heater, due to the temperature dependence of the resistance. This resistance oscillation at 2ω leads to a third harmonic component in the heater voltage. By measuring the phase and amplitude of this third harmonic, the temperature rise of the heater due to the modulating power input can be determined and, from this, the thermal conductivity of the film can be determined. This is called the 3ω method.

(a) Assuming a power input of the form of A sin $(2\omega t)$, derive an expression for the in-phase (sine function) and out-of-phase (cosine function) components of the heater temperature rise. Assume that all the thermal properties (thermal diffusivity, thermal conductivity, and specific heat) of the film and the substrate are known.

(b) One additional advantage of the 3ω method is that the substrate thermal conductivity can be determined from the frequency dependency of the temperature response under appropriate conditions. Try to identify these conditions.

(c) Another advantage of the 3ω method is that the radiation loss can be minimized, which is particularly important for low thermal conductivity materials and measurements at extreme temperatures (low and high). Explain why.

1.5 *Thermal diffusivity determination of thin films: laser pulse method.* One method for determining the thermal diffusivity of a thin film is to use a short laser pulse to heat up the front side of the film and to measure the decay of the front side temperature by monitoring the change in reflectance of a probe laser beam (see figure P1.5). The short pulse concentrates temperature drop in the film rather than across the substrate. In this case, it is not the absolute surface temperature rise that is measured but the normalized profile of the surface temperature decay as a function of time. For a heating pulse of the following profile,

$$q = \begin{cases} 0 & t < 0 \\ q_0 & 0 < t < t_p \\ 0 & t > t_p \end{cases}$$

(a) Derive an expression for the temporal response of the front surface temperature, assuming all thermal properties (thermal conductivity k, thermal diffusivity a, and specific heat c) are known for both the film and the substrate.

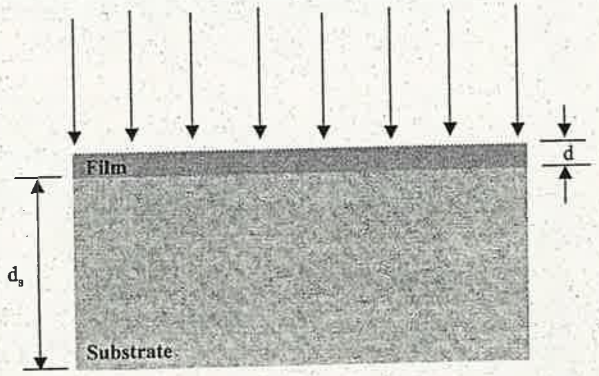

Figure P1.5 Figure for problem 1.5.

(b) What are the requirements on the pulse width that will maximize the sensitivity for measuring the thermal diffusivity of the film?

1.6 *Lumped heat capacitance and time constant.* Develop a lumped capacitance model for a solid sphere at uniform temperature T_i that is suddenly immersed inside a liquid at temperature T_0. In such a model, the temperature of the solid is assumed to be uniform, and the heat transfer coefficient between the solid object and the fluid is taken to be h. Other known parameters are the surface area A, the volume V, the density ρ, and specific heat c of the solid.

(a) Derive the differential equation governing the temperature history of the solid.

(b) Solve the equation and find the time constant of the process.

(c) Investigate how the time constant varies with the diameter of the solid sphere.

1.7 *$\kappa_B T$ energy.* One unit for energy is the electron-volt (eV). It is the energy difference of one electron under a potential difference of 1 V. Convert 1 $\kappa_B T$ at 300 K into milli-eV (meV).

1.8 *Thermal conductivity of gases.* Estimate the thermal conductivity of air and argon as a function of temperature between 300 K and 1000 K at 1 atm.

1.9 *Mean free path in air.* Estimate the mean free path of air molecules as a function of temperature at atmospheric pressure on the basis of (a) kinetic theory and (b) experimental data on the thermal conductivity and specific heat of air.

1.10 *Speed of electrons.* Estimate the average random speed of an electron gas in a semiconductor at 300 K.

1.11 *Thermal conductivity of liquid.* Although the application of kinetic theory to a dense liquid is questionable, estimate the thermal conductivity of water at room temperature on the basis of a simple derivation for the mean free path and the results from the kinetic theory. This estimation is typically smaller than experimental values because, for liquid, potential energy exchange contributes to heat conduction.

1.12 *Phonon mean free path and relaxation time.* Given the thermal conductivity of Si at room temperature as 145 $\mathrm{W\,m^{-1}K^{-1}}$, the speed of sound as 6400 $\mathrm{m\,s^{-1}}$, the volumetric specific heat as $1.66 \times 10^6\ \mathrm{J\,m^{-3}K^{-1}}$,

(a) Estimate the phonon mean free path in Si at room temperature from the kinetic theory. In reality, this estimation usually leads to a much shorter mean free path (about a factor of 10 shorter) than with more sophisticated modeling.

(b) Estimate the relaxation time of phonons in silicon.

1.13 *Fick's law of diffusion.* Using a simple kinetic argument that is similar to the derivation of the Fourier law, derive the Fick law of diffusion, which gives the mass flux for species i under a concentration gradient as

$$J_i = -\rho D \frac{dm_i}{dx}$$

where D is the mass diffusivity, ρ is the density of the mixture, and m_i the local mass fraction of species i.

1.14 *Newton's shear stress law.* Using a simple kinetic argument that is similar to the derivation of the Fourier law, derive the Newton law of shear stress (in one-dimensional form). Hint: consider the momentum exchange across a plane parallel to the flow.

1.15 *Energy quantization.*

(a) Assuming a person weighing 100 kg trapped deep inside a two-dimensional ditch 1 m in width, estimate the energy difference between the first and second quantized energy levels. Compare this energy difference with the thermal fluctuation energy $\kappa_B T$ for $T = 300$ K.

(b) Assuming an electron of mass 9.1×10^{-31} kg is trapped inside a two-dimensional infinitely high potential well, plot the first and second energy levels of the electron as a function of well width between 10 and 100 Å. Also mark the thermal energy $\kappa_B T$ on the graph for $T = 300$ K.

2

Material Waves and Energy Quantization

For macroscopic systems, we take the continuity of many variables for granted, including the continuity in energy. For example, the heat flux along a rod through conduction, according to the Fourier law, can be continuously varied to any desired value by controlling the temperature difference and the material properties. The microscopic picture of energy, however, is entirely different. According to quantum mechanical principles, the permissible energy levels of matter (electrons, crystals, molecules, and so on) are often discontinuous. Differences in allowable energy levels among materials are major factors that distinguish them from each other. For example, why is glass transparent in the visible light range but not silicon, and why are some materials electrical insulators but others are conductors?

In this chapter, we introduce the basic quantum mechanical concepts necessary to appreciate various energy states found in different materials. It should be remembered that these energy states represent the range of possibilities for the matter but do not tell which state the matter will be in. The latter depends on the temperature, a topic we will discuss in chapter 4. Important concepts that should be mastered through this chapter include the wave–particle duality, the Schrödinger equation and the meaning of the wavefunction, the Pauli exclusion principle, quantum states, and degeneracy. Solutions of the Schrödinger equation for various simple yet very common potentials will be given. Key concepts and results of this chapter are summarized in the last section of the chapter.

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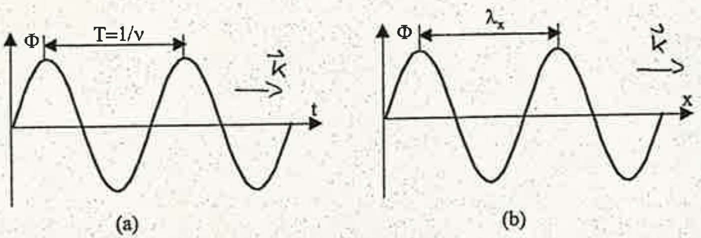

Figure 2.1 Traveling wave: (a) temporal variation at a fixed point; and (b) spatial variation at a fixed time.

2.1 Basic Wave Characteristics

Let's start by reviewing some basic characteristics of waves. We consider a harmonic wave (such as an electric or a magnetic field) represented by a sine function traveling along the positive x-direction,* → prefer to use cos

harmonic wave fct.

$$\Phi = A\sin\left(2\pi\nu t - \frac{2\pi x}{\lambda_x}\right)\hat{\mathbf{y}} = A\sin(\omega t - k_x x)\,\hat{\mathbf{y}} \tag{2.1}$$

where A is the amplitude and $\hat{\mathbf{y}}$ is a unit vector in the y-coordinate direction. Such a wave has two kinds of periodicity: one in space and one in time. The periodicity in time is characterized by the frequency ν, which equals the inverse of the period in time. The angular frequency $\omega = 2\pi\nu$ is often used instead of frequency to avoid writing the 2π factor. At any fixed point, the temporal variation of the field is a sine function, as shown in figure 2.1(a). The periodicity along the x-direction is characterized by the wavelength λ_x. Taking a snapshot of the field in space at any fixed time, the field is a sine function as shown in figure 2.1(b). The inverse of the wavelength $1/\lambda_x$ is called the wavenumber. The wave represented by eq. (2.1) is propagating along the x-direction, but the field is vibrating along the y-direction. When the field vibration direction (the direction of the electric field oscillation or the atomic displacement) is perpendicular to the wave propagation direction, the wave is said to be a transverse wave. When the wave propagation and the field vibration are along the same direction, the wave is called a longitudinal wave. The wavevector, **k**, represents the wave propagation direction and has a magnitude of $k_x = 2\pi/\lambda_x$ so that for a wave propagating along the x-direction as shown in figure 2.1(b),

$$\mathbf{k} = \frac{2\pi}{\lambda_x}\hat{\mathbf{x}} = k_x\hat{\mathbf{x}} \tag{2.2}$$

For the wave represented by Eq. (2.1), the constant phase plane in the x–t space is

$$\underline{\text{constant phase plane}} \quad \omega t - k_x x = \text{const.} \tag{2.3}$$

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*We will discuss waves in more detail in chapter 5.

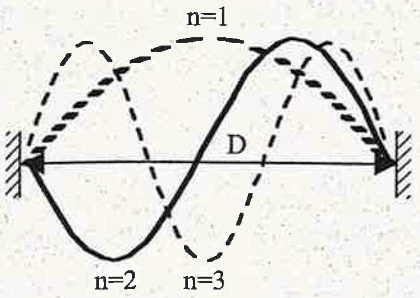

Figure 2.2 Standing waves, with vanishing amplitude at the boundaries.

This constant phase plane propagates along the positive x direction at the speed

$$\underline{\text{phase velocity}}: \quad v_{p,x} = \frac{dx}{dt} = \frac{\omega}{k_x} = \nu\lambda_x \tag{2.4}$$

which is called the phase velocity. Eq. (2.1) therefore represents a transverse *traveling wave* along the positive x-direction. For such a simple wave, the constant phase plane is also the constant amplitude plane, as is shown by substituting eq. (2.3) into (2.1). The frequency and wavevector of a wave are not independent of each other. The relationship between ω and **k**, or $\omega(\mathbf{k})$, is called the dispersion relation and may be different along different wavevector directions. For electromagnetic waves, we know that v_p is the speed of light, c, and eq. (2.4) gives $\omega = ck$. The dispersion relations for electrons and phonons are not this simple, as we indicated in table 1.3 and will discuss in more detail in chapter 3. !!

Sometimes, it is convenient to use the complex representation of the sine and cosine functions

↗ rotation!

$$\Phi_c = Ae^{-i(\omega t - k_x x)}\hat{\mathbf{y}} = A[\cos(\omega t - k_x x) - i\sin(\omega t - k_x x)]\hat{\mathbf{y}} \tag{2.5}$$

where $i = \sqrt{-1}$ is the unit imaginary number. This is because mathematical operations with the exponential function are much easier to manipulate than those with sine and cosine functions. In a typical mathematical operation using the complex representation, it is implicitly assumed that either the real or the imaginary part of the final solution is the true solution to the problem of interest. Which one of the two parts is the desired solution depends on whether the input (such as the initial or the boundary conditions) is in terms of a sine (imaginary part) or a cosine (real part).

let's stick to the real part

A *standing wave* has fixed boundary points, as shown in figure 2.2. We can create such a standing wave by superimposing two traveling waves along the positive and negative x-directions (assuming that the problem is linear such that the superposition principle applies),

$$\Phi = A[\sin(\omega t - k_x x) + \sin(\omega t + k_x x)]\hat{\mathbf{y}} = -2A\cos(\omega t)\sin(k_x x)\hat{\mathbf{y}} \tag{2.6}$$

Unlike a traveling wave, eq. (2.6) has fixed nodes in space such that $\Phi = 0$ at all times. Also, we see that the magnitude of Φ at different locations is a cosine function in time. Equation (2.6) is a simple form of a standing wave. It is a good representation of a wave inside a cavity of length D that requires the amplitude of the wave to vanish at the cavity boundaries, that is, $\Phi(x = 0) = \Phi(x = D) = 0$, which leads to

$$\sin\left(\frac{2\pi}{\lambda_x}D\right) = 0 \qquad (2.7)$$

or

$$D = \frac{n\lambda_x}{2} \qquad (n = 1, 2, 3, \ldots) \qquad (2.8)$$

Thus, for a stable wave to form inside a cavity that vanishes completely outside the cavity, the cavity length D must be multiples of the half wavelength.

The energy contained in a wave is usually proportional to the square of the field,

Energy of wave

$$U \propto |\Phi|^2 \qquad (2.9)$$

One can understand this point intuitively by imagining that eq. (2.1) represents the instantaneous displacement of a particle. Its velocity is the derivative of this displacement with respect to time and the kinetic energy is proportional to the square of this velocity. Classically, the allowable energy of the wave can change continuously since there is no limit on the amplitude of vibration. This picture, however, is no longer true under quantum mechanical principles.

2.2 Wave Nature of Matter

!!

From the previous section, we see that a wave is characterized by its frequency and wavelength, and its energy is determined by the magnitude of the wave. We also know that a particle is characterized by its energy and momentum. Waves and particles are two completely different and unrelated phenomena in classical mechanics and electrodynamics. In quantum mechanics, however, they are interrelated and are two aspects of matter.

2.2.1 Wave–Particle Duality of Light

Quantum mechanics started with the explanation of blackbody radiation and the absorption spectra of gases. By the end of the 19th century, classical Newtonian mechanics and electromagnetism were well established as two separate entities: Newtonian mechanics is based on the particle picture of materials, and electromagnetism is based on the wave picture. Interestingly, Sir Isaac Newton believed that radiation was particle-like in nature rather than wave-like, as we are more familiar with today. It was the discovery and explanation of interference and diffraction phenomena, from the work of Christian Huygens (1629–1695), Thomas Young (1773–1829), Augustin Jean Fresnel (1788–1827), and others, followed by Maxwell (1831–1879) and his celebrated equations, that solidified the foundation of the wave nature of the electromagnetic field.

The Maxwell equations, however, fail to explain the emission and absorption processes, such as the experimentally observed fine spectra of absorption in various gases, and the blackbody radiation (figure 2.3). According to classical theory, the blackbody emissive power should be proportional to $(\lambda T)^{-5}$, which approaches infinity at short wavelengths, while the experimental blackbody spectrum is reduced to zero as the wavelength decreases, as shown in figure 1.7. The discrete absorption lines in the hydrogen spectrum also cannot be explained by continuum mechanics. To explain blackbody radiation, Max Planck (1858–1948) introduced a radical hypothesis that the allowable energy of the electromagnetic field at a frequency ν_p is not continuous, but is a multiple of the following basic energy unit*

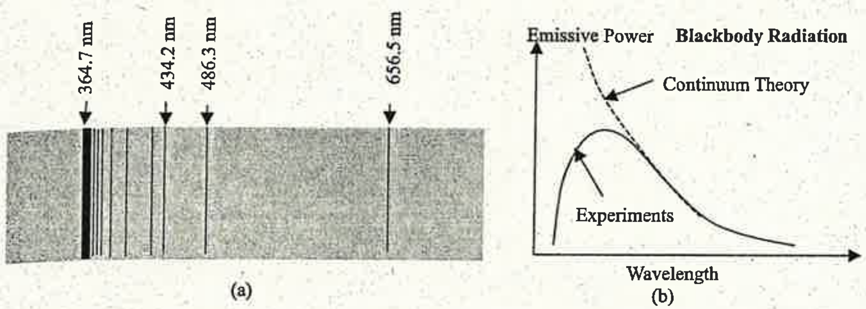

Figure 2.3 (a) An example of the hydrogen emission spectrum for the final state of $n = 2$. Classical mechanics fails to explain discrete lines in the emission spectrum. (b) Experimental measurement on blackbody radiation contradicts the predictions of continuum theory.

(particle) energy

$$E_p = h\nu_p \qquad (2.10)$$

frequency (wave)

where h is called the Planck constant and has a value $h = 6.6 \times 10^{-34}$ J s. We will show later how the idea of photon energy quantization leads to the Planck law. His success led Albert Einstein (1879–1955) to consider that the electromagnetic field also has particle (granular or corpuscular) characteristics such as momentum (Einstein, 1905, 1906).** The basic energy unit as given by eq. (2.10) was later called a photon (Lewis, 1926). Einstein used the corpuscular characteristics of electromagnetic radiation to explain some puzzling results from the basic photoelectricity experiment shown in figure 2.4. It was found that when light is incident on one of two metal electrodes separated by a vacuum, a current can be generated in the loop. The current generation, however, occurs only when the wavelength is shorter than a certain value. No current can be generated for wavelengths longer than this value, even at high light intensities. This experimental observation could not be explained from the classical wave point of view, according to which the energy of an electromagnetic wave is proportional to its intensity, as implied by eq. (2.8). On the basis of the photon particle concept, Einstein reasoned that one photon can excite an electron out of the metal surface only when the photon energy is higher than the electrode workfunction $A(= E_v - E_f)$, which is the energy difference between electrons at the vacuum level, E_v, and inside the metal, E_f,

$$h\nu_p \geq E_v - E_f \qquad (2.11)$$

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*We will neglect the zero point energy in the discussion here.

**Einstein developed theories on special relativity, particle characteristics of photons, and Brownian motion before age 26, while he worked at a patent office.

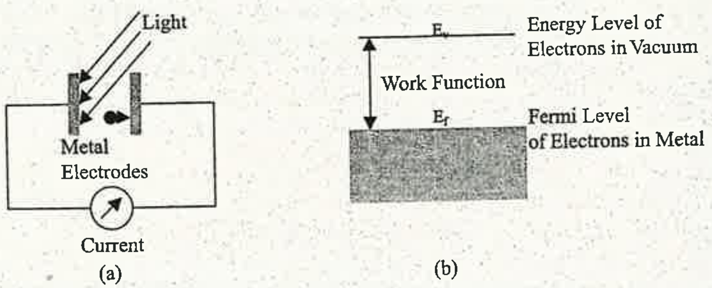

Figure 2.4 (a) Electron emission due to light excitation is called the photoelectric effect. The effect was explained by Einstein through the introduction of corpuscular properties of light. (b) Electrons in a metal have energy close to the Fermi level and their emission out of the metal surface into vacuum is possible only when the photon energy is larger than the work function.

Einstein reasoned that although a photon does not have a rest mass it has a moving mass determined through the relation $E = mc^2$. Its corresponding momentum is $p = mc = E_p/c = h\nu/c$, such that

(particle) momentum

$$p = \hbar k = \frac{h}{\lambda} \tag{2.12}$$

wavelenth/ wavevector (wave)

where $\hbar = h/(2\pi)$. This $\hbar$ is used more often than the Planck constant h because angular frequency and wavevector include the 2π factor. Equations (2.10) and (2.12) are called the Planck–Einstein relations. These two relations thus relate the energy and momentum, which we normally associate with particles, to the frequency and wavevector, which we normally associate with waves. Electromagnetic radiation, and thus photons, has both wave and particle characteristics. This wave–particle duality of light led to the development of quantum mechanics. Einstein also discovered many new properties of photons, such as stimulated emission which forms the basis of all lasers.

!!!

2.2.2 Material Waves

The wave–particle duality of light triggered de Broglie, who was a graduate student then, to postulate that a material particle also has wave properties (Broglie, 1925).* On the basis of an analogy with the Planck–Einstein relations, he proposed that the wavelength of any particle is

$$\lambda = h/p \tag{2.13}$$

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*Quantum mechanics was developed by a group of young researchers. Louis de Broglie (1892–1987) developed the material wave concept in 1923 when he was doing his Ph.D. research. He received the Nobel prize in 1929 at age 38. Werner Heisenberg (1901–1976) developed the matrix formulation of quantum mechanics in 1925, immediately after he finished his Ph.D. thesis on turbulence in 1923, and won the Nobel prize for his work in quantum mechanics in 1932 at age 31. Paul Dirac (1902–1984) developed relativistic quantum mechanics and won the Nobel prize in 1933 at age 31. Erwin Schrödinger (1887–1961) developed his famous equation in 1926 and received the Nobel prize in 1933 at age 46.

where p is the magnitude of the particle momentum. To see how large this wavelength is for a macroscopic object, let's assume $p = mv \approx 1$ kg m s^{-1}, leading to $\lambda \approx 6.6 \times 10^{-34}$ m which is impossible to detect even with current technology. On the other hand, an electron with a velocity of 1 m s^{-1} and a mass of 9.1×10^{-31} kg yields $\lambda \approx 0.7 \times 10^{-3}$ m; a quite long wavelength. The first proof of the wave properties of particles came from the electron diffraction experiment performed by Davisson and Germer (1927).

Now let's consider a simple example to illustrate the consequence of material waves. Consider an electron as a wave that is situated inside a one-dimensional cavity of length D surrounded by an infinite potential. Outside this cavity, the wave amplitude must be zero since an infinitely high potential means that no electrons can have an energy larger than this potential height. This means that the electron wave inside the cavity must be a standing wave and its wavelength must satisfy eq. (2.8),

$$\lambda = \frac{2D}{n} \qquad (n = 1, 2, 3, \ldots) \tag{2.14}$$

The momentum and energy of the electron are

$$p_n = \frac{nh}{2D} \text{ and } E_n = \frac{p^2}{2m} = \frac{1}{2m}\left(\frac{nh}{2D}\right)^2 \qquad (n = 1, 2, 3, \ldots) \tag{2.15}$$

which are discontinuous, or quantized. Later, we will derive the same result from solving the Schrödinger equation.

2.2.3 The Schrödinger Equation

Two basic methods have been developed to describe the material waves. The first was the matrix method developed by Heisenberg (1925). Shortly after, Schrödinger developed the famous equation that bears his name. These two descriptions are equivalent among themselves, so we will focus on the Schrödinger equation (Schrödinger, 1926), which states that the wavefunction of any matter obeys the following:

$$-\frac{\hbar^2}{2m}\nabla^2\Psi_t + U\Psi_t = i\hbar\frac{\partial \Psi_t}{\partial t} \tag{2.16}$$

where m is the mass, t is the time, U is the potential energy constraint that the matter is subject to and $\Psi_t(t, \mathbf{r})$ is called the wavefunction of the matter and is a function of time and coordinate $\mathbf{r}$. If $U = 0$, that is, a matter with no potential constraint, the Schrödinger equation becomes

$$-\frac{\hbar^2}{2m}\nabla^2\Psi_t = i\hbar\frac{\partial \Psi_t}{\partial t} \tag{2.17}$$

One may think that the equation is a parabolic type of equation similar to the transient heat conduction equation [eq. (1.19)], but the "magic" imaginary unit i really gives rise to wave behavior. Schrödinger himself did not come up with an explanation for the meaning of wavefunction. The right explanation was given by Born, who suggested that Ψ_t itself is not an observable quantity, but that $\Psi_t\Psi_t^*$ is the probability density function to find the matter at location $\mathbf{r}$, where "*" means complex conjugate. The normalization requirement for the probability function is then

$$\int_{-\infty}^{\infty} \Psi_t \Psi_t^* dx = 1 \tag{2.18}$$

for the one-dimensional case. For three-dimensional problems, the integration should be over the volume. The probabilistic interpretation is difficult to appreciate since we are most used to deterministic events in mechanics. Einstein, and even Schrödinger himself, rejected this interpretation. However, this interpretation has endured the test of experiments and time. Since $\Psi_t \Psi_t^*$ is a probability, the quantum world is full of uncertainties. Any quantities, such as energy, momentum, and location, are no longer a deterministic quantity but have an average, or expectation, value and uncertainties. The expectation value (or most probable value) of any quantity can be calculated from

$$\langle \Omega \rangle = \int_{-\infty}^{\infty} \Psi_t^* \Omega \Psi_t dx \tag{2.19}$$

where $\langle \Omega \rangle$ is the expectation value and Ω is the operator for this quantity. The operators for position, momentum, and energy of matter are

position operator:

$$\Omega = \mathbf{r} \tag{2.20}$$

momentum operator:

$$\begin{aligned} \Omega = \mathbf{p} &= -i\hbar\nabla \\ &= -i\hbar\left(\frac{\partial}{\partial x}\hat{\mathbf{x}} + \frac{\partial}{\partial y}\hat{\mathbf{y}} + \frac{\partial}{\partial z}\hat{\mathbf{z}}\right) \\ &= p_x\hat{\mathbf{x}} + p_y\hat{\mathbf{y}} + p_z\hat{\mathbf{z}} \end{aligned} \tag{2.21}$$

and the energy operator:

$$\begin{aligned} \Omega = H &= \frac{\mathbf{p} \bullet \mathbf{p}}{2m} + U = \frac{\mathbf{p}^2}{2m} + U \\ &= -\frac{\hbar^2}{2m}\nabla^2 + U = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) + U \end{aligned} \tag{2.22}$$

The first term in eq. (2.22) corresponds to the kinetic energy operator and the second term to the potential energy. In classical mechanics, the kinetic energy plus the potential energy of an energy-conserve system is called the Hamiltonian of the system. In quantum mechanics, the Hamiltonian becomes an operator, according to eq. (2.22). In a Cartesian coordinate system, the gradient operator ∇ and the Laplace operator ∇^2 are given by

$$\nabla = \hat{\mathbf{x}}\frac{\partial}{\partial x} + \hat{\mathbf{y}}\frac{\partial}{\partial y} + \hat{\mathbf{z}}\frac{\partial}{\partial z}, \quad \nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \tag{2.23}$$

The differentials in the operators are applied to the function immediately following the operator. Thus the order cannot be exchanged, which is similar to the matrix operation. Heisenberg's matrix formulation of quantum mechanics naturally possesses such characteristics. In eq. (2.19), $\Psi_t^* \Omega \Psi_t$ inside the integral means that the operator Ω is first applied to Ψ_t and the obtained function is multiplied by Ψ_t^*. As another example,

$$p_x p_x \Psi_t = -i\hbar\frac{\partial}{\partial x}\left(-i\hbar\frac{\partial \Psi_t}{\partial x}\right) = -\hbar^2\frac{\partial^2 \Psi_t}{\partial x^2} \tag{2.24}$$

which explains the way of expressing H in terms of $\mathbf{p}$ in eq. (2.22).

The Schrödinger equation is time dependent. When the potential energy is independent of time, we can derive the steady-state Schrödinger equation using the separation-of-variables method. Assuming $\Psi_t(\mathbf{r}, t) = \Psi(\mathbf{r})Y(t)$ and substituting into the Schrödinger equation, we get

$$\frac{1}{\Psi}\left[-\frac{\hbar^2}{2m}\nabla^2\Psi + U\Psi\right] = i\hbar\frac{1}{Y}\frac{dY}{dt} = E \tag{2.25}$$

where E is a constant (eigenvalue) since Ψ depends on $\mathbf{r}$ only and Y depends on t only, and its meaning will be explained later. Solving for Y leads to

$$Y = C_1 \exp\left[-i\frac{E}{\hbar}t\right] \tag{2.26}$$

The governing equation for $\Psi(\mathbf{r})$ is called the steady-state Schrödinger equation

$$-\frac{\hbar^2}{2m}\nabla^2\Psi + (U - E)\,\Psi = 0 \tag{2.27}$$

This is an eigenvalue equation with the eigenvalue E and eigenfunction Ψ determined by the potential energy profile U and the boundary conditions. On the basis of eqs. (2.19) and (2.22), we can prove that the expected energy of a system is

$$\langle H \rangle = \int_{-\infty}^{\infty} \Psi_t^* H \Psi_t dx = E \tag{2.28}$$

So the separation-of-variable constant E, or the eigenvalue, actually represents the energy states of the system. Correspondingly, we could write the time-dependent part as $Y = e^{-i\omega t}$, with $E = \hbar\omega$. So the material waves obey the Planck–Einstein relation, eq. (2.10).

Because $\Psi_t \Psi_t^*$ is a probability and the physical observable quantities are only the expectation values, there are also standard deviations for these expectations, such as the standard deviations in location Δx, momentum Δp, energy ΔE, and time Δt. It can be proven that, for any solution of the Schrödinger equation, the following relationship holds

$$\Delta p_x \bullet \Delta x \geq \hbar/2 \quad \text{and} \quad \Delta E \bullet \Delta t \geq \hbar/2 \tag{2.29}$$

This is the famous Heisenberg uncertainty principle, which means that position and momentum, or energy and time, cannot be accurately determined simultaneously in the quantum world. Because $\hbar$ is a very small number, the uncertainty represented by eq. (2.29) for a macroscopic object is very small. For example, if we decide that an object with a momentum of 1 kg m s^{-1} has an uncertainty of 10^{-10} kg m s^{-1}, the corresponding uncertainty in determining its position is $\sim 10^{-24}$ m, a negligible quantity. This uncertainty, however, becomes quite appreciable for small particles such as electrons.

For our further use, we need also to have an expression for the flux of the matter being considered. This can be obtained by (1) first multiplying the Schrödinger equation, (2.16), by Ψ_t^*, (2) taking the complex conjugate of the Schrödinger equation and multiplying the obtained equation by Ψ_t, and (3) subtracting the two resulting equations, which leads to

$$\frac{\partial |\Psi_t|^2}{\partial t} + \nabla \bullet \mathbf{J} = 0 \tag{2.30}$$

where **J** is

$$\mathbf{J} = \frac{i\hbar}{2m}(\Psi_t \nabla \Psi_t^* - \Psi_t^* \nabla \Psi_t) \tag{2.31}$$

Since the first term in eq. (2.30) is the rate of the change of the probability of finding the matter at each location, the second term in eq. (2.30) must be the net rate of matter flowing out of the point. Equation (2.30) is the particle conservation equation and **J** [m^{-2}s^{-1}] is understood as the current density (or flux) of the material wave.

The wavefunction is a difficult concept to grasp at first sight and this is not strange, since even Schrödinger himself was not able to explain the meaning of the wavefunction. However, Schrödinger was successful in using the equation to show that the energy states of electrons are quantized, as we will see later. Born's explanation of the wavefunction products $\Psi_t \Psi_t^*$ as a probability density of matter implies that material particles have spatial extent with some ambiguity, as we will see from the example solutions of the Schrödinger equation.

2.3 Example Solutions of the Schrödinger Equation

In this section, we will give solutions to the Schrödinger equation for several important cases that we will use later.

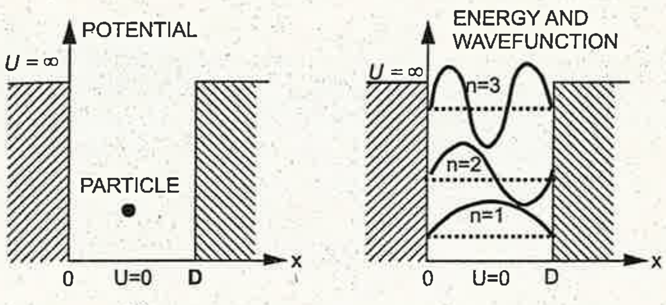
2.3.1 Free Particles

A free particle is one that it is not subject to any potential constraints; that is, $U = 0$. We can think of this free particle as a free electron. For the particle traveling along the x-direction, eq. (2.27) becomes

$$-\frac{\hbar^2}{2m}\frac{d^2\Psi}{dx^2} - E\Psi = 0 \tag{2.32}$$

The solution of the above equation is

$$\Psi(x) = A\exp(-ikx) + B\exp(ikx) \tag{2.33}$$



(a)

(b)

Figure 2.5 (a) One-dimensional potential well with infinite potential heights on both sides and zero potential inside the box. (b) Particle energy quantization in the box and wavefunction for the first three levels.

where $k = \sqrt{2Em/\hbar^2}$. When combined with the time-dependent factor, eq. (2.26), the time-dependent wavefunction is found to be

$$\Psi_t(x,t) = Ae^{-i(\omega t + kx)} + Be^{-i(\omega t - kx)} \tag{2.34}$$

where C_1 in eq. (2.26) is absorbed into A and B. The first term represents a free particle traveling in the negative x-direction and the second term along the positive x-direction.

Interested readers may ask what the Heisenberg uncertainty principle means for a free electron with a given momentum and energy. Equation (2.34) shows that the wavefunction for a right traveling wave extends from $x = -\infty$ to $x = \infty$, with equal probability everywhere, which means that its position is not determined at all. Similarly, the wave has fixed energy but spans time from negative infinity to positive infinity, that is, the whole time history. Thus, the Heisenberg uncertainty principle holds true for this simple case.

2.3.2 Particle in a One-Dimensional Potential Well

On the basis of the requirement for standing waves, we derived eq. (2.15) which shows the quantization of the allowable energy levels for a material wave inside a one-dimensional cavity of length D. Now let's start from the Schrödinger equation and demonstrate that eq. (2.15) is a natural solution of the equation. We consider the case of a particle in a one-dimensional potential well, which can be, for example, an electron subject to an electric potential field as shown in figure 2.5(a). The steady-state Schrödinger equation for the particle in such a potential profile is

$$-\frac{\hbar^2}{2m}\frac{d^2\Psi}{dy^2} + (U - E)\Psi = 0 \tag{2.35}$$

The solution of the above equation is

$$\Psi = A\exp\left[-ix\sqrt{\frac{2mE}{\hbar^2}}\right] + B\exp\left[ix\sqrt{\frac{2mE}{\hbar^2}}\right] \text{ (for } 0 < x < D\text{)} \tag{2.36}$$

$$\Psi = 0 \text{ (for other } x \text{ where } U \to \infty\text{)} \tag{2.37}$$

!!

The general boundary conditions are the continuity of the wavefunctions and their first-order derivatives at the boundaries. The continuity of the wavefunction states that the probability density of finding the matter cannot be double valued at the same location. The continuity of the first-order derivative of the wavefunction can be derived by integrating eq. (2.16) over an infinitely thin control volume encompassing the boundary, and this condition implies the continuity of the particle flux. For the current problem, the continuity of the first derivatives is not required because the wavefunction at the boundaries is already known to be zero. Applying the continuity of the wave function for $x = 0$ and $x = D$, we have at $x = 0$

$$A + B = 0 \tag{2.38}$$

at $x = D$

$$A \exp\left[-iD\sqrt{\frac{2mE}{\hbar^2}}\right] + B \exp\left[iD\sqrt{\frac{2mE}{\hbar^2}}\right] = 0 \tag{2.39}$$

Simultaneous solution of eqs. (2.38) and (2.39) yields

$$\sin\left(D\sqrt{\frac{2mE}{\hbar^2}}\right) = 0 \tag{2.40}$$

so that multiple solutions for E exist at

$$D\sqrt{\frac{2mE_n}{\hbar^2}} = n\pi \qquad (n = 1, 2, 3...) \tag{2.41}$$

Here we take only positive values of n since the negative values give the same electron probability distribution functions and are thus identical to the positive solutions. The value $n = 0$ is excluded since taking this value will lead to $\Psi = 0$, which means no particle exists inside the region. The integer n is called the quantum number. Each n corresponds to a wavefunction and an energy level. For multidimensional problems, which we will encounter later, there will be more quantum numbers, including the spin quantum number for electrons. From eq. (2.41), the allowable energy levels are

$E_n \propto n^2$

$$E_n = \frac{1}{2m}\left(\frac{\pi\hbar n}{D}\right)^2 = \frac{1}{2m}\left(\frac{hn}{2D}\right)^2 \qquad (n = 1, 2, 3, \ldots) \tag{2.42}$$

which is the same result as eq. (2.15). The material wave function inside the potential well is

$$\Psi_n = -2iA \sin\left(\frac{n\pi x}{D}\right) \tag{2.43}$$

To find the coefficient A, we use the normalization condition

$$\int_{-\infty}^{\infty} \Psi_n \Psi_n^* dx = 1 \tag{2.44}$$

the normalization gives: $|A| = 1/\sqrt{2D}$ we then chose → i to get a real Ψ_n.

which gives $A = i/\sqrt{2D}$, and thus

$$\Psi_n = \sqrt{\frac{2}{D}} \sin\left(\frac{n\pi x}{D}\right) \tag{2.45}$$

These wavefunctions are standing waves, as shown in figure 2.5(b). The separation between successive energy levels depends on the width D of the potential well, the mass, and the order of the energy level. When D is large, the energy separation is very small. The observation of such energy separation requires sensitive tools that can discern small energy separation. When the energy separation is larger than the thermal energy fluctuation, the quantization effect can be easily observed. For electrons with a small mass, this requires in general that D is smaller than 100 Å.

Let us now show that the Heisenberg principle is satisfied for $n = 1$. The most probable position and the standard deviation in its position can be calculated following eq. (2.19):

$$\langle x \rangle = \int_0^D \Psi_1^* x \Psi_1 dx = 4A^2 \int_0^D x \sin^2\left(\frac{\pi x}{D}\right) dx = \frac{D}{2} \tag{2.46}$$

$$\Delta x = \langle (x - \langle x \rangle)^2 \rangle^{1/2} = \left[\int_0^D \Psi_1^* (x - \langle x \rangle)^2 \Psi_1 dx\right]^{1/2} = D\sqrt{\frac{1}{12} - \frac{1}{2\pi^2}} \tag{2.47}$$

Similarly, the most probable momentum and the uncertainty standard deviation in its momentum are

$$\langle p \rangle = -\int_0^D \Psi_1^* i\hbar \frac{d\Psi_1}{dx} dx = 0 \tag{2.48}$$

$$\Delta p = \langle (p - \langle p \rangle)^2 \rangle^{1/2} = \left[\int_0^D \Psi_1^* (-\hbar^2) \frac{d^2\Psi_1}{dx^2} dx\right]^{1/2} = \frac{\pi\hbar}{D} \tag{2.49}$$

From eqs. (2.47) and (2.49), we obtain $\Delta x \Delta p = 0.57\hbar$, thus satisfying the Heisenberg uncertainty principle. This example shows although the electron at $n = 1$ energy level is most probably positioned in the middle of the potential well ($x = D/2$) and has zero average momentum, it can also be at other locations, as the wavefunction suggests.

Although the above solution for an electron in a potential well is one of the simplest solutions of the Schrödinger equation, the experimental realization of such a system came only in the 1970s, after the concept of superlattices was proposed (Esaki and Tsu, 1970) and the molecular-beam-epitaxy (MBE) thin-film growth technique was invented. The MBE technique allows the controlled growth of thin films to an accuracy of one atomic layer or less. Since then, studies of man-made quantum structures have become one of

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On the basis of the allowable values of α and β, we can determine the allowable energy levels as

$$E_{\ell n} = \frac{(\ell^2 + n^2)\pi^2\hbar^2}{2mD^2} \qquad (\ell, n = 1, 2, \ldots) \tag{E2.1.10}$$

Corresponding to each set of ℓ and n, there is a distinct wavefunction

$$\Psi_{\ell n} = C_{\ell n} \sin\left(\frac{n\pi x}{D}\right) \sin\left(\frac{\ell \pi y}{D}\right) \tag{E2.1.11}$$

We can further determine that the constant $C_{\ell n} = 2/D$ using normalization condition (2.44)

Comment: For the above two-dimensional problem, we obtain two quantum numbers ℓ and n. Typically, the number of the quantum numbers is identical to the dimensionality of the problem. For a three-dimensional problem, there are three quantum numbers, as we will see later. Each set of quantum numbers determines a unique wavefunction. The energy levels for different sets of ℓ and n, however, can be identical. For example, the wavefunction corresponding to $\ell = 1$ and $n = 2$ has the same energy as that corresponding to $\ell = 2$ and $n = 1$. These states that have different wavefunctions but the same energy are said to be degenerate.

2.3.3 Electron Spin and the Pauli Exclusion Principle

Each wavefunction obtained from the Schrödinger equation, as exemplified in the previous sections represents a possible quantum mechanical state at which a particle can exist under the given potential. The solutions of the Schrödinger equation, however, do not tell the entire story regarding the quantum state of a particle. For example, the equation cannot predict the spin of a particle. The spin is a property that preserves the particle's rotational symmetry and can only be derived from relativistic quantum mechanics, developed originally by Dirac. It is an intrinsic property of the particle and should not be understood, simply for example, as the rotation of an electron around a nucleus. For electrons, corresponding to each wavefunction obtained from the Schrödinger equation, there are two quantum states (or two relativistic wavefunctions), which are usually denoted by an additional quantum number s that can have the following values

$$s = \frac{1}{2} \text{ or } -\frac{1}{2} \tag{2.50}$$

where $s = 1/2$ is called spin up and $s = -1/2$ is called spin down. The spin quantum numbers for other types of particle are different. Interested readers should consult quantum mechanics textbooks (Feynman, 1965; Cohen-Tannoudji et al., 1977; Landau and Liftshitz, 1977).

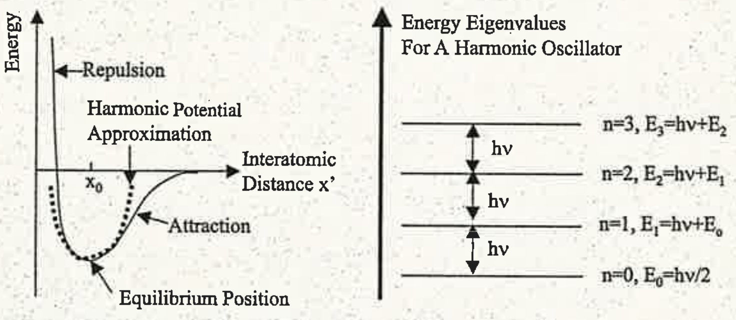
We can combine this spin quantum number with the wavefunctions obtained from the Schrödinger equation to denote the complete set of wavefunctions that a particle can have. For an electron in a one-dimensional box, the wavefunction can be denoted as $\Psi_{n,s}$. Each set of quantum numbers n and s represents a quantum state. For each n, there are two quantum states ($s = 1/2$ or $s = -1/2$) with identical energy. The number of wavefunctions, that is, the number of quantum states, at an identical energy level is called the level degeneracy. Thus, the electron in a one-dimensional box at any energy level n has a degeneracy of two. The *Pauli exclusion principle* says that each quantum state can be occupied by at most one electron. This principle determines how the allowable energy levels, such as those given by eqs. (2.42) and (E2.1.10), will actually be occupied by electrons. Although eq. (2.42) [or (E2.1.10)] is derived under the assumption of one electron in an infinite potential, the solution should be valid if there is more than one electron inside the well, under the approximation that the interactions of these electrons do not change the potential profile. From the principles of thermodynamics, we know that electrons tend to occupy the lowest energy states. If there are five electrons in the potential well and the temperature is at absolute zero (to avoid thermal fluctuations), two electrons will take the lowest E_1 energy level ($\Psi_{1,1/2}$ and $\Psi_{1,-1/2}$ quantum states), and another two will occupy the next lowest level E_2 ($\Psi_{2,1/2}$,$\Psi_{2,-1/2}$ quantum states). The fifth electron will occupy either the $\Psi_{3,1/2}$ or the $\Psi_{3,-1/2}$ state. The occupation of a quantum state at non-zero temperatures will be discussed in chapter 4.

2.3.4 Harmonic Oscillator

→ change in the potential form

Two main factors govern the Schrödinger equation and the consequent energy eigenvalues and wavefunctions: the potential distribution and the boundary conditions. The rectangular potential profile for the particle-in-a-box (problem discussed in section 2.3.2) gives energy eigenvalues that depend on the square of the quantum numbers, as represented by eqs. (2.42) and (E2.1.10). In this section, we will study the energy levels and eigenfunctions of a harmonic oscillator, which is a very useful model for describing the atomic vibrations in simple molecules, such as H_2 and CO, or the atomic vibrations in solids. We can appreciate this by considering the general shape of the interatomic potential, shown in figure 2.7(a). If the vibrational amplitude of the atom is not large, we can expand the potential around the equilibrium position, x_0, such that

$$U(x') = U(x_0) + \frac{1}{2}\left[\frac{d^2U}{dx'^2}\right]_{x'=x_0} (x' - x_0)^{2} + O[(x' - x_0)^3] \tag{2.51}$$



(a) (b)

Figure 2.7 (a) The harmonic oscillator model approximates the potential at equilibrium by a parabola. (b) The energy levels of a harmonic oscillator.

where we have used the fact that $dU/dx' = 0$ at the equilibrium point $x' = x_0$ (the minimum of a curve). Neglecting the higher order term $O[(x' - x_0)^3]$, the force acting on the atom thus becomes

$$F = -dU/dx' = -K(x' - x_0) = -Kx \tag{2.52}$$

where $x(= x' - x_0')$ represents the displacement from the equilibrium position rather than the separation between atoms, and $K = (d^2U/dx'^2)_{x=x_0}$is the spring constant such that $U = Kx^2/2$. This potential represents a classical mass–spring system, the Schrödinger equation for the system is

$$-\frac{\hbar^2}{2m}\frac{d^2\Psi}{dx^2} + \left(\frac{Kx^2}{2} - E\right)\Psi = 0 \tag{2.53}$$

Boundary conditions for the above equation are

$$\Psi(x \to \infty) = \Psi(x \to -\infty) = 0 \tag{2.54}$$

because as $x \to \pm\infty$, the potential $U \to \infty$, which requires vanishing wavefunction values in these limits. Solving eq. (2.53) involves a coordinate transformation and a series expansion, and will not be pursued here (see Landau and Lifshitz, 1977). Final results for the energy levels and wavefunctions are

$E_n \propto n$

$$E_n = \left(n + \frac{1}{2}\right)h\nu = \left(n + \frac{1}{2}\right)\hbar\omega \qquad (n = 0, 1, 2, \ldots) \tag{2.55}$$

$$\psi_n(x) = \left[\sqrt{\frac{m\omega}{\pi\hbar}}\frac{1}{2^n n!}\right]^{1/2} H_n\left[\left(\frac{m\omega x^2}{\hbar}\right)^{\frac{1}{2}}\right]\exp\left(-\frac{m\omega x^2}{2\hbar}\right) \tag{2.56}$$

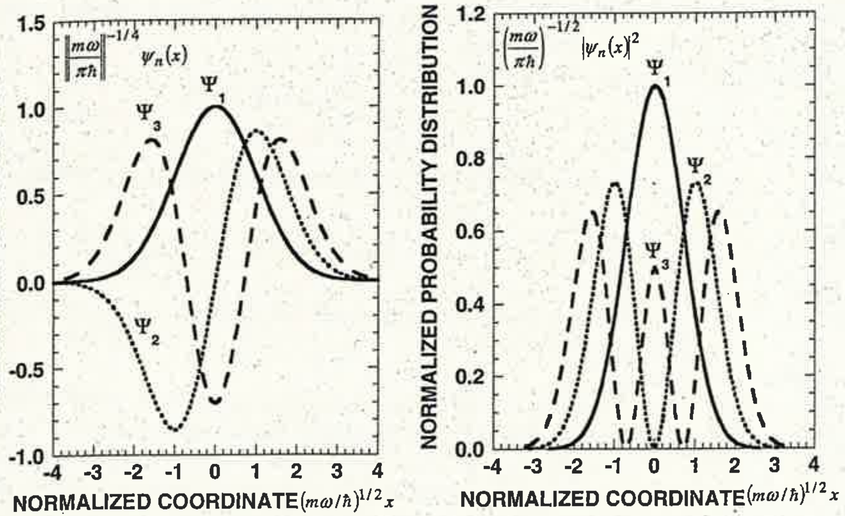
where

$$\nu = \frac{1}{2\pi}\sqrt{\frac{K}{m}} \tag{2.57}$$

$\omega = 2\pi\nu$ is the angular frequency, and H_n is a standard function called the Hermite polynomial, given by

$$H_n(\xi) = (-1)^n \exp(\xi^2)\frac{d^n}{d\xi^n}[\exp(\xi^{-2})] \tag{2.58}$$

We see that ν is the fundamental vibration frequency that we get from classical mechanics for a mass–spring system. In classical mechanics, however, the mass–spring system energy, which equals the sum of the kinetic and the potential energy, can be a continuous function of the amplitude of the oscillator. Equation (2.55) says, however, that the energy of the harmonic oscillator is quantized and can only be a multiple number of $h\nu$ plus $\frac{1}{2}h\nu$, which means that the separation between adjacent energy levels is constant and equal to $h\nu$, as shown in figure 2.7(b). The $\frac{1}{2}h\nu$ term in eq. (2.55a) is called the zero point energy, which is unimportant for most heat transfer problems. It is a manifestation of the Heisenberg uncertainty principle. In figure 2.8, we show the wavefunctions (Ψ)



(a) (b)

Figure 2.8 (a) Normalized wavefunction and (b) normalized probability distribution for a harmonic oscillator.

and the probability density distributions ($|\Psi|^2$) of the harmonic oscillator states. The latter shows the probability of finding the vibrating atom at position x. As the quantum number n increases, $|\Psi|^2$ spreads wider which means that the potential energy grows with increasing n. The kinetic energy also increases with increasing n.

The harmonic oscillator model is important for understanding the absorption characteristics of gases in the infrared spectrum. When a photon interacts with the gas, absorption occurs only when the photon energy equals the energy difference between the final state and the initial state of the molecule,

$$E_p = h\nu_p = E_f - E_i \tag{2.59}$$

where the subscript p represents photons. For the vibrational modes of a molecule, eqs (2.55) and (2.59) lead to $\nu_p = \nu\Delta n$. Further quantum mechanical consideration limits $\Delta n = \pm 1$ (the minus sign corresponds to emission), which is called the selection rule. The absorption or emission of a photon occurs when the photon frequency equals the molecular vibration frequency (also called an absorption line),

$$\nu_p = \frac{1}{2\pi}\sqrt{\frac{K}{m}} \tag{2.60}$$

The relative vibration of atoms in a polyatomic molecule can be modeled as a harmonic oscillator. When applying the above expression to a diatomic molecule with two atoms of mass m_1 and m_2, the reduced mass should be used,

$$m = \frac{m_1 m_2}{m_1 + m_2} \tag{2.61}$$

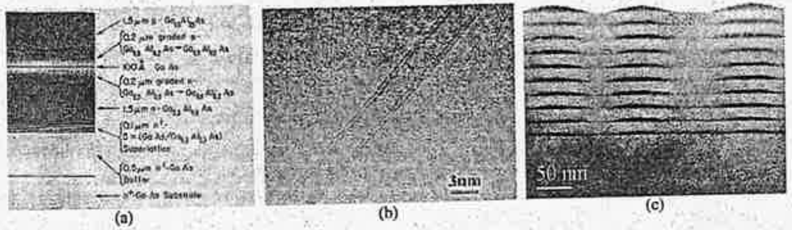


Figure 2.6 (a) Quantum well laser (Yariv, 1989; courtesy of Wiley). (b) A carbon nanotube (courtesy of Dr. Z.F. Ren). (c) Ge quantum dots in silicon (Liu et al., 2001).

the most active areas of research. Figure 2.6(a) shows a practical quantum well made of a very thin solid layer of gallium arsenide (GaAs) semiconductor. It is sandwiched between other materials in which the potential energy for the electrons is higher than that in the GaAs layer. The allowed electron energy states inside the GaAs layer become discrete. This quantum size effect has been used to make better semiconductor lasers and detectors. In addition to thin films, in which the quantum effect occurs in the direction of film thickness, other quantum structures, such as quantum wires, carbon nanotubes, and dots (quantum dots), are also being actively studied, as shown in figures 2.6(b) and (c), respectively. The potentials in the surrounding for these cases may not be infinite as in the preceding simple example. Thus, the energy levels may be more complicated than given by eq. (2.42).

Example 2.1 *Electron energy levels inside a square nanowire*

Determine the allowable energy levels of an electron in a two-dimensional square quantum wire, assuming the potential inside the quantum wire is $U = 0$ and outside is $U = \infty$.

Solution: We establish a coordinate system as shown in figure E2.1. Clearly, outside the potential well, we have $\Psi = 0$ because $U = \infty$. We thus focus on the solution inside the potential well. The Schrödinger equation inside the well ($U = 0$) is

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2\Psi}{\partial x^2}+\frac{\partial^2\Psi}{\partial y^2}\right)-E\Psi=0 \tag{E2.1.1}$$

with the following boundary conditions

$$\begin{array}{ll} x = 0 \text{ or } D, & \Psi = 0 \\ y = 0 \text{ or } D, & \Psi = 0 \end{array} \tag{E2.1.2}$$

We use the separation-of-variables technique. Assuming $\Psi(x, y) = X(x)Y(y)$ and substituting into the above equation lead to

$$\frac{1}{X}\frac{d^2X}{dx^2}+\frac{1}{Y}\frac{d^2Y}{dy^2}+\frac{2mE}{\hbar^2}=0 \tag{E2.1.3}$$

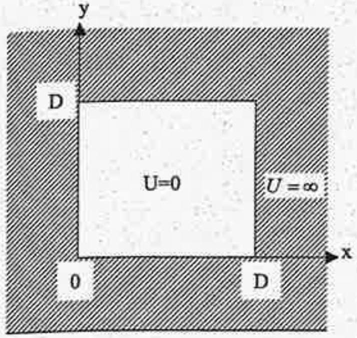


Figure E2.1 A square potential well.

In this equation, the first term depends on x and the second term on y. The third term is a constant. This leads to the requirement that both the first and the second term must be a constant. Since E is positive, we can show that neither of the first two terms can be positive (see what happens if you assume one of them is positive). Thus, we write

$$\frac{1}{X}\frac{d^2X}{dx^2}=-\alpha^2 \tag{E2.1.4}$$

$$\frac{1}{Y}\frac{d^2Y}{dy^2}=-\beta^2$$

The solution for X is

$$X(x) = A\sin(\alpha x) + B\cos(\alpha x) \tag{E2.1.5}$$

To satisfy the boundary condition that $\Psi = 0$ at $x = 0$ and $x = D$, we must have $X = 0$ at $x = 0$ and $x = D$. Applying these boundary conditions, we see that

$$\alpha = \frac{n\pi}{D} \quad (n = 1, 2, \ldots) \tag{E2.1.6}$$

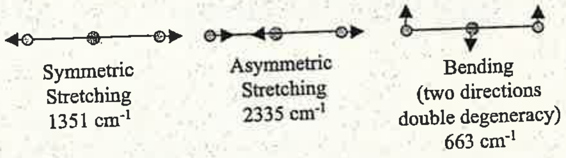
$$X_n(x) = A_n \sin\left(\frac{n\pi}{D}x\right) \tag{E2.1.7}$$

Similarly, for Y, we have

$$\beta = \frac{\ell\pi}{D} \quad (\ell = 1, 2, \ldots) \tag{E2.1.8}$$

$$Y_\ell(y) = B_\ell \sin\left(\frac{\ell\pi}{D}y\right) \tag{E2.1.9}$$

(a) Water Molecule



(b) CO_2 Molecule

Figure 2.9 Vibrational normal modes of (a) H_2O and (b) CO_2 molecules. Arrows represent atom vibration direction at one instant.

$\nu_p = \frac{1}{2\pi}\sqrt{K/m} =$

Consider, for example, an H_2 molecule having $K = 1113$ Nm^{-1} and a reduced mass of 1.67×10^{-27} kg. The corresponding vibrational frequency is 1.319×10^{14} Hz, or, in terms of wavelengh, $\lambda = 2.3$ μm, and wavenumber, $\eta = 1/\lambda = 4401$ cm^{-1} (wavenumber equals the inverse of wavelength). Experimentally, we can determine the absorption frequency using spectroscopy techniques and thus use eq. (2.60) to estimate the effective spring constant of the interatomic bonds in such molecules.

For polyatomic molecules (larger than two atoms), there exists more than one vibrational frequency. In general, the complex vibrational patterns can be decomposed into normal modes. Each normal mode can be thought of as one harmonic oscillator with a corresponding fundamental frequency. Examples of the normal modes for water and carbon dioxide (CO_2) are shown in figures 2.9(a) and (b). These fundamental normal modes can be superimposed to form new absorption lines. For example, the difference between the asymmetric and symmetric stretching gives the familiar absorption line of CO_2 at ~ 10 μm, which is a major factor in global warming because this absorption line is near the peak of terrestrial thermal radiation.

The harmonic oscillator model also represents quantized electromagnetic fields and atomic vibrations in solids. For an electromagnetic field at frequency ν, the allowable energy levels are

$$E_p = h\nu_p\left(n + \frac{1}{2}\right) \qquad (n = 0, 1, 2, \ldots) \tag{2.62}$$

where n is the number of photons in the field having frequency ν_p. This expression is consistent with our previous discussion on the quantized electromagnetic field eq. (2.10). In the next chapter, we will show that atomic vibrations in a crystalline solid can also be decomposed into normal modes and that the energy of each mode obeys eq. (2.62) as well.

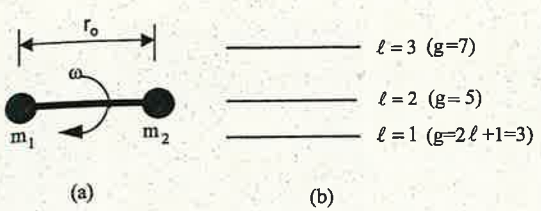


Figure 2.10 (a) A rigid rotor. (b) Energy levels in a rigid rotor.

2.3.5 The Rigid Rotor

In diatomic and polyatomic molecules, the atoms can vibrate relative to each other or rotate as a whole. The relative vibration can be treated by the harmonic oscillator approximation. Let us consider the rotation only and assume that the distance between the two masses of a diatomic molecule is constant (rigid rotation), as shown in figure 2.10(a).

In classical mechanics, a quantity often used to describe the rotation is the moment of inertia. For the two-mass system shown in figure 2.10 rotating relative to its mass center, the moment of inertia is

$$I = \frac{m_1 m_2 r_0^2}{m_1 + m_2} \tag{2.63}$$

where r_0 is the effective separation between the two atoms. In classical mechanics, we often use the angular momentum equations to solve rotational problems. In quantum mechanics, there are also corresponding angular momentum equations that govern the wavefunctions and energy eigenvalues for rotation. Here, we will skip the details but give the solutions for the wavefunction (Landau and Lifshitz, 1977)

$$Y_\ell^m(\theta, \varphi) = \varepsilon i^\ell \left[\frac{(2\ell+1)(\ell-|m|)!}{4\pi(\ell+|m|)!}\right]^{1/2} P_\ell^{|m|}(\cos\theta)\, e^{im\varphi}, \tag{2.64}$$

θ and φ are polar and azimuthal angles, respectively, in a spherical coordinate system, where $\varepsilon = (-1)^m$ for $m \geq 0$ and $\varepsilon = 1$ for $m \leq 0$, and P is the associated Legendre polynomial

$$P_\ell^m(\xi) = \frac{(1-\xi^2)^{m/2}}{2^\ell \ell!}\frac{d^{\ell+m}}{d\xi^{\ell+m}}(\xi^2-1)^\ell$$

The functions $Y_\ell^m(\theta, \phi)$ are called the spherical harmonics. The energy eigenvalues are

$$E_\ell = \frac{\hbar^2}{2I}\ell(\ell+1) = hB\ell(\ell+1) \quad (\text{for } |m| \leq \ell,\ \ell = 0, 1, 2, \ldots) \tag{2.65}$$

where $B = h/(8\pi^2 I)$ [Hz] is called the rotational constant. For H_2, $B = 1.8 \times 10^{12}$ Hz. The corresponding wavelength for this rotational state alone is very small (~ 100 μm). Because there are two degrees of freedom for the rigid rotational motion (polar and azimuthal directions in a spherical coordinate system), we see that two quantum numbers emerge, that is, ℓ and m. Each set of ℓ and m gives a unique wavefunction and thus a unique quantum state (spin quantum number not included). The energy levels given by eq. (2.65), however, do not depend on the magnitude of m. For each ℓ, there are $(2\ell + 1)$ values of m, that is, $(2\ell + 1)$ wavefunctions having the same energy level. The energy level E_ℓ is thus $(2\ell + 1)$-fold degenerate, similar to the degeneracy of a particle in a two-dimensional box discussed in example 2.1, because there are $(2\ell + 1)$ rotational orbits. We use g to denote the *degeneracy* so that, for the rotational level at energy E_ℓ we have

$$g(\ell) = 2\ell + 1 \tag{2.66}$$

Similar to the case of harmonic oscillators, the photon absorption by rigid rotors occurs only when the separation of the energy levels of the oscillators matches the photon energy. The selection rule in quantum mechanics further limits the photon to two adjacent energy levels ($\Delta\ell = 1$),

$$\nu_p = (E_{\ell+1} - E_\ell)/h = 2B(\ell + 1) \tag{2.67}$$

where B in the unit of wavelength is of the order of 100 μm for hydrogen molecules; thus pure rotational modes have long wavelengths and are typically unimportant in thermal energy transfer, but they can be important in the microwave range. Since a diatomic molecule can have both vibrational and rotational modes, we can approximate their allowable energy states as the superposition of the rotational and vibrational energy levels, forming vibrational–rotational states. Assuming, for simplicity, that the rotational and vibrational motions are independent, we can then write

$$E(\text{vib} + \text{rot}) = E_n(\text{vib}) + E_\ell(\text{rot}) \tag{2.68}$$

and, correspondingly, the absorption lines of the combined vibrational–rotational states can be written as

$$\nu_p = \nu \pm 2B(\ell + 1) \tag{2.69}$$

where the positive sign means that accompanying the increase of the vibrational energy level due to the photon absorption, the rotational energy also increases by one level, while the negative sign means that the rotational energy decreases by one level. Thus, surrounding each fundamental vibrational frequency ν of polyatomic molecules, spectral lines with fine structures due to molecular rotations are formed. These lines often overlap due to various broadening and interaction mechanisms (such as thermal vibrations) so that the absorption of gases effectively occurs over certain bandwidths (called bands), rather than only at sharp discrete lines. Figure 2.11 illustrates the absorption bands of CO_2 molecules at 0.5 atm and 300 K.

2.3.6 Electronic Energy Levels of the Hydrogen Atom

The vibrational and rotational energy levels that we previously obtained are for the atomic motion of polyatomic molecules. Now let's consider the electronic energy levels of an atom. We use hydrogen atom as an example since there is only one electron surrounding the nucleus. The solution we will find, however, can be used as a basis for understanding the energy levels of other atoms having multiple electrons. The nucleus of a hydrogen

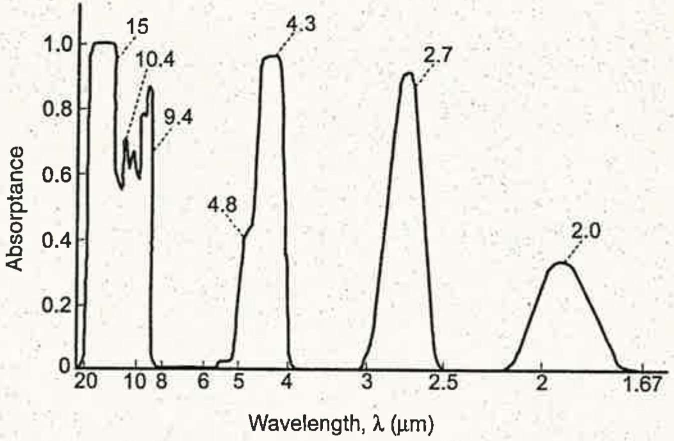


Figure 2.11 Vibrational-rotational absorption bands of CO_2 molecules (Siegel and Howell, 1992; courtesy of J.R. Howell).

atom can be treated as stationary because its mass is relatively heavy compared to that of the electron. The interaction between the nucleus and the orbiting electron is governed by the Coulomb electrostatic force

$$F = \frac{1}{4\pi\varepsilon_0}\frac{e^2}{r^2} = \frac{c_1}{r^2} \tag{2.70}$$

where $c_1 = e^2/4\pi\varepsilon_0$ and the electron charge is $e = 1.6 \times 10^{-19}$[C], while $\varepsilon_0 = 1.124 \times 10^{-10}/4\pi\,[\mathrm{C^2\,m^{-2}\,N^{-1}}]$ is the electrical permittivity of the vacuum. The potential is

$$U = -\int_r^\infty F\,dr = -\frac{c_1}{r} \tag{2.71}$$

Since the nucleus is stationary, we can take it as the origin of the coordinate system. The Schrödinger equation then becomes

$$-\frac{\hbar^2}{2m}\nabla^2\Psi + \left(-\frac{c_1}{r} - E\right)\Psi = 0 \tag{2.72}$$

In spherical coordinates, the Laplace operator is

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\varphi^2} \tag{2.73}$$

The solution of eq. (2.72) can then be separated into a radial wavefunction $R_{n\ell}(r)$ and into spherical harmonics Y_ℓ^m (Griffiths, 1994)

$$\Psi_{n\ell m} = R_{n\ell}(r)Y_\ell^m(\theta, \varphi) \tag{2.74}$$

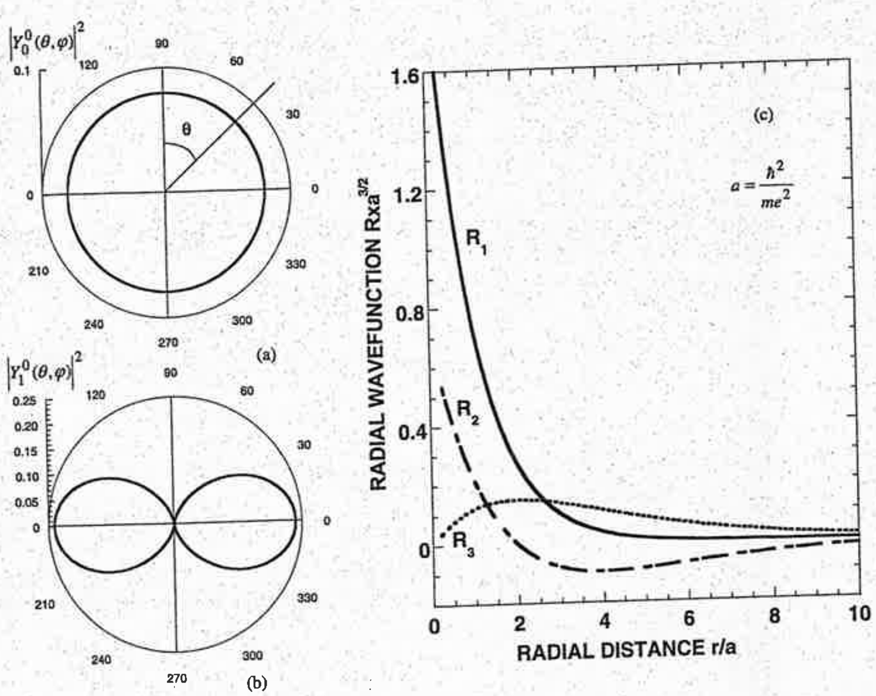


Figure 2.12 (a) and (b) Amplitude square of spherical harmonic functions in polar coordinate θ. The φ direction is axisymmetric around the $\theta = 0$ axis and (c) normalized radial wavefunction of the hydrogen atom.

where Y_ℓ^m is given by eq. (2.64). Because of the three degrees of freedom in space, there are three quantum numbers n, ℓ, and m in the wavefunction. We will skip the analytical expressions for the radial wavefunction, but give a few graphical examples of $R_{n\ell}(r)$ and $|Y_\ell^m|^2$ in figure 2.12. The allowable energy levels of the electron–nucleus system are

$$E_n^{\mathrm{el}} = -\frac{mc_1^2}{2\hbar^2 n^2} = -\frac{13.6\ \mathrm{eV}}{n^2}(n \geq 1, n \geq \ell + 1, \text{ and } |m| \\ \leq \ell, \ell = 0, 1, 2, \ldots) \tag{2.75}$$

where n is an integer called principal quantum number. We note that the energy levels depend on n but not on ℓ or m. The allowable values of ℓ and m are, however, restricted by the value of n. Let us recall the concept of degeneracy; this means that the energy levels are degenerate. The three quantum numbers are as follows: n is the principal quantum number, ℓ is the quantum number of total angular momentum, and m is the magnetic quantum number. Corresponding to each set of n, l, m quantum numbers, there are two wave functions $\Psi_{n,l,m,s}$, where $s = \pm 1/2$ is for the electron spin, which determine two quantum states. For $n = 1$, the allowable values for ℓ and m are 0. The wave functions for this set of n, l, m values are $\Psi_{1,0,0,s}$ and are called the 1s-orbital (s-shell),

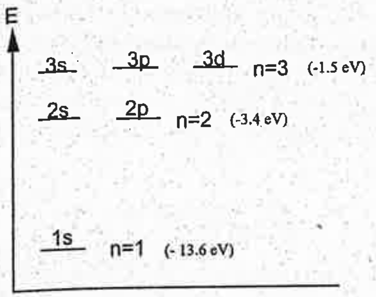


Figure 2.13 Illustration of first three energy levels of the hydrogen atom.

where "1" in front of s represents $n = 1$ and "s" following 1 represents $\ell = 0$. Since a maximum of one electron is allowable for each quantum state (Pauli exclusion principle), the 1s-orbital can have a maximum of two electrons as a result of the two possible values of the spin ($s = 1/2, -1/2$). For $n = 2$, the following values of ℓ and m are possible

$$n = 2 \rightarrow \begin{cases} l = 0 \quad m = 0 & 2s \quad \text{orbital} \\ l = 1 \quad m = -1, 0, 1 & 2p \quad \text{orbital} \end{cases}$$

Two electrons are allowed for the 2s-orbital and six electrons in total are allowable for the three quantum states in the 2p-orbital (p-shell). A total of eight electrons is thus allowed for the $n = 2$ states. In general, the degeneracy for a hydrogen atom of any arbitrary n is

$$g = 2n^2 \tag{2.76}$$

Figure 2.13 shows the energy levels of a hydrogen atom. An alphabetical symbol is assigned for each value of ℓ, which is inherited from the historical studies of absorption spectra of hydrogen before quantum mechanics was developed:

$$\ell = 0 \leftrightarrow s;\ \ell = 1 \leftrightarrow p;\ \ell = 2 \leftrightarrow d;\ \ell = 3 \leftrightarrow f;\ \ell = 4 \leftrightarrow g$$

The allowable hydrogen energy levels provide a framework for understanding the periodic table. Since the electron–ion interaction dominates the potential, the existence of more electrons in other atoms does not alter very much the major picture of the allowable energy levels and we can assume that the energy levels of a hydrogen atom also apply to other atoms for qualitative understanding. As a start, let's fill the electronic energy states, as shown in figure 2.13, according to the thermodynamics principle that the lowest level will be occupied first and each quantum state can have at most one electron. The one electron in hydrogen will occupy one of the two 1s orbitals. The two electrons in a helium atom will fully occupy the two 1s quantum states. Lithium has three electrons and the first two will fill the 1s-orbital and its third electron will fill one 2s-orbital, and so on.

Table 2.1 lists the electron orbital occupancy of elemental atoms. Up to the argon atom, it is always the case that quantum states with smaller orbital quantum number

Table 2.1 Electron configuration of first 30 elements in the periodic table

Atomic Number	Element	Electron Configuration									
		1s	2s	2p	3s	3p	3d	4s	4p	4d	4f
1	H hydrogen	1									
2	He helium	2									
3	Li lithium	Filled (2)	1								
4	Be beryllium		2								
5	B boron		2	1							
6	C carbon		2	2							
7	N nitrogen		2	3							
8	O oxygen		2	4							
9	F fluorine		2	5							
10	Ne neon		2	6							
11	Na sodium	Filled (2)	Filled (8)		1						
12	Mg magnesium				2						
13	Al aluminum				2	1					
14	Si silicon				2	2					
15	P phosphor				2	3					
16	S sulfur				2	4					
17	Cl chlorine				2	5					
18	A argon				2	6					
19	K potassium				2	6		1			
20	Ca calcium				2	6		2			
21	Sc scandium				2	6	1	2			
22	Ti titanium				2	6	2	2			
23	V vanadium				2	6	3	2			
24	Cr chromium				2	6	5	1			
25	Mn manganese				2	6	5	2			
26	Fe iron				2	6	6	2			
27	Co cobalt				2	6	7	2			
28	Ni nickel				2	6	8	2			
29	Cu copper				2	6	10	1			
30	Zn zinc				2	6	10	2			

are filled first. Starting with potassium, however, we begin to see deviations from this trend. Rather than filling the 3d-orbital, one electron actually fills the 4s-orbital first. This effect is due to electron–electron interaction such that the energy levels for the same n (for example, 3s, 3p, and 3d have the same $n = 3$) are no longer the same. This change is called the lifting of the degeneracy, and is because the 3d levels have a slightly higher energy than the 4s level. Therefore, the extra electron in potassium will fill the 4s-orbital rather than occupy one of the 3d-orbitals.

The filling of the electronic states determines the chemical activity of each atom. If all orbitals of the same principal quantum number n are filled, the atom is inert because the energy difference to the next level of n is much larger than $\kappa_B T$ (26 meV at room temperature). Otherwise, the vacant quantum states within the same principal quantum number can accept other electrons or lose electrons to form a more stable state. For example, the H_2 molecule has two electrons sharing the two 1s quantum states in the hydrogen atom, such that each atom "feels" that it has two electrons. In various acids, the hydrogen atom is also happy to give up its electrons. We call the electrons in the outermost principal orbitals the valence electrons.

Using eq. (2.75), we can calculate the absorption lines of hydrogen atoms as

$$h\nu_p\,(n_1 \rightarrow n_2) = 13.6\left(\frac{1}{n_2^2}-\frac{1}{n_1^2}\right)\text{eV} \tag{2.77}$$

Example 2.2

Determine the photon frequency and wavelength for series of allowable emission from all other states to the $n = 1$ states from the hydrogen atom. This series is called the Lyman series.

Solution: The emission occurs when the energy of the hydrogen atom drops from a high energy state to a low one. From eq. (2.77), the emission spectrum is

$$\begin{aligned}\nu_p &= \frac{13.6\text{ eV}}{h}\left(1-\frac{1}{n^2}\right)\\ &= 3.288\times10^{15}\left(1-\frac{1}{n^2}\right)\text{Hz}(n=2,3,4,\ldots)\end{aligned} \tag{E2.2.1}$$

The emitted photon frequency and wavelength are listed in the following table. These numbers are in excellent agreement with experiments.

n	$\nu_p(n \rightarrow 1)\times10^{15}$ Hz	$\lambda_p(n \rightarrow 1)$(nm)
2	2.466	121.57
3	2.9227	102.57
4	3.8025	97.255
⋮	⋮	⋮
∞	3.288	91.177

Now we are in a position to discuss the total energy of an atom or molecule. The total energy can be approximated as the summation of translational, vibrational, rotational, and electronic energies:

$$E^{\text{tot}} = E^{\text{trans}} + E^{\text{el}} + E^{\text{vib}} + E^{\text{rot}} \tag{2.78}$$

For a monatomic gas, there are no vibrational or rotational energy levels. Although we did not discuss the translational energy levels much, the particle in a potential well model describes the allowable translational energy levels of an atom or molecule. Parallel to example 2.1, the translational energy level of an atom (or a molecule) in a three-dimensional potential well can be expressed as

$$E^{\text{trans}} = \frac{h^2}{8m}\left(\frac{n_x^2}{D_x^2}+\frac{n_y^2}{D_y^2}+\frac{n_z^2}{D_z^2}\right) \quad (n_x, n_y, n_z = 1, 2, 3, \ldots) \tag{2.79}$$

where D_x, D_y, D_z are the lengths of the potential well in the x, y, and z directions, respectively. Since the mass of an atom is typically much larger than that of an electron, the separations between translational energy levels are very small. Thus the translational energy can be considered as a continuous variable and is often simply expressed as the kinetic energy;

$$E^{\text{trans}} = \frac{m}{2}(v_x^2 + v_y^2 + v_z^2) \tag{2.80}$$

Comparing eqs. (2.80) and (2.79), we see that

$$mv_x = \frac{hn_x}{2D_x} \tag{2.81}$$

and this is similar for y and z directions. The left-hand side of eq. (2.81) is momentum p_x. The right-hand side, according eqs. (2.8) or (1.38), is h/λ_x. Thus, eq. (2.81) is a consequence of the Planck–Einstein relation, eq. (2.12), between momentum and wavelength.

2.4 Summary of Chapter 2

In this chapter, we have introduced the wave–particle duality of electromagnetic radiation. It was through the work of Planck and Einstein that the particle characteristics of electromagnetic radiation were revealed. Planck suggested that the energy of an electromagnetic wave at frequency ν must be an integral multiple of $E = h\nu$. Einstein further showed that this basic energy unit has particle characteristics, and this basic quantum of energy was eventually named photon. The momentum and energy relations between waves and particles are called the Planck–Einstein relations

$$E = h\nu, \quad p = \frac{h}{\lambda}$$

On the basis of the wave–particle duality of light, de Broglie further suggested that matter has wave characteristics that follow the same Planck–Einstein relations. This suggestion led to the development of quantum mechanics. The Schrödinger equation describes material waves,

$$-\frac{\hbar^2}{2m}\nabla^2\Psi_t + U\Psi_t = i\hbar\frac{\partial\Psi_t}{\partial t}$$

where Ψ_t is the wavefunction. The meaning of the wavefunction is that $\Psi_t\Psi_t^*$ gives the probability that matter will be found at location $\mathbf{r}$ and time t. In the quantum mechanics world, things are uncertain and the most probable value of any quantity is calculated from the operator for that quantity, including its location, momentum, energy, and

so on. The uncertainties of the location and momentum, and of time and energy, obey the Heisenberg uncertainty principle

$$\Delta p \Delta x \geq \hbar/2 \text{ and } \Delta E \Delta t \geq \hbar/2$$

Solution of the Schrödinger equation leads to eigenvalues that are identified as the (most probable) energies of the system. We have given solutions for the following potential fields:

1. Free electrons. The free electron energy level is a continuous variable.
2. Particle in an infinite one-dimensional potential well. The particle energies are quantized and their wavefunctions form standing waves. Research on artificial quantum structures has become a mainstream research field and has led to many exciting applications.
3. Harmonic oscillator. The energy levels of a harmonic oscillator are quantized according to

   $$E^{\text{vib}} = h\nu\left(n+\frac{1}{2}\right) \text{ where } \nu = \frac{1}{2\pi}\sqrt{\frac{K}{m}} \qquad (n = 0, 1, 2, \ldots)$$

   The harmonic oscillator represents a wide range of phenomena such as the vibrational energy levels in polyatomic molecules, an electromagnetic field, and atom vibrations in solids.
4. Rigid rotor. The energy levels of a rigid rotor are given by

   $$E_\ell = \frac{\hbar^2}{2I}\ell(\ell+1) \quad (\text{for } |m| \leq \ell, \ell = 0, 1, 2, \ldots)$$

   where ℓ and m are integers. Because there are multiple ℓ and m values that give the same energy, and each set of ℓ and m represents one quantum state, the rotational energy levels are degenerate. The degeneracy is $g(\ell) = 2\ell + 1$. The energy separation between rotational energy levels is very small. They are typically observed together with vibrational energy levels.
5. Hydrogen atom. The electron energy levels of a hydrogen atom are

   $$E_n^{\text{el}} = -\frac{mc_1^2}{2\hbar^2 n^2} = -\frac{13.6\,\text{ev}}{h^2} \quad (n \geq 1, n \geq \ell + 1, \text{ and } |m| \leq \ell, \ell = 0, 1, 2, \ldots)$$

   where, again, each set of (n, m, ℓ), plus the spin quantum number s, determines a quantum state. Because the energy level depends on n only, the energy levels are degenerate, the degeneracy being $g(n) = 2n^2$. The electron energy levels in the hydrogen atom provide a basis for understanding the periodic table and the chemical activity of atoms.
6. For an atom or molecule, the total energy is the sum of translational, electronic, rotational, and vibrational energy levels (the latter two are for polyatomic molecules only).
7. A photon interacts with matter (absorption or emission) only when the photon energy and allowable energy levels of the matter satisfy the following relation

   $$E_{\text{photon}} = h\nu_{\text{photon}} = E_f - E_i$$

In addition, we should understand that each wavefunction determines one quantum state. Electrons also have spin, which cannot be obtained from solving the Schrödinger equation. The two spin quantum numbers for an electron are $s = 1/2$ and $-1/2$. The Pauli exclusion principle dictates that each quantum state can have a maximum of one electron.

2.5 Nomenclature for Chapter 2

A	wave amplitude
B	rotational constant, Hz; or undetermined coefficient in the wavefunction
c	constant in eq. (2.70), N m^2
D	width of potential well, m
e	charge per electron, C
F	force, N
g	degeneracy
h	Planck constant, J s
$\hbar$	Planck constant divided by 2π, J s
H	system Hamiltonian, J
I	moment of inertia, kg m^2
$\mathbf{J}$	particle flux, m^{-2} s^{-1}
k	magnitude of wavevector, m^{-1}
$\mathbf{k}$	wavevector, m^{-1}
K	spring constant, N m^{-1}
ℓ	quantum number
m	mass, kg; quantum number
n	quantum number
p	magnitude of the momentum, kg m s^{-1}
$\mathbf{p}$	momentum operator, kg m s^{-1}
r_0	effective distance between two atoms
r	radial distance from origin, m
$\mathbf{r}$	position vector
s	spin quantum number
t	time, s
U	system energy or potential energy, J
x, y, z	Cartesian coordinates
X	separation of variable component
$\hat{\mathbf{y}}$	unit vector in y direction
Y	separation of variable component; spherical harmonics

α	separation of variable constant
β	separation of variable constant
Δx	standard deviation in x from the expected value
∇	gradient operator
∇^2	Laplace operator
ε_0	electrical permittivity of vacuum, C^2 N^{-1} m^{-2}
κ_B	Boltzmann constant, J K^{-1}
λ	wavelength, m
ν	frequency, s^{-1}
$\mathbf{\Phi}$	vector waveform
$\mathbf{\Phi}_c$	complex waveform
Ψ	wavefunction
ω	angular frequency, rad s^{-1}
Ω	operator
$\langle\rangle$	expectation value

Subscripts

0	equilibrium position
f	Fermi level
ℓ	quantum number
m	quantum number
n	quantum number
p	photon
s	spin quantum number
t	total
v	vacuum level
x, y, z	Cartesian components

Superscripts

$\hat{}$	unit vector
$*$	complex conjugate

2.6 References

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2.7 Exercises

2.1 *Planck–Einstein relations*. (a) An argon laser emits light at 514 nm and at a power of 1 W. Calculate (1) the frequency of the photons in Hz, (2) their wavelength, expressed as a wavenumber, (3) the energy of each photon, (4) the momentum of each photon, and (5) the number of photons generated per second.
(b) If the photons are completely absorbed by a 1 mm^2 surface, calculate (1) the pressure exerted on the surface by the photons, and (2) the heat flux generated by the photon absorption.

2.2 *Transmission electron microscope*. Electron beams are used to study the atomic structure of crystals, as in the transmission electron microscope (TEM). The resolution of the microscope depends on the energy of the electrons, which determines the corresponding wavelength of the electrons. The minimum focal point of the electron beam depends on its wavelength. Determine the electron wavelength if they have an energy of (a) 100 keV and (b) 1 MeV.

2.3 *Spring constant and interatomic distance between H atoms in H_2*. The fundamental vibrational frequency of the H_2 molecule is 4401 cm^{-1} and the rotational constant is 59.32 cm^{-1}. Estimate the effective spring constant and the interatomic distance between the two hydrogen atoms. What are the photon wavelength and frequency corresponding to the vibration transition?

2.4 *Expectation value of Hamiltonian*. Prove that E in the separation of variables of the time-dependent Schrödinger equation represents the system energy; in other words, prove eq. (2.28).

2.5 *Particle Flux*. Derive the material wave continuity equation (2.30) and the flux expression (2.31).

2.6 *Photon emission wavelength*. Calculate the emitted photon wavelength if an electron falls from the $n = 2$ state into $n = 1$ state inside an infinite potential quantum well of width $D = 20$ Å.

2.7 *Heisenberg uncertainty principle.* For the $n = 2$ state of an electron inside an infinite potential well, prove that the Heisenberg uncertainty relation $\Delta p \Delta x \geq \hbar/2$ is satisfied.

2.8 *Spring constant of C—O bonds.* The absorption by a CO molecule at 5.61 μm is its fundamental vibrational mode. Determine the effective spring constant of C—O bonds.

2.9 *Vibrational-rotational energy levels.* The fundamental vibrational frequency of the H_2 molecule is 4401 cm^{-1} and its rotational constant is 59.32 cm^{-1}. Determine the photon emission wavelengths due to combined vibrational–rotational modes in H_2 near the fundamental vibrational mode.

2.10 *Electron reflection.* As shown in figure P2.10, an electron of energy E moving from left to right encounters a potential barrier of height δ. The electron wave can be reflected or transmitted.

(a) Show that the proper forms of the incoming, reflected, and transmitted wave functions are

$$\Psi_i = Ae^{-i(\omega t - k_1 x)},\ \Psi_r = Be^{-i(\omega t + k_1 x)},\ \Psi_t = Ce^{-i(\omega t - k_2 x)},$$

respectively, where

$$k_1 = \sqrt{\frac{2mE}{\hbar^2}} \text{ and } k_2 = \sqrt{\frac{2m(E-\delta)}{\hbar^2}}$$

and A, B, C are constants to be determined from the interface conditions at $x = 0$.

(b) At the interface $x = 0$, the wavefunction and its first derivative must be continuous. Using these conditions, derive expressions for B/A and C/A.

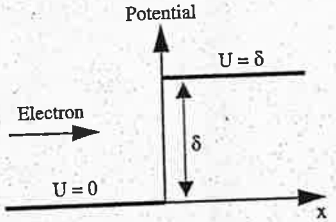

Figure P2.10 Figure for problem 2.10.

(c) The reflectivity R is defined as the ratio of the reflected particle flux divided by the incoming particle flux, and similarly for transmissivity T,

$$R = \frac{J_r}{J_i} \text{ and } T = \frac{J_t}{J_i}$$

Derive expressions for R and T.

(d) For $E = 1.2$ eV and $\delta = 1$ eV, calculate the electron reflectivity and transmissivity.

(e) For $E = 1$ eV and $\delta = 1.2$ eV, show that the transmissivity T is zero, and also show that Ψ_t is not zero. This nonzero wavefunction that does not carry a material flux is called an evanescent wave.

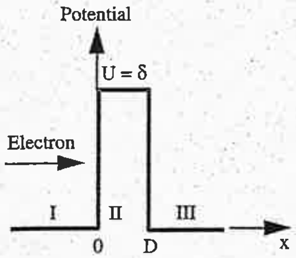

Figure P2.11 Figure for problem 2.11.

2.11 *Electron tunneling through a potential barrier.* An electron moving from left in region I encounters a potential barrier of finite width D and barrier height δ (region II), as shown in figure P2.11. The electron has a certain probability of traversing the potential barrier and entering region III. The objective of this exercise is to derive expressions for the electron reflectivity and transmissvity. To complete the derivation, go through the following steps:

(a) Solve the Schrödinger equation for each region. Identify which parts of the solution represent the incoming, reflected, and transmitted waves.

(b) Use the continuity of the wavefuction and its first-order derivative at the two interfaces to relate the solutions in the three regions.

(c) Use the definitions of reflectivity and transmissivity that are discussed in problem 2.10 to derive expressions for the electron reflectivity and transmissivity through the barrier region.

(d) Examine the solutions and show that even if the incoming electron energy E is lower than the Barrier height δ, there is still a nonzero probability that the transmissivity is not zero. The phenomenon that an electron with energy lower than the barrier height can transverse the barrier is called tunneling.

2.12 *Electron energy quantization in a potential well of finite barrier height.*

(a) Derive expressions determining the electron energy levels in a potential well surrounded by a barrier of finite height, as shown in figure P2.12.

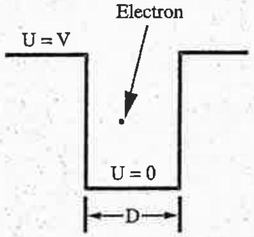

Figure P2.12 Figure for problem 2.12.

(b) For $D = 50$ Å, determine the first three energy levels for $V = 0.5$ eV and 1 eV.

2.13 *Electron energy states in a quantum dot.* Determine (a) the energy levels of an electron in a cubic quantum dot of length D, assuming an infinitely high potential barrier around the cube, (b) the allowable energy levels for $D = 100$ Å, and (c) the degeneracy of the first four energy levels.

2.14 *Electron energy states in a potential wire.* Determine (a) the energy levels of an electron in a two-dimensional square box of length D, assuming an infinitely high potential barrier around the box, (b) the allowable energy levels for $D = 50$ Å, and (c) the degeneracy of the first four energy levels.

2.15 *Wave function in a one-dimensional potential well.* Plot the most probable electron distribution in a one-dimensional infinite potential well for $n = 1, 2, 3$.

2.16 *Degeneracy of electron energy levels in a hydrogen atom.* Prove that the electron degeneracy in a hydrogen atom is $2n^2$.

2.17 *Translational energy level.* A 10 cm^3 box contains a H_2 molecule at 300 K.
  (a) Estimate the average translational energy of the H_2 molecule.
  (b) How do the first few translational energy levels compare with $\kappa_B T$?
  (c) Can you think about a way to count the degeneracy of the translational energy levels corresponding to this average energy?

3

Energy States in Solids

↑ See ch 2 for photon etc.

The previous chapter introduced the energy levels in simple potential fields, such as quantum wells, harmonic oscillators, atoms, and molecules. In this chapter, we will discuss energy levels in solids. We focus our discussion on single crystals, which are the simplest form of solids because the atoms are regularly arranged. As we will see, crystal periodicity plays a central role in determining the energy levels. So we will start by discussing crystal structures, including lattices and the potentials binding the atoms into a crystal. Since atoms in solids are packed closely, the electron wavefunctions of individual atoms overlap and form new wavefunctions and, correspondingly, new electron energy levels. The interatomic forces bond nuclei together so that the vibration of the atoms inside the crystal is strongly coupled. The collective atomic vibration can be decomposed into normal modes extending over the crystal and the basic energy quantum of each normal mode is called a phonon, in the same way of that the basic energy quantum of an electromagnetic mode is called a photon. Each electron and phonon wavefunction is characterized by a frequency (or energy) and a wavevector. The relationship between the energy and the wavevector is called the dispersion relation, which plays a central role in determining the properties of the crystal. We limit mathematical derivations to the dispersion relations of electrons and phonons in one-dimensional periodic structures and explain the energy levels in real crystals without a more detailed mathematical derivation, because the dispersion relation in a real crystal can be appreciated on the basis of a sound understanding of the behavior of a one-dimensional periodic system. The energy levels in crystals are highly degenerate. A very useful tool that takes into account the degeneracy of the energy states is the density of states, which will be used repeatedly throughout the book and should be mastered. !!

Degeneracy can be appreciated calculating the DOS.

3.1 Crystal Structure

A perfect bulk crystal is a three-dimensional periodic arrangement of atoms. To describe a crystal, we use an atomless lattice—a periodic array of mathematical points that replicate the inherent periodicity of the actual crystal. Every point in the lattice is identical to other points. To form an actual crystal, a basis consisting of one or several atoms (or a molecule) is attached to each lattice point, i.e.

$$\text{crystal} = \text{lattice} + \text{basis} \tag{3.1}$$

The exact position of the basis relative to the lattice point is not important, as long as the relative position between the basis and the lattice point is the same for all the lattice points. Many crystals have the same lattice structure; in fact, there is only a limited number of possible lattice types. Thus, we will first discuss the description of lattices in real space, followed by an introduction of the concept of reciprocal lattice, which is the Fourier transform of the real space lattice. The binding between atoms in real crystals will then be discussed.

3.1.1 Description of Lattices in Real Space

Consider a two-dimensional lattice as shown in figure 3.1. From a mathematical point of view, the location of each a point can be described by a vector. Because of the periodic arrangement of lattice points, we can choose a basic set of vectors, called the *primitive lattice vectors*, to construct all other vectors in the lattice. In a three-dimensional lattice, $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$ are primitive lattice vectors if, from any point, we could reach all other lattice points by a proper choice of integers through the following construction

Restriction on the symmetries

$$\mathbf{R} = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3 \qquad (n_1, n_2, n_3 \text{ cover all integers}) \tag{3.2}$$

The magnitudes of $\mathbf{a}_1$, $\mathbf{a}_2$, and $\mathbf{a}_3$ are called the lattice constants. A lattice constructed according to eq. (3.2) is often called a Bravais lattice. Primitive lattice vectors are not unique. We have drawn two sets of primitive lattice vectors in figure 3.1 with primitive unit vectors denoted by $\mathbf{a}_1$ and $\mathbf{a}_2$. The other set of vectors, $\mathbf{a}_1'$ and $\mathbf{a}_2'$, are not primitive lattice vectors because we cannot use them to construct all other lattice points by a two-dimensional version of eq. (3.2). For example, we cannot reach point 1 through any linear integer combination of $\mathbf{a}_1'$ and $\mathbf{a}_2'$.

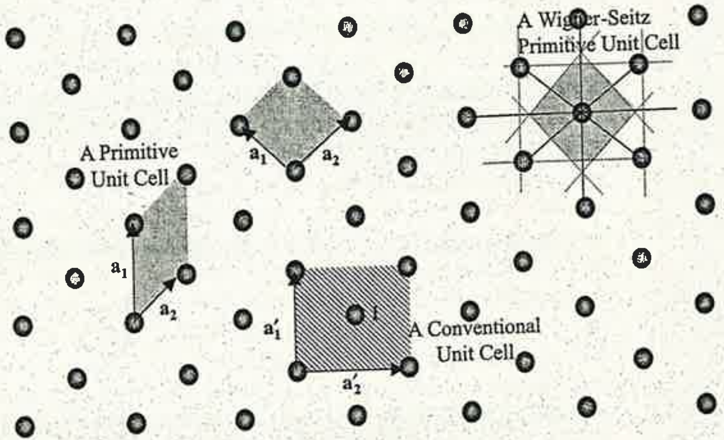

Figure 3.1 A two-dimensional lattice. Different choices of primitive lattice vectors $\mathbf{a}_1$ and $\mathbf{a}_2$ and primitive unit cells (gray areas) are possible. The Wigner-Seitz primitive unit cell is one way to uniquely construct a primitive unit cell. Vectors $\mathbf{a}_1'$ and $\mathbf{a}_2'$ are not a set of primitive lattice vectors and the shaded area is not a primitive unit cell. This area is, however, often used due to its regular shape and is called a conventional unit cell.

1 lattice point × primitive cell.

A primitive unit cell is the parallelepiped defined by the primitive lattice vectors. There is only one lattice point (equivalently speaking) per primitive unit cell. For example, each of the four lattice points in the two parallelograms formed by the two sets of primitive lattice vectors in figure 3.1 is shared by four unit cells and thus the number of equivalent lattice points in each parallelogram is one. These are thus primitive unit cells. On the other hand, the shaded rectangle formed by $\mathbf{a}_1'$ and $\mathbf{a}_2'$ is not a primitive unit cell because there are two lattice points in such a rectangle: the center point plus the four corners, each of the latter being shared by four cells. Because the choice of primitive lattice vectors is not unique, there can be different ways to draw a primitive unit cell, as shown by the two examples in figure 3.1. One method to construct a unit cell uniquely is the Wigner–Seitz cell (see figure 3.1), which is constructed by connecting all the neighboring points surrounding an arbitrary lattice point (as shown by the solid lines in figure 3.1) and drawing the bisecting plane (shown by dashed lines in the figure) perpendicular to each connection line. The smallest space formed by all the bisecting planes is a Wigner–Seitz cell, as indicated in the figure.

Sometimes, it is more convenient to describe a lattice by the *conventional unit cell*. For example, in figure 3.1, the rectangle formed by $\mathbf{a}_1'$ and $\mathbf{a}_2'$ is more convenient than the parallelogram formed by the primitive lattice vectors. This unit cell has two lattice points and is called a conventional unit cell. The crystal can also be constructed by repeating such a cell.

A general unit cell in the three-dimensional space is designated by three lattice vectors and the three angles formed between them. In the most general case, these three lattice vectors are of different lengths and the three angles are all oblique, as shown in figure 3.2(a). This lattice is called a triclinic lattice and does not have much symmetry. The symmetry of a lattice is often characterized by the symmetry operations, which include rotation of the unit cell around a fixed lattice point, reflection of the unit cell along a specific plane, and inversion with respect to a lattice point. A fundamental requirement on the lattice is that one can fill the entire space by placing a primitive unit cell at every lattice point. This requirement puts a limitation on the symmetric operations of a lattice. For example, the allowable rotational symmetry operations are 2π, π, $2\pi/3$, $2\pi/4$, and $2\pi/6$. No lattice, however, can have $2\pi/7$ or $2\pi/5$ rotational symmetry.* Given these conditions, it turns out that there are 13 other types of lattice that have special symmetry operations on top of the π and 2π rotational symmetry of

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*Some quasicrystals can have five-fold symmetry patterns but they do not satisfy the definition of a crystal discussed in this section (Kittel, 1996).