

Chapter 23: The Foundations of Quantum Mechanics

Why does a confined particle have quantized energy levels?

Why do atoms stick together to form chemical bonds? What principles govern the formation of the chemical bond? The structure of a molecule is determined by the chemical bonds that hold the atoms together. The key to understanding molecular structure is to determine the electronic structure of atoms and the bonds that the atoms form.

Atomic and molecular structure are aspects of the microscopic world, a world beyond the direct reach of our senses. In the microscopic world, light and matter behave in ways that are difficult to anticipate based on our daily experience. Light is the principal tool for unraveling the intricacies of the microscopic world. What can the interaction of light with matter tell us about atomic and molecular structure? Can we control the fate of chemical reactions using light? The principle goal of the next chapters is to develop the theory of chemical bonding so that we can determine the influence of chemical bonding on the structure and properties of molecules. The branch of science that concerns the microscopic structure of matter is **quantum mechanics**.

Structure-function relationships are the primary tools for solving problems using chemistry. Thermodynamics shows the interrelationships among thermochemistry, chemical equilibrium, and electrochemistry. The laws of thermodynamics govern all chemical phenomena, in a completely general way. However, because thermodynamics is model free, we must look beyond thermodynamics to further develop structure-function relationships. Atomic and molecular structure are aspects of the microscopic world. Reaction equilibria and kinetics are aspects of the macroscopic world. To develop practical applications of molecular systems, we need to understand the underlying principles of the microscopic world and then bridge the microscopic and macroscopic viewpoints of chemical reactivity. Our goal is to understand atomic and molecular structure and then predict thermodynamic and kinetic properties.

The microscopic behavior of atoms and molecules became evident at the turn of the 19th century through a series of experiments that determined that matter has quantized energy levels, that light has a particle nature, and that particles have a wave nature. A review of these experiments will help us understand the nature of quantization and wave-particle duality. These fundamental ideas lead to current theories of chemical bonding.

23.1 A Brief Review of Classical Mechanics

The classical view of matter and light clearly distinguishes particle-like and wave-like behavior. Particles are discrete, localized, and countable. Particles are characterized by their mass, charge, momentum, and kinetic energy. Particle properties are measured using collision-type experiments. At the beginning of the 20th century, electrons, protons, atoms, and molecules were considered particles. In contrast, waves are delocalized or “fuzzy.” Waves are characterized by their frequency, wavelength, and amplitude. Wave properties are measured using interference experiments, including wave length determination using diffraction experiments.

Newton's Laws of Motion: The momentum of a particle, p , is given by the mass of the particle, m , and the velocity, v . In one-dimension, $p = mv$ and the kinetic energy is given by $E_k = \frac{1}{2} mv^2 = p^2/2m$. The trajectory of a particle, $x(t)$, is calculated using Newton's Second Law by determining the forces that act on the particle:

$$p(t) = m \frac{dx(t)}{dt} \quad F = ma = m \frac{dv(t)}{dt} = m \frac{d^2x(t)}{dt^2} = \frac{dp(t)}{dt} \quad 23.1.1$$

This last equation can be read as: “a force is necessary to change the momentum of the particle.” For example, integrating these last equations for a constant force gives:

$$p(t) = p(t_0) + F(t - t_0) \quad (F(x) = F) \quad 23.1.2$$

where $p(t_0)$ is the initial momentum at time t_0 . A free particle experiences no forces, and therefore has a constant momentum and a constant velocity. Integrating $p(t) = m(dx/dt)$ for a constant momentum gives:

$$x(t) = x(t_0) + p/m(t - t_0) = x(t_0) + v(t - t_0) \quad (F(x) = 0) \quad 23.1.3$$

where $x(t_0)$ is the initial position at time t_0 . A free particle experiences straight-line motion with constant velocity. The force is the negative of the gradient of the potential energy:

$$F = - \frac{dV(x)}{dx} \quad 23.1.4$$

where $V(x)$ is the potential energy of the system as a function of position. The equations of motion for a classical particle are completely deterministic. If the position of the particle is known at some initial time, t_0 , and the potential energy function is known, then the trajectory of the particle, $x(t)$, is exactly determined for all future times. Please review the treatment of the classical harmonic oscillator, Addendum 8.12, for an important example of integrating Newton’s Laws of motion. We will refer to the classical harmonic oscillator repeatedly in this and subsequent chapters. Newton’s Laws of motion can also be expressed in a rearranged form that is often convenient, giving the classical Hamiltonian.

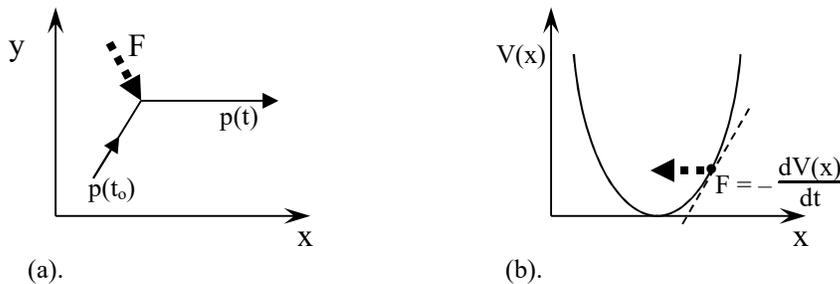


Figure 23.1.1: (a). A force is necessary to change the momentum of the particle. (b). A force is determined by the negative of the gradient of the potential energy function. The slope is positive at the chosen point, giving a force in the negative direction.

The Classical Hamiltonian is the Sum of the Kinetic and Potential Energy: The total energy of a particle is the sum of the kinetic and potential energies:

$$\begin{aligned} E_k + V(x) &= E \\ \frac{1}{2}mv^2 + V(x) &= E \\ p^2/2m + V(x) &= E \end{aligned} \quad 23.1.5$$

kinetic energy + potential energy = total energy

The total energy of the particle is conserved, is constant, in the absence of external forces. The sum of the kinetic energy and the potential energy is called the **classical Hamiltonian**, $\mathcal{H} = E_k + V$. The kinetic energy is often alternately represented in other texts as T and the Hamiltonian is then $\mathcal{H} = T + V$. Consider, again, the free particle example. For a free particle, $V(x) = 0$, and then using Eq. 23.1.5:

$$p^2/2m = E \quad \text{giving: } p = \sqrt{2mE} \quad (V(x) = 0) \quad 23.1.6$$

The momentum is constant. The trajectory of the particle is then given by Eq. 23.1.3, as before. The classical Hamiltonian form of the equations of motion is an important foundation for the development of quantum mechanics.

Energy is Often Expressed in Electron Volts: **Electron volts** are convenient units for expressing energies. An electron volt, eV, is the amount of kinetic energy that is gained by an electron that is accelerated by a potential difference of one volt. Consider a beam of electrons that is produced by a hot filament under vacuum, Figure 23.1.2. A grid placed in the path of the electrons with a positive potential attracts the electrons and imparts kinetic energy to the electrons given by the product of the charge on the electron and the applied potential, $E_k = eV$. The kinetic energy expressed in electron volts is just equal to the acceleration potential. For example, in an electron microscope, electrons are accelerated by a potential of 5,000-400,000 V, giving an electron energy of 5,000 eV – 400,000 eV. To convert eV to joules, remember that $1 \text{ J} = 1 \text{ C V}$, where the unit of charge is the coulomb, C. The charge of an electron is $-e$, with $e = 1.60217733 \times 10^{-19} \text{ C}$. The conversion from eV to joules is given by:

$$1 \text{ eV} = e (1\text{V}) = 1.60218 \times 10^{-19} \text{ C} (1\text{V}) = 1.60218 \times 10^{-19} \text{ J} \quad 23.1.7$$

The conversion constant is just the charge on the electron. For a mole of electrons:

$$1 \text{ eV} = 1.60218 \times 10^{-19} \text{ J} (6.0221367 \times 10^{23} \text{ mol}^{-1}) (1 \text{ kJ}/1000 \text{ J}) = 96.485 \text{ kJ mol}^{-1} \quad 23.1.8$$

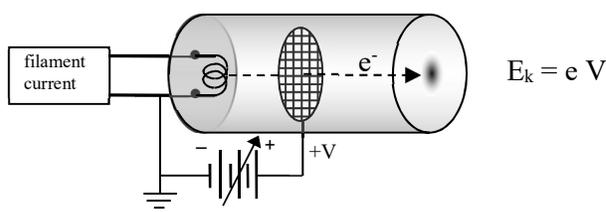


Figure 23.1.2: An electron volt is the kinetic energy of an electron after acceleration across a potential of 1V.

Waves Show Oscillatory Behavior: The frequency, ν , and wave length, λ , of a wave are related by $\nu\lambda = v$, where v is the propagation velocity of the wave. For light in vacuum the propagation velocity is c , giving $\nu\lambda = c$. The classical formulation of wave-like motion gives the energy carried by the wave as proportional to the amplitude of the wave squared, $E \propto A^2$, as we showed for the harmonic oscillator, Eq. 8.13.15. Consider throwing a rock into a pond and then

observing the displacement of the surface of the water at some fixed spot, Figure 23.1.3. A plot of the displacement, up and down, as a function of time is given by:

$$f(t) = A \sin 2\pi vt \quad \text{or} \quad f(t) = A \cos 2\pi vt \quad 23.1.9$$

with v the frequency in cycles per second and A the amplitude. The frequency is also often expressed in radians per second, $\omega = 2\pi v$. Both “cycles” and “radians” are unitless; we include them only for our convenience. The units of frequency are s^{-1} for both v and ω . If the initial observation catches the wave with zero displacement, then the sine form of Eq. 23.1.9 is appropriate. If the initial observation catches the wave at its maximum displacement, then the cosine form is appropriate. The cosine and sine forms differ only by a 90° phase shift.

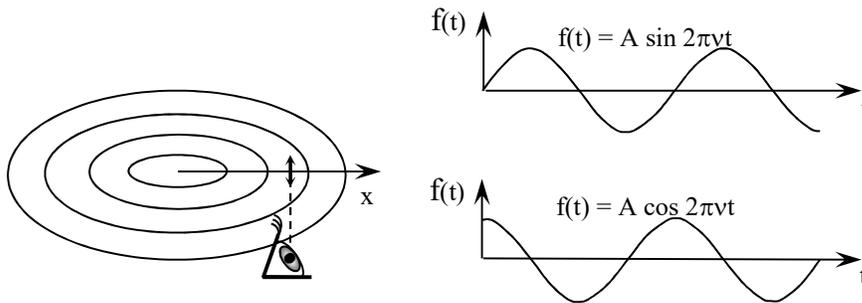


Figure 23.1.3: Time dependence of the wave displacement at a fixed point. Wave behavior is either sinusoidal or cosinusoidal depending on the phase of the wave.

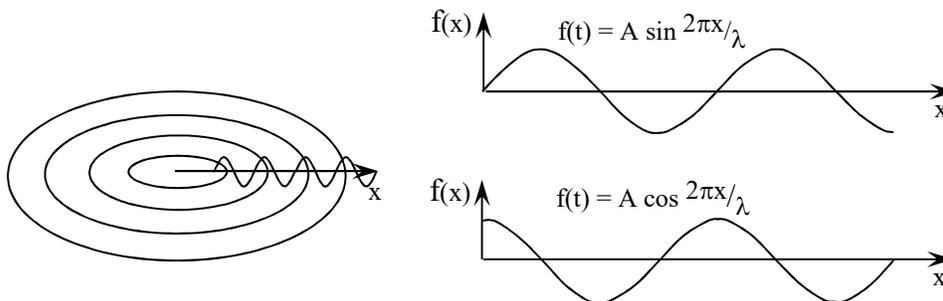


Figure 23.1.4: Distance dependence of the wave displacement at a fixed time. The frequency and wave length are related by $v\lambda = v$, where v is the propagation velocity.

Now consider taking a “snap shot” of the wave at a fixed time, Figure 23.1.4. A plot of the displacement as a function of distance is given by:

$$f(x) = A \sin(2\pi x/\lambda) \quad \text{or} \quad f(x) = A \cos(2\pi x/\lambda) \quad 23.1.10$$

Waves can be Represented by Complex Waveforms: The differential equation representing the classical harmonic oscillator, for a particle with mass m and force constant k_s is:

$$m \frac{d^2x(t)}{dt^2} = -k_s x(t) \quad (8.13.1)$$

In Sec. 8.13, we chose the sinusoidal solution for the classical harmonic oscillator, Eq. 8.13.9, $x(t) = A \sin[(\kappa/m)^{1/2}t]$. We should also have considered the cosine based solution for completeness: $x(t) = A \cos[(\kappa/m)^{1/2}t]$. Both the sine and cosine forms are equivalent solutions, differing only by a 90° phase shift in the start of observation. Both the sine and cosine forms are **particular solutions** to the differential equation. The general theory of differential equations specifies that the general solution to a differential equation is found by taking a linear combination of all the particular solutions that have the same energy. The general form of a **linear combination** of two functions $f(x)$ and $g(x)$ is:

$$h(x) = a f(x) + b g(x) \quad 23.1.11$$

with a and b constants. Remembering to find all possible particular solutions for wave-like differential equations can be bothersome. For differential equations of the form of Eq. 8.13.1, a convenient linear combination that guarantees that both sine and cosine solutions are considered with equal weighting is given by:

$$f(t) = \cos 2\pi vt + i \sin 2\pi vt = e^{i2\pi vt} \quad 23.1.12$$

where $i = \sqrt{-1}$. Eq. 23.1.12 is a specific example of the **Euler identity**. We can develop a useful visual representation of the Euler identity. Consider a vector rotating around the unit circle with angle $\phi = 2\pi vt$ radians with respect to the real-axis, Figure 23.1.5. The horizontal axis is the real axis and the vertical axis is the imaginary axis. The real projection of the rotating vector is maximal at $\phi = 0$ and the imaginary projection is maximal at $\pi/2$, which represents the 90° phase shift between the cosine and sine terms. For a review of complex variables, please consult Addendum 23.9. In short, i is treated just like any other number, with $i^2 = -1$. The ability of complex exponential functions, $e^{i\phi}$, to keep track of phase relationships will be very useful.

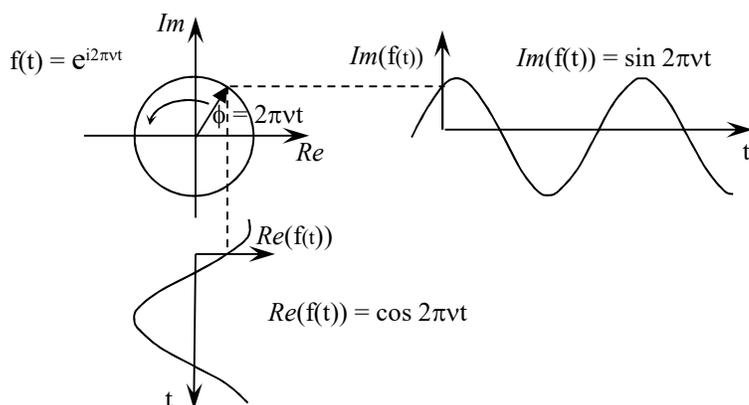


Figure 23.1.5: The Euler identity automatically accounts for cosine and sine relationships for wave-like behavior. The projection of a vector rotating on the unit circle onto the real axis is the cosine component and the projection onto the imaginary axis is the sine component.

Light is an **electromagnetic wave**, which is composed of an oscillating electric field and, perpendicular to the electric field, an oscillating magnetic field, Figure 23.1.6a. Light is produced by the oscillatory motion of charged particles. For example, charging a plastic rod with static electricity and then waving the rod up and down creates a vertically oscillating electric field and the acceleration of the electrons creates an oscillating magnetic field, perpendicular to the plane

of vibration, creating light. For many purposes the interaction of the electric field of light with matter is orders of magnitude larger than the interaction with the magnetic field, and to a good approximation we often need only consider the electric component. Light spans the electromagnetic spectrum from radiowaves to γ -rays, the only difference being the frequency, Figure 23.1.6b. Each region of the electromagnetic spectrum has utility in probing molecular systems. The corresponding types of spectroscopy are included in the figure.

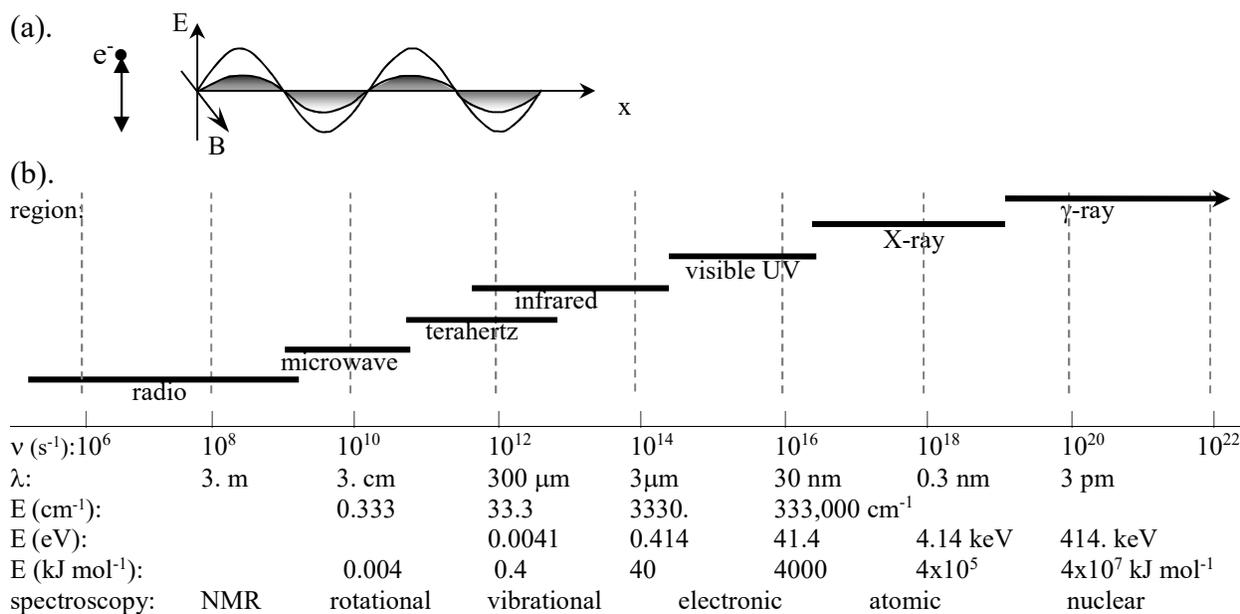


Figure 23.1.6: (a). An oscillating charge creates electromagnetic radiation. (b). The electromagnetic spectrum. The visible region is from 750 to 390 nm, 4.0×10^{14} to 7.9×10^{14} s^{-1} , or 1.65-3.18 eV. The ultraviolet, UV, region extends to 10 nm, 3×10^{16} s^{-1} , or 124 eV.

Experimental methods to determine wave properties are based on interference phenomena. The double slit diffraction experiment is an excellent example. Consider a monochromatic, phase coherent light source illuminating two slits with spacing d . If the light rays emerging from the two slits are in phase, constructive interference results, giving a bright spot on a screen placed beyond the double slits, Figure 23.1.7.

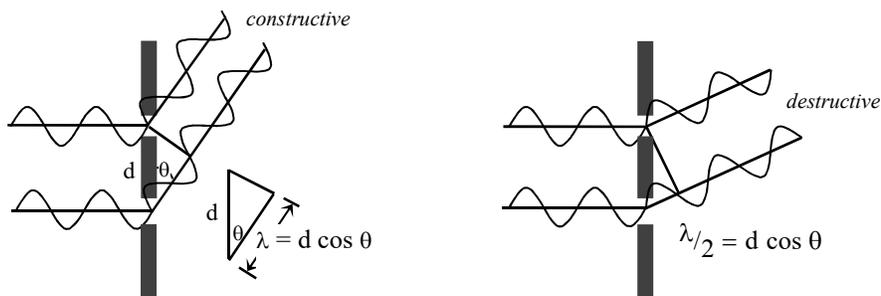


Figure 23.1.7: Bragg's Law of diffraction. Constructive interference results if the path length difference is an integer number of wave lengths.

If the exit angle of two beams is θ , then the requirement for constructive interference is the bottom wave must travel an integer number of wave lengths further than the top beam:

$$n\lambda = d \cos \theta \quad 23.1.13$$

This relationship is called **Bragg's Law**. If the difference in path length between the two beams is an integer multiple of $\lambda/2$, then destructive interference cancels the intensity of the two superimposed beams. The constructive and destructive interference of waves is an important phenomenon in describing microscopic behavior.

23.2 Steps Toward Quantum Theory

In 1897, J. J. Thomson discovered that the electron was a fundamental particle in matter carrying a negative charge, $-e$, and mass, m_e , which is small relative to the mass of an atom:

$$\begin{aligned} e &= 1.60217733 \times 10^{-19} \text{ C} \\ m_e &= 9.1093897 \times 10^{-31} \text{ kg} \end{aligned}$$

However, the concept of an atom wasn't widely accepted until the scattering experiments of Ernest Rutherford in 1911 showed that matter was composed of atoms with a dense positive nuclear core surrounded by electrons. Concurrent with the unraveling of the structure of the atom, the nature of the allowed energies states of matter and the nature of light led to a profound shift in the understanding of the microscopic world. The discovery of quantized energy levels, the particle nature of light, and the wave nature of particles led to the development of quantum mechanics by Werner Heisenberg in 1925 and Erwin Schrödinger in 1926. These experiments provide a window into the microscopic world and understanding these results helps us to learn how to think quantum mechanically.¹

Matter Has Quantized Energy Levels: The first clue that matter has quantized energy levels came from the failure of the Equipartition Theorem, Sec. 8.9. A vibration contributes less than the expected equipartition value of R to the heat capacity, because molecular vibration energy levels are quantized. The emission of light from hot bodies also proved critical in determining the quantum nature of microscopic phenomena.

All objects emit light. The detailed emission spectrum of an object is dependent on geometry and surface characteristics. However, if light emitted from a small cavity in a substance is observed, the spectrum is identical for all substances at a given temperature. The emission spectrum from a small cavity is called **blackbody radiation**, Figure 23.2.1. Consider a metal as an example. The application of the Equipartition Theorem to the electrons oscillating on the surface of the cavity predicts that the emission intensity should increase with decreasing wavelength. To resolve the discrepancy with experiment, Max Planck suggested in 1901 that the energy levels for the electron oscillators in the walls of the cavity are quantized. **Planck's Law** gives the energy levels as multiples of $h\nu$, where ν is the frequency of oscillation of the electron and h is Planck's constant:

$$\begin{aligned} E_n &= n h \nu & h &= 6.6260755 \times 10^{-34} \text{ J s} \\ E_n &= n \hbar \omega & \hbar &= h/2\pi = 1.054573 \times 10^{-34} \text{ J s} \end{aligned} \quad 23.2.1$$

with the angular frequency $\omega = 2\pi\nu$. Planck's constant divided by 2π often occurs in equations and is given a special symbol, \hbar , read as "h bar." The variable n is called a **quantum number**,

because the value is restricted to an integer. Using the Boltzmann distribution, Eq. 8.10.5, to determine the number of electron oscillators in a given vibrational energy state gives the intensity of the emitted blackbody radiation per unit wavelength increment as:

$$I(\lambda) = \frac{2\pi hc^2}{\lambda^5} \left(\frac{1}{e^{hc/kT\lambda} - 1} \right) \quad 23.2.2$$

This distribution is plotted in Figure 23.2.1. Even at 600 K, negligible light is emitted in the visible region of the spectrum, < 750 nm. As temperature increases the maximum emission wavelength shifts to the blue and the intensity increases. The total light flux emitted from the blackbody is the integral of Eq. 23.2.2 over the entire spectrum, which gives the Stefan-Boltzmann equation, $J = \sigma T^4$, Eq. 11.2.16. Subsequent to Planck's discovery, Einstein applied the idea of quantized energy levels and Eq. 23.2.1 to calculate the heat capacity of a solid. The discovery of the quantized nature of the energy levels in matter was a critical step in the development of quantum mechanics. Even more striking was the discovery that light, which was generally recognized as a wave phenomena, can also behave as a particle.

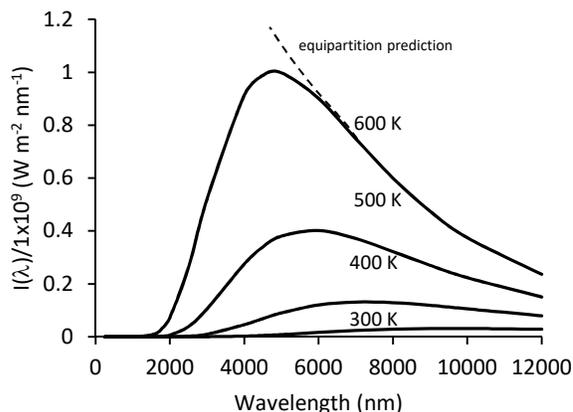


Figure 23.2.1: The spectrum for blackbody emission. As temperature increases the maximum emission wavelength shifts to the blue and the total intensity increases.

Light Has a Particle Nature – Photoelectric Effect: In a photoelectric effect experiment, a metal is placed in an evacuated container, Figure 23.2.2. Electrons are ejected from the metal when light of sufficient energy shines on the metal surface. The electrons are detected by measuring the current flowing through a circuit that includes the metal as the cathode and a collection anode. The kinetic energy of the emitted electrons is determined by placing a charged grid between the metal surface and the collection anode. The voltage on the grid is increased until the photoelectron current drops to zero. At that voltage, which is called the **stopping potential**, the electrons no longer have sufficient kinetic energy to overcome the electrostatic repulsion with the grid. Given the charge on the electron, $-e$, and the stopping potential, V_s , the kinetic energy of the photoelectrons is given by:

$$E_k = \frac{1}{2} mv^2 = eV_s \quad 23.2.3$$

The following observations are made concerning the frequency and intensity of the light source.

1. Current flows only if the light has greater than a minimum frequency, ν_0 .

2. Current is finite and instantaneous even if the light intensity is small.
3. Kinetic energy of ejected electrons is not a function of the intensity.
4. Current is proportional to intensity $= A^2$, where A is the amplitude of the exciting light.

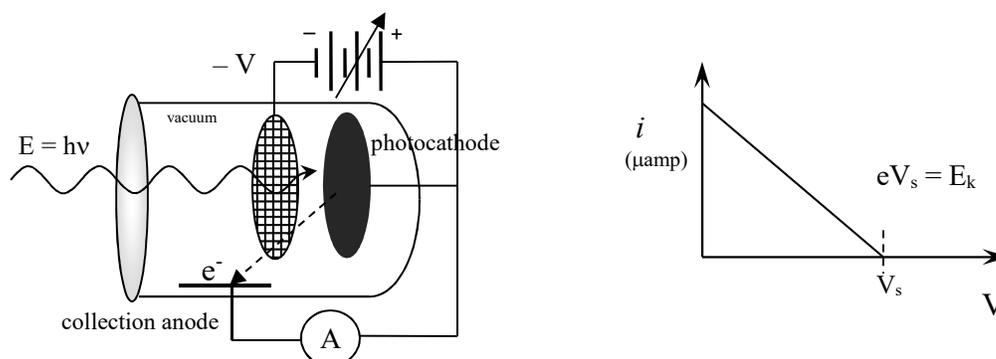


Figure 23.2.2: The photoelectric effect: a monochromatic light source illuminates a metal surface in a vacuum. An ammeter measures the photoelectron current between the photocathode and anode. The kinetic energy of the ejected electrons is measured by determining the potential placed on an intermediate grid that just prevents the flow of electrons to the anode.

Einstein's explanation of these observations provides the clearest introduction into the quantum nature of the microscopic world. The classical expectation is that the photoelectron current should be proportional to the intensity of the light, with the intensity $= A^2$. However, even very bright light sources fail to produce photoelectrons if the light frequency is less than a critical value, ν_0 . Einstein reasoned that the energy of light must be related to the frequency by $E = h\nu$, which is in concordance with the Planck expression for particle energy quantization. For this result to be true, Einstein argued that the light must act as a particle, rather than as a wave. The particles of light are called **photons**, and the energy of a photon depends only on the frequency. This realization is supported by the second observation. Classically, the results of wave action build over time, like the erosion of beach sands during storms. However, the photocurrent is instantaneous upon turning on the light source, even for light with low intensity. The instantaneous current suggests that a photoelectron is ejected immediately upon absorption of a light particle; the action of the light does not need to accumulate over time. The light is not acting as a diffuse source of energy; rather the energy is supplied as an impulse as the photon collides with the metal surface. Light behaves as a discrete quantum of energy. Observation 3 is also consistent with the particle nature of light; the energy arrives in a single quantum packet that supplies the energy necessary to remove the electron from the metal. The energy necessary to remove an electron from the metal surface is called the **work function**, Φ . Any residual energy from the photon not needed to overcome the work function of the metal is released as kinetic energy of the ejected electron, E_k :

$$E = h\nu = E_k + \Phi = \frac{1}{2} m_e v^2 + \Phi \quad (\Phi \text{ in joules}) \quad 23.2.4$$

The units of the work function are joules. The work function can also be expressed in volts, Γ , and then the energy necessary to remove the electron from the metal is given as $e\Gamma$:

$$E = h\nu = \frac{1}{2} m_e v^2 + e\Gamma \quad (\Gamma \text{ in volts}) \quad 23.2.5$$

The minimum frequency corresponds to the photon supplying just enough energy to remove the electron from the metal surface with no additional kinetic energy, $E_{\min} = h\nu_0 = \Phi$.

The energy of a photon can also be expressed in eV:

$$E = h\nu/e \quad (E \text{ in eV}) \quad 23.2.6$$

We can also directly express the energy of light in terms of the wave length, using $\nu = c/\lambda$, and the wavenumber, defined as $\tilde{\nu} \equiv 1/\lambda$ (also see Sec. 8.10 and Eq. 8.10.2):

$$E = hc/\lambda = hc\tilde{\nu} \quad 23.2.7$$

Einstein's explanation of the photoelectric effect is in stark contrast to classical expectations and is worthy of careful thought as a means of understanding quantized phenomena. Light certainly acts as a wave, as it does in diffraction experiments. But, light also acts like a particle, as it does in the photoelectric effect. This behavior is called **wave-particle duality**. In essence, the expectations of the experimenter determine the type of behavior. If an experiment is run that is designed to measure wave-like properties, then light behaves as a wave. If an experiment is run that is designed to measure particle-like properties, then light behaves as a particle. The energy of the light is confined to a short particle-like impulse with energy $E = h\nu$.

The intensity of light is determined by the number of photons emitted from the source per unit time. The intensity of the light must have some effect on the photocurrent, and observation 4 is consistent with classical expectations. However, the quantum explanation is that the intensity of the light determines the number of photons striking the surface in a given time interval. A greater number of photons per unit time produces a greater number of electrons per unit time, which is measured as the current. Einstein's theory for the photoelectric effect is an important window on the quantized nature of the microscopic world. The photoelectric effect also has important practical utility. The photoelectric effect using metals such as cesium that have low work functions is the basis for sensitive light detectors called phototubes and photomultipliers. If the sample is a gas instead of a metal, the experiment is called **photoelectron spectroscopy, PES**, or specifically using light in the ultraviolet region of the spectrum, **ultraviolet photoelectron spectroscopy, UPS**. UPS is an important spectroscopic technique that allows the ionization potentials of atoms and molecules to be accurately determined. Fundamentally, however, the wave-particle duality of light raises the question if particles can also have wave-like behavior.

Example 23.2.1:

Calculate the energy in eV and kJ mol^{-1} of a 500.0 nm blue-green photon. Calculate the energy in kJ mol^{-1} of a 40.0 keV electron in a scanning electron microscope, SEM. Are these energies sufficient to break chemical bonds?

Answer: For the blue-green photon in eV:

$$\begin{aligned} E &= h\nu/e = hc/\lambda \quad (1 \text{ eV}/1.6022 \times 10^{-19} \text{ J}) \\ &= 6.626 \times 10^{-34} \text{ J s} (2.998 \times 10^8 \text{ m s}^{-1}) / 500.0 \times 10^{-9} \text{ m} \quad (1 \text{ eV}/1.6022 \times 10^{-19} \text{ J}) = 2.480 \text{ eV} \end{aligned}$$

and in kJ mol^{-1} :

$$\begin{aligned} E &= N_A hc/\lambda \\ &= 6.022 \times 10^{23} \text{ mol}^{-1} (6.626 \times 10^{-34} \text{ J s}) (1 \text{ kJ}/1000 \text{ J}) (2.998 \times 10^8 \text{ m s}^{-1}) / 500.0 \times 10^{-9} \text{ m} \\ &= 239.3 \text{ kJ mol}^{-1} \end{aligned}$$

This energy is on the low end of typical single chemical bonds.

For the electrons in a SEM:

$$E = 40.0 \times 10^3 \text{ eV} (96.485 \text{ kJ mol}^{-1}/1 \text{ eV}) = 3859. \text{ kJ mol}^{-1}$$

which suggests that a sample will suffer considerable damage from the electron beam. In a SEM, damage increases with acceleration potential, since much of the beam energy is absorbed.

Particles Have a Wave Nature: If light can act as a particle, then a photon must carry momentum and have a corresponding effective mass. Louis de Broglie in 1924 reasoned that if the energy of a wave is $E = h\nu$, then the Einstein relationship for mass and energy equivalence, $E = mc^2$, can be used to find the effective mass and momentum of a photon. Setting the two equations for the energy equal to each other gives:

$$E = h\nu = mc^2 \quad 23.2.8$$

Solving for the effective mass of a photon, using $\nu = c/\lambda$, and calculating the momentum of a photon from $p = mv = mc$ gives:

$$m = \frac{h\nu}{c^2} = \frac{h}{\lambda c} \quad p = \frac{h}{\lambda} \quad 23.2.9$$

This last relationship is called the **de Broglie relationship**. The result shows that light carries momentum. As the wave length of light decreases, the frequency increases, and the momentum increases. The de Broglie relationship is fundamentally important because it gives the relationship between the particle-like property of momentum and the wave-like property of wave length. The de Broglie relationship is a direct representation of wave-particle duality. de Broglie, most importantly, also reasoned that if light can act as a particle, then particles can also act like waves. de Broglie postulated that $p = h/\lambda$ applies equally to light and particles; giving particles a corresponding wave-like nature. However, direct experimental confirmation of the wave nature of particles is necessary.

Clinton Davisson and Lester Germer in 1927, while working on vacuum tube based communications technology, discovered the wave-like nature of particles by accident. The modern version of their experiment is the determination of electron diffraction patterns using a transmission electron microscope. A rough schematic of the experiment is given in Figure 23.2.3. A hot filament produces a beam of electrons that are accelerated across a set potential to give a known kinetic energy. The beam of electrons strikes a thin crystalline sample. The predicted scattering pattern based on particle-like behavior is a diffuse pattern with decreasing intensity with increasing scattering angle. The experimental scattering pattern, however, is a regular array of spots of high intensity that mirror the symmetry of the arrangement of atoms in the crystal lattice. The pattern is the result of wave-like interference. Analysis of the spot-to-spot spacing as a function of the kinetic energy of the electrons confirms that electrons diffract

according to Bragg's Law with a wave length given by the de Broglie relationship, $p = h/\lambda$. This experiment conclusively shows that both light and particles have a wave-particle duality.

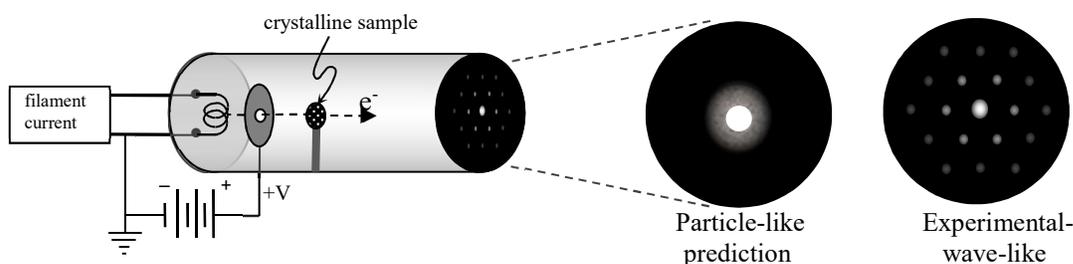


Figure 23.2.3: Electron diffraction in a transmission electron microscope. The example diffraction pattern is for a face-centered cubic metal with the (111)-face perpendicular to the electron beam. Electron diffraction is used to characterize nano-structured materials.

Electronic Structure of the Atom: The emission spectrum of hydrogen atoms, which have been excited in a high voltage electric discharge, provides a direct determination of the quantum nature of hydrogen-atom energy levels, Figure 23.2.4. The transitions in the visible region of the spectrum are called the **Balmer series**.

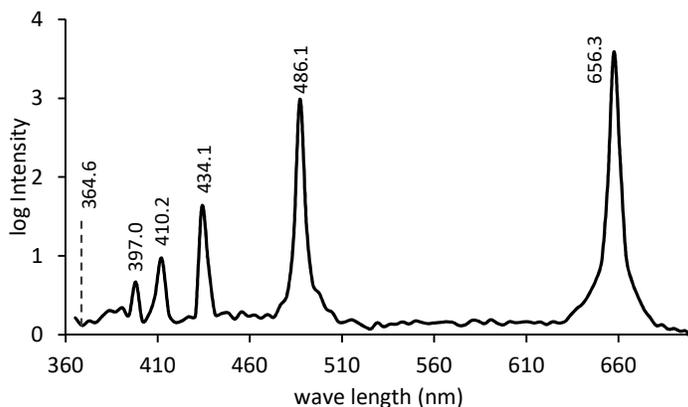


Figure 23.2.4: Balmer series: the hydrogen atom visible emission spectrum. Log intensity is plotted because the transitions have large differences in intensity.

The electronic emission and absorption spectra of all atoms in the gas phase consist of series of transitions at discrete, well-defined frequencies. The narrow range in wave length of each transition directly reflects the quantized energy levels for the electronic states of the atom. The absorption and emission spectra of an atom are unique and diagnostic for each element. Many elements were discovered through their electronic spectra. The first five emission lines for atomic hydrogen in the visible region of the spectrum are 656.3 nm, 486.1 nm, 434.1 nm, 410.2 nm, and 397.0 nm with additional weak lines ending at the convergence limit at 364.6 nm. A series of hydrogen lines also occur in the UV, called the Lyman series, and in the infrared, called the Paschen series. Additional series lie further in the infrared. Johannes Rydberg empirically determined that the emission lines for the hydrogen atom fit the expression:

$$\tilde{\nu} = \mathfrak{R}_h \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right) \quad \text{for hydrogen, } ^1\text{H}, \quad \mathfrak{R}_h = 109677.5 \text{ cm}^{-1} \quad 23.2.10$$

For the Lyman series, $n_f = 1$, for the Balmer series, $n_f = 2$, and for the Paschen series, $n_f = 3$. The value for n_i is also restricted to an integer, which is greater than n_f . The variables n_i and n_f are, accordingly, quantum numbers. Rydberg had no theoretical justification for the expression, and the first-principles derivation of the Rydberg formula was one of the major goals of early quantum theory.

Neils Bohr used Planck's idea of quantized energy levels and the de Broglie relationship to develop the first useful model for the hydrogen atom. The nucleus of the hydrogen atom is just a proton, $Z = 1$. The electrostatic attraction of the electron and the nucleus is given by the Coulomb potential, Eq. 8.8.18, with the charge on the nucleus Ze and the charge on the electron $-e$, in vacuum:

$$V(r) = -\frac{Ze^2}{4\pi\epsilon_0 r} \quad \text{with } \epsilon_0 = 8.85419 \times 10^{-12} \text{ J}^{-1} \text{ C}^2 \text{ m}^{-1} \quad 23.2.11$$

which is plotted in Figure 8.8.7 and where ϵ_0 is the vacuum permittivity. Treating the electron as a wave with wave length given by $p = h/\lambda$, Bohr suggested that the electron occupies stable orbits only at specific radii. The specific radii allow the constructive overlap of the electron waves when placed around the circumference of the orbit, Figure 23.2.5a. Constructive overlap gives a fixed energy **stationary-state**. For constructive overlap, the circumference must be an integer multiple of the wave length:

$$2\pi r = n\lambda \quad 23.2.12$$

where n is called the **principle quantum number**, with the range $n = 1, 2, 3, \dots \infty$.

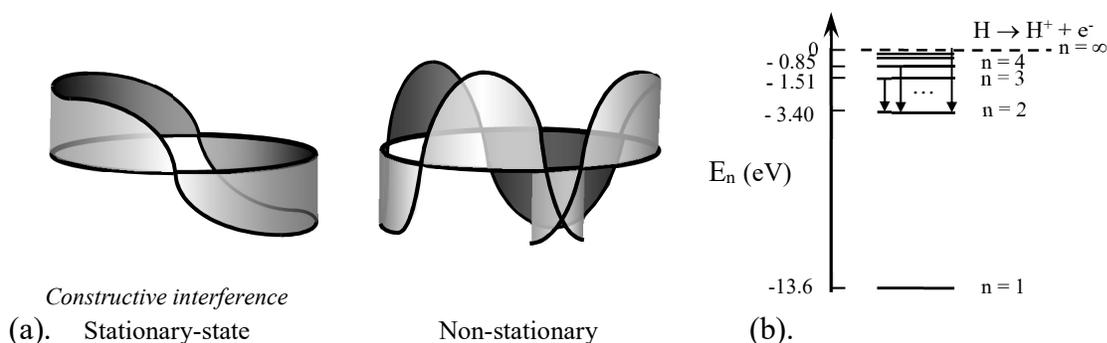


Figure 23.2.5: (a). Constructive overlap restricts the radius of the orbital to fixed values.

(b). Energy level diagram for the hydrogen atom: the zero in energy is the atomic dissociation limit. Balmer transitions are to $n_f = 2$. The first two Balmer transitions and the transition that corresponds to the convergence limit, $\infty \rightarrow 2$, are shown.

The lowest energy state, which is called the **ground state**, is for $n = 1$. Using the de Broglie relationship in the form $\lambda = h/m_e v$ gives the allowed values of the radius as:

$$r = \frac{nh}{2\pi m_e v} \quad \text{or} \quad m_e v r = nh \quad 23.2.13$$

where v is the velocity of the electron, and $m_e v r$ is the angular momentum of the electron around the nucleus. The requirement of constructive overlap results in the quantization of the angular momentum and energy of the electron. The energy of each orbital is given by:

$$E_n = -\frac{e^4 m_e}{32\pi^2 \epsilon_0^2 \hbar^2} \left(\frac{Z^2}{n^2}\right) = -109737.2 \text{ cm}^{-1} \left(\frac{Z^2}{n^2}\right) = -13.606 \text{ eV} \left(\frac{Z^2}{n^2}\right) = -1312.7 \text{ kJ mol}^{-1} \left(\frac{Z^2}{n^2}\right) \quad 23.2.14$$

where $Z = 1$ for the hydrogen atom. The radius of the first-Bohr orbit, for the $n = 1$ ground state, is given the symbol a_0 :

$$a_0 = \frac{4\pi\epsilon_0\hbar}{m_e e^2} = 0.5291772 \text{ \AA} \quad 23.2.15$$

Electronic transitions are given by the difference in energy for the initial and final energy levels:

$$\Delta E = E_f - E_i = -13.606 \text{ eV} Z^2 \left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right) \quad 23.2.16$$

For absorption, the energy of the photon is absorbed by the atom, $E_{\text{photon}} = h\nu = \Delta E$. For emission, the energy is released from the atom, $E_{\text{photon}} = h\nu = -\Delta E$. Eq. 23.2.16 matches the Rydberg formula and provides an explanation for the narrow emission lines in the Balmer spectrum by quantization of the energy states of the atom. Bohr's theory suffers from several fundamental problems and has been replaced by theory based on the Schrödinger equation. However, the Bohr approach helped lay the ground work for quantum theory.

The wave-like nature of fundamental particles is the key insight into the underlying principles of the microscopic world. In particular, the de Broglie relationship applies to electrons in atoms and molecules and is the foundation for the Schrödinger equation. The Schrödinger equation is the basis of the quantum theory of atomic and molecular structure.

Example 23.2.2:

Why don't we normally observe the wave behavior of particles in our daily experience? Calculate the de Broglie wavelength of (a) a 70.0 kg human traveling at 2.00 km hr⁻¹ and (b) a 13.6 eV electron, which is the electron kinetic energy for the ground state of the hydrogen atom.

Answer: (a). The momentum of the human is:

$$p = 70.0 \text{ kg}(2.0 \times 10^3 \text{ m hr}^{-1})(1 \text{ hr}/3600 \text{ s}) = 38.89 \text{ kg m s}^{-1}$$

The de Broglie relationship, $p = h/\lambda$, gives the effective wavelength:

$$\lambda = h/p = 6.6261 \times 10^{-34} \text{ J s}/38.89 \text{ kg m s}^{-1} = 1.70 \times 10^{-35} \text{ m}$$

which is too small to give macroscopically observable wave-like interactions.

(b). The momentum and wave length of the 13.6 eV electron is:

$$p = \sqrt{2mE_k} = [2(9.109 \times 10^{-31} \text{ kg})(13.6 \text{ eV})(1.6022 \times 10^{-19} \text{ J/1 eV})]^{1/2} = 1.992 \times 10^{-24} \text{ kg m s}^{-1}$$

$$\lambda = h/p = 6.6261 \times 10^{-34} \text{ J s} / 1.992 \times 10^{-24} \text{ kg m s}^{-1} = 3.33 \times 10^{-10} \text{ m} = 3.33 \text{ \AA}$$

which is on the order of the size of the hydrogen atom. An electron acts as a wave in an atom.

23.3 Free Particle Motion

The Schrödinger Equation: We begin by considering a one-dimensional system, in the x -direction, and later we will build to 3-dimensions. Consider a particle, such as an electron, moving in the x -direction under the influence of the potential energy, $\hat{V}(x)$. The **Schrödinger equation** provides a fundamental description of the properties of chemical systems given the total energy of the system, E , and the **wave function**, $\Psi(x)$. The wave function contains all the information necessary to describe the system and is the analytical representation of the particle wave. The wave function is the solution to the Schrödinger equation:

$$-\frac{\hbar^2}{2m} \frac{d^2\Psi(x)}{dx^2} + \hat{V}(x) \Psi(x) = E \Psi(x) \quad 23.3.1$$

kinetic energy + potential energy = total energy

where m is the mass of the particle. The first term gives the kinetic energy of the particle, the second term gives the potential energy, and the sum of the kinetic energy and the potential energy gives the total energy of the particle, E . The classical kinetic energy is $p^2/2m$, which bears a resemblance to the kinetic energy term in both the division by $2m$ and the correspondence of the square of the momentum with the appearance of a second derivative. The wave function, as a solution of the Schrödinger equation, automatically obeys the de Broglie relationship, $p = h/\lambda$. Schrödinger postulated the equation rather than deriving the relationship from other principles. The validity of the equation is established by applying the equation to many different physical systems and showing the results to be consistent with experimental evidence. In the same way, our understanding of the equation is best guided by considering a series of simple examples. We first consider a free particle.

A free particle is a particle that experiences no potential energy, $\hat{V}(x) = 0$. The Schrödinger equation then reduces to:

$$-\frac{\hbar^2}{2m} \frac{d^2\Psi(x)}{dx^2} = E \Psi(x) \quad (V(x) = 0) \quad 23.3.2$$

This equation has the same analytical form as the classical harmonic oscillator, Eq. 8.13.1; the second derivative of the function returns the same function, multiplied by a constant. Both $\cos kx$ and $\sin kx$, with k a constant, satisfy this relationship. The most convenient way to consider both forms of the solution is to use the Euler identity (see Eq. 23.1.12):

$$\Psi(x) = \cos kx + i \sin kx = e^{ikx} \quad 23.3.3$$

Using this form of the wave function, taking the derivatives gives:

$$\frac{d\Psi(x)}{dx} = ik e^{ikx} \quad \text{and} \quad \frac{d^2\Psi(x)}{dx^2} = (ik)^2 e^{ikx} = -k^2 e^{ikx} \quad 23.3.4$$

Substitution of the second derivative into the left side of Eq. 23.3.2 and $\Psi(x) = e^{ikx}$ into the right side and subsequently dividing both sides of the equation by e^{ikx} gives:

$$-\frac{\hbar^2}{2m} (-k^2 e^{ikx}) = E e^{ikx} \quad \text{and then} \quad E = \frac{\hbar^2 k^2}{2m} \quad (V(x) = 0) \quad 23.3.5$$

Eqs. 23.3.5 show that $\Psi(x) = e^{ikx}$ is a valid solution of the Schrödinger equation for a free particle. We next need to explore the physical validity of this analytic result. Is this solution to the Schrödinger equation consistent with the de Broglie relationship? The constant k is determined by the total energy; solving for k from Eqs. 23.3.5 gives:

$$k = \frac{\sqrt{2mE}}{\hbar} \quad 23.3.6$$

A free particle has no potential energy; the total energy is the kinetic energy, $E = E_k = p^2/2m$, giving $p = \sqrt{2mE}$. The numerator of Eq. 23.3.6 is the momentum:

$$k = \frac{p}{\hbar} \quad \text{or rearranging} \quad p = \hbar k \quad 23.3.7$$

The constant k is called the **wave vector**, because for 3-dimensional problems k is a vector, one component for each of the x , y and z directions: $\vec{p} = \hbar\vec{k} = \vec{i}\hbar k_x + \vec{j}\hbar k_y + \vec{k}\hbar k_z$. Comparing the general form for wave-like behavior from Eq. 23.1.10 with the free-particle wave function, Eq. 23.3.3, shows the relationship of k to the effective wave length of the particle:

$$\begin{array}{ccc} \cos(2\pi/\lambda x) & \text{or} & \sin(2\pi/\lambda x) \\ \downarrow & & \downarrow \\ \Psi(x) = e^{ikx} = \cos kx & + & i \sin kx \end{array} \quad \text{giving: } k = 2\pi/\lambda \quad 23.3.8$$

Substituting $k = 2\pi/\lambda$ into Eq. 23.3.7 gives the de Broglie relationship:

$$p = \hbar k = \hbar \frac{2\pi}{\lambda} = \frac{h}{2\pi} \frac{2\pi}{\lambda} = h/\lambda \quad 23.3.9$$

This last result shows that solutions to the Schrödinger equation obey the de Broglie relationship, which is necessary for the wave function to be consistent with experiment.

Example 23.3.1:

A **superposition** of two wave functions is given by a linear combination. Show that the superpositions $\Psi_1 = 1/2 (e^{ikx} + e^{-ikx})$ and $\Psi_2 = 1/2i (e^{ikx} - e^{-ikx})$ are real. What are the momenta and energies of the two components of the superpositions?

Answer: For e^{ikx} , the momentum is in the forward direction, $p = \hbar k$. For e^{-ikx} , the momentum is in the backward direction, $p = -\hbar k$. The given superpositions have equal weight combining a wave with forward momentum and a wave with backward momentum:

$$\begin{array}{ccc} \Psi_1 = 1/2 (e^{ikx} + e^{-ikx}) & & \Psi_2 = 1/2i (e^{ikx} - e^{-ikx}) \\ \text{direction:} & \rightarrow & \leftarrow & & \text{direction:} & \rightarrow & \leftarrow \end{array}$$

The forwards and backwards waves have the same energy; they are degenerate. Using the Euler identity for each term and noting the signs (e.g. Eq. 23.9.10) gives:

$$\begin{aligned}\Psi_1 &= \frac{1}{2} (e^{ikx} + e^{-ikx}) = \frac{1}{2} [\cos(kx) + i \sin(kx) + \cos(-kx) + i \sin(-kx)] \\ &= \frac{1}{2} [\cos(kx) + i \sin(kx) + \cos(kx) - i \sin(kx)] = \cos kx\end{aligned}$$

and
$$\begin{aligned}\Psi_2 &= \frac{1}{2i} (e^{ikx} - e^{-ikx}) = \frac{1}{2i} [\cos(kx) + i \sin(kx) - \cos(-kx) - i \sin(-kx)] \\ &= \frac{1}{2i} [\cos(kx) + i \sin(kx) - \cos(kx) + i \sin(kx)] = \sin kx\end{aligned}$$

The linear combination of two degenerate solutions to the Schrödinger equation is also a solution: both $\cos kx$ and $\sin kx$ satisfy the free-particle Schrödinger equation, Eq. 23.3.2. The two superpositions show how to convert complex wave functions to real wave functions.

Kinetic Energy is Given by the Curvature of the Wave Function: In the Schrödinger equation, the kinetic energy of a particle is determined by the second derivative of the wave function. The second derivative is called the curvature. The curvature determines the “wiggleness” of the function. As the curvature of the wave function increases, the “wiggleness” of the wave function increases, the frequency of the wave function increases, and the kinetic energy increases. Combining these observations with Eqs. 23.3.7-23.3.9 also shows that as the curvature increases, the momentum increases and the wave vector increases, Figure 23.3.1.

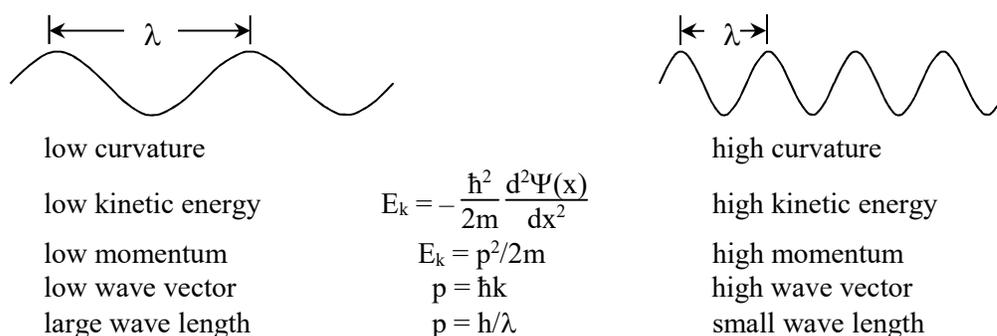


Figure 23.3.1: Curvature is a measure of the kinetic energy, momentum, and wave vector. As the momentum increases, the wave length of a particle decreases.

The curvature or “wiggleness” of a wave function provides a convenient visual interpretation of the Schrödinger equation. Consider a particle that experiences a constant potential $\hat{V}(x) = V$.

The Schrödinger equation is:

$$-\frac{\hbar^2}{2m} \frac{d^2\Psi(x)}{dx^2} + V \Psi(x) = E \Psi(x) \quad (V(x) = V) \quad 23.3.10$$

Subtracting the potential energy term from both sides of the equation gives:

$$-\frac{\hbar^2}{2m} \frac{d^2\Psi(x)}{dx^2} = (E - V) \Psi(x) \quad (V(x) = V) \quad 23.3.11$$

which is in the same form as the free particle except that k is given by:

$$k = \frac{\sqrt{2m(E - V)}}{\hbar} \quad (V(x) = V) \quad 23.3.12$$

where $(E - V)$ is the kinetic energy. The wave function for a free particle with energy E is shown in Figure 23.3.2a. The kinetic energy of a particle with a positive potential is decreased giving a longer wavelength, Figure 23.3.2b. A conventional depiction of wave functions is to superimpose the wave function onto a plot of the potential energy function, with the zero for the wave function amplitude plotted at the value for the total energy of the particle.

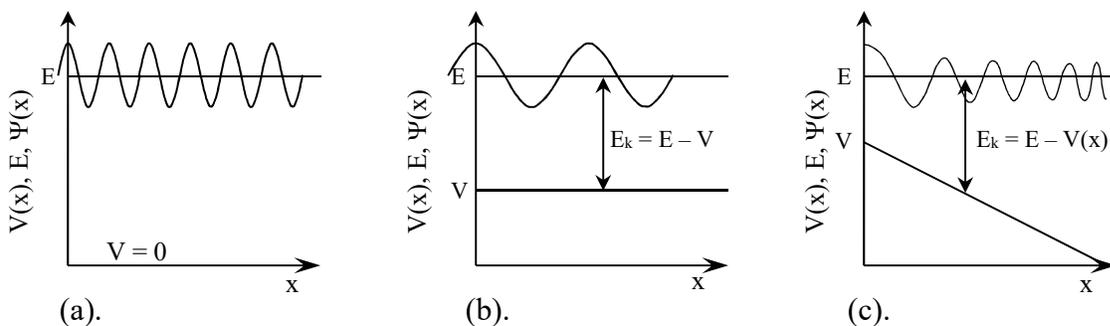


Figure 23.3.2: (a). Wave function for a free particle shown superimposed on the energy level diagram. (b). Wave function for a particle in a constant positive potential. (c). Wave function for a linear potential.

For a potential energy that decreases linearly with distance, the wave function has a long wave length in regions of high potential energy and short wave length in regions with low potential energy, Figure 23.3.2c. The wave function is more “wiggly” in regions with lower potential energy. The harmonic oscillator wave functions show the same dependence of the curvature on the potential energy, Figure 23.3.3.

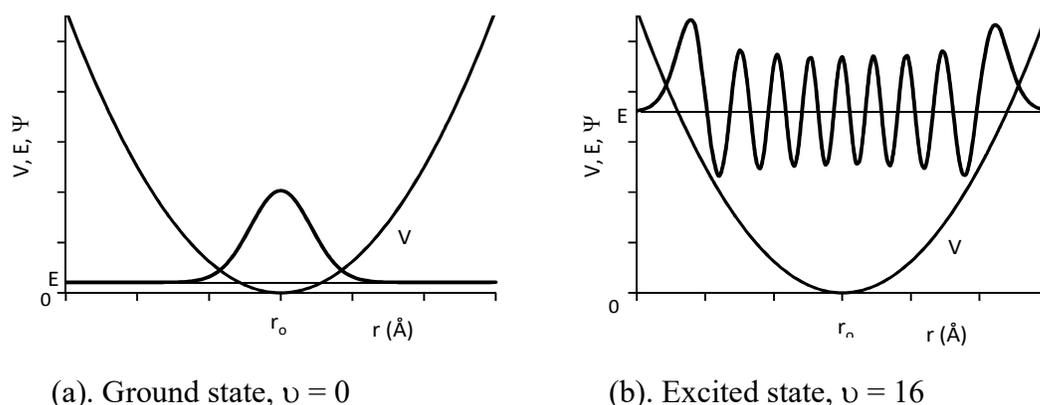


Figure 23.3.3: Harmonic oscillator wave functions have high curvature in regions with low potential energy. The quantum number for vibration is ν .

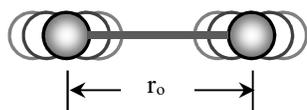
The Square of the Wave Function Determines the Probability of Finding a Particle at a Given Point: The wave function is a complete description of the system. The wave function represents the particle and determines the energy and spatial extent. However, a more visual interpretation of the wave function is often helpful in understanding the solutions to the Schrödinger equation. In the Einstein interpretation of the photoelectric effect, the intensity of a light wave determines the number of photons emitted from the light source per unit time. The larger the intensity of light, the larger is the probability of finding a photon. The intensity of the wave is given by the square of the amplitude. Max Born noted the similarity between light and particle waves and postulated that the probability of finding a particle in an interval $[x, x+dx]$ is given by the square of the wave function:

$$P(x) dx = \Psi_n^2 dx \quad (\Psi \text{ is real valued}) \quad 23.3.13$$

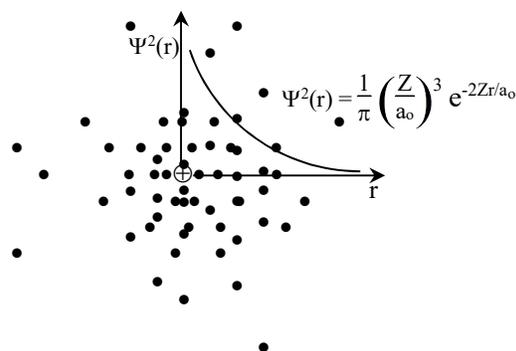
For complex valued wave functions, $\Psi^* \Psi$ must be used, where Ψ^* is the complex conjugate of the wave function:

$$P(x) dx = \Psi_n^* \Psi_n dx \quad (\Psi \text{ is complex valued}) \quad 23.3.14$$

For a real valued wave function, $\Psi_n^* = \Psi_n$, and Eqs. 23.3.13 and 23.3.14 are equivalent. For example, consider the ground state of the harmonic oscillator, Figure 23.3.3a. The square of the wave function is maximal at the equilibrium bond length, r_0 . On successive observations of the bond length, the most probable bond length is the equilibrium bond length. Longer or shorter bond lengths are also found, but with lower probability, Figure 23.3.4a.



(a). Harmonic oscillator ground state



(b). Hydrogen atom ground state, 1s-orbital.

Figure 23.4.4: (a). “Snap shots” of the harmonic oscillator are superimposed. The most probable bond length is the equilibrium bond length, r_0 . (b). “Snap shots” of the position of the electron in the ground state of the hydrogen atom are superimposed. The result is called a “dot density” diagram. The electron is most likely near the nucleus.

The probability of finding a free particle at a specified position is given using Eq. 23.3.3 as:

$$\Psi^* \Psi = e^{-ikx} e^{ikx} dx = dx \quad (\text{free particle}) \quad 23.3.15$$

The probability of finding the particle is constant for all values of x from $-\infty$ to ∞ . The position of a free particle is completely unknown. As another example, consider the wave function for the ground state of the hydrogen atom, the 1s-orbital:

$$\Psi(r) = \frac{1}{\sqrt{\pi}} \left(\frac{Z}{a_0} \right)^{3/2} e^{-Zr/a_0} \quad (\text{H atom}) \quad 23.3.16$$

with Z the charge on the nucleus, a_0 the Bohr radius, and r is the radial distance between the nucleus and the electron, $r = \sqrt{x^2 + y^2 + z^2}$. The wave function decreases exponentially with distance from the nucleus, giving a spherical electron distribution. The probability of finding the electron in a small interval around the position x , y , and z is given by the wave function squared:

$$P(x,y,z) dx dy dz = \Psi^2(r) dx dy dz = \frac{1}{\pi} \left(\frac{Z}{a_0} \right)^3 e^{-2Zr/a_0} dx dy dz \quad (\text{H atom}) \quad 23.3.17$$

The square of the wave function decreases exponentially with increasing distance from the nucleus, Figure 23.3.4b. The wave function is fuzzy and delocalized, but the probability is large for short distances and small for long distances. The electron in a hydrogen atom can be many meters away from the nucleus, however at vanishingly small probability. The electron is most likely found near the nucleus of the atom, because of the Coulomb attractions of the positive charge of the nucleus and the negative charge of the electron. The interpretation of the square of the wave function as the probability of finding the particle is called the **Born interpretation**. Treating the square of the wave function as a probability places several important restrictions on the wave function.

The integral over the probability of finding the particle over all space is unity, since the total probability of finding the particle should be 100%. This requirement is called **normalization**. In one-dimension, the wave function must be normalized by:

$$\int_{-\infty}^{\infty} \Psi_n^2 dx = 1 \quad \text{if } \Psi_n \text{ is real} \quad \text{or} \quad \int_{-\infty}^{\infty} \Psi_n^* \Psi_n dx = 1 \quad \text{if } \Psi_n \text{ is complex} \quad 23.3.18$$

The integral limits are over all the allowable values of the position of the particle, “over all space.” The integrals in Eqs. 23.3.18 are called the **normalization integrals**. To be normalizable, the wave function must be:

- (1). Finite
- (2). Continuous
- (3). Single-valued
- (4). Square integrable

In essence, these analytical stipulations require the wave function to be “smooth.” Examples of the disallowed behaviors are shown in Figure 23.3.5.

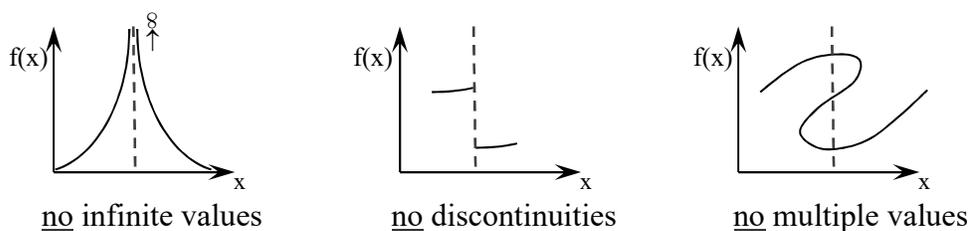


Figure 23.3.5: The wave function must be finite, continuous, single-valued, and square integrable.

(1). The wave function must be finite across the allowable range of positions, because a probability can't exceed 1. (2). The wave function must be continuous, because a discontinuity is unphysical for wave-like behavior. The probability of a particle being at positions x and $(x + 0.00001 \text{ \AA})$ should vary smoothly with x and not make big jumps; wave phenomena are smoothly varying. (3). The wave function must be single valued, because the probability can't have more than one value at a given position. The probability of a particle being at $x = 1.00 \text{ \AA}$ can't be both 10% and 80%. (4). The wave function must be square integrable, because the normalization integral would otherwise be undefined. This last requirement is the weakest analytical stipulation for the "smooth" behavior of the wave function.

Example 23.3.2:

Which of the following functions cannot be a valid wave function over the specified range? (a). e^{-kx} with $0 \leq x \leq \infty$, (b). e^{-kx} with $-\infty \leq x \leq \infty$, (c). $e^{im\phi}$ for m not an integer with $0 \leq \phi \leq 2\pi$.

Answer: (a). $\Psi = e^{-kx}$ with $0 \leq x \leq \infty$ is acceptable since the function is finite, continuous, and square integrable: $\int_0^\infty \Psi^2 dx = \int_0^\infty e^{-2kx} dx = 1/2k$. (b). However, with $-\infty \leq x \leq \infty$, $\Psi = e^{-k(-\infty)}$ is infinite, so it is not acceptable over the wider range. (c). For m non-integer, $\Psi = e^{im\phi}$ is not single valued. At $\phi = 0$ and 2π , for example, the function should have the same value: $e^{im0} = e^{im2\pi}$. However, $e^{im0} = 1$, so $e^{im2\pi} = \cos 2\pi m + i \sin 2\pi m$ is equal to one only if m is an integer.

23.4 Confined Particle Motion

Our next example of the application of the Schrödinger equation is to consider a particle that is confined in a potential energy well. This example is important because it introduces all of the important concepts that govern quantum phenomena. Confined particle motion helps us to learn how to think quantum mechanically.¹ The confined particle is a useful model for the electronic transitions in conjugated molecules and is a model for the translational degree of freedom of atoms and molecules.

The Model for a Confined Particle is the Particle in a Box: Consider a potential energy function that is zero inside a box of length a and infinite at the edges of the box, Figure 23.4.1a.

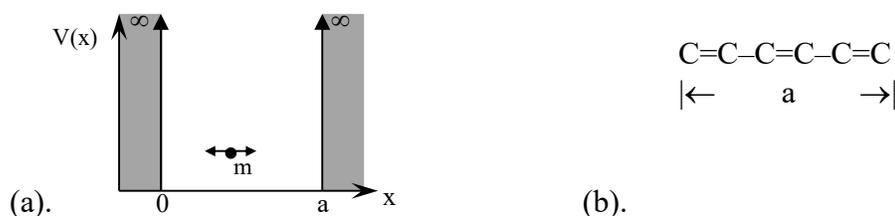


Figure 23.4.1: (a). The particle in a box model has a potential energy of zero inside the box and infinite at the walls. (b). The π -electrons in a conjugated molecule can be modeled as a particle in a box, where the length of the molecule is the box length a .

The resulting model is called the **particle in a box**. The particle may be an electron, an atom, or a molecule. One interesting application of the particle in a box is the description of the motion of the π -electrons in a conjugated molecule, Figure 23.4.1b. Because the potential energy is infinite at the walls of the box, the electron has zero probability of being found outside the box. As a consequence the position of the particle is restricted to $0 \leq x \leq a$. Within this range of positions the potential energy is zero and the Schrödinger equation reduces to:

$$-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \Psi = E \Psi \quad (0 \leq x \leq a) \quad 23.4.1$$

This equation is equivalent to the free-particle case, and the possible wave functions are $A \sin kx$ and $B \cos kx$, with k a constant and amplitudes A and B . The derivatives are:

$$\text{for } A \sin kx : \quad \frac{d\Psi}{dx} = A k \cos kx \quad \frac{d^2\Psi}{dx^2} = -A k^2 \sin kx \quad 23.4.2$$

$$\text{for } B \cos kx : \quad \frac{d\Psi}{dx} = -B k \sin kx \quad \frac{d^2\Psi}{dx^2} = -B k^2 \cos kx$$

Taking the sine possibility first, substitution of $A \sin kx$ into both sides of Eq. 23.4.1 gives:

$$-\frac{\hbar^2}{2m} (-A k^2 \sin kx) = E A \sin kx \quad (0 \leq x \leq a) \quad 23.4.3$$

Solving for the energy and the constant k gives:

$$E = \frac{\hbar^2 k^2}{2m} \quad k = \frac{\sqrt{2mE}}{\hbar} \quad (0 \leq x \leq a) \quad 23.4.4$$

Since the potential energy is zero for a particle in a box, the total energy is all kinetic energy. Repeating the last three steps with the cosine possibility gives the same result. Since both the sine and cosine terms are particular solutions to the Schrödinger equation, the general solution is the linear combination:

$$\Psi(x) = A \sin kx + B \cos kx \quad (0 \leq x \leq a) \quad 23.4.5$$

Eqs. 23.4.4 are the same as for the free particle, Eqs. 23.3.5 and 23.3.6. The difference for a confined particle is that we need to apply boundary conditions at the walls of the box, $\Psi(0) = 0$ and $\Psi(a) = 0$, since the particle has zero probability of being outside the box.

Consider first the boundary condition at the left-hand boundary, $\Psi(x) = 0$. Since the $\cos(0) = 1$, the value of B in the general solution must be zero. Only the sine term is a valid solution for the problem. At the right-hand boundary, $x = a$:

$$\Psi(a) = A \sin ka = 0 \quad (0 \leq x \leq a) \quad 23.4.6$$

The value of k is restricted to integer multiples of π/a as shown in Figure 23.4.2a:

$$k = n\pi/a \quad (0 \leq x \leq a) \quad 23.4.7$$

where n is a quantum number. The particle in a box wave function is then:

$$\Psi = A \sin\left(\frac{n\pi x}{a}\right) \quad (0 \leq x \leq a) \quad 23.4.8$$

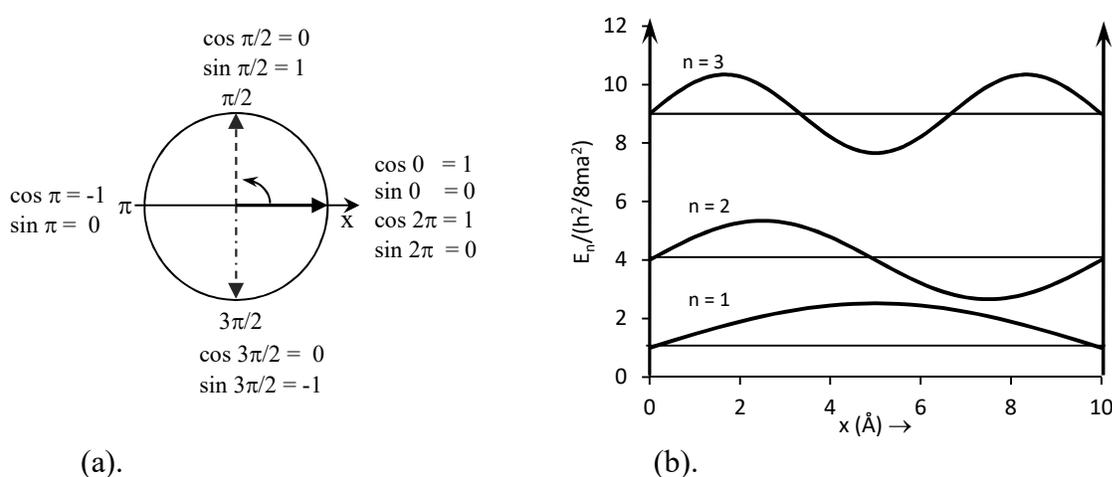


Figure 23.4.2: (a). The values of $\cos \phi$ and $\sin \phi$ on the unit circle; $\sin \phi = 0$ at $n\pi$ radians. (b). Particle-in-a-box wave functions for the three lowest energy states. The particle-in-a-box has a zero point energy, $E_1 = h^2/8ma^2$.

For example, for $n = 1$ setting $x = a$ gives $kx = ka = \pi$ so that the wave progresses through one-half cycle, Figure 23.4.2b. For $n = 2$ at $x = a$, $kx = ka = 2\pi$, and the wave progresses through one full cycle. Substituting Eq. 23.4.7 into the energy expression, Eqs. 23.4.4, gives the allowed energy levels for the particle in a box as:

$$E_n = \frac{\hbar^2 \pi^2 n^2}{2ma^2} = \frac{h^2 n^2}{8ma^2} \quad 23.4.9$$

The energy is quantized with the quantum number n , with $n = 1, 2, 3, \dots, \infty$. The quantum number is commonly given as a subscript for the energy, E_n . A useful visual way of judging the kinetic energy of a particle is to note the curvature. As the “wiggleness” or curvature of the wave function increases, the kinetic energy increases. The curvature can be easily determined by counting the number of nodes for the wave function, Figure 23.4.2b. As the number of nodes increases, the curvature or the “wiggleness” increases, and the energy of the particle increases. For the ground state, with $n = 1$, there are no nodes in the middle of the box. The number of nodes is $n-1$ for the particle in a box. Notice that the energy levels diverge, become further apart, as $n \rightarrow \infty$. The energy levels are closer together for larger mass particles or for longer length boxes.

The quantum number for the particle in a box cannot be zero, because if n is zero, the wave function vanishes for all values of x , $\Psi(x) = A \sin(0) = 0$. If $n = 0$, a particle has no kinetic energy, the wave function has no curvature, and the wave function vanishes; there is no particle. A non-zero ground state energy is called the **zero-point energy**. The zero-point energy for the particle in a box is E_1 . At zero degrees K, the particle is in the lowest possible energy state. Even at absolute zero the system has translational energy. This result is the reason that we describe absolute zero as, not the absence of all motion, but rather the absence of all **quenchable** motion.

One remaining step is to determine the constant A . The constant A is called a **normalization constant** and is determined by ensuring the probability of finding the particle over all space is unity. The integral limits for the particle in a box can be reduced to 0 to a , since the wave

function is zero outside the box. Substituting the Eq. 23.4.8 into the normalization integral, Eq. 23.3.18, gives:

$$\int_{-\infty}^{\infty} \Psi^2 dx = A^2 \int_0^a \sin^2\left(\frac{n\pi x}{a}\right) dx = 1 \quad (0 \leq x \leq a) \quad 23.4.10$$

This integral can be put into general form using the substitution:

$$y = \frac{n\pi x}{a} \quad \text{and then} \quad \frac{dy}{dx} = \frac{n\pi}{a} \quad 23.4.11$$

Solving these two equations for x and dx gives, respectively:

$$x = \frac{a}{n\pi} y \quad \text{and} \quad dx = \frac{a}{n\pi} dy \quad 23.4.12$$

For the integral limits, when x varies from 0 to a , then y varies from 0 to $n\pi$. Substituting Eqs. 23.4.12 into Eq. 23.4.10 changes variables to give:

$$A^2 \left(\frac{a}{n\pi}\right) \int_0^{n\pi} \sin^2(y) dy = 1 \quad 23.4.13$$

Integral tables give the integral as: $\int \sin^2(x) dx = -\frac{1}{2} \sin x \cos x + \frac{1}{2} x$:

$$A^2 \left(\frac{a}{n\pi}\right) \left(-\frac{1}{2} \sin y \cos y + \frac{1}{2} y\right) \Big|_0^{n\pi} = 1 \quad 23.4.14$$

Note that $\sin(0) = 0$ and $\sin(n\pi) = 0$. Evaluating the result at the endpoints gives:

$$A^2 \left(\frac{a}{n\pi}\right) \left(\frac{n\pi}{2}\right) = 1 \quad \text{and then} \quad A = \left(\frac{2}{a}\right)^{1/2} \quad 23.4.15$$

Substituting the normalization constant into Eq. 23.4.8, the normalized wave function is:

$$\Psi_n(x) = \left(\frac{2}{a}\right)^{1/2} \sin\left(\frac{n\pi x}{a}\right) \quad 23.4.16$$

The wave function contains all the information necessary to describe the system. For example, what is the most probable position of the particle in a box? The most probable position corresponds to the maximum of the squared wave function, $d\Psi^2/dx = 0$. For the ground state, the most probable position is half-way through the box, $x_{mp} = 0.5 a$. The particle in a box is an excellent example of many of the fundamental issues in quantum mechanics.

The Solutions to the Schrödinger Equation are Orthogonal: The set of solutions to the Schrödinger equation have another important property, they are mutually **orthogonal**. Two solutions of the Schrödinger equation, Ψ_m and Ψ_n , are orthogonal if the integral:

$$\int_{-\infty}^{\infty} \Psi_m^* \Psi_n dx = 0 \quad 23.4.17$$

is equal to zero. The integral is called the **orthogonality** integral. Notice the similarity to the normalization integral, Eq. 23.3.18. Orthogonality can be interpreted as that the two wave functions are as “different as possible” from each other.

An analogy with vectors may be helpful. The orthogonality integral is analogous to the dot product for vectors. The dot product for two vectors $\vec{u} \cdot \vec{v}$ is equal to zero if the vectors are perpendicular to each other. In this specific sense, two perpendicular vectors are as different from each other as possible. The normalization integral is analogous to the square of the vector length, $\vec{v} \cdot \vec{v}$. A normalized vector has unit length. A complete set of orthogonal and normalized vectors are called a **basis set**. The unit vectors \vec{i} , \vec{j} , and \vec{k} are an example of a basis set in three-Cartesian dimensions. Any general solution to a vector problem may be expressed as a linear combination of the basis set. In the same way, any general solution to a quantum mechanical problem may be expressed as a linear combination of the orthogonal and normalized solutions to the Schrödinger equation. Wave functions that are both orthogonal and normalized are said to be **orthonormal**. The complete set of solutions to the Schrödinger equation for a given problem are said to be the **orthonormal basis set** for the problem. The orthonormal solutions to the Schrödinger equation are a complete representation that span the entire range of possible solutions. The particle in a box is an excellent example.

Example 23.4.1 The Particle in a Box Wave functions are Orthogonal

Show that the particle in a box wave functions are orthogonal.

Answer: Consider two different solutions, Ψ_m and Ψ_n . Substituting the wave functions from Eq. 23.4.16 into the orthogonality integral gives:

$$\int_{-\infty}^{\infty} \Psi_m^* \Psi_n dx = \left(\frac{2}{a}\right) \int_0^a \sin\left(\frac{m\pi x}{a}\right) \sin\left(\frac{n\pi x}{a}\right) dx$$

Using the substitution $y = \pi x/a$ gives $dy/dx = \pi/a$ or $dx = a/\pi dy$ with the range 0 to π :

$$\int_{-\infty}^{\infty} \Psi_m^* \Psi_n dx = \left(\frac{2}{a}\right) \left(\frac{a}{\pi}\right) \int_0^{\pi} \sin(my) \sin(ny) dy \quad (m \text{ and } n = \text{integers})$$

Tables give this integral as zero. However, a visual inspection is quite instructive. For example, consider $m = 2$ and $n = 1$, Figure 23.4.3. Ψ_2 is odd about the midpoint of the integral and Ψ_1 is even; the product is odd about the midpoint giving a vanishing integral.

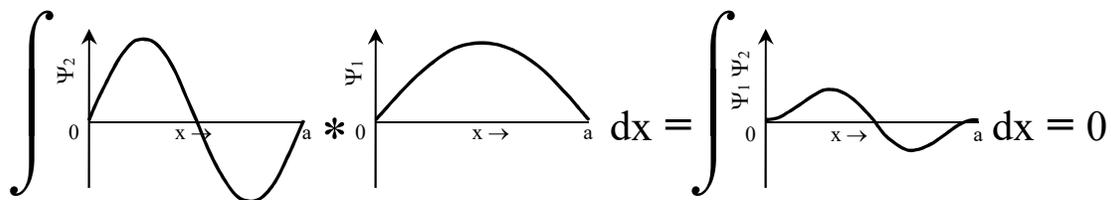


Figure 23.4.3: A pictorial representation of the orthogonality integral for $m = 2$ and $n = 1$ shows the integral vanishes. The product of the two wave functions is taken point-by-point. The two solutions are as “different as possible.”

The particle in a box also provides a useful model for the absorption spectra of conjugated molecules, which is helpful in learning how to think quantum mechanically.

Confined Particles are a Model for the Spectra of Conjugated Molecules: Electrons in delocalized π -electron systems can be modeled as particles in a box. Consider 1,3,5-hexatriene, Figure 23.4.4. The length of the box is approximated as the terminal carbon to carbon distance. The average C-C bond length in conjugated molecules is roughly 1.39 Å, giving the box length as $a = 5(1.39 \text{ Å}) = 6.95 \times 10^{-10} \text{ m}$. Each sp^2 hybridized carbon atom donates one electron to the π -system, for a total of 6 electrons. Remember from General Chemistry that the Pauli Exclusion Principle specifies that each orbital can hold two electrons, one spin up and one spin down. Three orbitals are then required. The highest occupied molecular orbital, or **HOMO**, corresponds to $n = 3$ for hexatriene, Figure 23.4.4. The lowest unoccupied molecular orbital, or **LUMO**, is then $n = 4$. The lowest energy electronic transition is to promote an electron from the HOMO to the LUMO. For hexatriene the HOMO to LUMO transition is $n_i = 3$ to $n_f = 4$, which is symbolized as $4 \leftarrow 3$ for absorption. The energy difference for the transition, using Eq. 23.4.9, determines the maximum absorption wave length:

$$\Delta E = h\nu = hc/\lambda = E_f - E_i = \frac{h^2}{8ma^2} (n_f^2 - n_i^2) \quad 23.4.18$$

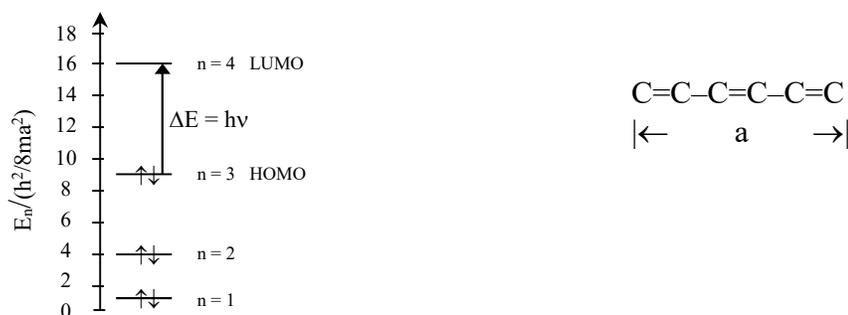


Figure 23.4.4: Particle in a box energy level diagram for the π -system in 1,3,5-hexatriene. The lowest energy electronic transition in absorption is from the HOMO to the LUMO.

Example 23.4.2: Absorption Spectra of Conjugated Polyenes

Determine the energy difference in J, kJ mol^{-1} , cm^{-1} , and eV for the lowest energy electronic transition in 1,3,5-hexatriene. Determine the maximum absorption wave length.

Answer: The $4 \leftarrow 3$, HOMO to LUMO transition for 1,3,5-hexatriene using Eq. 23.4.18 occurs at:

$$\begin{aligned} \Delta E &= hc/\lambda = E_4 - E_3 = \frac{h^2}{8ma^2} (4^2 - 3^2) = \frac{h^2}{8ma^2} (7) \\ &= \frac{(6.626 \times 10^{-34} \text{ J s})^2}{8(9.109 \times 10^{-31} \text{ kg})(6.95 \times 10^{-10} \text{ m})^2} (7) = 8.731 \times 10^{-19} \text{ J} \end{aligned}$$

$$\Delta E N_A (1 \text{ kJ}/1000 \text{ J}) = 526. \text{ kJ mol}^{-1}$$

$$\tilde{\nu} = \Delta E/hc = \frac{8.731 \times 10^{-19} \text{ J}}{6.626 \times 10^{-34} \text{ J s} (2.998 \times 10^8 \text{ m})} (1 \text{ m}/100 \text{ cm}) = 44000 \text{ cm}^{-1}$$

$$\Delta E/e = 5.46 \text{ eV}$$

$$\lambda = hc/\Delta E = 6.626 \times 10^{-34} \text{ J s} (2.998 \times 10^8 \text{ m s}^{-1}) / 8.731 \times 10^{-19} \text{ J} (1 \text{ nm}/1 \times 10^{-9} \text{ m}) = 228. \text{ nm}$$

This transition is in the UV region of the spectrum. The literature value is significantly redder at 258 nm, giving a large error for the theoretical model. However, the accuracy of the model improves for longer chain lengths. A better prediction often results if the box length is assumed to extend $\frac{1}{2}$ -bond length beyond the terminal carbons. While the particle in a box model for the absorption spectra of conjugated systems is superseded by more advanced theories, the simple model provides a good didactic example.

The Schrödinger Equation is an Eigenvalue Equation: The left side of the Schrödinger equation, Eq. 23.3.1, is the quantum mechanical analog of the classical Hamiltonian. The Schrödinger equation in one-dimension is represented in terms of the quantum mechanical Hamiltonian, \hat{H} , as:

$$\hat{H}\Psi_n(x) = E_n \Psi_n(x) \quad \text{with} \quad \hat{H} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \hat{V}(x) \quad 23.4.19$$

The Hamiltonian acting on the wave function gives the total energy of the particle. The Schrödinger equation is in the general form of an **eigenvalue** equation. The term “eigen” in German means “the same.” The action of the Hamiltonian on the wave function returns the same wave function multiplied by a constant. The constant is the eigenvalue. The set of solutions to an eigenvalue equation are called the **eigenvectors**, **eigenfunctions**, or **eigenstates** of the system. The allowed wave functions are the eigenfunctions of the Hamiltonian and the corresponding eigenvalues are the energies. The eigenstates of the system are also called **stationary states**; in the absence of an external perturbation, systems in a stationary state remain in that state.

The general form of an eigenvalue equation for the observable property \hat{o} is:

$$\hat{o} \Psi = o \Psi \quad 23.4.20$$

\uparrow observable \uparrow

The eigenvalue corresponds to the observed value for the property. For the specific case of the Hamiltonian, the observed property is the total energy. The momentum of the particle can also be calculated from the wave function. The kinetic energy is given using $\hat{E}_k \Psi = -(\hbar^2/2m) d^2\Psi/dx^2$. Solving for the momentum using $p = \sqrt{2mE_k}$ gives:

$$\hat{p} \Psi = \frac{\hbar}{i} \frac{d\Psi}{dx} \quad 23.4.21$$

For example, the free particle is an eigenfunction of the momentum. The free particle wave function is $\Psi = e^{ikx}$; substitution into Eq. 23.4.21 gives:

$$\hat{p} \Psi = \frac{\hbar}{i} \frac{d(e^{ikx})}{dx} = \hbar k e^{ikx} \quad 23.4.22$$

Substituting back in for the wave function $\Psi = e^{ikx}$ simplifies Eq. 23.4.22 to give:

$$\hat{p} \Psi = \hbar k \Psi \quad 23.4.23$$

Notice the correspondence that is established by the last equation, as based on Eq. 23.4.20:

$$\begin{array}{l} \hat{p} \Psi = \hbar k \Psi \\ \uparrow \qquad \uparrow \\ \hat{p} \Psi = p \Psi \end{array} \quad 23.4.24$$

The momentum is a constant, the eigenvalue, with $p = \hbar k$. Not only is the free particle wave function an eigenfunction of the Hamiltonian, the free particle is also an eigenfunction of the momentum. See *General Pattern* § 6, Sec. 6.3, for further information on eigenvalue equations.

Observable Properties are Eigenvalues or Expectation Values: The wave function provides the information necessary to determine all the observable properties of the system. Two possibilities arise for the determination of observable properties. For some observable properties, the measurements are exactly the same for each repetition. For example, the energy of a particle in a box is exactly the same for each measurement, because the energy is the eigenvalue of the Hamiltonian. For some properties, each measurement is different and average values must be determined. For example, each time the position of a particle in a box is measured, a different result is found and the average position must be determined, $\langle x \rangle$. Averages in quantum mechanical problems are called **expectation values**. For a given property, \hat{o} , the expectation value is defined by the integral over all space:

$$\langle o \rangle = \frac{\int_{-\infty}^{\infty} \Psi^* \hat{o} \Psi dx}{\int_{-\infty}^{\infty} \Psi^* \Psi dx} \quad 23.4.25$$

The order in the integrand is important for the general case, and will be discussed further in Sec. 23.6. For a normalized wave function, the denominator is equal to one. For the average position of the particle in a box, $\hat{o} = x$, giving the expectation value as $\langle x \rangle = \int \Psi^* x \Psi dx$, for a normalized wave function. Substitution of Eq. 23.4.16 into the expectation integral gives the average position as:

$$\langle x \rangle = \int_{-\infty}^{\infty} \underbrace{\left(\frac{2}{a}\right)^{1/2} \sin\left(\frac{n\pi x}{a}\right)}_{\text{average } x} x \underbrace{\left(\frac{2}{a}\right)^{1/2} \sin\left(\frac{n\pi x}{a}\right)}_{\Psi^2 dx = \text{probability distribution}} dx \quad 23.4.26$$

For this example, the integral simplifies to:

$$\langle x \rangle = \int_{-\infty}^{\infty} x \underbrace{\left(\frac{2}{a}\right) \sin^2\left(\frac{n\pi x}{a}\right)}_{\Psi^2 dx = \text{probability distribution}} dx \quad 23.4.27$$

\uparrow *average x* \uparrow

This last result shows that the expectation value is in the same form as any statistical average, a form not specific to quantum mechanics. The probability distribution, for a real wave function, is $\Psi^2 dx$. The integral in Eq. 23.4.27 is converted to standard form with the same substitution that we used for the normalization integral, Eqs. 23.4.12:

$$\langle x \rangle = \left(\frac{2}{a}\right) \left(\frac{a}{n\pi}\right)^2 \int_0^{n\pi} y \sin^2(y) dy \quad 23.4.28$$

Integral tables give the integral as: $\int x \sin^2(x) dx = \frac{x^2}{4} - \frac{x \sin 2x}{4} - \frac{\cos 2x}{8} :$

$$\langle x \rangle = \left(\frac{2}{a}\right) \left(\frac{a}{n\pi}\right)^2 \left[\frac{y^2}{4} - \frac{y \sin 2y}{4} - \frac{\cos 2y}{8} \right]_0^{n\pi} \quad 23.4.29$$

Note that $\sin(0) = \sin(2n\pi) = 0$ and $\cos(0) = \cos(2n\pi) = 1$. Evaluating the integral at the limits:

$$\langle x \rangle = \left(\frac{2a}{n^2\pi^2}\right) \left(\frac{n^2\pi^2}{4}\right) = \frac{a}{2} \quad 23.4.30$$

The average position is half-way through the box, independent of quantum number. In the next chapter, we will see that expectation values of the position are useful for determining the size of atomic orbitals. For a second example, the momentum of the particle in a box must also be determined using expectation values.

Example 23.4.3: Momentum for the Particle in a Box

Determine the expectation value of the momentum of the particle in a box.

Answer: Using the normalized wave function gives $\int_{-\infty}^{\infty} \Psi^* \Psi dx = 1$ and the expectation value of the momentum is:

$$\langle p \rangle = \frac{\int_{-\infty}^{\infty} \Psi^* \hat{p} \Psi dx}{\int_{-\infty}^{\infty} \Psi^* \Psi dx} = \int_{-\infty}^{\infty} \Psi^* \left(\frac{\hbar}{i} \frac{d}{dx} \right) \Psi dx \quad (\text{normalized } \Psi) \quad 23.4.31$$

For the particle in a box, Eqs. 23.4.16 and 23.4.21 give:

$$\hat{p} \Psi = \frac{\hbar}{i} \frac{d\Psi}{dx} = \frac{\hbar}{i} \left(\frac{2}{a}\right)^{1/2} \frac{d \sin(n\pi x/a)}{dx} = \frac{\hbar}{i} \left(\frac{2}{a}\right)^{1/2} \left(\frac{n\pi}{a}\right) \cos\left(\frac{n\pi x}{a}\right) \quad 23.4.32$$

Combining Eqs. 23.4.31 and 23.4.32, the expectation value of the momentum is:

$$\langle p \rangle = \frac{\hbar}{i} \left(\frac{2}{a}\right) \left(\frac{n\pi}{a}\right) \int_0^a \sin\left(\frac{n\pi x}{a}\right) \cos\left(\frac{n\pi x}{a}\right) dx \quad 23.4.33$$

Using the substitution $y = n\pi x/a$ as before gives:

$$\langle p \rangle = \frac{\hbar}{i} \left(\frac{2}{a}\right) \left(\frac{n\pi}{a}\right) \left(\frac{a}{n\pi}\right) \int_0^{n\pi} \sin y \cos y dy = 0 \quad 23.4.34$$

because: $\int_0^{n\pi} \sin y \cos y dy = \left[\frac{1}{2} \sin^2 y \right]_0^{n\pi} = 0$. The average momentum of the particle is zero.

The particle in a box wave functions are analogous to classical standing waves. A standing wave is interpreted as the constructive interference of a wave with forward momentum and a wave with negative momentum, Example 23.3.1. Because the particle in a box wave function is

not an eigenfunction of the momentum, each observation of the momentum gives a different result. The average momentum is zero because the wave is moving forwards half the time and backwards half the time. However, for a free particle, the wave function is an eigenfunction of the momentum. An expectation value is not required to find the momentum of a free particle. Repeated observations of the momentum of a free particle give the same exact result, $\hbar k$.

The distinction between eigenvalues and expectation values has several implications. Eigenvalues can be determined exactly, but is there an inherent uncertainty in observations represented by expectation values?

Particles are Fuzzy – Position and Momentum Can't Both be Determined with High Precision: Particles act as waves in the microscopic world. Waves by their nature are diffuse, so the position of a particle is necessarily uncertain. The uncertainties in the position and momentum of a particle are governed by the **Heisenberg Uncertainty** principle, which for one-dimension is:

$$\sigma_x \sigma_{p_x} \geq \hbar/2 \quad \text{or equivalently} \quad \delta x \delta p_x \geq \hbar/2 \quad 23.4.35$$

where the standard deviations of the position and the momentum are σ_x and σ_{p_x} , or δx and δp_x , respectively. The average values are given by the expectation values, $\bar{x} = \langle x \rangle$ and $\bar{p} = \langle p \rangle$. The standard deviations are defined using the expectation values of the squared deviations of the position and momentum from their average values:

$$\sigma_x = \langle (x - \bar{x})^2 \rangle^{1/2} = (\langle x^2 \rangle - \langle x \rangle^2)^{1/2} \quad \text{and} \quad \sigma_{p_x} = \langle (p - \bar{p})^2 \rangle^{1/2} = (\langle p^2 \rangle - \langle p \rangle^2)^{1/2} \quad 23.4.36$$

The expectation values are determined using the integrals in Eq. 23.4.24.

Consider the free particle as a first example. The momentum of a free particle is exactly known, $p_x = \hbar k$, giving $\delta p_x = 0$. The uncertainty in the position must then be infinite, since solving Eq. 23.4.35 for the uncertainty in the position gives $\delta x \geq \hbar/(2\delta p_x)$. The position of a free particle cannot be determined, in agreement with Eq. 23.3.15. The free particle is an extreme case; most systems have a finite uncertainty for both position and momentum. A Gaussian distribution, such as the ground state of the harmonic oscillator, is an example (Figure 23.3.3a).

Example 23.4.4: Heisenberg Uncertainty for a Gaussian Distribution

Find σ_{p_x} for a Gaussian distribution, Figure 23.4.3. Verify that the Heisenberg uncertainty relationship holds for this distribution. A Gaussian wave function with standard deviation σ_x is:

$$\Psi(x) = N e^{-x^2/4\sigma_x^2} \quad \text{with the normalization constant} \quad N = \frac{1}{(2\pi)^{1/4} \sigma_x^{1/2}}$$

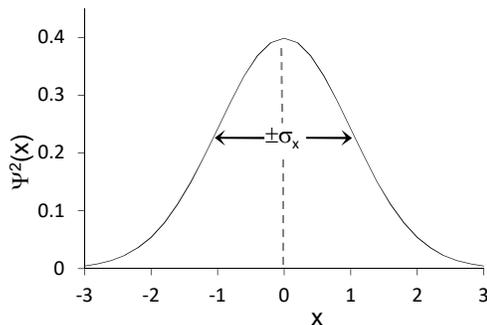


Figure 23.4.3: Gaussian probability distribution, $\Psi^2(x)$, with positional uncertainty σ_x .

Answer: Inspection of the shape of the Gaussian distribution shows that the average momentum is zero, $\langle p \rangle = 0$, because the distribution is symmetrical about zero. The remaining task is to find $\langle p^2 \rangle$ to substitute into Eq. 23.4.35 for the uncertainty in the momentum. The wave function is normalized, giving the expectation value of the squared momentum as:

$$\langle p^2 \rangle = \int_{-\infty}^{\infty} \Psi^* \hat{p}^2 \Psi \, dx \quad (\Psi \text{ normalized}) \quad 23.4.37$$

The derivative of the wave function is: $\frac{d\Psi}{dx} = N \left(\frac{-2x}{4\sigma_x^2} \right) e^{-x^2/4\sigma_x^2} = \left(\frac{-x}{2\sigma_x^2} \right) \Psi$ 23.4.38

(see *General Pattern* §5 for an introduction to the Gaussian distribution and its derivatives).

Using Eq. 23.4.21, the first application of \hat{p} on the wave function gives:

$$\hat{p} \Psi = \frac{\hbar}{i} \frac{d\Psi}{dx} = \left(\frac{-\hbar}{2i\sigma_x^2} \right) x \Psi \quad 23.4.39$$

The second application of \hat{p} , using the product rule and Eq. 23.4.38, then results in:

$$\begin{aligned} \hat{p}^2 \Psi &= \hat{p} \hat{p} \Psi = \frac{\hbar}{i} \frac{d}{dx} \left(\frac{-\hbar}{2i\sigma_x^2} \right) x \Psi = \left(\frac{\hbar^2}{2\sigma_x^2} \right) \left(x \frac{d\Psi}{dx} + \Psi \frac{dx}{dx} \right) \\ &= \left(\frac{\hbar^2}{2\sigma_x^2} \right) \left(\frac{-x^2}{2\sigma_x^2} + 1 \right) \Psi = -\hbar^2 \left(\frac{x^2}{4\sigma_x^2} - \frac{1}{2\sigma_x^2} \right) \Psi \end{aligned} \quad 23.4.40$$

Substitution into Eq. 23.4.37 gives: $\langle p^2 \rangle = -\hbar^2 N^2 \int_{-\infty}^{\infty} \left(\frac{x^2}{4\sigma_x^2} - \frac{1}{2\sigma_x^2} \right) e^{-x^2/2\sigma_x^2} \, dx$ 23.4.41

Luckily the integrals are standard forms and available from integral tables:

$$\int_0^{\infty} x^2 e^{-x^2/2\sigma_x^2} \, dx = \frac{2\sigma_x^2}{4} (2\pi)^{1/2} \sigma_x \quad \int_0^{\infty} e^{-x^2/2\sigma_x^2} \, dx = \frac{1}{2} (2\pi)^{1/2} \sigma_x \quad 23.4.42$$

Substitution of the integrals into Eq. 23.4.41 gives:

$$\langle p^2 \rangle = -2 \hbar^2 \left(\frac{1}{(2\pi)^{1/2} \sigma_x} \right) \left(\frac{2\sigma_x^2}{16\sigma_x^4} (2\pi)^{1/2} \sigma_x - \frac{1}{4\sigma_x^2} (2\pi)^{1/2} \sigma_x \right) = \frac{\hbar^2}{4\sigma_x^2} \quad 23.4.43$$

Using $\langle p \rangle = 0$, the standard deviation of the momentum is then $\sigma_{px} = (\langle p^2 \rangle - \langle p \rangle^2)^{1/2} = \hbar/2\sigma_x$.

The product of the uncertainty of the position and momentum is correspondingly:

$$\sigma_x \sigma_{px} = \sigma_x (\hbar/2\sigma_x) = \hbar/2 \quad 23.4.44$$

as required by the Heisenberg uncertainty relationship. This result is the ideal limit; experimental measurements give higher uncertainty. For the harmonic oscillator, x is the displacement with $x = r - r_0$. Several end of the chapter problems cover the uncertainties for the particle in a box.

The energy of a given state of an atom or molecule and the lifetime of that state are also governed by an uncertainty relationship:

$$\delta E \delta t \geq \hbar/2 \quad 23.4.45$$

where δE is the uncertainty in the energy of the state and δt is the lifetime of the state. States with a short lifetime have a larger energy uncertainty. The uncertainty in the energy of the state determines the width of the corresponding transition in an absorption or emission spectrum, Figure 23.4.4. The uncertainty broadening of spectral transitions is called **lifetime broadening**. The line width given by the uncertainty relationship is called the **intrinsic spectral width**. Motion makes additional large contributions to spectral broadening near room temperature.

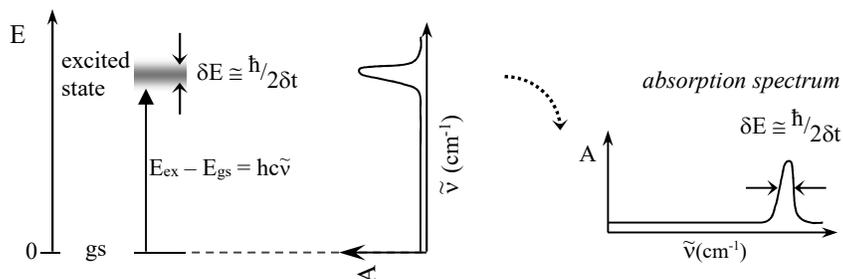


Figure 23.4.4: A finite lifetime for an electronic state gives a finite line width in the absorption or emission spectra. An absorption transition from the ground state, gs, is illustrated.

Example 23.4.5: Heisenberg Uncertainty for Spectroscopic Transitions

Determine the line width of the fluorescence spectrum for a transition at 253. nm with an excited state lifetime of 2.50 ns. Give the spectral width in cm^{-1} and nm.

Answer: A transition at 253. nm corresponds to $\tilde{\nu} = 1/\lambda$ (1 m/100 cm) = 39,500 cm^{-1} . Using Eq. 23.4.45, the excited state lifetime of 2.50 ns corresponds to an uncertainty in wave numbers of:

$$\begin{aligned} \delta\tilde{\nu} &= \delta E/hc \cong \frac{\hbar}{2hc\delta t} = \frac{1}{4\pi c\delta t} \text{ (1 m/100 cm}^{-1}\text{)} & 23.4.46 \\ &= \frac{1}{4\pi \cdot 2.998 \times 10^8 \text{ m s}^{-1} \cdot (2.50 \times 10^{-9} \text{ s})} \text{ (1 m/100 cm)} = 1.062 \times 10^{-3} \text{ cm}^{-1} \end{aligned}$$

The spectral line width is a very small fraction of the transition energy. This spectral width corresponds to a frequency uncertainty of $\delta\nu = c \delta\tilde{\nu} = 32$ MHz. To determine the spectral width in nm, consider transitions that are one standard deviation above and below the wave length of maximum absorption, λ_+ and λ_- , respectively. The spectral width in wavenumbers and in nm are related by Eq. 23.2.7:

$$\delta E/hc = \delta\tilde{\nu} = \left(\frac{1}{\lambda_-} - \frac{1}{\lambda_+} \right) = \left(\frac{\lambda_+ - \lambda_-}{\lambda_+ \lambda_-} \right) \cong \left(\frac{\delta\lambda}{\lambda_{\text{max}}^2} \right) \quad 23.4.47$$

The approximation in the denominator, $\lambda_+ \cong \lambda_- \cong \lambda_{\text{max}}$, is generally valid because the intrinsic line width is a small fraction of the transition energy or wave length. Solving Eq. 23.4.47 for $\delta\lambda$, the spectral width in nm is given using Eq. 23.4.46 as:

$$\begin{aligned}\delta\lambda &= \delta\tilde{\nu} \lambda_{\max}^2 (100 \text{ cm/1 m})(1 \text{ nm}/1 \times 10^{-9} \text{ m}) \\ &= 1.062 \times 10^{-3} \text{ cm}^{-1} (253. \times 10^{-9} \text{ m})^2 (100 \text{ cm/1 m})(1 \text{ nm}/1 \times 10^{-9} \text{ m}) = 6.80 \times 10^{-6} \text{ nm}\end{aligned}\quad 23.4.48$$

The intrinsic line width makes a small contribution to the experimental spectral width. The intrinsic line width is negligible except at temperatures near absolute zero K where motions are quenched.

Zero Point Energy is a Result of the Uncertainty Relationship: The particle in a box has finite uncertainties for both position and momentum. The observed momentum is different for each replicate measurement with an average of zero. The momentum of the particle cannot always be zero, because the momentum would be precisely known. The standard deviation of the momentum for the particle in a box is given by $\sigma_{p_x} = (\langle p^2 \rangle)^{1/2}$. The expectation value of the square of the momentum cannot be zero. The energy of the particle in a box is given by $E_k = \langle p^2 \rangle / 2m$, which is then necessarily non-zero. The result is the energy for the lowest energy state is non-zero. The lowest energy is the zero point energy. The occurrence of a zero point energy is a direct result of the Heisenberg uncertainty relationship. Another surprising quantum mechanical phenomenon related to the uncertainty relationship is the ability of particles to tunnel into and through potential energy barriers.

23.5 Tunneling – Particles Can Penetrate Into Barriers

The Tunneling Probability Depends on the Barrier Height and Width: The continuity requirements of the Born interpretation and the uncertainty relationship are manifested in the ability of particles to penetrate into regions where the total energy of the particle is less than the potential energy. Barrier penetration, with $E < V$, is not possible in classical theory. Consider a particle with total energy E incident from the left on a potential energy barrier of height V , Figure 23.5.1a. The position of the boundary is assigned as $x = 0$. The overall solution is composed of three parts, the incident wave with amplitude a , Ψ_{incident} , a reflected wave with amplitude b , $\Psi_{\text{reflected}}$, and a transmitted wave inside the barrier with amplitude c , $\Psi_{\text{transmitted}}$.

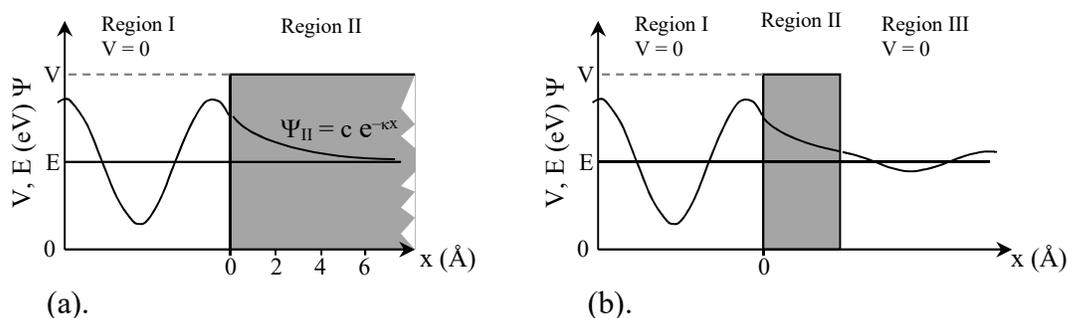


Figure 23.5.1: (a). The particle probability extends into the region where $E < V$. In this classically forbidden region the wave function is exponentially damped. $V = 2 \text{ eV}$ and $E = 1 \text{ eV}$ for an electron. (b). For a narrow barrier some probability remains at the second boundary. Free particle motion holds in regions I and III with the same wave length.

In region I, the incident and reflected waves experience no potential energy. In region I, the Schrödinger equation corresponds to a free particle that has an oscillatory wave function with wave vector k , from Eq. 23.3.6:

$$k = \frac{\sqrt{2mE}}{\hbar} \quad \Psi_{\text{incident}} = a e^{ikx} \quad \Psi_{\text{reflected}} = b e^{-ikx} \quad (\text{Region I}) \quad (23.3.6)$$

The wave function for region I is the superposition of the incident and reflected wave:

$$\Psi_I = \Psi_{\text{incident}} + \Psi_{\text{reflected}} = a e^{ikx} + b e^{-ikx} \quad (\text{Region I}) \quad 23.5.1$$

In region II, the transmitted wave experiences potential energy V . The potential is constant giving a wave vector k' , from Eq. 23.3.12:

$$k' = \frac{\sqrt{2m(E - V)}}{\hbar} \quad (\text{Region II}) \quad (23.3.12)$$

However, since $E < V$, the square root is of a negative number. Factoring out $\sqrt{-1}$ gives:

$$k' = i \frac{\sqrt{2m(V - E)}}{\hbar} = i\kappa \quad \text{where} \quad \kappa = \frac{\sqrt{2m(V - E)}}{\hbar} \quad (\text{Region II}) \quad 23.5.2$$

In region II inside the barrier, the wave function is then an exponentially decreasing real function:

$$\Psi_{\text{transmitted}} = c e^{ik'x} = c e^{-\kappa x} \quad (\text{Region II}) \quad 23.5.3$$

Region II is called the **classically forbidden** region. At the boundary the wave function must be continuous and smooth:

$$\text{at } x = 0: \quad a e^{ikx} + b e^{-ikx} = c e^{-\kappa x} \quad \text{or} \quad a + b = c \quad (\text{continuous}) \quad 23.5.4$$

To be smooth the slopes must match at the boundary:²

$$\frac{d}{dx} (a e^{ikx} + b e^{-ikx}) = \frac{d}{dx} (c e^{-\kappa x}) \quad \text{or} \quad iak - ibk = -c\kappa \quad (\text{smooth}) \quad 23.5.5$$

Solving Eq. 23.5.4 for $b = c - a$, substitution into Eq. 23.5.5, and solving for c gives:

$$c = \left(\frac{2ik}{ik - \kappa} \right) a \quad 23.5.6$$

The particle has a finite amplitude in the classically forbidden region. The particle can penetrate into the potential energy barrier, which is quite unexpected from our everyday experience (you can't insert your hand into a solid wall, for example). Penetration into the barrier results because the wave must vary smoothly and the position of the particle is uncertain at the boundary. The uncertainty extends into the classically forbidden region.

In many practical cases, the potential energy barrier has a finite width. If the width of the barrier is sufficiently thin, the transmitted wave has a small but significant amplitude at the end of the barrier. The particle can then propagate freely in the potential free region beyond the barrier, region III-Figure 23.5.1b. This process is called **tunneling**, which is a purely quantum mechanical phenomenon. Matching of the wave function amplitudes and slopes at both sides of the barrier gives the probability of tunneling of the particle through the barrier of thickness L as:

$$T = \left[\frac{(e^{\kappa L} - e^{-\kappa L})^2}{16\varepsilon(1 - \varepsilon)} + 1 \right]^{-1} \quad 23.5.7$$

where the ratio of the total energy of the particle to the barrier height is $\varepsilon = E/V$. The tunneling probability increases as the mass of the particle decreases and the energy of the particle increases. The probability also increases as the barrier thickness decreases. Tunneling may seem bizarre, but the phenomenon is widespread.

The copper or aluminum metal in electrical conductors is covered with a thin metal oxide film. Metal oxides are good insulators. Electrons can travel from one wire to another by tunneling through the insulating oxide barrier. Many enzymes have a metal cofactor that is oxidized or reduced in electron transfer reactions. Redox processes in enzymes occur by electron tunneling through the insulating layer of amino acids that exist between the solution and the metal center. Proton transfer reactions are faster than predicted by classical theories; protons are sufficiently light to tunnel through thin potential energy barriers. Deuterium tunneling is slower than proton tunneling, because of the larger mass, which is one source of the deuterium isotope effect. The hydrogen over-potential at metal electrodes in electrochemical cells is caused by the slow rate of electron tunneling from solution to the metal electrode. Electron tunneling is the basis of **scanning tunneling microscopy, STM**, which is capable of imaging individual atoms.

Example 23.5.1: Tunneling and Internal Rotation

Methyl groups have a low torsional barrier to internal rotation, Figure 8.8.5c. The barrier to internal rotation in ethane is roughly 3.3 kJ mol^{-1} for a single H atom and the barrier width can be estimated as 1.00 \AA . Calculate the tunneling probability for a proton across the torsional barrier at 298.2 K . The average energy is then $E \cong RT = 2.48 \text{ kJ mol}^{-1}$.

Answer: The ratio of the energy to the barrier height is $\varepsilon = 2.48/3.3 = 0.7515$. Using Eq. 23.5.2 gives κ ; for a proton $m_p = 1.673 \times 10^{-27} \text{ kg}$:

$$\kappa = \frac{\sqrt{2m(V - E)}}{\hbar} = \frac{\sqrt{2(1.673 \times 10^{-27} \text{ kg})(3300 \text{ J mol}^{-1} - 2480 \text{ J mol}^{-1})(1 \text{ mol}/6.022 \times 10^{23})}}{1.055 \times 10^{-34} \text{ J s}^{-1}}$$

$$\kappa = 2.023 \times 10^{10} \text{ m}^{-1}$$

giving for $L = 1.00 \text{ \AA} = 1.00 \times 10^{-10} \text{ m}$:

$$e^{-\kappa L} = e^{-2.023 \times 10^{10}(1 \times 10^{-10})} = 0.1323 \quad \text{and} \quad \frac{(e^{\kappa L} - e^{-\kappa L})^2}{4} = 13.81$$

The tunneling probability is given by Eq. 23.5.7:

$$T = \left[\frac{(e^{\kappa L} - e^{-\kappa L})^2}{16\varepsilon(1 - \varepsilon)} + 1 \right]^{-1} = \left[\frac{13.81}{4(0.7515)(1 - 0.7515)} + 1 \right]^{-1} = 0.0513 \quad \text{or} \quad 5.13\%$$

The protons in the methyl group tunnel across the rotational barrier with surprisingly high probability. Liquid helium temperatures, $\sim 4.5 \text{ K}$, are needed to stop methyl group rotation.

Scanning Tunneling Microscopy Can Image Single Atoms: Microscopy is playing an increasingly important role in the characterization of nano-scale materials. In scanning tunneling microscopy, **STM**, an atomically sharp tip is placed near a sample surface so that electrons can tunnel from the tip to the sample. The sample is scanned under the tip in an x-y raster pattern, Figure 23.5.2. As the sample is moved laterally, the height of the sample in the z-direction is adjusted to maintain a constant tunneling current. STM imaging is done in air or under high vacuum. The positioning of the sample and the height of the sample tip are controlled using piezoelectric actuators. Piezoelectric ceramics, such as barium titanate and lead zirconate titanate, change dimensions with an applied voltage. The voltage across a piezoelectric actuator is scanned to move the sample in a given direction. The tunneling current is measured by placing a small bias voltage across the tip and the sample. The surface of the sample must be conductive for STM imaging. The tip does not touch the surface, rather electrons tunnel across the 4-7 Å insulating air or vacuum gap between the tip and the surface.

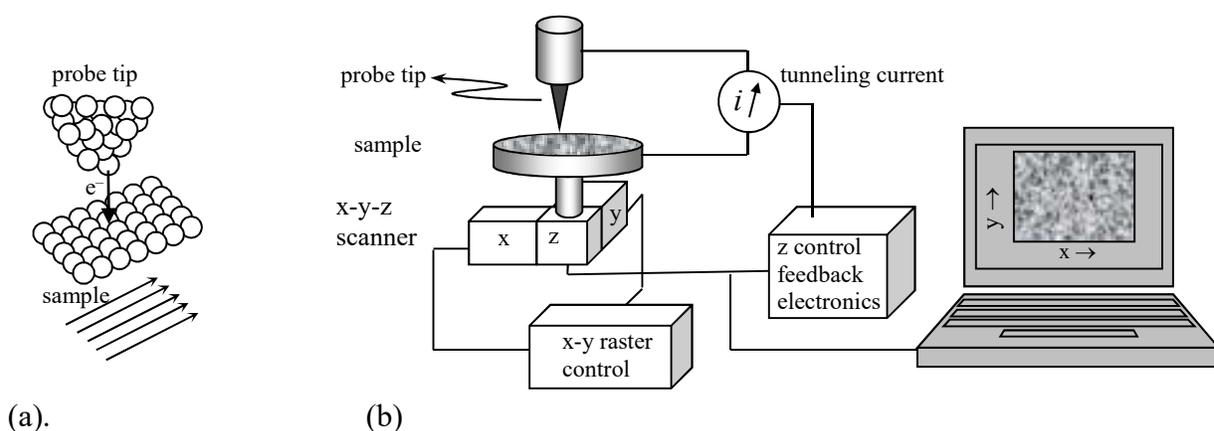


Figure 23.5.2: Scanning Tunneling Microscope. (a). The sample surface is scanned under a sharp metallic tip. (b). The tunneling current is monitored in a closed-loop feedback circuit that adjusts the sample height to maintain a constant tunneling current. The sample height is plotted as a function of position to produce an image.

The z-axis sensitivity is 0.1 \AA and the lateral resolution approaches 1 \AA . The resolution is determined by the sharpness of the tip. The tip is usually made by electrochemically etched tungsten or platinum-iridium alloy wire that has been mechanically sheared to produce a sharp tip. The tunneling current is determined by the tip to sample distance and the **local density of states** of the electronic energy levels.

Consider a two-dimensional particle in a box as an analogy for the surface of a metal. The allowed quantum states are closely spaced for an extended metal surface. The density of states counts the number of quantum states in a given energy range. The larger the number of states, the greater is the tunneling probability. An STM image is a plot of the accessibility of electronic states on the surface for electrons from the sample tip. The STM image of graphite, Figure 23.5.3a, shows a hexagonal lattice for the sheets of carbon atoms, however individual atoms cannot be resolved. Rather the intensity maxima correspond to roughly pairs of atoms. Single-walled carbon nano-tubes show the same graphitic hexagonal pattern, Figure 23.5.3b. Individual

atoms of iron on a copper surface have been imaged under ultra-high vacuum, Figure 23.5.3c. The copper surface inside the rectangle shows the variation of the density of states. The nodal patterns are analogous to the two-dimensional particle in a box wave functions.

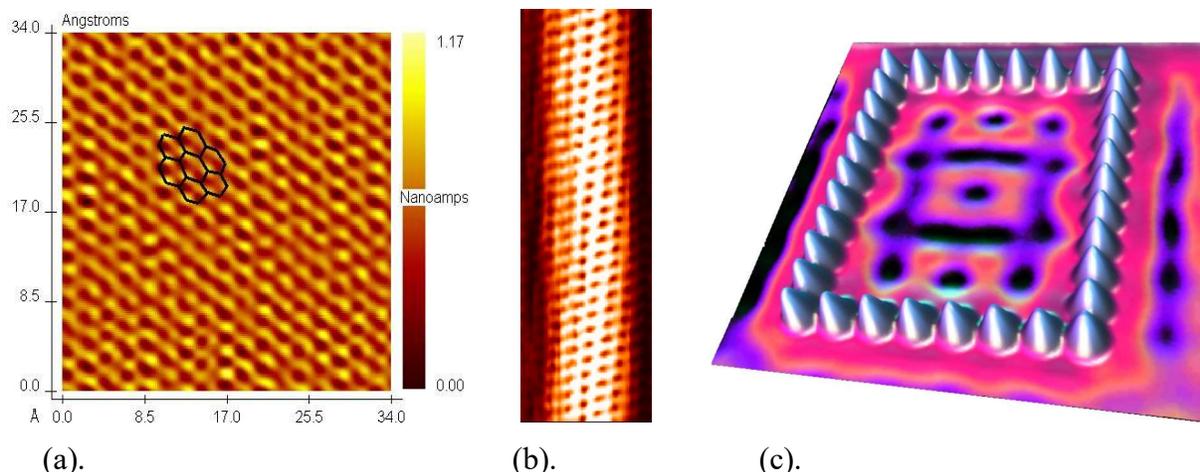


Figure 23.5.3: STM images: (a). Graphite, (b). A single-walled carbon nano-tube (<http://www.ncnr.nist.gov/staff/taner/nanotube/types.html>), (c). Iron atoms on copper. (<http://www.almaden.ibm.com/vis/stm/images/square3.tif>)

23.6 Particle in a 3-Dimensional Box

For Separable Potentials, $\Psi(x,y,z)$ is a Product of One-Dimensional Wave Functions: So far we have focused on one-dimensional problems. Solutions to the Schrödinger equation for several dimensions can often be constructed from one-dimensional wave functions. The 3-dimensional particle in a box is a case in point. The 3-D particle in a box is the model for the translational degree of freedom of atoms and molecules. In three spatial dimensions, the Schrödinger equation for a particle of mass m is:

$$-\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial x^2} \Psi + \frac{\partial^2}{\partial y^2} \Psi + \frac{\partial^2}{\partial z^2} \Psi \right) + \hat{V}(x,y,z)\Psi = E\Psi \quad 23.6.1$$

The curvature of the wave function is given the symbol ∇^2 , which is read as “del-squared”:

$$\nabla^2 = \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \quad 23.6.2$$

The Schrödinger equation is correspondingly written as:

$$-\frac{\hbar^2}{2m} \nabla^2 \Psi + \hat{V}(x,y,z)\Psi = E\Psi \quad 23.6.3$$

For the 3-dimensional particle in a box with side lengths a , b , and c , the potential energy is zero within the box for $0 \leq x \leq a$, $0 \leq y \leq b$, and $0 \leq z \leq c$:

$$-\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial x^2} \Psi + \frac{\partial^2}{\partial y^2} \Psi + \frac{\partial^2}{\partial z^2} \Psi \right) = E \Psi \quad 23.6.4$$

A multi-dimensional wave function can be built up from one dimensional wave functions if the potential energy is separable. The problem is separable if the potential energy can be written as the sum of terms in x, y, and z alone. This requirement is met for this case with zero potential. The 3-dimensional wave function is then the product of one-dimensional wave functions:

$$\Psi(x,y,z) = \Psi_x(x)\Psi_y(y)\Psi_z(z) \quad 23.6.5$$

The one-dimensional wave functions are functions of a single variable. The partial derivatives in the curvature operate on only one variable, the other variables are held constant. For example, the x-derivative gives:

$$\frac{\partial^2}{\partial x^2} \Psi(x,y,z) = \Psi_y(y)\Psi_z(z) \frac{d^2\Psi_x(x)}{dx^2} \quad 23.6.6$$

The final second derivative is a one-dimensional derivative. Completing the derivatives gives:

$$-\frac{\hbar^2}{2m} \left(\Psi_y(y)\Psi_z(z) \frac{d^2\Psi_x(x)}{dx^2} + \Psi_x(x)\Psi_z(z) \frac{d^2\Psi_y(y)}{dy^2} + \Psi_x(x)\Psi_y(y) \frac{d^2\Psi_z(z)}{dz^2} \right) = E\Psi_x(x)\Psi_y(y)\Psi_z(z) \quad 23.6.7$$

This equation is shown to be separable by dividing each term by the product wave function, $\Psi_x(x)\Psi_y(y)\Psi_z(z)$:

$$-\frac{\hbar^2}{2m} \left(\frac{1}{\Psi_x(x)} \frac{d^2\Psi_x(x)}{dx^2} + \frac{1}{\Psi_y(y)} \frac{d^2\Psi_y(y)}{dy^2} + \frac{1}{\Psi_z(z)} \frac{d^2\Psi_z(z)}{dz^2} \right) = E \quad 23.6.8$$

The resulting relationship is the sum of three terms, each a function of only one variable. The particle in the box moves independently in each direction and covers the entire range in each direction. How can the sum of three independent terms always add to give the same value of E? The equation is satisfied over the full range of x, y, and z only if each term is separately equal to a constant. The energy in the x, y, and z directions is given as E_x , E_y , and E_z , respectively:

$$E = E_x + E_y + E_z \quad 23.6.9$$

For separable problems, the one-dimensional wave functions multiply and the energies add. This result will be used repeatedly as we tackle more complex problems. Eq. 23.6.8 then separates into three independent one-dimensional problems:

$$-\frac{\hbar^2}{2m} \frac{1}{\Psi_x(x)} \frac{d^2\Psi_x(x)}{dx^2} = E_x \quad -\frac{\hbar^2}{2m} \frac{1}{\Psi_y(y)} \frac{d^2\Psi_y(y)}{dy^2} = E_y \quad -\frac{\hbar^2}{2m} \frac{1}{\Psi_z(z)} \frac{d^2\Psi_z(z)}{dz^2} = E_z \quad 23.6.10$$

These equations can be recast into familiar form by multiplying through by the corresponding wave function:

$$-\frac{\hbar^2}{2m} \frac{d^2\Psi_x(x)}{dx^2} = E_x \Psi_x(x) \quad -\frac{\hbar^2}{2m} \frac{d^2\Psi_y(y)}{dy^2} = E_y \Psi_y(y) \quad -\frac{\hbar^2}{2m} \frac{d^2\Psi_z(z)}{dz^2} = E_z \Psi_z(z) \quad 23.6.11$$

The results are equivalent to the one-dimensional particle in a box, Eq. 23.4.1, but written in terms of the x, y, and z coordinates. Using Eqs. 23.4.9 and 23.4.16 in each dimension gives:

$$\Psi_x(x) = \left(\frac{2}{a}\right)^{1/2} \sin \frac{n_x\pi x}{a} \quad E_x = \frac{\hbar^2}{8m} \frac{n_x^2}{a^2} \quad 23.6.12$$

$$\Psi_y(y) = \left(\frac{2}{b}\right)^{1/2} \sin \frac{n_y \pi y}{b} \quad E_y = \frac{h^2}{8m} \frac{n_y^2}{b^2} \quad 23.6.13$$

$$\Psi_z(z) = \left(\frac{2}{c}\right)^{1/2} \sin \frac{n_z \pi z}{c} \quad E_z = \frac{h^2}{8m} \frac{n_z^2}{c^2} \quad 23.6.14$$

where n_x , n_y , and n_z are the quantum numbers for the corresponding dimensions. The final 3-D wave function is the product of the one-dimensional wave functions:

$$\Psi(x,y,z) = \left(\frac{8}{abc}\right)^{1/2} \sin \frac{n_x \pi x}{a} \sin \frac{n_y \pi y}{b} \sin \frac{n_z \pi z}{c} \quad 23.6.15$$

and the energy is the sum of the one-dimensional energies:

$$E = E_x + E_y + E_z = \frac{h^2}{8m} \left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2} \right) \quad 23.6.16$$

Each new dimension adds an additional quantum number, compared to the one-dimensional case. For the special case of a cubical box, with side length a , the energy is given by:

$$E = \frac{h^2}{8ma^2} (n_x^2 + n_y^2 + n_z^2) \quad 23.6.17$$

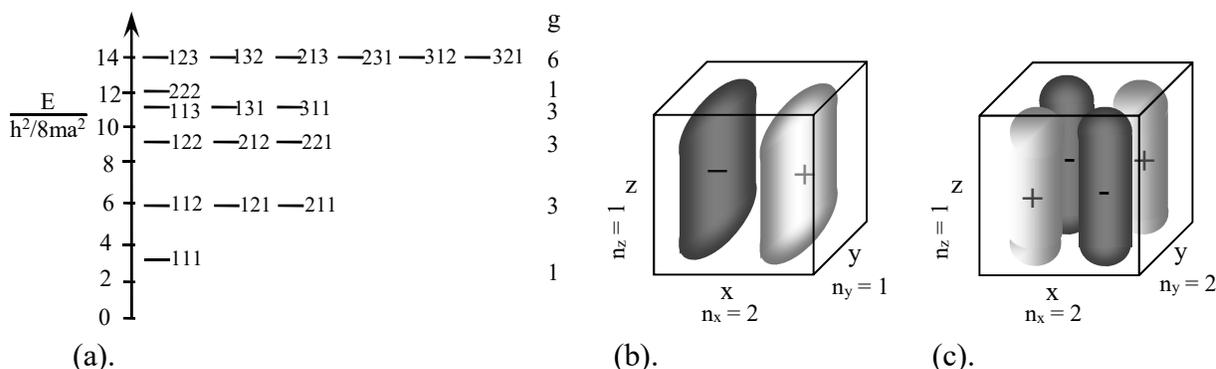


Figure 23.6.1: (a). A 3-D cubical box has degenerate energy levels. (b). The $(n_x, n_y, n_z) = (2, 1, 1)$ wave function has one node in the x -direction and no nodes in the y - and z -directions. The shaded regions are areas of high probability of finding the particle. (c). The $(2, 2, 1)$ wave function has one node in both the x - and y -directions and no nodes in the z -direction.

Many energy levels now have the same energy, Figure 23.6.1. For example, $(n_x, n_y, n_z) = (2, 1, 1)$, $(1, 2, 1)$, and $(1, 1, 2)$ have the same energy. States with the same energy are called degenerate and the degeneracy is listed as g . Degeneracy is a common feature in many quantum mechanical problems. Diagrammatic examples of 3D-wave functions are also shown.

Example 23.6.1: Boltzmann Distribution of Translational Energy Levels

Use the particle in a box model to find the translational energy levels for a helium atom confined in cubical box, in J, kJ mol^{-1} , and cm^{-1} . The size of the cavity inside a C_{60} buckyball roughly

corresponds to a cube, 5.0 Å on a side. Find the relative Boltzmann populations of the first two energy levels for a 5.0 Å side length and a 10.0 cm side length at 298 K.

Answer: For He atoms, $m = 4.003 \text{ g mol}^{-1}(1 \text{ mol}/6.022 \times 10^{23})(1 \text{ kg}/1000 \text{ g}) = 6.647 \times 10^{-27} \text{ kg}$. Using Eq. 23.6.17 then gives for $a = 5.00 \text{ Å}$:

$$E = \frac{(6.626 \times 10^{-34})^2}{8(6.647 \times 10^{-27} \text{ kg})(5.0 \times 10^{-10} \text{ m})^2} (n_x^2 + n_y^2 + n_z^2) = 3.303 \times 10^{-23} \text{ J} (n_x^2 + n_y^2 + n_z^2)$$

$$E N_A (1 \text{ kJ}/1000 \text{ J}) = 0.01989 \text{ kJ mol}^{-1} (n_x^2 + n_y^2 + n_z^2)$$

$$E/hc (1 \text{ m}/100 \text{ cm}) = 1.663 \text{ cm}^{-1} (n_x^2 + n_y^2 + n_z^2)$$

and for 10.0 cm: $\frac{h^2}{8ma^2} = 8.26 \times 10^{-40} \text{ J} = 4.97 \times 10^{-19} \text{ kJ mol}^{-1} = 4.16 \times 10^{-17} \text{ cm}^{-1}$

The lowest energy level is (1,1,1) with $(n_x^2 + n_y^2 + n_z^2) = 3$ and the next energy level is triply degenerate with (1,1,2) and $(n_x^2 + n_y^2 + n_z^2) = 6$. Room temperature corresponds to $kT = 1.38065 \times 10^{-23} \text{ J K}^{-1}(298.2 \text{ K}) = 4.116 \times 10^{-21} \text{ J} = 207.2 \text{ cm}^{-1}$ or $RT = 8.3145 \text{ J K}^{-1} \text{ mol}^{-1}(298.2 \text{ K}) = 2.479 \text{ kJ mol}^{-1}$. Using Eq. 8.10.8 and taking into account the degeneracies, the relative populations of the lowest two energy levels for a 5 Å box is:

$$\frac{n_{(112)(121)(211)}}{n_{(111)}} = 3 e^{-[3.303 \times 10^{-23} \text{ J} (6 - 3)/4.116 \times 10^{-21} \text{ J}]} = e^{-[1.663 \text{ cm}^{-1}(6 - 3)/207.2 \text{ cm}^{-1}]} = 2.93$$

and for the 10.0 cm box: $\frac{n_{(112)(121)(211)}}{n_{(111)}} = 3 e^{-[4.16 \times 10^{-17} \text{ cm}^{-1}(6 - 3)/207.2 \text{ cm}^{-1}]} = 3.000$

Because of degeneracy there are more atoms in the second energy level than the first. The energy spacing is so small for the 10.0 cm box that the levels are essentially continuous, and classical approximations are excellent.

Many of the purely mathematical features that we have been discussing were well known to mathematicians and physicists before the advent of quantum mechanics. The theory of operators and functional analysis provide a rigorous mathematical foundation that we can use as a guide in solving quantum mechanical problems. The theory of quantum mechanics can be summarized in just a few general postulates. We have illustrated these general principles using the free particle and particle in a box as explicit examples.

23.7 The Postulates of Quantum Mechanics

The wave functions for a problem describe the system as completely as possible. The allowed wave functions are the eigenfunctions of the Hamiltonian, $\hat{H}\Psi_n(\mathbf{x}) = E_n \Psi_n(\mathbf{x})$, and the corresponding eigenvalues are the energies. The Hamiltonian, the kinetic energy, the potential energy, and other observables such as the momentum are represented by operators.

Operators Have Properties Independent of the Function They Operate On: An operator is an instruction for action upon a function. As an example, the operator for the derivative of $f(\mathbf{x})$ is to “take the derivative:”

$$\text{with } \hat{o} = \frac{d}{dx} \quad \hat{o} f(x) = \frac{df(x)}{dx} \quad 23.7.1$$

With \hat{o} operating on the function $f(x)$, the result is “take the derivative” of $f(x)$. Operators are symbolized with a “^”. The concept of an operator may, at first, seem unnecessary. However, operators have properties, apart from the functions that they act upon. The properties greatly simplify problem solving. The quantum mechanical Hamiltonian is the operator that corresponds to the total energy. The operator corresponding to the momentum in one-dimension is:

$$\hat{p} = \frac{\hbar}{i} \left(\frac{d}{dx} \right) = -i\hbar \left(\frac{d}{dx} \right) \quad 23.7.2$$

Multiplication of a function can also be considered as an operator. In determining the expectation value for the position of the particle in the particle in a box, Eqs. 23.4.25 and 23.4.26, the position operator is “multiply by x”:

$$\text{with } \hat{x} = x \cdot \quad \hat{x} \Psi(x) = x \Psi(x) \quad 23.7.3$$

Operators have properties independent of the wave function upon which they operate.

One important class of operators is **linear operators**. For functions $f(x)$ and $g(x)$ and constants a and b , a linear operator gives:

$$\hat{o} (a f(x) + b g(x)) = a \hat{o} f(x) + b \hat{o} g(x) \quad 23.7.4$$

Taking derivatives and multiplication by a function are linear operators. The position operator is a linear operator. A sum of linear operators is also a linear operator. So the Hamiltonian is a linear operator. In contrast, absolute value and square root are not linear, $|a+b| \neq |a| + |b|$ and $\sqrt{a+b} \neq \sqrt{a} + \sqrt{b}$. Linear behavior has important consequences for the operators in quantum mechanics.

Example 23.7.1: The Hamiltonian is a Linear Operator

Consider two degenerate wave functions as particular solutions to the Schrödinger equation, $\hat{H}\Psi_n = E\Psi_n$ and $\hat{H}\Psi_m = E\Psi_m$. Prove that the linear combination of two degenerate solutions to the Schrödinger equation is also a solution.

Answer: This property is guaranteed because the Hamiltonian is a linear operator:

$$\hat{H}(a\Psi_n + b\Psi_m) = a\hat{H}\Psi_n + b\hat{H}\Psi_m \quad 23.7.5$$

Then using the fact that Ψ_n and Ψ_m are separately eigenfunctions of the Hamiltonian gives:

$$\hat{H}(a\Psi_n + b\Psi_m) = a\hat{H}\Psi_n + b\hat{H}\Psi_m = a E\Psi_n + b E\Psi_m = E(a\Psi_n + b\Psi_m) \quad 23.7.6$$

We used this property in the solution of the free particle and particle in a box problems when we stated that the linear combination of the particular solutions is a general solution to the Schrödinger equation. The Euler identity is one specific linear combination.

The Order of Operations Can Make a Difference: Operators do not necessarily commute, so the order of operations is important. For example, consider the two operators $\hat{o}_1 = d/dx$ and $\hat{o}_2 = x \cdot$ and the function $f(x) = 6x$. For the product of two operators, $\hat{o}_1 \hat{o}_2 f(x)$, the right-most operator is applied first. Applying the two operators in either order gives different results:

$$\begin{aligned}\hat{o}_1 \hat{o}_2 f(x) &= \frac{d}{dx} x \cdot f(x) = \frac{d}{dx} 6x^2 = 12x \\ \hat{o}_2 \hat{o}_1 f(x) &= x \cdot \frac{d}{dx} f(x) = x \cdot \frac{d}{dx} 6x = 6x\end{aligned}\tag{23.7.7}$$

The derivative operator and multiplication by x do not commute. The lack of commutivity, in general, is the reason that the order of operations in the integral for expectations values, Eq. 23.4.24, is specific. The **commutator** of two operators is defined as:

$$[\hat{o}_1, \hat{o}_2] = \hat{o}_1 \hat{o}_2 - \hat{o}_2 \hat{o}_1\tag{23.7.8}$$

If the commutator is non-zero then the order of operations is important. Commutators can often be assigned values that are independent of the functions upon which they operate.

Example 23.7.2: *The Commutation Relationship for Position and Momentum*

Find the commutator for the position and momentum of a particle in one-dimension, $[\hat{x}, \hat{p}_x]$.

Answer: The approach is to apply the commutator as an operator for an arbitrary function, $f(x)$. The commutator is $[\hat{x}, \hat{p}_x] = (\hat{x} \hat{p}_x - \hat{p}_x \hat{x})$. The operator for position is just “multiply by x ”: $\hat{x} = x \cdot$. The operator for momentum is $\hat{p}_x = (\hbar/i)(d/dx)$. With $f(x)$ as an arbitrary function of x :

$$[\hat{x}, \hat{p}_x] f = (x \hat{p}_x - \hat{p}_x x) f = x \hat{p}_x f - \hat{p}_x x f = (\hbar/i) \left(x \frac{df}{dx} - \frac{d(xf)}{dx} \right)$$

Using the product rule for the last derivative:

$$[\hat{x}, \hat{p}_x] f = (\hbar/i) \left(x \frac{df}{dx} - x \frac{df}{dx} - f \frac{dx}{dx} \right) = -(\hbar/i) f$$

Dividing both sides of this expression by f gives the final result:

$$[\hat{x}, \hat{p}_x] = -(\hbar/i)\tag{23.7.9}$$

This result holds for any wave function, which shows the usefulness of operator relationships.

Quantum mechanical systems are characterized by five postulates, which apply to all quantum mechanical problems.^{3,4} Different problems use different coordinate systems. To make the postulates more general, we specify the volume element in general terms, $d\tau$, and the integrals are over all space for each dimension. For example, for one Cartesian dimension $d\tau = dx$ and for three-dimensions $d\tau = dx dy dz$. For rotation in a plane with angle ϕ , $d\tau = d\phi$, with $0 \leq \phi \leq 2\pi$.

I. The physical state of the system is described by a wave function as completely as possible. The wave function is derived from an orthonormal set of eigenfunctions of the Hamiltonian. The normalization integral is $\int \Psi_n^* \Psi_n d\tau = 1$ and the orthogonality integral is $\int \Psi_n^* \Psi_m d\tau = 0$.

II. Any observable may be represented by a linear operator. The results should be a real number. The least restrictive requirement is that the operator must be Hermitian:

$$\int \Psi_j^* \hat{o} \Psi_i d\tau = \int \Psi_i (\hat{o} \Psi_j)^* d\tau = \int \Psi_i \hat{o}^* \Psi_j^* d\tau \quad 23.7.10$$

The observable operator is constructed from the following table.

Table 23.7.1: The Correspondence of Quantum Mechanical Operators with Classical Observables.

Classical	Quantum Operator
x	\hat{x}
p	$\hat{p} = \frac{\hbar}{i} \left(\frac{\partial}{\partial x} \right) = -i\hbar \left(\frac{\partial}{\partial x} \right)$
t	\hat{t}
E vs. time	$\hat{E} = i\hbar \left(\frac{\partial}{\partial t} \right)$

III. If the wave function is an eigenfunction of the observable, repeated measurements of the observable always give the same result. The repeated result is the eigenvalue; if $\hat{o} \Psi = o \Psi$ then each measurement gives the result, o.

(See for example the momentum of a free particle, Eq. 23.4.23.)

IV. If the wave function is not an eigenfunction of the observable, the measurement gives a different result each time. The “average” or expectation value is given by:

$$\langle o \rangle = \frac{\int_{-\infty}^{\infty} \Psi_n^* \hat{o} \Psi_n d\tau}{\int_{-\infty}^{\infty} \Psi_n^* \Psi_n d\tau} \quad (23.4.24) \quad 23.7.11$$

(See for example the position and momentum of a particle in a box, Eqs. 23.4.30 and 23.4.34.)

V. The wave function evolves in time according to:

$$\hat{H}\Psi(x,t) = i\hbar \left(\frac{\partial \Psi(x,t)}{\partial t} \right) \quad 23.7.12$$

Example 23.7.3: Potential Energy Operator for the Harmonic Oscillator

Give the quantum mechanical operator for the potential energy of the harmonic oscillator in terms of the displacement, $x = r - r_o$, where r_o is the equilibrium bond length.

Answer: The classical potential for a harmonic oscillator is $V(x) = \frac{1}{2} kx^2$. Since the classical operator involves only multiplications, Table 23.7.1 shows the quantum mechanical operator has the same form with x replaced by the operator \hat{x} : $\hat{V}(x) = \frac{1}{2} k\hat{x}^2$. The action of $V(x)$ on a wave function is then simply $\hat{V}(x)\Psi = \frac{1}{2} k\hat{x}^2 \Psi = \frac{1}{2} kx^2 \Psi$. The potential energy operator is a Hermitian, linear operator. All the potential energy operators that we will need for our study of atomic and molecular structure and spectroscopy are multiplicative, so the classical and quantum operators are equivalent.

The Eigenvalues for Quantum Mechanical Operators are Real: The Hermitian property guarantees that eigenvalues for operators corresponding to quantum mechanical observables are real. To prove that the eigenvalues of Hermitian operators are real, consider the Hermitian operator \hat{o} and one of its eigenfunctions Ψ_n :

$$\hat{o} \Psi_n = o \Psi_n \quad 23.7.13$$

To show that the eigenvalue is real we need to show that $o^* = o$. Multiplication of Eq. 23.7.13 from the left by Ψ_n^* and integration over all space in one-dimension gives:

$$\int \Psi_n^* \hat{o} \Psi_n dx = \int \Psi_n^* o \Psi_n dx = o \int \Psi_n^* \Psi_n dx \quad 23.7.14$$

where the eigenvalue factors in front of the integral because it is a constant. Now we need to work on o^* . The complex conjugate of Eq. 23.7.13 is:

$$\hat{o}^* \Psi_n^* = o^* \Psi_n^* \quad 23.7.15$$

Multiplication of the last equation from the left by Ψ_n and integration over all space gives:

$$\int \Psi_n \hat{o}^* \Psi_n^* dx = \int \Psi_n o^* \Psi_n^* dx = o^* \int \Psi_n \Psi_n^* dx \quad 23.7.16$$

Given that \hat{o} is Hermitian, by Eq. 23.7.10, $\int \Psi_n^* \hat{o} \Psi_n dx = \int \Psi_n \hat{o}^* \Psi_n^* dx$. Then Eqs. 23.7.14 and 23.7.16 are equal:

$$o \int \Psi_n^* \Psi_n dx = o^* \int \Psi_n \Psi_n^* dx \quad 23.7.17$$

The wave function is just a function, so the order does not matter, $\int \Psi_n^* \Psi_n dx = \int \Psi_n \Psi_n^* dx$. The integrals cancel from both sides of Eq 23.7.17 giving $o = o^*$. The eigenvalues of Hermitian operators are real, therefore the eigenvalues for quantum mechanical observables are real.

Example 23.7.4: The Momentum Operator is Hermitian

Show that the momentum operator is Hermitian.

[Hint: use integration by parts: $\int u dv = uv - \int v du$]

Answer: The goal is to show that:

$$\int_{-\infty}^{\infty} \Psi_j^* \left(-i\hbar \frac{d}{dx} \right) \Psi_i dx = \int_{-\infty}^{\infty} \Psi_i \left(-i\hbar \frac{d}{dx} \right)^* \Psi_j^* dx \quad 23.7.18$$

Starting with the left hand integral:

$$\int_{-\infty}^{\infty} \Psi_j^* \left(-i\hbar \frac{d}{dx} \right) \Psi_i dx = -i\hbar \int_{-\infty}^{\infty} \Psi_j^* d\Psi_i \quad 23.7.19$$

Integration by parts, with $u = \Psi_j^*$ and $dv = d\Psi_i$, gives:

$$-i\hbar \int_{-\infty}^{\infty} \Psi_j^* d\Psi_i = -i\hbar \left[\Psi_j^* \Psi_i \Big|_{x=-\infty}^{x=\infty} - \int_{-\infty}^{\infty} \Psi_i d\Psi_j^* \right] \quad 23.7.20$$

For a confined particle, the product $\Psi_j^* \Psi_i$ goes to zero at each endpoint, since the wave function approaches zero for long distances. Substituting this last equation back into Eq. 23.7.19 gives:

$$\int_{-\infty}^{\infty} \Psi_j^* \left(-i\hbar \frac{d}{dx} \right) \Psi_i dx = i\hbar \int_{-\infty}^{\infty} \Psi_i d\Psi_j^* = \int_{-\infty}^{\infty} \Psi_i \left(i\hbar \frac{d}{dx} \right) \Psi_j^* dx \quad 23.7.21$$

Finally, $(-i\hbar d/dx)^* = (i\hbar d/dx)$ so that the last equation reduces to Eq. 23.7.18. The “i” in the definition of the momentum is necessary for the momentum operator to be Hermitian.

The Time Dependent Schrödinger Equation is Separable for Time-Independent Potentials: The potential energy operator may change as a function of time. For example, the atoms in a chemical reaction follow a trajectory that results in changing Coulomb interactions. The time dependent Schrödinger equation is:

$$-\frac{\hbar^2}{2m} \nabla^2 \Psi + \hat{V}(x,y,z,t) \Psi = i\hbar \left(\frac{\partial \Psi(t)}{\partial t} \right) \quad 23.7.22$$

On the right side of the equation, the time dependent energy operator is given from Table 23.7.1 as $\hat{E} \Psi = i\hbar (\partial \Psi / \partial t)$. The spatial coordinates are held constant for the partial derivative with respect to time. For the determination of the translational, rotational, vibrational, and electronic states of isolated atoms or molecules, the potential energy operator is independent of time, $\hat{V}(x,y,z,t) = \hat{V}(x,y,z)$. The Schrödinger equation is then separable; the solution with respect to time is independent of the spatial coordinates. For the separable case, the wave function is given as the product of a spatially dependent wave function multiplied by a time dependent wave function:

$$\Psi(x,y,z,t) = \Psi(x,y,z) \Psi(t) \quad 23.7.23$$

Review the treatment of the 3D-particle in a box for the procedure in separable cases. The curvature operator, ∇^2 , is only a function of the spatial coordinates, $\nabla^2 \Psi(x,y,z) \Psi(t) = \Psi(t) \nabla^2 \Psi(x,y,z)$. The time dependent energy operator is only a function of the time, $\hat{E} \Psi(x,y,z) \Psi(t) = \Psi(x,y,z) \hat{E} \Psi(t)$. Eq. 23.7.22 then simplifies to:

$$\frac{1}{\Psi(x,y,z)} \left(-\frac{\hbar^2}{2m} \nabla^2 \Psi(x,y,z) + \hat{V}(x,y,z) \Psi(x,y,z) \right) = \frac{1}{\Psi(t)} i\hbar \left(\frac{\partial \Psi(t)}{\partial t} \right) \quad 23.7.24$$

The terms on the left are only a function of the spatial coordinates. The term on the right is only a function of time. The spatial operators comprise the time independent Hamiltonian in 3-dimensions, Eqs. 23.4.18 and 23.6.1:

$$\frac{1}{\Psi(x,y,z)} \hat{H}\Psi(x,y,z) = \frac{1}{\Psi(t)} i \hbar \left(\frac{\partial \Psi(t)}{\partial t} \right) \quad 23.7.25$$

The only way that the spatial terms and the time dependent term may be equal, for all values of the spatial coordinates and for all times, is for each side to separately equal a constant. The constant is the total energy. The problem then separates into two equations, one in the spatial coordinates and one in time only:

$$\frac{1}{\Psi(x,y,z)} \left(\frac{-\hbar^2}{2m} \nabla^2 \Psi(x,y,z) + \hat{V}(x,y,z) \Psi(x,y,z) \right) = E \quad 23.7.26$$

$$E = \frac{1}{\Psi(t)} i \hbar \left(\frac{\partial \Psi(t)}{\partial t} \right) \quad 23.7.27$$

Time independent Eq. 23.7.26 is the basis for the previous sections in this chapter, $\hat{H}\Psi = E\Psi$. We need to solve the time dependent equation only once. The form of the time dependence applies to any problem with a time independent potential energy operator. Multiplying Eq. 23.7.27 through by the wave function gives:

$$i\hbar \left(\frac{\partial \Psi(t)}{\partial t} \right) = E \Psi(t) \quad 23.7.28$$

We can separate variables in the same fashion as in chemical kinetics by dividing both sides of the equation by $\Psi(t)$ and multiplying by dt :

$$\frac{d\Psi(t)}{\Psi(t)} = \frac{E}{i\hbar} dt \quad \text{or} \quad \frac{d\Psi(t)}{\Psi(t)} = -\frac{iE}{\hbar} dt \quad 23.7.29$$

Integrating both sides of the last equation gives:

$$\ln \Psi(t) = -\frac{iE}{\hbar} t \quad 23.7.30$$

Exponentiating both sides solves for the wave function:

$$\Psi(t) = e^{-iEt/\hbar} \quad 23.7.31$$

The complete wave function is the product of the spatial and time dependent parts, Eq. 23.7.23:

$$\Psi(x,y,z,t) = \Psi(x,y,z) e^{-iEt/\hbar} \quad 23.7.32$$

The time dependent wave function is the same for any translational, rotational, vibrational, or electronic wave function for any isolated atom or molecule. We can gain further insight into the time dependence by expanding the complex exponential using the Euler identity:

$$e^{-iEt/\hbar} = \cos\left(\frac{Et}{\hbar}\right) - i \sin\left(\frac{Et}{\hbar}\right) \quad 23.7.33$$

$$\begin{array}{ccc} \uparrow & & \uparrow \\ \cos 2\pi\nu t & + & i \sin 2\pi\nu t \end{array}$$

Comparing the time dependence to the general form of an oscillating function gives the frequency as:

$$2\pi\nu = \frac{E}{\hbar} \quad \text{or} \quad E = h\nu \quad 23.7.34$$

Of course, $E = h\nu$ is the familiar Planck formula. Eqs. 23.7.22-23.7.34 provide a rigorous derivation of the Planck relationship. In subsequent chapters we will work primarily with time independent potentials, so we will usually not mention the time dependent part of the complete wave function. Mentioned or not, the complete wave function always oscillates in time with the frequency given by $E = h\nu$. For example, for the $n = 2$ state of the particle in a box, the wave function oscillates in time as shown in Figure 23.7.1.

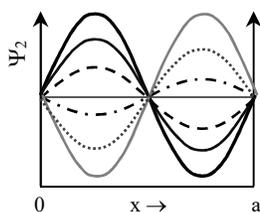


Figure 23.7.1: The time dependence for time independent potential energy operators is oscillation with the frequency given by $E = h\nu$. The $n = 2$ wave function for the particle in a box is shown in successive time snapshots.

Complementary Observables Obey an Uncertainty Relationship: To finish our overview of the properties of quantum mechanical systems, we need to make one final connection between uncertainty relationships and the commutator for two observable properties. Commuting observables can be simultaneously specified with arbitrary precision. If the operators for two observables do not commute then the observables cannot be simultaneously specified to arbitrary precision. A generalized Heisenberg uncertainty relationship is then defined by:

$$\sigma_A \sigma_B \geq \left| \frac{1}{2i} \int \Psi^* [\hat{A}, \hat{B}] \Psi \, dx \right| \quad 23.7.35$$

where $||$ is the absolute value. The uncertainty relationship for position and momentum is a special case of the more general principle. The commutator for position and momentum is given by Eq. 23.7.9, $[\hat{x}, \hat{p}_x] = -(\hbar/i)$. Substitution of the commutator into Eq. 23.7.35 for a normalized wave function gives $\sigma_x \sigma_{p_x} \geq \hbar/2$. At this point you might have the feeling that quantum mechanics is very strange. Quantum mechanics is weird, but is it that weird?

Does Quantum Mechanics Work? The Correspondence Principle: The picture of the microscopic world presented by quantum mechanics is often unexpected. However, to be useful and meaningful we must require that when quantum solutions are scaled to macroscopic size, quantum solutions should agree with classical physics. For example, consider a particle in a box in the ground state. The most probable position for a particle in a box, for $n = 1$, is in the middle of the box. Consider a classical ball rolling in a macroscopic box with a fixed kinetic energy. The ball rolls between the two walls where collisions occur and the momentum reverses sign upon each collision. In the middle of the box the momentum and velocity of the ball are constant, giving a uniform probability of finding the ball at any position. For the ground state, the quantum and classical views are very different. However, if we take the **classical limit** of the quantum

mechanical problem by letting the quantum number approach infinity, then the quantum solution should agree with classical expectations. For the particle in a box, the number of nodes increases as $n \rightarrow \infty$, so that the peaks in the probability distribution merge to give a constant probability in agreement with classical expectations, Figure 23.7.2

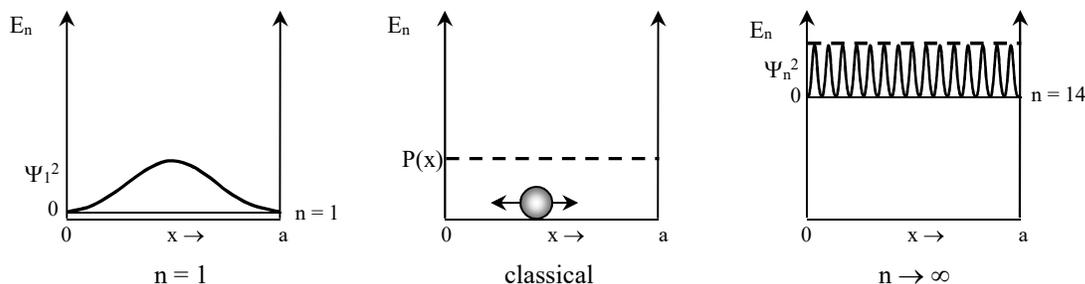


Figure 23.7.2: The Correspondence Principle: In the classical limit, $n \rightarrow \infty$, quantum mechanical expressions should agree with classical expectations.

23.8 Summary – Looking Ahead

The view of the microscopic world presented by quantum mechanics is strikingly different from our everyday experience. The wave behavior of particles is the central insight in thinking quantum mechanically. Consider the $n = 2$ level of the particle in a box with its central node, Figure 23.7.1. The node is a point with zero probability of finding the particle. Students often ask how the particle is able to pass from one side of the node to the other. The answer is that the particle is on both sides of the node at the same time. The particle doesn't need to pass through the node. The particle acts as a wave and waves are diffuse by nature. An analogy is a wave on a pond. A wave on the surface of the water is delocalized over a large area. The wave is at many positions at once.

The wave nature of particles results in an inherent uncertainty in the observable properties of the system. This uncertainty is unavoidable. Better instruments cannot decrease the inherent uncertainty given by the Heisenberg uncertainty relationship. The fundamental inability to measure a property accurately is perhaps the most important departure from classical mechanics. In classical mechanics the trajectory of a particle can be precisely known. The wave behavior of particles places fundamental limits on our ability to measure the properties of the system. Even so, quantum mechanics gives us an excellent ability to predict the properties of a system within those fundamental limits. Consider a schematic experiment that uses light scattering to determine the position of a free electron, Figure 23.8.1. Initially the momentum of the free electron is precisely given by $p = \hbar k$. However, after a collision with a photon the momentum of the particle is changed, to conserve momentum. The act of observation changes the properties of the system. To localize the particle, the momentum of the particle necessarily becomes uncertain. The important insight from quantum mechanics is that the observer is not separated from the experiment. We cannot observe the world without changing the properties we are trying to measure. Philosophers in the 19th century believed that scientists were dispassionate objective observers, separated from nature. We now understand that humans and the environment are intricately interrelated. People are inseparable from their surroundings.

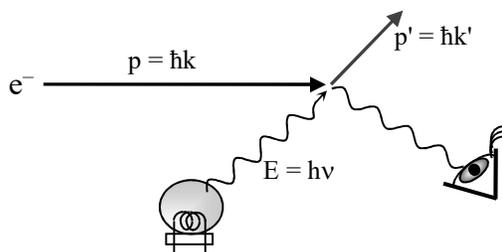


Figure 23.8.1: The act of observation changes the system. Conservation of momentum requires that the momentum of the particle change after the collision with an observing photon. Neither the position nor the momentum are then precisely known.

In the next chapter we develop the theory of the quantum mechanical harmonic oscillator and the rigid rotor. The harmonic oscillator is a model for molecular vibration and infrared spectroscopy. The rigid rotor is a model for molecular rotation and microwave spectroscopy. Our focus then shifts to the electronic structure of atoms and molecules, which provides the theory of the chemical bond and electronic spectroscopy. The foundations represented by the postulates of quantum mechanics are the key to understanding the microscopic world.

23.9 Addendum: Complex Variables

The physical properties of systems are often conveniently represented by complex numbers and functions. All laboratory observations must be real quantities; however, complex variables allow phase relationships to be easily expressed. A complex number, $z = a + ib$, has a real and imaginary part with $i = \sqrt{-1}$ and $i^2 = -1$:

$$z = a + ib \quad \text{with } \text{Re}(z) = a \quad \text{and} \quad \text{Im}(z) = b \quad 23.9.1$$

Complex variables are conveniently diagrammed as a vector with the real part plotted along the horizontal axis and the imaginary part plotted along the vertical axis, Figure 23.9.1a. A purely real value and a purely complex value are related by a 90° phase difference.

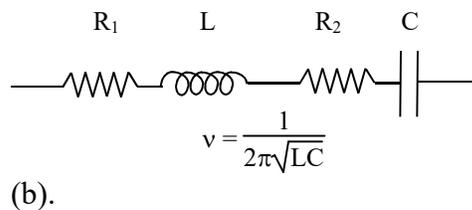
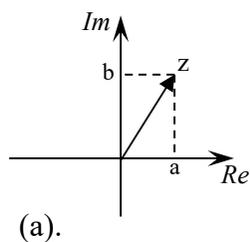


Figure 23.9.1: (a). A complex number is represented as a vector with components along the real and imaginary axes. (b). A series inductor and capacitor have a resonance when the imaginary parts of the impedances cancel.

For example, the phase difference between the excitation and response in spectroscopy is 90° . For another example, the resistance and inductive reactance in an electronic circuit differ by $+90^\circ$ and the resistance and capacitive reactance differ by -90° :

$$\text{resistance and inductance} \quad z_1 = R_1 + i 2\pi\nu L \quad 23.9.2$$

$$\text{resistance and capacitance} \quad z_2 = R_2 - i \frac{1}{2\pi\nu C} \quad 23.9.3$$

A series inductor and capacitor are in resonance when the combined impedance is purely real:

$$z = R_1 + i 2\pi\nu L + R_2 - i \frac{1}{2\pi\nu C} = R_1 + R_2 \quad \text{with} \quad \frac{1}{2\pi\nu C} = 2\pi\nu L \quad \text{or} \quad \nu = \frac{1}{2\pi\sqrt{LC}} \quad 23.9.4$$

NMR probes are made from an LC circuit at resonance. The inductor is just a coil of wire. The sample sits inside the inductor, which acts as a radio-frequency antenna.

The algebra of complex quantities is accomplished by keeping the imaginary terms separate from the real terms:

$$z_1 + z_2 = (a_1 + i b_1) + (a_2 + i b_2) = (a_1 + a_2) + i (b_1 + b_2) \quad 23.9.5$$

$$z_1 z_2 = (a_1 + i b_1)(a_2 + i b_2) = a_1 a_2 + i a_1 b_2 + i b_1 a_2 + i^2 b_1 b_2 = (a_1 a_2 - b_1 b_2) + i(a_1 b_2 + b_1 a_2)$$

The complex conjugate of a complex number, indicated by a “*”, is obtained by changing the sign in front of every i:

$$\text{if } z = a + i b \quad \text{then} \quad z^* = a - i b \quad \text{if } z = e^{i\phi} \quad \text{then} \quad z^* = e^{-i\phi} \quad 23.9.6$$

The “size” or “length” or **magnitude** or **norm** of a complex number is given by:

$$|z| = \sqrt{z^* z} \quad 23.9.7$$

The complex conjugate is necessary to ensure the result is real:

$$|z| = \sqrt{z^* z} = \sqrt{(a - ib)(a + ib)} = \sqrt{a^2 + b^2} \quad 23.9.8$$

as expected from the Pythagorean theorem. For complex functions, the norm is given by $|\Psi| = (\int_{-\infty}^{\infty} \Psi^* \Psi dx)^{1/2}$. For a normalized function, the magnitude or norm is equal to one.

The Euler identity gives the relationship of the real and imaginary parts of a complex number as a phase angle, Figure 23.9.2a:

$$e^{i\phi} = \cos \phi + i \sin \phi \quad 23.9.9$$

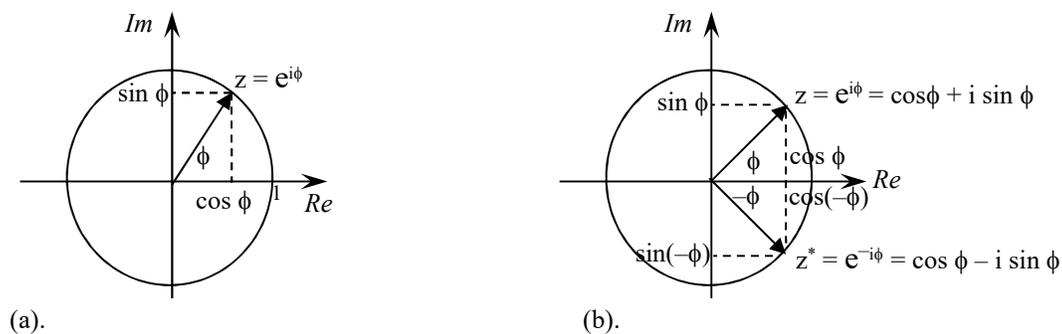


Figure 23.9.2: (a). The Euler identity expresses the relationship of the real and imaginary parts as a phase angle, ϕ . The vector lies on the unit circle. (b). The cosine of a negative angle is unchanged and the sine of a negative angle changes sign.

The complex conjugate of $e^{i\phi}$ occurs often. Note that $\cos(-\phi) = \cos \phi$ and that $\sin(-\phi) = -\sin \phi$, Figure 23.9.2b. The complex conjugate of $e^{i\phi}$ is then:

$$(e^{i\phi})^* = e^{-i\phi} = \cos(-\phi) + i \sin(-\phi) = \cos \phi - i \sin \phi \quad 23.9.10$$

as expected by changing the sign in front of the i in Eq. 23.9.9. The real and imaginary parts of a complex exponential wave function are given using Eq. 23.9.10 as:

$$\text{real part: } \cos \phi = \frac{1}{2} (e^{i\phi} + e^{-i\phi}) \quad \text{imaginary part: } \sin \phi = \frac{1}{2i} (e^{i\phi} - e^{-i\phi}) \quad 23.9.11$$

Example 23.9.1: *The Magnitude of $e^{i\phi}$*

Find the magnitude of $e^{i\phi}$.

Answer: Using the Euler identity, the square of the magnitude of $e^{i\phi}$ is given using Eq. 23.9.10:

$$|e^{i\phi}|^2 = (e^{i\phi})^* e^{i\phi} = (\cos \phi - i \sin \phi)(\cos \phi + i \sin \phi) = \cos^2 \phi + \sin^2 \phi = 1$$

Alternatively, using the exponential form directly: $|e^{i\phi}|^2 = (e^{i\phi})^* e^{i\phi} = e^{-i\phi} e^{i\phi} = e^0 = 1$.

For an equivalent point of view, the graphical vector representation of $e^{i\phi}$ shows the vector lying on the unit circle, Figure 23.9.2.

The Euler identity may be proved by expanding $\cos \phi$, $\sin \phi$, and $e^{i\phi}$ as Taylor series. From Addendum 1.5:

$$e^{i\phi} = 1 + i\phi + \frac{1}{2!} (i\phi)^2 + \frac{1}{3!} (i\phi)^3 + \frac{1}{4!} (i\phi)^4 + \dots + \frac{1}{n!} (i\phi)^n \quad 23.9.12$$

and the trigonometric functions expand as:

$$\sin \phi = \phi - \frac{1}{3!} \phi^3 + \frac{1}{5!} \phi^5 - \dots + (-1)^n \frac{1}{(2n+1)!} \phi^{2n+1} \quad 23.9.13$$

$$\cos \phi = 1 - \frac{1}{2!} \phi^2 + \frac{1}{4!} \phi^4 - \dots + (-1)^n \phi^{2n} \quad 23.9.14$$

Multiplying the sine expansion by i gives:

$$i \sin \phi = i\phi - \frac{1}{3!} i\phi^3 + \frac{1}{5!} i\phi^5 - \dots + (-1)^n \frac{1}{(2n+1)!} i\phi^{2n+1} \quad 23.9.15$$

Noting that $i \cdot i = -1$ gives:

$$i \sin \phi = i\phi + \frac{1}{3!} (i\phi)^3 + \frac{1}{5!} (i\phi)^5 + \dots + \frac{1}{(2n+1)!} (i\phi)^{2n+1} \quad 23.9.16$$

$$\cos \phi = 1 + \frac{1}{2!} (i\phi)^2 + \frac{1}{4!} (i\phi)^4 + \dots + \frac{1}{(2n)!} (i\phi)^{2n} \quad 23.9.17$$

Combining the $\cos \phi$ and $(i \sin \phi)$ expansions, Eqs. 23.9.16 and 23.9.17, gives:

$$\cos \phi + i \sin \phi = 1 + i\phi + \frac{1}{2!} (i\phi)^2 + \frac{1}{3!} (i\phi)^3 + \frac{1}{4!} (i\phi)^4 + \frac{1}{5!} (i\phi)^5 + \dots \quad 23.9.18$$

which is the same expansion as for $e^{i\phi}$, Eq. 23.9.12.

Chapter Summary

1. Wave-like behavior in time and distance are, respectively:

$$f(t) = A \sin 2\pi vt + B \cos 2\pi vt \quad \text{and} \quad f(x) = A \sin 2\pi x/\lambda + B \cos 2\pi x/\lambda$$

2. The Euler identity allows phase relationships to be treated in algebraic equations:

$$e^{i\phi} = \cos \phi + i \sin \phi \quad \text{and} \quad e^{i2\pi vt} = \cos 2\pi vt + i \sin 2\pi vt \quad \text{where } i = \sqrt{-1}$$

3. The Bragg equation for constructive interference and diffraction is $n\lambda = d \cos \theta$, for n an integer, λ the wave length of the diffracted light or particle, d the spacing between diffracting centers or slits, and θ the diffraction angle.

4. Planck postulated the energy levels in matter are quantized in units of $h = 6.62608 \times 10^{-34}$ J s: $E_n = n h \nu$ or $E_n = n \hbar \omega$, with angular frequency $\omega = 2\pi \nu$ and $\hbar = h/2\pi = 1.05457 \times 10^{-34}$ J s.

5. The blackbody intensity per unit wavelength increment is: $I(\lambda) = \frac{2\pi hc^2}{\lambda^5} \left(\frac{1}{e^{hc/kT\lambda} - 1} \right)$

6. The total light flux emitted from the blackbody is the integral over the spectrum: $J = \sigma T^4$.

7. For incident frequency ν , metal work function Φ , and ejected kinetic energy $E_k = \frac{1}{2} m_e \nu^2$, the Einstein photoelectric effect relationship is:

$$E = h\nu = E_k + \Phi = \frac{1}{2} m_e \nu^2 + \Phi \quad (\Phi \text{ in joules}) \quad \text{or} \quad \Phi = e\Gamma \quad (\Gamma \text{ in volts})$$

8. Photon energy, frequency, wave length, and wavenumber are related by: $E = h\nu = hc/\lambda = hc\tilde{\nu}$.

9. All objects have a wave-particle duality with momentum and wavelength related by the de Broglie relationship: $p = h/\lambda$.

10. Spectroscopic transitions in one-electron atoms and ions are related by the Rydberg formula:

$$\tilde{\nu} = \mathfrak{R}_h \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right) \quad \text{for hydrogen, } ^1\text{H, } \mathfrak{R}_h = 109677.5 \text{ cm}^{-1}$$

11. The Coulomb potential, with nuclear charge Ze and electron charge $-e$, is:

$$V(r) = -\frac{Ze^2}{4\pi\epsilon_0 r} \quad \text{with } \epsilon_0 = 8.85419 \times 10^{-12} \text{ J}^{-1} \text{ C}^2 \text{ m}^{-1} \text{ and } Z = 1 \text{ for } ^1\text{H or } ^2\text{H}$$

12. For the Bohr model of the hydrogen atom, the circumference must be an integer multiple of the wave length, $2\pi r = n\lambda$, giving the energy for principle quantum number n as:

$$E_n = -\frac{e^4 m_e}{32\pi^2 \epsilon_0^2 \hbar^2} \left(\frac{Z^2}{n^2} \right) = -109737.2 \text{ cm}^{-1} \left(\frac{Z^2}{n^2} \right) = -13.606 \text{ eV} \left(\frac{Z^2}{n^2} \right) = -1312.749 \text{ kJ mol}^{-1} \left(\frac{Z^2}{n^2} \right)$$

13. The radius of the first-Bohr orbit is: $a_0 = \frac{4\pi\epsilon_0 \hbar}{m_e e^2} = 0.5291772 \text{ \AA}$.

14. Electronic transitions in the Bohr model are given by the initial and final quantum numbers:

$$\Delta E = E_f - E_i = -13.606 \text{ eV } Z^2 \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right) \quad \text{matching the Rydberg formula}$$

The Postulates of Quantum Mechanics:

I. The physical state of the system is described by a wave function as completely as possible.

15. The Hamiltonian is the total energy operator; in one-dimension: $\hat{H} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \hat{V}(x)$
16. A wave function is an eigenfunction of the Hamiltonian: $\hat{H}\Psi_n = E_n\Psi_n$.
17. The eigenfunctions are orthogonal and normalized, or orthonormal.
18. The allowed wave functions are finite, continuous, single-valued, and square integrable.
19. The normalization integral is $\int \Psi_n^* \Psi_n d\tau = 1$ and the orthogonality, $\int \Psi_n^* \Psi_m d\tau = 0$.
20. The eigenvectors, eigenfunctions, or eigenstates of the Hamiltonian are stationary states.
21. The Born interpretation is that the probability of finding a particle in an interval $[x, x+dx]$ is given by the square of the wave function: $P(x) dx = \Psi_n^* \Psi_n dx$.

II. Any observable may be represented by a linear operator. The results should be a real number; the observable operator must be Hermitian: $\int \Psi_j^* \hat{o} \Psi_i d\tau = \int \Psi_i (\hat{o} \Psi_j)^* d\tau = \int \Psi_i \hat{o}^* \Psi_j^* d\tau$

22. A linear operator gives $\hat{o} (a f(x) + b g(x)) = a \hat{o} f(x) + b \hat{o} g(x)$, for functions $f(x)$ and $g(x)$ and constants a and b .

23. The observable operator is constructed from the following table.

Classical	Quantum Operator
x	\hat{x}
p	$\hat{p} = \frac{\hbar}{i} \left(\frac{\partial}{\partial x} \right) = -i\hbar \left(\frac{\partial}{\partial x} \right)$
t	\hat{t}
E vs. time	$\hat{E} = i\hbar \left(\frac{\partial}{\partial t} \right)$

24. The momentum, kinetic, potential, and Hamiltonian operators are linear Hermitian.
25. The classical and quantum operator are equivalent for purely multiplicative potentials.
26. The eigenvalues for quantum mechanical observables are real.

III. If the wave function is an eigenfunction of the observable, repeated measurements of the observable always give the same result. The repeated result is the eigenvalue of $\hat{o} \Psi = o \Psi$.

IV. If the wave function is not an eigenfunction of the observable, the measurement gives a different result each time. The “average” or expectation value is given by:

$$\langle o \rangle = \frac{\int_{-\infty}^{\infty} \Psi_n^* \hat{o} \Psi_n d\tau}{\int_{-\infty}^{\infty} \Psi_n^* \Psi_n d\tau}$$

V. The wave function evolves in time according to: $\hat{H}\Psi(x,t) = i\hbar \left(\frac{\partial \Psi(x,t)}{\partial t} \right)$

27. For time independent potentials, the wave function factors into a purely spatially dependent part and a purely time dependent part: $\Psi(x,y,z,t) = \Psi(x,y,z)\Psi(t)$ with $\Psi(t) = e^{-iEt/\hbar}$ having oscillation frequency $E = h\nu$.

28. The commutator of two operators is defined as: $[\hat{O}_1, \hat{O}_2] = \hat{O}_1 \hat{O}_2 - \hat{O}_2 \hat{O}_1$. If the commutator is non-zero then the order of operations is important.

29. Complementary observables obey an uncertainty relationship: $\sigma_A \sigma_B \geq \left| \frac{1}{2i} \int \Psi^* [\hat{A}, \hat{B}] \Psi dx \right|$

30. For position and momentum, $[\hat{x}, \hat{p}_x] = -(\hbar/i)$ and $\sigma_x \sigma_{p_x} \geq \hbar/2$.

31. The standard deviations are defined by the expectation values:

$$\sigma_x = \langle (x - \bar{x})^2 \rangle^{1/2} = (\langle x^2 \rangle - \langle x \rangle^2)^{1/2} \quad \text{and} \quad \sigma_{p_x} = \langle (p - \bar{p})^2 \rangle^{1/2} = (\langle p^2 \rangle - \langle p \rangle^2)^{1/2}$$

32. For energy and lifetime: $\delta E \delta t \geq \hbar/2$ with $\delta \tilde{\nu} = \delta E/hc$ and $\delta \tilde{\nu} \cong \delta \lambda / \lambda_{\max}^2$.

33. The wave function and energy for a free particle are not quantized; for wave vector k :

$$\Psi(x) = e^{ikx} \quad p = \hbar k \quad \text{and} \quad E = \frac{\hbar^2 k^2}{2m}$$

34. The kinetic energy is given by the curvature; in one-dimension: $E_k = -\frac{\hbar^2}{2m} \frac{d^2 \Psi(x)}{dx^2}$.

35. The wave function and energy for a particle in a box with length a and quantum number n :

$$\Psi_n(x) = \left(\frac{2}{a}\right)^{1/2} \sin\left(\frac{n\pi x}{a}\right) \quad \text{and} \quad E_n = \frac{\hbar^2 \pi^2 n^2}{2ma^2} = \frac{\hbar^2 n^2}{8ma^2} \quad \text{with } n = 1, 2, 3, \dots, \infty$$

36. The quantum restriction for a particle in a box results from the boundary conditions.

37. The transition energy and absorption frequency for a particle in a box are:

$$\Delta E = h\nu = hc/\lambda = E_f - E_i = \frac{\hbar^2}{8ma^2} (n_f^2 - n_i^2)$$

38. The occurrence of a zero point energy is a direct result of the Heisenberg uncertainty relationship. The zero point energy for a particle in a box is for $n = 1$: $E_1 = \hbar^2/8ma^2$

39. A wave with incident amplitude a and energy E in an infinite barrier of potential V is:

$$\Psi_{\text{transmitted}} = c e^{-\kappa x} \quad \text{with} \quad c = \left(\frac{2ik}{ik - \kappa}\right) a \quad \text{and} \quad \kappa = \frac{\sqrt{2m(V - E)}}{\hbar}$$

40. The probability of tunneling of a particle through a barrier of thickness L is:

$$T = \left[\frac{(e^{\kappa L} - e^{-\kappa L})^2}{16\varepsilon(1 - \varepsilon)} + 1 \right]^{-1}$$

where the ratio of the total energy of the particle to the barrier height is $\varepsilon = E/V$.

41. Scanning tunneling microscopy, STM, achieves sub-atomic height sensitivity by monitoring the tunneling current from a sharp metallic tip to a conducting surface as the sample is rastered.

42. For separable potentials, the constituent one-dimensional wave functions multiply and the energies add.

43. For a 3D-particle in a box of side lengths a , b , and c :

$$\Psi(x,y,z) = \left(\frac{8}{abc}\right)^{1/2} \sin \frac{n_x \pi x}{a} \sin \frac{n_y \pi y}{b} \sin \frac{n_z \pi z}{c} \quad \text{and} \quad E = \frac{\hbar^2}{8m} \left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2} \right)$$

44. For a cubical box, the translational energy levels have a degeneracy of g .

45. The translational energy levels for macroscopic scale boxes are closely spaced in energy and essentially continuous.

46. The Correspondence principle is that quantum solutions should agree with classical expectations in the classical limit, $n \rightarrow \infty$.

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Chapter 23: Foundations of Quantum Mechanics Problems

1. A typical mid-infrared spectrophotometer for studying molecular vibrations has a wavenumber range from $4000. \text{ cm}^{-1}$ to $400. \text{ cm}^{-1}$. (NaCl cell windows have a 460 cm^{-1} long-wavelength cutoff and KBr has a 345 cm^{-1} cutoff.) Calculate the frequency and energy range for the mid-IR. Express the energy units in J, eV, and kJ mol^{-1} .
2. Complete the following table. For the region, choose from radiowave, microwave, infrared, visible, and ultraviolet.

λ (cm)	λ (μm)	λ (nm)	ν (s^{-1})	E (J)	E (eV)	E (kJ mol^{-1})	$\tilde{\nu}$ (cm^{-1})	region
			100 MHz					
			10 GHz					microwave
							1	
	10							
		1000						
					2			
						200		
		500						
		350						
		190						
							100,000	

3. All else being equal, the wavelength of the light in a photoelectric effect experiment is halved. Describe the effect on the photoelectron current and the kinetic energy of the photoelectrons.
4. Calculate the kinetic energy of a photoelectron emitted by sodium metal when light of wavelength 400.0 nm is incident on it. The work function of sodium is 2.28 eV.
5. The work function for cesium metal is 2.10 eV. Cesium is used as a coating for photodetector tubes in some older spectrophotometers. Calculate the long wavelength limit for photoelectron production for a cesium coated phototube.
6. Rephrase the four experimental observations for the photoelectric effect assuming light is only wave-like (not particle-like) and the electrons in atoms are harmonically bound.
7. Electron microscopes can be used to determine the electron diffraction pattern of crystalline materials, in a similar fashion to X-ray diffraction. (a). Calculate the de Broglie wavelength for electrons that are accelerated to 10.0 keV. (b). Calculate the wavelength for 8.046 keV X-rays from a Cu X-ray tube. The effective wavelength for the electrons or X-rays determines the limiting spatial resolution for the diffraction study.
8. Why don't we normally notice the wave behavior of particles in the macroscopic world that we directly experience? (a). Calculate the de Broglie wavelength of a 58.0 g tennis ball traveling at 80.0 km hr⁻¹ and a 70.0 kg human traveling at 2 km hr⁻¹. (b). Calculate the de Broglie wavelength of an O₂ molecule based on the overall translational energy at room temperature. The average speed (rms) of an O₂ molecule at room temperature is 482. m s⁻¹.
9. Calculate the photon energy, in electron volts and wavenumbers, and the wavelength for the hydrogen atomic emission lines for the transitions: (a) n = 3 to n = 2, (b). n = 3 to n = 1. However, before you do the numerical calculations predict the transition that is "bluer."
10. (a). Calculate the energy and wavelength for the lowest energy absorption transition for ground state atomic hydrogen. (b). Calculate the ionization potential and the corresponding wavelength of the transition that ionizes ground state hydrogen atoms. Report the energies in eV and wavenumbers. Report the wavelengths in nm. In what region of the electromagnetic spectrum are these two transitions?
11. Li²⁺ is a one-electron ion, which is well described using the Bohr formula. Compare the wavelength of the n = 3 to n = 2 emission lines for H-atoms and Li²⁺. Before you do the numerical calculation, determine qualitatively which transition is "bluer."
12. The spectrum of the sun incident on the earth is shown in the table below and Figure P23.1.² Gases in the atmosphere absorb infrared light through vibrational transitions and ultraviolet light through electronic transitions. Gas molecular absorption and scattering by atmospheric particulates reduce the solar intensity at sea level compared to outside the atmosphere. Using the data in the following table, show that the solar irradiance outside the earth's atmosphere is well modeled by the Planck blackbody expression at 5800 K:

$$H(\lambda) = \frac{2\pi hc^2}{\lambda^5} \left(\frac{1}{e^{hc/kT\lambda} - 1} \right)$$

where k is Boltzmann's constant, $k = R/N_A = 1.3807 \times 10^{-23} \text{ J K}^{-1}$. The irradiance is the energy flux per unit wavelength interval; that is, the energy emitted from a unit area per unit time per unit wavelength interval. A square meter cross section of the earth captures a tiny fraction of the total energy output of the sun, so a small scale factor must be applied to match the overall intensity to the experimental data.

λ (nm)	250.	375.	460.	500.	625.	750.	1000.	1250.	1500.	1750.
H_λ ($\text{W m}^{-2} \text{ nm}^{-1}$)	0.034	1.193	2.032	1.929	1.667	1.279	0.742	0.445	0.263	0.166

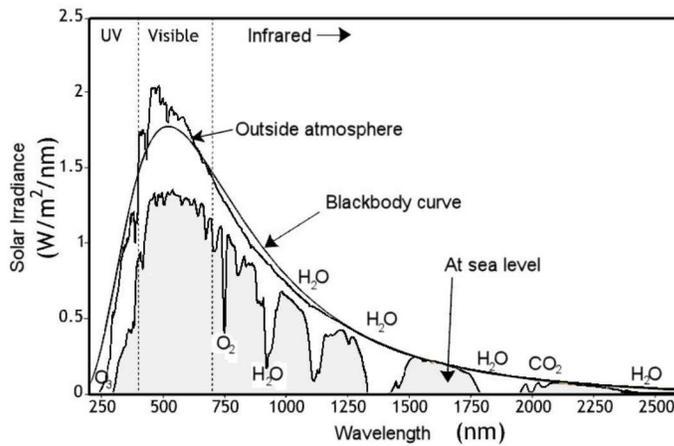


Figure P23.1: The solar irradiance incident on the earth at the top of the atmosphere and at sea level. The irradiance is given in watts for a one-meter surface placed perpendicular to the incident angle of the sun for a 1 nm range in wavelength, λ to $\lambda+d\lambda$, given in nm.

13. The Planck blackbody expression in terms of frequency is:

$$I(\nu) = \frac{2\pi h \nu^3}{c^2} \left(\frac{1}{e^{h\nu/kT} - 1} \right)$$

Show that the total flux radiated by a blackbody is $J = \sigma T^4$, where $\sigma = 5.6704 \times 10^{-8} \text{ W m}^{-2} \text{ K}^{-4}$ (see Section 11.2 and Eq. 11.2.16). [Hint: $\int_0^\infty (x^3/(e^x - 1)) dx = \pi^4/15$]

14. The Planck blackbody expression in terms of frequency is given in the last problem. This expression gives the intensity of radiation in an interval of frequency from ν to $\nu+d\nu$:

$$I(\nu) d\nu = \frac{2\pi h \nu^3}{c^2} \left(\frac{1}{e^{h\nu/kT} - 1} \right) d\nu$$

Apply a change in variables to show that the distribution in terms of wavelength is given by:

$$I(\lambda) d\lambda = \frac{2\pi hc^2}{\lambda^5} \left(\frac{1}{e^{hc/kT\lambda} - 1} \right) d\lambda$$

15. The total flux radiated by a blackbody is $J = \sigma T^4$, where $\sigma = 5.6704 \times 10^{-8} \text{ W m}^{-2} \text{ K}^{-4}$ (see Section 11.2 and Eq. 11.2.16). This flux is the energy emitted per unit area of the emitter per unit time. The solar constant is the energy from the sun falling on the top of earth's atmosphere per unit area per unit time. The solar constant is 1.37 kW m^{-2} . The surface area of the sun is $6.09 \times 10^{18} \text{ m}^2$. A square meter cross section of the earth captures a tiny fraction of the total energy output of the sun. The average distance of the earth from the sun is 93×10^6 miles, giving the surface area of a sphere at that radius of $2.79 \times 10^{23} \text{ m}^2$. Calculate the effective blackbody temperature of the surface of the sun.

16. (This problem expands on material in Chapter 12, using the partition function for vibration.) Planck's treatment of blackbody radiation and Einstein's treatment of the heat capacity of a solid are based on the assumption of quantized energy levels. Assume the energy levels for the electrons in a metal or for the vibration of atoms in a solid are equally spaced with $\epsilon_j = j h\nu$, where ν is a fundamental vibration frequency for the motion and j is an integer. The probability of an electron or atom having energy ϵ_j is given by the Boltzmann distribution, $n_j/N = e^{-\beta \epsilon_j}/q$, where $\beta = 1/kT$. The average energy is given by Eq. 12.2.6:

$$\langle \epsilon \rangle = \frac{\sum_{j=0}^{\infty} \epsilon_j e^{-\beta \epsilon_j}}{q} \quad \text{where } q \text{ is the partition function: } q = \sum_{j=0}^{\infty} e^{-\beta \epsilon_j}$$

(a). Show that the average energy can also be expressed as:

$$\langle \epsilon \rangle = - \frac{1}{q} \left(\frac{\partial q}{\partial \beta} \right)_V$$

(b). Show that the partition function reduces to: $q = \frac{1}{1 - e^{-\beta h\nu}}$

Note that the infinite power series can be summed as: $\sum_{j=0}^{\infty} a^j = 1 + a + a^2 + a^3 + \dots = \frac{1}{1 - a}$

(c). Using the partition function, show that the average energy is: $\langle \epsilon \rangle = \frac{h\nu}{(e^{\beta h\nu} - 1)}$

17. The Wein relationship for the spectral distribution of blackbody radiation is:

$$I(\nu) = \frac{2\pi\nu^2}{c^2} \langle \epsilon \rangle$$

where ν is the frequency of the light emitted, and $\langle \epsilon \rangle$ is the average energy of an electron oscillator in the walls of the cavity of the solid. The radiation in the cavity is assumed to be in thermodynamic equilibrium with the electron oscillators in the cavity walls. Using the equipartition theorem for the average energy of an electron oscillator gives $\langle \epsilon \rangle = RT$. However, classical result is found to vastly overestimate the blackbody intensity in the ultraviolet. Show that the assumption of quantized oscillators and the corresponding average energy derived in the previous problem gives the Planck distribution function, which was given in Problems 13 and 14.

18. The heat capacity of an oscillator can be determined from the derivative of the average energy versus temperature: $C_v = (\partial U / \partial T)_v = N_A (\partial \langle \varepsilon \rangle / \partial T)_v$. The average energy of a one-dimensional quantized oscillator was derived in Problem 16:

$$\langle \varepsilon \rangle = \frac{h\nu}{(e^{\beta h\nu} - 1)}$$

Einstein estimated that the heat capacity of a simple solid is $C_v = 3N_A (\partial \langle \varepsilon \rangle / \partial T)_v$, where the factor of three results since the atoms in a solid can oscillate in the x, y, and z directions. Derive the Einstein relationship for the heat capacity of an atomic solid. Plot the relationship versus temperature for $\tilde{\nu} = 100. \text{ cm}^{-1}$.

19. (a). Assume the uncertainty for the one-dimensional linear position of an electron is 1.00 \AA . Calculate the uncertainty of the momentum using $\delta x \delta p_x \geq \hbar/2$. (b). The average momentum for a confined particle, such as the particle in a box, is zero: $\langle p \rangle = 0$. The uncertainty in the momentum, as measured by the standard deviation, then reduces to just the root-mean-squared momentum, $\sigma_{p_x} = (\langle p^2 \rangle - \langle p \rangle^2)^{1/2} = (\langle p^2 \rangle)^{1/2} = p_{\text{rms},x}$. The root-mean-squared momentum can be used to estimate the kinetic energy of the particle, $E_{k,x} \approx (p_{\text{rms},x})^2 / 2m$. Estimate the kinetic energy of a confined electron with a positional uncertainty of 1 \AA . (c). The kinetic energy of a particle confined in a cubical box is determined by adding the kinetic energy in each direction, $E_k = E_{k,x} + E_{k,y} + E_{k,z} = 3 E_{k,x}$, for a cubical box. The diameter of an atom is about 1 \AA (the Bohr radius of the H atom is 0.529 \AA). Assume the hydrogen atom is approximated by a 1 \AA cubical box. Use the kinetic energy from part (b) to estimate an approximate kinetic energy of the ground state of the H atom in eV and kJ mol^{-1} . Is this resulting energy chemically significant? In other words, is the magnitude comparable to or greater than typical enthalpy changes for chemical reactions?

20. (a). The momentum of a 10.0 eV electron is known to 10%. Calculate the minimum uncertainty in the position of the electron. (b). The speed of a 58.0 g tennis ball traveling at 80.0 km hr^{-1} is known to 10%. Calculate the uncertainty in the position of the tennis ball. Does this uncertainty contribute to the difficulty in returning an 80.0 km hr^{-1} tennis serve?

21. (a). What are the quantum numbers for the energy levels that are involved in the lowest energy electronic transition for the molecule, $\text{H}_2\text{C}=\text{CH}-\text{CH}=\text{CH}-\text{CH}=\text{CH}-\text{CH}=\text{CH}_2$? Base your answer on the particle in a box model. (b). Calculate the wavelength of the light absorbed in nm. Calculate the energy change for the transition in wavenumbers, cm^{-1} . The average bond length for a conjugated double bond is 1.39 \AA . Lengthen the box by one-half of a bond beyond each terminal C atom to take into account that the π orbital doesn't end exactly at the nucleus of the terminal C atoms.

22. Two restrictions are placed on the solutions to the Schrödinger equation that take the form of integrals. Name the two restrictions, the two integrals, and the values that define these restrictions.

23. Show that the $n = 2$ and $n = 3$ wave functions for the particle in the box are orthogonal. Show that the $n = 2$ wave function is normalized.

24. The harmonic oscillator ground state has a Gaussian wave function of the form $\Psi(x) = N e^{-x^2/4\sigma_x^2}$. Normalize the wave function over $-\infty \leq x \leq \infty$.

25. What is the probability that a particle is in the left side of the particle in a box, for a box of length a and quantum number n ?

26. Show that $\langle x^2 \rangle$ for a particle in a box of length a and quantum number n is:

$$\langle x^2 \rangle = a^2 \left(\frac{1}{3} - \frac{1}{2n^2\pi^2} \right)$$

27. Using the result from the last problem, find the uncertainty in the position of the particle in box, for box length a and quantum number n . Express the result as the standard deviation, $\sigma_x = (\langle x^2 \rangle - \langle x \rangle^2)^{1/2}$.

28. Find the average momentum for a particle in a box, with box length a and quantum number n .

29. Show that $\langle p_x^2 \rangle$ for a particle in a box of length a and quantum number n is:

$$\langle p_x^2 \rangle = \hbar^2 \left(\frac{n\pi}{a} \right)^2$$

30. Using the results of Problems 28 and 29, find the standard deviation of the momentum of a particle in a box:

$$\sigma_{p_x} = (\langle p_x^2 \rangle - \langle p_x \rangle^2)^{1/2} = \hbar \left(\frac{n\pi}{a} \right)$$

Rationalize the results on the basis of the Heisenberg uncertainty principle.

31. Using the results of Problems 27 and 30, show that $\sigma_x \sigma_p \geq \hbar/2$ for a particle in a box, in concordance with the Heisenberg uncertainty principle.

32. Determine the standard deviation of the position, $(\langle x^2 \rangle - \langle x \rangle^2)^{1/2}$, for the Gaussian wave function:

$$\Psi(x) = \frac{1}{(2\pi)^{1/4} \sigma_x^{1/2}} e^{-x^2/4\sigma_x^2} \quad \text{over } -\infty \leq x \leq \infty$$

33. Consider a particle in a box of length a with a potential that goes to infinity at $-a/2$ and $+a/2$. The general form of the wave function as given by Eq. 23.4.5 also applies for $-a/2 \leq x \leq +a/2$. Apply the boundary conditions to determine the wave function for the particle.

34. Give the wave function and energy for a 3D-particle in a box with quantum numbers (1,1,2) and side lengths a , b , and c for a particle of mass m .

35. Why does a confined particle have quantized energy levels?

36. Find the average penetration depth of a particle of mass m and energy E into an infinite barrier of constant potential V . Assume the total energy is less than the potential energy, Figure 23.5.1a. Given the amplitude of the incident wave, a , show that the average penetration depth is:

$$\langle x \rangle = \left(\frac{4k^2}{k^2 + \kappa^2} \right) \frac{a^2}{4\kappa^2}$$

37. Find the tunneling probability for a 1.00 eV electron into a 2.00 eV potential energy barrier of thickness 10.0 Å.

38. Show that $\Psi = N e^{-\alpha x}$ is an eigenfunction of the operator d^2/dx^2 . What is the eigenvalue? Normalize the wave function for $x \geq 0$.

39. (a). Show that $\Psi(x) = e^{-ikx}$ is an eigenfunction of the momentum and kinetic energy operators, but not an eigenfunction of the position operator, for motion in one-dimension. (b). Will repeated measurements of the position, momentum, and kinetic energy give the same result or different results?

40. What are the restrictions on the wave functions that may represent physical systems? Can the following be valid wave functions? (a). $\Psi(x) = N \ln x$ for $0 \leq x \leq \infty$, (b). $\Psi(x) = N e^{ax^2}$ for $-\infty \leq x \leq \infty$, and (c). $\Psi(x) = N x e^{-ax}$ with $a > 0$ and the range $0 \leq x \leq \infty$.

41. Show that a linear combination of two eigenfunctions of the momentum that have the same momentum is also an eigenfunction of the momentum.

42. Determine the value for the commutation relationship between the observation time and total energy of a particle, $[\hat{t}, \hat{E}]$. [Hint: apply the commutator as an operator for an arbitrary function, $f(t)$]

43. Consider a two-dimensional problem, such as the two-dimensional particle in a box. Determine the value for the commutation relationship between the position in the x -direction and the momentum in the y -direction, $[\hat{x}, \hat{p}_y]$. [Hint: apply the commutator as an operator for an arbitrary function, $f(x,y)$]

44. Determine the value for the commutation relationship between the momentum and kinetic energy of a particle in one-dimension, $[\hat{p}_x, \hat{E}_k]$. [Hint: apply the commutator as an operator for an arbitrary function, $f(x)$]

45. Find the absolute values for the following:

(a). $2 + i6$, (b). $e^{-i\alpha x^2}$, (c). $\cos(n\pi x/a) + i \sin(n\pi x/a)$, (d). $e^{-i n\pi x/a}$ and (e). $-\hbar/i$.

46. Using explicit summations, show that $\sigma_x^2 = \langle (x - \langle x \rangle)^2 \rangle$ is equivalent to $\sigma_x^2 = \langle x^2 \rangle - \langle x \rangle^2$. Use the trial data set $x = \{2,3,3,4,1,2,2\}$.

47. Prove that $\sigma_x = \langle (x - \bar{x})^2 \rangle^{1/2} = (\langle x^2 \rangle - \langle x \rangle^2)^{1/2}$, Eq. 23.4.36.

48. The moments of a probability distribution characterize the distribution. The first moment is the mean, $\langle x \rangle = \bar{x}$. The second central moment is the standard deviation, $\sigma_x = [\langle (x - \bar{x})^2 \rangle]^{1/2}$. Central moments are evaluated using the deviations from the mean ($x - \bar{x}$). The third central moment is defined as $[\langle (x - \bar{x})^3 \rangle]^{1/3}$. The third central moment is a measure of the asymmetry about the mean for the distribution. For example, for a Gaussian distribution the third central moment is zero. (a). Prove that the third central moment can be calculated using:

$$\langle (x - \bar{x})^3 \rangle = \langle x^3 \rangle - 3 \bar{x} \langle x^2 \rangle + 2 \bar{x}^3$$

(b). Verify the formula using explicit summations with the trial data set listed in Problem 23.46.

49. Use Eq. 23.7.35 to determine the product of the uncertainty in the position and momentum for a one-dimensional particle in a box of length a for $n = 2$.

50. Show that the commutator for the position and kinetic energy of a particle, in one-dimension, is $[\hat{x}, \hat{E}_k] = -(\hbar/m) \hat{p}$.

Can position and kinetic energy be simultaneously defined to high precision? [Hint: find the result of the commutator operating on an arbitrary function $f(x)$.]

51. Is the operator $\hat{o} = (d/dx)$ Hermitian? [Hint: use integration by parts: $\int u dv = uv - \int v du$]

52. (*Challenge Problem*) Show that the operator (d^2/dx^2) is Hermitian. Is the kinetic energy operator also Hermitian? Do the problem using the following intermediate steps. (a). Show that: [Hint: use integration by parts, $\int u dv = uv - \int v du$.]

$$\int_{-\infty}^{\infty} \Psi_j^* \left(\frac{d^2}{dx^2} \right) \Psi_i dx = - \int_{-\infty}^{\infty} \left(\frac{d\Psi_i}{dx} \right) d\Psi_j^* = - \int_{-\infty}^{\infty} \left(\frac{d\Psi_i}{dx} \right) \left(\frac{d\Psi_j^*}{dx} \right) dx$$

(b). Show that: [Hint: use integration by parts again.]

$$\int_{-\infty}^{\infty} \Psi_j^* \left(\frac{d^2}{dx^2} \right) \Psi_i dx = \int_{-\infty}^{\infty} \Psi_i \left(\frac{d}{dx} \right) \left(\frac{d\Psi_j^*}{dx} \right) dx$$

(c). Finally show that (d^2/dx^2) is Hermitian by proving that:

$$\int \Psi_j^* \left(\frac{d^2}{dx^2} \right) \Psi_i dx = \int \Psi_i \left(\frac{d^2}{dx^2} \right)^* \Psi_j^* dx$$

(d). Is the kinetic energy operator also Hermitian?

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