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Quantum Mechanics I

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Teaching

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Table of Contents

Chapter 1: Introduction

Chapter 2: The One-Dimensional Wave Equation

Chapter 3: The Schrödinger Equation and a Particle in a Box

Chapter 1

Introduction:

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

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

At about the same time, in the 1860's, Maxwell and Boltzmann gave a brilliant account of the properties of gases by assuming that they were made up of weakly interacting molecules flying about in a container, bouncing off the sides, with a statistical distribution of energies so that the probability of a molecule having energy E was proportional to $exp(-E/kT)$, kk being a universal constant known as Boltzmann's constant. Boltzmann generalized this result from a box of gas to any system. For example, a solid can be envisioned classically as a lattice of balls (the atoms) connected by springs, which can sustain oscillations in many ways, each such mode can be thought of as a simple harmonic oscillator, with reasonable approximations concerning the properties of the springs, etc. Boltzmann's work leads to the conclusion that each such mode of oscillation, or degree of freedom, would at temperature T have average energy kT, made up of $1/2kT$ potential energy, $1/2kT$ kinetic energy. Notice that this average energy is independent of the strength of the springs, or the masses! *All* modes of vibration, which will vibrate at very different rates, contain the same energy at the same temperature. This equal sharing is called *the Equipartition of Energy*. It is not difficult to check this for a one-dimensional classical harmonic oscillator, averaging the energy by integrating over all displacements and momenta (independently) with the weighting factor $exp(-E/kT)$, (which of course needs to be normalized). The result doesn't depend on the spring constant or the mass. Boltzmann's result gave an excellent account of the specific heats of a wide range of materials over a wide temperature range, but there *were* some exceptions, for example hydrogen gas at low temperatures, and even solids at low enough temperatures. Still, it was generally felt these problems could be handled within the existing framework, just as the slightly odd behavior of Mercury was likely caused by a small planet, named Vulcan, closer to the sun, and so very hard to observe.

- ✓ **What was Wrong with Classical Mechanics?**

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

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

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

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

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

- ✓ **Black Body Radiation**

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

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

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

- ✓ **The Photoelectric Effect**

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

- ✓ **The Bohr Atom**

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

$$1/\lambda = R_H(1/4 - 1/n^2)$$

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

$$En = -hcR_H/n^2$$

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

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

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

$$R_H = \frac{m\,e^4}{8\,{\varepsilon_0}^2 c h^3}$$

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

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

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

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

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

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

✓ De Broglie Waves

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

✓ The Nature of Matter

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

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

1: The Dawn of the Quantum Theory

"With the recognition that there is no logical reason why Newtonian and classical principles should be valid outside the domains in which they have been experimentally verified has come the realization that departures from these principles are indeed necessary. Such departures find their expression through the introduction of new mathematical formalisms, new schemes of axioms and rules of manipulation, into the methods of theoretical physics." - P. A. M. Dirac,

1.1 Blackbody Radiation Cannot Be Explained Classically:

✓ **Learning Objectives**

One experimental phenomenon that could not be adequately explained by classical physics was blackbody radiation. Objectives for this section include

- Be familiar with black-body radiators
- Apply Stefan-Boltzmann's Law to estimate total light output from a radiator
- Apply Wien's Displacement Law to estimate the peak wavelength (or frequency) of the output from a black body radiator
- Understand the Rayleigh-Jeans Law and how it fails to properly model black-body radiation

All normal matter at temperatures above absolute zero emits electromagnetic radiation, which represents a conversion of a body's internal thermal energy into electromagnetic energy and is therefore called *thermal radiation*. Conversely, all normal matter *absorbs* electromagnetic radiation to some degree. An object that absorbs ALL radiation falling on it, at all wavelengths, is called a blackbody. When a blackbody is at a uniform temperature, its emission has a characteristic frequency distribution that depends on the temperature. This emission is called *blackbody radiation*.

A room temperature blackbody appears black, as most of the energy it radiates is infra-red and cannot be perceived by the human eye. Because the human eye cannot perceive light waves at lower frequencies, a black body, viewed in the dark at the lowest just faintly visible temperature, subjectively appears grey, even though its objective physical spectrum peaks in the infrared range. When it becomes a little hotter, it appears dull red. As its temperature increases further it becomes yellow, white, and ultimately blue-white.

Figure 1.1: Blackbody Radiation. When heated, all objects emit electromagnetic radiation whose wavelength (and color) depends on the temperature of the object. A relatively low-temperature object, such as a horseshoe forged by a blacksmith, appears red, whereas a higher-temperature object, such as the surface of the sun, appears yellow or white. Images used with permission from Wikipedia.

Blackbody radiation has a characteristic, continuous frequency spectrum that experimentally depends only on the body's temperature. In fact, we can be much more precise:

A body emits radiation at a given temperature and frequency exactly as well as it absorbs the same radiation.

This statement was proved by Gustav Kirchhoff: the essential point is that if we *instead* suppose a particular body can absorb better than it emits, then in a room full of objects all at the same temperature, it will absorb radiation from the other bodies better than it radiates energy back to them. This means it will get hotter, and the rest of the room will grow colder, contradicting the second law of thermodynamics. *Thus, a body must emit radiation exactly as well as it absorbs the same radiation at a given temperature and frequency in order to not violate the second law of thermodynamics.*

Anybody at any temperature above absolute zero will radiate to some extent, the intensity and frequency distribution of the radiation depending on the detailed structure of the body. To begin analyzing heat radiation, we need to be specific about the body doing the radiating: *the simplest possible case is an idealized body which is a perfect absorber, and therefore also (from the above argument) a* *perfect emitter.* So how do we construct a perfect absorber in the laboratory? In 1859 Kirchhoff had a good idea: a small hole in the side of a large box is an excellent absorber, since any radiation that goes through the hole bounces around inside, a lot getting absorbed on each bounce, and has little chance of ever getting out again. So, we can do this *in reverse*: have an oven with a tiny hole in the side, and presumably the radiation coming out the hole is as good a representation of a perfect emitter as we're going to find (Figure 1.1.2).

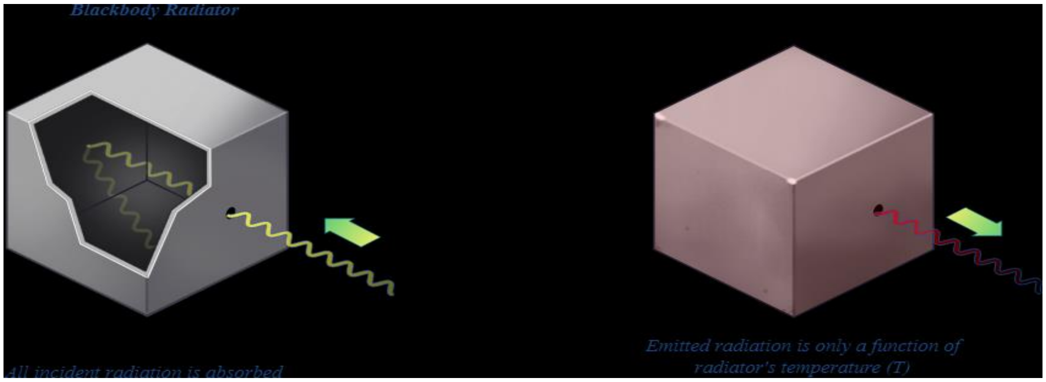


Figure 1.1.2: Blackbody radiator is any object that is a perfect emitter and a perfect absorber of radiation. (CC BY-NC; Ümit Kaya)

By the 1890's, experimental techniques had improved sufficiently that it was possible to make fairly precise measurements of the energy distribution of blackbody radiation. In 1895, at the University of Berlin, Wien and Lummer punched a small hole in the side of an otherwise completely closed oven and began to measure the radiation coming out. The beam coming out of the hole was passed through a diffraction grating, which sent the different wavelengths/frequencies in different directions, all towards a screen. A detector was moved up and down along the screen to find how much radiant energy was being emitted in each frequency range. They found a radiation intensity/frequency curve close to the distributions in Figure 1.1.3.

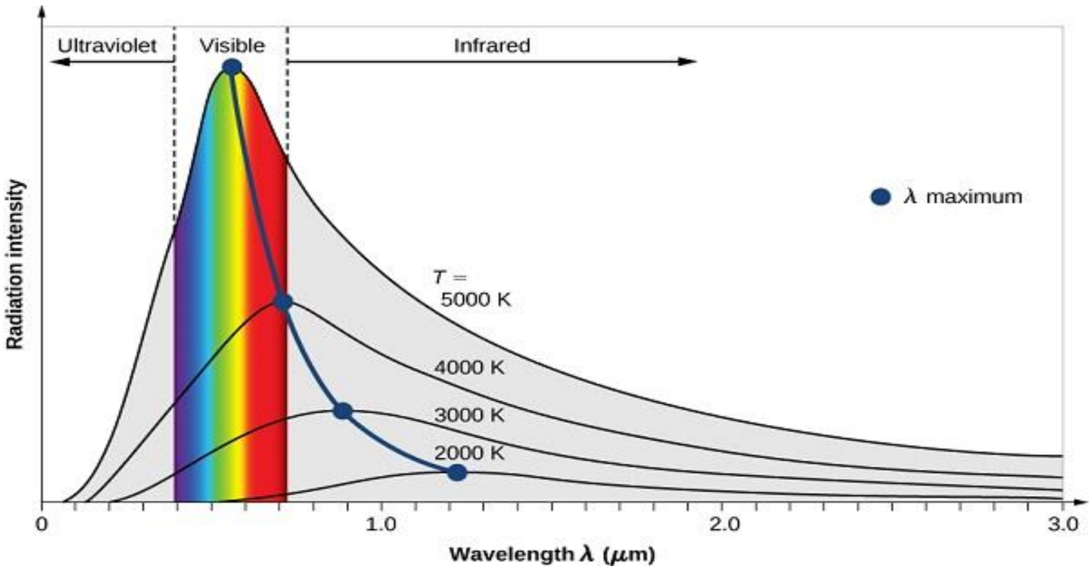
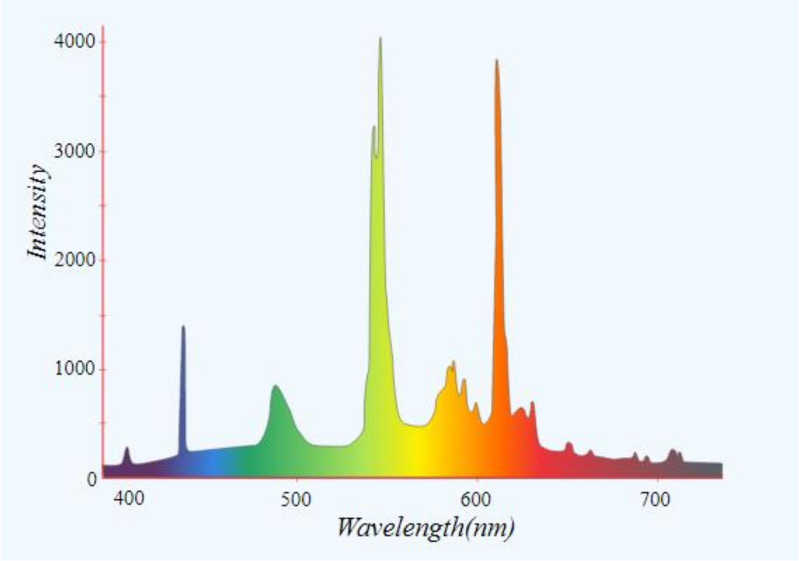


Figure 1.1.3: Graphic representation of spectral distribution of blackbody radiation at different temperatures. The Stefan-Boltzmann's Law is observed as the increase in the emission amplitude with increasing temperature and the Wien's Displacement Law is observed as the shift to smaller wavelength with increasing temperature. (CC-BY 4.0; OpenStax)

By measuring the blackbody emission curves at different temperatures (Figure 1.1.3), they were also able to construct two important phenomenological Laws (i.e., formulated from experimental observations, not from basic principles of nature): **Stefan-Boltzmann's Law** and **Wien's Displacement Law**.

- ✓ **Not all radiators are blackbody radiators**

The radiation of a blackbody radiator is produced by the thermal activity of the material, not the nature of the material, nor how it got thermally excited. Some examples of blackbodies include incandescent light bulbs, stars, and hot stove tops. The emission appears as a continuous spectrum (Figure 1.1.3) with multiple coexisting colors. However, not every radiator is a blackbody radiator. For example, the emission of a fluorescence bulb is not one. The following spectrum show the distribution of light from a fluoresce light tube and is a mixture of discrete bands at different wavelengths of light in contrast to the continuous spectra in Figure 1.1.3 for blackbody radiators.



Fluorescent lighting spectrum with emission peaks. Graph of Intensity (counts) vs. Wavelength (nm) in the visible spectrum. (CC BY-NC; Ümit Kaya).

Fluorescent light bulbs contain a mixture of inert gases (usually argon and neon) together with a drop of mercury at low pressure. A different mix of visible colors blend to produce a light that appears to us white with different shadings.

✓ The Stefan-Boltzmann Law

The first quantitative conjecture based on experimental observations was the **Stefan-Boltzmann Law** (1879) which states the total power (i.e., integrated over all emitting frequencies in Figure 1.1.3) radiated from one square meter of black surface goes as the *fourth power* of the absolute temperature (Figure 1.1.4):

$$P = \sigma T^4 \tag{1.1.1}$$

where

- P is the total amount of radiation emitted by an object per square meter ($Watts/m^2$)
- σ is a constant called the Stefan-Boltzman constant ($5.67 \times 10^{-8}\, Watts\ m^{-2} k^{-4}$)
- T is the absolute temperature of the object (in K)

The Stefan-Boltzmann Law is easily observed by comparing the integrated value (i.e., under the curves) of the experimental black-body radiation distribution in Figure 1.1.3 at different temperatures. In 1884, Boltzmann derived this T^4

behavior from theory by applying classical thermodynamic reasoning to a box filled with electromagnetic radiation, using Maxwell's equations to relate pressure to energy density. That is, the tiny amount of energy coming out of the hole (Figure 1.1.2) would of course have the same temperature dependence as the radiation intensity inside.

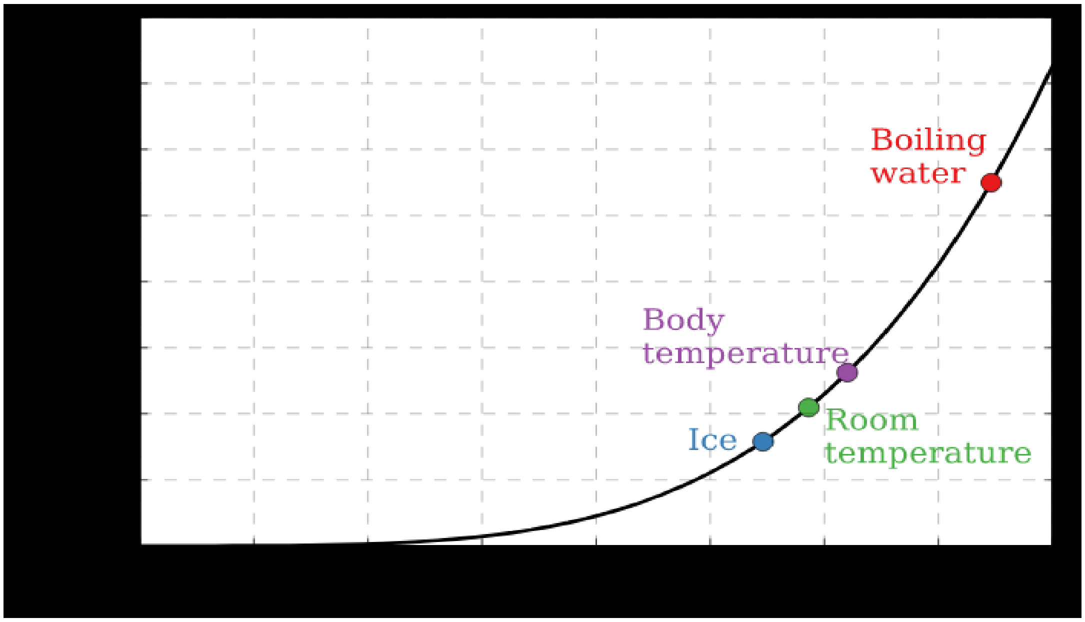


Figure 1.1.4: Graph of a function of total emitted energy of a blackbody proportional to the fourth power of its thermodynamic temperature *T* according to the Stefan–Boltzmann law. (CC BY-SA 4.0; Nicoguaro)

- ✓ **Example 1.1.1**

The sun's surface temperature is 5700 K.

a. How much power is radiated by the sun?
b. Given that the distance to earth is about 200 sun radii, what is the maximum power possible from a one square kilometer solar energy installation?

- ✓ **Solution**

(a) First, we calculate the area of the sun followed by the flux (power). The sun has a radius of 6.96×10^8m

The area of the sun is $A=4\pi R^2$.

$$A = 4(3.1416)(6.96 \times 10^{8} m)^{2}$$

$$= 6.08 \times 10^{18} m^{2}$$

The power radiated from the sun (via Stefan-Boltzmann Law) is $P=\sigma T^4$.

$$P = (5.67 \times 10^{-8}\ Watts\ m^{-2}\ k^{-4})(5700\ K)^{4}$$

$$= 5.98 \times 10^{7}\ Watts/m^{2}$$

This value is per square meter.

(b) To calculate the total power radiated by the sun is thus:

$$Ptotal = PA = (5.98 \times 10^{7}\ Watts/m^{2})(6.08 \times 10^{18} m^{2}) = 3.6 \times 10^{26}\ Watts$$

- ✓ **Wien's Displacement Law**

The second phenomenological observation from experiment was **Wien's Displacement Law**. Wien's law identifies the dominant (peak) wavelength, or color, of light coming from a body at a given temperature. As the oven temperature varies, so does the frequency at which the emitted radiation is most intense (Figure 1.1.3). In fact, that frequency is directly proportional to the absolute temperature:

$$vmax \propto T \tag{1.1.2}$$

where the proportionality constant is $5.879 \times 10^{10}\ Hz/K$.

Wien himself deduced this law theoretically in 1893, following Boltzmann's thermodynamic reasoning. It had previously been observed, at least semi-quantitatively, by an American astronomer, Langley. This upward shift in $vmax$ with T is familiar to everyone—when an iron is heated in a fire (Figure 1.1.1), the first visible radiation (at around 900 K) is deep red, the lowest frequency visible light. Further increase in *T* causes the color to change to orange then yellow, and finally blue at very high temperatures (10,000 K or more) for which the peak in radiation intensity has moved beyond the visible into the ultraviolet.

Another representation of Wien's Law (Equation 1.1.2) in terms of the peak wavelength of light is

$$\lambda max = b/T \tag{1.1.3}$$

where T is the absolute temperature in kelvin and b is a constant of proportionality called Wien's displacement constant, equal to $2.89 \times 10^{-3} m\, K$, or more conveniently to obtain wavelength in micrometers, $b \approx 2900\ \mu m \cdot\ K$. This is an inverse relationship between wavelength and temperature. So, the higher the temperature, the shorter or smaller the wavelength of the thermal radiation. The lower the temperature, the longer or larger the wavelength of the thermal radiation. For visible radiation, hot objects emit bluer light than cool objects.

- ✓ **Example 1.1.2**

If surface body temperature is 90 °F.

a. How much radiant energy in Wm^{-2} would your body emit?
b. What is the peak wavelength of emitted radiation?
c. What is the total radiant energy emitted by your body in Watts? Note: The average adult human male has a body surface area of about 1.9 m^2 and the average body surface area for a woman is about 1.6 m^2.

- ✓ **Solution**

(a) 90 °F is 305 K. We use Stefan-Boltzmann Law (Equation 1.1.1) The total amount of radiation emitted will be $P = \sigma\, T^4$.

$$P = (5.67\times10{-}8 \text{Watts } m^{-2}K^{-4})\ (305K)^4$$

$$= 491 \text{ W } m^{-2}$$

b) The peak wavelength of emitted radiation is found using Wien's Law:

$$\lambda max = 2.898\times10^{-3} m \cdot K/T$$

$$= 2.898\times10^{-3} m\cdot K/305K$$

$=9.5\times10^{-6}$ m=9.5 µm

c) The total radiant energy density in Watts is:

$\text{Energy}_{\text{male}}$= (491 W m^{-2}) (1.9 m^2) =933 W

$\text{Energy}_{\text{female}}$= (491 W m^{-2}) (1.6 m^2) =786 W

- ✓ **Example 1.1.3: The Temperature of the Sun**

For example, if the Sun has a surface temperature of 5700 K, what is the wavelength of maximum intensity of solar radiation?

- ✓ **Solution**

If we substitute 5700 K for *T* in Equation 1.1.3, we have

$$\lambda max = 0.0029/5700 = 5.1\times10^{-7}\text{ m}$$

Knowing that violet light has a wavelength of about 4.0×10^{-7} meters, yellow about 5.6×10^{-7} meters, and red about 6.6×10^{-7} meters, what can we say about the color of the Sun's peak radiation? The peak wavelength of the Sun's radiation is at a slightly shorter wavelength than yellow, so it is a slightly greenish yellow. To see this greenish tinge to the Sun, you would have to look at it from space. It turns out that the Earth's atmosphere scatters some of the shorter waves of sunlight, which shifts its peak wavelength to pure yellow.

Remember that thermal radiation always spans a wide range of wavelengths (Figure 1.1.2) and Equation 1.1.3 only specifies the single wavelength that is the peak of the spectrum. So, although the Sun appears yellowish-white, when you disperse sunlight with a prism you see radiation with all the colors of the rainbow. Yellow just represents a characteristic wavelength of the emission.

- ✓ **Exercise 1.1.1**

a. At what wavelength does the sun emit most of its radiation if it has a temperature of 5,778 K?
b. At what wavelength does the earth emit most of its radiation if it has a temperature of 288 K?

Answer a) 500 nm

Answer b)10.0 microns

- ✓ **The Rayleigh-Jeans Law:**

Lord Rayleigh and J. H. Jeans developed an equation which explained blackbody radiation at low frequencies. The equation which seemed to express blackbody radiation was built upon all the known assumptions of physics at the time. *The big assumption which Rayleigh and Jean implied was that infinitesimal amounts of energy were continuously added to the system when the frequency was increased*. Classical physics assumed that energy emitted by atomic oscillations could have any continuous value. This was true for anything that had been studied up until that point, including things like acceleration, position, or energy. Their resulting **Rayleigh-Jeans Law** was

$$d\rho(\nu,T) = \rho\nu(T)d\nu \tag{1.1.4}$$

$$= 8\pi k_B T\, \nu^2 d\nu\, /c^3 \tag{1.1.5}$$

Experimental data performed on the black box showed slightly different results than what was expected by the Rayleigh-Jeans law (Figure 1.1.5). The law had been studied and widely accepted by many physicists of the day, but the experimental results did not lie, something was different between what was theorized and what happens. The experimental results showed a bell type of curve, but according to the Rayleigh-Jeans law the frequency diverged as it neared the ultraviolet region (Equation 1.1.5). Ehrenfest later dubbed this the "ultraviolet catastrophe".

It is important to emphasizing that Equation 1.1.5 is a **classical** result: the only inputs are classical dynamics and Maxwell's electromagnetic theory. The charge e of the oscillator does not appear: the result is independent of the coupling strength between the oscillator and the radiation, the coupling only must be strong enough to ensure thermal equilibrium. The derivation of the law can be found here.

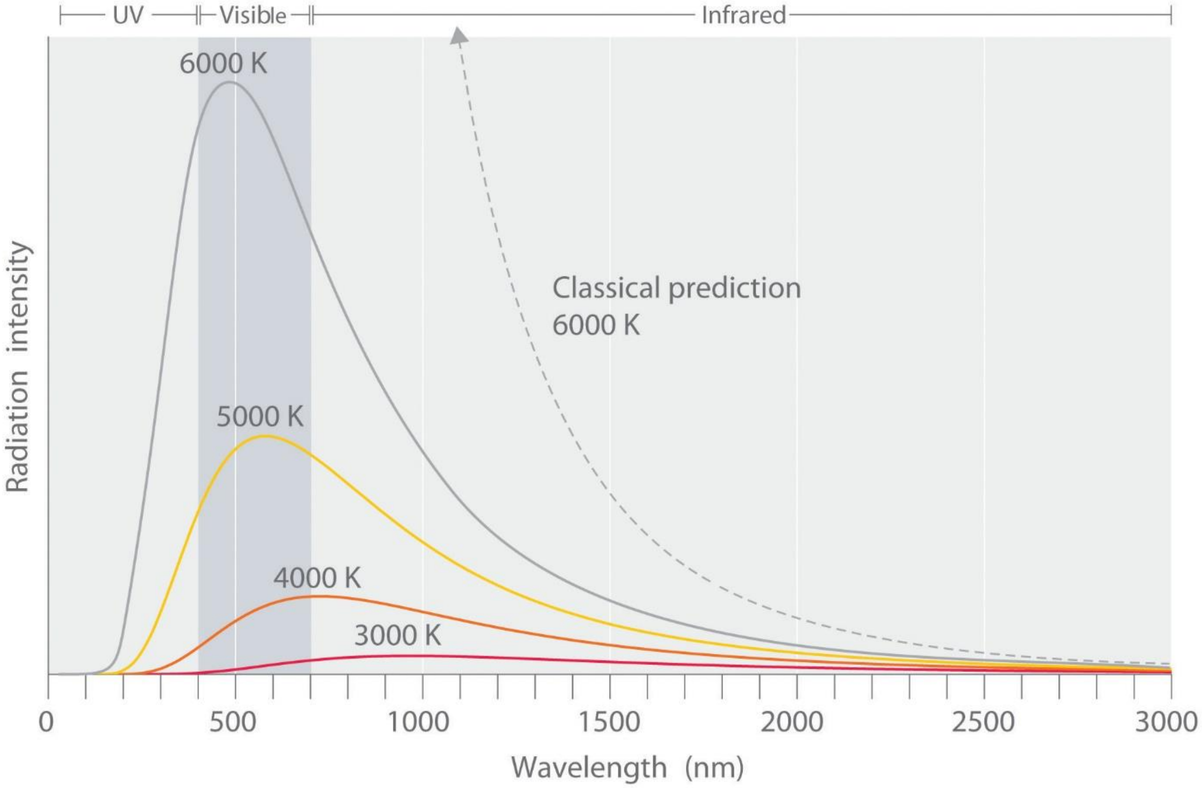


Figure 1.1.5: Relationship between the temperature of an object and the spectrum of blackbody radiation it emits. At relatively low temperatures, most radiation is emitted at wavelengths longer than 700 nm, which is in the infrared portion of the spectrum. The dull red glow of the hot metalwork in Figure 1.1.5 is due to the small amount of radiation emitted at wavelengths less than 700 nm, which the eye can detect. As the temperature of the object increases, the maximum intensity shifts to shorter wavelengths, successively resulting in orange, yellow, and finally white light. At high temperatures, all wavelengths of visible light are emitted with approximately equal intensities. (CC BY-SA-NC; anonymous)

- ✓ **Differential vs. Integral Representation of the Distribution:**

Radiation is understood as a continuous distribution of amplitude vs. wavelength or, equivalently, amplitude vs. frequency (Figure 1.1.5). According to Rayleigh-Jeans law, the intensity at a specific frequency ν and temperature is

$$\rho(\nu, T) = 8\pi k_B T \, \nu^2 d\nu \, / c^3.$$

However, in practice, we are more interested in frequency intervals. An exact frequency is the limit of a sequence of smaller and smaller intervals. If we make the assumption that, for a sufficiently small interval, $\rho(\nu, T)$ does not vary, we get your definition for the differential $d\rho(\nu, T)$ in Equation 1.1.5:

The assumption is fair due to the continuity of $\rho(\nu, T)$. This is the approximation of an integral on a very small interval $d\nu$ by the height of a point inside this interval ($8\pi k_B T\ \nu^2 d\nu\ /c^3$) times its length ($d\nu$). So, if we sum an infinite amount of small intervals like the one above we get an integral. The total radiation between $\nu 1$ and $\nu 2$ will be:

$$\int \nu 2 \nu 1 d\rho(\nu, T) = \int \nu 2 \nu 1 \rho(\nu, T) d\nu = \int \nu 2 \nu 1\ 8\pi k_B T\ \nu^2 d\nu\ /c^3$$
$$= 8\pi k_B T (\nu^3 2 - \nu^3 1)/3c^3$$

Observe that $\rho(\nu, T)$ is quadratic in ν.

- ✓ **Example 1.1.4: the ultraviolet catastrophe**

What is the total spectral radiance of a radiator that follows the Rayleigh-Jeans law for its emission spectrum?

- ✓ **Solution**

The total spectral radiance $\rho_{tot}(T)$ is the combined emission over all possible wavelengths (or equivalently, frequencies), which is an integral over the relevant distribution (Equation 1.1.5 for the Rayleigh-Jeans Law).

$$\rho tot(T) = \int_0^\infty d\nu = \int_0^\infty 8\pi k_B T\ \nu^2 d\nu\ /c^3$$

but the integral

$$\int_0^\infty x^2 dx$$

does not converge. Worse, it is infinite,

$$\lim_{k \to \infty} \int_0^k x^2 dx = \infty$$

Hence, the classically derived Rayleigh-Jeans law predicts that the radiance of a blackbody is infinite. Since radiance is power per angle and unit area, this also implies that the total power and hence the energy a blackbody emitter gives off is infinite, which is patently absurd. This is called the ultraviolet catastrophe because the absurd prediction is caused by the classical law not predicting the behavior at high frequencies/small wavelengths correctly (Figure 1.1.5).

1.2 Quantum Hypothesis Used for Blackbody Radiation Law

✓ **Learning Objectives**

- To understand how energy is quantized in blackbody radiation

By the late 19th century, many physicists thought their discipline was well on the way to explaining most natural phenomena. They could calculate the motions of material objects using Newton’s laws of classical mechanics, and they could describe the properties of radiant energy using mathematical relationships known as Maxwell’s equations, developed in 1873 by James Clerk Maxwell, a Scottish physicist. The universe appeared to be a simple and orderly place, containing matter, which consisted of particles that had mass and whose location and motion could be accurately described, and electromagnetic radiation, which was viewed as having no mass and whose exact position in space could not be fixed. Thus, matter and energy were considered distinct and unrelated phenomena. Soon, however, scientists began to look more closely at a few inconvenient phenomena that could not be explained by the theories available at the time.

One experimental phenomenon that could not be adequately explained by classical physics was blackbody radiation (Figure 1.2.1). Attempts to explain or calculate this spectral distribution from classical theory were complete failures. A theory developed by Rayleigh and Jeans predicted that the intensity should go to infinity at short wavelengths. Since the intensity drops to zero at short wavelengths, the Rayleigh-Jeans result was called the **ultraviolet catastrophe** (Figure 1.2.1dashed line). There was no agreement between theory and experiment in the ultraviolet region of the blackbody spectrum.

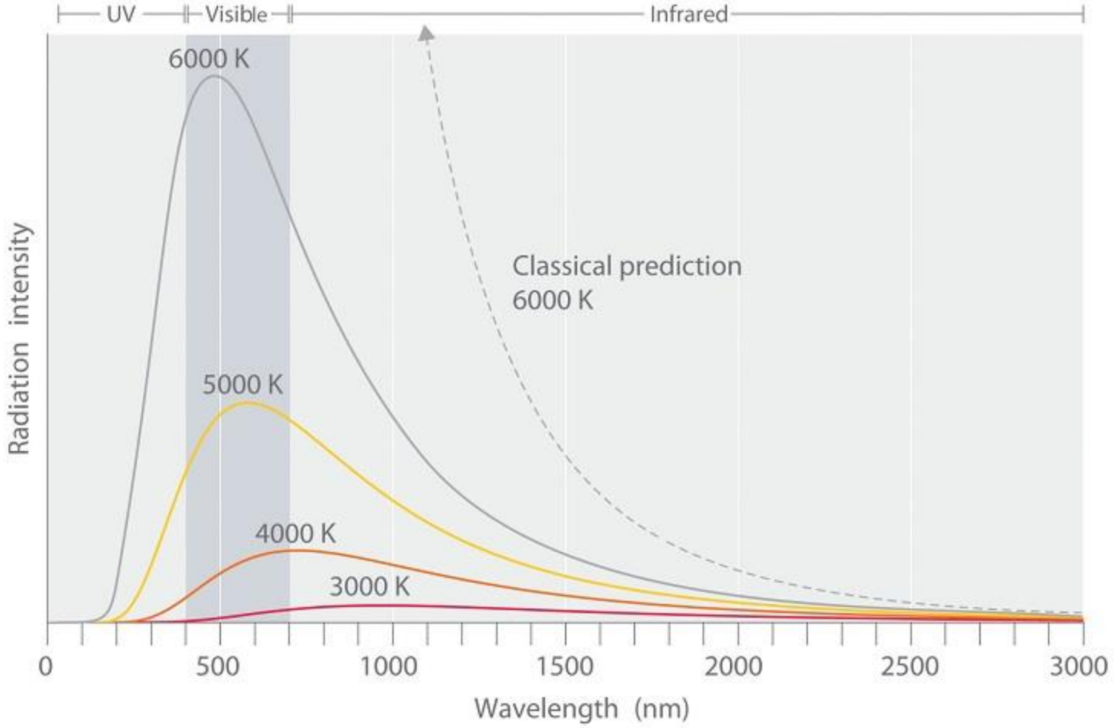


Figure 1.2.1: Relationship between the temperature of an object and the spectrum of blackbody radiation it emits. At relatively low temperatures, most radiation is emitted at wavelengths longer than 700 nm, which is in the infrared portion of the spectrum. As the temperature of the object increases, the maximum intensity shifts to shorter wavelengths, successively resulting in orange, yellow, and finally white light. At high temperatures, all wavelengths of visible light are emitted with approximately equal intensities. The white light spectrum shown for an object at 6000 K closely approximates the spectrum of light emitted by the sun. Note the sharp decrease in the intensity of radiation emitted at wavelengths below 400 nm, which constituted the ultraviolet catastrophe. The classical prediction fails to fit the experimental curves entirely and does not have a maximum intensity. (CC BY-SA-NC; anonymous by request).

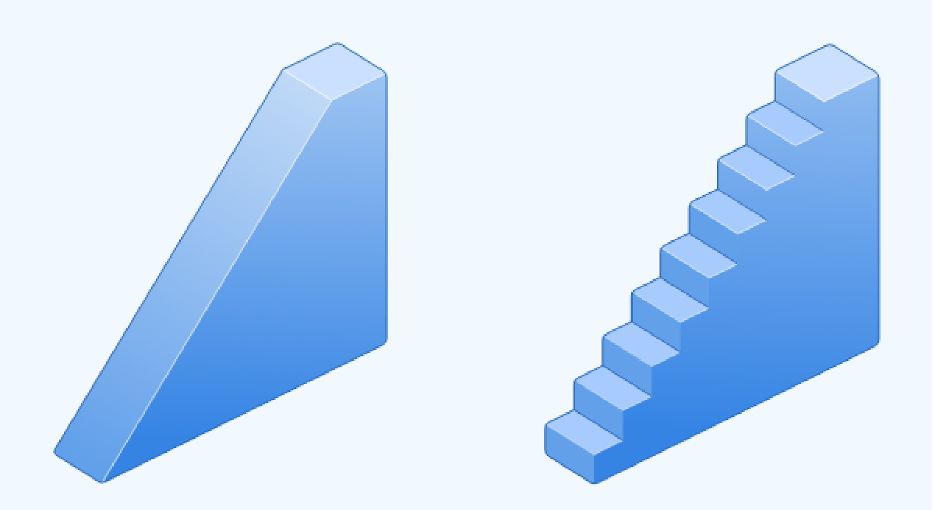
✓ Quantizing Electrons in the Radiator

In 1900, the German physicist Max Planck (1858–1947) explained the ultraviolet catastrophe by proposing that the energy of electromagnetic waves is *quantized* rather than continuous. This means that for each temperature, there is a maximum intensity of radiation that is emitted in a blackbody object, corresponding to the peaks in Figure 1.2.1, so the intensity does not follow a smooth curve as the temperature increases, as predicted by classical physics.

Thus, energy could be gained or lost only in integral multiples of some smallest unit of energy, a quantum (the smallest possible unit of energy). Energy can be gained or lost only in integral multiples of a quantum.

- ✓ **Quantization**

Although quantization may seem to be an unfamiliar concept, we encounter it frequently in quantum mechanics (hence the name). For example, US money is integral multiples of pennies. Similarly, musical instruments like a piano or a trumpet can produce only certain musical notes, such as C or F sharp. Because these instruments cannot produce a continuous range of frequencies, their frequencies are quantized. It is also like going up and down a hill using discrete stair steps rather than being able to move up and down a continuous slope. Your potential energy takes on discrete values as you move from step to step. Even electrical charge is quantized: an ion may have a charge of −1 or −2, but not −1.33 electron charges.



A continuous vs. a quantized (gravitationaly) potential energy system. In the continuous case (left) a system can have any potential energy, but in the quantized case (right), a system can only have certain values (other values are not allowed). (CC BY-NC; Ümit Kaya)

Planck's quantization of energy is described by his famous equation:

$$E = h\nu \tag{1.2.1}$$

where the proportionality constant h is called **Planck’s constant**, one of the most accurately known fundamental constants in science

$$h = 6.626070040(81) \times 10^{-34}\, J \cdot s$$

However, for our purposes, its value to four significant figures is sufficient:

$$h \;=\; 6.626 \;\times 10^{-34}\, J \cdot s$$

As the frequency of electromagnetic radiation increases, the magnitude of the associated quantum of radiant energy increases. By assuming that energy can be emitted by an object only in integral multiples of $h\nu$, Planck devised an equation that fit the experimental data shown in Figure 1.2.1. We can understand Planck's explanation of the ultraviolet catastrophe qualitatively as follows: At low temperatures, radiation with only relatively low frequencies is emitted, corresponding to low-energy quanta. As the temperature of an object increases, there is an increased probability of emitting radiation with higher frequencies, corresponding to higher-energy quanta. At any temperature, however, it is simply more probable for an object to lose energy by emitting many lower-energy quanta than a single very high-energy quantum that corresponds to ultraviolet radiation. The result is a maximum in the plot of intensity of emitted radiation versus wavelength, as shown in Figure 1.2.1, and a shift in the position of the maximum to lower wavelength (higher frequency) with increasing temperature.

At the time he proposed his radical hypothesis, Planck could not explain *why* energies should be quantized. Initially, his hypothesis explained only one set of experimental data—blackbody radiation. If quantization were observed for many different phenomena, then quantization would become a law. In time, a theory might be developed to explain that law. As things turned out, Planck's hypothesis was the seed from which modern physics grew.

Max Planck explains the spectral distribution of blackbody radiation as result from oscillations of electrons. Similarly, oscillations of electrons in an antenna produce radio waves. Max Planck concentrated on modeling the oscillating charges that must exist in the oven walls, radiating heat inwards and—in thermodynamic equilibrium—themselves being driven by the radiation field. He found he could account for the observed curve if he required these oscillators not to radiate energy continuously, as the classical theory would demand, but they could **only** loss or gain energy in chunks, called **quanta**, of size $h\nu$, for an oscillator of frequency ν (Equation 1.2.1).

With that assumption, Planck calculated the following formula for the radiation energy density inside the oven:

$$d\rho(\nu,T) = \rho_{\nu}(T)d\nu \tag{1.2.2}$$

$$= (2h\nu_{3/c2)} \cdot \frac{1}{exp(h\nu\,/kBT)-1} d\nu \tag{1.2.3}$$

with

- $\pi = 3.14159$
- $h = 6.626 \times 10^{-34}\, J \cdot s$
- $c = 3.00 \times 10^{8}\, m/s$
- $\nu = 1/s$
- $k_B = 1.38 \times 10^{-23}\, J/K$
- $T\, isabsolutetemperature(inKelvin)$

Planck's radiation energy density (Equation 1.2.3) can also be expressed in terms of wavelength λ.

$$\rho(\lambda,T)d\lambda = (2hc2/\lambda 5)\frac{1}{exp(hc\backslash\lambda kBT)-1} d\lambda \tag{1.2.4}$$

Planck's equation (Equation 1.2.4) gave an excellent agreement with the experimental observations for all temperatures (Figure 1.2.2).

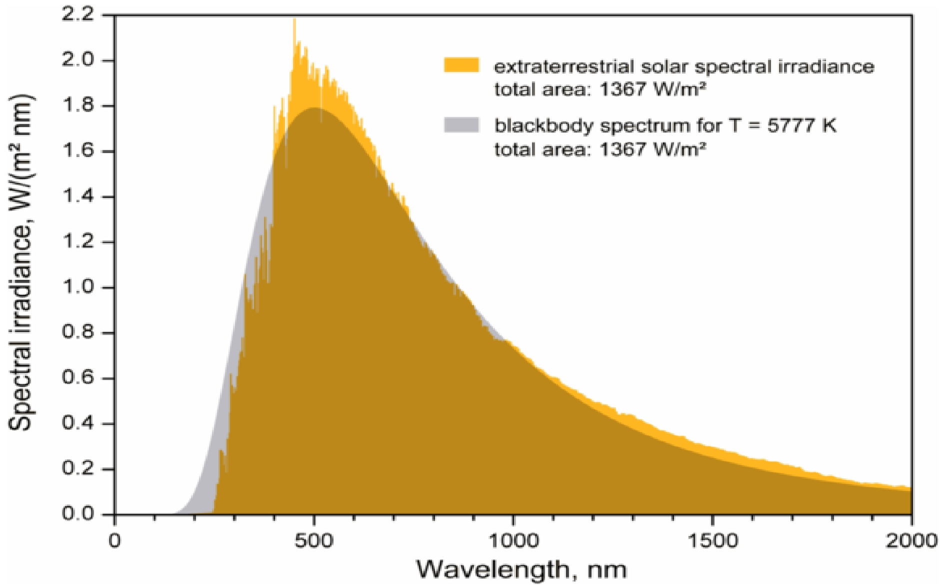
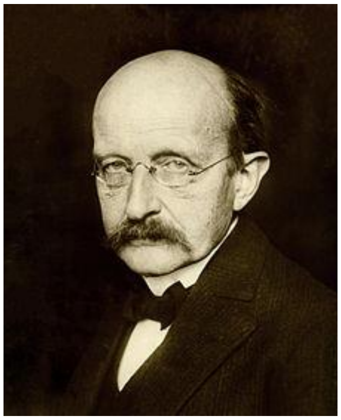


Figure 1.2.2: The Sun is an excellent approximation of a blackbody. Its effective temperature is ~5777 K. (CC-SA-BY 3.0; Sch).

✓ Max Planck (1858–1947)

Planck made many substantial contributions to theoretical physics, but his fame as a physicist rest primarily on his role as the originator of quantum theory. In addition to being a physicist, Planck was a gifted pianist, who at one time considered music as a career. During the 1930s, Planck felt it was his duty to remain in Germany, despite his open opposition to the policies of the Nazi government.



(left) The German physicist Max Planck had a major influence on the early development of quantum mechanics, being the first to recognize that energy is sometimes quantized. Planck also made important contributions to special relativity and classical physics. (Public Domain; Library of Congress via Wikimedia)
(left) The society's logo features Minerva, the Roman goddess of wisdom. (Fair use)

One of his sons was executed in 1944 for his part in an unsuccessful attempt to assassinate Hitler and bombing during the last weeks of World War II destroyed Planck’s home. After WWII, the major German scientific research organization was renamed the Max Planck Society.

✓ Exercise 1.2.1

Use Equation 1.2.4 to show that the units of $\rho(\lambda, T) d\lambda$ are $J/m3$ as expected for an energy density.

The near perfect agreement of this formula with precise experiments (e.g., Figure 1.2.3), and the consequent necessity of energy quantization, was the most important advance in physics in the century. His blackbody curve was completely accepted as the correct one: more and more accurate experiments confirmed it time and again, yet the radical nature of the quantum assumption did not sink in. Planck was not to upset—he didn't believe it either, he saw it as a technical fix that (he hoped) would eventually prove unnecessary.

Part of the problem was that Planck's route to the formula was long, difficult, and implausible—he even made contradictory assumptions at different stages, as Einstein pointed out later. However, the result was correct anyway!

The mathematics implied that the energy given off by a blackbody was not continuous, but given off at certain specific wavelengths, in regular increments. If Planck assumed that the energy of blackbody radiation was in the form

$$E = nh\nu$$

Where, n is an integer, then he could explain what the mathematics represented. This was indeed difficult for Planck to accept, because at the time, there was no reason to presume that the energy should only be radiated at specific frequencies. Nothing in Maxwell's laws suggested such a thing. It was as if the vibrations of a mass on the end of a spring could only occur at specific energies. Imagine the mass slowly coming to rest due to friction, but not in a continuous manner. Instead, the mass jumps from one fixed quantity of energy to another without passing through the intermediate energies.

To use a different analogy, it is as if what we had always imagined as smooth inclined planes were, in fact, a series of closely spaced steps that only presented the illusion of continuity.

- ✓ **Summary**

The agreement between Planck's theory and the experimental observation provided strong evidence that the energy of electron motion in matter is quantized. In the next two sections, we will see that the energy carried by light also is quantized in units of $\overline{h\nu}$. These packets of energy are called "photons."

1.3 Photoelectric Effect Explained with Quantum Hypothesis

✓ **Learning Objectives**

- To be familiar with the photoelectron effect for bulk materials
- Understand how the photoelectron kinetic energy and intensity vary as a function of incident light wavelength
- Understand how the photoelectron kinetic energy and intensity vary as a function of incident light intensity
- Describe what a workfunction is and relate it to ionization energy
- Describe the photoelectric effect with Einstein's quantized photon model of light

Nature, it seemed, was quantized (non-continuous, or discrete). If this was so, how could Maxwell’s equations correctly predict the result of the blackbody radiator? Planck spent a good deal of time attempting to reconcile the behavior of electromagnetic waves with the discrete nature of the blackbody radiation, to no avail. It was not until 1905, with yet another paper published by Albert Einstein, that the wave nature of light was expanded to include the particle interpretation of light which adequately explained Planck’s equation.

The photoelectric effect was first documented in 1887 by the German physicist Heinrich Hertz and is therefore sometimes referred to as the Hertz effect. While working with a spark-gap transmitter (a primitive radio-broadcasting device), Hertz discovered that upon absorption of certain frequencies of light, substances would give off a visible spark. In 1899, this spark was identified as light-excited electrons (called **photoelectrons**) leaving the metal's surface by J.J. Thomson (Figure 1.3.1).

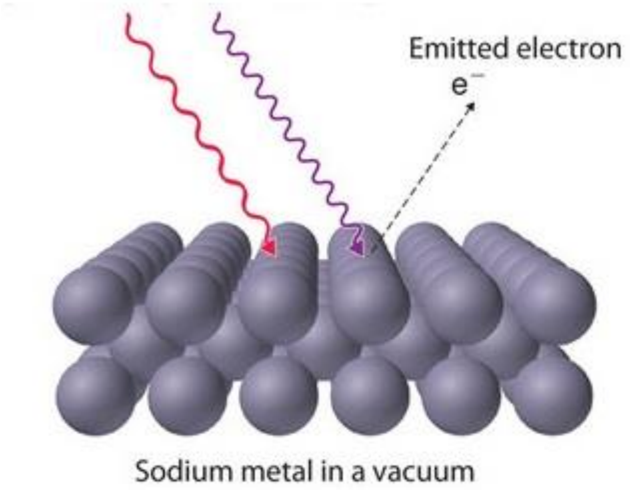


Figure 1.3.1: The photoelectric effect involves irradiating a metal surface with photons of sufficiently high energy to cause the electrons to be ejected from the metal. (CC BY-SA-NC; anonymous)

The classical picture underlying the photoelectron effect was that the atoms in the metal contained electrons, that were shaken and caused to vibrate by the oscillating electric field of the incident radiation. Eventually some of them would be shaken loose and would be ejected from the cathode. It is worthwhile considering carefully how the *number* and *speed* of electrons emitted would be expected to vary with the *intensity* and *color* of the incident radiation along with the time needed to observe the photoelectrons.

- Increasing the intensity of radiation would shake the electrons more violently, so one would expect more to be emitted, and they would shoot out at greater speed, on average.
- Increasing the frequency of the radiation would shake the electrons faster, so it might cause the electrons to come out faster. For very dim light, it would take some time for an electron to work up to a sufficient amplitude of vibration to shake loose.

✓ Lenard's Experimental Results (Intensity Dependence)

In 1902, Hertz's student, Philipp Lenard, studied how the energy of the emitted photoelectrons varied with the intensity of the light. He used a carbon arc light and could increase the intensity a thousand-fold. The ejected electrons hit another metal plate, the collector, which was connected to the cathode by a wire with a sensitive ammeter, to measure the current produced by the illumination (Figure 1.3.21.3.2). To measure the energy of the ejected electrons, Lenard charged the collector plate negatively, to repel the electrons coming towards it. Thus, only electrons ejected with enough kinetic energy to get up this potential hill would contribute to the current.

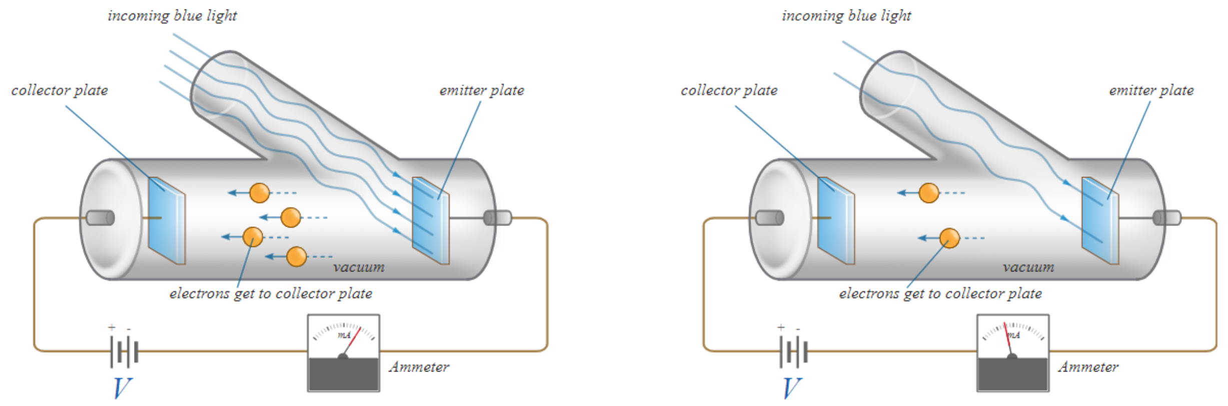


Figure 1.3.2: Lenard's photoelectric experiment. (left) High light intensity increase photocurrent (number of collected photoelectrons). (right) Low light intensity has reduced photocurrent. However, the kinetic energy of the ejected electrons is independent of incident light intensity. (CC BY-NC; Ümit Kaya)

Lenard discovered that there was a well-defined minimum voltage that stopped any electrons getting through ($Vstop$). To Lenard's surprise, he found that $Vstop$ did not depend at all on the intensity of the light! Doubling the light intensity doubled the *number* of electrons emitted but did not affect the *kinetic energies* of the emitted electrons. The more powerful oscillating field ejected more electrons, but the maximum individual energy of the ejected electrons was the same as for the weaker field (Figure 1.3.2).

✓ Millikan's Experimental Results (Wavelength Dependence)

The American experimental physicist Robert Millikan followed up on Lenard's experiments and using a powerful arc lamp, he was able to generate sufficient light intensity to separate out the colors and check the photoelectric effect using light of different colors. He found that the maximum energy of the ejected electrons *did* depend on the color - the shorter wavelength, higher frequency light ejects photoelectrons with greater kinetic energy (Figures 1.3.3).

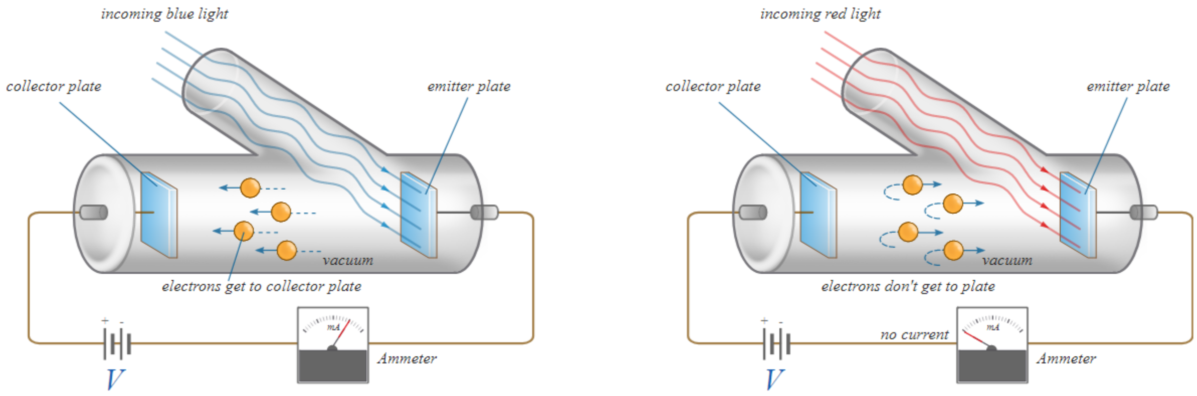


Figure 1.3.3: Millikan's photoelectric experiment. (left) Incident high-energy blue light. The battery represents the potential Lenard used to charge the collector plate negatively, which would be a variable voltage source. Since the electrons ejected by the blue light are getting to the collector plate, the potential supplied by the battery is less than $Vstop$, for blue light. (right) Indicent low-energy red light. Since the electrons ejected by the red light are not getting to the collector plate, the potential supplied by the battery exceeds $Vstop$ for red light. (CC BY-NC; Ümit Kaya)

As shown in Figure 1.3.4, just the opposite behavior from classical is observed from Lenard's and Millikan's experiments. The intensity affects the number of electrons, and the frequency affects the kinetic energy of the emitted electrons. From these sketches, we see that

- the kinetic energy of the electrons is linearly proportional to the frequency of the incident radiation above a threshold value of $\nu 0$ (no current is observed below $\nu 0$), and the kinetic energy is independent of the intensity of the radiation, and
- the number of electrons (i.e., the electric current) is proportional to the intensity and independent of the frequency of the incident radiation above the threshold value of $\nu 0$ (i.e., no current is observed below $\nu 0$).

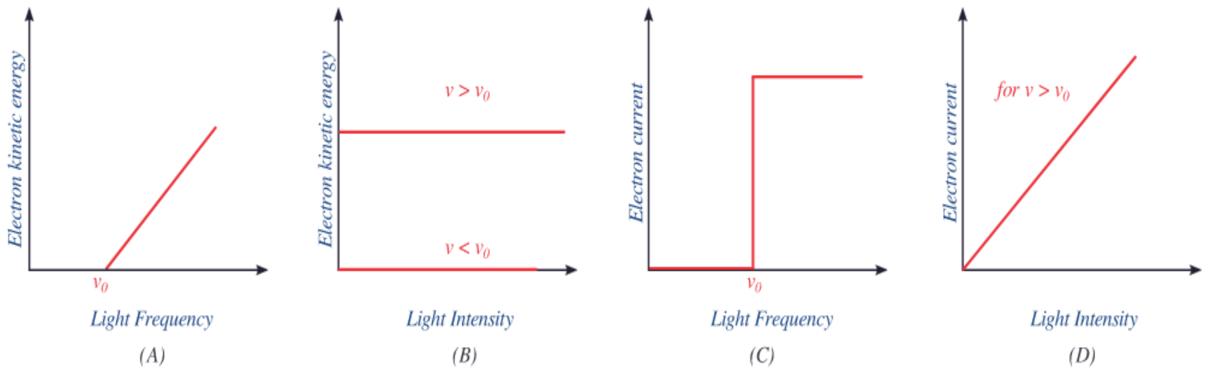


Figure 1.3.4: Schematic drawings showing the characteristics of the photoelectric effect from Lenard's and Millikan's experiments. (A) The kinetic energy of any single emitted electron increases linearly with frequency above some threshold value (B) The electron kinetic energy is independent of the light intensity above the threshold frequency and zero below. (C) The number of electrons emitted per second (i.e., the electric current) is independent of light frequency above the threshold frequency and zero below. (D) The number of electrons increases linearly with the light intensity. (CC BY-NC; Ümit Kaya)

✓ Classical Theory does not Describe Experiment

Classical theory predicts that energy carried by light is proportional to its amplitude independent of its frequency, and this fails to correctly explain the observed wavelength dependence in Lenard's and Millikan's observations.

As with most of the experimental results we discuss in this text, the behavior described above is a simplification of the true experimental results observed in the laboratory. A more complex description involves a greater introduction of more complex physics and instrumentation, which will be ignored for now.

✓ Einstein's Quantum Picture

In 1905 Einstein gave a very simple interpretation of Lenard's results and borrowed Planck's hypothesis about the quantized energy from his blackbody research and assumed that the incoming radiation should be thought of as quanta of energy $h\nu$, with ν the frequency. In photoemission, one such quantum is absorbed by one electron. If the electron is some distance into the material of the cathode, some energy will be lost as it moves towards the surface. There will always be some electrostatic cost as the electron leaves the surface, which is the workfunction, Φ. The most energetic electrons emitted will be those very close to the surface, and they will leave the cathode with kinetic energy

$$KE = h\nu - \Phi \tag{1.3.1}$$

On cranking up the negative voltage on the collector plate until the current just stops, that is, to $Vstop$, the highest kinetic energy electrons (KEe) must have had energy $eVstop$ upon leaving the cathode. Thus,

$$eV_{stop} = h\nu - \Phi \tag{1.3.2}$$

Thus, Einstein's theory makes a very definite quantitative prediction: if the frequency of the incident light is varied, and $Vstop$ plotted as a function of frequency, the slope of the line should be h/e (Figure 1.3.4A). It is also clear that there is a minimum light frequency for a given metal νo, that for which the quantum of energy is equal to Φ (Equation 1.3.1). Light below that frequency, no matter how bright, will not eject electrons.

According to both Planck and Einstein, the energy of light is proportional to its frequency rather than its amplitude, there will be a minimum frequency $\nu 0$ *needed to eject an electron with no residual energy.*

Since every photon of sufficient energy excites only one electron, increasing the light's intensity (i.e., the number of photons/sec) only increases the *number* of released electrons and not their kinetic energy. In addition, no time is necessary for the atom to be heated to a critical temperature and therefore the release of the electron is nearly instantaneous upon absorption of the light. Finally, because the photons must be above a certain energy to satisfy the work function, a threshold frequency exists below which no photoelectrons are observed. This frequency is measured in units of Hertz (1/second) in honor of the discoverer of the photoelectric effect.

Einstein's Equation 1.3.1 explains the properties of the photoelectric effect quantitatively. A strange implication of this experiment is that light can behave as a kind of massless "particle" now known as a *photon* whose energy $E = h\nu$ can be transferred to an actual particle (an electron), imparting kinetic energy to it, just as in an elastic collision between to massive particles such as billiard balls.

Robert Millikan initially did not accept Einstein's theory, which he saw as an attack on the wave theory of light, and worked for ten years until 1916, on the photoelectric effect. He even devised techniques for scraping clean the metal surfaces inside the vacuum tube. For all his efforts he found disappointing results: he confirmed Einstein's theory after ten years. In what he writes in his paper, Millikan is still desperately struggling to avoid this conclusion. However, by the time of his Nobel Prize acceptance speech, he has changed his mind rather drastically!

Einstein's simple explanation (Equation 1.3.1) completely accounted for the observed phenomena in Lenard's and Millikan's experiments (Figure 1.3.4) and began an investigation into the field we now call *quantum mechanics*. This new field seeks to provide a quantum explanation for classical mechanics and create a more unified theory of physics and thermodynamics. The study of the photoelectric effect has also lead to the creation of new field of photoelectron spectroscopy. Einstein's theory of the photoelectron presented a completely different way to measure Planck's constant than from black-body radiation.

✓ The Workfunction (Φ)

The **workfunction** is an intrinsic property of the metal. While the workfunctions and ionization energies appear as similar concepts, they are independent. The workfunction of a metal is the minimum amount of energy (E) necessary to remove an electron from the surface of the bulk (*solid*) metal (sometimes referred to as **binding energy**).

$$M(s) + \Phi \rightarrow M^{+}(s) + e^{-} \quad (free\ with\ no\ kinetic\ energy) \tag{1.3.3}$$

The workfunction is qualitatively like ionization energy (IE), which is the amount of energy required to remove an electron from an atom or molecule in the *gaseous* state.

$$M(g) + IE \rightarrow M^{+}(g) + e^{-} \quad (free\ with\ no\ kinetic\ energy) \qquad (1.3.4)$$

However, these two energies differ in magnitude (Table 1.3.11.3.1). For instance, copper has a workfunction of about 4.7 eV, but has a higher ionization energy of 7.7 eV. Generally, the ionization energies for metals are greater than the corresponding workfunctions (i.e., the electrons are less tightly bound in bulk metal).

✓ **Example 1.3.1: Calcium**

a. What is the energy in joules and electron volts of a photon of 420-nm violet light?
b. What is the maximum kinetic energy of electrons ejected from calcium by 420-nm violet light, given that the workfunction for calcium metal is 2.71 eV?

✓ **Strategy**

To solve part (a), note that the energy of a photon is given by $E = h\nu$. For part (b), once the energy of the photon is calculated, it is a straightforward application of Equation 1.3.1 to find the ejected electron's maximum kinetic energy, since Φ is given.

Solution for (a) Photon energy is given by

$$E = h\nu$$

Since we are given the wavelength rather than the frequency, we solve the familiar relationship $c = \nu\lambda$ for the frequency, yielding

$$\nu = c/\lambda$$

Combining these two equations gives the useful relationship

$$E = hc/\lambda$$

Now substituting known values yields

$$E = (6.63 \times 10^{-34} J \cdot s)(3.00 \times 10^{8} m/s)/420 \times 10^{-9} m$$

$$= 4.74 \times 10^{-19} J$$

Converting to eV, the energy of the photon is

$$E = (4.74 \times 10^{-19} J)(1 eV/1.6 \times 10^{-19}\ J)$$

$$= 2.96\ eV.$$

Solution for (b)

Finding the kinetic energy of the ejected electron is now a simple application of Equation 1.3.1 Substituting the photon energy and binding energy yields

$$KEe = h\nu - \Phi$$

$$= 2.96\ eV - 2.71\ eV$$

$$= 0.246\ eV.$$

- ✓ **Discussion**

The energy of this 420-nm photon of violet light is a tiny fraction of a joule, and so it is no wonder that a single photon would be difficult for us to sense directly—humans are more attuned to energies on the order of joules. But looking at the energy in electron volts, we can see that this photon has enough energy to affect atoms and molecules. A DNA molecule can be broken with about 1 eV of energy, for example, and typical atomic and molecular energies are on the order of eV, so that the UV photon in this example could have biological effects.

The ejected electron (called a photoelectron) has a rather low energy, and it would not travel far, except in a vacuum. The electron would be stopped by a retarding potential of 0.26 eV. In fact, if the photon wavelength were longer and its energy less than 2.71 eV, then the formula would give a negative kinetic energy, an impossibility. This simply means that the 420-nm photons with their

2.96-eV energy are not much above the frequency threshold. You can show for yourself that the threshold wavelength is 459 nm (blue light). This means that if calcium metal is used in a light meter, the meter will be insensitive to wavelengths longer than those of blue light. Such a light meter would be insensitive to red light, for example.

- ✓ **Exercise 1.3.1: Silver**

What is the longest-wavelength electromagnetic radiation that can eject a photoelectron from silver? Is this in the visible range?

- ✓ **Answer**

Given that the workfunction is 4.72 eV from Table 1.3.1, then only photons with wavelengths lower than 263 nm will induce photoelectrons (calculated via $E = h\nu$). This is ultraviolet and not in the visible range.

- ✓ **Exercise 1.3.2**

Why is the workfunction of an element generally lower than the ionization energy of that element?

- ✓ **Answer**

The workfunction of a metal refers to the minimum energy required to extract an electron from the surface of a (bulk) metal by the absorption a photon of light. The workfunction will vary from metal to metal. In contrast, ionization energy is the energy needed to detach electrons from atoms and varies with each particular atom, with the valence electrons require less energy to extract than core electrons (i.e., from lower shells) that are more closely bound to the nuclei. The electrons in the metal lattice there less bound (i.e., free to move within the metal) and removing one of these electrons is much easier than removing an electron from an atom because the metallic bond of the bulk metal reduces their binding energy. As we will show in subsequent chapters, the more delocalized a particle is, the lower its energy.

✓ Summary

Although Hertz discovered the photoelectron in 1887, it was not until 1905 that a theory was proposed that explained the effect completely. The theory was proposed by Einstein, and it made the claim that electromagnetic radiation had to be thought of as a series of particles, called photons, which collide with the electrons on the surface and emit them. This theory ran contrary to the belief that electromagnetic radiation was a wave and thus it was not recognized as correct until 1916 when Robert Millikan experimentally confirmed the theory

The photoelectric effect is the process in which electromagnetic radiation ejects electrons from a material. Einstein proposed photons to be quanta of electromagnetic radiation having energy $E = h\nu$ is the frequency of the radiation. All electromagnetic radiation is composed of photons. As Einstein explained, all characteristics of the photoelectric effect are due to the interaction of individual photons with individual electrons. The maximum kinetic energy KEe of ejected electrons (photoelectrons) is given by $KEe = h\nu - \Phi$, where $h\nu$ is the photon energy and Φ is the workfunction (or binding energy) of the electron to the particular material.

✓ Conceptual Questions

1. Is visible light the only type of electromagnetic radiation that can cause the photoelectric effect?
2. Which aspects of the photoelectric effect cannot be explained without photons? Which can be explained without photons? Are the latter inconsistent with the existence of photons?
3. Is the photoelectric effect a direct consequence of the wave character of electromagnetic radiation or of the particle character of electromagnetic radiation? Explain briefly.
4. Insulators (nonmetals) have a higher Φ than metals, and it is more difficult for photons to eject electrons from insulators. Discuss how this relates to the free charges in metals that make them good conductors.

5. If you pick up and shake a piece of metal that has electrons in it free to move as a current, no electrons fall out. Yet if you heat the metal, electrons can be boiled off. Explain both facts as they relate to the amount and distribution of energy involved with shaking the object as compared with heating it.

1.4: Matter Has Wavelike Properties

✓ **Learning Objectives**

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

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

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

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

✓ **Deriving the de Broglie Wavelength**

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

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

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

$$E = pc.$$

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

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

Solving for the wavelength λ gives Equation 1.6.1:

$$\lambda = h/p = h/mv \tag{1.4.3}$$

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

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

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

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

✓ **Example 1.4.1: Electron Waves**

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

✓ **Solution**

To calculate the de Broglie wavelength (Equation 1.4.3), the momentum of the particle must be established and requires knowledge of both the mass and velocity of the particle. The mass of an electron is 9.109383×10–^{28}g and the velocity is obtained from the given kinetic energy of 1000 eV:

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

Solve for momentum

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

convert to SI units

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

expanding definition of joule into base SI units and cancel

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

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

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

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

$$\lambda = h/p$$

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

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

✓ **Exercise 1.4.1: Baseball Waves**

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

✓ **Answer**

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

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

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

The de Broglie wavelength of this fast ball is:

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

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

1.5: de Broglie Waves can be Experimentally Observed

✓ **Learning Objectives**

- To present the experimental evidence behind the wave-particle duality of matter

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

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

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

✓ Diffraction of Light (Light as a Wave)

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

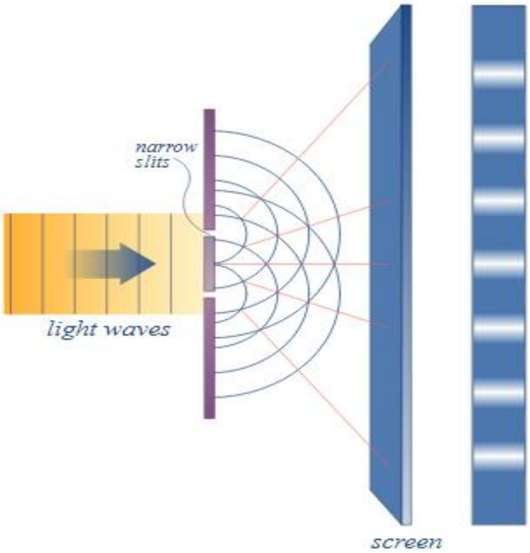


Figure 1.5.1: Young double slit experiment. Two slits are illuminated by a plane light waves. (CC BY-NC; Ümit Kaya)

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

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

- ✓ **Diffraction of Electrons (Electrons as Waves)**

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

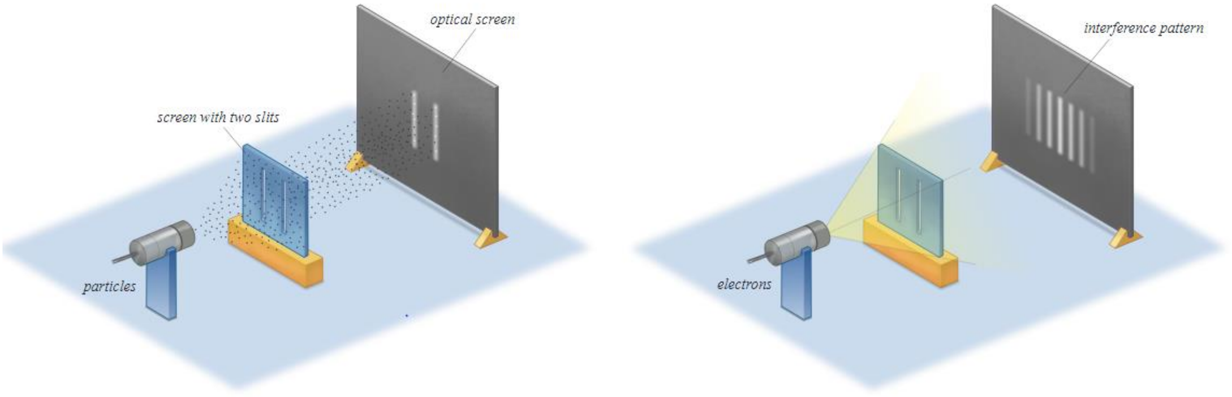


Figure 1.5.2: (left) classical model of electrons. (right) wave property of electrons. (CC BY-NC; Ümit Kaya)

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

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

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

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

✓ Is Matter a Particle or a Wave?

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

✓ Neutrons Diffraction (Neutrons as Waves)

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

Example 1.7.1: Neutron Diffraction

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

- ✓ **Solution**

This is a simple use of de Broglie's equation

$$\lambda = h/p$$

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

$$p = h/\lambda$$

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

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

The relationship for kinetic energy is

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

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

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

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

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

1.6: The Heisenberg Uncertainty Principle

✓ **Learning Objectives**

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

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

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

✓ **Probability**

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

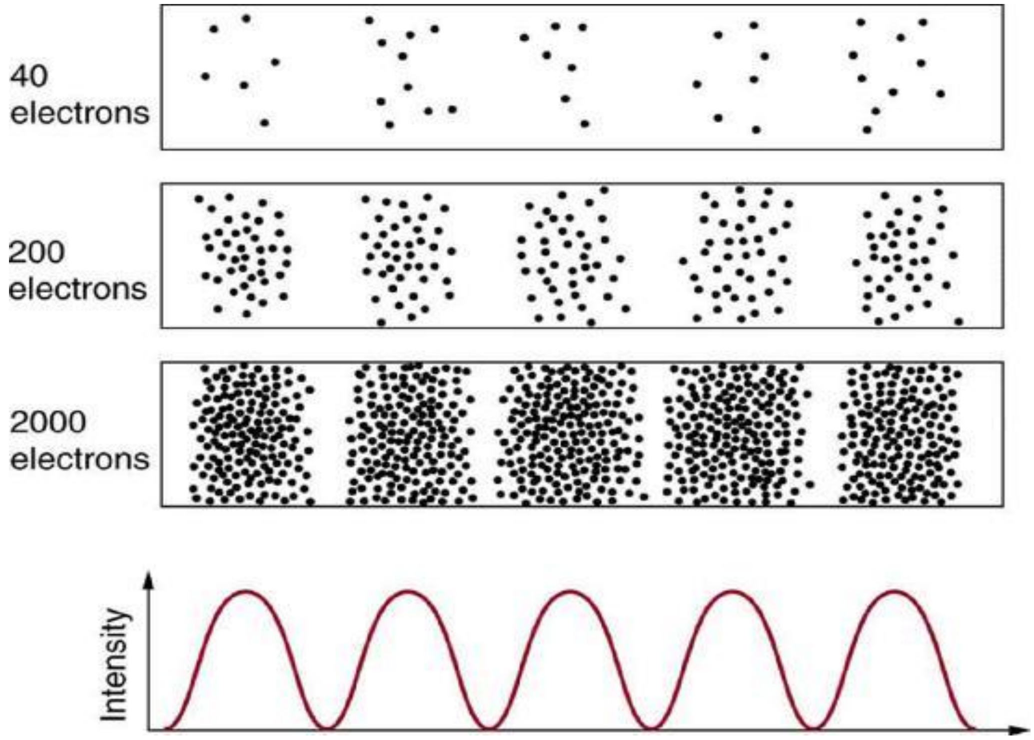


Figure 1.6.1: The building up of the diffraction pattern of electrons scattered from a crystal surface. Each electron arrives at a definite location, which cannot be precisely predicted. The overall distribution shown at the bottom can be predicted as the diffraction of waves having the de Broglie wavelength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

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

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

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

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

✓ Heisenberg's Uncertainty Principle

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

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

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

By substituting $\varDelta x$ for λ into Equation 1.6.1, we derive

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

or,

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

early form of uncertainty principle

✓ A Common Trend in Quantum Systems

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

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

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

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

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

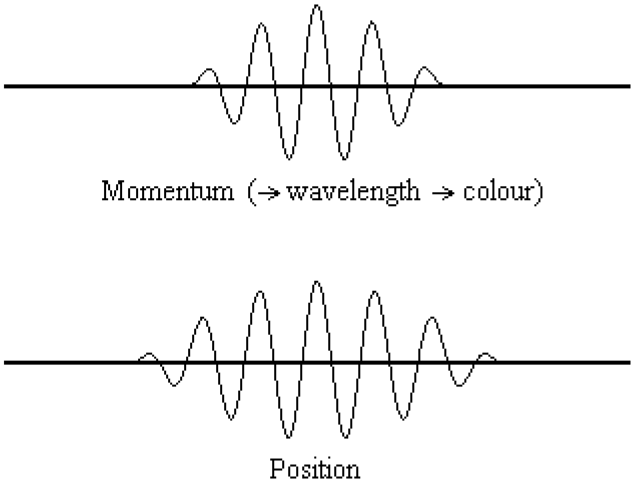


Figure 1.6.2: The animation shows the relevant spreads in the uncertainty for position and momentum of light/photons (light wave's corresponding photon particle). From the result of de Broglie, we know that for a particle with known momentum, pp will have a precise value for its de Broglie wavelength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

✓ What is the Proper Definition of Uncertainty?

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

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

✓ Example 1.6.1

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

- ✓ **Solution**

The uncertainty principle (Equation 1.6.5):

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

can be written

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

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

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

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

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

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

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

- ✓ **Exercise 1.6.1**

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

- ✓ **Answer**

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

- ✓ **Example 1.6.2**

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

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

- ✓ **Solution**

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

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

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

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

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

- ✓ **Exercise 1.6.2**

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

- ✓ **Answer**

We need to quantify the uncertainty of the electron in position. We can estimate that as ±5×10^{-10} m. Hence, substituting the relevant numbers into Equation 1.6.5 and solving for Δv we get

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

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

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

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

Heisenberg get pulled over for speeding by the police. The officer asks him "Do you know how fast you were going?"
Heisenberg replies, "No, but we know exactly where we are!"

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

Chapter 2

2.1: The One-Dimensional Wave Equation

✓ **Learning Objectives**

- To introduce the wave equation including time and position dependence

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

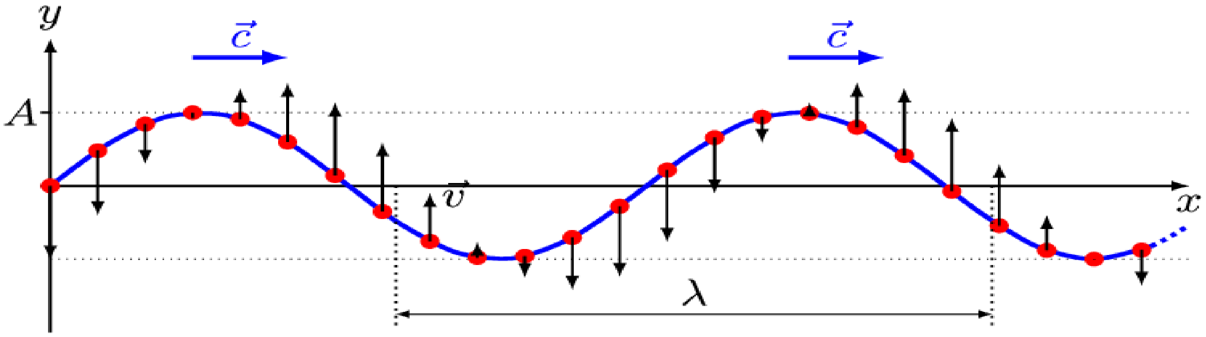


Figure 2.1.1: A simple translational (transverse) wave. (CC BY-SA 4.0 International; And 1mu via Wikimedia Commons)

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

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

Where,

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

- ϕ is the phase constant.

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

✓ Traveling Waves

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

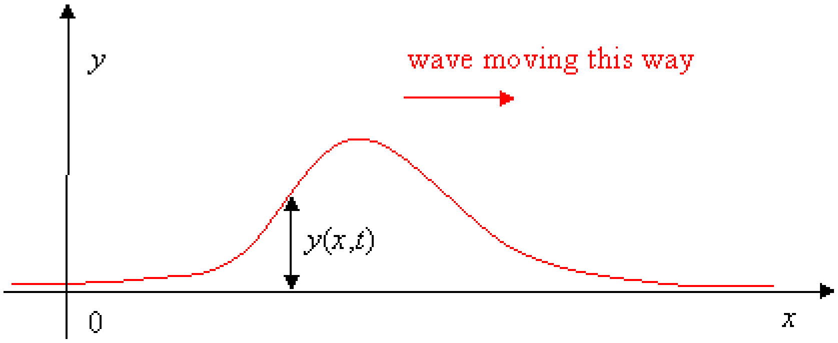


Figure 2.1.2: A one-dimensional traveling wave at one instance of time t.

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

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

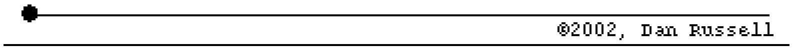


Figure 2.1.3: A one-dimensional traveling wave at as a function of time. Traveling waves propagate energy from one spot to another with a fixed velocity vv. (CC BY-NC-ND; Daniel A. Russell).

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

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

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

✓ Standing Waves

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

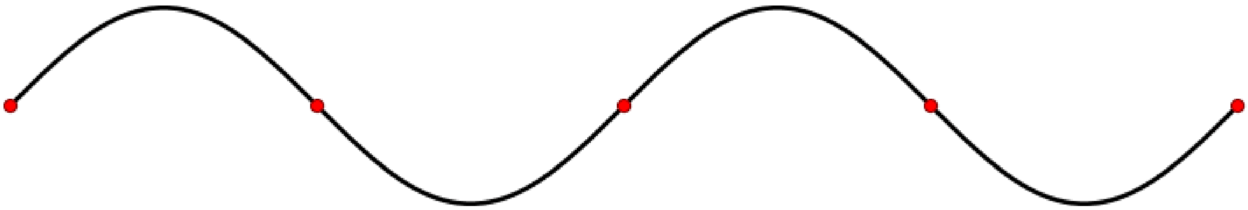


Figure 2.1.4: Animation of standing wave in the stationary medium with marked wave nodes (red circles). (Public domain; Lucas VB).

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

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

✓ The Wave Equation

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

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

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

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

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

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

and

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

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

✓ Summary

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

Chapter 3

The Schrödinger Equation and a Particle in a Box

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

3.1: The Schrödinger Equation

✓ **Learning Objectives**

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

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

✓ The Schrödinger Equation: A Better Approach

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

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

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

$$\nabla^2 = \partial^2/\partial x^2 + \partial^2/\partial y^2 + \partial^2/\partial z^2 \qquad (3.1.2)$$

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

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

$$\Psi(x) = f(2\pi x/\lambda) \qquad (3.1.3)$$

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

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

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

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

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

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

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

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

Where,

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

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

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

Thus from a simple comparison of Equations 3.1.7 and 3.1.9

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

or analogously differentiation of Equation 3.1.9 with respect to x

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

and then the second derivative

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

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

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

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

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

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

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

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

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

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

time-dependent Schrödinger equation in 1D

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

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

(3.1.17)

time-dependent Schrödinger equation in 3D

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

- ✓ **The Laplacian Operator**

The three second derivatives in parentheses together are called the Laplacian operator, or del-squared,

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

$$= (\partial 2/\partial x 2 + \partial 2/\partial y 2 + \partial 2/\partial z 2) \qquad (3.1.18)$$

with the del operator,

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

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

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

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

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

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

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

time-independent Schrödinger equation

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

✓ Time Dependence to the Wavefunctions

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

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

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

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

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

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

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

3.2: Linear Operators in Quantum Mechanics

✓ **Learning Objectives**

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

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

$$[-(\hbar_2/2m)\nabla_2 + V(\vec{r})]\psi(\vec{r}) = E\psi(\vec{r}) \tag{3.2.1}$$

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

$$\hat{H} = -(\hbar_2/2m)\nabla_2 + V(\vec{r}) \tag{3.2.2}$$

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

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

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

✓ Fundamental Properties of Operators

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

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

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

The product of two operators is defined by

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

Two operators are equal if

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

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

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

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

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

The *associative law* holds for operators

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

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

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

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

✓ Definition: The Commutator

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

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

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

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

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

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

✓ Linear Operators

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

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

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

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

Condition A

and

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

Condition B

where

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

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

✓ Example 3.2.1

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

✓ Solution

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

Condition A (Equation 3.2.15):

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

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

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

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

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

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

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

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

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

- ✓ **Exercise 3.2.1**

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

- ✓ **Answer**

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

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

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

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

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

- ✓ **Hermitian Operators**

An important property of operators is suggested by considering the Hamiltonian

for the particle in a box:

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

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

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

Now, using integration by parts,

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

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

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

It follows therefore that

$$\int_0^a f(x)H^\wedge g(x)dx = \int_0^a g(x)H^\wedge f(x)dx \qquad (3.2.21)$$

An obvious generalization for complex functions will read

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

In mathematical terminology, an operator A^ for which

$$\int f * A^\wedge \, g \, d\tau = (\int g * A^\wedge \, f \, d\tau) * \qquad (3.2.23)$$

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

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

3.3: The Schrödinger Equation is an Eigenvalue Problem

✓ **Learning Objectives**

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

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

$$A\hat{}\psi \propto \psi \tag{3.3.1}$$

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

$$A\hat{}\psi = k\psi \tag{3.3.2}$$

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

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

$$A\hat{}\psi = a\psi \tag{3.3.3}$$

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

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

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

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

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

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

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

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

and the time-independent Schrödinger equation

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

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

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

✓ Correspondence Principle

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

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

✓ Common Operators

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

- **Linear Momentum:**

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

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

  and can be generalized in three dimensions:

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

- **Position**

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

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

and can be generalized in three dimensions:

$$r^{\rightarrow}\hat{} = r^{\rightarrow} \tag{3.3.12}$$

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

- **Kinetic Energy**

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

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

Quantum mechanically, the corresponding kinetic energy operator is

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

and can be generalized in three dimensions:

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

- **Angular Momentum:**

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

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

- **Hamiltonian:**

The Hamiltonian operator corresponds to the total energy of the system

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

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

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

- **Total Energy:**

The energy operator from the time-dependent Schrödinger equation

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

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

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

This aspect will be discussed in more detail elsewhere.

✓ **Eigenstate, Eigenvalues, Wavefunctions, Measurables and Observables**

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

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

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

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

This will be discussed in more detail in later sections.

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

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

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

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

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

- ✓ **Example 3.3.1**

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

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

- ✓ **Strategy**

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

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

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

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

- ✓ **Solution**

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

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

and compare to the right side of Equation 3.3.22

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

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

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

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

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

and compare to the right side

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

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

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

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

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

and the right side of Equation 3.3.22

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

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

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

$$-(\hbar 2/2m)\ \ \partial 2/\partial x2\ N\ exp(-ix/\hbar) = +i(\hbar/2m)\ \ \partial/\partial x\ N\ exp(-ix/\hbar)$$
$$= +1/2m\ \ N\ exp(-ix/\hbar)$$

and the right side

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

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

$$KE = 1/2m$$

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

✓ **Exercise 3.3.1**

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

✓ **Answer**

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

3.4: Wavefunctions Have a Probabilistic Interpretation

✓ **Learning Objectives**

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

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

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

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

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

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

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

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

$$P(x \in [a,b]) = \int_a^b |\psi(x)|2dx \qquad (3.4.3)$$

In three dimensions, Equation 3.4.3 is represented differently

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

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

- Cartesian:

$$d\tau = dx\ dy\ dz \qquad (3.4.5)$$

- Spherical:

$$d\tau = r2\ sin\phi\ dr\ d\theta\ d\phi \qquad (3.4.6)$$

- Cylindrical:

$$d\tau = r\ dr\ d\phi\ dz \qquad (3.4.7)$$

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

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

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

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

✓ Required Properties of Wavefunction

- The wavefunction must be a single-valued function of all its coordinates since the probability density ought to be uniquely determined at each point in space.
- The wavefunction should be both finite as an infinite probability has no meaning.
- The wavefunction should be continuous everywhere, as expected for a physically meaningful probability density.

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

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

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