:

$$\int |\psi|^2 \, dx = \int |\phi|^2 \, dk. \tag{15.4}$$

This allows us to interpret the quantity

$$|\phi(k,t)|^2 \, dk \tag{15.5}$$

as the probability to find the particle with wavenumber between k and $k+dk$, or, using the de Broglie relation $p = \hbar k$, the probability to find the particle with momentum between p and $p + dp$.

15.3 We now see how to find the expectation value of the momentum of the particle. We must use the momentum space wavefunction! The rules of probability then tell us that

$$\boxed{\langle p \rangle = \langle \hbar k \rangle = \int \hbar k \phi^*(k,t)\phi(k,t) \, dk}. \tag{15.6}$$

15.4 This is all nice and fine, but we would like to write all our equations in terms of $\psi(x,t)$ rather than $\phi(k,t)$, because this is what is more familiar to us. How can we do this? Well, let us substitute into (15.6) using (15.3) to get

$$\begin{aligned}
\langle p \rangle &= \int \hbar k \left[\frac{1}{\sqrt{2\pi}} \int \psi(x,t) e^{-ikx} \, dx \right]^* \phi(k,t) \, dk \\
&= \frac{1}{\sqrt{2\pi}} \int dx \, dk \; (\hbar k) \psi^*(x,t) \phi(k,t) e^{ikx} \\
&= \hbar \int dx \, \psi^*(x,t)(-i) \frac{\partial}{\partial x} \left[\frac{1}{\sqrt{2\pi}} \int \phi(k,t) e^{ikx} \, dk \right] \\
&= \int dx \, \psi^*(x,t) \left(-i\hbar \frac{\partial}{\partial x} \right) \psi(x,t).
\end{aligned}$$

[24] Indeed, when you learn more about quantum theory you will discover that the transformation from (15.2) to (15.3) may be thought of as an infinite dimensional change of basis.

15.5 Now comparing this with (14.6) we see that, instead of thinking of momentum as a **number**, we should think of it as a **differential operator** that acts on wavefunctions:

$$\boxed{\widehat{p} := -i\hbar \frac{\partial}{\partial x}}\,. \tag{15.7}$$

We call it the **momentum operator in the position representation**. The little hat indicates that it is an operator rather than a simple variable. It follows that the rule for computing the expectation value of the momentum (in position space) is

$$\boxed{\langle p \rangle =: \langle \widehat{p} \rangle = \int \psi^*(x,t) \widehat{p} \psi(x,t)\, dx}\,. \tag{15.8}$$

15.6 This association allows you to compute the expectation value of any function of momentum, such as the kinetic energy. You simply express the kinetic energy in terms of the momentum, then substitute in the momentum operator $\widehat{p}$ everywhere for the momentum p. That is

$$\langle KE \rangle = \int \psi^*(x,t) \frac{\widehat{p}^2}{2m} \psi(x,t)\, dx. \tag{15.9}$$

16. Operators vs. Dynamical Variables

16.1 If, instead of looking for an expression for the momentum in position space you were to look for an expression for the position in momentum space, you would find that $\widehat{x} = i\hbar\partial/\partial p$. This leads you to suspect that **all dynamical variables in quantum theory must be represented by operators**. And this is indeed one of the postulates of quantum theory. [25]

16.2 In this course we will always work in position space, with position space wave functions $\psi(x,t)$. In position space, the position operator $\widehat{x}$ acts simply by ordinary multiplication by x:

$$\boxed{\widehat{x} := x\cdot}\,. \tag{16.1}$$

[25] Actually, there is a restriction on the sorts of operators that are allowed. They must be what are called **Hermitian** operators. See below.

We can see this by comparing (14.2) and, say, (15.8). Because of this, we may simply commute the x and $\psi^*(x,t)$ in (14.2) and express the expectation value of x in a manner parallel to that of (15.8). Indeed, for any operator $\widehat{A}$ representing some dynamical variable A we write

$$\boxed{\langle A\rangle = \langle \widehat{A}\rangle = \int \psi^*(x,t)\widehat{A}\psi(x,t)\,dx}\,. \tag{16.2}$$

16.3 Let us make certain we understand this point. A dynamical variable is something like the position of a particle or its momentum or its energy. In classical physics these quantities are represented by numerical variables, *i.e.,* by quantities whose values are real numbers. In quantum theory, the uncertainty principle forces us to represent dynamical variables by operators that act on wavefunctions. This could be viewed as the essential difference between classical and quantum theory.

16.4 The **commutator** $[\widehat{A},\widehat{B}]$ of two operators is defined by

$$\boxed{[\widehat{A},\widehat{B}]\psi = \widehat{A}\widehat{B}\psi - \widehat{B}\widehat{A}\psi}\,. \tag{16.3}$$

An essential feature that distinguishes quantum theory from classical theory is that, whereas in classical theory two dynamical variables commute, *i.e.,* $xp = px$, this is no longer the case in quantum theory where dynamical variables are represented by quantum operators.

16.5 Exercise. Show that $[\widehat{x},\widehat{x}] = [\widehat{p},\widehat{p}] = 0$ (trivial) and $[\widehat{x},\widehat{p}] = i\hbar$. These are called the **Heisenberg commutation relations**, because they are responsible for the Heisenberg uncertainty principle.

16.6 Exercise. Show that the commutator is antisymmetric, bilinear, and that it acts as a **derivation** on products of operators. That is, prove that, for complex constants a, b, and c, and operators $\widehat{A}$, $\widehat{B}$, and $\widehat{C}$:

$$1) \qquad [\widehat{A},\widehat{B}] = -[\widehat{B},\widehat{A}] \tag{16.4}$$

$$2) \qquad [\widehat{A}, b\widehat{B} + c\widehat{C}] = b[\widehat{A},\widehat{B}] + c[\widehat{A},\widehat{C}] \tag{16.5}$$

$$2') \qquad [a\widehat{A} + b\widehat{B},\widehat{C}] = a[\widehat{A},\widehat{C}] + b[\widehat{B},\widehat{C}] \tag{16.6}$$

$$3) \qquad [\widehat{A},\widehat{B}\widehat{C}] = [\widehat{A},\widehat{B}]\widehat{C} + \widehat{B}[\widehat{A},\widehat{C}]. \tag{16.7}$$

17.1 Because certain particular combinations of symbols occur so often, we introduce some shorthand notation. Let us define, for any two complex functions f and g the **inner product** of f and g as follows:

$$\boxed{(f,g) := \int f^*(x)g(x)\,dx}\,. \tag{17.1}$$

The nomenclature arises because the expression (17.1) really is an inner product, in that it satisfies the following three axioms of an inner product. For any complex functions f and g and complex scalar λ we have

$$\begin{aligned} &(i) && (f,\lambda g) = \lambda(f,g) && \text{(linearity on second entry)} \\ &(ii) && (f,g) = (g,f)^* && \text{(Hermiticity)} \\ &(iii) && (f,f) \geq 0, = 0 \Leftrightarrow f = 0 && \text{(positive definiteness).} \end{aligned}$$

You can think of the inner product as a sort of infinite dimensional dot product.

17.2 Exercise. Show from the axioms that the inner product is **antilinear** on the first entry:

$$(\lambda f, g) = \lambda^*(f,g). \tag{17.2}$$

17.3 Exercise. Show from the axioms that the inner product satisfies the *Cauchy-Schwarz inequality*

$$|(f,g)|^2 \leq (f,f)(g,g). \tag{17.3}$$

[Hint: Consider minimizing $(f+\lambda g, f+\lambda g)$ with respect to λ. Assume λ is a complex variable and to differentiate with respect to it. When so doing, you may treat λ^* as if it were independent of λ. The result will be an equation in λ^*, which you should substitute back into your original equation.]

17.4 Exercise. Prove that the expression (17.1) really defines an inner product, by verifying that is satisfies all the axioms.

17.5 Using this new notation, we see that the expectation value of an operator $\widehat{A}$ is given by

$$\langle \widehat{A} \rangle = (\psi, \widehat{A}\psi), \tag{17.4}$$

provided

$$(\psi, \psi) = 1. \tag{17.5}$$

If ψ is not normalized, then we write

$$\boxed{\langle \widehat{A} \rangle = \frac{(\psi, \widehat{A}\psi)}{(\psi, \psi)}}. \tag{17.6}$$

Alternatively, we can normalize ψ by replacing ψ by $\psi/(\psi, \psi)^{1/2}$. If we can do this (*i.e.,* if (ψ, ψ) exists) we say that ψ is **normalizable**.

18. Hermiticity

We need one technical

Definition. An operator $\widehat{A}$ is said the be **Hermitian** provided

$$\boxed{(\psi, \widehat{A}\psi) = (\widehat{A}\psi, \psi)}. \tag{18.1}$$

for all possible wavefunctions ψ. Hermitian operators have all sorts of nice properties, including the fact that their expectation values are always real.

18.1 Exercise. Prove this.

For now we only need to know that, in quantum theory, dynamical variables are always represented by Hermitian operators.

18.2 Exercise. Show that, in order for a one-dimensional wavefunction ψ to be normalizable, it must fall off at least as fast as $x^{-1/2}$. [Hint: Show that (ψ, ψ) does not exist if this condition is not satisfied.]

18.3 Exercise. Prove that, when acting in the space of all normalizable wavefunctions, the momentum operator (15.7) is Hermitian.

19. The Standard Deviation

19.1 We learned that, in the case of a finite number of measurements of a system, the expectation value or average measurement is given by

$$\langle x \rangle = \frac{1}{N} \sum_i x_i$$

where the x_i are all the data points. [26] If we wish to measure the spread of these data points about the mean, we need another indicator, or **statistic**. Such a statistic is provided by the **standard deviation**. Let us recall what this is.

19.2 We might imagine measuring how far each data point is from the mean and then averaging these deviations. That is, define

$$d_i := x_i - \bar{x} \tag{19.1}$$

to be the deviation of the i^{th} measurement from the mean. Then the average deviation is

$$\langle d \rangle = \frac{1}{N} \sum_i d_i. \tag{19.2}$$

The problem with this is that it is always zero! Obviously, this statistic is not too helpful.

19.3 Exercise. Prove the average deviation is identically zero.

19.4 Instead of using the average deviation as our measure of the spread of values from the mean, we could use the average of the absolute values of the deviations. But it turns out to be much more useful to define the standard deviation σ, which is the square root of the average of the square of the deviations. In other words, σ is the root mean square deviation:

$$\sigma := \sqrt{\frac{1}{N} \sum_i (x_i - \bar{x})^2}. \tag{19.3}$$

19.5 In the continuum limit, we already saw that the average becomes the expectation value

$$\langle x \rangle = \int x P(x)\, dx.$$

[26] Here we temporarily revert back to the original meaning of the x_i.

Similarly, the **variance** (the square of the standard deviation) becomes

$$\boxed{\sigma^2 = \int (x - \langle x \rangle)^2 P(x)\, dx}, \tag{19.4}$$

and the standard deviation is obtained upon taking the square root.

19.6 Exercise. Show that the variance can be written as

$$\sigma^2 = \langle x^2 \rangle - \langle x \rangle^2. \tag{19.5}$$

19.7 Exercise. Compute the standard deviation of the exponential probability distribution (10.8).

20. Uncertainty Revisited

20.1 Let us now return to quantum theory. According to Equation (17.4) the expectation value of the dynamical variable A in the (normalized) state represented by ψ is

$$\langle A \rangle = \langle \widehat{A} \rangle = (\psi, \widehat{A}\psi)$$

We now define the **uncertainty** ΔA of the observable A in the state ψ to be simply the standard deviation (*cf.* Equation (19.5)):

$$\boxed{\Delta A = \left(\langle \widehat{A}^2 \rangle - \langle \widehat{A} \rangle^2 \right)^{1/2}}. \tag{20.1}$$

20.2 What does all this mean? Suppose the particle is in a state represented by the wavefunction ψ. We can then ask certain questions about it. For example, we might want to know what is the expected value of its position. The answer to this question is $\langle x \rangle = (\psi, x\psi)$. On the other hand, we might wish to know how uncertain we are of its position. We might imagine measuring the location of the particle again and again, and computing its standard deviation. This is precisely what we have called the uncertainty in the position of the particle, and it is given by Δx.

20.3 The problem is, you cannot do this in general! That is, most measurements of the location of a particle require destroying the particle, so there is no way you can measure

its position repeatedly. So what is the ontological significance of the uncertainty? Well, we can imagine preparing the particle in exactly the same way 100 times, then measuring the positions of each of the 100 particles. Then the spread of values of the position of the particle about the mean is given by what we have called the uncertainty. Of course, we do not actually do this. For this reason, the state ψ is often said to represent a **virtual ensemble** of particles, the word 'virtual' implying that we do not actually perform all 100 experiments.

20.4 At this point you might wonder what this has to do with Heisenberg's Uncertainty Principle, if anything. Starting from the definition (20.1) one can show (see Appendix B) that:

$$\Delta x \Delta p_x \geq \frac{\hbar}{2}. \tag{13.8}$$

Of course, this is precisely the Heisenberg Uncertainty Principle. Indeed, it is the most precise statement of that principle.

20.5 But there is one major difference. Previously, we argued the Heisenberg Uncertainty Principle applied to a **single particle**, while in this context it seems to apply to a **virtual ensemble** of particles. Before, the Heisenberg principle seemed to be a statement about a single particle, namely the fact that it does not simultaneously possess well defined position and momentum. In the current context, it seems to be a statement about a virtual ensemble of particles. It seems to say that, the more precisely you measure the **distribution** of particle positions, the less precisely you can know the **distribution** of particle momenta. It makes it appear to be a statement about **measurement**, an interpretation we previously eschewed.

20.6 So, which is it? And what does the wavefunction ψ mean, anyway? Does it represent a single particle, or a virtual ensemble of identically prepared particles? Well, all the available evidence suggests that it is both! Both interpretations can be sustained. Indeed, there is no necessary conflict between the two. At present, the difference seems to be one of interpretation only.

Does this mean we are free to reject the first interpretation of the Heisenberg Uncertainty Principle? No. It can be shown experimentally that assuming particles have well defined properties leads to conclusions that disagree with reality. By like token, the second interpretation is also workable. If we perform an experiment in which we actually do repeat a measurement over and over, the ensemble interpretation gives the correct answer.

20.7 Exercise. Compute the uncertainty Δx in the position of the particle represented by the normalized version of the wavefunction $\psi = Ce^{-\alpha x^2/2}$ that you computed in Exercise **10.5** above. Show that the normalized Gaussian represents the **minimum uncertainty wavepacket**, namely the wavepacket with the smallest possible uncertainty product $\Delta x\, \Delta p_x$. [Hint: You must compute Δp using the wavefunction ψ and the momentum operator (15.7).]

21. Eigenvalues and Eigenfunctions

21.1 At this point, you might think that everything in the subatomic world is probabilistic, *i.e.,* that measurements always yield a spread in values. But this is false. For example, the wavefunction $\psi(x,t) = Ae^{i(kx-\omega t)}$ represents a particle with a perfectly well-defined momentum. More physically, atoms have well-defined energy levels. Any state or wavefunction ψ with such a sharply defined value for a dynamical variable A will be called an **eigenstate** or **eigenfunction** of the operator $\widehat{A}$. Technically we have the

Definition. An **eigenstate** ψ is a state in which one or more dynamical variables have vanishing uncertainty.

21.2 Suppose, for example, that the state ψ is an eigenstate of the operator $\widehat{A}$. Let us define a new operator [27]

$$\bar{A} := \widehat{A} - \langle \widehat{A} \rangle \tag{21.1}$$

21.3 Exercise. Prove that, if A is a dynamical variable (so that the operator $\widehat{A}$ that represents it in quantum theory is Hermitian) then the operator $\bar{A}$ is also Hermitian.

Then we have

$$0 = (\Delta A)^2 = (\psi, (\widehat{A} - \langle \widehat{A} \rangle)^2 \psi) = (\psi, \bar{A}^2 \psi) = (\bar{A}\psi, \bar{A}\psi)$$

where the last step used the Hermiticity of $\bar{A}$. The properties of the inner product then guarantee that $\bar{A}\psi = 0$ and so

$$(\widehat{A} - \langle \widehat{A} \rangle)\psi = 0$$

[27] Technically, we must write $\bar{A} = \widehat{A} - \langle \widehat{A} \rangle \widehat{1}$ where $\widehat{1}$ is the **identity operator** which does nothing to wavefunctions $\widehat{1}\psi = \psi$. But if you just imagine $\langle \widehat{A} \rangle$ to be a number that multiplies wavefunctions, everything will work out fine.

But $\langle \widehat{A} \rangle = a$, a definite number. So we conclude that, if the uncertainty of the operator $\widehat{A}$ in the state ψ is zero, the following equation holds:

$$\boxed{\widehat{A}\psi = a\psi}\,. \tag{21.2}$$

This is called an **eigenvalue equation**. [28] We say that ψ is an **eigenstate** of the operator $\widehat{A}$ with eigenvalue a.

21.4 Exercise. Show that the family of wavefunctions of the form

$$\psi(x,t) = Ae^{i(kx-\omega t)} \tag{21.3}$$

are **momentum eigenstates**:

$$\widehat{p}\psi = p\psi.$$

Each one represents a particle with a precisely defined momentum $\hbar k$.

21.5 Exercise. Show that the wavefunction given by

$$\psi(x,t) = Ae^{i(k_1x-\omega_1 t)} + Ae^{i(k_2x-\omega_2 t)} \tag{21.4}$$

does not have a definite value for its momentum by showing that it is not a momentum eigenstate.

21.6 Exercise. Let us introduce a new operator, called the **energy operator**, defined as follows:

$$\boxed{\widehat{E} := i\hbar\frac{\partial}{\partial t}}\,. \tag{21.5}$$

Show that the momentum eigenstates (21.3) are also **energy eigenstates**:

$$\widehat{E}\psi = E\psi$$

This is one justification for the name "energy operator" for the differential operator given in (21.5).

[28] From the German, **eigenwert**, meaning proper or characteristic value.

22. The Schrödinger Equation for an Interacting Particle

22.1 The energy and momentum of a free non-relativistic particle satisfy the relation

$$E = \frac{p^2}{2m}$$

Let us multiply both sides of this equation by ψ

$$E\psi = \frac{p^2}{2m}\psi$$

Now, arguing heuristically that in quantum theory dynamical variables are represented by operators, we could replace E and p with their operator counterparts to get

$$\widehat{E}\psi = \frac{\widehat{p}^2}{2m}\psi$$

which, if you plug in the definitions (15.7) and (21.5) is precisely the Schrödinger equation for a free, non-relativistic particle! Indeed, we could view this as an alternative "derivation" of that equation.

22.2 The chief utility of this heuristic argument is in discovering the appropriate generalization of Schrödinger's equation in the interacting case. Suppose we have a particle subject to various forces. Recall from classical mechanics that conservative forces can be derived from a potential energy, *e.g.,*

$$F_x = -\frac{\partial V}{\partial x}$$

where $V(x)$ is the potential energy of the particle. Now, we believe that all fundamental forces in nature are conservative. Certainly we know this to be true for the gravitational and electrostatic forces; and we know that friction, for example, which is not conservative, is not a fundamental force, but rather is electrostatic in origin.

22.3 This argument suggests that we may introduce interactions via a potential energy term. That is, we now write the total energy of the particle as

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

A priori $V = V(x,t)$ can vary in both space and time, although we will primarily be concerned with cases in which $V = V(x)$ is time independent. Again, by analogy with what we did above, we can multiply by ψ to obtain

$$E\psi = \frac{p^2}{2m}\psi + V\psi$$

22.4 Now we introduce a **potential energy operator** $\widehat{V}(x)$ via the definition

$$\widehat{V}(x) := V(\widehat{x}). \tag{22.1}$$

Under the present circumstances this definition is rather pedantic, as we already agreed that, as long as we stick with wavefunctions in the position representation, the position operator $\widehat{x}$ is just multiplication by x when acting on wavefunctions. So $\widehat{V}(x)$ acting on wavefunctions is just multiplication by $V(x)$.

22.5 Pressing onwards, we promote the dynamical variables to operators to yield

$$\widehat{E}\psi = \frac{\widehat{p}^2}{2m}\psi + \widehat{V}\psi, \tag{22.2}$$

or, substituting from (15.7), (21.5), and (22.1),

$$\boxed{i\hbar\frac{\partial\psi}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} + V\psi}\,. \tag{22.3}$$

Equation (22.2), or equivalently (22.3), is called the **time-dependent Schrödinger equation in one dimension in the position representation**. This is the equation, discovered by Schrödinger in 1926, that governs the behavior of de Broglie waves. It is more fundamental than Newton's Laws, in that the latter can be proved to be a consequence of the former!

22.6 For future reference let us record the three dimensional generalization of (22.3), namely

$$i\hbar\frac{\partial\psi}{\partial t} = -\frac{\hbar^2}{2m}\overrightarrow{\nabla}^2\psi + V\psi, \tag{22.4}$$

where

$$\overrightarrow{\nabla}^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

is the Laplacian operator.

22.7 By analogy with classical mechanics, we introduce the **Hamiltonian operator** $\widehat{H}$ via

$$\boxed{\widehat{H} := \frac{\widehat{p}^2}{2m} + \widehat{V}}\,. \tag{22.5}$$

Then Schrödinger's equation reads

$$\boxed{\widehat{H}\psi = \widehat{E}\psi}\,, \tag{22.6}$$

which reveals its close connection to the energy of the system. [29]

23. Probability Current Density and The Conservation of Probability

23.1 We now turn to an investigation of the flow of probability in quantum theory, in order to gain some understanding of the motion of particulate systems. We begin by computing the rate of change of probability in a given volume. In one dimension, a volume is just an interval, so we write

$$\begin{aligned}\frac{\partial}{\partial t}\int_a^b P(x,t)\,dx &= \frac{\partial}{\partial t}\int_a^b \psi^*\psi\,dx \\ &= \int_a^b \left(\frac{\partial\psi^*}{\partial t}\psi + \psi^*\frac{\partial\psi}{\partial t}\right)\,dx.\end{aligned} \tag{23.1}$$

Taking the complex conjugate of Schrödinger's equation (22.3) we have

$$-i\hbar\frac{\partial\psi^*}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2\psi^*}{\partial x^2} + V\psi^*. \tag{23.2}$$

Observe that we have assumed the potential energy operator V to be real. [30] Using (22.3) and (23.2) in Equation (23.1) yields

$$\begin{aligned}\frac{\partial}{\partial t}\int_a^b P(x,t)\,dx &= \int_a^b \left[\frac{1}{-i\hbar}\left(-\frac{\hbar^2}{2m}\frac{\partial^2\psi^*}{\partial x^2} + V\psi^*\right)\right]\psi \\ &\qquad + \psi^*\left[\frac{1}{i\hbar}\left(-\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} + V\psi\right)\right] \\ &= \frac{\hbar}{2im}\int_a^b dx\,\left(\frac{\partial^2\psi^*}{\partial x^2}\psi - \psi^*\frac{\partial^2\psi}{\partial x^2}\right) \\ &= \frac{\hbar}{2im}\int_a^b dx\,\frac{\partial}{\partial x}\left(\frac{\partial\psi^*}{\partial x}\psi - \psi^*\frac{\partial\psi}{\partial x}\right).\end{aligned} \tag{23.3}$$

[29] Note that (22.6) is **not** an eigenvalue equation (at least, not yet), because both sides are operator equations. We will eventually reduce it to one, however.

[30] It can be shown that, if V is complex, probability leaks out of the universe. We may interpret this physically by arguing that, in this case, the particle is decaying. That is, it really is disappearing!

23.2 To interpret (23.3) physically, we introduce the **probability current density vector** (in one dimension):

$$j(x,t) := \frac{\hbar}{2im}\left(\psi^*\frac{\partial\psi}{\partial x} - \frac{\partial\psi^*}{\partial x}\psi\right). \tag{23.4}$$

With this definition, Equation (23.3) can be written (by stripping off the integrals)

$$\frac{\partial P}{\partial t} = -\frac{\partial j}{\partial x} \qquad \text{or} \qquad \frac{\partial P}{\partial t} + \frac{\partial j}{\partial x} = 0. \tag{23.5}$$

In integral form, Equation (23.3) becomes

$$\frac{\partial}{\partial t}\int_a^b P(x,t)\,dx = -\left(j(b) - j(a)\right). \tag{23.6}$$

Physically, the left side represents the rate of change of probability in the interval $[a,b]$, while the right hand side gives the rate at which probability is carried into a minus the rate at which it is carried out of b. That is, equation (23.6) embodies the **Law of Conservation of Probability**. The differential form (23.5) is often referred to as a **continuity equation** by analogy with similar equations in fluid dynamics and electrodynamics. This allows us to picture probability as a sort of fluid that flows continuously!

The probability current density vector $j(x,t)$ may be interpreted as the *flux* of probability. This is particularly clear in three dimensions, where the analogues of (23.4), (23.5), and (23.6) are

$$\mathbf{j}(x,t) := \frac{\hbar}{2im}\left(\psi^*\vec{\nabla}\psi - \psi\vec{\nabla}\psi^*\right), \tag{23.7}$$

$$\frac{\partial P}{\partial t} + \vec{\nabla}\cdot\mathbf{j} = 0, \tag{23.8}$$

and

$$\frac{\partial}{\partial t}\int_V P(\mathbf{r},t)\,d^3r = -\int_{\partial V}\mathbf{j}\cdot d\mathbf{S}. \tag{23.9}$$

respectively.

23.3 From our knowledge of electrodynamics, we see that $\mathbf{j}(x,t)$ really does play the role of a probability current density vector, representing the probability per unit time per unit area crossing a given surface. In one dimension $j(x,t)$ has units of probability per unit time, and it represents the rate of flow of probability at a point. If we multiply it by the number of particles in our ensemble, it gives the average number of particles moving past a given point per unit time.

23.4 Exercise. Compute the probability current density associated with the wave

$$\psi(x,t) = Ae^{i(kx-\omega t)}.$$

Verify that it can be written in the form $j = vP$, where $P = |\psi|^2$ is the probability density of the wave and v is the particle velocity. Interpret this equation physically. [Hint: Reason by analogy with (one-dimensional) fluid dynamics. Interpret j as the fluid flux density, *i.e.,* the mass per unit time crossing a given point, and interpret v and P as the fluid velocity and mass density, respectively.]

23.5 Exercise. Calculate the probability current density vector associated to the wave-function

$$\psi(x,t) = Ae^{-i\omega t}\sin kx.$$

What is the physical interpretation of this result?

24. Hermiticity of the Hamiltonian

24.1 Let us now take the interval of interest to be $[-\infty,\infty]$. Assuming there are no particle decays, we cannot have particles spontaneously disappearing from the universe, so we must have $j(\pm\infty) = 0$. That is, no probability leaks out of the universe at the edges. It then follows that (using the shorthand notation of the inner product)

$$\begin{aligned} 0 &= \frac{\partial}{\partial t}\int_{-\infty}^{\infty} P(x,t)\,dx \\ &= \frac{\partial}{\partial t}(\psi,\psi) \\ &= (\dot{\psi},\psi) + (\psi,\dot{\psi}) \\ &= (\frac{1}{i\hbar}\widehat{H}\psi,\psi) + (\psi,\frac{1}{i\hbar}\widehat{H}\psi) \\ &= \frac{1}{i\hbar}[(\psi,\widehat{H}\psi) - (\widehat{H}\psi,\psi)], \end{aligned} \tag{24.1}$$

where we employed the Hamiltonian operator introduced in (22.5) together with the properties of the inner product. It follows that, in order for probability to be conserved, the Hamiltonian operator must be Hermitian, *i.e.,*

$$(\psi,\widehat{H}\psi) = (\widehat{H}\psi,\psi). \tag{24.2}$$

This condition will be important in what follows. It is also serves as an important constraint when one is trying to construct the Hamiltonian operator that describes a physical system.

25. Ehrenfest's Theorem

25.1 In 1927, just after Schrödinger wrote down his equation (22.3), Paul Ehrenfest demonstrated that Newton's Laws can be deduced from Schrödinger's wave mechanics. Newton's Laws for a single particle may be written in the following form:

$$\frac{dx}{dt} = \frac{p}{m} \qquad \text{and} \qquad \frac{dp}{dt} = -\frac{\partial V}{\partial x}. \tag{25.1}$$

According to the principles of wave mechanics, particles do not simultaneously possess well defined positions and momenta, so they cannot be said to travel along definite trajectories. Hence equations (25.1) cannot hold precisely. Instead, Ehrenfest showed that the *expectation values* of the particle's position and momentum are related by Newton's Laws. More precisely, Ehrenfest showed that

$$\frac{d}{dt}\langle x\rangle = \frac{\langle p\rangle}{m} \qquad \text{and} \qquad \frac{d}{dt}\langle p\rangle = -\langle\frac{\partial V}{\partial x}\rangle. \tag{25.2}$$

It is in this sense that Newton's Laws are a consequence of quantum theory.

25.2 To begin, we develop an expression for the time rate of change of an expectation value: [31]

$$\begin{aligned}
\frac{d}{dt}\langle A\rangle &= \frac{d}{dt}(\psi, \widehat{A}\psi) \\
&= (\frac{\partial\psi}{\partial t}, \widehat{A}\psi) + (\psi, \frac{\partial\widehat{A}}{\partial t}\psi) + (\psi, \widehat{A}\frac{\partial\psi}{\partial t}) \\
&= (\frac{1}{i\hbar}\widehat{H}\psi, \widehat{A}\psi) + (\psi, \frac{\partial\widehat{A}}{\partial t}\psi) + (\psi, \widehat{A}\frac{1}{i\hbar}\widehat{H}\psi) \\
&= -\frac{1}{i\hbar}(\widehat{H}\psi, \widehat{A}\psi) + \langle\frac{\partial\widehat{A}}{\partial t}\rangle + \frac{1}{i\hbar}(\psi, \widehat{A}\widehat{H}\psi) \\
&= -\frac{1}{i\hbar}(\psi, [\widehat{H}\widehat{A} - \widehat{A}\widehat{H}]\psi) + \langle\frac{\partial\widehat{A}}{\partial t}\rangle,
\end{aligned}$$

where we used Schrödinger's equation (22.6) and the Hermiticity of $\widehat{H}$. Therefore we can write

$$\frac{d}{dt}\langle A\rangle = \langle\frac{\partial\widehat{A}}{\partial t}\rangle + \frac{1}{i\hbar}\langle[\widehat{A}, \widehat{H}]\rangle. \tag{25.3}$$

25.3 Exercise. Finish the proof of Ehrenfest's theorem.

Remark. Technically, the classical trajectory of the particle is approximated by $\langle x\rangle$. So, to agree with Newton's Laws (25.1) we must show that $\langle\partial V/\partial x\rangle = \partial V(\langle x\rangle)/\partial\langle x\rangle$. But this is approximately true whenever the particle is well described by a localized wavepacket.

[31] As always, unless stated otherwise, we assume ψ to be normalized.

26. Steady State Solutions to the Wave Equation

26.1 In this section we begin to investigate the nature of the solutions to Schrödinger's equation (22.3). It turns out that there is a big difference in the nature of the solutions, depending on whether the potential energy $V(x,t)$ is or is not a function of time. For the next while, therefore, we will assume that $V = V(x)$ is time-independent. In this case, we may employ a technique called **separation of variables** to reduce the time-dependent Schrödinger equation (22.3) to a time-independent equation.

26.2 The technique of separation of variables is basically a fancy way of guessing that, under certain circumstances, a function of two variables may be written as a simple product of two functions of one variable. We therefore assume that we may write [32]

$$\psi(x,t) = u(x)f(t). \tag{26.1}$$

The function $u(x)$ is often called the **time-independent wave function**, although we will see there is also another term for it.

26.3 Plugging Equation (26.1) into the time-dependent Schrödinger equation (22.3) gives

$$i\hbar u(x)\frac{\partial f}{\partial t} = -\frac{\hbar^2}{2m}\left(\frac{\partial^2 u}{\partial x^2}\right) f(t) + Vu(x)f(t)$$

Dividing through by the product $u(x)f(t)$ then gives

$$i\hbar\frac{1}{f(t)}\frac{\partial f}{\partial t} = \frac{1}{u(x)}\left[-\frac{\hbar^2}{2m}\frac{\partial^2 u}{\partial x^2} + Vu(x)\right] =: E. \tag{26.2}$$

The left side is a function of t only, while the middle is a function of x only. The only way an arbitrary function of t can equal an arbitrary function of x for all values of x and t is if they are both equal to a fixed constant, called a **separation constant**. We have called this separation constant E, because, as we will see, it will turn out to be the energy of the system.

26.4 The equation for $f(t)$ is now trivial:

$$i\hbar\frac{1}{f}\frac{\partial f}{\partial t} = E \Longrightarrow f(t) = Ae^{-i(E/\hbar)t}, \tag{26.3}$$

[32] Many authors denote the functions $u(x)$ by $\psi(x)$, and reserve $\Psi(x,t)$ for what we have called $\psi(x,t)$. I choose not to do this for the simple reason that I find the distinction between capital Ψ and small ψ awkward to make on a blackboard.

while the other equation, using the definition (22.5) of the hamiltonian operator becomes

$$\boxed{\widehat{H}u_E(x) = Eu_E(x)}\,. \tag{26.4}$$

This is an eigenvalue equation in which $u_E(x)$ is the eigenfunction of the Hamiltonian operator corresponding to the eigenvalue E. It is often called the **time-independent Schrödinger equation**. The solutions $u_E(x)$ are called **energy eigenfunctions**, for reasons that will become clear.

26.5 By absorbing the constant A into the function $u_E(x)$ and recalling Equation (26.1) we have arrived at one particular solution to the time-dependent Schrödinger equation (22.3)

$$\boxed{\psi(x,t) = u_E(x)e^{-i(E/\hbar)t}}\,, \tag{26.5}$$

provided $u_E(x)$ satisfies the time-independent Schrödinger equation (26.4). The solution (26.5) is called a **stationary state**, because the expectation value of any time-independent operator $\widehat{A}$ in such a state is time-independent.

26.6 Exercise. Prove this.

26.7 First, let us observe that E really is the energy of the system in the state ψ given by (26.5). Recall that, to do this, it suffices to show that ψ is an eigenstate of the energy operator with eigenvalue E. This will demonstrate that (i) the expectation value of $\widehat{E}$ in the state ψ is E, and (ii) the uncertainty ΔE of $\widehat{E}$ in the state ψ is zero, *i.e.,* the state ψ has definite energy E. But this is easy:

$$\widehat{E}\psi = i\hbar\frac{\partial\psi}{\partial t} = E\psi$$

26.8 One minor point is: how do we know the energy is real? That is, E was introduced above as a separation constant. What guarantees that E is a real number and not a complex number? Well, this follows because of the following

26.9 Theorem. *The eigenvalues of a Hermitian operator are real.*

Proof. Let $\widehat{A}$ be a Hermitian operator, and let ψ be an eigenstate of $\widehat{A}$ with eigenvalue a. Then, by definition of Hermiticity

$$(\psi, \widehat{A}\psi) = (\widehat{A}\psi, \psi)$$

But ψ is an eigenstate of $\widehat{A}$ with eigenvalue a, so we have

$$(\psi, a\psi) = (a\psi, \psi)$$

By the properties of the inner product, this yields

$$a(\psi, \psi) = a^*(\psi, \psi)$$

whence $a = a^*$ and a is real. ∎

We therefore conclude that E really is the energy of the state ψ.

27. General Solution to the Time-Dependent Schrödinger Equation for a Time Independent Potential

27.1 We have seen that the stationary state ψ given in Equation (26.5) is a particular solution to the time-dependent Schrödinger equation (22.3), and that it corresponds to a particle with a definite energy E. I now claim that the most general solution to the time-dependent Schrödinger equation is a **superposition** of stationary states. I will not prove this claim (indeed, it can only be proved in certain cases), but I hope to make it plausible.

27.2 Before we proceed, we need a bit of terminology. So we make the following

Definition. Two states ψ and χ are said to be **orthogonal** if

$$(\psi, \chi) = 0$$

The terminology follows that of ordinary vectors. Think of ϕ and χ as vectors in some large space (possibly infinite dimensional). Then they are orthogonal if the dot product between them is zero. This brings us to the following:

27.3 Theorem. *The eigenstates of a Hermitian operator corresponding to distinct eigenvalues are orthogonal.*

Proof. Let $\widehat{A}$ be a Hermitian operator, and suppose $\widehat{A}\psi = a\psi$ and $\widehat{A}\chi = b\chi$. Then

$$(\widehat{A}\psi, \chi) = (a\psi, \chi) = a^*(\psi, \chi) = a(\psi, \chi)$$

where the last step follows from Theorem 26.9. Similarly

$$(\psi, \widehat{A}\chi) = (\psi, b\chi) = b(\psi, \chi)$$

By Hermiticity, the leftmost expressions of both these equations are equal. Subtracting one equation from the other thus yields

$$(a - b)(\psi, \chi) = 0$$

The conclusion now follows, as a and b are distinct. ∎

27.4 Consider now the entire set $\{u_E(x)\}$ of energy eigenfunctions of a system, where E runs through all possible values of the energy. We suppose they are normalized, so that

$$(u_E, u_E) = 1$$

By the previous theorem, we have

$$(u_E, u_{E'}) = 0$$

if $E \neq E'$. Hence we can write

$$\boxed{(u_E, u_{E'}) = \delta_{EE'} := \begin{cases} 1 & \text{if } E = E', \\ 0 & \text{otherwise.} \end{cases}} \tag{27.1}$$

($\delta_{EE'}$ is called the **Krönecker delta function**.)

27.5 What is the point of this? Well, because of (27.1) we can now think of the energy eigenfunctions as a set of basis elements in an infinite dimensional space. [33] To see this, recall how things work in $\mathbb{R}^3$. There, we have the basis vectors e_1, e_2, and e_3. Any vector in $\mathbb{R}^3$ can be written as a linear combination of these basis vectors:

$$v = v_1 e_1 + v_2 e_2 + v_3 e_3$$

The vectors e_1, e_2, and e_3 are basis vectors because they are linearly independent, and span the space. This is guaranteed by the **orthonormality conditions**

$$(e_i, e_j) = \delta_{ij}$$

[33] Technically, there is a *caveat*. It is possible that one might have different energy eigenfunctions corresponding to the same energy eigenvalue. Such an subset of energy eigenfunctions is said to be **degenerate**. In that case, Theorem 27.3 does not apply. But, using something called **Gram-Schmidt orthogonalization**, one can make the entire set of energy eigenfunctions orthogonal to each other, even those that correspond to the same energy. In this case, Equation (27.1) can be generalized.

where (e_i, e_j) is the ordinary dot product of vectors in $\mathbb{R}^3$.

27.6 EXERCISE. Show that $(e_j, v) = v_j$, where (u, v) is the ordinary dot product. [Hint: Use the linearity and orthonormality properties.]

27.7 Therefore, by analogy with vector spaces, we **postulate** that the entire set of energy eigenfunctions $\{u_E(x)\}$ is **complete**, *i.e.,* that it forms a basis for the space of solutions to the time-dependent Schrödinger equation: [34]

$$\psi(x,t) = \sum_E c_E(t) u_E(x). \tag{27.2}$$

In this expression, the coefficients $c_E(t)$ are, in general, time-dependent. If the potential energy $V = V(x)$ is a function of position only, it is easy to show, starting from (27.2) that the coefficients have a very special form. In that case we may write

$$\boxed{\psi(x,t) = \sum_E c_E u_E(x) e^{-i(E/\hbar)t}}, \tag{27.3}$$

where the c_E are now **constants**. Comparing this equation to (26.5) we see that, as long as the potential energy is time-independent, *the general solution to the time-dependent Schrödinger equation is a superposition of stationary states.*

27.8 The coefficients c_E appearing in (27.3) may be given a physical interpretation, as follows. Let us compute the expectation value of the energy in the state ψ given by (27.3):

$$\begin{aligned}
\langle E \rangle = \langle \widehat{E} \rangle &= \langle \widehat{H} \rangle = (\psi, \widehat{H}\psi) \\
&= \sum_{E,E'} (c_{E'} u_{E'} e^{-i(E'/\hbar)t}, \widehat{H} c_E u_E e^{-i(E/\hbar)t}) \\
&= \sum_{E,E'} c^*_{E'} c_E e^{it(E'-E)/\hbar} (u_{E'}, \widehat{H} u_E) \\
&= \sum_{E,E'} c^*_{E'} c_E e^{it(E'-E)/\hbar} (u_{E'}, E u_E) \\
&= \sum_{E,E'} c^*_{E'} c_E e^{it(E'-E)/\hbar} E \delta_{EE'} \\
&= \sum_E |c_E|^2 E.
\end{aligned} \tag{27.4}$$

[34] In general, there may be a continuum of energy eigenvalues, not just a discrete set. In that case one should replace all the sums below with a combination of sums and integrals.

27.9 Comparing this expression with the expression (10.2) for the expectation value of a dynamical variable, we see that we may interpret the quantity $|c_E|^2$ as **the probability that the system represented by the state ψ has the energy E**:

$$P(E) = |c_E|^2. \tag{27.5}$$

Note that this assumes the state ψ is normalized, which, in turn, requires

$$\sum_E |c_E|^2 = 1, \tag{27.6}$$

as befits a probability distribution.

27.10 EXERCISE. Starting from the condition $(\psi, \psi) = 1$ show that $\sum_E |c_E|^2 = 1$.

Observe that, if $c_{E_0} = 1$ and all the others are zero, then the system is in a stationary state with the precise energy E_0.

27.11 EXERCISE. Let $u_1(x)$, $u_2(x)$, and $u_3(x)$ denote the normalized energy eigenfunctions of some one dimensional system. Let $\psi(x,t)$ be the wave function of the system, and suppose it is given at $t = 0$ by

$$\psi(x,0) = \frac{1}{\sqrt{2}} e^{i\alpha_1} u_1(x) + \frac{1}{\sqrt{3}} e^{i\alpha_2} u_2(x) + \frac{1}{\sqrt{6}} e^{i\alpha_3} u_3(x)$$

where the α_i are constants.

a) Write down the wavefunction $\psi(x,t)$ at time t.

b) Verify that $\psi(x,t)$ is normalized.

c) Find the probability that at a time t the measurement of the energy of the system gives the value E_2.

d) Compute $\langle x \rangle$. Notice that it is time-dependent, even though x is not. Compute $E = \langle H \rangle$. Does it vary with time?

28. The Free Particle

28.1 In Section **27.7** we discovered that the general solution to the Schrödinger equation in the case of a time independent potential was a superposition of stationary states (*cf.* (27.3)). Clearly, then, in this case we need only solve the time independent Schrödinger equation (26.4), then put these solutions into (27.3) to obtain the general solution. Of course, even this is a difficult task, and we will be able to complete it in only a few special cases. But the special cases satisfy two important conditions. First, they illustrate the general principles, and second, they are surprisingly robust, in that they may be employed as rather successful approximations under certain circumstances.

28.2 We begin our study of the physical implications of the formalism of wave mechanics with the simplest example, namely the free particle. In this case, the particle is moving in a constant potential, which we may, without essential loss of generality, take to be zero, whence Schrödinger's equation becomes

$$-\frac{\hbar^2}{2m}\frac{d^2u}{dx^2} = Eu. \tag{28.1}$$

We may rewrite this as

$$\frac{d^2u}{dx^2} + k^2u = 0, \tag{28.2}$$

where

$$k^2 = \frac{2mE}{\hbar^2}. \tag{28.3}$$

The most general solution to this equation is a superposition of states of the form

$$u(x) = Ae^{ikx} + Be^{-ikx}, \tag{28.4}$$

where A and B are constants.

28.3 The stationary state solution corresponding to the solution (28.4) is

$$\begin{aligned}\psi(x,t) &= u(x)e^{-iEt/\hbar} \\ &= (Ae^{ikx} + Be^{-ikx})e^{-i\omega t} \\ &= Ae^{i(kx-\omega t)} + Be^{-i(kx+\omega t)},\end{aligned} \tag{28.5}$$

where we have used the de Broglie relation $E = \hbar\omega$. Of course, the two terms of this equation are simply the harmonic wave solutions with which we began our journey into

quantum theory. We say that the solution (28.4) represents a superposition of waves (traveling right and left, respectively), but we really mean the corresponding stationary state (28.5). Following tradition, we shall use the same (somewhat sloppy) terminology below. You just have to remember that you must multiply the energy eigenfunctions by the appropriate factors of $e^{i\omega t}$ to get the wavefunction.

28.4 Two remarks are in order. First, these solutions are *waves*—that is, they are oscillatory, because E is positive, so k is real (*cf.* (28.3)). We will see later that E will be negative in some cases, in which case k will become imaginary, and the solutions will decay. Second, the **spectrum** (the set of possible frequencies $\omega = E/\hbar$) is **continuous**, that is, ω can take a continuum of possible values, as E is not restricted in any way. Again, we will see later that this is not always the case. Indeed, one of the hallmarks of quantum theory is the restriction of various dynamical variables to discrete values in certain contexts.

28.5 Let us compute the probability current density vector for this solution. We get

$$\begin{aligned} j &= \frac{\hbar}{2im}\left[\psi^*\frac{\partial\psi}{\partial x} - \frac{\partial\psi^*}{\partial x}\psi\right] \\ &= \frac{\hbar}{2im}[(Ae^{i(kx-\omega t)} + Be^{-i(kx+\omega t)})^*(ikAe^{i(kx-\omega t)} - ikBe^{-i(kx+\omega t)}) \\ &\qquad - (-ikA^*e^{-i(kx-\omega t)} + ikB^*e^{i(kx+\omega t)})(Ae^{i(kx-\omega t)} + Be^{-i(kx+\omega t)})] \\ &= \frac{\hbar}{2im}[2ik|A|^2 - 2ik|B|^2] \\ &= \frac{\hbar k}{m}[|A|^2 - |B|^2] \\ &= v[|A|^2 - |B|^2], \end{aligned} \tag{28.6}$$

where v is the speed of the particle. Similarly we find, for the probability density,

$$\begin{aligned} P(x,t) &= \psi^*\psi \\ &= [Ae^{i(kx-\omega t)} + Be^{-i(kx+\omega t)}]^*[Ae^{i(kx-\omega t)} + Be^{-i(kx+\omega t)}] \\ &= |A|^2 + |B|^2 + A^*Be^{-2ikx} + B^*Ae^{2ikx} \\ &= |A|^2 + |B|^2 + 2\,\mathrm{Re}[A^*Be^{-2ikx}]. \end{aligned} \tag{28.7}$$

28.6 Next we consider some special cases. Suppose, for example, that the particle is prepared in a state in which $B = 0$. Then we have

$$P(x,t) = |A|^2 \qquad \text{and} \qquad j = v|A|^2 = vP$$

which, as we discovered in Exercise **19.4**, has the following interpretation. Suppose we have N particles, each of which is prepared in the state ψ given by (28.5) with $B = 0$. Then the flux of particles (in one dimension, the number of particles per unit time) crossing the point x at time t and moving to the right equals, on average, jN. Similarly, if $A = 0$ we get the same interpretation, only the particles are moving to the left.

28.7 Suppose that $A = \pm B$. Then

$$\begin{aligned} P &= |A|^2 + |B|^2 + 2\,\mathrm{Re}[A^* B e^{-2ikx}] \\ &= 2|A|^2[1 \pm \cos 2kx] \\ &= 2|A|^2 \times \begin{cases} 2\cos^2 kx & (+) \\ 2\sin^2 kx & (-), \end{cases} \end{aligned}$$

and, from (28.6) we see that $j = 0$. These are **standing waves**. On the average, the particle is neither moving right nor left. This is entirely consistent with, *e.g.,* waves on a string, in which standing waves are a superposition of left and right moving waves with the same frequency and amplitude.

28.8 Observe that the wavefunction (28.5) is not normalizable. (Try integrating (28.7) over all space.) To get a normalizable solution to Schrödinger's equation, we would have to superpose these solutions to form a wavepacket, which would then have finite norm. But as any wavepacket can be built of harmonic waves, and as harmonic waves are simple and easy to deal with, we will continue to use them. We must simply remember to use only **relative probabilities**, and everything will be all right. We will see how this works in the next section.

29. The Potential Step

29.1 Suppose the particle is initially traveling to the right when it encounters a **potential barrier**. What this means is that the particle encounters a region in which it experiences a force back the way it came. This force may be represented mathematically as a region in which its potential energy gradient is positive, as shown:

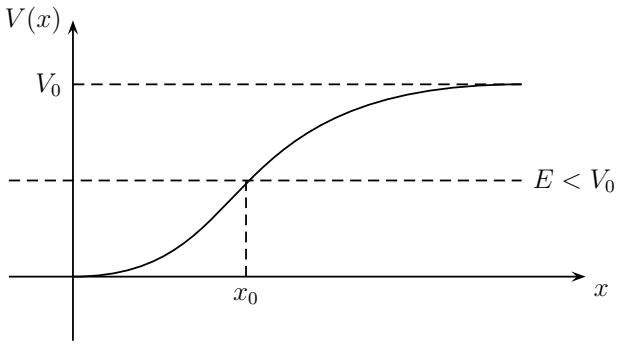

Figure 23. A realistic potential barrier.

Qualitatively, what do we expect? Suppose the total energy E of the particle were less than the maximum potential energy V_0. Well, if the particle were classical, it would hit a **turning point**, which is the point x_0 at which its energy equals its potential energy. At that point its kinetic energy is zero, so the particle would stop and turn around (hence the name). In other words, the particle would be **reflected** by the barrier. On the other hand, if its total energy E were greater than V_0, it would continue to the right, but at diminished speed (its kinetic energy being the difference between E and V_0). That is, the particle would be **transmitted** past the barrier.

29.2 We shall see that, according to wave mechanics, the particle is **partly transmitted** and **partly reflected**, depending on the shape of the barrier. In order to make the problem tractable, we replace the realistic barrier in Figure 23 with the idealized "step potential" of Figure 24:

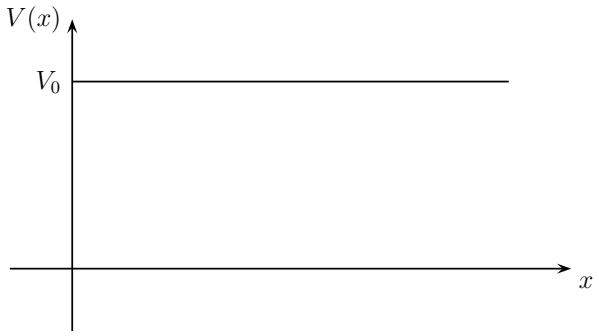

Figure 24. An idealized step potential.

The potential energy function describing this barrier is

$$V(x) = \begin{cases} 0 & x < 0 \\ V_0 & x > 0 \end{cases}. \tag{29.1}$$

Although this semi-infinite barrier is unphysical, it does have properties that mimic those of real barriers. We will solve Schrödinger's equation in the case in which $0 < E < V_0$, leaving the other case as an exercise.

29.3 To begin, we write down the Schrödinger equation in the two regions $x < 0$ and $x > 0$. For the region $x < 0$ we have (*cf.* (28.2))

$$\frac{d^2u}{dx^2} + k^2u = 0 \qquad \text{with} \qquad k^2 = \frac{2mE}{\hbar^2}. \tag{29.2}$$

On the other hand, in the region $x > 0$ we have (from (26.4))

$$\frac{d^2u}{dx^2} - \kappa^2u = 0 \qquad \text{with} \qquad \kappa^2 = \frac{2m}{\hbar^2}(V_0 - E), \tag{29.3}$$

where κ^2 is a positive constant, so κ is real. These two differential equations have quite different solutions. In particular, as we already discovered, the solutions to (29.2) are of the form

$$u(x) = Ae^{ikx} + Be^{-ikx} \qquad\qquad x < 0. \tag{29.4}$$

On the other hand, the solutions to (29.3) are of the form

$$u(x) = Ce^{\kappa x} + De^{-\kappa x} \qquad\qquad x > 0. \tag{29.5}$$

29.4 Exercise. Verify that Equation (29.5) solves Equation (29.3).

29.5 Before we proceed, we may simplify the solutions somewhat. In particular, we see from Equation (29.5) that, if C were not zero, the wavefunction would grow without bound in the positive x direction. This would mean the probability density to find the particle would approach infinity to the right of the barrier, which is obviously unphysical. So, on physical grounds, we set $C = 0$.

29.6 The next step is to employ what are called **matching conditions** or **boundary conditions**. We demand that, at an interface, the following two conditions obtain:

- ψ is continuous across the boundary
- $\dfrac{\partial\psi}{\partial x}$ is continuous across the boundary

The significance of these conditions is as follows. On physical grounds we expect that the probability to find the particle does not jump discontinuously from one point to the next. This accounts for the first condition. The second condition follows because, if the spatial derivative of ψ (and therefore $u(x)$) were to be discontinuous, the second derivative $\frac{\partial^2\psi}{\partial x^2}$ would be infinite. According to the Schrödinger equation (26.4), the energy of the particle would then be infinite—an impossibility.

29.7 So, applying the matching conditions at the point $x = 0$, we find the following relations must hold. First, the continuity of ψ at $x = 0$ requires

$$A + B = D, \tag{29.6}$$

while the continuity of the first derivative at $x = 0$ requires

$$ik(A - B) = -\kappa D. \tag{29.7}$$

We have two equations and three unknowns, which is good, for the part of the solution in (29.4) multiplying A represents a particle incident on the barrier from the left, and we control the amplitude (which, as we discussed above, is proportional to the probability flux of particles). Combining (29.6) and (29.7) we get

$$A = \frac{1}{2}(1 + i\frac{\kappa}{k})D = (re^{i\theta})D \tag{29.8}$$

and

$$B = \frac{1}{2}(1 - i\frac{\kappa}{k})D = (re^{-i\theta})D, \tag{29.9}$$

where

$$r = \frac{1}{2}\sqrt{1 + (\kappa/k)^2} \qquad \text{and} \qquad \theta = \tan^{-1}\frac{\kappa}{k}. \tag{29.10}$$

29.8 Plugging (29.8) and (29.9) into (29.4) we have, on the left of the barrier

$$\begin{aligned} u(x) &= rD(e^{ikx}e^{i\theta} + e^{-ikx}e^{-i\theta}) \\ &= 2rD\cos(kx + \theta), \end{aligned} \tag{29.11}$$

while on the right side of the barrier we have

$$u(x) = 2rD\left(\frac{e^{-\kappa x}}{2r}\right). \tag{29.12}$$

We have pulled out the same factor in front of both of these solutions because, as we discussed before, the wavefunction has meaning only up to an overall complex constant in front. This solution (remember, (29.11) and (29.12) represent a *single* solution in different regions) is illustrated in Figure 25.

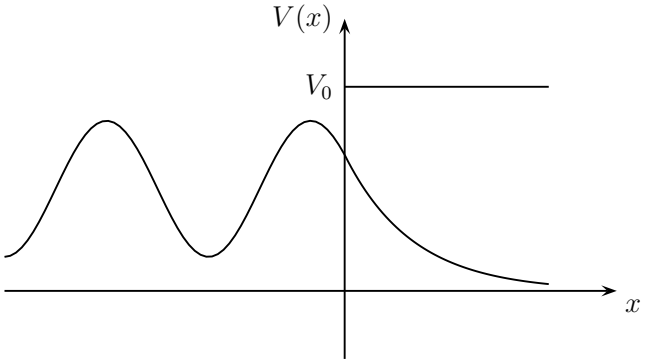

Figure 25. The wavefunction for the step potential.

Comparing the two forms (29.11) and (29.12), and thinking about the discussion in Section **28.7**, we see that what appears on the left of the barrier are **standing waves** with a net current density of zero. Another way to think about this is that we have particles impinging upon the barrier and reflecting from it at the same rate, so that, on average, there is no net flow of particles.

29.9 One final way to see the same thing is to compute the **reflection coefficient** R for the barrier, which is defined to be the ratio of the reflected "intensity" (equivalently, the probability flux density, which is just the probability current density) to the incident "intensity". That is,

$$R := \left| \frac{j_{\text{reflected}}}{j_{\text{incident}}} \right|. \tag{29.13}$$

The reflection coefficient gives the probability that a particle will be reflected from the barrier.

In the case of the step potential above, the part of the wave (29.4) with the A coefficient is the right-moving, or "incident", wave, while the part of the wave (29.4) with the B coefficient is the left-moving, or "reflected", wave. So, recalling Equation (28.6) we see that

$$R = \frac{v|B|^2}{v|A|^2} = \frac{|B|^2}{|A|^2} = \left| \frac{B}{A} \right|^2 = |e^{-2i\theta}|^2 = 1. \tag{29.14}$$

In other words, the reflection is *total*. Every particle incident on the barrier reflects back.

29.10 For later use we define the **transmission coefficient** for the barrier. Not surprisingly, this is defined as the ratio of the transmitted intensity to the incident intensity:

$$T := \left| \frac{j_{\text{transmitted}}}{j_{\text{incident}}} \right|. \tag{29.15}$$

The value of T is the probability that a particle incident on a barrier is transmitted through the barrier. In the case of the step potential, this probability is zero.

29.11 EXERCISE. Verify that $T = 0$ for the step potential.

29.12 What is the meaning, then, of the "transmitted" wave (29.12)? Clearly, there is **something** in the barrier. Moreover, according to classical physics it should not be there! This wave illustrates the ubiquitous quantum phenomenon known as **barrier penetration**. There is some probability, however small, to find the particle inside the classically forbidden region. But, inside the barrier, the particle is not a traveling wave. Furthermore, the probability to find the particle drops off exponentially with distance. Finally, you cannot actually *measure* the particle inside the barrier. The reason is that, to observe the particle inside the barrier we would have to localize it in a region

$$\Delta x \sim \kappa^{-1}$$

where the probability to find it is appreciable. But then its momentum would be uncertain by an amount

$$\Delta p \geq \frac{\hbar}{\Delta x} \sim \hbar\kappa = \sqrt{2m(V_0 - E)}$$

in which case the uncertainty in its kinetic energy would be

$$\Delta KE \sim \frac{(\Delta p)^2}{2m} \geq V_0 - E$$

and we could no longer say that the total energy of the particle is less than the barrier height V_0!

29.13 EXERCISE. Suppose now that $E > V_0$.

(a) Find the solution to the Schrödinger equation assuming, as above, that the particle is incident on the barrier from the left.

(b) Compute the reflection R and transmission T coefficients for the barrier in terms of the energy E and the potential energy V_0. Prove that $R+T = 1$ as required by conservation of probability.

30. Quantum Tunneling Through a Potential Barrier

30.1 The potential step we investigated in the previous section was rather artificial, as it extended all the way to infinity. In that case we found that, although there was technically some probability for the particle to be inside the barrier, we could never actually measure it there. In this section we consider a much more useful problem, namely the one in which the potential barrier is of finite size. We will find that, although the wavefunction is exponentially decreasing within the barrier, if the barrier has a finite size, there is some nonzero probability for the particle to be found on the other side!

30.2 The finite (idealized) barrier looks like this:

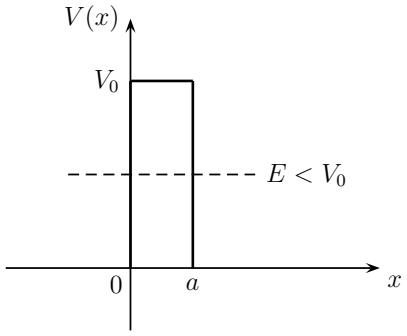

Figure 26. A finite potential barrier.

and has the mathematical form

$$V(x) = \begin{cases} 0 & x < 0 \\ V_0 & 0 < x < a \\ 0 & x > a \end{cases}, \tag{30.1}$$

where a is the width of the barrier. Once again, we assume that the particle is incident from the left and has a total energy E less than V_0, the height of the barrier.

30.3 We now have a more complicated problem than before, because there are three different regions to consider. As E is greater than 0, it is clear that, to the left and right of the barrier, the solutions to Schrödinger's equation will be traveling waves:

$$u(x) = \begin{cases} Ae^{ikx} + Be^{-ikx} & x < 0 \\ Ce^{ikx} + De^{-ikx} & x > a \end{cases}, \tag{30.2}$$

where k satisfies equation (28.3). We can make one simplification from the start, which is to set $D = 0$. We may do this because there are no particles incident from the right,

which is what this term represents. Inside the barrier, the same analysis as in Section **29.3** applies, and the solution is of the form

$$u(x) = Fe^{\kappa x} + Ge^{-\kappa x} \qquad\qquad 0 < x < a, \tag{30.3}$$

where κ is as in (29.3). Note that we cannot automatically discard the increasing exponential term (*i.e.,* we cannot set $F = 0$) because the finite width of the barrier ensures that this term will never blow up.

30.4 The matching conditions must be enforced at $x = 0$ and $x = a$. At $x = 0$ we have, from continuity of the wavefunction

$$A + B = F + G, \tag{30.4}$$

while continuity of the first derivative yields

$$ik(A - B) = \kappa(F - G). \tag{30.5}$$

Similarly, at $x = a$ we get

$$Ce^{ika} = Fe^{\kappa a} + Ge^{-\kappa a} \tag{30.6}$$

and

$$ikCe^{ika} = \kappa(Fe^{\kappa a} - Ge^{-\kappa a}). \tag{30.7}$$

Solving these four simultaneous equations yields

$$\frac{B}{A} = \frac{(k^2 + \kappa^2)(e^{2\kappa a} - 1)}{e^{2\kappa a}(k + i\kappa)^2 - (k - i\kappa)^2} \tag{30.8}$$

and

$$\frac{C}{A} = \frac{4ik\kappa e^{-ika}e^{\kappa a}}{e^{2\kappa a}(k + i\kappa)^2 - (k - i\kappa)^2}, \tag{30.9}$$

from which we conclude that

$$\begin{aligned} R &= \left[1 + \frac{4k^2\kappa^2}{(k^2 + \kappa^2)^2 \sinh^2(\kappa a)}\right]^{-1} \\ &= \left[1 + \frac{4E(V_0 - E)}{V_0^2 \sinh^2(\kappa a)}\right]^{-1} \end{aligned} \tag{30.10}$$

and

$$\begin{aligned} T &= \left[1 + \frac{(k^2 + \kappa^2)^2 \sinh^2(\kappa a)}{4k^2\kappa^2}\right]^{-1} \\ &= \left[1 + \frac{V_0^2 \sinh^2(\kappa a)}{4E(V_0 - E)}\right]^{-1}. \end{aligned} \tag{30.11}$$

One can check that $R + T = 1$. The solution is represented schematically in Figure 27.

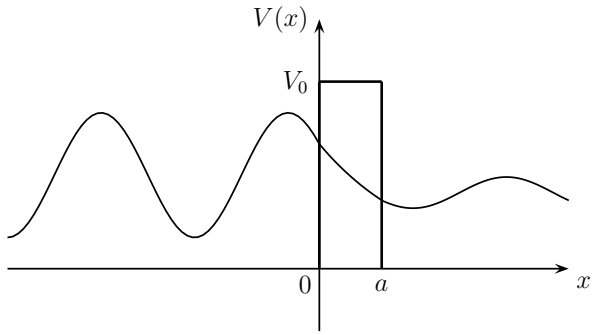

Figure 27. A wavefunction for the finite potential barrier.

30.5 The most striking feature of the solution is that T is not zero! That is, there is some finite probability that the particle will **tunnel** through the barrier. Classically, the particle would hit the potential barrier and bounce back, but quantum mechanically it mysteriously makes it through to the other side. This phenomenon of quantum tunneling explains a great many otherwise inexplicable phenomena.

30.6 Typically, we have

$$\kappa a >> 1. \tag{30.12}$$

When this holds,

$$\sinh(\kappa a) \approx \frac{1}{2} e^{\kappa a}$$

so Equation (30.11) reduces to

$$T \approx \frac{16E(V_0 - E)}{V_0^2} e^{-2\kappa a} << 1. \tag{30.13}$$

30.7 The phenomenon of quantum tunneling is what permits the operation of the **scanning tunneling microscope** or STM. In the STM, a metal probe is held within a few nanometers of some metallic surface, and a voltage difference is applied between the probe and the surface. Ordinarily, the electrons in the surface will not be ripped off unless the potential difference between the probe and the surface exceeds the **work function** of the surface, typically several electron volts. In the STM a potential difference of only about 10 mV is applied, but this is sufficient to lower the potential barrier enough so that quantum tunneling will take place. The electrons on the surface tunnel from the surface to the tip, establishing a current that is detectable.

We saw in Equation (30.13) that the tunneling probability depends exponentially on the barrier width. Hence, small changes in the barrier width cause measurable changes in the tunneling current. Typically, these changes are on the order of 0.01 nm, or one twentieth of a typical atomic diameter! By scanning the probe over the surface while maintaining the tunneling current via a feedback loop, the topographical features of the electron density of the surface are mapped out. The STM has allowed us to form images of individual atoms for the very first time. It is for good reason that the inventors of the STM, Gert Binning and Heinrich Rohrer, were awarded the Nobel Prize in 1986.

30.8 Exercise. *Ceteris paribus* [35], which particle has greater probability to tunnel through a barrier, an electron or a proton? Compute the ratio of the two probabilities.

30.9 Exercise. A continuous beam of 10^6 electrons per second is incident on a potential barrier 5 eV high and 0.4 nm wide. If the electrons have a wavelength of 10 nm, what is the expected tunneling current?

30.10 To get the transmission probability through a non-square barrier we must resort to approximation techniques. The correct way to proceed is to use the notorious WKB approximation, [36] but we will employ a simpler method instead. We assume that we can treat a general barrier as a series of thin rectangular barriers of varying height. Then, treating the transmission through each one of these barriers as an independent event, we simply multiply the transmission probabilities for each one. We assume that the potential function $V(x)$ is slowly varying, so that the prefactor in (30.13) remains more or less constant. (Obviously this will fail badly near the turning points where $E = V_0$, but this represents only a very small part of the potential.) Hence we conclude that

$$\begin{aligned} T \approx T_1 T_2 \cdot T_n &\approx \exp\left\{-2\sum_{i=1}^{n} \kappa(x_i)\Delta x\right\} \\ &\approx \exp\left\{-2\int dx \sqrt{(2m/\hbar^2)(V(x)-E)}\right\}. \end{aligned} \tag{30.14}$$

30.11 A classic example of the application of (30.14) is to the decay of radioactive nuclei. A nucleus can decay by emitting one of three types of particles, denoted by the symbols α, β, and γ. We focus here on α decay only. An α particle is a helium nucleus, consisting of

[35] Other things being equal.
[36] Named after G. Wentzel, H. Kramers, and L. Brillouin.

two protons and two neutrons bound tightly together. A typical decay process is radium decaying to radon:

$$\mathrm{Ra}_{88}^{226} \longrightarrow \mathrm{Rn}_{86}^{222} + \alpha$$

The half life of radium-226 is 1622 years, which means that after 1622 years have elapsed, half the atoms in a given sample (on the average) will have decayed. From the point of view of nuclear timescales, this is unnaturally long. First we note that, based on scattering experiments, the size of a nucleus with atomic mass number A (which counts the total number of protons plus neutrons ('nucleons')) is approximately

$$r = r_0 A^{1/3}, \tag{30.15}$$

where $r_0 = 1.2$ fm (1 fm = 1 Fermi = 10^{-15} m). Second we note that typical subatomic speeds are within a factor of 100 or so of the speed of light. Hence, the typical time for a nuclear process should be around r/c, which is approximately 10^{-23} seconds. The natural lifetime of radium-226 is about 33 orders of magnitude greater. In fact, the half lives of radioactive nuclei vary tremendously, from 10^{-7} seconds to 10^{9} years. How do we explain this?

30.12 According to a very crude model, we can imagine that the protons and neutrons in the nucleus act together to create a kind of cage that traps alpha particles inside and prevents them from escaping. For $r < R$ the potential is constant, so the alpha particle experiences no forces, but outside it is repelled by the Coulomb force (because both the alpha particle and the nucleus are positively charged).

Let Z denote the atomic number of the parent nucleus, and let R denote its radius. Then the daughter nucleus will have atomic number $Z' = Z - 2$ and the alpha particle will have atomic number 2, so according to this model the potential energy function can be written

$$V(r) = \begin{cases} -V_0 & \text{if } 0 \le r \le R, \\ \dfrac{z}{r} & \text{if } r > R, \end{cases} \tag{30.16}$$

where

$$z := \frac{Z' e^2}{2\pi\epsilon_0}. \tag{30.17}$$

The potential curve is sketched in Figure 28.

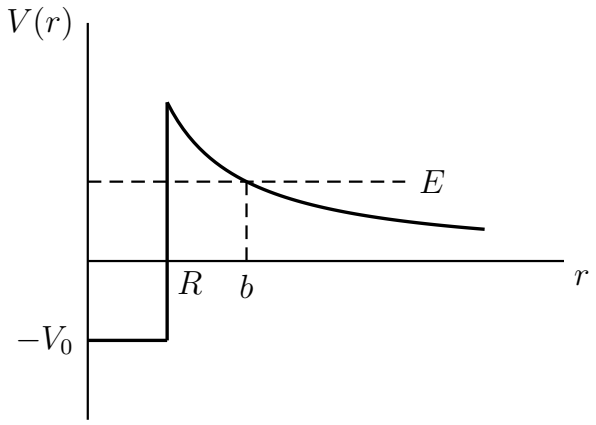

Figure 28. A model nuclear potential.

An alpha particle with energy E has the two turning points R and $b = z/E$. Hence, by (30.14), the tunneling probability can be written

$$T = \exp\left\{-2\sqrt{\frac{2mz}{\hbar^2}}\int_R^b dr\sqrt{\frac{1}{r}-\frac{1}{b}}\right\}. \tag{30.18}$$

The integral is

$$\int_R^b dr\sqrt{\frac{1}{r}-\frac{1}{b}} = \sqrt{b}\left[\arccos\left(\frac{R}{b}\right)^{1/2} - \left(\frac{R}{b}-\frac{R^2}{b^2}\right)^{1/2}\right]. \tag{30.19}$$

At low energies compared to $V(R)$, $b \gg R$, so we can write

$$\ln T \approx -2\sqrt{\frac{2mzb}{\hbar^2}}\left[\frac{\pi}{2} - \left(\frac{R}{b}\right)^{1/2}\right] = -\frac{1.7Z'}{\sqrt{E(\mathrm{MeV})}} + CZ'^{2/3}, \tag{30.20}$$

for some constant C on the order of unity (assuming $A = 5Z/2$, which is approximately true for most heavy nuclei).

30.13 In keeping with our naive model, we assume that the alpha particle is bouncing back and forth inside the nucleus with some speed $v = \sqrt{2mE}$. Each time it hits the barrier it has a probability of T to tunnel through to the other side and escape the nucleus. On the average, it will need to hit the barrier about $1/T$ times before it escapes. It makes one attempt in a time $2R/v$, so the average time before decay is

$$\tau = \frac{2R}{vT} = \frac{2R}{T\sqrt{2mE}}. \tag{30.21}$$

Taking logarithms gives

$$\log \tau = -\log T - \frac{1}{2}\log E + C', \tag{30.22}$$

for some approximately constant C'. The second term varies much more slowly than the first, as a function of E, so to a good approximation we just have

$$\log \tau = \frac{C_1 Z'}{\sqrt{E}} - C_2 Z'^{2/3} + C_3. \tag{30.23}$$

This is a very good approximation to the data for various alpha emitters provided one chooses $C_1 = C_2 = 1.6$ and $C_3 = -28.9$ and one measures lifetimes in years. The extraordinary thing about this equation is that it gives good agreement with the data for lifetimes ranging over 30 orders of magnitude! Some of these data are plotted in Figure 29 below.

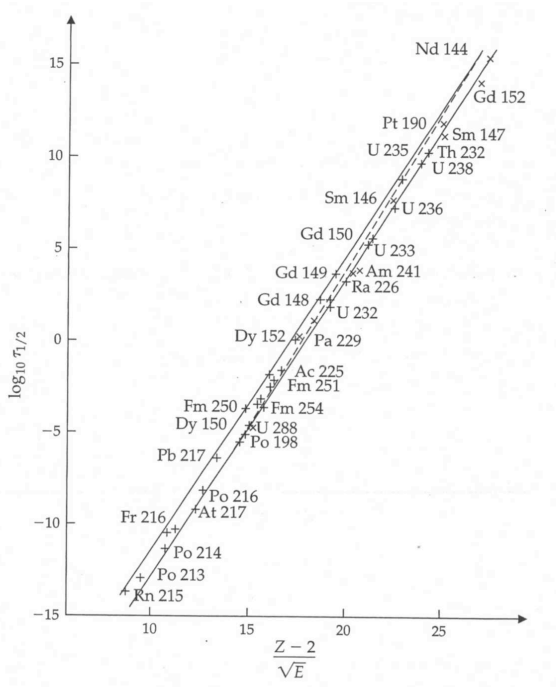

Figure 29. Plot of log of half life versus $Z'/\sqrt{E}$ for various alpha emitters. (From J. Bernstein, P. Fishbane, and S. Gasiorowicz, *Modern Physics*, Addison-Wesley, Reading, MA, 2000.)

31. The Infinite Square Well

31.1 Suppose we put a particle into a box with infinitely strong walls. Then we would certainly not expect the particle to escape. This is true both classically and quantum mechanically. The potential energy function for such a box would look something like this:

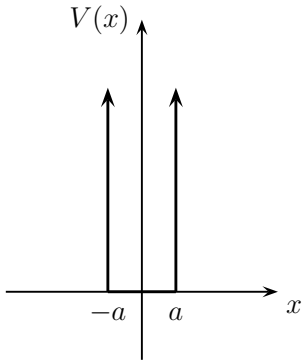

Figure 30. The infinite square well.

The mathematical representation for the potential is

$$V(x) = \begin{cases} 0 & \text{if } |x| < a, \\ \infty & \text{if } |x| > a. \end{cases} \tag{31.1}$$

This is clearly unphysical, but serves as a first approximation for a more realistic **potential well**.

31.2 The boundary conditions require that $u(x) = 0$ at $x = \pm a$, because the probability to find the particle inside either wall should be zero. But we must have $\frac{\partial u}{\partial x} \neq 0$ at $x = \pm a$ because otherwise $u(x)$ would vanish everywhere inside the box. This means that $u(x)$ exhibits some sort of jump discontinuity at the walls, but this does not contradict the boundary conditions we established previously, as $V(x)$ also experiences an infinite jump at the walls.

31.3 In any event, the Schrödinger equation (26.4) becomes

$$\frac{d^2u}{du^2} + k^2 u = 0 \qquad\qquad k^2 = \frac{2mE}{\hbar^2}. \tag{31.2}$$

We choose to write the solution to (31.2) in terms of sines and cosines:

$$u(x) = A\cos kx + B\sin kx. \tag{31.3}$$

31.4 Exercise. Starting from the general solution to (31.2) of the form

$$u(x) = Ce^{ikx} + De^{-ikx},$$

derive the form (31.3). What is the relation between A, B, C, and D?

Applying the boundary conditions to (31.3) we see that

$$A\cos ka = B\sin ka = 0. \tag{31.4}$$

31.5 Exercise. Derive Equations (31.4).

31.6 We now see there are two exclusive classes of solution, corresponding to the cases $A = 0$ or $B = 0$. If $B = 0$, we have $\cos ka = 0$ which means

$$k_n = \frac{n\pi}{2a} = \frac{n\pi}{L} \qquad n = 1, 3, 5, ..., \tag{31.5}$$

where $L = 2a$ is the width of the well. The normalized wavefunctions in this case are

$$u_n(x) = \frac{1}{\sqrt{a}} \cos \frac{n\pi x}{2a}. \tag{31.6}$$

On the other hand, if $A = 0$, we have $\sin ka = 0$ which means

$$k_n = \frac{n\pi}{2a} = \frac{n\pi}{L} \qquad n = 2, 4, 6, ..., \tag{31.7}$$

and the corresponding normalized wavefunctions are

$$u_n(x) = \frac{1}{\sqrt{a}} \sin \frac{n\pi x}{2a}. \tag{31.8}$$

31.7 The most important feature of these solutions is that, unlike the classical situation, only certain discrete energies are allowed. That is, the energy levels are **quantized**. We may interpret this by saying that only certain types of standing waves are permitted in the box, namely those that satisfy the condition

$$k_n = \frac{n\pi}{L} \Longrightarrow \lambda_n = \frac{2\pi}{k_n} = \frac{2L}{n}. \tag{31.9}$$

This is merely the statement that only an integral number of wavelengths will fit in the box. The corresponding energy levels are

$$E_n = \frac{(\hbar k_n)^2}{2m} = \frac{\hbar^2 \pi^2 n^2}{2mL^2}. \tag{31.10}$$

The number n is called the **principal quantum number**, and the solutions $u_n(x)$ are precisely the **energy eigenfunctions**.

31.8 EXERCISE. In Section **27.4** we proved that the energy eigenstates form an orthonormal set (*cf.* Equation (27.1)). Verify that this is true here by showing that $(u_n, u_m) = \delta_{nm}$ where δ_{nm} is the Krönecker delta.

31.9 One interesting feature of the solutions to the particle-in-a-box is that the energy eigenfunctions come in two types, even and odd. That is, they have definite **parity**. If a function $f(x)$ satisfies the property

$$f(-x) = f(x) \tag{31.11}$$

then the function is said to be **even** or have **even parity** or be **parity invariant**. If a function satisfies the property

$$f(-x) = -f(x) \tag{31.12}$$

then it is said to be **odd** or have **odd parity**. Most functions are neither even nor odd (**indefinite parity**), but the energy eigenfunctions above are of one type or the other (**definite parity**). This particular feature of the energy eigenfunctions can be traced to the fact that the potential energy is even:

$$V(-x) = V(x). \tag{31.13}$$

31.10 THEOREM. *If the potential energy $V(x)$ is parity invariant, we can choose all the eigenfunctions of the Hamiltonian operator to have definite parity.*

Proof. If $V(-x) = V(x)$ then the Hamiltonian operator $\widehat{H}$ is invariant under a parity transformation (one that sends x to $-x$) because the Laplacian operator is invariant under parity (see Exercise **27.11**). It follows that, under a parity transformation

$$\widehat{H}u(x) = Eu(x) \longrightarrow \widehat{H}u(-x) = Eu(-x). \tag{31.14}$$

This means that, if $u(x)$ is an eigenfunction of the Hamiltonian operator with eigenvalue E, $u(-x)$ is also.

This state of affairs leads to two possibilities, depending upon whether E is or is not degenerate. If E is a degenerate eigenvalue, then there are at least two distinct eigenfunctions corresponding to the same eigenvalue. If E is non-degenerate, then there is only one eigenfunction (up to a constant scalar multiple) corresponding to the eigenvalue E.

In the case that E is non-degenerate, we must have

$$u(-x) = \alpha u(x), \tag{31.15}$$

for some constant α. But then, using (31.15) twice we get

$$u(x) = \alpha u(-x) = \alpha^2 u(x), \tag{31.16}$$

from which it follows that $\alpha^2 = 1$. This, in turn, implies that $\alpha = \pm 1$, in which case we conclude

$$u(-x) = \pm u(x). \tag{31.17}$$

In other words, the eigenfunctions have a definite parity, and we are done.

If E is a degenerate eigenvalue, then there are two sub-cases. In the first case, $u(x)$ and $u(-x)$ represent two distinct functions, each of which has a definite parity. In this case we are done. In the second case, neither $u(x)$ nor $u(-x)$ has definite parity. But we may construct two linear combinations of these two functions which are eigenfunctions of the Hamiltonian operator and which do have definite parity. These will be perfectly acceptable substitutes for the original eigenfunctions, because as you recall, the most general wavefunction is a linear combination of the energy eigenfunctions, so we are free to choose the basis eigenfunctions as we please, provided they are indeed energy eigenfunctions. We construct the new eigenfunctions as follows:

$$u_+(x) = \frac{1}{2}[u(x) + u(-x)] \tag{31.18}$$

and

$$u_-(x) = \frac{1}{2}[u(x) - u(-x)]. \tag{31.19}$$

The proof is complete. ∎

31.11 Exercise. Verify that the Laplacian operator is invariant under a parity transformation.

31.12 Exercise. Prove that $u_+(x)$ and $u_-(x)$ are (i) eigenfunctions of the Hamiltonian operator with eigenvalue E and (ii) even and odd, respectively.

31.13 The advantage of Theorem 31.10 is that it can occasionally simplify our lives, as we shall see in the next section. In particular, for a particle moving in a parity invariant

potential, we need only solve for the eigenfunctions in the region $x > 0$, because the eigenfunctions in the region $x < 0$ may be constructed by the appropriate parity transformation.

31.14 Exercise. Suppose that, along the positive x-axis, a certain eigenfunction looks like this

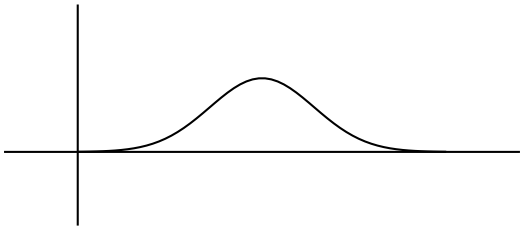

Figure 30. Half of an eigenfunction.

Sketch the continuation of this function to negative values of x in the case that the eigenfunction is (a) even and (b) odd.

31.15 Exercise. Prove that an odd function necessarily vanishes at the origin. Prove than even function necessarily has vanishing slope at the origin.

32. The Finite Square Well

32.1 We now turn to a slightly more realistic approximation of an attractive potential energy profile, the finite square well. This function has the following shape:

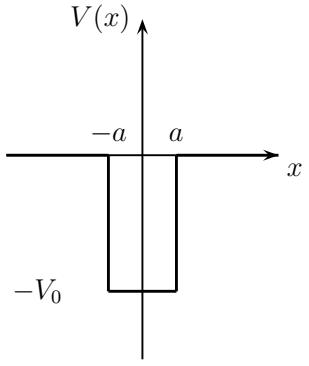

Figure 31. The finite square well.

and algebraic form

$$V(x) = \begin{cases} -V_0 & |x| < a \\ 0 & |x| > a \end{cases}. \tag{32.1}$$

Once again, we consider only the case in which the particle begins in the well, namely the case $-V_0 < E < 0$. In this case, we expect the particle to be trapped in the well, so we expect to find what are called **bound states** (as opposed to **unbound states**, such as those of a free particle).

32.2 As the potential energy function is even, Theorem 31.10 applies, and we may limit ourselves to a consideration of the region $x > 0$, the rest of the wavefunction being obtained by a suitable reflection about the origin. Furthermore, again by Theorem 31.10, we may consider the even and odd eigenfunctions separately. Schrödinger's equation (26.4) then becomes

$$\frac{\partial^2 u}{\partial x^2} + \alpha^2 u = 0 \qquad 0 < x < a, \tag{32.2}$$

where

$$\alpha^2 = \frac{2m}{\hbar^2}(V_0 + E) = \frac{2m}{\hbar^2}(V_0 - |E|), \tag{32.3}$$

and

$$\frac{\partial^2 u}{\partial x^2} - \beta^2 u = 0 \qquad x > a, \tag{32.4}$$

where

$$\beta^2 = -\frac{2m}{\hbar^2}E = \frac{2m}{\hbar^2}|E|. \tag{32.5}$$

The even solution to these equations is given by

$$u(x) = \begin{cases} A\cos\alpha x & 0 < x < a \\ Ce^{-\beta x} & x > a \end{cases}, \tag{32.6}$$

where we threw out the increasing exponential term in the region $x > a$ because it is unphysical. [37]

32.3 Next we apply the matching conditions. Once more, thanks to Theorem 31.10, we need only apply the matching condition at the boundary $x = a$, whereupon the one at $x = -a$ is automatically satisfied. Continuity of the wavefunction and its first derivative at $x = a$ yields the equation

$$\alpha \tan \alpha a = \beta. \tag{32.7}$$

32.4 Exercise. Derive Equation (32.7).

[37] It may not look as though the solution (32.6) is even. The cosine part is even, but the exponential looks worrisome. But this is an illusion. We will eventually reflect the solution about the origin in such a way that the entire solution is even. We do the same thing below with the odd solution. Theorem 31.10 guarantees that, after reflection, the resulting function is indeed an energy eigenfunction.

32.5 Exercise. Find the corresponding odd eigenfunction. Show that the matching conditions require that, for the odd eigenfunctions,

$$\alpha \cot \alpha a = -\beta. \tag{32.8}$$

32.6 To obtain the possible discrete energy levels we must solve the two equations (32.7) and (32.8). These are **transcendental equations**, which means that they have no analytic solution. Instead, we must solve them numerically, as follows. First, define two dimensionless variables

$$\xi = \alpha a \qquad \text{and} \qquad \eta = \beta a. \tag{32.9}$$

Then (32.7) and (32.8) become

$$\xi \tan \xi = \eta \qquad \text{for the even states} \tag{32.10}$$

and

$$\xi \cot \xi = -\eta \qquad \text{for the odd states.} \tag{32.11}$$

Observe that

$$\xi^2 + \eta^2 = a^2(\alpha^2 + \beta^2) = \frac{2ma^2V_0}{\hbar^2} =: \gamma^2. \tag{32.12}$$

That is, ξ and η are not independent, but satisfy the constraint (32.12). The allowed energy eigenvalues are then found at the intersection of the circles $\xi^2 + \eta^2 = \gamma^2$ and the curves given by (32.10) and (32.11).

32.7 Exercise. Make a graph, either by hand or using a computer, of η versus ξ for the two curves (32.10) and (32.11). Show that, for the case $\gamma = 5$, there are four bound states, two even and two odd. Using numerical analysis, show that the energy of ground state is $E = -0.93V_0$.

33. The Harmonic Oscillator

33.1 Recall that the force on a mass attached to a spring with spring constant K is given by Hooke's Law:

$$F = -Kx. \tag{33.1}$$

Applying Newton's Second Law we get the equation of motion

$$-Kx = ma = m\frac{d^2x}{dx^2}$$

which has solution

$$x(t) = A\cos(\omega t + \phi), \tag{33.2}$$

where

$$\omega = 2\pi\nu = \sqrt{\frac{K}{m}}. \tag{33.3}$$

The mass undergoes simple harmonic motion. Of course, harmonic motion is a very special kind of motion. Most oscillations of a particle will not be of this type. But, if the oscillation is small enough, the particle **will** oscillate simple harmonically! In other words, for sufficiently small oscillations about equilibrium **everything oscillates simple harmonically**.

33.2 We prove this as follows. Suppose we have a particle moving under the influence of some force. We agreed that, as all fundamental forces seem to be conservative, this force is derivable from some potential energy function $V(x)$. Consider the following potential energy function:

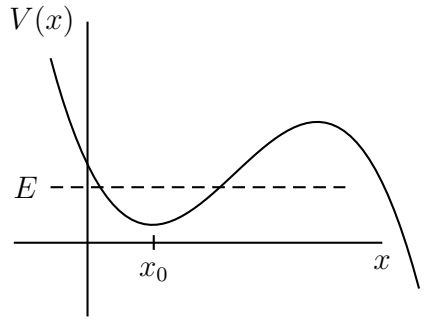

Figure 32. A potential energy function.

The point x_0 is a point of **stable equilibrium**. It is an equilibrium, because a particle placed at this point will experience no net force: $F = -\frac{\partial V}{\partial x} = 0$. It is stable because, if we displace the particle to the right or left, the force will always be in the opposite direction. In other words, the force is **restorative**—it acts to restore particle to its original position.

33.3 Now, let us expand the potential energy function $V(x)$ in a Taylor series around the point x_0:

$$V(x) = V(x_0) + V'(x_0)(x - x_0) + \frac{1}{2}V''(x_0)(x - x_0)^2 + ... \tag{33.4}$$

By redefining the zero of potential energy, we can set $V(x_0) = 0$. Also, the point x_0 is an equilibrium point, so the first derivative of the potential energy vanishes there: $V'(x_0) = 0$. This means that, in a sufficiently small neighborhood of the equilibrium point x_0, the potential energy function has the form

$$V(x) = \frac{1}{2}V''(x_0)(x - x_0)^2$$

For convenience, let us redefine our coordinate system so that $x_0 = 0$. Then the potential energy function has the form

$$V(x) = \frac{1}{2}Kx^2, \tag{33.5}$$

where we set $K = V''(0)$. But (33.5) is just the potential energy function for a harmonic oscillator! We can see this because the force on the particle in this potential is simply Hooke's Law: $F = -\partial V/\partial x = -Kx$. It is this **universality** of the harmonic oscillator that makes it such an important example of an attractive potential.

33·4 We now analyze the harmonic oscillator according to quantum theory. Schrödinger's equation (26.4) for a particle in a harmonic oscillator potential reads

$$-\frac{\hbar^2}{2m}\frac{d^2u}{dx^2} + \frac{1}{2}Kx^2u = Eu. \tag{33.6}$$

Let us introduce two new dimensionless parameters:

$$\lambda := \frac{2E}{\hbar\omega}, \tag{33.7}$$

where

$$\omega = \sqrt{K/m}, \tag{33.8}$$

and

$$\xi = \alpha x, \tag{33.9}$$

where

$$\alpha = \left(\frac{m\omega}{\hbar}\right)^{1/2} = \left(\frac{mK}{\hbar^2}\right)^{1/4}. \tag{33.10}$$

Then Equation (33.6) can be written

$$\frac{d^2\tilde{u}(\xi)}{d\xi^2} + (\lambda - \xi^2)\tilde{u}(\xi) = 0, \tag{33.11}$$

where

$$\tilde{u}(\xi) := u(\xi/\alpha) = u(x). \tag{33.12}$$

33.5 The solution of equation (33.11) is somewhat involved, so we will have to be content with the final answer. It turns out that, in order for the equation (33.11) to yield well-behaved solutions, we must have

$$\lambda = 2n + 1 \qquad\qquad n = 0, 1, 2, 3, ... \tag{33.13}$$

It then follows from (33.7) that the allowed energy levels are given by

$$E_n = (n + \frac{1}{2})h\nu. \tag{33.14}$$

Two notable features of (33.14) are (i) the energy levels of the harmonic oscillator are evenly spaced, unlike those of the other potentials we have studied, and (ii) the smallest energy, the so-called **zero-point energy**, is $E_0 = \frac{1}{2}h\nu$. The zero-point energy is called this because, at 0 Kelvins, when all thermal motion should cease according to classical thermodynamics, there is residual vibration of atoms in solids, equal to this energy. It is the zero-point energy that prevents helium-3 from solidifying even as the temperature approaches absolute zero.

33.6 Finally we turn to the wavefunctions themselves. After some messy analysis, we discover that the (normalized) wavefunctions are of the form

$$u_n(x) = \left[\frac{\alpha}{\sqrt{\pi}2^n n!}\right]^{1/2} e^{-\alpha^2 x^2/2} H_n(\alpha x), \tag{33.15}$$

where the $H_n(\xi)$ are polynomials in ξ called **Hermite polynomials**, after the French mathematician Charles Hermite (1822-1901). [38] The first few Hermite polynomials are listed below:

$$H_0(\xi) = 1 \qquad H_1(\xi) = 2\xi \qquad H_3(\xi) = 4\xi^2 - 2, \tag{33.16}$$

and a general formula is given by

$$H_n(\xi) = (-1)^n e^{\xi^2} \frac{d^n}{d\xi^n} e^{-\xi^2}. \tag{33.17}$$

(See any good quantum mechanics book for pictures of the eigenfunctions (33.15).)

33.7 EXERCISE. Compute the expectation values $\langle x \rangle$ and $\langle x^2 \rangle$ for the first two states of the harmonic oscillator.

33.8 EXERCISE. Using the results of the previous problem, prove that $\langle V \rangle = E/2$ for both the first and second states of the harmonic oscillator. How does this compare to the classical expectation?

[38] The same person who brought you 'Hermiticity' and 'Hermitian'.

Appendix A: Gaussian Integrals

Let

$$J := \int_{-\infty}^{\infty} e^{-\alpha x^2}\, dx, \tag{A.1}$$

for some constant α. To evaluate this integral we first square both sides to get

$$J^2 = \int_{-\infty}^{\infty} e^{-\alpha x^2}\, dx \int_{-\infty}^{\infty} e^{-\alpha y^2}\, dy = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} dx\, dy\, e^{-\alpha(x^2+y^2)}. \tag{A.2}$$

Next, we change variables to plane polar coordinates to get:

$$J^2 = \int_0^{2\pi} d\theta \int_0^{\infty} dr\, r e^{-\alpha r^2} = \frac{2\pi}{-2\alpha} e^{-\alpha r^2}\Big|_0^{\infty} = \frac{\pi}{\alpha}, \tag{A.3}$$

from which it follows that

$$\boxed{\int_{-\infty}^{\infty} e^{-\alpha x^2}\, dx = \sqrt{\frac{\pi}{\alpha}}}. \tag{A.4}$$

Often one needs to evaluate an integral of the following type:

$$\int_{-\infty}^{\infty} e^{-\alpha x^2+\beta x}\, dx, \tag{A.5}$$

In this case we complete the square to get

$$\int_{-\infty}^{\infty} e^{-\alpha(x^2-(\beta/\alpha)x)}\, dx = \int_{-\infty}^{\infty} e^{-\alpha(x-\beta/2\alpha)^2+\beta^2/4\alpha}\, dx. \tag{A.6}$$

Changing variables to $x' = x - (\beta/2\alpha)$ and using (A.4) gives

$$\boxed{\int_{-\infty}^{\infty} e^{-\alpha x^2+\beta x}\, dx = e^{\beta^2/4\alpha}\sqrt{\frac{\pi}{\alpha}}}. \tag{A.7}$$

The *moments* of the Gaussian distribution are

$$I_n := \int_{-\infty}^{\infty} x^n e^{-x^2}\, dx.$$

By symmetry, these moments vanish when n is odd. The even moments can be evaluated by integrating by parts. Set

$$u = x^{n-1} \quad \text{and} \quad dv = x e^{-x^2}\, dx,$$

so that

$$du = (n-1)x^{n-2}\,dx \quad \text{and} \quad v = -\frac{1}{2}e^{-x^2}.$$

Then we have

$$I_n = -\frac{1}{2}x^{n-1}e^{-x^2}\Big|_{-\infty}^{\infty} + \frac{1}{2}(n-1)\int_{-\infty}^{\infty} x^{n-2}e^{-x^2}\,dx.$$

The first term vanishes, so we find

$$I_n = \frac{1}{2}(n-1)I_{n-2}.$$

Plug this equation into itself to get

$$I_n = \frac{1}{2}(n-1)\cdot\frac{1}{2}(n-3)I_{n-4}.$$

Continuing this process ('running out the recurrence') yields, for any natural number m,

$$\boxed{I_{2m} = \frac{m!!}{2^m}\sqrt{\pi}},$$

where

$$m!! := 1\cdot 3\cdot 5\cdots(2m-1)$$

is the so-called *double factorial function.*

Appendix B: Proof of the Generalized Heisenberg Uncertainty Principle

We will prove the generalized uncertainty principle for incompatible (noncommuting) observables A and B, namely

$$\boxed{\Delta A\,\Delta B \geq \frac{1}{2}|\langle[\widehat{A},\widehat{B}]\rangle|}, \tag{B.1}$$

where the expectation value is computed using any normalized wavefunction ψ. Equation (B.1), together with the result of Exercise **12.5**, implies the usual position-momentum uncertainty principle:

$$\Delta x\,\Delta p_x \geq \frac{1}{2}|\langle[\widehat{x},\widehat{p}_x]\rangle| = \frac{\hbar}{2}.$$

To prove (B.1) we first we introduce the shifted Hermitian operators

$$\bar{A} := \widehat{A} - \langle\widehat{A}\rangle \qquad \text{and} \qquad \bar{B} := \widehat{B} - \langle\widehat{B}\rangle. \tag{B.2}$$

By construction,

$$\langle \bar{A} \rangle = \langle \bar{B} \rangle = 0, \tag{B.3}$$

so

$$(\Delta A)^2 = \langle \bar{A}^2 \rangle \qquad \text{and} \qquad (\Delta B)^2 = \langle \bar{B}^2 \rangle. \tag{B.4}$$

Because operators commute with multiples of the identity,

$$[\bar{A}, \bar{B}] = [\widehat{A}, \widehat{B}]. \tag{B.5}$$

Now define a new family of operators

$$\widehat{C} := \bar{A} + i\lambda \bar{B} \tag{B.6}$$

depending on a real constant λ. By the Hermiticity of the shifted operators we have

$$\widehat{C}^\dagger = \bar{A} - i\lambda \bar{B}, \tag{B.7}$$

where $\widehat{C}^\dagger$ is the *adjoint* of $\widehat{C}$, defined by the equality

$$(\widehat{C}^\dagger \psi, \phi) = (\psi, \widehat{C}\phi) \tag{B.8}$$

for any states ψ and ϕ. (Note that, by the properties of the inner product, $\widehat{C}^{\dagger\dagger} = \widehat{C}$.) From (B.6), (B.8), and the properties of the inner product, we have

$$(\psi, \widehat{C}^\dagger \widehat{C} \psi) = (\widehat{C}\psi, \widehat{C}\psi) \geq 0. \tag{B.9}$$

Hence

$$\langle (\bar{A} - i\lambda \bar{B})(\bar{A} + i\lambda B) \rangle = \langle \bar{A}^2 + \lambda^2 \bar{B}^2 + i\lambda [\bar{A}, \bar{B}] \rangle =: f(\lambda) \tag{B.10}$$

is a *real* and *nonnegative* function of λ. By virtue of (B.4) and (B.5) we can write

$$\begin{aligned} f(\lambda) &= \langle \bar{A}^2 \rangle + \lambda^2 \langle \bar{B}^2 \rangle + i\lambda \langle [\bar{A}, \bar{B}] \rangle \\ &= \langle \bar{A}^2 \rangle + \lambda^2 \langle \bar{B}^2 \rangle + i\lambda \langle [\widehat{A}, \widehat{B}] \rangle \end{aligned} \tag{B.11}$$

which shows that $\langle [\widehat{A}, \widehat{B}] \rangle$ must be *pure imaginary.*

By differentiating we see that $f(\lambda)$ has a minimum at

$$\lambda_0 = -\frac{i}{2} \frac{\langle [\widehat{A}, \widehat{B}] \rangle}{(\Delta B)^2} \tag{B.12}$$

at which point

$$f(\lambda_0) = (\Delta A)^2 + \frac{1}{4}\frac{\langle[\widehat{A},\widehat{B}]\rangle^2}{(\Delta B)^2}. \tag{B.13}$$

As observed, this must be nonnegative, so

$$(\Delta A)^2(\Delta B)^2 \geq -\frac{1}{4}\langle[\widehat{A},\widehat{B}]\rangle^2. \tag{B.14}$$

Now take the square root and use the fact that $\langle[\widehat{A},\widehat{B}]\rangle$ is pure imaginary to get

$$(\Delta A)(\Delta B) \geq \frac{1}{2}|\langle[\widehat{A},\widehat{B}]\rangle|, \tag{B.14}$$

which proves (B.1).

Appendix C: Some Constants

Planck's constant	$h = 6.626068 \times 10^{-34}$ J·s
Speed of light	$c = 2.997925 \times 10^{8}$ m/s
Charge of electron	$e = 1.60218 \times 10^{-19}$ C
Mass of electron	$m = 9.10938 \times 10^{-31}$ kg
Mass of proton	$m_p = 1.67262 \times 10^{-27}$ kg
Mass of neutron	$m_n = 1.67493 \times 10^{-27}$ kg
Unified atomic mass unit	$u = 1.660539 \times 10^{-27}$ kg
Boltzmann's constant	$k = 1.38065 \times 10^{-23}$ J/K
Rydberg constant for hydrogen	$\widetilde{R}_H = 1.09678 \times 10^{7}$ m^{-1}