

TOPIC 6: LATTICE VIBRATIONS AND THERMAL PROPERTIES**PRIMARY READING ASSIGNMENT**

"Lattice Vibrations and Thermal Properties of Crystals", from *Solid State and Semiconductor Physics*, J.P. McKelvey

SUPPLEMENTARY REFERENCE

"Phonons II: Thermal Properties" from *Introduction to Solid State Physics*, Charles Kittel
"Outline of Quantum Mechanics" from *Solid State and Semiconductor Physics*, J.P. McKelvey

LECTURE PROGRAM

1. Classical Calculation of Specific Heat
2. Einstein Theory of Specific Heat
3. Debye Theory of Specific Heat
4. The Phonon
5. Thermal Expansion of Solids
6. Lattice Thermal Conductivity of Solids

LATTICE VIBRATIONS AND THE THERMAL PROPERTIES OF CRYSTALS

6.1 CLASSICAL CALCULATION OF LATTICE SPECIFIC HEAT

In Section 4.4, we have already outlined some of the problems which arise when the specific heat of a crystal is calculated on the assumption that the atoms of the crystal behave as independent classical harmonic oscillators. We must now examine these problems in detail, and study how they may be resolved, using the results obtained in Chapters 3-5 relating to lattice dynamics, quantum mechanics, and statistical mechanics. We shall throughout these investigations deal with a crystal composed of N atoms which are held together in a periodic array. These atoms are assumed to be free to vibrate about their equilibrium positions subject to constraining forces which, to a first approximation, obey Hooke's law. It is also assumed that there are no free electrons, such as one might find in a metal, and that the entire heat capacity of the crystal is due to the excitation of thermal vibrations of the lattice. When free electrons are present, their motion may also be excited by an external heat source, and so they also will contribute to the observed specific heat, but this electronic contribution will be discussed in a later chapter.

The classical calculation assumes that each atom is a classical three-dimensional harmonic oscillator which vibrates independently of all other atoms in the crystal. Under these circumstances, one may calculate the total internal thermal energy of the crystal by finding the average energy of a single oscillator and multiplying the result by N . For a single three-dimensional isotropic harmonic oscillator, the total energy is

$$\varepsilon = \frac{p^2}{2m} + V(\mathbf{r}) \quad (6.1-1)$$

with $V(\mathbf{r}) = \frac{1}{2}m\omega_0^2(x^2 + y^2 + z^2) = \frac{1}{2}m\omega_0^2r^2$, (6.1-2)

where m is the mass and ω_0 the natural frequency of the oscillator. If we assume that the distribution of the oscillators in energy obeys the Maxwell-Boltzmann distribution law, then the distribution function which expresses the probability for an oscillator

to have a certain energy ε is

$$f(\varepsilon) = Ae^{-\varepsilon/kT} = Ae^{-\frac{p^2}{2mkT}}e^{-\frac{m\omega_0^2 r^2}{2kT}} = f(p, q) \quad (6.1-3)$$

where A is a constant. According to (5.2-4), the average energy will be given by

$$\langle \varepsilon \rangle = \frac{\int_p \int_r \left(\frac{p^2}{2m} + \frac{1}{2} m\omega_0^2 r^2 \right) e^{-\frac{p^2}{2mkT}} e^{-\frac{m\omega_0^2 r^2}{2kT}} \cdot p^2 \sin \theta_p dp d\theta_p d\phi_p \cdot r^2 \sin \theta dr d\theta d\phi}{\int_p \int_r e^{-\frac{p^2}{2mkT}} e^{-\frac{m\omega_0^2 r^2}{2kT}} \cdot p^2 \sin \theta_p dp d\theta_p d\phi_p \cdot r^2 \sin \theta dr d\theta d\phi} \quad (6.1-4)$$

Here we have chosen to use spherical coordinates (r, θ, ϕ) in coordinate space, and (p, θ_p, ϕ_p) in momentum space for the purposes of integration, which, of course, must be taken over all phase space. Since the integrand has no dependence upon θ, ϕ, θ_p , or ϕ_p , the integration over these variables may be performed very simply, giving a factor $(4\pi)^2$ in both numerator and denominator, and leaving

$$\langle \varepsilon \rangle = \frac{\frac{1}{2m} \int_0^\infty p^4 e^{-\frac{p^2}{2mkT}} dp + \frac{m\omega_0^2}{2} \int_0^\infty r^4 e^{-\frac{m\omega_0^2 r^2}{2kT}} dr}{\int_0^\infty p^2 e^{-\frac{p^2}{2mkT}} dp + \int_0^\infty r^2 e^{-\frac{m\omega_0^2 r^2}{2kT}} dr} = \langle \varepsilon_k \rangle + \langle \varepsilon_p \rangle. \quad (6.1-5)$$

In the first term of (6.1-5), each double integral in (6.1-4) has been expressed as a product of a p -integral and an r -integral; the r -integrals in the numerator and denominator are the same, and cancel, giving the first term of the expression shown above. The second term is treated in the same way, but here the p -integrals in numerator and denominator cancel. It is clear that the first term above represents the average kinetic energy and the second the average potential energy. Evaluating the integrals with the help of Table 5.1, one finds

$$\langle \varepsilon_k \rangle = \langle \varepsilon_p \rangle = \frac{3}{2} kT \quad \text{whence} \quad \langle \varepsilon \rangle = 3kT. \quad (6.1-6)$$

For an assembly of N independent oscillators, the total internal energy U is simply

$$U = N \langle \varepsilon \rangle = 3NkT, \quad (6.1-7)$$

and the heat capacity C_v is, by definition,

$$C_v = (\partial U / \partial T)_v = 3Nk. \quad (6.1-8)$$

The specific heat is simply the heat capacity per gram (or per unit volume). The heat capacity is found simply to be a constant, independent of temperature. For a mole of any substance N is equal to Avogadro's number N_a and the molar heat capacity C_{vm} is given by

$$C_{vm} = 3N_a k = 5.96 \text{ cal/mole} \cdot ^\circ \text{K}. \quad (6.1-9)$$

This result is known as the law of Dulong and Petit and is familiar to students of elementary chemistry as the basis of a rudimentary way of estimating the atomic weight of an unknown element. The law of Dulong and Petit agrees fairly well with experimental results for most substances at and above room temperature, but breaks

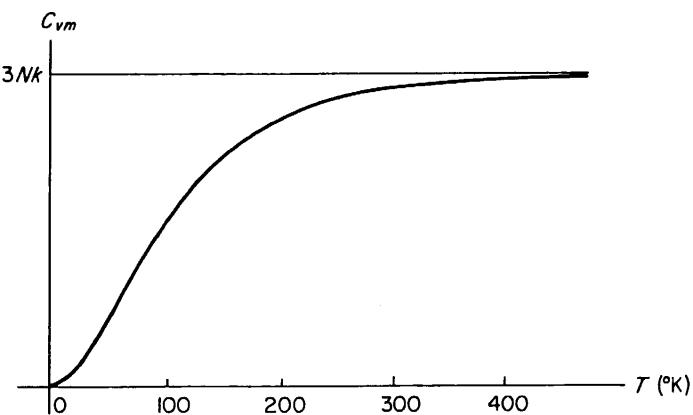


FIGURE 6.1. The heat capacity of a typical solid substance plotted as a function of temperature.

down seriously at low temperatures. In the low-temperature range, the specific heat of all substances is found to approach zero, being proportional to T^3 as T approaches zero, as shown in Figure 6.1.

6.2 THE EINSTEIN THEORY OF SPECIFIC HEAT

The discrepancies in the classical theory of specific heat were investigated by Einstein, who in 1911 succeeded in explaining, qualitatively, at least, the experimentally observed form of the specific heat as a function of temperature. In the Einstein theory, the atoms are again regarded as identical independent harmonic oscillators with a single natural vibration frequency ω_0 , but they are regarded as *quantum* harmonic oscillators which may have only discrete energy values¹ such that

$$\varepsilon_n = (n + \frac{1}{2})\hbar\omega_0 \quad (n = 0, 1, 2, \dots), \quad (6.2-1)$$

as given by (4.12-27). The oscillators may still be regarded as having the Maxwell-Boltzmann distribution of energies, since they form an assembly of systems which are *distinguishable* or identifiable by virtue of their location at separate and distinct lattice sites, and since *any number* of oscillators may be in the same quantum state of

¹ Originally, of course, Einstein used the Planck result $\varepsilon_n = n\hbar\omega$ rather than the wave-mechanical result as given by (6.2-1) for the energy levels of a harmonic oscillator. If the original Planck result is used, the final expressions for internal energy and specific heat which are obtained differ from the results derived here only in the absence of a temperature-independent zero-point energy contribution to the internal energy.

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the system. Thus, although the atoms are quantized oscillators, the classical Maxwell-Boltzmann distribution is still the appropriate one with which to describe their statistical behavior. The actual quanta of vibrational energy which are absorbed or emitted, by the oscillators, on the other hand, are not distinguishable entities, and therefore Bose-Einstein statistics must be used to describe their statistical behavior. As we shall see later, the same results can be obtained by discussing the properties of the system of oscillators using Maxwell-Boltzmann statistics, or by treating the dynamics of the quanta of vibrational energy themselves using Bose-Einstein statistics.

For the sake of simplicity, we shall assume that the crystal contains $3N$ one-dimensional harmonic oscillators, whose energy levels are given by (6.2-1), rather than N three-dimensional isotropic oscillators. This assumption is justified by the fact that there are indeed three independent vibrational degrees of freedom associated with each atom of the crystal, and that according to the principle of equipartition, the available vibrational energy is distributed equally, on the average, among these three degrees of freedom. If the oscillators are distributed in energy according to the Boltzmann law, then the number of oscillators at energy ϵ is proportional to $e^{-\epsilon/kT}$, and the average energy is

$$\langle \epsilon \rangle = \frac{\sum_{n=0}^{\infty} \epsilon_n e^{-\epsilon_n/kT}}{\sum_{n=0}^{\infty} e^{-\epsilon_n/kT}} = \hbar\omega_0 \frac{\sum_n (n + \frac{1}{2}) e^{(n+\frac{1}{2})x}}{\sum_n e^{(n+\frac{1}{2})x}} \quad (6.2-2)$$

where

$$x = -\hbar\omega_0/kT. \quad (6.2-3)$$

Equation (6.2-2) can, however, be written as

$$\begin{aligned} \langle \epsilon \rangle &= \hbar\omega_0 \frac{\frac{1}{2}e^{\frac{1}{2}x} + \frac{3}{2}e^{\frac{3}{2}x} + \frac{5}{2}e^{\frac{5}{2}x} + \dots}{e^{\frac{1}{2}x} + e^{\frac{3}{2}x} + e^{\frac{5}{2}x} + \dots} = \hbar\omega_0 \frac{d}{dx} \ln[e^{\frac{1}{2}x}(1 + e^x + e^{2x} + \dots)] \\ &= \hbar\omega_0 \frac{d}{dx} [\frac{1}{2}x - \ln(1 - e^x)] = \hbar\omega_0 \left[\frac{1}{2} + \frac{1}{e^{\hbar\omega_0/kT} - 1} \right]. \end{aligned} \quad (6.2-4)$$

The internal energy is obtained by multiplying the average energy per oscillator by the number of oscillators, as before, whereby

$$U = 3N\langle \epsilon \rangle = \frac{3N\hbar\omega_0}{2} + \frac{3N\hbar\omega_0}{e^{\hbar\omega_0/kT} - 1} \quad (6.2-5)$$

and

$$C_v = \left(\frac{\partial U}{\partial T} \right)_v = 3Nk \left(\frac{\hbar\omega_0}{kT} \right)^2 \frac{e^{\hbar\omega_0/kT}}{(e^{\hbar\omega_0/kT} - 1)^2}. \quad (6.2-6)$$

This result can be expressed in a somewhat simpler way by defining an "Einstein Temperature" Θ_E such that

$$\hbar\omega_0 = k\Theta_E. \quad (6.2-7)$$

Substituting $k\Theta_E$ for $\hbar\omega_0$ in (6.2-6), one finds

$$C_v = 3Nk \left(\frac{\Theta_E}{T} \right)^2 \frac{e^{\Theta_E/T}}{(e^{\Theta_E/T} - 1)^2}. \quad (6.2-8)$$

For temperatures high enough that $T \gg \Theta_E$, $e^{\Theta_E/T} \approx 1$; by using the power series expansion for the exponential and retaining only first-order terms it is easily seen that in this limit C_v approaches the classical result $3Nk$. For low temperatures ($T \ll \Theta_E$), $e^{\Theta_E/T} \gg 1$ and (6.2-8) can be approximated by

$$C_v = 3Nk \left(\frac{\Theta_E}{T} \right)^2 e^{-\Theta_E/T} \quad (6.2-9)$$

which approaches zero as T approaches zero, although it does not agree with the observed T^3 behavior at low temperatures. The first term in (6.2-5) represents the contribution of the zero-point energy of the oscillators to the internal energy of the system. Since it is independent of temperature, it makes no contribution to the specific heat.

Physically, the reason that the specific heat becomes quite small at low temperatures can be understood by assuming that the crystal is placed in contact with an external heat bath consisting of an ideal monatomic gas at some given temperature, and allowed to absorb energy from the atoms of the ideal gas. The average energy of the gas atoms is $\frac{3}{2}kT$, and if the temperature of the system is high enough so that kT is of the order of, or larger than, the energy $\hbar\omega_0$ required to excite one of the vibrating atoms of the crystal to a higher energy state, then such excitations will occur frequently when gas atoms from the heat bath collide with the crystal. These collisions will then be *inelastic* in the mechanical sense, and energy initially belonging to the gas atoms will readily be transferred to the crystal lattice as vibrational energy. On the other hand, at sufficiently low temperatures, kT will be much smaller than the excitation energy $\hbar\omega_0$ and only an occasional gas atom having much higher energy than the average will be capable of effecting such an excitation and thus transferring heat to the crystal lattice. The crystal is then relatively incapable of absorbing heat from its surroundings, and a unit temperature change in the surroundings will transfer but little heat to the crystal, compared to that which may be transferred under similar conditions at a higher temperature. As the temperature approaches absolute zero, the fraction of atoms in the heat bath possessing the minimum excitation energy $\hbar\omega_0$ approaches zero, and consequently so also does the specific heat.

The Einstein temperature, $\Theta_E = \hbar\omega_0/k$ can easily be computed if ω_0 is known. This natural vibrational frequency can be calculated from the atomic mass and the observed elastic constants of the crystal.² For many metallic elements the value thus calculated is of the order of 100–200°K, and thus the transition from the low temperature to high temperature behavior should occur in this temperature range. Experimentally, the Einstein theory is found to fit the observations fairly well at all but very low temperatures, where the observed T^3 behavior is not obtained. The calculated values of Θ_E and those obtained by fitting the theoretical expression (6.2-8) to observed data also generally agree moderately well. Obviously, the Einstein theory provided a

² See Chapter 3, Exercise 6.

(6.2-8)

much better explanation of the experimental data than the classical theory, despite the fact that the agreement with experiment is by no means perfect. The discrepancy between theory and the low temperature experimental results was removed, and the general fit to the experimental data improved by the Debye theory of 1912. In the Debye theory, interactions between atoms which result in there being a range of possible values of vibrational frequency rather than just a single value ω_0 , as described in Chapter 3, are taken into account.

(6.2-9)

6.3 THE DEBYE THEORY OF SPECIFIC HEAT

The Debye theory of specific heat, first proposed in 1912,³ treated the atoms of the crystals as oscillators which were coupled together and which were capable of propagating elastic waves whose frequency might vary over a wide range of values, as predicted by the calculations of Chapter 3. Although still involving certain approximations, it was found to be superior to the Einstein model in predicting the specific heat of substances in the low-temperature region, and has formed the basis for a number of subsequent and more detailed investigations.

Since the atoms of the crystal no longer vibrate independently of one another, it is more convenient to work with the normal modes of vibration of the system than with the vibrational motion of a single atom. We have already seen (in Section 3.3 and Exercise 7, Chapter 3) that for a one-dimensional linear chain of N atoms there are essentially N normal modes of vibration. For a three-dimensional crystal of N atoms, each atom can vibrate independently along three coordinate directions, so that for this system there are $3N$ possible normal modes. Since any vibrational motion of the system can be thought of as a superposition of independent normal-mode vibrations, the normal modes can be regarded as independent harmonic oscillations whose allowed energy levels are given by (6.2-1) and whose average energy is given by (6.2-4), provided that the number of excited normal modes are distributed in energy according to the Maxwell-Boltzmann distribution law.

Suppose now that in a frequency range $d\omega$ about some frequency ω there are $g(\omega) d\omega$ normal modes of vibration of the crystal. The quantity $g(\omega)$ must thus represent the number of normal modes per unit frequency at frequency ω . The contribution to the internal vibrational energy of the crystal from these modes of vibration is then given by

$$dU = \langle \epsilon(\omega) \rangle g(\omega) d\omega \quad (6.3-1)$$

where $\langle \epsilon(\omega) \rangle$ is the average energy of a vibrational mode of frequency ω , as given by the formula (6.2-4). It is somewhat more convenient to calculate the number of normal modes $g(k) dk$ in an interval dk about wave number k , and since $dk = (dk/d\omega) d\omega$, we may write (6.3-1) as

$$dU = \langle \epsilon(\omega(k)) \rangle g(k) dk = \langle \epsilon(\omega) \rangle g(k) \frac{dk}{d\omega} d\omega. \quad (6.3-2)$$

³ P. Debye, *Ann. Physik* **39**, 789 (1912).

In order to calculate $g(k)$, we may assume a rectangular crystal of dimensions (L_x, L_y, L_z) and assume that the origin is at a corner of the crystal, the crystal edges coinciding with the $+x$, $+y$, and $+z$ axes. The equations of motion for the mechanical vibrational amplitude $u(x, y, z, t)$ then lead to vibrational solutions of the form

$$u(x, y, z, t) = Ae^{i(\mathbf{k} \cdot \mathbf{r} - \omega t)} = Ae^{i(k_x x + k_y y + k_z z - \omega t)}. \quad (6.3-3)$$

If periodic boundary conditions of the form

$$u(L_x, y, z, t) = u(0, y, z, t)$$

$$u(x, L_y, z, t) = u(x, 0, z, t) \quad (6.3-4)$$

$$u(x, y, L_z, t) = u(x, y, 0, t)$$

are applied to (6.3-3), then it is clear that $k_x L_x = 2\pi n_x$, $k_y L_y = 2\pi n_y$, $k_z L_z = 2\pi n_z$, or

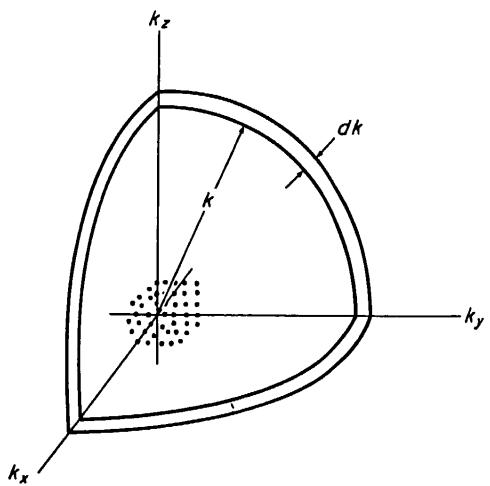
$$k_x = 2\pi n_x / L_x$$

$$k_y = 2\pi n_y / L_y \quad (6.3-5)$$

$$k_z = 2\pi n_z / L_z$$

where n_x, n_y, n_z are positive or negative *integers*. The allowed values (k_x, k_y, k_z) , to each of which corresponds a single normal mode of vibration satisfying periodic boundary conditions, can be plotted as points in an orthogonal k -space, such as that shown in Figure 6.2. The allowed normal modes form a simple orthorhombic lattice in such a space, the dimensions of the unit cell being $(2\pi/L_x, 2\pi/L_y, 2\pi/L_z)$.

FIGURE 6.2. Spherical surfaces corresponding to constant values of propagation constant k and $k + dk$ plotted in a (k_x, k_y, k_z) coordinate system.



If the crystal dimensions L_x, L_y, L_z are sufficiently large, the unit cell will become small, the points representing allowed normal modes crowding together very closely in a diagram such as Figure 6.2. In this case one may calculate $g(k) dk$ by evaluating the volume of k -space between the spherical surface of radius k

$$k_x^2 + k_y^2 + k_z^2 = k^2 \quad (6.3-6)$$

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which is the locus of all points corresponding to wave number k , and another spherical surface of radius of $k + dk$ which is the locus of all points whose wave number is $k + dk$. The required volume is simply the volume between the two spheres of Figure 6.2 or $4\pi k^2 dk$. The number of allowed normal modes is then obtained by dividing this quantity by the volume of the unit cell corresponding to a single normal mode of the system. This volume is simply $8\pi^3/(L_x L_y L_z) = 8\pi^3/V$, where V is the volume of the crystal. This procedure leads to the value

$$g(k) dk = \frac{k^2 V}{2\pi^2} dk.$$

(6.3-4)

Actually, however, there are *three* independent normal modes for each allowed point in k -space, one corresponding to a longitudinal vibration (and discussed above), and two others corresponding to two mutually orthogonal *transverse* vibrations, which we have not included in our reckoning so far. To take these possibilities into account, the right-hand side of the above equation should be increased by a factor of 3, giving finally

$$g(k) dk = \frac{3k^2 V}{2\pi^2} dk. \quad (6.3-7)$$

At this point, what one would wish to do would be to use some relation such as (3.3-7) which expresses the variation of k as a function of ω for a monatomic lattice, find $dk/d\omega$, and substitute these results along with (6.3-7) and (6.2-4) into (6.3-2), integrating finally over ω . This procedure was first outlined by Born and von Kármán.⁴ Unfortunately, the mathematical form of the equation is such that the resulting expression is very cumbersome and cannot be integrated in closed form or handled numerically in any convenient way. To get around this difficulty, Debye approximated the sinusoidal function (3.3-7) as a linear function, writing

$$\omega(k) = v_0 k \quad (6.3-8)$$

where v_0 is a (constant) phase velocity equal, in principle, to the velocity of long-wave sound in the crystal. This is simply what is given by (3.3-7) for wavelengths long enough to satisfy the condition $ka \ll \pi$, although Debye used it to describe the behavior of *all* the vibrations which can be propagated in the crystal.

The integration over ω indicated in (6.3-2) is performed between the limits zero and a *maximum frequency* ω_m which is chosen in such a way that the *total number* of normal modes of frequency less than ω_m shall be just $3N$, since it is known that that is the actual number of normal modes which exist for a crystal of N atoms.⁵ Corresponding to ω_m there is a wave number k_m , and all the normal modes for which $k < k_m$ have frequencies $\omega < \omega_m$, according to (3.3-7) or (6.3-8). There must, therefore, be just $3N$ normal modes of oscillation within a sphere of radius k_m in k -space. Since the volume

⁴ M. Born and T. von Kármán, *Physikalische Zeitschrift* **13**, 297 (1912).

⁵ Had it been possible to use an exact expression for relating ω and k , the integration would have been carried out within the limits of the first Brillouin zone. This would have guaranteed that the condition that the total number of normal modes equal $3N$ would have been satisfied *automatically*.

of k -space occupied by a single normal mode is $8\pi^3/3V$, we may thus write

$$\frac{4}{3}\pi k_m^3 = 3N \cdot \frac{8\pi^3}{3V}$$

or

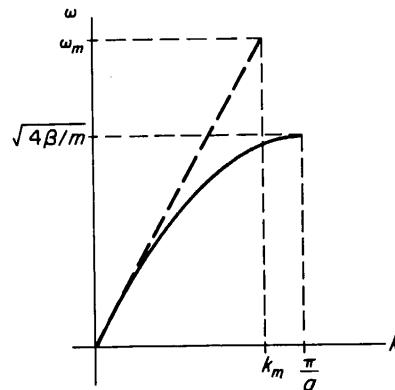
$$k_m = (6N\pi^2/V)^{1/3} \quad (6.3-9)$$

whence, using the Debye approximation (6.3-8)

$$\omega_m = v_0 k_m = v_0 (6N\pi^2/V)^{1/3}. \quad (6.3-10)$$

The variation of ω with k as assumed by the Debye approximation is shown in comparison with the value given by (3.3-7) in Figure 6.3. We are assuming in (6.3-10) that

FIGURE 6.3. The actual dispersion relation (solid curve) and the dispersion relation (dotted curve) according to the Debye approximation.



the velocity v_0 is the same for longitudinal and transverse elastic waves. This is not generally true, but the difference is not usually great enough to affect the final result significantly.

If we now substitute (6.2-4) and (6.3-7) into (6.3-2), using (6.3-8) wherever necessary to express k in terms of ω , and integrate from zero to ω_m , we obtain

$$U = \frac{3\hbar V}{2\pi^2 v_0^3} \int_0^{\omega_m} \left[\frac{\omega^3}{2} + \frac{\omega^3}{e^{\hbar\omega/kT} - 1} \right] d\omega = \frac{3\hbar\omega_m^4 V}{16\pi^2 v_0^3} + \frac{3\hbar V}{2\pi^2 v_0^3} \int_0^{\omega_m} \frac{\omega^3 d\omega}{e^{\hbar\omega/kT} - 1}. \quad (6.3-11)$$

The integral of the first term above is easily evaluated and gives rise to a zero-point contribution to the internal energy which, however, is independent of temperature and contributes nothing to the specific heat. The integral of the second term cannot be evaluated in closed form but must be worked out numerically.

It is customary to express these results in a slightly different form. If one lets

$$x = \hbar\omega/kT, \quad (6.3-12)$$

$$x_m = \hbar\omega_m/kT = \frac{\hbar v_0}{kT} \left(\frac{6N\pi^2}{V} \right)^{1/3} \quad (6.3-13)$$

ite
and

$$\Theta = \frac{\hbar\omega_m}{k} = \frac{\hbar v_0}{k} \left(\frac{6N\pi^2}{V} \right)^{1/3} \quad (6.3-14)$$

then (6.3-12) can be written in the form

$$(6.3-9) \quad U = \frac{9}{8} Nk\Theta + 9NkT \left(\frac{T}{\Theta} \right)^3 \int_0^{\Theta/T} \frac{x^3 dx}{e^x - 1}.$$

(6.3-10)
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6.3-10) that

The parameter Θ is seen to have the dimensions of temperature and to play the role of a characteristic temperature in (6.3-15) in much the same way as does the Einstein Temperature in (6.2-8). Θ is usually referred to as the *Debye temperature*. It is, of course, independent of temperature, except for the slight temperature variation introduced by the variation of V and v_0 with temperature.

By differentiating (6.3-11) under the integral with respect to temperature, the heat capacity can be found; the result is easily shown to be

$$(6.3-16) \quad C_v = \frac{3\hbar^2 V}{2\pi^2 v_0^3 k T^2} \int_0^{\omega_m} \frac{\omega^4 e^{\hbar\omega/kT} d\omega}{(e^{\hbar\omega/kT} - 1)^2} = 9Nk \left(\frac{T}{\Theta} \right)^3 \int_0^{\Theta/T} \frac{x^4 e^x dx}{(e^x - 1)^2}.$$

The integral in (6.3-16), which is a function of Θ/T alone, can be evaluated numerically, yielding a function a plot of which is shown in Figure 6.4. At high temperatures,

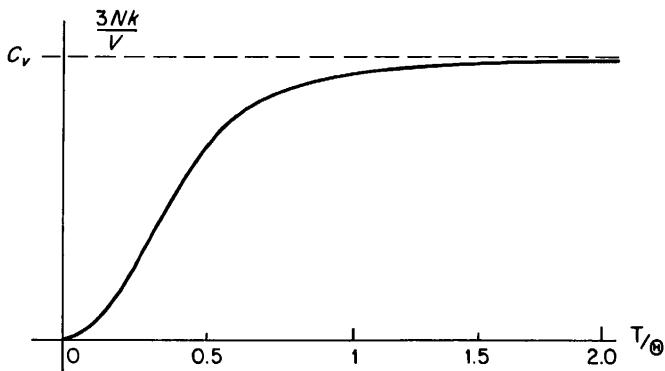


FIGURE 6.4. The heat capacity of a monatomic insulating solid according to the Debye theory plotted against the reduced temperature variable T/Θ .

$T \gg \Theta$ and the exponential term in the center expression of (6.3-16) can be expanded just as was done in connection with (6.2-8), giving an expression which is easily integrated; subsequently, using (6.3-10) it is easy to show that the classical result $C_v = 3Nk$ is obtained. At low temperatures, in the right-hand expression of (6.3-15), the limit of the integral approaches infinity, and the resulting definite integral can be shown by methods of contour integration to equal $\pi^4/15$, giving

$$(6.3-17) \quad \left(\frac{\partial U}{\partial T} \right)_v = C_v = \frac{12\pi^4}{5} Nk \left(\frac{T}{\Theta} \right)^3 \quad (T \ll \Theta).$$

This is the well-known “Debye T^3 Law”; its predictions for specific heats in the low

temperature region are in good agreement with experimental data for many substances.

The value of the Debye temperature may be calculated from (6.3-14), or obtained experimentally by choosing that value for Θ which leads to the best fit between the experimental data and the theoretical expression (6.3-16). The calculated and experimentally determined values are generally in fairly good agreement for substances which obey the assumptions which have been made in the Debye theory. For the more common metallic elements the Debye temperature generally lies in the range 150–450°K. A table of Debye temperatures and a detailed discussion of the agreement between experimentally determined and calculated values of the Debye temperature is given by Seitz.⁶

In the preceding development, a crystal containing N identical atoms was assumed. In a crystal where the atoms are not all identical, such as NaCl, elastic vibrations belonging to either optical or acoustical mode can be excited and the results calculated by this procedure are no longer directly applicable. In such a crystal, however, it is possible to treat the acoustical modes and optical modes separately. The acoustical modes may be treated by the above procedure, while the variation of ω with k for the optical modes as shown, for example by Figure 3.11, is so small that it is usually a fairly good approximation to regard the optical modes as vibrations of a single frequency given by (3.4-10). The optical modes may then be treated by the Einstein method developed in the preceding section, and the contributions from optical and acoustical modes combined to give the total heat capacity of the crystal. These and other corrections to the simple Debye theory have been considered in some detail by Blackman,^{7,8} who concluded that in certain specific cases the Debye procedure might lead to significant errors, and that under these circumstances the more exact Born-von Kármán procedure would have to be used instead.

It is customary to think of a metallic substance as possessing a large number of free electrons which may serve to produce a flow of current under an applied electric field, thus accounting for the very high electrical conductivity of metals. On the basis of this picture, one might expect that these free electrons would acquire additional kinetic energy when the crystal is exposed to an external heat source, and in this way contribute significantly to the specific heat. Actually, and somewhat surprisingly, this contribution to the specific heat is so small as to be negligible at temperatures greater than about 5°K. Below this temperature in metallic crystals, it is possible to distinguish a linear variation of specific heat with temperature, which is indeed due to the free electrons. The reasons for this rather peculiar behavior of the electronic specific heat will be discussed in detail in the next chapter.

6.4 THE PHONON

So far, we have discussed the specific heat of solid materials in terms of quantum harmonic oscillators, and calculated the internal energy by ascertaining the number of oscillators, on the average, in each allowed energy state. If the vibrations of the lattice can be treated in this way, then there must exist quanta of vibrational energy

⁶ F. Seitz, *Modern Theory of Solids*, McGraw-Hill Book Co., Inc., New York (1940), pp. 110–111.

⁷ M. Blackman, Z. Physik **86**, 421 (1933).

⁸ M. Blackman, Proc. Roy. Soc. **148**, 384 (1935); **159**, 416 (1937).

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which are emitted or absorbed when transitions between one quantum state and another occur. It is a result of the quantum mechanics of the harmonic oscillator that to a first order of approximation transitions occur only between *adjacent* states of the system;⁹ in other words, in any such transition the quantum number of the oscillator may change only by ± 1 . Accordingly the energy change $\Delta\epsilon$ of the oscillator, corresponding to the energy of the quantum which is absorbed or emitted must be

$$\Delta\epsilon = \Delta n \cdot \hbar\omega = \pm \hbar\omega \quad (6.4-1)$$

where ω is the frequency of the oscillator. The plus sign in (6.4-1) refers to absorption, the minus sign to emission.

Such a quantum of acoustical energy is commonly referred to as a *phonon*, in analogy with the terminology *photon* for a quantum of electromagnetic energy. A phonon must be regarded as having characteristics both of a wave and a particle, just as does the photon; in fact it is quite possible to treat the interaction between two phonons or between a phonon and an electron as a scattering "collision" between two particles. The Debye result for the specific heat can indeed be obtained by regarding the lattice vibrations of the crystal as a *gas of phonons*. Since the phonons are indistinguishable particles, the Bose-Einstein distribution function must be used to describe the distribution of particles among the energy states of the system, and since the number of phonons in the system is not constant with respect to temperature the form which the distribution function takes is (5.6-9), in which $\alpha = 0$.

The number of phonons in the frequency range $d\omega$ about ω (corresponding to an energy range $d\epsilon$ about $\epsilon = \hbar\omega$) is then

$$N(\omega) d\omega = \frac{g(\omega) d\omega}{e^{\hbar\omega/kT} - 1} \quad (6.4-2)$$

where $g(\omega) d\omega$ is the number of possible normal vibrations of the system in the range $d\omega$ about ω . But in (6.3-2) and (6.3-7) we have already shown that

$$g(\omega) d\omega = g(k) \frac{dk}{d\omega} d\omega = \frac{3k^2 V}{2\pi^2} \frac{dk}{d\omega} d\omega. \quad (6.4-3)$$

Using the Debye approximation (6.3-8) to express k and $dk/d\omega$ in terms of ω , (6.4-2) becomes

$$N(\omega) d\omega = \frac{3V}{2\pi^2 v_0^3} \frac{\omega^2 d\omega}{e^{\hbar\omega/kT} - 1}. \quad (6.4-4)$$

The contribution of the internal energy from the frequency range $d\omega$ about ω is just the quantum energy $\hbar\omega$ times the number of quanta in that frequency range. Thus

$$\begin{aligned} dU &= \epsilon(\omega) N(\omega) d\omega = \hbar\omega N(\omega) d\omega \\ &= \frac{3\hbar V}{2\pi^2 v_0^3} \frac{\omega^3 d\omega}{e^{\hbar\omega/kT} - 1}. \end{aligned} \quad (6.4-5)$$

⁹ For a derivation of this *selection rule* see R. B. Leighton, *Principles of Modern Physics*, McGraw-Hill Book Co., Inc., New York (1959), pp. 211-222.

Integrating over all allowed frequencies from zero to the Debye maximum frequency ω_m , one obtains immediately the result (6.3-11). The zero-point energy term, of course, is not obtained when the internal energy is calculated in this way, since the zero-point energy is not connected with the distribution of phonons in any way. This term, however, does not contribute to the specific heat and the two methods lead to the same value (6.3-16) for the specific heat, the result which is of physical interest and accessible to measurement. One may thus treat the system as an ensemble of distinguishable harmonic oscillators, obeying Maxwell-Boltzmann statistics, or as a gas of phonons or vibrational energy quanta, which are indistinguishable, and which obey Bose-Einstein statistics.

6.5 THERMAL EXPANSION OF SOLIDS

The picture of a solid as a system of atoms which are free to vibrate about a periodic array of equilibrium positions, which has been developed in the preceding sections to account for the observed behavior of the specific heat, also suffices to explain the thermal expansion of solids. In this case, however, it is found that if the atoms of the crystal are ideal simple harmonic oscillators, there is no thermal expansion at all, either by classical or quantum mechanical reckoning, and the entire thermal expansion effect in a real crystal depends upon the *anharmonicity* of the lattice vibrations.

This result can be understood qualitatively by considering the potential energy of interaction between neighboring atoms, which must have the form shown in Figure 6.5 as a function of interatomic distance. The minimum in the potential energy curve, at B , is the classical equilibrium position of the atom in question if it is at rest. If the interatomic forces were such that the atom if set in motion thermally would vibrate about its equilibrium position as an ideal classical harmonic oscillator, then the potential curve would be a perfect parabola whose vertex would be located at B . In such a potential "well," the atom would execute harmonic vibrations about the equilibrium point B , the maximum excursions from the equilibrium point in either direction being equal, and the average interatomic distance $\langle x \rangle$ would be equal to the zero-temperature lattice constant a . There would thus be no thermal expansion whatever.

In reality, however, since the crystal can be torn apart by the expenditure of a finite amount of energy, the potential well in which the atoms vibrate, must have approximately the appearance shown in Figure 6.5. In this case, although *nearly* parabolic about the minimum point B , the actual well deviates from the parabolic form more and more as the distance from the minimum point increases. If the atom has energy ε_0 , it should, according to the classical picture vibrate between the extreme amplitude limits A and C , the vibrations being somewhat anharmonic in character. But the distance DC between the equilibrium position and the maximum extension position is now greater than the distance AD between the equilibrium position and the maximum compression position. The average interatomic distance $\langle x \rangle$ is thus *greater* than the zero-temperature lattice constant, and thermal expansion is observed. This classical view of the effect can be shown to lead to the conclusion that the thermal expansion $\langle x \rangle - a$ is directly proportional to the temperature, or that the coefficient

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of thermal expansion $d(\langle x \rangle - a)/dT$ is independent of temperature. This is in fairly good agreement for most substances in the room temperature range or above.

At low temperatures, however, the observed thermal expansion coefficient for most materials becomes much smaller than the classical value, and indeed approaches

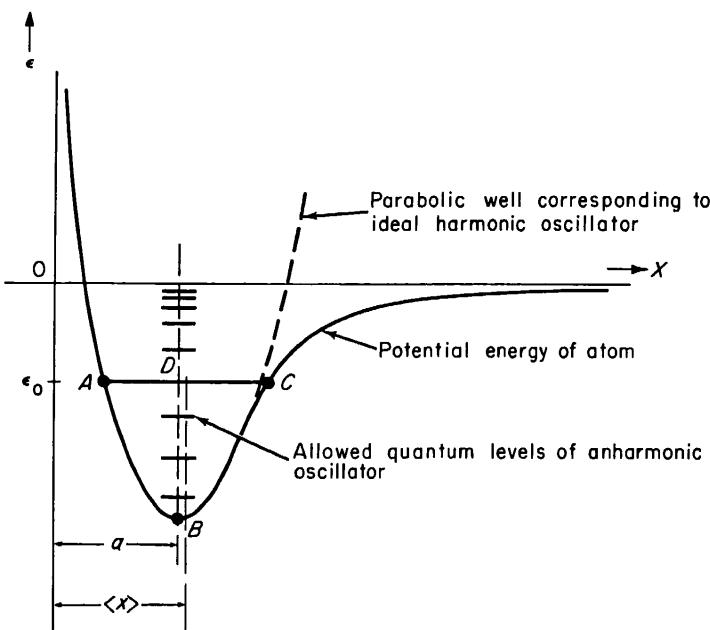


FIGURE 6.5. A representation of the potential energy of a single atom of the crystal as a function of interatomic spacing, illustrating the role of the anharmonic component in the thermal expansion.

zero as the absolute temperature approaches zero. Here again the classical picture breaks down, and the atoms of the crystal must be regarded as quantum oscillators rather than classical ones. In order to calculate the thermal expansion one must first solve Schrödinger's equation using an anharmonic potential (it is usually sufficient to modify the harmonic potential (4.12-6) by the addition of a cubic term in x) to obtain the energy levels ϵ_n and wave functions corresponding to this modified potential, and then find the expectation value $\langle x \rangle_n$ for each allowed energy state by (4.8-11). The interatomic distance, averaged over a Maxwell-Boltzmann distribution may then be written (in analogy with (6.2-1)) as

$$\langle x \rangle = \frac{\sum_n \langle x \rangle_n e^{-\epsilon_n/kT}}{\sum_n e^{-\epsilon_n/kT}}, \quad (6.5-1)$$

the sum being taken over all the levels of the anharmonic oscillator. The details of this procedure are rather involved and will not be presented here. The coefficient of thermal expansion calculated by this method approaches zero as the absolute temperature approaches zero, and is in reasonably good agreement with experiment over a wide range of temperature.

6.6

LATTICE THERMAL CONDUCTIVITY OF SOLIDS

The conduction of heat in solids is a process in which the lattice vibrations also play an important role. In metallic crystals, where large concentrations of free electrons are present, the free electrons contribute significantly to the thermal conductivity, and indeed provide the dominant mechanism for the transport of thermal energy through the crystal. The discussion of electronic thermal conductivity in metals is best presented in connection with the free-electron theory of metals, and hence will be postponed to a later chapter. In nonmetallic substances, however, the lattice vibrations are solely responsible for the transport of heat through the crystal.

The thermal conductivity is customarily defined in terms of a one-dimensional heat flow situation in which a temperature difference ΔT exists over a distance Δx , causing a flow of heat ΔQ over an area A in a time Δt . The thermal conductivity is the coefficient of proportionality between the heat flow per unit area and the temperature gradient. In accord with this definition, one may write

$$J_{qx} = \frac{1}{A} \frac{\Delta Q}{\Delta t} = -K \frac{\Delta T}{\Delta x}, \quad (6.6-1)$$

where K is the thermal conductivity coefficient and J_{qx} the heat flow per unit area or thermal current density. The minus sign is required since K is regarded as a positive quantity and since a positive temperature gradient leads to a negative thermal current. If thermal energy is conserved, then the thermal current must everywhere obey a continuity equation of the form

$$\nabla \cdot \mathbf{J}_q = \frac{\partial J_{qx}}{\partial x} = -\frac{\partial Q}{\partial t}. \quad (6.6-2)$$

By combining (6.6-2) and (6.6-1) it is easily seen that the temperature (hence the thermal energy per atom) must obey a differential equation of the form

$$\frac{K}{c_v} \frac{\partial^2 T}{\partial x^2} = \frac{\partial T}{\partial t}. \quad (6.6-3)$$

This is a partial differential equation which is essentially the same as the equation which describes the *diffusive* transport of mobile particles in a medium in which a concentration gradient exists. It differs from the equation for radiative propagation (3.1-12) in that the right-hand side is a first derivative with respect to time rather than a second derivative. Its characteristic solutions have an exponential rather than harmonic behavior with respect to time, as we shall see in a later chapter.

In a system made up of *ideal* harmonic oscillators, the various normal modes of oscillation of the system are completely independent of one another, there being no coupling whatever between different normal modes of vibration. If a given normal mode of such a system is excited, the system will vibrate in a stable fashion in that same normal mode for an indefinite period of time. In such a system the energy of vibration is propagated directly by acoustical *radiation* rather than by the much slower process which is associated with thermal conduction. Energy thus flows through the system with the velocity of sound, there is no mechanism by which this energy is

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randomized and by which thermal resistance is created, and the thermal conductivity of the specimen is essentially infinite. These observations are true for quantum oscillators as well as classical oscillators. This state of affairs can be described in terms of phonons by the statement that phonons corresponding to different normal-mode harmonic vibrations do not interact with one another at all—or that their mutual interaction cross-section is zero.

If a small amount of anharmonicity is introduced into such a system, then a *coupling* between the various normal modes arises. In this case, if a single normal mode is excited at the outset, the energy initially belonging to this mode will gradually be transferred to the other possible normal modes of the system and thus randomized. In the language of phonons, one may say that phonons representing the various normal-mode vibrations of the system interact (or *collide*) with one another. In other words, a group of phonons corresponding to a single normal mode of the harmonic system will now interact (or be *scattered* by) one another in such a way that after a time their individual momenta and propagation directions will be altered in an essentially random fashion. The phonon distribution is thus converted to one which represents a more or less random selection of normal modes of the system, within the restrictions imposed by conservation of energy and momentum in the individual interactions.

It is clear from this that the thermal conductivity would be infinite were it not for the anharmonicity of the lattice vibrations. The strength of the anharmonic component of the interatomic potential is thus a major factor in determining the thermal conductivity. Since the magnitude of the anharmonicity increases with vibration amplitude, one would expect that the thermal conductivity would decrease as this amplitude increases, leading to a decrease of lattice thermal conductivity with increasing temperature. This effect is quite generally observed in experiment at sufficiently high temperatures. An inverse measure of the strength of the anharmonic interaction between atoms of the crystal is given by the average distance which a phonon can travel between randomizing collisions or scattering events involving other phonons. This distance is referred to as the *mean free path* for phonon-phonon interactions, and the thermal conductivity of solids can be understood quite easily on a qualitative basis in terms of the mean free path. We shall have occasion to deal with the mean free path in a rather more precise and quantitative way in later sections.

The thermal conductivity of solids is most easily understood by regarding the crystal as a container enclosing a “gas” of phonons. We shall first develop a formula for the thermal conductivity of an ideal monatomic gas and then examine how it may be applied to the lattice of a crystalline solid. To begin with, we must find the number of particles of an ideal gas having velocity in the range dv about v , which cross an area element dS per unit time from a direction lying within an angular range $d\theta$ about a polar angle θ . This number is just half the number within that velocity range inside a column of cross section $dS \cos \theta$ (which is the projection of the area dS onto a plane normal to the θ -direction) which lie with a distance of v centimeters from the area element itself. This situation is illustrated in Figure 6.6. The factor one-half is included because on the average only half the particles within the column going along the θ -direction are headed *toward* the area element, the rest going in the opposite direction. If $n(v) dv$ is the number of particles per unit volume having velocity in the range dv about v , then the number crossing the area element is

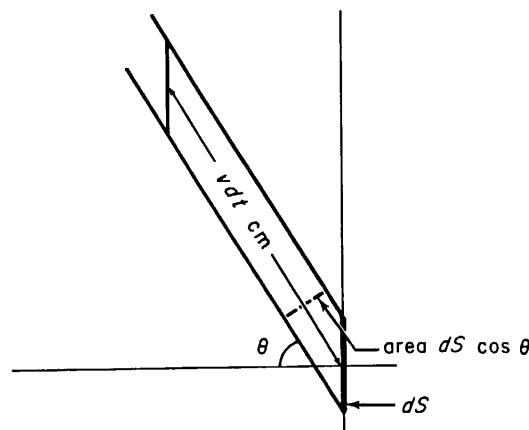
$$dn = \frac{1}{2}v \cdot n(v) dv \cdot \frac{4\pi \sin \theta d\theta}{4\pi} \cdot dS \cos \theta = \frac{1}{2}vn(v) \sin \theta \cos \theta dv d\theta dS. \quad (6.6-4)$$

The factor involving $\sin \theta$ above represents the ratio of the solid angle subtended by the element $d\theta$ about θ to the solid angle 4π subtended by all space; it is clear that this factor also must appear in the expression. Integrating over v , using the Maxwell-Boltzmann distribution (5.4-14) (and remembering that the velocity distribution is independent of θ), one may obtain

$$n(\theta) d\theta = \frac{1}{2} n \bar{c} \sin \theta \cos \theta d\theta dS \quad (6.6-5)$$

with \bar{c} given by (5.4-20), as the desired result.

FIGURE 6.6. Geometry of particles streaming across a plane used in the calculations of Section 6.6.



It should be noted at this point that since the problem of thermal conduction always involves a flow of energy and a temperature gradient, one always has to deal with a system which is *not* in a state of thermal equilibrium. For this reason it is not strictly correct to use the statistical distribution functions which apply to systems at equilibrium. If the temperature gradient in the system is so small that the fractional variation of absolute temperature over a mean free path is small, however, the use of the equilibrium distribution as an approximation is justified. We shall in all cases limit ourselves to a discussion of systems of this sort. The question of the use of statistical distributions in systems which are not in equilibrium will be considered further in the next chapter.

Consider now the situation illustrated in Figure 6.7. A temperature gradient is assumed to exist along the x -axis, so that particles at the origin have average energy ε and those at a short distance to the left have average energy $\varepsilon + \Delta\varepsilon$. Suppose that a particle starts out a distance l away from the origin and gives up its energy to the distribution at the origin in a collision which takes place there. By Taylor's expansion the energy of this particle is

$$\varepsilon + \Delta\varepsilon = \varepsilon + \frac{\partial\varepsilon}{\partial x} \Delta x = \varepsilon + (l \cos \theta) \frac{\partial\varepsilon}{\partial x}. \quad (6.6-6)$$

For each such particle, of course, there will be a particle going in the opposite direction which transports energy ε from the origin to the starting point of the first particle. The *net* transport of energy is just $\Delta\varepsilon = (l \cos \theta)(\partial\varepsilon/\partial x)$, and since the average value of l is simply the *mean free path* between randomizing collisions, which we shall call λ , the

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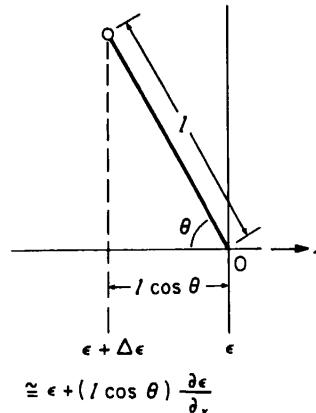
net energy transport per particle, averaged over the distribution of path lengths l , is

$$\Delta\epsilon = (\lambda \cos \theta) \frac{\partial\epsilon}{\partial x}. \quad (6.6-7)$$

For particles of polar angle θ , according to (6.6-5) and (6.6-7), a net energy flux ΔF per unit area arises, where

$$\Delta F = \frac{\Delta\epsilon \cdot n(\theta) d\theta}{dS} = \frac{1}{2} n\bar{c}\lambda \frac{\partial\epsilon}{\partial x} \cos^2 \theta \sin \theta d\theta. \quad (6.6-8)$$

FIGURE 6.7. The path of a particle in a system containing a temperature gradient along the x -direction.



Integrating over the polar angle θ between limits of 0 and π , it is easily seen that the total energy flux must be $\frac{1}{2}n\bar{c}\lambda(\partial\epsilon/\partial x)$. But from the definition of the thermal conductivity K (6.6-1) this must also equal $K(\partial T/\partial x)$. Accordingly,

$$K \frac{\partial T}{\partial x} = \frac{1}{2} n\bar{c}\lambda \frac{\partial\epsilon}{\partial x} = \frac{1}{3} n\bar{c}\lambda \frac{\partial\epsilon}{\partial T} \frac{\partial T}{\partial x}, \quad (6.6-9)$$

whereby

$$K = \frac{1}{3} n\bar{c}\lambda \frac{\partial\epsilon}{\partial T} = \frac{1}{3} c_v \lambda \bar{c}, \quad (6.6-10)$$

since, by definition, the specific heat c_v is just $n(\partial\epsilon/\partial T)$.

This result, derived above for an ideal Maxwell-Boltzmann gas, is also good for a distribution of phonons, provided that the velocity \bar{c} is understood to refer to an average phonon velocity, that is, to an average *sound* velocity in the crystal. [It will be recalled that the Boltzmann distribution was used only to average velocities in obtaining (6.6-5).] According to (6.6-10), then, the problem of determining the lattice thermal conductivity may be reduced essentially to determining the mean free path for phonons in the crystal, since the sound velocity and the specific heat are easily measured or calculated. This problem, unfortunately, is not an easy one, and to reproduce the work involved in its calculation is quite beyond the scope of the present work. The problem was first solved by Peierls,¹⁰ who found λ to be proportional to

(6.6-6)

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¹⁰ R. Peierls, Ann. Physik 3, 1055 (1929).

$1/T$ at high temperatures and to $e^{\Theta/2T}$ at low temperatures. According to this, the thermal conductivity would become infinitely large as the temperature approaches absolute zero, since the product of c_v and λ would diverge to infinity in this limit. Actually, however, at very low temperatures, the phonon mean free path ceases to be limited by phonon-phonon interactions, and is instead limited by scattering of phonons by impurities and imperfections in the crystal, or, in very pure crystals, by the surfaces of the crystal sample itself. In the latter case, it is found that the thermal conductivity of the crystal is a function of the size of the sample! In either instance, the mean free path tends to some finite limit as T approaches zero, and the thermal conductivity approaches zero as T approaches zero, due to the fact that c_v vanishes in the zero-temperature limit. With increasing temperature, then, the thermal conductivity rises from zero to some maximum value, then decreases as the temperature is further increased. This qualitative behavior is indeed observed experimentally in most instances, the magnitudes of the values calculated by (6.6-10) from calculated values of λ agreeing with experimental data in order of magnitude. The effect of scattering by crystal boundaries was first considered by Casimir,¹¹ and the effect of certain types of imperfections has been treated in detail by Klemens.¹²

EXERCISES

1. Show explicitly, using Maxwell-Boltzmann statistics, that the average energy of a three-dimensional classical harmonic oscillator is just three times that of a one-dimensional classical harmonic oscillator at the same temperature, and that it is thus immaterial whether a crystal of N atoms is regarded as an assembly of N three-dimensional oscillators or $3N$ one-dimensional oscillators.
2. Calculate by the Debye method the heat capacity of a two-dimensional periodic crystal lattice containing N identical atoms, and show that at low temperatures the heat capacity varies with temperature as T^2 . What is the high-temperature limit for the heat capacity?
3. Calculate the Debye temperature Θ for (a) diamond, (b) germanium, (c) copper, and (d) lead, and compare your results with published values derived from experimental heat capacity data.
4. Using the Planck relation to express the energy of a phonon in terms of its frequency and the de Broglie relation to express the momentum in terms of the wave number, find an expression for the equivalent "mass" of a phonon of average thermal energy at 300°K, and compare this value with the electronic mass. You may assume that k is small enough so that dispersion effects may be neglected.
5. Prove that the average value $\langle x \rangle_n$ of the amplitude of a quantum harmonic oscillator in the n th energy state is zero.
6. Show, using the laws of thermodynamics, that the difference between the specific heat of a substance at constant pressure and at constant volume is given by

$$c_p - c_v = \frac{9\alpha^2 VT}{K_{iso}}$$

¹¹ H. B. G. Casimir, *Physica* **5**, 495 (1938).

¹² P. G. Klemens, *Proc. Roy. Soc. A* **208**, 108 (1951).

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where α is the linear coefficient of expansion and K_{iso} is the isothermal compressibility $-V^{-1}(\partial V/\partial P)_T$. Hint: note that, by Maxwell's relations, $(\partial S/\partial P)_T = -(\partial V/\partial T)_P$.

7. Consider an assembly of N identical systems having just two energy levels, at energies zero and ε_0 . Assuming that the systems are distinguishable, find (a) the internal energy of the assembly, (b) the heat capacity, (c) approximate expressions for the heat capacity in the high- and low-temperature limits. Plot the heat capacity as a function of temperature.

8. For the assembly of systems discussed in connection with Exercise 7, prove that the heat capacity reaches a maximum value at a temperature T_0 for which

$$x \tanh x = 1$$

where $x = \varepsilon_0/2kT$. Show also that the heat capacity at this temperature is given by

$$c_v(\text{max}) = Nk(x_0^2 - 1)$$

where $x_0 = \varepsilon_0/2kT_0$. Contributions to the heat capacity from systems of this sort are often encountered at low temperatures in paramagnetic substances, and are referred to as *Schottky anomalies*.

9. From the quantum-mechanical expression $\varepsilon = (\frac{3}{2} + n_x + n_y + n_z)\hbar\omega_0$ (where n_x, n_y , and n_z may be zero or positive integers) for the energy levels of a three-dimensional harmonic oscillator, show, in the limit of large energies where $\varepsilon \gg \hbar\omega_0$ and $d\varepsilon \gg \hbar\omega_0$, that the number of quantum states in a range $d\varepsilon$ about energy ε is given by $g(\varepsilon) d\varepsilon = \varepsilon^2 d\varepsilon / (2(\hbar\omega_0)^3)$.

10. Using the result obtained in Problem 9 above, show that the expression $\langle \varepsilon \rangle = 3kT$ for the average energy of a *classical* three-dimensional harmonic oscillator in a system whose members are distributed in energy according to the Boltzmann law may be obtained simply by evaluating the expression

$$\langle \varepsilon \rangle = \frac{\int \varepsilon f(\varepsilon) g(\varepsilon) d\varepsilon}{\int f(\varepsilon) g(\varepsilon) d\varepsilon}.$$

Compare critically the physical aspects of this method and the one used to obtain the same result in Section 6.1.

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CHAPTER 4

OUTLINE OF QUANTUM MECHANICS

4.1 INTRODUCTION

In the latter part of the nineteenth century and the early years of the twentieth century scientists were confronted with a large number of experimentally observed effects which could not be properly explained on the basis of classical mechanics and classical electrodynamics. Among these poorly understood phenomena were some of the more basic thermal and electrical properties of solids. For example, the question of why some solids are very good insulators, with specific resistivities in excess of 10^{12} ohm-cm, and others are excellent conductors having resistivities of the order of 10^{-5} ohm-cm could not be understood classically at all. Starting in 1901 with Max Planck's explanation of the spectral distribution of radiation from incandescent hot bodies, however, nearly all of these puzzling experimental results were found to be consistent with the predictions of a revised scheme of mechanics, which differs in many important respects from Newtonian mechanics, but which reduces to Newtonian mechanics in the limit where the masses and energies of the particles involved become relatively large. This new and expanded scheme of mechanics, which has been particularly successful in describing events which take place on an atomic scale, is called *quantum mechanics*. Although it is manifestly impossible to present a comprehensive account of this subject here, we shall discuss some of its more important aspects, in order to obtain a working knowledge of how to solve simple dynamical problems quantum mechanically, and in order to be able to appreciate the results of calculations concerning more complex systems which are involved in explaining the physical behavior of actual crystals.

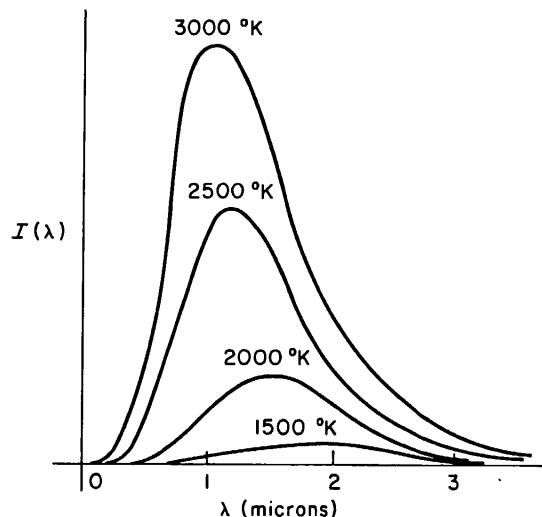
4.2 BLACK BODY RADIATION

The experimentally determined spectral distribution of radiation intensity emitted by an ideal incandescent "black body" radiator is shown in Figure 4.1. A number of attempts were made late in the nineteenth century to explain these results on the basis of classical mechanics and electromagnetic theory, by treating the radiation field as a fluid having thermodynamic properties such as temperature, pressure, entropy, etc., which were determined by the laws of classical electrodynamics and thermodynamics. This fluid was assumed to be in equilibrium with the atoms of the radiating substance, which were regarded as classical harmonic oscillators. None of these attempts was successful in describing the short wavelength part of the curves, although quite good agreement with the experimental data was obtained in the limit of long wavelengths.

(the Rayleigh-Jeans law). The classical calculations, which were always based upon the notion that energy could be absorbed or emitted by the atomic oscillators continuously in any amount, large or small, invariably predicted infinite spectral intensity in the short wavelength limit. This resulted in the emission of infinite total radiation energy per unit time, a result which was clearly absurd.

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FIGURE 4.1. Schematic representation of the frequency distribution of radiation emitted by an incandescent black body radiator at several different values of temperature.



In 1901 Max Planck succeeded in explaining the form of the spectral radiation intensity curves for black body radiation by hypothesizing that the atomic oscillators could radiate or absorb energy only in discrete packets or bundles (called *photons*) whose energy was given by

$$\varepsilon = h\nu = \hbar\omega, \quad (4.2-1)$$

where

$$\hbar = h/2\pi. \quad (4.2-2)$$

Here ν is the frequency of the oscillator (or of the radiation absorbed or emitted), $\omega = 2\pi\nu$, and \hbar is a universal atomic constant (Planck's constant) of magnitude

$$h = 6.625 \times 10^{-27} \text{ erg-sec}$$

$$\hbar = h/2\pi = 1.054 \times 10^{-27} \text{ erg-sec.}$$

The oscillators are thus pictured as existing only in certain *allowed energy states* of total energy $0, \hbar\omega, 2\hbar\omega, 3\hbar\omega, \dots, n\hbar\omega, \dots$, the transitions between these allowed states being accomplished by the absorption or emission of photons of energy $\hbar\omega$.

The quantum hypothesis seemed rather bizarre to some of the scientists of that era, who were accustomed to the ideas of classical mechanics, but the agreement which was obtained thereby with the experimental data was excellent, and the value of h which Planck obtained by fitting his theory to experimental data (6.55×10^{-27} erg-sec) is only about 1 percent less than the currently accepted value. More important, however, subsequent successes of the quantum hypothesis in explaining very different phenomena left no doubt of its essential validity. In the light of present knowledge it is not difficult to accept the fact that energy as well as matter may be composed of discrete and indivisible particles.

4.3 THE PHOTOELECTRIC EFFECT

When light is allowed to fall upon the surface of a metal, electrons may be ejected from the metal into a vacuum where they may be collected by an anode, as shown in Figure 4.2(a). The maximum initial energy of these emitted photoelectrons may be measured by inserting a grid between the photocathode and the anode, and determining the retarding potential which must be applied between grid and cathode to reducing the photocurrent to zero, as illustrated in Figure 4.2(b). It can be demonstrated in thi

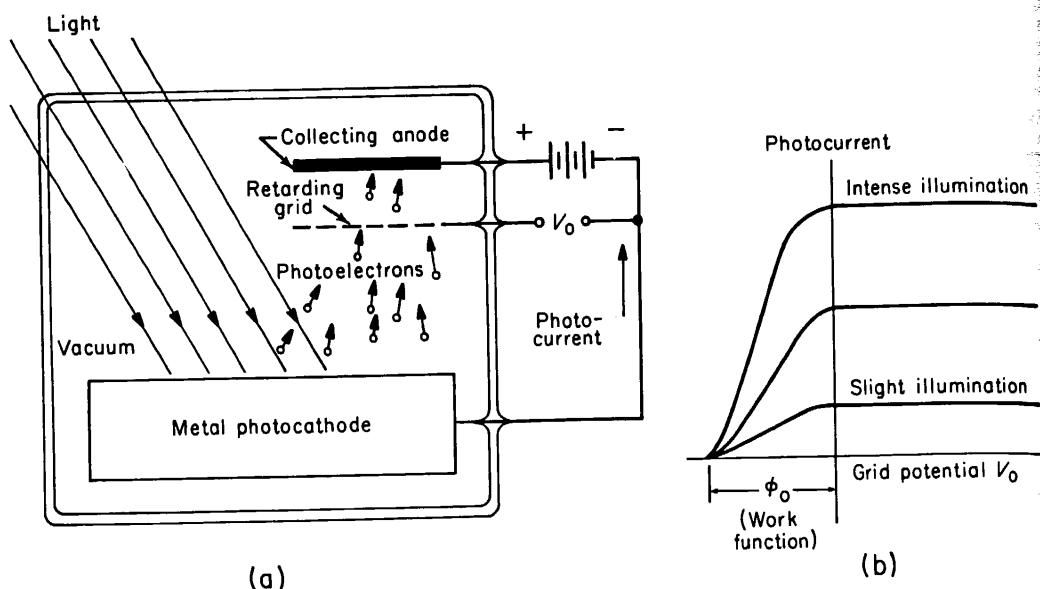


FIGURE 4.2. (a) Schematic diagram of the apparatus used to study the photoelectric effect in metals, (b) a plot of observed photocurrent *versus* retarding potential for several levels of incident light intensity.

way that if the incident light is of frequency less than a given threshold frequency ω_0 there is no photoelectric effect whatsoever, no matter how *intense* the light may be. For incident radiation of frequency greater than ω_0 , photoelectrons are emitted in numbers proportional to the intensity of the incident illumination, causing a photocurrent proportional to light intensity to flow in the external circuit. The maximum initial energy of these electrons as measured by the retarding potential method is strictly proportional to $\omega - \omega_0$, where ω is the frequency of the incident light.

The existence of the threshold frequency cannot be explained on the basis of classical physics, and it was not until 1905 that the physical nature of the photoelectric effect was described by Einstein on the basis of Planck's quantum hypothesis. According to Einstein's explanation, the electrons inside the metal must have lower potential energy than electrons at rest in the vacuum outside the metal surface; otherwise, they would be emitted spontaneously in the dark. This fact leads to a conceptual picture of a metal such as that shown in Figure 4.3. In order to be emitted as photoelectrons, the electrons in the metal must overcome a potential energy barrier of magnitude $e\phi_0$, at least. The potential ϕ_0 , called the *vacuum work function*, is a characteristic property of the emitting cathode material. According to Planck's quantum ideas, the absorption of a photon whose energy is less than $e\phi_0$ by the metal

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cannot excite an electron into the vacuum, but will only impart to it some kinetic energy which is finally dissipated inside the metal in the form of heat by collisions.

On the other hand, if the absorbed photon has energy $e\phi_0$, it can just excite a photoelectron into vacuum with zero kinetic energy, and if the photon energy is

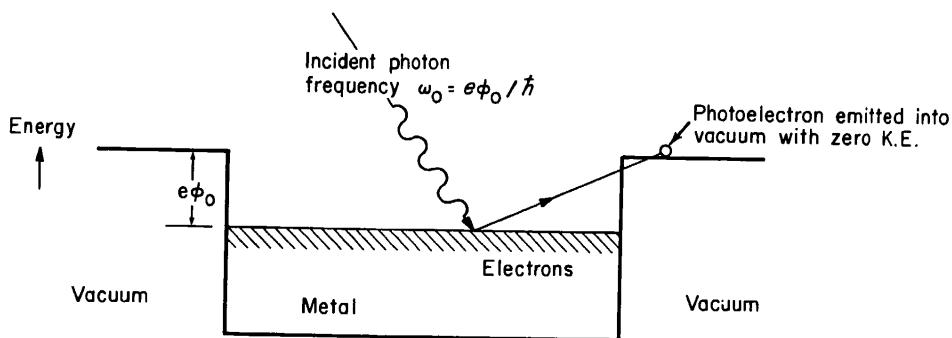


FIGURE 4.3. Simplified conceptual model of a metal as a potential well containing free electrons upon which the Einstein theory of the photoelectric effect is based.

greater than $e\phi_0$, it can excite a photoelectron into vacuum with excess kinetic energy which may be as large as $\hbar\omega - e\phi_0$, $\hbar\omega$ being the incident photon energy. The maximum energy of the emitted photoelectrons will thus be seen to be

$$\varepsilon_m = \hbar\omega - e\phi_0 = \hbar(\omega - \omega_0), \quad (4.3-1)$$

where the threshold frequency ω_0 must be given by

$$\omega_0 = e\phi_0/\hbar. \quad (4.3-2)$$

This is all in agreement with the experimental facts which were described previously. In addition, Equation (4.3-1) predicts that the slope of the curve giving ε_m as a function of ω will be the constant value \hbar . When this slope is evaluated from the experimental data, it is indeed found to be constant and gives a value for \hbar which is in exact agreement with the value derived by Planck from experimental data pertaining to black body radiation! The photoelectric effect thus provided, within a few years, a striking confirmation of the quantum theory in a field which was quite unrelated to the original application.

4.4 SPECIFIC HEAT OF SOLIDS

Classical physics regarded a solid crystal as an assembly of atoms held together in a periodic array by certain attractive forces. The atoms were assumed to be free to vibrate about their equilibrium positions under the constraints of the resultant forces, and to a first approximation, forces and atomic displacements would be related by Hooke's law. The effect of thermal energy, then, would be to set these atoms into

vibration as harmonic oscillators about their equilibrium positions. It is an elementary result of classical kinetic theory that if the energies of an assembly of classical harmonic oscillators are distributed according to the Boltzmann law in thermal equilibrium, the average energy of an oscillator is kT for each vibrational degree of freedom, where T is the absolute temperature and k is Boltzmann's constant (equal to 1.380×10^{-16} erg/ $^{\circ}\text{K}$). We shall see in a later section how this result is derived. On the basis of classical physics, then, since there are three independent vibrational degrees of freedom per atom, we should expect the total internal thermal energy of a crystal composed of N identical atoms to be

$$U = 3NkT. \quad (4.4-1)$$

The *heat capacity* at constant volume, C_v , is by definition the rate of increase of internal energy per unit temperature rise, measured under conditions of constant volume, or for this case

$$C_v = (\partial U / \partial T)_v = 3Nk. \quad (4.4-2)$$

According to the classical formula (4.4-2) the heat capacity should be independent of the temperature. If, in (4.4-2), N is set equal to Avogadro's number N_A (equal to 6.025×10^{-23} mole $^{-1}$), it can be seen that the *molar* heat capacity of all solid chemical elements should have the same value $3N_A k$, equal to about 6 cal $^{\circ}\text{K}^{-1}$ mole $^{-1}$. This result is known as the Law of Dulong and Petit, and is in fairly good agreement with experiment for many elements *at and above room temperature*. At low temperatures

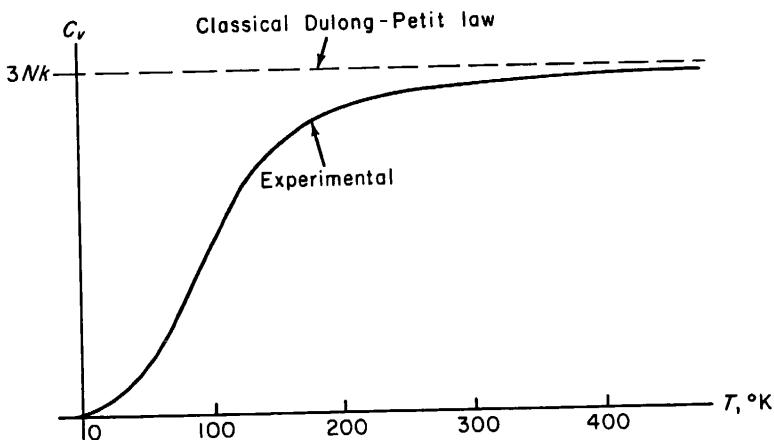


FIGURE 4.4. Typical experimental data for the specific heat of a solid substance as a function of temperature, in comparison with the classical Dulong-Petit result.

the classical result does *not* agree with experiment, the experimental data showing that the heat capacity approaches zero as the temperature approaches zero on the absolute scale, as shown in Figure 4.4. The same general remarks, of course, apply to the specific heat at constant volume c_v , which is defined simply as

$$c_v = (\partial U / \partial T)_v / V. \quad (4.4-3)$$

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4.5 THE BOHR ATOM

One of the most puzzling aspects of atomic behavior to physicists of the nineteenth century was the emission and absorption spectra of the elements. The sharp, discrete spectral lines which are observed could not be understood at all in terms of classical mechanics and electromagnetic theory. In 1913, however, Niels Bohr proposed a model of the hydrogen atom, based on Planck's quantum hypothesis, which described with amazing accuracy the main features of the spectrum of atomic hydrogen.

In Bohr's model, which was founded upon the concept of the nuclear atom advanced by Rutherford in 1910, an electron of mass m and charge $-e$ is assumed to move in an orbit around a much more massive nucleus of charge $+Ze$, where Z is an integer. The introduction of the factor Z allows one to account not only for hydrogen ($Z = 1$), but also for certain other hydrogen-like ions, such as He^+ ($Z = 2$), Li^{++} ($Z = 3$), Be^{+++} ($Z = 4$), etc., which consist of a single electron and a heavy nucleus.

According to classical electrodynamics, accelerated charges always radiate energy, and a system such as that considered by Bohr, wherein the electron is always subjected to a central acceleration, should lose energy constantly by radiation, the electron spiralling gradually inward toward the nucleus. Bohr nevertheless assumed that the electron could exist in stable orbits about the nucleus without radiating energy at all, if only the *angular momentum* associated with the motion were quantized so as to have only the allowed values $n\hbar$, where n is a positive integer. Transitions between allowed steady states n and m would then be accompanied by the instantaneous emission or absorption of a photon of frequency ω_{mn} such that

$$\hbar\omega_{mn} = |\varepsilon_m - \varepsilon_n|, \quad (4.5-1)$$

where ε_m is the energy associated with the state of angular momentum $n\hbar$ and ε_n the energy associated with the state of angular momentum $n\hbar$.

Dynamically, of course, the orbit of the electron about the nucleus could be either circular or elliptical, but for simplicity we shall assume that the orbit is circular. The allowed values of angular momentum L are restricted to integer multiples of \hbar ,

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so that

$$L_n = mr_n^2\omega_n = n\hbar \quad (n = 1, 2, 3, \dots), \quad (4.5-2)$$

where r_n is the radius of the orbit with angular momentum $n\hbar$ and ω_n is the angular velocity of the electron in that orbit. For a steady orbit, the radius r_n must be such that the electrostatic force of attraction between the electron and the nucleus, Ze^2/r_n^2 , is just the centripetal force mv_n^2/r_n required to hold the electron in the circular orbit, whence,

$$Ze^2/r_n^2 = mv_n^2/r_n = mr_n\omega_n^2. \quad (4.5-3)$$

Equations (4.5-2) and (4.5-3) may now be solved as simultaneous equations for r_n and ω_n , giving

$$r_n = \frac{n^2\hbar^2}{Zme^2} \quad (4.5-4)$$

and

$$\omega_n = \frac{Z^2me^4}{n^3\hbar^3}. \quad (4.5-5)$$

The kinetic energy of the system, ε_k , is given by

$$\varepsilon_k = \frac{1}{2}mv_n^2 = \frac{1}{2}mr_n^2\omega_n^2 = \frac{Z^2me^4}{2n^2\hbar^2}. \quad (4.5-6)$$

The potential energy, ε_p , is

$$\varepsilon_p = -Ze^2/r_n = -\frac{Z^2me^4}{n^2\hbar^2}. \quad (4.5-7)$$

The total energy of the system is then

$$\varepsilon_n = \varepsilon_k + \varepsilon_p = -\frac{Z^2me^4}{2n^2\hbar^2} \quad (n = 1, 2, 3, \dots). \quad (4.5-8)$$

The energy of the system is seen to be restricted to certain discrete values or *energy levels* corresponding to $n = 1, 2, 3, \dots$. If $Z = 1$, the system corresponds to the hydrogen atom, and the resulting energy level diagram is as represented in Figure 4.5. Transitions between the energy levels are accomplished by the absorption or emission of a photon whose frequency is given by (4.5-1), each such transition corresponding to a possible spectrum line. The Bohr theory accounts quite successfully for the spectrum of hydrogen and hydrogen-like ions, the agreement between observed and predicted spectral frequencies being very close.

In the preceding development we have assumed the electron orbits to be circular. In general the orbits may be elliptical, and it can indeed be shown that there are regular series of allowed elliptical orbits which satisfy the quantum condition (4.5-2). These elliptical orbits, however, contribute no new energy levels, but merely represent

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OUTLINE OF QUANTUM MECHANICS

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orbits for which the angular momentum has a value $m\hbar$ where m is an integer less than n ; the system thus has energy ϵ_n as given by (4.5-8), but its angular momentum, though still an integral multiple of \hbar , is less than the maximum value $n\hbar$ which corresponds to a circular orbit. We have also regarded the nucleus as being fixed, which is true only in the limit where the ratio of the nuclear to electronic mass becomes infinite. For finite nuclear mass, the nucleus and the electron would rotate about

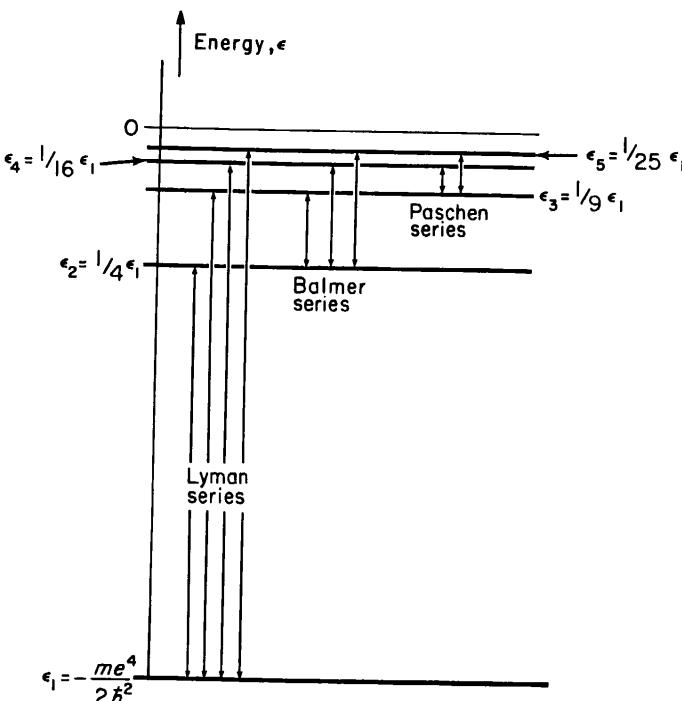


FIGURE 4.5. Energy levels of the hydrogen atom as predicted by the Bohr theory. Transitions corresponding to certain prominent spectral lines are indicated.

their common center of mass. This effect is easily taken into account, the result being that the quantity m in the preceding equations should be replaced by a *reduced mass* μ given by

$$\mu = \frac{mM}{m + M}, \quad (4.5-9)$$

M being the nuclear mass. In the case of the hydrogen atom, the reduced mass differs from the electron mass by about 1 part in 1850.

Numerous attempts were made to extend the Bohr model to explain the spectra of helium and of more complex atoms during the decade following its introduction. These attempts were fraught with difficulty because there was no simple way of determining what the orbits should be. In general, the results of these calculations were not in good agreement with experiment; nor did the Bohr theory provide any explanation for why some transitions between electronic states in complex atoms seemed to be forbidden. Nevertheless the Bohr model provided for the first time a simple,

coherent and accurate explanation of the spectra of one-electron atoms, and served as a conceptual framework for visualizing certain aspects of atomic behavior which persists even to the present time.

4.6 DE BROGLIE'S HYPOTHESIS AND THE WAVELIKE PROPERTIES OF MATTER

In 1924 de Broglie suggested that with a particle of momentum p one might associate a wave of wavelength λ such that

$$p = \frac{h}{\lambda} = \frac{h}{2\pi} \frac{2\pi}{\lambda} = \hbar k. \quad (4.6-1)$$

The Bohr quantum condition follows directly from this hypothesis if one assumes that the allowed orbits of the previous section accommodate an integral number of particle wavelengths as defined by (4.6-1). Since the path length of the orbit is $2\pi r_n$, we must find, according to this idea,

$$n\lambda = \frac{nh}{mv_n} = 2\pi r_n \quad (4.6-2)$$

or

$$n\hbar = mv_n r_n = L_n.$$

It was shown experimentally by Davisson and Germer that electrons could indeed be diffracted from crystals, giving the same pattern for a given crystal as that produced by X-rays of wavelength $\lambda = h/p$, as proposed by de Broglie. The condition for the diffraction of electrons from crystal planes is just the Bragg condition, with λ equal to h/p ;

$$n\lambda = nh/p = 2d \sin \theta. \quad (4.6-3)$$

It has since been shown that neutral atoms, protons, positive ions and other particles exhibit the same wavelike behavior, the de Broglie relation (4.6-1) being satisfied in each case.

4.7 WAVE MECHANICS

In 1926, Schrödinger developed a unified scheme of mechanics based upon the physical notions of Planck's quantum theory and utilizing de Broglie's ideas of the wavelike nature of matter. This scheme, which is called *wave mechanics*, is a very general revision of the laws of mechanics which is designed to extend that subject into the realm of atomic and nuclear phenomena. It has been very successful, and as far as

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one can tell at present, it is a correct way of describing the physical behavior of matter on the atomic scale, or, in fact, on any scale, since the results of wave mechanics reduce to those of classical Newtonian mechanics for the relatively large and massive systems which are observable macroscopically. Almost at the same time, an alternative system of quantum mechanics, called *matrix mechanics*, based upon the same physical ideas as wave mechanics, was devised by Heisenberg. Although quite different from Schrödinger's wave mechanics in its mathematical formulation, it was later shown to be precisely equivalent to Schrödinger's theory. We shall confine our discussions for the most part to the Schrödinger wave mechanical description, which is simpler and more easily related to physically observable situations.

In Schrödinger's formulation of quantum mechanics a complex quantity Ψ , called the *wave function* is associated with a dynamical system. This quantity is a function of three space coordinates for each particle of the system, and the time. The dynamical properties of the system are closely related to the properties of the Ψ function, and the dynamical behavior of the system can be ascertained when the Ψ function for the system is known. For a single-particle system, to which our discussion will be largely restricted, the properties of the wave function Ψ can be expressed in terms of these five postulates:¹

1. Associated with the particle is a complex wave function $\Psi(x,y,z,t)$, where x, y, z are space coordinates and t is the time.
2. The classical expression for the total energy ε of the system (which is called the classical *Hamiltonian* of the system), given by

$$\frac{p^2}{2m} + V(x,y,z) = \varepsilon, \quad (4.7-1)$$

where p is the momentum of the particle, m its mass and $V(x,y,z)$ its potential energy, may be converted into a *wave equation* by associating certain *operators* with the classical dynamical quantities and allowing these operators to operate on the wave function as directed by (4.7-1). The operators corresponding to the pertinent dynamical quantities are

dynamical variable associated operator

$$x, y, \text{ or } z \rightarrow x, y, \text{ or } z$$

$$f(x,y,z) \rightarrow f(x,y,z)$$

$$p \rightarrow \frac{\hbar}{i} \nabla \quad (4.7-2)$$

$$\varepsilon \rightarrow -\frac{\hbar}{i} \frac{\partial}{\partial t}.$$

Since the cartesian components of the ∇ operator are $(\partial/\partial x, \partial/\partial y, \partial/\partial z)$, it is

¹ C. W. Sherwin, *Introduction to Quantum Mechanics*, Holt, Rinehart and Winston, New York (1959), p. 14, pp. 62-63. See also for the extension of these postulates to systems of more than one particle.

clear that the operators corresponding to the momentum components p_x , p_y , p_z are $(\hbar/i)(\partial/\partial x)$, $(\hbar/i)(\partial/\partial y)$ and $(\hbar/i)(\partial/\partial z)$, respectively. Also, since $p^2 = \mathbf{p} \cdot \mathbf{p}$, the corresponding p^2 operator should be $-\hbar^2(\nabla \cdot \nabla)$ or $-\hbar^2\nabla^2$, where ∇^2 represents the Laplacian operator $\partial^2/\partial x^2 + \partial^2/\partial y^2 + \partial^2/\partial z^2$. Replacing the dynamical quantities p^2 , $V(x,y,z)$ and ϵ in (4.7-1) with their corresponding operators and allowing them to operate upon the wave function Ψ , we obtain the wave equation

$$-\frac{\hbar^2}{2m} \nabla^2 \Psi + V(x,y,z)\Psi = -\frac{\hbar}{i} \frac{\partial \Psi}{\partial t}. \quad (4.7-3)$$

This is Schrödinger's equation for the wave function. It is often written in the form

$$\mathcal{H}\Psi = -\frac{\hbar}{i} \frac{\partial \Psi}{\partial t}, \quad (4.7-4)$$

where \mathcal{H} represents the Hamiltonian operator

$$\mathcal{H} = -\frac{\hbar^2}{2m} \nabla^2 + V(x,y,z). \quad (4.7-5)$$

3. The quantities $\Psi(x,y,z,t)$ and $\nabla\Psi$ must be finite, continuous and single-valued for all values of x,y,z and t .

4. The quantity $\Psi^*\Psi$, where Ψ^* is the complex conjugate of Ψ , is always a *real* quantity. This quantity is interpreted as a probability density, in the sense that $\Psi^*\Psi dv$ is the probability that the particle will be found in the volume element dv at time t . This is all the information about the actual location of the particle we can ever obtain from the wave function; the question of just where the particle is at a given time and what its trajectory is cannot be answered precisely, according to quantum mechanics. Of course, for a large or massive object, $\Psi^*\Psi$ will be large only within the classical boundaries of the object and will move in time as predicted by Newton's laws, but on an atomic scale it will be impossible to locate a particle precisely and to follow its trajectory in precise detail. Since $\Psi^*\Psi dv$ is a probability density and since the probability that the particle will be found *somewhere* in space is unity, we must require that the wave function be *normalized* such that

$$\int_v \Psi^*\Psi dv = 1, \quad (4.7-6)$$

the integral being taken over all space.

5. The average or *expectation* value $\langle \alpha \rangle$ of any dynamical variable α , with which is associated an operator $\alpha_{op.}$, is defined by

$$\langle \alpha \rangle = \int_v \Psi^* \alpha_{op.} \Psi dv, \quad (4.7-7)$$

the integral again being taken over all space.

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The essential features of all of wave mechanics are contained in these five postulates. The remainder of our treatment of the subject will be devoted to exploring their implications and applying them to specific problems. There is no way of *proving* them except to state that their consequences, whenever they have been subjected to test by experiment, have been shown to be in agreement with observations within the limits of experimental uncertainty, which in many cases have been extremely small. We shall, of course, try to demonstrate that the results of wave mechanics are in line with some of the dictates of intuition and correspond whenever it can be expected to the results of classical mechanics.

In regard to the latter subject, we are already in a position to show that wave mechanics gives the same results as classical mechanics insofar as the average or expectation values of dynamical quantities are concerned. Let us for simplicity consider a one-dimensional situation where the dynamical system is confined to the x -axis. The expectation value of the momentum p_x , according to (4.7-7), is then

$$\langle p_x \rangle = \int_{-\infty}^{\infty} \Psi^*(x, t) \cdot -\frac{\hbar}{i} \frac{\partial}{\partial x} \Psi(x, t) dx, \quad (4.7-8)$$

whereby, taking a time derivative and differentiating under the integral sign on the right,

$$\frac{d\langle p_x \rangle}{dt} = \frac{\hbar}{i} \int_{-\infty}^{\infty} \frac{\partial \Psi^*}{\partial t} \frac{\partial \Psi}{\partial x} dx + \frac{\hbar}{i} \int_{-\infty}^{\infty} \Psi^* \frac{\partial^2 \Psi}{\partial x \partial t} dx. \quad (4.7-9)$$

Now the value of $\partial \Psi / \partial t$ is given by the wave equation (4.7-3), and the value of $\partial \Psi^* / \partial t$ can be expressed in a similar form by writing the wave equation in terms of Ψ^* rather than Ψ . This can be done by writing the complex function $\Psi(x, t)$ as a sum of real and imaginary parts,

$$\Psi(x, t) = u(x, t) + iv(x, t), \quad (4.7-10)$$

substituting this form for Ψ into (4.7-3), and equating real and imaginary parts on either side of the resulting expression, to obtain two equations of the form

$$-\frac{\hbar^2}{2m} \nabla^2 u + uV = -\hbar \frac{\partial v}{\partial t}$$

$$-\frac{\hbar^2}{2m} \nabla^2 v + vV = \hbar \frac{\partial u}{\partial t}. \quad (4.7-11)$$

Multiplying the second of these equations by $-i$ and adding it to the first, we get a wave equation for Ψ^* ($= u - iv$) of the form

$$-\frac{\hbar^2}{2m} \nabla^2 \Psi^* + V\Psi^* = \frac{\hbar}{i} \frac{\partial \Psi^*}{\partial t}. \quad (4.7-12)$$

In equation (4.7-9), if we express $\partial \Psi / \partial t$ by (4.7-3) and $\partial \Psi^* / \partial t$ by (4.7-12), we obtain

$$\begin{aligned}
 \frac{d\langle p_x \rangle}{dt} &= -\frac{\hbar^2}{2m} \int_{-\infty}^{\infty} \left[\frac{\partial^2 \Psi^*}{\partial x^2} \frac{\partial \Psi}{\partial x} - \Psi^* \frac{\partial^3 \Psi}{\partial x^3} \right] dx + \int_{-\infty}^{\infty} \left[V \Psi^* \frac{\partial \Psi}{\partial x} - \Psi^* \frac{\partial}{\partial x} (V \Psi) \right] dx \\
 &= -\frac{\hbar^2}{2m} \int_{-\infty}^{\infty} \left[\frac{\partial}{\partial x} \left(\frac{\partial \Psi}{\partial x} \frac{\partial \Psi^*}{\partial x} - \Psi^* \frac{\partial^2 \Psi}{\partial x^2} \right) \right] dx - \int_{-\infty}^{\infty} \Psi^* \frac{\partial V}{\partial x} \Psi dx \\
 &= -\frac{\hbar^2}{2m} \left[\frac{\partial \Psi^*}{\partial x} \frac{\partial \Psi}{\partial x} - \Psi^* \frac{\partial^2 \Psi}{\partial x^2} \right]_{-\infty}^{\infty} - \int_{-\infty}^{\infty} \Psi^* \frac{\partial V}{\partial x} \Psi dx. \tag{4.7-13}
 \end{aligned}$$

From postulate (4) above, the integral of the quantity $\Psi^* \Psi = u^2 + v^2$ over the range ∞ to $-\infty$ must exist; this means that both u and v , as well as their derivatives must approach zero as x approaches either ∞ or $-\infty$. Thus Ψ and $\partial \Psi / \partial x$ approach zero in these limits, and the first term in (4.7-13) vanishes. But, according to postulate (5) above, the second term in (4.7-13) represents the expectation value of the quantity $-\partial V / \partial x$, which is the classical force on the particle. We have thus

$$\frac{d\langle p_x \rangle}{dt} = \langle -\partial V / \partial x \rangle = \langle F_x \rangle, \tag{4.7-14}$$

which is simply Newton's Law of motion. It is clear, then, that insofar as the expectation values are concerned, wave mechanics is in agreement with the equations of classical mechanics.

4.8 THE TIME DEPENDENCE OF THE WAVE FUNCTION

Let us assume that the Schrödinger equation (4.7-3) can be solved by the usual mathematical technique of separation of variables. Accordingly we shall assume solutions of the form

$$\Psi(x, y, z, t) = \psi(x, y, z)\phi(t), \tag{4.8-1}$$

where ψ depends only on the space coordinates and ϕ only upon the time. Differentiating (4.8-1) and substituting back into (4.7-3), it is easily seen that

$$-\frac{\hbar^2}{2m} \phi \nabla^2 \psi + V \phi \psi = -\frac{\hbar}{i} \psi \frac{d\phi}{dt}. \tag{4.8-2}$$

Dividing both sides of this equation by $\Psi = \phi\psi$, we find

$$-\frac{\hbar^2}{2m} \frac{\nabla^2 \psi}{\psi} + V(x, y, z) = -\frac{\hbar}{i} \frac{1}{\phi} \frac{d\phi}{dt} = \epsilon. \tag{4.8-3}$$

In (4.8-3), the left-hand side is a function of the space coordinates alone, while the

$$\frac{\partial}{\partial x} (V\Psi) \Big] dx$$

center expression is a function of time only. The only way in which this equality can hold for all values of the variables is for each expression separately to be equal to a constant, called a separation constant and denoted by ϵ in (4.8-3). There are really two separate equations, one for $\phi(t)$, the other for $\psi(x,y,z)$, thus

$$(4.8-4) \quad d\phi/dt = -\frac{i\epsilon}{\hbar} \phi(t)$$

(4.7-13)

$$\text{and } \nabla^2\psi + \frac{2m}{\hbar^2} (\epsilon - V(x,y,z))\psi(x,y,z) = 0. \quad (4.8-5)$$

Equation (4.8-4) can easily be integrated to give

$$(4.8-6) \quad \phi(t) = e^{-i\epsilon t/\hbar}.$$

(4.7-14)

The integration constant which would normally appear as a multiplicative factor in (4.8-6) is arbitrarily set equal to unity. There is no loss in generality sustained in doing this. According to (4.8-1) the time-dependent wave function Ψ can now be written

$$(4.8-7) \quad \Psi(x,y,z,t) = \psi(x,y,z)e^{-i\epsilon t/\hbar},$$

where $\psi(x,y,z)$ is a solution of (4.8-5).

Equation (4.8-5) is called the *time-independent Schrödinger equation*, and its solutions $\psi(x,y,z)$ are called *time-independent wave functions* or *stationary state wave functions*. Equation (4.8-5) can also be written as

$$(4.8-8) \quad \mathcal{H}\psi = \epsilon\psi,$$

where \mathcal{H} is the Hamiltonian operator given by (4.7-5). It is usually more convenient, when possible, to solve the time-independent equation (4.8-6) and deal as much as possible with the time-independent wave functions only. The time dependences, whenever needed, can be expressed using (4.8-7).

In order to be able to do this conveniently, we should take note of certain results which follow when the wave function is of the form (4.8-7). First of all, if the wave function has this form, then

$$(4.8-9) \quad \Psi^*\Psi = \psi^*e^{i\epsilon t/\hbar}\psi e^{-i\epsilon t/\hbar} = \psi^*\psi,$$

and $\Psi^*\Psi$ itself is time independent and equal to $\psi^*\psi$ —thus the terminology *stationary state* wave functions for wave functions of this sort. As a consequence of this result, $\psi^*\psi$ has the same probability density interpretation with respect to the time-independent wave functions as $\Psi^*\Psi$ has with respect to the time-dependent ones. In addition, from (4.8-9) it follows that

$$(4.8-10) \quad \int_v \Psi^*\Psi dv = \int_v \psi^*\psi dv = 1,$$

and that the normalization condition for the time-independent functions (4.8-7) is thus the same as that for the time-dependent functions. Finally, if the wave functions have the form (4.8-7) and if $\alpha_{\text{op.}}$ depends only on the coordinates and not *explicitly* upon the time, the expectation value of the dynamical variable represented by the operator $\alpha_{\text{op.}}$ can be expressed as

$$\langle \alpha \rangle = \int_v \Psi^* \alpha_{\text{op.}} \Psi dv = \int_v \psi^* \alpha_{\text{op.}} \psi dv, \quad (4.8-11)$$

since the exponential time factors cancel out just as in (4.8-9) if $\alpha_{\text{op.}}$ has no explicit time dependence. If $\alpha_{\text{op.}}$ depends explicitly upon time, then the time-dependent wave functions must in general be used to evaluate $\langle \alpha \rangle$.

It should be noted that these results are applicable only when the total wave function is of the form (4.8-7). If the total wave function Ψ is a *superposition* of functions of the form (4.8-7), as it well may be while still satisfying the time-dependent wave equation, these three results are no longer true, and the time dependent wave functions must generally be used to calculate the properties of the system.

It is easily shown, using the wave function (4.8-7) in (4.7-7), employing the time-dependent energy operator $-(\hbar/i)(\partial/\partial t)$, that the expectation value of the energy of a system in a state represented by a wave function of this type is just the value of the separation constant ϵ . The notation chosen for the separation constant has, of course, anticipated this result. It can also be shown from (4.8-8) that the expectation value of the Hamiltonian operator \mathcal{H} for a system in a state represented by this sort of wave function (which, since \mathcal{H} is a time-independent operator can be calculated using the time-independent wave function according to (4.8-11)) is just equal to ϵ , the expectation value of the energy.

Neither (4.8-4) nor (4.8-5) places any restriction upon the value of ϵ , since for *any* ϵ there exists a Ψ which satisfies these equations. However, the requirements of continuity, finiteness, and single-valuedness *may* select out of the infinite continuum of possible solutions only certain individual ones satisfying these conditions, which correspond to *certain discrete values* of the separation constant (thus the energy) ϵ . We may find in this way that only a certain set of solutions $\psi_n(x, y, z)$ which are related to an associated set of energy levels ϵ_n are acceptable as wave functions for the system, because only these functions satisfy the wave equation *and the boundary conditions*. These acceptable wave functions are called the *eigenfunctions* of the system (from the German *eigen*, meaning *own* or *characteristic*), and the associated energy levels are called *energy eigenvalues*. The discrete energy levels of the Planck oscillator and the Bohr atom are really eigenvalues of this sort. From (4.8-6) it is easily seen that the frequency of the wave function always obeys Planck's relation

$$\epsilon = \hbar\omega. \quad (4.8-12)$$

In some instances, both the wave equation and the associated boundary conditions may be satisfied for *any* value of ϵ , or at least for any value of ϵ in a given finite interval. In such cases there is a *continuous* range of permitted energies or a *continuum* of energy levels. We shall see in due time in what particular circumstances either of these possible situations arises.

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4.9 THE FREE PARTICLE AND THE UNCERTAINTY PRINCIPLE

We now wish to examine the wave function of a free particle, that is, one which is subject to no forces, and which, therefore, moves in a region of constant potential. We shall again limit ourselves to a one-dimensional geometry in which motion is restricted to the x -axis. For convenience, and without loss of generality, the potential may be taken to be zero, in which case the wave equation (4.8-5) becomes

$$\frac{d^2\psi}{dx^2} + k^2\psi(x) = 0, \quad (4.9-1)$$

where

$$k = \sqrt{2m\epsilon/\hbar^2}. \quad (4.9-2)$$

Equation (4.9-1) is a familiar differential equation which has solutions of the form

$$\psi(x) = Ae^{\pm ikx}, \quad (4.9-3)$$

where A is an arbitrary constant. These solutions satisfy all the requirements for wave functions except, in a strict sense, integrability on the interval $-\infty < x < \infty$. We shall nevertheless have to accept them, although, as we shall see, certain difficulties will arise in satisfying the normalization requirement. The time-dependent wave functions for the system, according to (4.8-7), will be

$$\Psi(x,t) = Ae^{i(\pm kx - \omega t)}, \quad (4.9-4)$$

where, from (4.9-2), $\omega = \epsilon/\hbar = \frac{\hbar k^2}{2m}. \quad (4.9-5)$

The time dependent solutions (4.9-4) represent running waves; if the $+$ sign is chosen, the propagation direction is along the $+x$ -axis, and if the $-$ sign is chosen, the propagation direction is reversed. Accordingly, the same choice of signs for the time-independent functions (4.9-3) may be made to represent waves propagating (in time) in those respective directions. The expectation value of the momentum of the particle, according to (4.8-11), is given by

$$\langle p_x \rangle = \int_{-\infty}^{\infty} \psi^* \frac{\hbar}{i} \frac{\partial}{\partial x} \psi dx. \quad (4.9-6)$$

However, from (4.9-3) it is easily seen that $\partial\psi/\partial x = \pm ik\psi$, whereby (4.9-6) becomes

$$\langle p_x \rangle = \pm \hbar k \int_{-\infty}^{\infty} \psi^* \psi dx = \pm \hbar k = \pm \frac{\hbar}{\lambda}. \quad (4.9-7)$$

This expression is simply a statement of de Broglie's relation (4.6-1); the de Broglie relation for free particles is thus implicitly contained in the postulates of wave

mechanics. In addition, from (4.9-5) it is clear that

$$\varepsilon = \frac{\hbar^2 k^2}{2m} = \frac{\langle p^2 \rangle}{2m}, \quad (4.9-8)$$

in agreement with the classical result.

In attempting to normalize the wave function (4.9-3) in accord with the requirements of (4.8-10) it is found that the value of A^*A must be chosen to be infinitesimally small in order that the integral (4.8-10) not diverge. Since from (4.9-3) the probability $\psi^*\psi dx$ of finding the particle within an interval dx about a point x is the same at all points and equal to $A^*A dx$, and since the *a priori* classical probability of finding a free particle within some specific finite region of an infinite line is infinitesimally small, it is not surprising that this situation should have arisen. It is, in fact, in agreement with what we should have expected physically. We shall not attempt to deal with this difficulty in a more rigorous manner, but we shall merely note that no serious trouble arises through application of the normalization condition (4.8-10) as long as we recognize the singular nature of the circumstances which govern the magnitude of A^*A and do not attempt to evaluate this quantity explicitly in numerical terms.

The solutions of the time-independent Schrödinger equation (4.8-5) yield wave functions of the form (4.9-3) or (4.9-4) which represent plane waves propagating along the $\pm x$ -directions. Since the probability density $\Psi^*\Psi$ associated with these functions is independent of time, the solutions (4.9-3) are stationary-state wave functions. Each stationary-state wave function is associated with a unique value of energy ε , and thus, according to (4.9-8) and (4.9-7), represents a state whose propagation constant has a unique value k and whose momentum has a unique value $p_x (= \hbar k)$. However, since the amplitude of the waves is constant, the waves run uniformly from ∞ to $-\infty$, and thus have *no unique location* in space. Because the boundary conditions of continuity, finiteness, single-valuedness, etc., are satisfied equally well for any value of ε or k , there is a *continuous* range of allowed values for these parameters.

It is quite possible by superposing solutions of this type, each of which corresponds to a different value of ε and k , to construct wave functions of the form

$$\Psi(x,t) = A_1 e^{i(k_1 x - \omega_1 t)} + A_2 e^{i(k_2 x - \omega_2 t)}. \quad (4.9-9)$$

Due to the *linearity* of the time-dependent Schrödinger equation, such superposition wave functions are perfectly good solutions to the time-dependent equation (4.7-3), although they do *not* satisfy the time-independent equation (4.8-3) because they are not of the form (4.8-7). The probability amplitude associated with such solutions is not independent of time, as it is for the stationary-state solutions. The process of superposition may be extended so that an infinite number of stationary-state solutions are combined into a wave function of the form

$$\Psi(x,t) = \sum_n A_n e^{i(k_n x - \omega_n t)}. \quad (4.9-10)$$

Finally, the values k_n may be chosen very close together, separated only by intervals dk , and the values A_n may assume the values of any given function of k at these points, in which case the superposition (4.9-10) may become in the limit an integral of the form

$$\Psi(x,t) = \int_{-\infty}^{\infty} A(k) e^{i(kx - \omega t)} dk. \quad (4.9-11)$$

(4.9-8)

The reader may as an exercise easily verify the fact that this is still a solution to the time-dependent Schrödinger equation (4.7-3). The function $A(k)$ in (4.9-11) may be any function of k whatsoever, so long as the integral exists.

Suppose now that at some instant of time, say $t = 0$, one tries to form a wave function whose probability density $\Psi^* \Psi$ is localized in a particular region of the x -axis, for instance between the points $x = a/2$ and $x = -a/2$, as illustrated in Figure 4.6. This can be accomplished by constructing a superposition of solutions

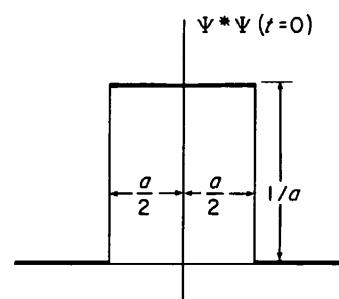


FIGURE 4.6. The probability density function for a particle which is somehow constrained to be along the region of the x -axis extending between $-a/2$ and $+a/2$.

of the stationary-state form (4.9-4), belonging to different values of k , according to (4.9-11). Let us choose

$$A(k) = C \frac{\sin \frac{1}{2}(k - k_0)a}{\frac{1}{2}(k - k_0)a}, \quad (4.9-12)$$

where C and k_0 are constants. It will be seen directly that this choice for $A(k)$ is the correct one if $\Psi^* \Psi$ is to be as represented in Figure 4.6. Substituting (4.9-12) into (4.9-11) and setting t equal to zero, it is clear that

$$\Psi(x,0) = C \int_{-\infty}^{\infty} \frac{\sin \frac{1}{2}(k - k_0)a}{\frac{1}{2}(k - k_0)a} e^{ikx} dk. \quad (4.9-13)$$

(4.9-9)

Letting

$$q = k - k_0, \quad (4.9-14)$$

this can be written in the form

$$\Psi(x,0) = C e^{ik_0 x} \int_{-\infty}^{\infty} \frac{\sin \frac{1}{2}qa}{\frac{1}{2}qa} e^{iqx} dq. \quad (4.9-15)$$

Now, according to the Fourier Integral Theorem² an arbitrary function $f(x)$ can be expressed as a *Fourier integral* by

$$f(x) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{iqx} dq \int_{-\infty}^{\infty} f(x') e^{-iqx'} dx'. \quad (4.9-16)$$

² See, for example, R. V. Churchill, *Fourier Series and Boundary Value Problems*, McGraw-Hill Book Co. Inc., New York (1941), Chapter V.

(4.9-10)

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If the function shown as $\Psi^*\Psi$ in Figure 4.6, that is,

$$(x) = \begin{cases} 1/a & (-a/2 < x < a/2) \\ 0 & (x > a/2; x < -a/2) \end{cases} \quad (4.9-17)$$

is expressed in integral form by using (4.9-16), it can be shown in a straightforward manner that

$$f(x) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \frac{\sin \frac{1}{2}qa}{\frac{1}{2}qa} e^{iqx} dq = \begin{cases} 1/a & (-a/2 < x < a/2) \\ 0 & (x > a/2; x < -a/2). \end{cases} \quad (4.9-18)$$

Using this result to express the integral in (4.9-15) in simpler form, we find³

$$\Psi(x,0) = \frac{2\pi C}{a} e^{ik_0 x} \quad (-a/2 < x < a/2) \\ = 0 \quad (x > a/2; x < -a/2). \quad (4.9-19)$$

The normalizing constant C must now be chosen so as to satisfy (4.7-6), whereby

$$\frac{4\pi^2 C^2}{a^2} \int_{-\frac{1}{2}a}^{\frac{1}{2}a} dx = \frac{4\pi^2 C^2}{a} = 1$$

or $C = \sqrt{a}/(2\pi).$ (4.9-20)

Then $\Psi(x,0) = \frac{1}{\sqrt{a}} e^{ik_0 x} \quad (-a/2 < x < a/2) \\ = 0 \quad (x > a/2; x < -a/2) \quad (4.9-21)$

In other words, if $A(k)$ is chosen as in (4.9-12), with $C = \sqrt{a}/(2\pi)$, the wave function at time $t = 0$, given by (4.9-15) is ultimately expressable in the simple form (4.9-21). The probability amplitude $\Psi^*(x,0)\Psi(x,0)$ existing at $t = 0$ is then simply that of Figure 4.6, and the "particle" is localized within a distance $\Delta x = a$ about the origin. To accomplish this localization, however, we were forced to introduce a superposition of stationary-state wave functions corresponding to various values of k , hence to various values of momentum $\hbar k$. The relative amplitudes of the various momentum components in the superposition is given by the function $A(k)$, thus by (4.9-12) with $C = \sqrt{a}/(2\pi)$. A plot of these momentum contribution amplitudes *versus* ka

³ Although all the superposition functions $A(k)e^{i(kx-\omega t)}$ satisfy the continuity requirement for wave functions, the actual summation as expressed by (4.9-19) does not satisfy this requirement for $x = \pm a$. This violation of the formal requirements, however, introduces no error into the calculations, since obviously the square pulse function (4.9-19) could be "rounded off" very slightly near $x = \pm a$ so as to satisfy the continuity condition without introducing any very significant alteration into the shape of the function $A(k)$.

(4.9-17)

is shown in Figure 4.7. The principal momentum contributions are from the region near $k = k_0$, and the momentum contribution falls off quite rapidly for values of k much larger than or smaller than k_0 . We may regard the contributions to the superposition from values of k larger than $k_0 + \frac{1}{2}\Delta k$ and smaller than $k_0 - \frac{1}{2}\Delta k$ as negligible, where Δk is a parameter which expresses the effective width of that part of the $A(k)$

straightforward

(4.9-18)

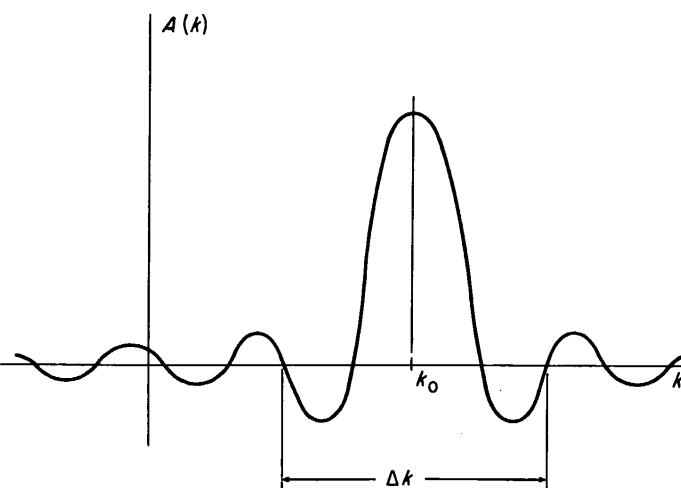


FIGURE 4.7. Momentum amplitude distribution corresponding to the probability amplitude of Figure 4.6.

curve where $A(k)$ takes on values which are not small compared to the maximum value $A(k_0)$. If we arbitrarily choose Δk such that $\Delta(k\alpha) = 8\pi$, a position corresponding to the second zero of the curve on either side of $k = k_0$, which is a reasonable choice by the above criterion, we find

$$\Delta k = 8\pi/a. \quad (4.9-22)$$

The product of the distance Δx within which the particle may be considered to be localized and the uncertainty Δk in momentum which is introduced by the superposition of states required to accomplish this localization is

$$\Delta k \cdot \Delta x = \frac{8\pi}{a} \cdot a = 8\pi,$$

or, since $k = p/\hbar$,

$$\Delta p \cdot \Delta x = 8\pi\hbar. \quad (4.9-23)$$

Neglecting the numerical factors which result from the arbitrary choice of a cutoff point for Δk , and using the symbol \sim to mean "of the order of," we may write

$$\Delta p \cdot \Delta x \sim \hbar. \quad (4.9-24)$$

For a free particle whose momentum is characterized by a single unique value of k , the "particle" extends over all space. If the particle is required to be within a given region of space, then its wave function, which must now be regarded as a superposition of stationary-state functions related to different values of k , is characterized by a "spread" of momentum values as illustrated by Figure 4.6, such that (4.9-24) is

obeyed. This is a specific illustration of an effect known as the *Heisenberg Uncertainty Principle* which is a very general consequence of the wave-mechanical description of nature. The uncertainty principle states that the position of a particle and its momentum cannot *simultaneously* be defined with arbitrary precision; any experiment which is performed to ensure that the particle will be localized within a given region of space will inevitably *introduce* an uncertainty into its momentum which will be given by (4.9-24). It should be emphasized that this effect is independent of the experimental precision with which the quantities involved can be measured; it is really a property of matter under observation.

It can be shown quite generally that uncertainty relations such as (4.9-24) exist between all pairs of conjugate dynamical variables which classically could be used to specify completely the state of motion of the system. A complete and thorough discussion of this subject is given by Powell and Craseman.⁴ If in (4.9-24) we write $\Delta x = v \Delta t$, where v is the velocity, we obtain

$$v \Delta p \Delta t \sim \hbar. \quad (4.9-25)$$

Since for a free particle, $\epsilon = p^2/2m$, $\Delta\epsilon = p\Delta p/m = v\Delta p$, (4.9-25) may be expressed as

$$\Delta\epsilon \cdot \Delta t \sim \hbar. \quad (4.9-26)$$

The Heisenberg relation (4.9-24) may thus also be written in terms of the uncertainty in energy of the wave train times its duration.

It should be noted that the behavior of the "wave packet" which was considered above may be expressed as a function of time by (4.9-11) with $A(k)$ as given by (4.9-12). It can be shown that the maximum of the probability amplitude $\Psi^*\Psi$ moves with constant velocity $\hbar k_0/m$, corresponding to a constant momentum $\hbar k_0$ as predicted by classical mechanics. In addition to this classical motion of the packet as a whole, it is also found that the packet spreads out as time elapses, in such a way that the uncertainty relation (4.9-24) is always satisfied. For wave packets representing large or massive objects which are localized within macroscopically observable distances, this spreading effect is found to be so slow as to be undetectable on a reasonable time scale.⁵

4.10 A PARTICLE IN AN INFINITELY DEEP ONE-DIMENSIONAL POTENTIAL WELL

In this example we shall examine the behavior of a particle in the one-dimensional potential well shown in Figure 4.8. For such a system we have

$$\begin{aligned} V(x) &= 0 & (0 < x < a) \\ &= \infty & (x < 0; x > a). \end{aligned} \quad (4.10-1)$$

⁴ J. L. Powell and B. Craseman, *Quantum Mechanics*, Addison-Wesley, Reading, Mass. (1961), pp. 69-76; pp. 182-184.

⁵ E. Ikenberry, *Quantum Mechanics for Mathematicians and Physicists*, Oxford University Press, New York (1962), p. 64.

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In the region ($0 < x < a$), where $V = 0$, the time-independent Schrödinger equation (4.8-5) can again be written

$$\frac{d^2\psi}{dx^2} + k^2\psi = 0 \quad (4.10-2)$$

where

$$k = \sqrt{2me/\hbar^2}. \quad (4.10-3)$$

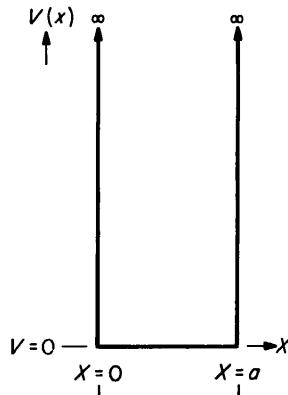


FIGURE 4.8. An infinitely deep potential "well."

In this region the particle is a free particle, and the solution to (4.10-2) could be written in the form (4.9-3). We shall find it more convenient, however, to write it in the equivalent form

$$\psi(x) = A \sin kx + B \cos kx \quad (0 < x < a), \quad (4.10-4)$$

where A and B are arbitrary constants. Since the particle is constrained by infinitely high potential barriers at $x = 0$ and $x = a$, we shall assume that

$$\psi(x) = 0 \quad (x < 0; x > a). \quad (4.10-5)$$

This assumption, which appears to be physically reasonable, will be justified further in the next section.

If it is required that $\psi(x)$ be continuous at the boundaries of the potential well at $x = 0$ and $x = a$, then (4.10-4) must reduce to zero at those two points. Substituting the values $x = 0$ and $x = a$ into (4.10-4) and setting the result equal to zero, it is clear that $B = 0$ and that

$$A \sin ka = 0. \quad (4.10-6)$$

This condition can be satisfied *only* when

$$ka = n\pi \quad (n = 1, 2, 3, \dots), \quad (4.10-7)$$

thus only for a discrete sequence of values of k , which we label k_n , where

$$k_n = n\pi/a \quad (n = 1, 2, 3, \dots). \quad (4.10-8)$$

Since k is related to the energy by (4.10-3), this condition defines a discrete set of allowed energy eigenvalues

$$\epsilon_n = \frac{\hbar^2 k_n^2}{2m} = \frac{n^2 \pi^2 \hbar^2}{2ma^2} \quad (n = 1, 2, 3, \dots). \quad (4.10-9)$$

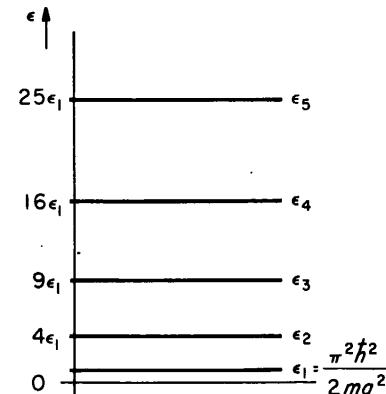


FIGURE 4.9. Allowed energy levels for a particle in the potential well illustrated in Figure 4.8.

Figure 4.9 shows an energy level diagram for this system. In view of the requirement (4.10-8), the wave functions of the system must be of the form

$$\begin{aligned} \psi_n(x) &= A_n \sin \frac{n\pi x}{a} \quad (0 < x < a), \\ &= 0 \quad (x < 0; x > a), \end{aligned} \quad (4.10-10)$$

the constants A_n being determined by the normalization requirement (4.8-10), according to which

$$\int_{-\infty}^{\infty} \psi_n^* \psi_n dx = A_n^2 \int_0^a \sin^2 \frac{n\pi x}{a} dx = 1 \quad (4.10-11)$$

giving $A_n = 1/\sqrt{a}$. (4.10-12)

The time dependence of the wave functions is easily determined from (4.8-7). The functions (4.10-10) are, of course, stationary state eigenfunctions, for which $\Psi^* \Psi$ is time-independent.

For this system we find that there is a system of *discrete* energy levels as given by (4.10-9). The Schrödinger equation (4.10-2) within the region of allowed motion is the same as that for a free particle (4.9-1), for which a *continuous* range of energy values are permitted, and the solutions (4.10-10) are simply linear combinations of free-particle solutions of the form (4.9-3) pertaining to the same energy. The difference between the two cases lies solely in the *boundary conditions*, which for the potential well can be satisfied only for a discrete set of energies.

The continuity condition upon the slope of the wave functions (4.10-10) is formally violated by these functions at $x = 0$ and $x = a$. This situation arises from the singularity in the potential function $V(x)$ at those points, and causes no difficulty in the physical

discrete set of

(4.10-9)

interpretation of the results. The behavior of the wave function at these points can be inferred as a limiting case of the results which will be discussed in the next section, confirming the calculations leading to (4.10-10).

The wave functions (4.10-10), which can be represented as

$$\psi_n(x) = \frac{A_n}{2i} (e^{n\pi ix/a} - e^{-n\pi ix/a}) \quad (4.10-13)$$

in the region ($0 < x < a$), are seen to be standing-wave superpositions of plane wave solutions for which $k = n\pi/a$ and $-n\pi/a$, thus superpositions of a wave propagating along the $+x$ -direction and one of equal amplitude going in the opposite direction. Since both components of the superposition have the *same* energy, the linear combination (4.10-13) is a solution to the time-independent Schrödinger equation (4.10-2) and thus still represents a stationary state of the system. The corresponding physical picture is that of a particle which is reflected elastically from the walls of the potential well at $x = 0$ and $x = a$ and oscillates rapidly back and forth in the potential well. The wave function and the probability amplitude for the particle in the lowest energy state and in a higher energy state are shown in Figure 4.10. According to the quantum

e requirement

(4.10-10)

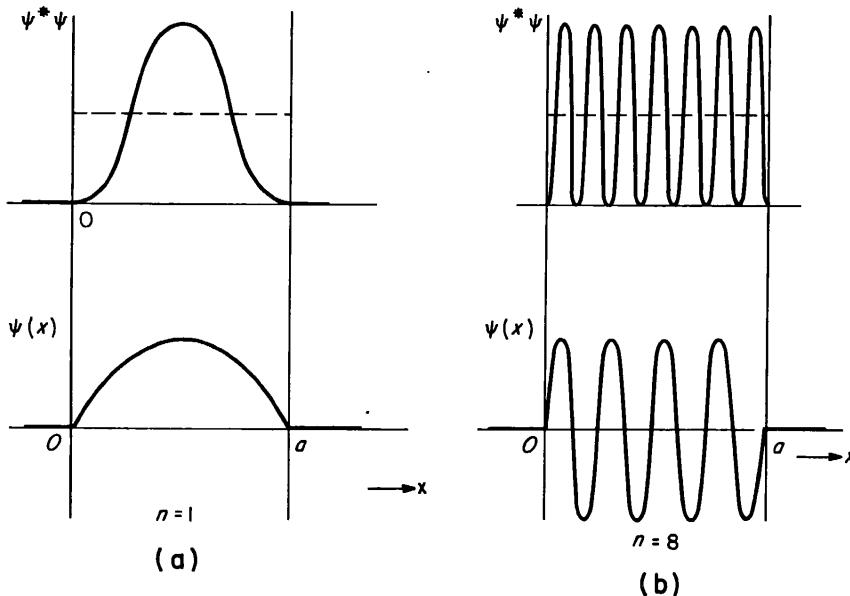


FIGURE 4.10. Wave functions and probability amplitudes for two particular allowed energy states of a particle in the infinitely deep well.

probability amplitude, the probability of finding the particle at certain points corresponding to the zeros of $\psi^* \psi$ (which for this example simply equals ψ^2 , since ψ is real) becomes vanishingly small. The quantum probability amplitude for the lower energy states is not in good agreement with the constant probability amplitude which would be expected classically and which in the figure is shown by the dashed curves. For higher energy states, however, apart from the rapid oscillation of the quantum amplitude about the classical value as an average, the agreement is good in the sense that the mean value of the quantum probability amplitude taken over any interval of appreciable length nearly equals the classical amplitude.

4.11 A PARTICLE IN A ONE-DIMENSIONAL WELL OF FINITE DEPTH

The behavior of a particle in a one-dimensional well of finite depth can be calculated along the general lines of approach which were used in Section 4.10. In this case we shall assume a potential well of the form shown in Figure 4.11, in which the depth of

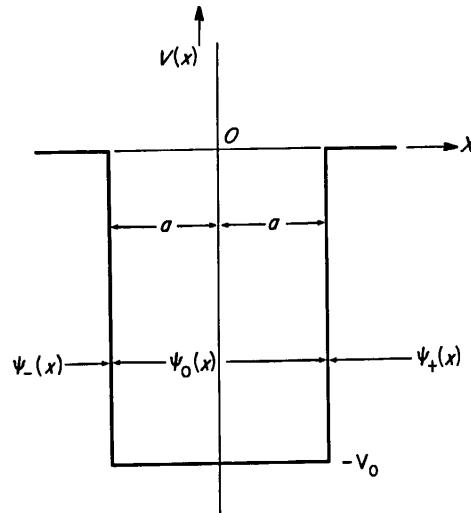


FIGURE 4.11. A potential well of finite depth.

the well is V_0 . We must solve separate equations for the wave function in the regions $(x < -a)$, $(-a < x < a)$ and $(x > a)$, and we shall call the wave function in those regions $\psi_-(x)$, $\psi_0(x)$ and $\psi_+(x)$, respectively. We shall first treat the case of a particle which is classically bound to remain within the well, that is, a particle for which $-V_0 < \varepsilon < 0$.

In the regions outside the well ($x < -a$; $x > a$), (4.8-5) becomes

$$\frac{d^2\psi_{\pm}}{dx^2} - k^2\psi_{\pm}(x) = 0 \quad (x < -a; x > a) \quad (4.11-1)$$

where

$$k = \sqrt{-2m\varepsilon/\hbar^2}, \quad (4.11-2)$$

while inside the well, where $V(x) = -V_0$, (4.8-5) becomes

$$\frac{d^2\psi_0}{dx^2} + k_0^2\psi_0(x) = 0 \quad (-a < x < a) \quad (4.11-3)$$

where

$$k_0 = \sqrt{2m(\varepsilon + V_0)/\hbar^2}. \quad (4.11-4)$$

As thus defined, under the condition $(-V_0 < \varepsilon < 0)$, k and k_0 are both real quantities. The general solutions to (4.11-1) and (4.11-3) may be written

$$\psi_+(x) = A_+e^{kx} + B_+e^{-kx} \quad (x > a) \quad (4.11-5)$$

$$\psi_0(x) = A_0 \sin k_0 x + B_0 \cos k_0 x \quad (-a < x < a) \quad (4.11-6)$$

$$\psi_-(x) = A_-e^{kx} + B_-e^{-kx} \quad (x < -a). \quad (4.11-7)$$

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(4.11-7)

The boundary conditions on the wave function demand that the wave function and its derivative be continuous at $x = \pm a$ and that the wave function approach zero as $x \rightarrow \pm \infty$. We must thus require

$$\psi_0(a) = \psi_+(a) \quad \psi'_0(a) = \psi'_+(a) \quad (4.11-8)$$

$$\psi_0(-a) = \psi_-(-a) \quad \psi'_0(-a) = \psi'_-(-a) \quad (4.11-9)$$

$$\psi_+(\infty) = 0 \quad \psi_-(\infty) = 0, \quad (4.11-10)$$

where the primes indicate derivatives with respect to x . It is obvious at once from (4.11-10) that $A_+ = B_- = 0$. The four remaining coefficients can be evaluated by substituting the solutions (4.11-5,6,7) into the four boundary conditions (4.11-8) and (4.11-9), whereby one obtains a set of four simultaneous equations of the form

$$\begin{aligned} A_0 \sin k_0 a + B_0 \cos k_0 a - B_+ e^{-ka} &= 0 \\ -A_0 \sin k_0 a + B_0 \cos k_0 a - A_- e^{-ka} &= 0 \\ A_0 k_0 \cos k_0 a - B_0 k_0 \sin k_0 a + B_+ k e^{ka} &= 0 \\ A_0 k_0 \cos k_0 a + B_0 k_0 \sin k_0 a - A_- k e^{-ka} &= 0. \end{aligned} \quad (4.11-11)$$

In order to solve the problem completely, the values of the four arbitrary constants A_0 , B_0 , A_- , and B_+ must be determined. The expressions (4.11-11) form a set of four homogeneous equations in these unknown coefficients. It is an elementary result of the theory of linear algebraic equations that such a set of equations can have no solution other than the trivial one $A_0 = B_0 = A_- = B_+ = 0$ unless the determinant of the coefficients of the system vanishes.⁶ This means that there are no solutions of physical significance unless

$$e^{-2ka} \begin{vmatrix} \sin k_0 a & \cos k_0 a & -1 & 0 \\ -\sin k_0 a & \cos k_0 a & 0 & -1 \\ k_0 \cos k_0 a & -k_0 \sin k_0 a & k & 0 \\ k_0 \cos k_0 a & k_0 \sin k_0 a & 0 & k \end{vmatrix} = 0. \quad (4.11-12)$$

To obtain this expression the quantity e^{-2ka} has been factored out of the third and fourth columns of the determinant of the coefficients of (4.11-11). Since e^{-2ka} does not vanish for any real value of ka , the determinant must vanish in order that (4.11-12) be satisfied. The determinant may be expanded in minors to give the equation

$$k_0^2 \sin k_0 a \cos k_0 a + k k_0 \sin^2 k_0 a - k k_0 \cos^2 k_0 a - k^2 \sin k_0 a \cos k_0 a = 0,$$

which may be written as

$$(k \sin k_0 a + k_0 \cos k_0 a)(k_0 \sin k_0 a - k \cos k_0 a) = 0,$$

⁶ See for example N. B. Conkwright, *Introduction to the Theory of Equations*, Ginn and Co., Boston (1941), pp. 144-145.

or, dividing by $\cos^2 k_0 a$,

$$(k \tan k_0 a + k_0)(k_0 \tan k_0 a - k) = 0. \quad (4.11-13)$$

This equation is satisfied if *either* factor vanishes. If we let

$$\mu^2 = 2mV_0/\hbar^2, \quad (4.11-14)$$

then, according to (4.11-4) and (4.11-2),

$$k^2 = \mu^2 - k_0^2. \quad (4.11-15)$$

Substituting this in (4.11-13) and equating either factor to zero, we find that (4.11-13) is satisfied if

either $\sqrt{\mu^2 - k_0^2} = -k_0 \operatorname{ctn} k_0 a$ (4.11-16)

or $\sqrt{\mu^2 - k_0^2} = k_0 \tan k_0 a.$

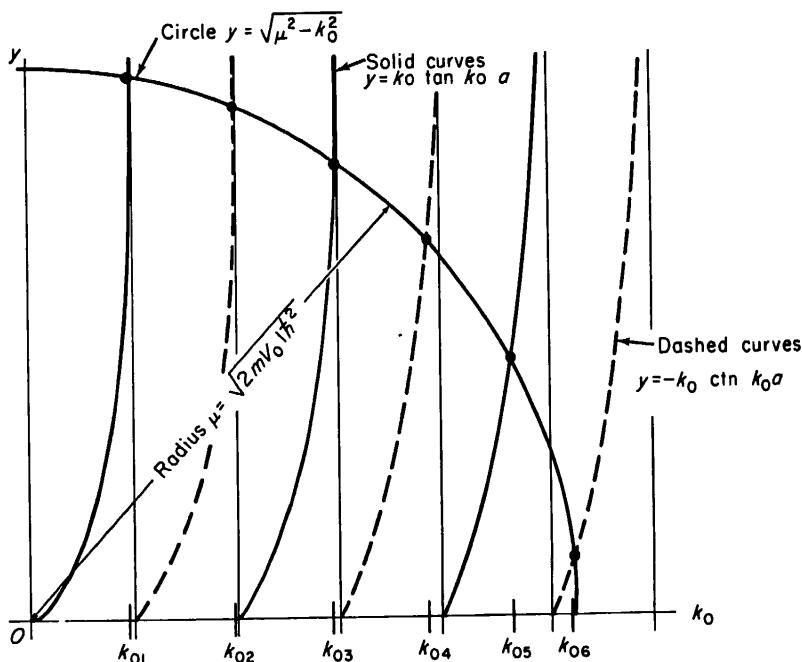


FIGURE 4.12. Diagram illustrating the solution of the transcendental equations for the energy eigenvalues associated with the potential well of Figure 4.11.

One or the other of these equations will be satisfied only for a certain set of values of k_0 , which we shall represent by $k_{01}, k_{02}, k_{03}, \dots, k_{0n}, \dots$. A set of energy eigenvalues ε_n is related to these values of k_0 , according to (4.11-4), by

$$\varepsilon_n = \frac{\hbar^2 k_{0n}^2}{2m} - V_0. \quad (4.11-17)$$

(4.11-13)

(4.11-14)

(4.11-15)

d that (4.11-13)

(4.11-16)

The eigenvalues k_{0n} can be obtained graphically by finding the intersections of the curves $y = -k_0 \operatorname{ctn} k_0 a$ and $y = k_0 \tan k_0 a$ with the circle $y = \sqrt{\mu^2 - k_0^2}$ as shown in Figure 4.12. For each intersection point one or the other of Equations (4.11-16) is satisfied. There is thus defined a finite set of values k_{0n} and a *finite* number of discrete energy levels corresponding to these values through (4.11-17). The radius of the circle $y = \sqrt{\mu^2 - k_0^2}$ in Figure 4.11 is simply μ , which is directly related by (4.11-14) to the depth of the potential well. For a very shallow well, $\mu \rightarrow 0$, and there will be one and only one energy level in the range $-V_0 < \epsilon < 0$. For deeper wells, the number of energy states increases, and for very deep wells may become very large. In a very deep well, as illustrated by Figure 4.12, the lower-lying levels are characterized by values of k_{0n} which are almost equally spaced, corresponding quite closely to the k_n values of the infinite well of Section 4.10, and giving rise to energy levels which, with respect to the bottom of the well, are close to those of the infinite well. The energy level diagrams for a number of finite wells are shown in Figure 4.13.

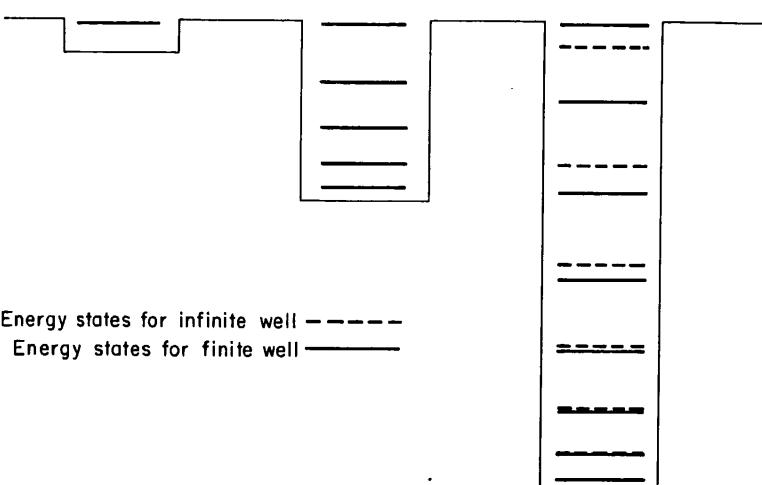


FIGURE 4.13. Schematic representation of the energy levels of potential wells of various depths.

The values k_{0n} for which (4.11-11) has physically meaningful solutions having been determined, the coefficients A_0 , B_0 , A_- and B_+ may be found. Since for the values k_{0n} which satisfy (4.11-16) the determinant of the homogeneous system (4.11-11) vanishes, the equations (4.11-11) are *no longer linearly independent* equations, and hence only the *ratios* of the coefficients can be obtained from (4.11-11) directly. The actual magnitudes of the coefficients may, however, be found by imposing the condition that

$$\int_{-\infty}^{\infty} \psi^* \psi dx = \int_{-\infty}^{-a} \psi_-^* \psi_- dx + \int_{-a}^a \psi_0^* \psi_0 dx + \int_a^{\infty} \psi_+^* \psi_+ dx = 1. \quad (4.11-18)$$

The wave functions themselves follow from (4.11-5,6,7) once the coefficients are known. The actual calculation of the coefficients is a laborious matter and will not be discussed in detail here. We shall, however, discuss some of the properties of the wave functions which are so obtained.

The wave functions for the bound energy states of this problem are illustrated

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(4.11-17)

in Figure 4.14. It will be noted first of all that the wave function *as a whole* is either an even function or an odd function of x . In the present example the lowest energy state is even, the next odd, the next even, and so forth, alternately. This comes about as a result of the fact that the potential $V(x)$ is itself an even function of x ; it can be shown quite generally that when this is so the eigenfunctions must be either even or odd functions of x .⁷

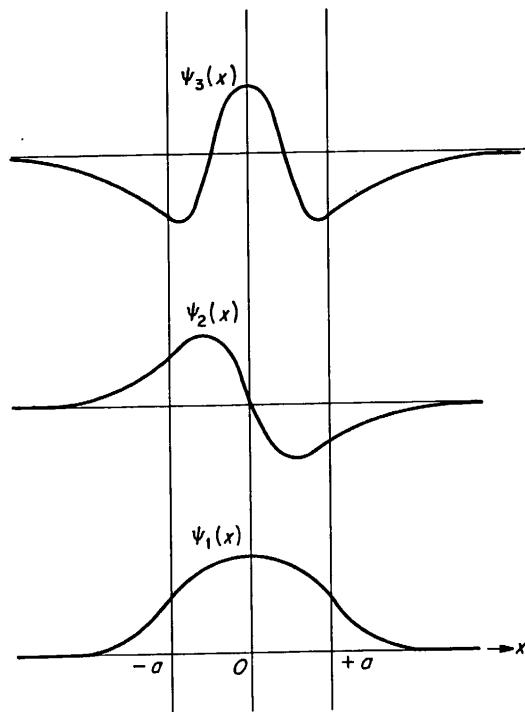


FIGURE 4.14. Schematic diagrams of the wave functions of the lowest energy states of the finite potential well of Figure 4.11.

From Figure 4.14 and from Equations (4.11-5) and (4.11-7) it can be seen that in spite of the fact that the total energy of the particle is negative and hence according to the classical picture the particle would never be able to surmount the potential barrier and appear outside the well, the wave function of the particle does indeed extend beyond the limits of the well. According to quantum mechanics, therefore, there is a definite probability that the particle will be found in the classically forbidden region beyond the actual boundaries of the well. The wave function of the particle is exponentially attenuated in this region and approaches zero far outside the well. This phenomenon, which is known as *barrier penetration*, is quite a common aspect of the quantum behavior of matter. A particle approaching a potential barrier of finite thickness and height as shown in Figure 4.15 has a certain probability of penetrating the barrier and appearing on the other side, even though this may be energetically forbidden on a classical basis. The wave function is attenuated within the barrier, and if the barrier is very high or quite thick, the attenuation becomes very strong and

⁷ See for example E. Merzbacher, *Quantum Mechanics*, John Wiley and Sons, New York (1961), p. 53.

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the probability of penetration becomes extremely small. This effect is called quantum mechanical *tunneling*, and has been observed experimentally in semiconductor devices and thin insulating films. Reflection effects are also predicted quantum mechanically for particles incident on a barrier such as that of Figure 4.15 which have *more* than enough energy to surmount the barrier classically. Quantum tunneling effects provide the generally accepted explanations for the electrical breakdown of insulators, reverse breakdown of semiconductor rectifiers and radioactive decay of α -emitting isotopes.

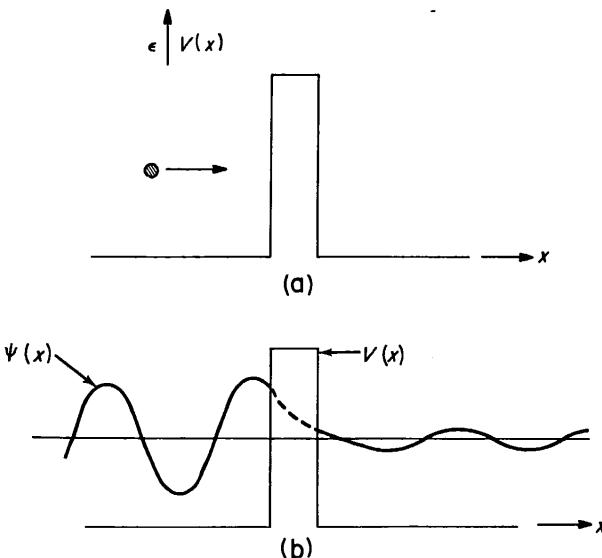


FIGURE 4.15. (a) Classical and (b) quantum mechanical pictures of a particle interacting with a potential barrier whose height is greater than the initial particle energy. The quantum picture (b) exhibits the phenomenon of *tunneling*.

So far, this discussion has been based exclusively upon the assumption that the total energy ϵ is negative, lying in the range $-V_0 < \epsilon < 0$. In the case where ϵ is positive, it is easy to see from (4.11-1) that the solutions ψ_{\pm} outside the well become oscillatory in nature, like the solution ψ_0 inside. In this instance, it turns out that the Schrödinger equation and all the boundary conditions can be satisfied for *any* positive value of ϵ . There is thus a *continuous* range of allowed energy states and corresponding eigenfunctions extending upward from $\epsilon = 0$ in Figure 4.13. These states are referred to as the "continuum states."

To see how this comes about, let us assume that the eigenfunctions in this energy range are either even or odd functions of x ; we have seen that this must be true if $V(x)$ is an even function. Then, for *even* eigenfunctions, we must have

$$\begin{aligned}\psi_0(x) &= A_0 \cos k_0 x & (-a < x < a) \\ \psi_+(x) &= A_+ \cos kx + B_+ \sin kx & (x > a) \\ \psi_-(x) &= \psi_+(-x), & (x < -a)\end{aligned}\quad (4.11-19)$$

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$$k = \sqrt{2m\varepsilon/\hbar^2} \quad (\varepsilon > 0). \quad (4.11-20)$$

The boundary conditions (4.11-8) and (4.11-9) still must apply, so that the values and slopes of $\psi_0(x)$ and $\psi_+(x)$ must be equal at $x = a$. From (4.11-19) this requires that

$$A_0 \cos k_0 a = A_+ \cos ka + B_+ \sin ka$$

and

$$-k_0 A_0 \sin k_0 a = -k A_+ \sin ka + k B_+ \cos ka. \quad (4.11-21)$$

Dividing both equations by A_0 and solving the resulting set of simultaneous equations for A_+/A_0 and B_+/A_0 , we find that

$$A_+/A_0 = \cos k_0 a \cos ka + \frac{k_0}{k} \sin k_0 a \sin ka \quad (4.11-22)$$

$$B_+/A_0 = \cos k_0 a \sin ka - \frac{k_0}{k} \sin k_0 a \cos ka.$$

It is thus always possible to find perfectly good values for A_+ and B_+ in terms of A_0 , whose value, in turn, is fixed by normalization requirements. This means that whatever value of ε or k is chosen initially, a solution for ψ_0 , ψ_+ , and ψ_- satisfying all the boundary conditions can be found, as asserted previously. A similar calculation can be made starting with the *odd* eigenfunctions, the same result being obtained. The general character of the wave functions for the continuum states is shown in Figure 4.16.

This state of affairs is illustrative of a much more general principle. If the total energy of the system is such that the particle is classically constrained by the potential $V(x)$ to move in a given finite region of space, then there will be a discrete set of eigenfunctions and energy levels which satisfy all the requirements for wave functions. On the other hand, for particle energies sufficiently large that a classical particle can escape from any potential minimum of the system to infinity in at least one direction, there will be a continuum of energy states and corresponding eigenfunctions.⁸

The results of Section 4.10 for the infinitely deep potential well can be obtained from the results of this section if V_0 is allowed to approach infinity. In particular, it is easily seen from (4.11-5) and (4.11-7) with $A_+ = B_- = 0$, that if k becomes indefinitely large, as it must for any state with a finite energy above the bottom of the well as $V_0 \rightarrow \infty$, the wave function outside the limits of the well approaches zero. As the well becomes very deep, the curvature of the wave function near $x = a$ and $x = -a$ where the solutions $\psi_+(x)$ and $\psi_-(x)$ are joined to the solution $\psi_0(x)$ becomes very large, although for a finite well depth, the slope is always continuous. It is only in the limit as the well depth approaches infinity that the discontinuity in the derivative of the wave function at these points, which was mentioned in Section 4.10, arises.

⁸ A simple proof of this assertion is given by L. Pauling and E. B. Wilson, *Introduction to Quantum Mechanics*, McGraw-Hill Book Co., Inc., New York (1935).

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Introduction to

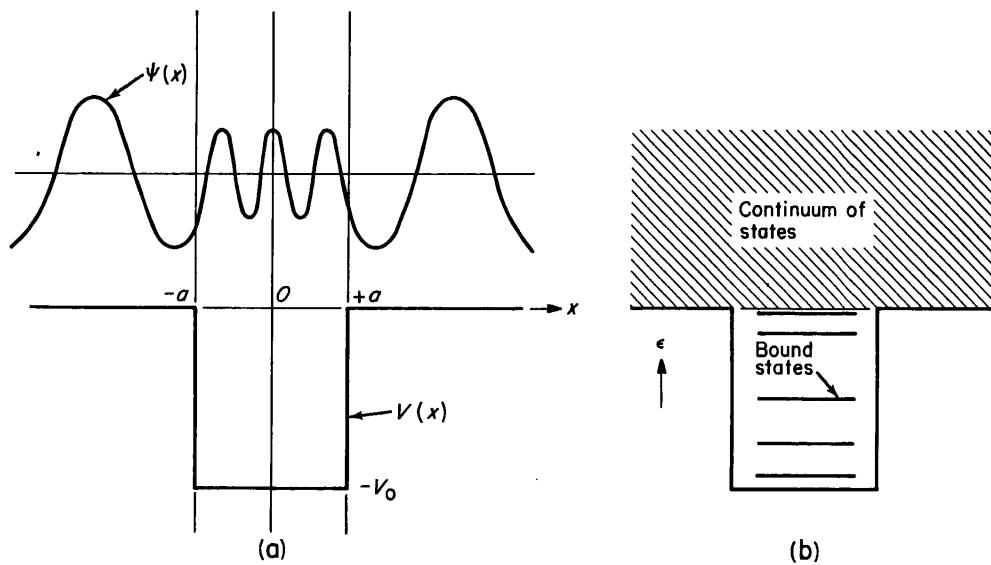


FIGURE 4.16. (a) Schematic representation of the wave function of a particle whose energy is sufficiently great that it would not in the classical picture be constrained to remain within the illustrated potential well. (b) Division of allowed energy levels for the finite potential well into a group of discrete levels corresponding to a classically bound particle and to a continuum of levels corresponding to a classically unbound particle. The wave function illustrated in (a) belongs to the latter group of levels.

4.12 THE ONE-DIMENSIONAL HARMONIC OSCILLATOR

A harmonic oscillator is a particle which is bound to an equilibrium position by a force which is proportional to the displacement from that position; this force may thus be expressed as

$$F = -kx = -dV(x)/dx. \quad (4.12-1)$$

The potential $V(x)$ must then be a parabola of the form

$$V(x) = \frac{1}{2}kx^2. \quad (4.12-2)$$

From (4.12-1) the classical equation of motion for a particle of mass m subjected to such a force is

$$m \frac{d^2x}{dt^2} = -kx \quad (4.12-3)$$

whose solution is an oscillatory function which can be written in the form

$$x(t) = A \sin(\omega_0 t - \delta), \quad (4.12-4)$$

where

$$\omega_0 = \sqrt{k/m} \quad (4.12-5)$$

is the *classical oscillator frequency*, and where A and δ are constants. Following this classical result, let us use (4.12-5) to express the force constant k in terms of ω_0 and m , and rewrite the potential $V(x)$ as

$$V(x) = \frac{1}{2}m\omega_0^2x^2. \quad (4.12-6)$$

We shall now proceed to solve Schrödinger's equation (4.8-5) using this potential function; (4.8-5) will then read

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2} [\varepsilon - \frac{1}{2}m\omega_0^2x^2]\psi(x) = 0. \quad (4.12-7)$$

To solve this equation, we first let

$$\alpha = m\omega_0/\hbar \quad (4.12-8)$$

$$\beta = 2\varepsilon/(\hbar\omega_0) \quad (4.12-9)$$

$$\xi = x\sqrt{\alpha}. \quad (4.12-10)$$

Then, from (4.12-8) and (4.12-9), it is clear that

$$\frac{d^2\psi}{dx^2} + (\alpha\beta - \alpha^2x^2)\psi(x) = 0, \quad (4.12-11)$$

and from (4.12-10), noting that $d^2\psi/dx^2 = \alpha d^2\psi/d\xi^2$,

$$\frac{d^2\psi}{d\xi^2} + (\beta - \xi^2)\psi(\xi) = 0. \quad (4.12-12)$$

For *large* values of $|\xi|$, such that $\xi^2 \gg \beta$, we may neglect β and write (4.12-12) as

$$\frac{d^2\psi}{d\xi^2} \cong \xi^2\psi. \quad (4.12-13)$$

This equation is satisfied approximately, for large ξ , by

$$\psi(\xi) = e^{-\xi^2/2}, \quad (4.12-14)$$

because then $d^2\psi/d\xi^2 = (\xi^2 - 1)\exp(-\xi^2/2)$, which satisfies (4.12-13) approximately if $\xi^2 \gg 1$. This suggests that the solutions $\psi(\xi)$ for (4.12-12) might be more simply expressed by writing

$$\psi(\xi) = e^{-\xi^2/2}H(\xi) \quad (4.12-15)$$

and transforming (4.12-12) to an equation for the function $H(\xi)$. This may be accomplished by simply substituting the form (4.12-15) into (4.12-12), the result being that (4.12-12) becomes

$$\frac{d^2H}{d\xi^2} - 2\xi \frac{dH}{d\xi} + (\beta - 1)H(\xi) = 0. \quad (4.12-16)$$

Following this
terms of ω_0 and

This differential equation may be solved by a power series technique, assuming initially that

(4.12-6)

$$H(\xi) = \sum_{k=0}^{\infty} a_k \xi^k, \quad (4.12-17)$$

ng this potential

whereby

(4.12-7)

$$\frac{d^2 H}{d\xi^2} = \sum_{k=0}^{\infty} (k+1)(k+2)a_{k+2}\xi^k$$

$$-2\xi \frac{dH}{d\xi} = \sum_{k=0}^{\infty} -2ka_k \xi^k \quad (4.12-18)$$

(4.12-8)

$$(\beta - 1)H(\xi) = \sum_{k=0}^{\infty} (\beta - 1)a_k \xi^k. \quad (4.12-9)$$

(4.12-10)

Adding these three equations and noting that the right-hand sides add to zero according to (4.12-16), we find

(4.12-11)

$$0 = \sum_{k=0}^{\infty} [(k+1)(k+2)a_{k+2} + [(\beta - 1) - 2k]a_k] \xi^k. \quad (4.12-19)$$

(4.12-12)

This equation must hold true for *all values* of ξ , and therefore the coefficient of *each power* of ξ must vanish separately. (This may be seen more clearly by evaluating the coefficients for the expansion of the function $f(\xi) = 0$ in McLaurin's power series; they are all zero.) This requirement at once establishes a *recursion relation* between the coefficients a_{k+2} and a_k , in which

(4.12-12) as

$$a_{k+2} = -\frac{\beta - 1 - 2k}{(k+1)(k+2)} a_k. \quad (4.12-20)$$

(4.12-13)

In the solution of any second-order ordinary differential equation there must be two arbitrary constants. Therefore, let us regard a_0 and a_1 as fundamental arbitrary constants, to be determined from boundary conditions, in the series expression (4.12-17) for $H(\xi)$, and express all the other coefficients in terms of these two by repeated application of the recursion relation (4.12-20). It is easily seen in this way that

(4.12-14)

$$a_2 = -\frac{\beta - 1}{2!} a_0 \quad a_3 = -\frac{(\beta - 3)}{3!} a_1$$

(4.12-15)

$$a_4 = -\frac{\beta - 5}{4 \cdot 3} a_2 = \frac{(\beta - 1)(\beta - 5)}{4!} a_0 \quad a_5 = \frac{(\beta - 3)(\beta - 7)}{5!} a_1 \quad (4.12-21)$$

(4.12-16)

$$a_6 = -\frac{(\beta - 1)(\beta - 5)(\beta - 9)}{6!} a_0 \quad a_7 = \frac{(\beta - 3)(\beta - 7)(\beta - 11)}{7!} a_1$$

etc.,

etc.

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the result being

According to (4.12-17), then, we must have

$$\begin{aligned} H(\xi) = a_0 & \left[1 - \frac{(\beta-1)}{2!} \xi^2 + \frac{(\beta-1)(\beta-5)}{4!} \xi^4 - \frac{(\beta-1)(\beta-5)(\beta-9)}{6!} \xi^6 + \dots \right] \\ & + a_1 \left[\xi - \frac{\beta-3}{3!} \xi^3 + \frac{(\beta-3)(\beta-7)}{5!} \xi^5 - \frac{(\beta-3)(\beta-7)(\beta-11)}{7!} \xi^7 + \dots \right]. \end{aligned} \quad (4.12-22)$$

If, in the recursion relation (4.12-20), $\beta - 1 - 2k$ should be zero for some value of the index k , then $a_{k+2} = 0$. But since a_{k+4} is a multiple of a_{k+2} and a_{k+6} is a multiple of a_{k+4} , etc., all the succeeding coefficients which are related to a_k by the recursion formula would then vanish, and one or the other of the bracketed series in (4.12-22) would terminate to become a polynomial of degree k . This phenomenon can occur only for certain integer values of β , in fact, from (4.12-20) only when $\beta - 1$ equals twice an integer, thus only when

$$\beta - 1 - 2n = 0$$

$$\text{or} \quad \beta = 2n + 1 \quad (n = 0, 1, 2, 3, \dots). \quad (4.12-23)$$

It is easily seen by inspection of (4.12-22) that this termination of one or the other series to produce a polynomial does indeed occur when $\beta = 1, 3, 5, 7, \dots$ as predicted by (4.12-23). It turns out that the only solutions of (4.12-16) which lead to acceptable wave functions via (4.12-15) will be these polynomial solutions.

In order to understand why this is so, let us first consider the series expansion for the function e^{ξ^2} , which can be written

$$e^{\xi^2} = 1 + \frac{\xi^2}{1!} + \frac{\xi^4}{2!} + \frac{\xi^6}{3!} + \dots = \sum_k b_k \xi^k. \quad (4.12-24)$$

For large values of ξ , the contributions of the initial terms of this series are negligible in comparison with those for which k is large. This is true also, of course, for the series in (4.12-22) for $H(\xi)$. For the series (4.12-24) the ratio of the coefficient b_{k+2} to the coefficient b_k is

$$\frac{b_{k+2}}{b_k} = \frac{(k/2)!}{\left[\frac{k}{2} + 1\right]!} = \frac{1}{\frac{k}{2} + 1},$$

and for large values of k

$$\frac{b_{k+2}}{b_k} \cong 2/k. \quad (4.12-25)$$

The ratio of the coefficients a_{k+2} and a_k for the series solutions of (4.12-16) is given by the recursion relation (4.12-20) and, for large values of k , is readily seen to be also approximately equal to $2/k$. The series solutions for $H(\xi)$, thus, when not terminated to polynomials, behave like e^{ξ^2} for large values of ξ . According to (4.12-15), however,

the actual wave functions are given by

$$\psi(\xi) = e^{-\xi^2/2} H(\xi) \cong e^{-\xi^2/2} e^{\xi^2} = e^{\xi^2/2} \quad (4.12-26)$$

for large values of ξ . Since these functions do not remain finite at $\pm\infty$ they are not acceptable as wave functions for the physical system. The only solutions which are acceptable are the solutions which terminate as polynomials, that is, the solutions for which (4.12-23) is obeyed. If one or the other of the two bracketed series of (4.12-22) terminates as a polynomial, the solution for $H(\xi)$ then takes the form

$$H(\xi) = a_0(\text{polynomial}) + a_1(\text{infinite series})$$

$$\text{or, } H(\xi) = a_0(\text{infinite series}) + a_1(\text{polynomial}).$$

In either case, in order that the solution $H(\xi)$ lead to a physically acceptable wave function, the arbitrary constant multiplying the series solution must be chosen to be zero, so that the total expression for $H(\xi)$ is simply a polynomial. Expressing β in (4.12-23) in terms of ϵ by (4.12-9), it is clear that the only solutions which yield the polynomial expressions for $H(\xi)$ are those corresponding to a discrete set of energy eigenvalues

$$\epsilon_n = (n + \frac{1}{2})\hbar\omega_0 \quad (n = 0, 1, 2, 3, \dots). \quad (4.12-27)$$

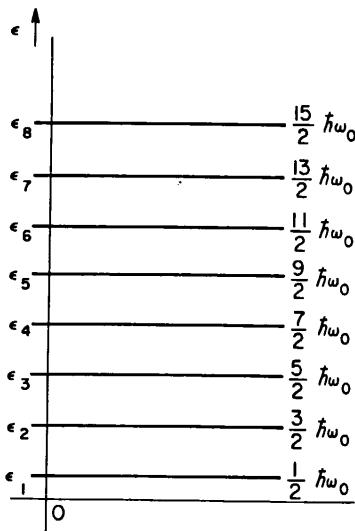


FIGURE 4.17. Energy levels of the one-dimensional quantum harmonic oscillator.

A notable feature of this system is that the lowest energy state of the system, for which $n = 0$, is characterized not by $\epsilon_0 = 0$, but by $\epsilon_0 = \frac{1}{2}\hbar\omega_0$. In other words, the lowest energy state of the harmonic oscillator is characterized not by the absence of vibrational motion but by a minimum “zero-point” vibrational energy $\frac{1}{2}\hbar\omega_0$. In his original theory of black body radiation, Planck assumed that the energy levels of a harmonic oscillator were given by $\epsilon_n = n\hbar\omega_0$ rather than by (4.12-27); in that particular instance, however, the zero-point energy makes no difference in the final result. It will be noted that the potential wells of the preceding sections also exhibit this zero-point energy effect. The energy level diagram for the harmonic oscillator is illustrated in Figure 4.17. The equal spacing of levels is a unique property of the parabolic potential well.

The polynomial solutions which represent the eigenfunctions of the system can be obtained from (4.12-22) by considering β to take on the values $1, 3, 5, \dots, 2n + 1, \dots$ in accord with (4.12-23). For each such value one or the other of the two bracketed series will terminate to a polynomial, all the coefficients beyond a certain point being zero. It is customary to choose the arbitrary constant a_0 or a_1 , as the case may be, which multiplies the resulting polynomial, such that the coefficient of the highest power of ξ in the polynomial is $2^n (= 2^{(\beta-1)/2})$. When this is done, a set of polynomial solutions $H_n(\xi)$ of the form

$$H_0(\xi) = 1$$

$$H_1(\xi) = 2\xi$$

$$H_2(\xi) = 4\xi^2$$

$$H_3(\xi) = 8\xi^3 - 12$$

$$H_4(\xi) = 16\xi^4 - 48\xi^2$$

$$H_5(\xi) = 32\xi^5 - 160\xi^3 + 120\xi$$

etc.,

(4.12-28)

is obtained. These polynomials are well known to mathematicians and are called the *Hermite polynomials*; Equation (4.12-16) is known as the Hermite equation. The Hermite polynomials may be defined as

$$H_n(\xi) = (-1)^n e^{\xi^2} \frac{d^n}{d\xi^n} (e^{-\xi^2}). \quad (4.12-29)$$

It can be shown that the definition (4.12-29) leads to the polynomials which satisfy the Hermite equation (4.12-16). The proof is assigned as an exercise.

The actual wave functions $\psi_n(x)$ are obtained from the polynomial solutions of the Hermite equation by (4.12-15) and (4.12-10), the result being

$$\psi_n(x) = N_n e^{-\xi^2/2} H_n(\xi) = N_n e^{-\alpha x^2/2} H_n(x \sqrt{\alpha}), \quad (4.12-30)$$

where α is given by (4.12-8) and where the normalization constant N_n is chosen such that

$$\int_{-\infty}^{\infty} \psi_n^* \psi_n dx = 1.$$

This condition can be shown⁹ to require that

$$N_n = \sqrt{\sqrt{\frac{\alpha}{\pi}} \cdot \frac{1}{2^n n!}}. \quad (4.12-31)$$

⁹ D. Bohm, *Quantum Mechanics*, Prentice-Hall, Englewood Cliffs, N.J. (1951), p. 305.

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The time-dependent wave functions $\Psi_n(x, t)$ are obtained from the expressions of (4.12-30) by multiplying by a factor $e^{-ie_n t/\hbar}$, in accord with (4.8-7).

Since we shall wish to compare the properties of the quantum oscillator with those of its classical counterpart, we must again briefly consider some characteristics of the classical oscillator and, in particular, we must compute the probability distribution associated with the classical oscillator. Since the displacement $x(t)$ of the classical particle is as given by (4.12-4), it follows that the kinetic and potential energy of the classical oscillator are given by

$$\epsilon_k = \frac{1}{2}m(dx/dt)^2 = \frac{1}{2}mA^2\omega_0^2 \cos^2(\omega_0 t - \delta)$$

$$\epsilon_p = \frac{1}{2}m\omega_0^2x^2 = \frac{1}{2}mA^2\omega_0^2 \sin^2(\omega_0 t - \delta),$$

respectively, whence the total energy must be

(4.12-28)

$$\epsilon = \epsilon_k + \epsilon_p = \frac{1}{2}mA^2\omega_0^2. \quad (4.12-32)$$

This equation may be solved for A in terms of ϵ , giving $A = \sqrt{2\epsilon/m\omega_0^2}$, and if the energy is assumed to have the value $(n + \frac{1}{2})\hbar\omega_0$ (as it must for the quantum oscillator to which we wish to make a direct comparison), we obtain for the amplitude of the *classical* oscillator having this energy

$$A = \sqrt{\frac{(2n + 1)\hbar}{m\omega_0}} = \sqrt{\frac{2n + 1}{\alpha}}, \quad (4.12-33)$$

where α is defined by (4.12-8).

(4.12-29)

The probability amplitude is the probability of finding the particle within a given region dx about the point x . For the classical oscillator, this is simply the ratio of the time dt which the particle spends in this region during the course of one vibration to the period of oscillation $T (= 2\pi/\omega_0)$. Since $dx = v(x)dt$, the time spent in this interval during one period is

(4.12-30)

$$2 dt = \frac{2dx}{v(x)}, \quad (4.12-34)$$

the particle passing through the region *twice* during a full period of the motion. Since, from (4.12-4), $v(t) = dx/dt = A\omega_0 \cos(\omega_0 t - \delta)$, and since $\omega_0 t - \delta = \sin^{-1}(x/A) = \cos^{-1}(1 - (x/A)^2)^{1/2}$, v can be expressed as a function of x by

$$v(x) = A\omega_0 \sqrt{1 - \frac{x^2}{A^2}}. \quad (4.12-35)$$

(4.12-31)

The fraction of time spent in dx is $P(x) dx$, where $P(x)$ is the classical probability amplitude, corresponding to the quantum mechanical quantity $\psi^*\psi$. Since this quantity is equal to $2dt/T$, we must have, in view of (4.12-34) and of the relation $T = 2\pi/\omega_0$,

$$P(x) dx = \frac{2 dt}{T} = \frac{\omega_0 dx}{\pi v(x)} = \frac{dx}{\pi \sqrt{A^2 - x^2}}. \quad (4.12-36)$$

Using (4.12-33), the probability amplitude of a classical oscillator having energy $(n + \frac{1}{2})\hbar\omega_0$ becomes

$$P(x) = \frac{1}{\sqrt{\frac{2n+1}{\alpha} - x^2}}. \quad (4.12-37)$$

We shall compare this quantity with the quantum probability amplitudes $\psi_n^* \psi_n$, obtained from (4.12-30).

Figure 4.18 shows the general behavior of the wave functions for the harmonic oscillator. It will be noted that here again the wave function penetrates into the region beyond the limits of amplitude of the classical motion. In addition, as we might

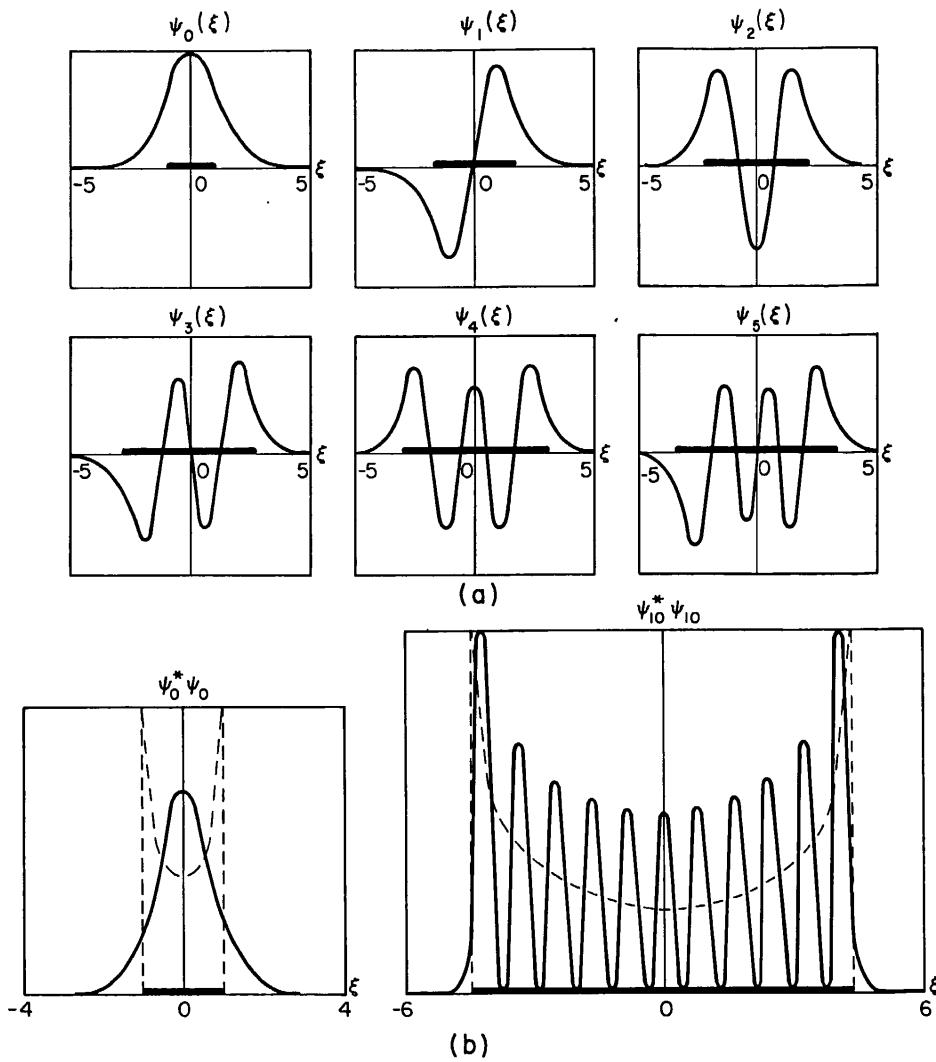


FIGURE 4.18. (a) Wave functions of the lowest energy states of the one-dimensional quantum harmonic oscillator. (b) Quantum probability amplitudes (solid curves) and classical probability distributions (dashed curves) for the one-dimensional harmonic oscillator at two energy values, $\frac{1}{2}\hbar\omega_0$ and $\frac{21}{2}\hbar\omega_0$. [After L. Pauling and E. B. Wilson, *Introduction to Quantum Mechanics*, McGraw-Hill, New York (1935).]

having energy

(4.12-37)

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expect from the fact that $V(x)$ is an even function of x , the wave functions are alternately even and odd functions of x for ascending values of n . For the lowest energy state the classical probability amplitude as computed from (4.12-37), shown as the dotted curve in the figure, does not resemble the quantum mechanical probability amplitude at all. The classical probability amplitude predicts that the particle is most likely to be found near the ends of the region of allowed motion, while the quantum result predicts that it will most likely be found at the center. For a state of larger amplitude and correspondingly higher energy, however, there is good agreement between the classical and quantum probability distributions, apart from the fact that, as usual, the quantum probability amplitude oscillates rapidly about a mean value close to the classical result. As the amplitude and energy associated with the motion become detectable on a macroscopic scale, the quantum and classical results are not appreciably different. There are, as usual, points along the classical track of the particle where the probability of finding the particle, as predicted by the quantum probability amplitude, becomes vanishingly small.

4.13 ORTHOGONALITY OF EIGENFUNCTIONS AND SUPERPOSITION OF STATES

It can be shown that eigenfunctions of the one-dimensional Schrödinger equation satisfying the physical requirements for wave functions, always exhibit the property of *orthogonality*, that is, they always obey the equation

$$\int_{-\infty}^{\infty} \psi_m^* \psi_n dx = 0 \quad (m \neq n) \\ = 1 \quad (m = n). \quad (4.13-1)$$

These relations are a characteristic property of the Schrödinger equation and the boundary conditions, and are found to hold *no matter what the potential function $V(x)$ is nor what mathematical form the wave functions are found to have*. That this must be true can be seen by writing the one-dimensional Schrödinger equation for ψ_n ,

$$\frac{d^2 \psi_n}{dx^2} - \frac{2m}{\hbar^2} [\epsilon_n - V(x)] \psi_n(x) = 0, \quad (4.13-2)$$

and the wave equation for ψ_m^* , which, from (4.7-12) and (4.8-6) must be

$$\frac{d^2 \psi_m^*}{dx^2} - \frac{2m}{\hbar^2} [\epsilon_m - V(x)] \psi_m^*(x) = 0. \quad (4.13-3)$$

Multiplying the first equation by ψ_m^* , the second by ψ_n , subtracting the two equations, and integrating from ∞ to $-\infty$, we obtain

$$\int_{-\infty}^{\infty} \left[\psi_m^* \frac{d^2 \psi_n}{dx^2} - \psi_n \frac{d^2 \psi_m^*}{dx^2} \right] dx = \frac{2m}{\hbar^2} (\epsilon_n - \epsilon_m) \int_{-\infty}^{\infty} \psi_m^* \psi_n dx. \quad (4.13-4)$$

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The integrand of the term on the left-hand side of this equation can be expressed as the derivative of $\psi_m^*(d\psi_n/dx) - \psi_n(d\psi_m^*/dx)$ with respect to x , whence (4.13-4) becomes

$$\left[\psi_m^* \frac{d\psi_n}{dx} - \psi_n \frac{d\psi_m^*}{dx} \right]_{-\infty}^{\infty} = \frac{2m}{\hbar^2} (\varepsilon_n - \varepsilon_m) \int_{-\infty}^{\infty} \psi_m^* \psi_n dx. \quad (4.13-5)$$

For physically well-behaved wave functions ψ and $d\psi/dx$ approach zero as $x \rightarrow \pm\infty$; therefore, the quantity on the left vanishes at both endpoints and

$$\frac{2m}{\hbar^2} (\varepsilon_n - \varepsilon_m) \int_{-\infty}^{\infty} \psi_m^* \psi_n dx = 0. \quad (4.13-6)$$

If the wave functions ψ_m^* and ψ_n are assumed to belong to two distinct energy levels, so that $\varepsilon_n \neq \varepsilon_m$, the only way in which (4.13-6) can be satisfied is if

$$\int_{-\infty}^{\infty} \psi_m^* \psi_n dx = 0 \quad (m \neq n). \quad (4.13-7)$$

For $m = n$, the factor $\varepsilon_n - \varepsilon_n$ in (4.13-6) vanishes; in this case from the way in which the wave functions are defined (4.8-10) we must have

$$\int_{-\infty}^{\infty} \psi_n^* \psi_n dx = 1. \quad (4.13-8)$$

The wave functions ψ_m, ψ_n thus exhibit the property of orthogonality. The property of orthogonality is not restricted to solutions of Schrödinger's equation, but is also associated with the characteristic solutions of a large class of differential equations including the heat equation, the equation of the vibrating string, and the electromagnetic wave equations. It is easily seen that the wave functions (4.10-10) associated with the infinitely deep potential well will satisfy the orthogonality conditions, because it is well known (and easily verified) that

$$\int_0^L \sin \frac{m\pi x}{L} \sin \frac{n\pi x}{L} dx = 0. \quad (m \neq n) \quad (4.13-9)$$

Although it is more difficult to prove for the finite well and for the harmonic oscillator, it is, of course, true that the wave functions (4.11-5,6,7) and (4.12-30) pertaining to these systems are also orthogonal.¹⁰

Suppose now that we have an infinite set of eigenfunctions $\psi_n(x)$ which are solutions of Schrödinger's equation for some particular potential $V(x)$. We know that these eigenfunctions must be orthogonal and normalized in accord with (4.8-10), so that they obey (4.13-1). It is possible to combine these eigenfunctions as a linear superposition in such a way that the sum will represent an *arbitrary* function of x , subject to certain mathematical restrictions which are not very severe. To show how this may be done, let us assume that an arbitrary function $f(x)$ may be represented as a

¹⁰ *Ibid.*, p. 219. See also R. V. Churchill, *Fourier Series and Boundary Value Problems*, McGraw-Hill, New York (1941), pp. 46-52.

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linear combination of the eigenfunctions, such that

$$f(x) = \sum_{n=0}^{\infty} a_n \psi_n(x). \quad (4.13-10)$$

so as $x \rightarrow \pm\infty$,

(4.13-6)

Multiplying this equation by $\psi_m^*(x)$ and integrating, we find

$$\int_{-\infty}^{\infty} f(x) \psi_m^*(x) dx = \sum_{n=0}^{\infty} \int_{-\infty}^{\infty} a_n \psi_m^*(x) \psi_n(x) dx. \quad (4.13-11)$$

In the summation all the integrals are zero by virtue of (4.13-1) except that for which $n = m$, which yields the value a_m . The final result is

(4.13-7)

$$a_m = \int_{-\infty}^{\infty} f(x) \psi_m^*(x) dx. \quad (4.13-12)$$

Substituting this value for a_m into (4.13-10) it is clear that $f(x)$ can be represented as

(4.13-8)

$$f(x) = \sum_n \left[\int_{-\infty}^{\infty} f(x') \psi_n^*(x') dx' \right] \psi_n(x), \quad (4.13-13)$$

where the dummy variable of integration x' has been substituted for x to avoid confusion.

For the sine eigenfunctions of Section 4.10, this expansion turns out to be nothing more than a Fourier series expansion. Similar expansions may be made in terms of the Hermite functions associated with the harmonic oscillator and in terms of other wave functions related to other potential functions. We have already seen in Section 4.9 an example of a situation where the eigenvalues and eigenfunctions are continuously distributed rather than discrete. In that case we found that an arbitrary function could be represented as an *integral* combination of the eigenfunctions in the form of a Fourier integral. This result can be generalized to eigenfunctions representing *any* system whose eigenvalues are continuously distributed, the result being expressable as Equation (4.13-13) in the limit where the eigenvalues crowd closely together, the sum in that equation then becoming an integral. Although this integral representation is important and must be mentioned for completeness, since we have no immediate use for it we shall not discuss it in detail. Its application to the case of free particle eigenfunctions should be clear from the discussion of Section 4.9.

A linear combination of eigenfunctions such as (4.13-10) is no longer a solution of the time independent Schrödinger equation associated with some particular value of energy ϵ_n , since it no longer has the form (4.8-7), but a linear combination of time-dependent eigenfunctions of the form

$$f(x,t) = \sum_{n=0}^{\infty} a_n \Psi_n(x,t) = \sum_{n=0}^{\infty} a_n \psi_n(x) e^{-i\epsilon_n t/\hbar}, \quad (4.13-14)$$

which reduces to (4.13-10) for $t = 0$ is indeed a solution to the *time dependent* Schrödinger equation (4.7-3). This can easily be verified directly, with the help of the fact that the time-independent eigenfunctions ψ_n always, according to (4.8-8) obey the

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relation $\mathcal{H}\psi_n = \epsilon_n\psi_n$. It is clear from this that although a superposition of wave functions which obeys the time-dependent Schrödinger equation can be constructed so as to represent any function or any probability amplitude *at a given time* ($t = 0$ in the above example), the superposition of wave functions will not, in general, *continue* to represent that same function or probability amplitude for later times, on account of the different time dependences of the individual components of the superposition. A superposition wave function thus does not generally represent a stationary state of the system. This state of affairs has been touched upon previously in Section 4.8.

If a superposition of eigenfunctions such as (4.13-14) is to serve as any sort of wave function for a physical system, it must be normalized so as to satisfy (4.7-6). Accordingly, for wave functions of the form (4.13-14) we must have

$$\int_{-\infty}^{\infty} f^*f dx = \sum_m \sum_n a_m^* a_n e^{i(\epsilon_n - \epsilon_m)t/\hbar} \int_{-\infty}^{\infty} \psi_m^* \psi_n dx = 1. \quad (4.13-15)$$

In view of (4.13-1), all the terms of the double summation are zero except those for which $m = n$, where the value of the integral is unity. It is found thus that the normalization requirement will be met provided that the coefficients are chosen such that

$$\sum_n a_n^* a_n = 1. \quad (4.13-16)$$

4.14 EXPECTATION VALUES AND QUANTUM NUMBERS

Suppose that a large number of measurements are made of a physical quantity f which is a property of some specific dynamical system. These measurements are always made upon the same system, or upon identical systems which are always in the same state. If the property f is conserved, that is, if it is constant with respect to the motion of the system, then (within experimental error, which we shall assume to be negligible) the same value for f will be obtained from every measurement, and a plot of the frequency $P(f)df$ with which a measured value in a range df about f is obtained will simply be a "spike" located at some value f_0 which is then the expectation value $\langle f \rangle$. This situation is shown in Figure 4.19(a). If the property f is not conserved in the motion, then we may expect to obtain different results from each measurement and a plot of the frequency with which values in a range df about f are observed as a function of f will exhibit a statistical "spread" about some average or expectation value $\langle f \rangle$, as shown in Figure 4.19(b). The extent of the statistical spread of the measurements can be expressed in terms of the standard deviation σ , defined as

$$\sigma^2 = \langle [f - \langle f \rangle]^2 \rangle. \quad (4.14-1)$$

From this it is clear that if f is always the same as $\langle f \rangle$, as for the "spike" distribution of Figure 4.19(a), then $\sigma = 0$, while if f and $\langle f \rangle$ are not always the same, then σ is the root-mean-square deviation of the values of f from the average. The expression (4.14-1) can be written in a different way by noting that

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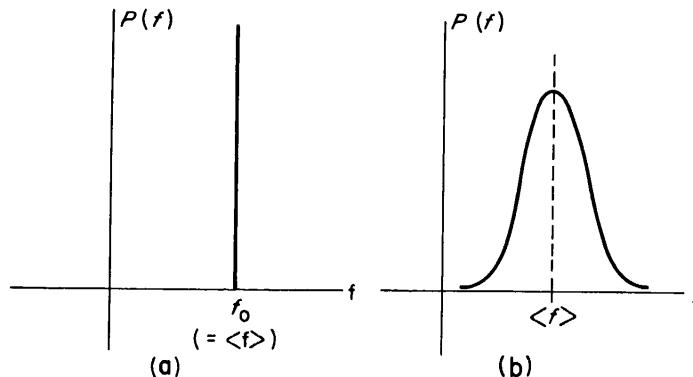


FIGURE 4.19. (a) Statistical distribution of many determinations of a quantity which is a constant of the motion. (b) Corresponding distribution for a quantity which is not a constant of the motion.

$$\text{whence}$$

$$\begin{aligned} [f - \langle f \rangle]^2 &= f^2 - 2f\langle f \rangle + \langle f \rangle^2 \\ \sigma^2 &= \langle f^2 \rangle - 2\langle f \rangle\langle f \rangle + \langle f \rangle^2 \\ &= \langle f^2 \rangle - \langle f \rangle^2. \end{aligned} \quad (4.14-2)$$

One of the fundamental postulates is that the expectation value of a dynamical quantity is given by

$$\langle f \rangle = \int_{-\infty}^{\infty} \Psi^* f_{op} \Psi dx, \quad (4.14-3)$$

where f_{op} is the operator corresponding to the dynamical variable f and where Ψ represents the wave function of the system for which f is being measured. Let us now investigate certain expectation values connected with the energy operator $(-\hbar^2/m)(\partial/\partial t)$, first for a system in one of its eigenstates and then for the same system in a state which is represented as a superposition of two eigenstates.

First of all, it is clear that for any system the expectation value of the energy, $\langle \epsilon \rangle$, can be calculated from the time-dependent wave function $\Psi(x,t)$ by (4.14-3), using also (4.7-4). The result is

$$\langle \epsilon \rangle = \int_{-\infty}^{\infty} \Psi^* \left(-\frac{\hbar^2}{m} \frac{\partial^2}{\partial x^2} \right) \Psi dx = \int_{-\infty}^{\infty} \Psi^* \mathcal{H} \Psi dx = \langle \mathcal{H} \rangle. \quad (4.14-4)$$

The expectation value of the energy is thus the same as the expectation value of the Hamiltonian operator, evaluated over the time dependent wave functions. If $\Psi(x,t)$ is a wave function which represents a stationary eigenstate of the system, and which is thus of the form (4.8-7), we may write (4.14-4) as

$$\langle \epsilon \rangle = \langle \mathcal{H} \rangle = \int_{-\infty}^{\infty} \psi^*(x) e^{i\epsilon t/\hbar} \mathcal{H} \psi(x) e^{-i\epsilon t/\hbar} dx = \int_{-\infty}^{\infty} \psi^*(x) \mathcal{H} \psi(x) dx. \quad (4.14-5)$$

The expectation value of the Hamiltonian operator, and thus of the energy, in this case is the same when taken over the time-independent wave functions $\psi(x)$ as over the time-dependent functions $\Psi(x,t)$. Since \mathcal{H} , according to (4.7-5) is a time-independent operator, it does not operate on the time factors in (4.14-5); these factors may thus be moved past the \mathcal{H} operator and cancelled one against the other.

If the wave function $\Psi(x,t)$ is a superposition of stationary state eigenfunctions of the form (4.13-14),

$$\Psi(x,t) = \sum_n a_n \psi_n(x) e^{-i\varepsilon_n t/\hbar}, \quad (4.14-6)$$

then, from (4.14-4), again noting that \mathcal{H} does not operate on the time factors,

$$\langle \varepsilon \rangle = \int_{-\infty}^{\infty} \Psi^* \mathcal{H} \Psi dx = \sum_m \sum_n e^{-i(\varepsilon_n - \varepsilon_m)t/\hbar} \int_{-\infty}^{\infty} a_m^* \psi_m^*(x) \mathcal{H}[a_n \psi_n(x)] dx. \quad (4.14-7)$$

Using (4.8-8), which tells us that $\mathcal{H}\psi_n = \varepsilon_n \psi_n$, we find

$$\langle \varepsilon \rangle = \sum_m \sum_n \varepsilon_n e^{-i(\varepsilon_n - \varepsilon_m)t/\hbar} \int_{-\infty}^{\infty} a_m^* a_n \psi_m^* \psi_n dx, \quad (4.14-8)$$

which, in view of the orthogonality property of the eigenfunctions, reduces to

$$\langle \varepsilon \rangle = \sum_n a_n^* a_n \varepsilon_n, \quad (4.14-9)$$

all the integrals in (4.14-8) vanishing except those for which $m = n$. This is, however, the same value which is obtained by taking the expectation value of the Hamiltonian operator \mathcal{H} over the *time-independent* wave function

$$\psi(x) = \Psi(x,0) = \sum_n a_n \psi_n(x), \quad (4.14-10)$$

because then, utilizing (4.8-8) and the orthogonality properties of the eigenfunctions

$$\begin{aligned} \langle \mathcal{H} \rangle &= \int_{-\infty}^{\infty} \psi^* \mathcal{H} \psi dx = \sum_m \sum_n a_m^* a_n \int_{-\infty}^{\infty} \psi_m^* \mathcal{H} \psi_n dx \\ &= \sum_m \sum_n a_m^* a_n \varepsilon_n \int_{-\infty}^{\infty} \psi_m^* \psi_n dx = \sum_n a_n^* a_n \varepsilon_n = \langle \varepsilon \rangle. \end{aligned} \quad (4.14-11)$$

The operator \mathcal{H} operating on the time-independent function (4.14-10) is thus seen to be fully equivalent to the operator $(-\hbar/i)(\partial/\partial t)$ operating on the time-dependent function (4.14-6). We shall utilize this result, which is due to the time-independence of the \mathcal{H} operator and the orthogonality of the eigenfunctions, when we calculate expectation values for superposition wave functions.

If the system is in one of its stationary eigenstates, its wave function is simply $\psi_n(x)$, and from (4.14-5),

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$$\langle \varepsilon \rangle = \langle \mathcal{H} \rangle = \int_{-\infty}^{\infty} \psi_n^* \mathcal{H} \psi_n dx = \int_{-\infty}^{\infty} \psi_n^* (\varepsilon_n \psi_n) dx = \varepsilon_n \int_{-\infty}^{\infty} \psi_n^* \psi_n dx = \varepsilon_n. \quad (4.14-12)$$

In like fashion, the expectation value of ε^2 may be found by evaluating the corresponding time-independent operator \mathcal{H}^2 over the time independent wave function,¹¹ whereby

$$\langle \varepsilon^2 \rangle = \langle \mathcal{H}^2 \rangle = \int_{-\infty}^{\infty} \psi_n^* \mathcal{H}(\mathcal{H} \psi_n) dx = \varepsilon_n \int_{-\infty}^{\infty} \psi_n^* \mathcal{H} \psi_n dx = \varepsilon_n^2. \quad (4.14-13)$$

The standard deviation associated with a series of determinations of energy upon a system in one of its stationary eigenstates will be, according to (4.14-2), (4.14-12), and (4.14-13),

$$\sigma^2 = \langle \varepsilon^2 \rangle - \langle \varepsilon \rangle^2 = \varepsilon_n^2 - \varepsilon_n^2 = 0. \quad (4.14-14)$$

A "spike" distribution will thus result, wherein every measurement will yield the same value of energy ε_n .

Now let us assume that the wave function of the system is a superposition of two eigenfunctions, of the form

$$\Psi(x,t) = a_m \psi_m(x) e^{-i\varepsilon_m t/\hbar} + a_n \psi_n(x) e^{-i\varepsilon_n t/\hbar}, \quad (4.14-15)$$

$$\text{so that} \quad \psi(x) = \Psi(x,0) = a_m \psi_m(x) + a_n \psi_n(x), \quad (4.14-16)$$

where, in accord with (4.13-16),

$$a_m^* a_m + a_n^* a_n = 1. \quad (4.14-17)$$

The expectation value of the energy may now be evaluated by computing the expectation value of the \mathcal{H} operator over the wave function (4.14-16). The results, of course, can be obtained as a special case of (4.4-11), whereby

$$\langle \varepsilon \rangle = a_m^* a_m \varepsilon_m + a_n^* a_n \varepsilon_n = \alpha \varepsilon_m + (1 - \alpha) \varepsilon_n \quad (4.14-18)$$

$$\text{where} \quad \alpha = a_m^* a_m \quad \text{and} \quad 1 - \alpha = a_n^* a_n. \quad (4.14-19)$$

Likewise, the expectation value of ε^2 can be found by evaluating $\langle \mathcal{H}^2 \rangle$ using the wave function (4.14-16), giving

$$\begin{aligned} \langle \mathcal{H}^2 \rangle &= \int_{-\infty}^{\infty} (a_m^* \psi_m^* + a_n^* \psi_n^*) \mathcal{H} \mathcal{H} (a_m \psi_m + a_n \psi_n) dx \\ &= \int_{-\infty}^{\infty} a_m^* a_m \psi_m^* \mathcal{H}(\mathcal{H} \psi_m) dx + \int_{-\infty}^{\infty} a_n^* a_n \psi_n^* \mathcal{H}(\mathcal{H} \psi_n) dx \\ &\quad + \int_{-\infty}^{\infty} a_m^* a_n \psi_m^* \mathcal{H}(\mathcal{H} \psi_n) dx + \int_{-\infty}^{\infty} a_n^* a_m \psi_n^* \mathcal{H}(\mathcal{H} \psi_m) dx. \end{aligned} \quad (4.14-20)$$

¹¹ Strictly speaking, this assertion should be (and can be) proved by the methods used in deriving (4.14-9) and (4.14-11).

But $\mathcal{H}\psi_m = \epsilon_m\psi_m$ and $H\psi_n = \epsilon_n\psi_n$; applying these formulas twice to each of the four integrals in (4.14-20), we obtain

$$\begin{aligned} \langle \mathcal{H}^2 \rangle &= a_m^* a_m \epsilon_m^2 \int_{-\infty}^{\infty} \psi_m^* \psi_m dx + a_n^* a_n \epsilon_n^2 \int_{-\infty}^{\infty} \psi_n^* \psi_n dx \\ &\quad + a_m^* a_n \epsilon_n^2 \int_{-\infty}^{\infty} \psi_m^* \psi_n dx + a_n^* a_m \epsilon_m^2 \int_{-\infty}^{\infty} \psi_n^* \psi_m dx. \end{aligned} \quad (4.14-21)$$

The first two integrals in (4.14-21) are unity, the second two zero, due to the orthogonality of the eigenfunctions ψ_n . The equation then reduces to

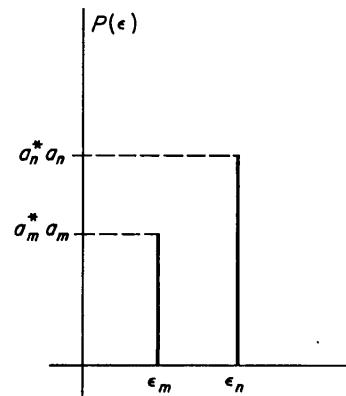
$$\langle \epsilon^2 \rangle = \langle \mathcal{H}^2 \rangle = a_m^* a_m \epsilon_m^2 + a_n^* a_n \epsilon_n^2 = \alpha \epsilon_m^2 + (1 - \alpha) \epsilon_n^2. \quad (4.14-22)$$

The standard deviation associated with measurements of energy on a system whose wave function is the superposition (4.14-15) is

$$\begin{aligned} \sigma^2 &= \langle \epsilon^2 \rangle - \langle \epsilon \rangle^2 = \alpha \epsilon_m^2 + (1 - \alpha) \epsilon_n^2 - [\alpha \epsilon_m + (1 - \alpha) \epsilon_n]^2 \\ &= \alpha(1 - \alpha)(\epsilon_m - \epsilon_n)^2. \end{aligned} \quad (4.14-23)$$

The standard deviation is zero only when $\alpha = 0$, $\alpha = 1$, or $\epsilon_m = \epsilon_n$; in each of these instances the wave function (4.14-16) reduces to a single eigenfunction of the system. In general, however, there will be some sort of "spread" associated with energy measurements on a system of this sort, the determinations not yielding the same value of

FIGURE 4.20. Statistical distribution of energies for systems whose wave functions are superpositions of the m th and n th eigenfunctions.



energy every time. As a matter of fact, a bit of reflection will serve to convince one that the "two-spike" frequency distribution of Figure 4.20 is consistent with the values of $\langle \epsilon \rangle$ and $\langle \epsilon^2 \rangle$ given by (4.14-18) and (4.14-22). A consideration of expectation values of higher powers of ϵ leads to the conclusion that this distribution is the *only* one which is consistent with all these expectation values.¹² The currently prevailing interpretation of this result is that when measurement of energy is made on a system, the system is forced by the act of measurement into one of its eigenstates, if it is no

¹² C. W. Sherwin, *op. cit.* pp. 118-122.

each of the four already in one of them, and that the probability that the measured value of energy will be that associated with one or the other eigenstate is proportional to the quantity $a_m^* a_m$ associated with that eigenstate in the superposition wave function.

If the quantity σ^2 associated with the expectation value of some dynamical quantity should be zero, then that quantity is said to be *conserved* in the motion, or to be a constant of the motion. From (4.14-14) it is clear that the energy of a system in one of its eigenstates is conserved. If we can find an operator A with the property that

(4.14-21)

$$A\psi_n = \lambda_n \psi_n, \quad (4.14-24)$$

where λ_n is a constant, it is said that λ_n is an eigenvalue of the operator A . For such an operator

(4.14-22)

$$\langle A \rangle = \int_{-\infty}^{\infty} \psi_n^* A \psi_n dx = \lambda_n \int_{-\infty}^{\infty} \psi_n^* \psi_n dx = \lambda_n \quad (4.14-25)$$

and $\langle A^2 \rangle = \int_{-\infty}^{\infty} \psi_n^* A A \psi_n dx = \lambda_n \int_{-\infty}^{\infty} \psi_n^* A \psi_n dx = \lambda_n^2,$ (4.14-26)

(4.14-23)

whereby $\sigma^2 = \langle A^2 \rangle - \langle A \rangle^2 = \lambda_n^2 - \lambda_n^2 = 0,$ (4.14-27)

and the dynamical quantity represented by A is conserved, the expectation value of the operator A being given by the eigenvalue λ_n . It is obvious that the Hamiltonian operator \mathcal{H} is just such an operator, whose eigenvalues are the energies ε_n . Any other operator A which has the property (4.14-24) with respect to the eigenfunctions of the system will always *commute* with the Hamiltonian operator, that is, it will always be found that

$$A\mathcal{H} = \mathcal{H}A, \quad (4.14-28)$$

since then

$$\mathcal{H}A\psi_n = \mathcal{H}(\lambda_n \psi_n) = \lambda_n \mathcal{H}\psi_n = \lambda_n \varepsilon_n \psi_n \quad (4.14-29)$$

and $A\mathcal{H}\psi_n = A(\varepsilon_n \psi_n) = \varepsilon_n A\psi_n = \varepsilon_n \lambda_n \psi_n = \mathcal{H}A\psi_n.$ (4.14-30)

The converse of this statement is also true; if an operator A commutes with the Hamiltonian operator, as in (4.14-28), then that operator has the property (4.14-24) with respect to the eigenfunctions ψ_n , and the dynamical variable which it represents is a constant of the motion, because then (4.14-27) will be satisfied.¹³

In dealing with more complex systems, such as the hydrogen atom, which we shall treat in the next section, the relations (4.14-24) and (4.14-28) are very useful in exhibiting the fact that certain dynamical quantities are constants of the motion. We shall see, by using (4.14-24) that the total orbital angular momentum of the electron in the hydrogen atom, and its z -component are constants of the motion.

¹³ For a proof of this converse statement, see E. Merzbacher, *op. cit.*, p. 160.

4.15 THE HYDROGEN ATOM

The hydrogen atom is a system consisting of a proton and a single electron, which interact through their mutual electrostatic attraction. The classical potential for this system is simply

$$V(r) = -e^2/r, \quad (4.15-1)$$

where e is the electronic charge and r is the distance between the electron and the proton. In our treatment we shall regard the mass of the proton as infinite compared to the electron mass. In this approximation, any motion of the proton is neglected, the motion being assumed to be that of the electron with respect to a fixed nucleus. Since the proton mass is some 1850 times the electron mass, the approximation is a good one. The motion of the proton can be taken into account through the use of reduced mass, as discussed in Section 4.5 in connection with the Bohr atom.

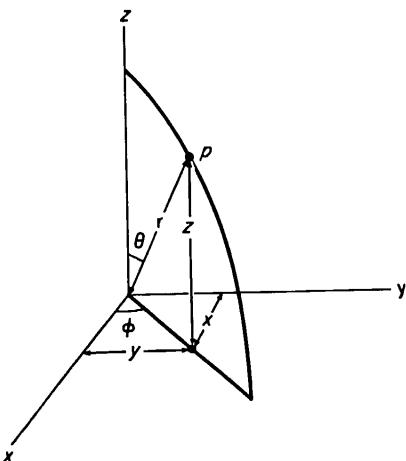
The spherical symmetry of the potential (4.15-1) suggests the use of the familiar spherical coordinate system, with

$$x = r \sin \theta \cos \phi$$

$$y = r \sin \theta \sin \phi$$

$$z = r \cos \theta,$$

FIGURE 4.21. Spherical coordinate system used in discussing the hydrogen atom.



as shown in Figure 4.21, in which we may write the time-independent Schrödinger equation as

$$\nabla^2 \psi + \frac{2m_0}{\hbar^2} \left[\epsilon + \frac{e^2}{r} \right] \psi(r, \theta, \phi) = 0, \quad (4.15-2)$$

with $\nabla^2 \psi = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \psi}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 \psi}{\partial \phi^2}. \quad (4.15-3)$

In (4.15-2), m_0 refers to the electron mass.

We may proceed by the familiar separation of variables technique, in which it is assumed that the solutions have the form

$$\psi(r,\theta,\phi) = R(r)\Theta(\theta)\Phi(\phi), \quad (4.15-4)$$

where $R(r)$ is a function of r alone, independent of θ and ϕ , $\Theta(\theta)$ is a function of θ alone and $\Phi(\phi)$ is a function of ϕ alone. Substituting this form for the solution into (4.15-2), noting that $\partial\psi/\partial r = \Theta\Phi dR/dr$, $\partial\psi/\partial\theta = R\Phi d\Theta/d\theta$ and $\partial\psi/\partial\phi = R\Theta d\Phi/d\phi$, multiplying the resulting equation by $r^2 \sin^2 \theta / (R\Theta\Phi)$, and transposing, we find

$$\frac{\sin^2 \theta}{R} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \frac{\sin \theta}{\Theta} \frac{d}{d\theta} \left(\sin \theta \frac{d\Theta}{d\theta} \right) + \frac{2m_0}{\hbar^2} \sin^2 \theta \left(\epsilon + \frac{e^2}{r} \right) = -\frac{1}{\Phi} \frac{d^2\Phi}{d\phi^2} = m^2. \quad (4.15-5)$$

Since the expression on the right, which is a function of r and θ only is equal to another expression which is a function of ϕ only, the two expressions must separately be equal to a constant, which for reasons which will presently become clear, will be denoted by m^2 .

Now let us confine our attention for the moment to the latter equality shown in (4.15-5). This may be rearranged slightly to read

$$\frac{d^2\Phi}{d\phi^2} = -m^2\Phi(\phi), \quad (4.15-6)$$

which is a simple differential equation whose solution may be written as

$$\Phi_m(\phi) = e^{\pm im\phi}. \quad (4.15-7)$$

Since the total wave function ψ must be single-valued, it must be required that $\Phi_m(\phi)$ be single-valued also. In other words, one must demand that

$$\Phi_m(\phi + 2\pi) = \Phi_m(\phi), \quad (4.15-8)$$

whereby, from (4.15-7),

$$e^{\pm im\phi} e^{\pm 2\pi mi} = e^{\pm im\phi}$$

$$\text{or } e^{\pm 2\pi mi} = 1. \quad (4.15-9)$$

This condition can be fulfilled only if m is a positive or negative *integer* or zero. The allowed values for m are thus restricted to

$$m = 0, \pm 1, \pm 2, \pm 3, \dots,$$

otherwise the wave function will be multiple-valued. It can now be seen why the separation constant was chosen to be m^2 . If m is a real number, then m^2 must be positive. Had the separation constant in (4.15-5) been negative, then the solutions (4.15-7) would have been exponential rather than sinusoidal in character, and the single-valuedness condition (4.15-8) could never have been fulfilled. The separation constant

was thus chosen in such a way as to insure that it would always have a positive value, so as to exclude at once such unwanted solutions.

In (4.15-5), the expression on the left may be set equal to m^2 , and the resulting equation divided through by $\sin^2 \theta$ and rearranged so as to read

$$\frac{1}{R} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \frac{2m_0 r^2}{\hbar^2} \left(\epsilon + \frac{e^2}{r} \right) = - \frac{1}{\Theta \sin \theta} \frac{d}{d\theta} \left(\sin \theta \frac{d\Theta}{d\theta} \right) + \frac{m^2}{\sin^2 \theta} = \beta, \quad (4.15-10)$$

Again, since the first expression is a function of r alone and the second a function of θ alone, the two must separately be equal to a constant β . The second equality of (4.15-10) may be written in the form

$$\frac{1}{\sin \theta} \frac{d}{d\theta} \left(\sin \theta \frac{d\Theta}{d\theta} \right) - \frac{m^2 \Theta}{\sin^2 \theta} + \beta \Theta(\theta) = 0. \quad (4.15-11)$$

This equation is a familiar one in mathematical physics, known as *Legendre's equation*. Without going into the mathematical details,¹⁴ we shall note that the only solutions of this equation which do not violate the requirements of finiteness for the wave functions are those for which β has the values $0, 2, 6, 12, 20, \dots$, thus for which

$$\beta = l(l+1) \quad \text{with } (l = 0, 1, 2, 3, \dots). \quad (4.15-12)$$

In these instances, the solution of (4.15-11) reduces to a polynomial in $\cos \theta$ and $\sin \theta$ in much the same way as the solutions of Hermite's equation reduce to polynomials under certain conditions. These polynomial solutions may be represented as the associated *Legendre functions* $P_l^m(\theta)$, defined by

$$P_l^m(\theta) = \sin^{l|m|} \theta \frac{d^{l|m|}}{d(\cos \theta)^{|m|}} P_l(\cos \theta) \quad (4.15-13)$$

$$\text{where } P_l(\cos \theta) = \frac{1}{2^l l!} \frac{d^l (\cos^2 \theta - 1)^l}{d(\cos \theta)^l}. \quad (4.15-14)$$

The functions $P_l(\cos \theta)$ are the so-called *Legendre polynomials*, the first few of which are

$$\begin{aligned} P_0(\cos \theta) &= 1 \\ P_1(\cos \theta) &= \cos \theta \\ P_2(\cos \theta) &= \frac{1}{2}(3 \cos^2 \theta - 1) \\ P_3(\cos \theta) &= \frac{1}{2}(5 \cos^3 \theta - 3 \cos \theta) \\ &\text{etc.} \end{aligned} \quad (4.15-15)$$

¹⁴ See, for example, R. B. Leighton, *Principles of Modern Physics*, McGraw-Hill Book Co., Inc., New York (1959), p. 168.

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When $m = 0$, of course, the associated functions $P_l^0(\theta)$ reduce to the simple Legendre polynomials $P_l(\cos \theta)$. The function $\Theta(\theta)$ of (4.15-11) is usually written in the form

$$\Theta_{lm}(\theta) = \sqrt{\frac{(2l+1)(l-m)!}{2(l+m)!}} P_l^m(\theta), \quad (4.15-16)$$

the factor multiplying $P_l^m(\theta)$ being a normalization constant. The *angular part* of the wave function, represented as a product of $\Theta_{lm}(\theta)$ and $\Phi_m(\phi)$ is often written in the form

$$\begin{aligned} Y_{lm}(\theta, \phi) &= \frac{(-1)^m}{\sqrt{2\pi}} \Theta_{lm}(\theta) \Phi_m(\phi) \\ &= (-1)^m \sqrt{\frac{(2l+1)(l-m)!}{4\pi(l+m)!}} P_l^m(\theta) e^{im\phi}. \end{aligned} \quad (4.15-17)$$

The functions $Y_{lm}(\theta, \phi)$ are referred to as *spherical harmonics*. For a central force, where the potential is a function of r alone, the angular part of the wave function is *always* given by (4.15-17), no matter what particular form $V(r)$ may take.

The radial part of Equation (4.15-10), taking $\beta = l(l+1)$ as required by (4.15-12) now becomes

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \frac{2m_0}{\hbar^2} \left(\epsilon + \frac{e^2}{r} \right) R(r) - \frac{l(l+1)R(r)}{r^2} = 0. \quad (4.15-18)$$

This equation is called the Laguerre equation. The only solutions whose behavior at $r = \infty$ is such as to qualify them as wave functions are those which may be expressed in terms of *Laguerre polynomials*. These functions, with which are associated *a discrete set of eigenvalues of the energy ϵ* , may be written

$$R_{nl}(r) = - \left[\left(\frac{2m_0 e^2}{n\hbar^2} \right)^3 \cdot \frac{(n-l-1)!}{(2n[n+l]!)^3} \right]^{1/2} e^{-\rho/2} \rho^l L_{n+l}^{2l+1}(\rho), \quad (4.15-19)$$

$$\text{where } n = 1, 2, 3, \dots. \quad (4.15-20)$$

$$\text{and where } \rho = \frac{2m_0 e^2}{n\hbar^2} r. \quad (4.15-21)$$

The functions $L_{n+l}^{2l+1}(\rho)$ are *associated Laguerre functions*, defined by

$$L_r^s(\rho) = \frac{d^s}{d\rho^s} L_r(\rho), \quad (4.15-22)$$

where $L_r(\rho)$ are the *Laguerre polynomials*, in turn defined as

$$L_r(\rho) = e^\rho \frac{d^r}{d\rho^r} (\rho^r e^{-\rho}). \quad (4.15-23)$$

The energies ε_n for which acceptable wave functions exist are related to the values of n in (4.15-19) by¹⁵

$$\varepsilon_n = -\frac{m_0 e^4}{2n^2 \hbar^2}. \quad (4.15-24)$$

Equation (4.15-24) for the energy levels of the hydrogen atom is in agreement with the result (4.5-8) of the Bohr theory; the energy levels as given by the Bohr theory and illustrated in Figure 4.5 are therefore the same as those predicted by wave mechanics.

There are three quantum numbers, n , l , and m in the wave mechanical treatment of the hydrogen atom. The possible values for n are given by (4.15-20). The Laguerre polynomials $L_r(\rho)$ of (4.15-23) are easily seen to be polynomials of degree r . Such polynomials may be differentiated just r times before the result of the repeated differentiation yields zero. Therefore, for nonzero wave functions of the form L_s^r to result from the polynomial L_r , the number of differentiations s required to generate the associated function L_s^r according to (4.15-22) must be less than or equal to r . For physically meaningful wave functions, then, in (4.15-22) we must have

$$s \leq r, \quad (4.15-25)$$

$$\text{or in (4.15-19)} \quad 2l + 1 \leq n + l. \quad (4.15-26)$$

Subtracting $l + 1$ from both sides of this inequality, (4.15-26) reduces to

$$l \leq n - 1. \quad (4.15-27)$$

In like fashion, the associated Legendre function $P_l^m(\theta)$ results from the Legendre polynomial $P_l(\cos \theta)$ by m -fold differentiation. For a nonzero wave function of the form $P_l^m(\theta)$, the number of differentiations m must be less than or equal to the degree l of the polynomial. We must then have

$$m \leq l \quad (4.15-28)$$

for wave functions of physical interest. Conditions (4.15-20), (4.15-27), and (4.15-28) together serve to define the well-known expressions for the possible range of values for n , l , and m ,

$$n = 1, 2, 3, 4, \dots$$

$$l = 0, 1, 2, 3, \dots n - 1 \quad (4.15-29)$$

$$m = 0, \pm 1, \pm 2, \pm 3, \dots \pm l.$$

It is customary to refer to the states for which $l = 0, 1, 2, 3$ as s, p, d , and f -states, respectively. Thus a state for which $n = 2$ and $l = 0$ is referred to as a $2s$ -state, while one for which $n = 3$ and $l = 2$ is called a $3d$ -state.

¹⁵ The mathematical details of this development are given by R. B. Leighton, *op. cit.*, pp. 171-175.

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The complete wave functions for the hydrogen atom, from (4.15-4), must be

$$\psi_{nlm}(r, \theta, \phi) = N_{nlm} R_{nl}(r) \Theta_{lm}(\theta) \Phi_m(\phi), \quad (4.15-30)$$

where $R_{nl}(r)$, $\Theta_{lm}(\theta)$, and $\Phi_m(\phi)$ are given by (4.15-7), (4.15-16), and (4.15-19), respectively, and where N_{nlm} is a normalization constant chosen so that

$$\int \psi_{nlm}^* \psi_{nlm} \cdot r^2 \sin \theta dr d\theta d\phi = 1. \quad (4.15-31)$$

The wave functions (4.15-30) will be found to be orthogonal, so that

$$\int \psi_{n'l'm'}^* \psi_{nlm} \cdot r^2 \sin \theta dr d\theta d\phi = 0, \quad (4.15-32)$$

unless $n = n'$, $l = l'$ and $m = m'$ simultaneously. The time-dependent wave functions are, as usual, obtained from the time-independent functions by multiplying by $e^{-ie_n t/\hbar}$.

TABLE 4.1.

Wave Functions for the Hydrogen Atom

$n = 1$	$l = 0$	$m = 0$	$\psi_{100} = N_{100} e^{-\frac{1}{2}\rho}$	1s
$n = 2$	$l = 0$	$m = 0$	$\psi_{200} = N_{200}(2 - \rho)e^{-\frac{1}{2}\rho}$	2s
	$l = 1$	$m = 0$	$\psi_{210} = N_{210}\rho e^{-\frac{1}{2}\rho} \cos \theta$	
	(4 states)		$\psi_{21\pm 1} = N_{211}\rho e^{-\frac{1}{2}\rho} \sin \theta e^{\pm i\phi}$	
$n = 3$	$l = 0$	$m = 0$	$\psi_{300} = N_{300}(6 - 6\rho + \rho^2)e^{-\frac{1}{2}\rho}$	3s
	$l = 1$	$m = 0$	$\psi_{310} = N_{310}\rho(4 - \rho)e^{-\frac{1}{2}\rho} \cos \theta$	
	(4 states)		$\psi_{31\pm 1} = N_{311}\rho(4 - \rho)e^{-\frac{1}{2}\rho} \sin \theta e^{\pm i\phi}$	
	$l = 2$	$m = 0$	$\psi_{320} = N_{320}\rho^2 e^{-\frac{1}{2}\rho}(3 \cos^2 \theta - 1)$	3p ³
	(9 states)		$\psi_{32\pm 1} = N_{321}\rho^2 e^{-\frac{1}{2}\rho} \sin \theta \cos \theta e^{\pm i\phi}$	
			$\psi_{32\pm 2} = N_{322}\rho^2 e^{-\frac{1}{2}\rho} \sin^2 \theta e^{\pm 2i\phi}$	
	$l = 1$	$m = 0$	$\psi_{410} = N_{410}\rho e^{-\frac{1}{2}\rho}(20 - 10\rho + \rho^2) \cos \theta$	4p ³
			$\psi_{41\pm 1} = N_{411}\rho e^{-\frac{1}{2}\rho}(20 - 10\rho + \rho^2) \sin \theta e^{\pm i\phi}$	
			$\psi_{41\pm 2} = N_{412}\rho^2(6 - \rho)e^{-\frac{1}{2}\rho}(3 \cos^2 \theta - 1)$	
$n = 4$	$l = 2$	$m = 0$	$\psi_{420} = N_{420}\rho^2(6 - \rho)e^{-\frac{1}{2}\rho} \sin \theta \cos \theta e^{\pm i\phi}$	4d ⁵
	(16 states)		$\psi_{42\pm 1} = N_{421}\rho^2(6 - \rho)e^{-\frac{1}{2}\rho} \sin \theta \cos \theta e^{\pm i\phi}$	
			$\psi_{42\pm 2} = N_{422}\rho^2(6 - \rho)e^{-\frac{1}{2}\rho} \sin^2 \theta e^{\pm 2i\phi}$	
	$l = 3$	$m = 0$	$\psi_{430} = N_{430}\rho^3 e^{-\frac{1}{2}\rho} (\frac{5}{3} \cos^3 \theta - \cos \theta)$	4f ⁷
			$\psi_{43\pm 1} = N_{431}\rho^3 e^{-\frac{1}{2}\rho} (5 \cos^2 \theta - 1) \sin \theta e^{\pm i\phi}$	
			$\psi_{43\pm 2} = N_{432}\rho^3 e^{-\frac{1}{2}\rho} \sin^2 \theta \cos \theta e^{\pm 2i\phi}$	
			$\psi_{43\pm 3} = N_{433}\rho^3 e^{-\frac{1}{2}\rho} \sin^3 \theta e^{\pm 3i\phi}$	

$$N_{nlm} = - \left[\left(\frac{2m_0 e^2}{n\hbar^2} \right)^3 \frac{(n-l-1)!(l-m)!(2l+1)}{4\pi(2n[n+l]!)^3(l+m)!} \right]^{\frac{1}{2}}$$

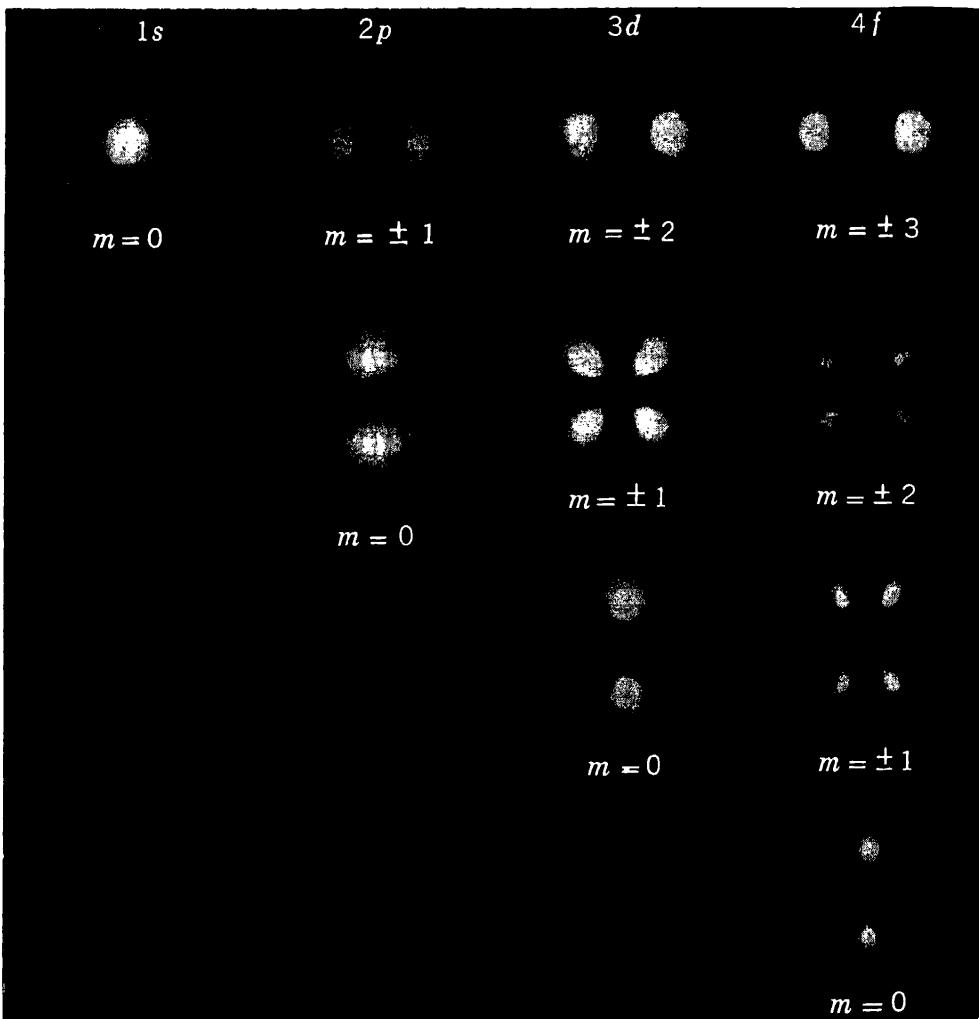


FIGURE 4.22. Photographic representations of the electron density associated with several eigenstates of the hydrogen atom. The polar axis lies in the plane of the page and is oriented vertically.

From (4.15-24) it is clear that the energy depends only upon the principal quantum number n in this particular system. There are in general many independent quantum states [corresponding to the various permitted values for l and m , according to (4.15-29)] which have the same principal quantum number n , and which thus belong to the *same* energy level. This phenomenon is called *degeneracy* and an energy level which contains more than one independent quantum state is referred to as a *degenerate* level. It can be seen from (4.15-29), simply by counting states, that the degeneracy or multiplicity associated with the level of energy ε_n , whose principal quantum number is n , is just n^2 .

The algebraic expressions for some of the wave functions of the hydrogen atom are given in Table 4.1, and some representations of the probability density for some of these states are shown in Figure 4.22. It will be noted that the *s*-states ($l = 0$) are always spherically symmetric, while the *p*-, *d*-, *f*-states, etc., have angular dependences which may be quite complex. The $2p$ -state for which $m = 0$ has two lobes which point along the $\pm z$ -directions, while the $2p$ -states for which $m = \pm 1$ are "doughnut-shaped" and symmetric about the z -axis. All the $2p$ -states thus result in probability

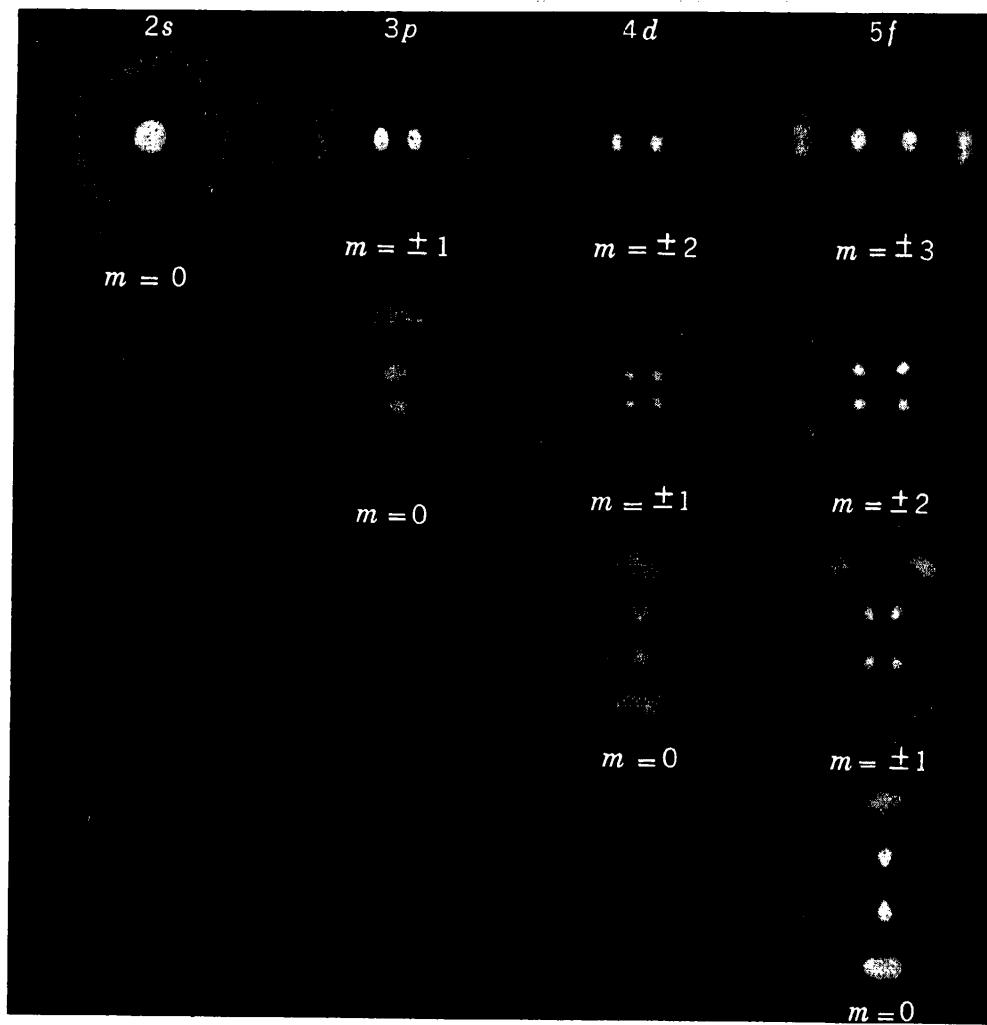


FIGURE 4.22 (Cont'd). The scale is not uniform among all the diagrams. [After R. B. Leighton, *Principles of Modern Physics*, McGraw-Hill, New York (1959).]

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amplitudes which are symmetric about the z -axis. The question of why the z -axis is thus seemingly favored or preferred may well arise. After all, the potential $V(r)$ is spherically symmetric, which permitted us in the first place to choose any polar axis at all for our spherical coordinate system, and we chose the one we did purely arbitrarily. Why, then does it appear in this seemingly favored aspect—or, more to the point, is it really a preferred axis in a physical sense?

We have noted in connection with Section 4.13 that linear superpositions of stationary state wave functions belonging to different energy levels no longer represent probability amplitudes which are independent of time. Since the different independent stationary state eigenfunctions belonging to the same degenerate energy level all have the same time dependence factor $e^{-i\epsilon_{\text{en}t}/\hbar}$, however, it follows that *states of this nature can be superposed* and the superposition probability amplitude will still be independent of time. We have already run across one example of this in Section 4.10 (in connection with equation (4.10-13)). It is clear, for example, from Table 4.1 and from (4.15-29) that there are *three* independent $2p$ states for the hydrogen atom. It makes no difference, however, whether we regard those three states as being those given in Table 4.1,

or as three linearly independent superpositions of those states. By properly superposing the three states given in Table 4.1, we could produce three independent superposition wave functions corresponding to probability amplitudes with lobes pointing along the x -, y - and z -axes, instead of the polar lobe and doughnut configuration of the functions in the table. By further proper linear superposition of these wave functions, these three lobes could be made to point in *any* three given orthogonal directions. It is clear from this that the wave functions of Table 4.1, in which an arbitrarily chosen polar axis seems to have a unique or preferred status, form only one *representation* of the wave functions of the system, and that by proper superposition of *degenerate* quantum states, one might form a representation in which the polar axis was in some other direction. In addition, of course, if we so desired, we could superpose the $2s$ state along with the three $2p$ states. We could *not*, however, add in a $3s$ or $3p$ state and still have a time-independent probability amplitude.

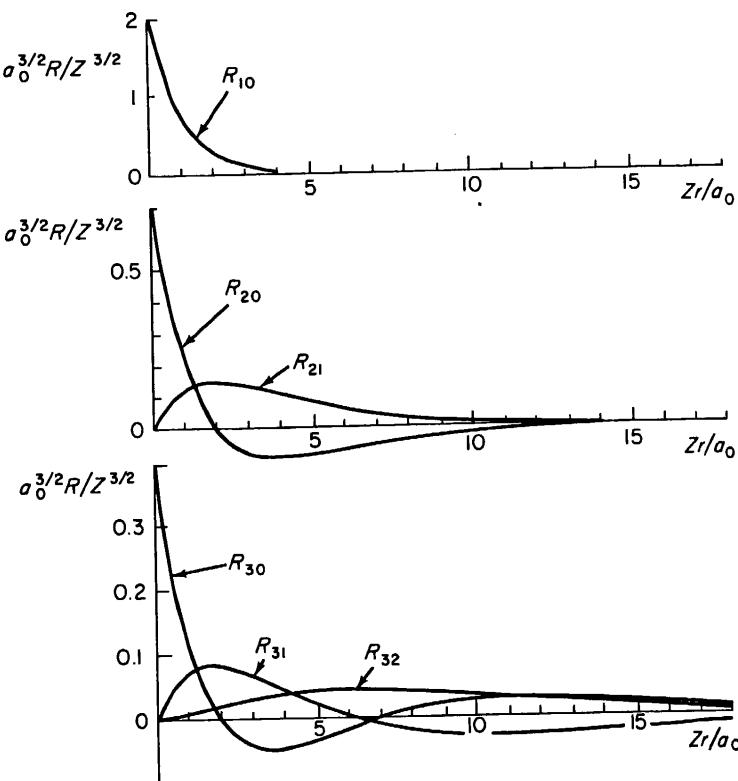


FIGURE 4.23. Plots of the radial wave function $R_{nl}(r)$ for several of the states of the hydrogen atom. [After R. B. Leighton, *Principles of Modern Physics*, McGraw-Hill, New York (1959).]

Figure 4.23 shows a plot of the radial wave function $R_{nl}(r)$ for several of the lower energy states of the hydrogen atom, and Figure 4.24 shows a plot of the radial probability density, which is the probability of finding the electron within a spherical shell of thickness dr about radius r . Since the volume of such a shell is $4\pi r^2 dr$, the radial probability density must be proportional to $r^2 R_{nl}^2(r)$. The proof of this statement is assigned as an exercise. The maxima in the radial probability density for the

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s-wave functions as shown in Figure 4.24 are in close (but not exact) agreement with the Bohr radii r_n as given by (4.5-4).

We have already noted from Equation (4.15-24) that the principal quantum number n is associated with the total energy of the system. We shall find that the quantum numbers l and m are related to the angular momentum of the system. In classical

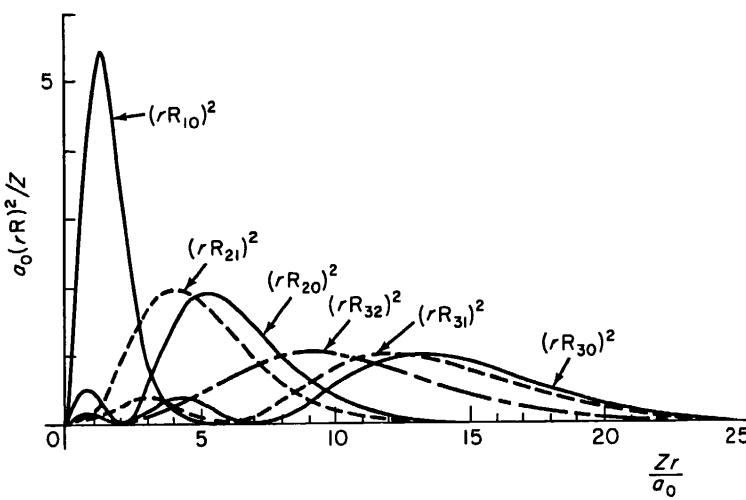


FIGURE 4.24. Plots of the radial probability distribution $r^2 R_{nl}^2(r)$ for several of the states of the hydrogen atom. [After R. B. Leighton, *Principles of Modern Physics*, McGraw-Hill, New York (1959).]

planetary motion, the orbital angular momentum is conserved, and this, as we shall soon see, is also true in the quantum mechanical treatment. The classical angular momentum \mathbf{L} of a particle is defined by

$$\mathbf{L} = \mathbf{r} \times \mathbf{p}, \quad (4.15-33)$$

where \mathbf{p} is the linear momentum and \mathbf{r} is the radius vector from some arbitrary origin to the particle. From this definition and from the definition of the linear momentum operators (4.7-2), a set of operators representing the Cartesian components of the angular momentum can be constructed in a very direct manner. The result is

$$\begin{aligned} L_x &= yp_z - zp_y = \frac{\hbar}{i} \left[y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right] \\ L_y &= zp_x - xp_z = \frac{\hbar}{i} \left[z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \right] \\ L_z &= xp_y - yp_x = \frac{\hbar}{i} \left[x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right]. \end{aligned} \quad (4.15-34)$$

These operators may be expressed in terms of the spherical coordinates (r, θ, ϕ) by a

tedious but straightforward coordinate transformation. The operators then become

$$L_x = \frac{\hbar}{i} \left[-\sin \phi \frac{\partial}{\partial \theta} - \operatorname{ctn} \theta \cos \phi \frac{\partial}{\partial \phi} \right]$$

$$L_y = \frac{\hbar}{i} \left[\cos \phi \frac{\partial}{\partial \theta} - \operatorname{ctn} \theta \sin \phi \frac{\partial}{\partial \phi} \right] \quad (4.15-35)$$

$$L_z = \frac{\hbar}{i} \frac{\partial}{\partial \phi}.$$

The operator representing the square of the total angular momentum can be obtained from (4.15-35) as

$$L^2 = L_x^2 + L_y^2 + L_z^2 = -\hbar^2 \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right]. \quad (4.15-36)$$

Now let us examine what happens when this operator operates upon the wave functions ψ_{nlm} of the hydrogen atom, as given by (4.15-30). We find then that

$$L^2 \psi_{nlm} = -\hbar^2 \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right] R_{nl}(r) \Theta_{lm}(\theta) \Phi_m(\phi). \quad (4.15-37)$$

The operator for L^2 , however, is independent of r , and operates on the product wave function (4.15-30) in such a manner that (4.15-37) can be written

$$L^2 \psi_{nlm} = -\hbar^2 R_{nl}(r) \left[\frac{\Phi_m(\phi)}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \Theta_{lm}}{\partial \theta} \right) + \frac{\Theta_{lm}(\theta)}{\sin^2 \theta} \frac{\partial^2 \Phi_m}{\partial \phi^2} \right]. \quad (4.15-38)$$

Applying, successively, the relations (4.15-6), (4.15-11), and (4.15-12) to this expression, it is evident that

$$\begin{aligned} L^2 \psi_{nlm} &= -\hbar^2 R_{nl}(r) \Phi_m(\phi) \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \Theta_{lm}}{\partial \theta} \right) - m^2 \frac{\Theta_{lm}(\theta)}{\sin^2 \theta} \right] \\ &= \hbar^2 R_{nl}(r) \Phi_m(\phi) \cdot \beta \Theta_{lm}(\theta) = \hbar^2 l(l+1) \psi_{nlm}. \end{aligned} \quad (4.15-39)$$

This equation shows that the operator L^2 is an operator which has the special property given by (4.14-24) with respect to the wave functions ψ_{nlm} . Therefore, according to (4.14-27) and (4.14-25), the dynamical variable associated with the operator must be a constant of the motion, and its expectation value must be $\hbar^2 l(l+1)$. The square of the angular momentum is thus conserved, whereby the angular momentum itself must be conserved, and the expectation value of the angular momentum must be

$$\langle L \rangle = \sqrt{\langle L^2 \rangle} = \hbar \sqrt{l(l+1)}. \quad (4.15-40)$$

In a similar manner, one can show that the z -component of the angular momentum

s then become

is conserved. In this case, from (4.15-35) and (4.15-30) we have

$$L_z \psi_{nlm} = \frac{\hbar}{i} \frac{\partial}{\partial \phi} R_{nl}(r) \Theta_{lm}(\theta) \Phi_m(\phi) = \frac{\hbar}{i} R_{nl}(r) \Theta_{lm}(\theta) \frac{\partial \Phi_m}{\partial \phi}. \quad (4.15-41)$$

(4.15-35) But $\partial \Phi_m / \partial \phi = im e^{im\phi} = im \Phi_m(\phi)$, whence (4.15-41) becomes

$$L_z \psi_{nlm} = \frac{\hbar}{i} \cdot im R_{nl}(r) \Theta_{lm}(\theta) \Phi_m(\phi) = m\hbar \psi_{nlm}. \quad (4.15-42)$$

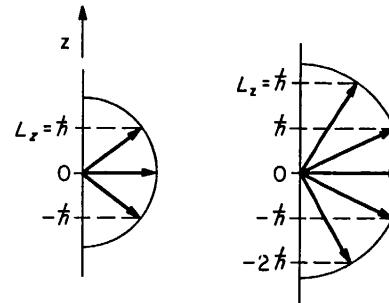
The operator L_z thus also has the special property (4.14-24), and L_z is therefore a constant of the motion whose expectation value must be

$$L_z = m\hbar. \quad (4.15-43)$$

The total angular momentum and its component along a polar axis (whose direction, as we have already seen, may be chosen arbitrarily) are simultaneously conserved. The quantum number l , which specifies the total orbital angular momentum is often referred to as the *orbital* quantum number. The quantum number m , which specifies the z -component of angular momentum, is sometimes called the *magnetic* quantum number because the degeneracy of the states having the same values for n and l but different values of m can be removed when a magnetic field is applied.

The possible orientations of the angular momentum vector \mathbf{L} under the restrictions imposed by the quantum conditions (4.15-40) and (4.15-43) are illustrated by Figure 4.25 for states for which $l = 0, 1$, and 2 . The \mathbf{L} vector must at the same time

FIGURE 4.25. Possible orientations for the angular momentum vector under the restrictions imposed by (4.15-40) and (4.15-43) for $l = 0, 1$, and 2 .



$l=0$	$l=1$	$l=2$
$L=0$	$L=\hbar\sqrt{2}$	$L=\hbar\sqrt{6}$
$L_z=0, \pm\hbar$	$L_z=0, \pm\hbar$	$L_z=0, \pm\hbar \pm 2\hbar$

have a total length given by (4.15-40) and a projection along the z -axis given by (4.15-43). This results in a discrete set of possible orientations for the vector, as shown in the diagrams. The extension of these diagrams to systems with higher values for l is obvious. It should also be clear that if a constant magnetic field is applied along the z -axis, the magnetic moment of the electron in its orbit (which is proportional to the total orbital angular momentum) will interact with the applied field in such a way that the atom will experience a force tending to align its magnetic moment vector (hence its orbital angular momentum vector) with the applied field. The states whose value of m permits partial or complete alignment then must lie *lower in*

energy than those corresponding to nearly antiparallel orientations. The quantum states having different m -values, which are degenerate in the absence of a magnetic field, will thus be split into m closely spaced but separate levels when the field is applied. This phenomenon is the well-known Zeeman effect.

These results serve to explain quite well the observed electric, magnetic, and spectroscopic properties of the hydrogen atom. More complex atoms can, in principle, be treated by the same methods, although since such atoms represent systems of three or more bodies, no closed-form analytic solutions can be obtained, and a perturbation approach must be adopted. Such an approach is based upon the technique of separating the Hamiltonian of the system into a major part whose solution is known or can be obtained analytically, and a smaller part, hopefully containing the terms which cause the analytical difficulties. The solution is then assumed to be of the form of a linear combination of eigenfunctions of the first part of the Hamiltonian, and the constants involved in the linear combination are determined in such a way that the wave function is an approximate eigenfunction of the complete Hamiltonian. These methods, while very useful in solving a variety of practical problems will not be discussed further here.¹⁶

4.16 ELECTRON SPIN, THE PAULI EXCLUSION PRINCIPLE AND THE PERIODIC SYSTEM

In the quantum mechanical calculation of the wave functions and energy levels of many-electron atoms (He, Be, Li, etc.), it is generally assumed that each electron moves in a spherically symmetric potential due to the nucleus and the average spatial distribution of all the other electrons. In this approximation the total wave function of the system may be expressed as a product of one-electron wave functions. The potential function for each electron is spherically symmetric, and the angular part of the one-electron wave functions is still expressable in terms of the spherical harmonics (4.15-17). The radial part of such wave functions, however, is more complex than that for the hydrogen atom. Due to the separability of the one-electron wave functions into radial and angular parts, each electron can be regarded as being represented by three quantum numbers, n , l , and m , just as in hydrogen. Since the radial wave function does not now have the form (4.15-19) corresponding to a simple Coulomb potential, however, states having the same value of n but a different value of l are no longer degenerate and the total energy of the electron depends upon the orbital quantum number l as well as upon n .

From these considerations the energy levels of complex atoms may be calculated and predictions regarding the spectra of those atoms made. These predictions, however, are not in complete agreement with experiment unless two additional corrections are made.

The first of these is the hypothesis of electron spin, which was introduced by Goudsmit and Uhlenbeck in 1925, in which every electron, in addition to whatever orbital angular momentum it may have, is assumed to have an *intrinsic* angular

¹⁶ For a complete treatment of this subject see for example C. W. Sherwin, *op. cit.*, Chapters 7-10, or E. Merzbacher, *op. cit.*, Chapters 16-20.

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momentum or *spin* angular momentum of magnitude $L_s = \frac{1}{2}\hbar\sqrt{3}$, whose component along any given field axis may have two possible values, $m_s = \pm\hbar/2$. The electron can thus exist in two "spin states" corresponding to the two possible values of m_s . These two spin states are often referred to as the "spin up" and "spin down" states. The electron can be regarded as having a total spin angular momentum quantum number s which can have only one value, $\frac{1}{2}$, in which case, in analogy with (4.15-40) the spin angular momentum is

$$\langle L_s \rangle = \hbar\sqrt{s(s+1)} = \hbar\sqrt{3}/2, \quad (4.16-1)$$

and a quantum number m_s representing the z -component of spin angular momentum which may have the values $\pm\frac{1}{2}$, so that in analogy with (4.15-43), the z -component of spin angular momentum is

$$\langle L_{sz} \rangle = m_s\hbar = \pm\hbar/2. \quad (4.16-2)$$

The degeneracy of all the electronic states in hydrogen and in more complex atoms is thus doubled by the existence of the two spin states of the electron. The intrinsic angular momentum of the electron is a consequence of relativity and is obtained from first principles when the wave equation is formulated in a relativistically covariant manner, as shown by Dirac in 1928. The incorporation of electron spin into the formalism of wave mechanics thus really involves no new *ad hoc* physical assumption at all.

The other factor which must be introduced into the wave-mechanical explanation of the behavior of many-particle systems is the *Pauli Exclusion Principle*, which states that in a given *system* (which may be an atom, a molecule, or a whole crystal made up of many interacting atoms), no two electrons may occupy the same quantum state, counting states of opposite spin as different states. Applied to a complex atom, this means that no two electrons in the atom can have quantum numbers n , l , m , and m_s , *all* of which are the same. For other systems, it means that no more than g electrons may occupy an energy level which is g -fold degenerate. Although electrons obey the Pauli principle, certain other particles, such as photons, do not. In general, particles such as electrons whose intrinsic spin is half-integral ($s = \frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \dots$) obey the Pauli principle, while those, such as photons, whose intrinsic spin is integral ($s = 0, 1, 2, \dots$) do not. This fact introduces very important differences into the statistical behavior of assemblies of electrons and photons, as we shall see in the next chapter.

The addition of electron spin and the Pauli principle to the wave-mechanical treatment of many-electron atoms made it possible to explain the periodic system of the elements on the basis of the successive occupation of electronic states of the atoms. This scheme is shown in Table 4.2, which lists the electronic configuration of each atom.

In this table, the simplest atom, H, is represented as having a single electron, which in the lowest energy configuration of the system must be in a $1s$ state. The next atom, He, with two electrons, in the lowest energy configuration (or *ground state*), may have two $1s$ electrons with opposite spins. This configuration is written $1s^2$. Since there are only two states associated with the level $n = 1$, $l = 0$, the next most complex atom, Li, must in accord with the Pauli principle have the ground state configuration $1s^22s$, the third electron going into the next lowest energy state, which is the $2s$ state. The fourth element, Be, adds another $2s$ electron, but since there are only two

2s states, the Pauli principle requires that the fifth element, B, have an electron in the 2p level, which save for the 1s and 2s is the lowest in energy; B thus has the ground state configuration $1s^2)2s^22p$. There are 6 possible 2p states, corresponding to quantum numbers $n = 2$, $l = 1$, $m = 0, \pm 1$ and $m_s = \pm \frac{1}{2}$. The next five elements, C, N, O F, and Ne, each add one additional 2p electron to fill the 2p level. The filled 2p shell

TABLE 4.2.
Electronic Configurations and the Periodic System

1s	H	1s
	He	$1s^2)$
2s	Li	$1s^2)2s$
	Be	$1s^2)2s^2$
	B	$1s^2)2s^22p$
	C	$1s^2)2s^22p^2$
	N	$1s^2)2s^22p^3$
	O	$1s^2)2s^22p^4$
	F	$1s^2)2s^22p^5$
	Ne	$1s^2)2s^22p^6)$
3s	Na	$1s^2)2s^22p^6)3s$
	Mg	$1s^2)2s^22p^6)3s^2$
3p	Al	$1s^2)2s^22p^6)3s^23p$
	Si	$1s^2)2s^22p^6)3s^23p^2$
	P	$1s^2)2s^22p^6)3s^23p^3$
	S	$1s^2)2s^22p^6)3s^23p^4$
	Cl	$1s^2)2s^22p^6)3s^23p^5$
	A	$1s^2)2s^22p^6)3s^23p^6)$
4s	K	$1s^2)2s^22p^6)3s^23p^6)4s$
	Ca	$1s^2)2s^22p^6)3s^23p^6)4s^2$
3d	Sc	$1s^2)2s^22p^6)3s^23p^63d)4s^2$
	Ti	$1s^2)2s^22p^6)3s^23p^63d^2)4s^2$
	V	$1s^2)2s^22p^6)3s^23p^63d^3)4s^2$
	Cr	$1s^2)2s^22p^6)3s^23p^63d^5)4s$
	Mn	$1s^2)2s^22p^6)3s^23p^63d^5)4s^2$
	Fe	$1s^2)2s^22p^6)3s^23p^63d^6)4s^2$
	Co	$1s^2)2s^22p^6)3s^23p^63d^7)4s^2$
	Ni	$1s^2)2s^22p^6)3s^23p^63d^8)4s^2$
	Cu	$1s^2)2s^22p^6)3s^23p^63d^{10})4s$
	Zn	$1s^2)2s^22p^6)3s^23p^63d^{10})4s^2$
4p	Ga	$1s^2)2s^22p^6)3s^23p^63d^{10})4s^24p$
	Ge	$1s^2)2s^22p^6)3s^23p^63d^{10})4s^24p^2$
	As	$1s^2)2s^22p^6)3s^23p^63d^{10})4s^24p^3$
	Se	$1s^2)2s^22p^6)3s^23p^63d^{10})4s^24p^4$
	Br	$1s^2)2s^22p^6)3s^23p^63d^{10})4s^24p^5$
	Kr	$1s^2)2s^22p^6)3s^23p^63d^{10})4s^24p^6)$... etc.

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is spherically symmetric and very stable, as is the filled 1s shell, and the elements Ne and He which have these configurations are inert gases. The succeeding elements then fill up the 3s and 3p shells as shown in the table, ending up with another inert gas, A, which has a full 3p shell containing 6 electrons. The elements which have similar arrangements of outer or valence electrons in the $n = 2$ and $n = 3$ groups have similar chemical properties.

When the 3p level is filled, the next two elements add electrons in the 4s states rather than in the 3d levels, as might have been expected. This is simply because the 4s state happens to fall lower in energy than the 3d state. There is then a series of eight "transition elements" which have an incompletely filled inner 3d-shell. When this 3d level is at length completely filled, the filling of the 4p shell resumes, ending with another inert gas, Kr. The rest of the table may be constructed along generally similar lines. In every case the outer shell structure of chemically related elements, such as Li, Na, K, Rb, and Cs is *identical*. The quantum theory is thus found to account satisfactorily not only for the spectroscopically observed energy level structure of complex atoms, but also for the arrangement of the atoms in the periodic system and the regularity of chemical properties associated with the periodic table of the elements.

EXERCISES

1. Show that the expectation value of the energy is equal to the separation constant ϵ for a system with time-dependent wave functions of the form (4.8-8). Show that the expectation value of the Hamiltonian operator taken over the time-independent wave function is equal to ϵ for this type of system.
2. Show that if z_1 and z_2 are any two complex numbers, then $(z_1 z_2)^* = z_1^* z_2^*$; show that the complex conjugate of a complex quantity expressed in polar form as $f e^{i\theta}$ (f, θ real) is $f^* e^{-i\theta}$.
3. For the free particle of Section 4.9, the phase velocity, from (4.9-5) is $\omega/k = \hbar k/2m = p/2m$. Classically, however, the velocity of a free particle is p/m . Explain the discrepancy of a factor of 2.
4. Verify directly that the wave function (4.9-11) for a free particle satisfies Schrödinger's equation (4.7-3) with $V = 0$.
5. By expressing the function of (4.9-17) as a Fourier integral with the help of (4.9-16), verify Equation (4.9-18).
6. Find $\langle x \rangle_n$, $\langle px \rangle_n$, $\langle p_x^2 \rangle_n$ for the n th eigenstate of the infinitely deep potential well of Section 4.10, and show explicitly that $\epsilon_n = \langle p_x^2 \rangle_n / 2m$, as for the free particle.
7. What is the ratio of the amplitudes of the *continuum* eigenfunctions of the finite potential well of Section 4.11 in the region $(-a < x < a)$ to the amplitude in the regions $(x < -a; x > a)$?
8. From the definition (4.12-29) prove that $dH_n(\xi)/d\xi = 2nH_{n-1}(\xi)$. Hint: Note that $d^n(xf(x))/dx^n = x d^n f/dx^n + nd^{n-1}f/dx^{n-1}$.
9. From (4.12-29), prove that $H_{n+1}(\xi) = 2\xi H_n(\xi) - 2nH_{n-1}(\xi)$.
10. From the results of Problems 8 and 9, show that the functions $H_n(\xi)$ satisfy Hermite's equation (4.12-16).
11. Find the expectation value of the potential energy $\langle V \rangle_n$ for the n th eigenstate of a 1-dimensional quantum harmonic oscillator. Hint: Use the orthogonality properties of the wave functions.
12. Find the expectation value of the kinetic energy $\langle K \rangle_n$ for the n th eigenstate of a

1-dimensional quantum harmonic oscillator, and using the result of Problem 11, show that $\langle V \rangle_n + \langle K \rangle_n = \hbar\omega_0(n + \frac{1}{2})$, in agreement with intuition.

13. Show by evaluating the standard deviation that the momentum of a free particle is a constant of the motion.

14. Show for the eigenstates of the hydrogen atom that the probability of finding the electron in a spherical shell of thickness dr and radius r is $r^2 R_{nl}^2(r)$. Assume that the spherical harmonics $Y_{lm}(\theta, \phi)$ are normalized.

15. Show directly that the standard deviation formula yields $\sigma = 0$ for the operators L^2 and L_z for the hydrogen atom.

16. Obtain the expression (4.15-36) for L^2 from the expressions (4.15-35) for L_x , L_y , and L_z .

17. Using the methods of Section 4.15, show that if $\langle \epsilon^n \rangle$ can be evaluated as $\langle \mathcal{H}^n \rangle$ using the time-independent wave functions, then $\langle \epsilon^{n+1} \rangle$ can be represented as $\langle \mathcal{H}^{n+1} \rangle$ using these same functions. Indicate how, by induction, this means that $\langle f(\epsilon) \rangle$ can be obtained from $\langle f(\mathcal{H}) \rangle$ using time-independent wave functions, where $f(\epsilon)$ is any function of ϵ which can be represented as a convergent power series.

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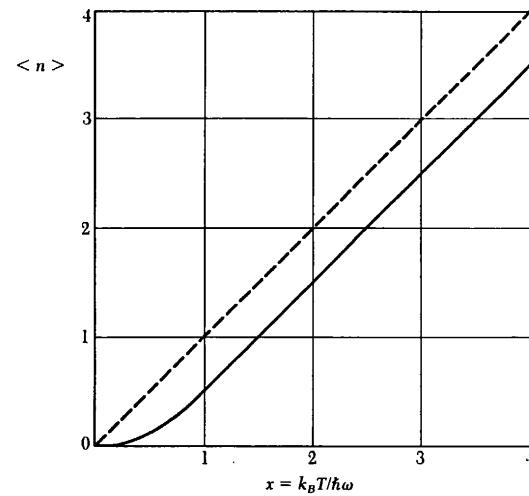


Figure 1 Plot of Planck distribution function. At high temperatures the occupancy of a state is approximately linear in the temperature. The function $\langle n \rangle + \frac{1}{2}$, which is not plotted, approaches the dashed line as asymptote at high temperatures. The dashed line is the classical limit.

CHAPTER 5: PHONONS II. THERMAL PROPERTIES

We discuss the heat capacity of a phonon gas and then the effects of anharmonic lattice interactions on the phonons and on the crystal. Thermal properties of metals are treated in Chapter 6, superconductors in Chapter 12, magnetic materials in Chapters 14 and 15, and noncrystalline solids in Chapter 17.

PHONON HEAT CAPACITY

By heat capacity we shall usually mean the heat capacity at constant volume, which is more fundamental than the heat capacity at constant pressure, which is what the experiments determine.¹ The heat capacity at constant volume is defined as $C_V \equiv (\partial U / \partial T)_V$, where U is the energy and T the temperature.

The contribution of the phonons to the heat capacity of a crystal is called the lattice heat capacity and is denoted by C_{lat} .

The total energy of the phonons at a temperature $\tau (= k_B T)$ in a crystal may be written as the sum of the energies over all phonon modes, here indexed by the wavevector K and polarization index p :

$$U = \sum_K \sum_p U_{K,p} = \sum_K \sum_p \langle n_{K,p} \rangle \hbar \omega_{K,p} , \quad (1)$$

where $\langle n_{K,p} \rangle$ is the thermal equilibrium occupancy of phonons of wavevector K and polarization p . The form of $\langle n_{K,p} \rangle$ is given by the Planck distribution function:

$$\langle n \rangle = \frac{1}{\exp(\hbar \omega / \tau) - 1} \quad (2)$$

where the $\langle \dots \rangle$ denotes the average in thermal equilibrium. A graph of $\langle n \rangle$ is given in Fig. 1.

Planck Distribution

Consider a set of identical harmonic oscillators in thermal equilibrium. The ratio of the number of oscillators in their $(n + 1)$ th quantum state of excitation to the number in the n th quantum state is

$$N_{n+1}/N_n = \exp(-\hbar \omega / \tau) , \quad \tau \equiv k_B T , \quad (3)$$

¹A thermodynamic relation gives $C_p - C_V = 9\alpha^2 B V T$, where α is the temperature coefficient of linear expansion, V the volume, and B the bulk modulus. The fractional difference between C_p and C_V is usually small and often may be neglected. As $T \rightarrow 0$ we see that $C_p \rightarrow C_V$, provided α and B are constant.

by use of the Boltzmann factor. Thus the fraction of the total number of oscillators in the n th quantum state is

$$\frac{N_n}{\sum_{s=0}^{\infty} N_s} = \frac{\exp(-\hbar\omega/\tau)}{\sum_{s=0}^{\infty} \exp(-s\hbar\omega/\tau)}. \quad (4)$$

We see that the average excitation quantum number of an oscillator is

$$\langle n \rangle = \frac{\sum_s s \exp(-s\hbar\omega/\tau)}{\sum_s \exp(-s\hbar\omega/\tau)}. \quad (5)$$

The summations in (5) are

$$\sum_s x^s = \frac{1}{1-x}; \quad \sum_s s x^s = x \frac{d}{dx} \sum_s x^s = \frac{x}{(1-x)^2}, \quad (6)$$

with $x = \exp(-\hbar\omega/\tau)$. Thus we may rewrite (5) as the Planck distribution:

$$\langle n \rangle = \frac{x}{1-x} = \frac{1}{\exp(\hbar\omega/\tau) - 1}. \quad (7)$$

Normal Mode Enumeration

The energy of a collection of oscillators of frequencies $\omega_{K,p}$ in thermal equilibrium is found from (1) and (2):

$$U = \sum_K \sum_p \frac{\hbar\omega_{K,p}}{\exp(\hbar\omega_{K,p}/\tau) - 1}. \quad (8)$$

It is usually convenient to replace the summation over K by an integral. Suppose that the crystal has $D_\lambda(\omega)d\omega$ modes of a given polarization λ in the frequency range ω to $\omega + d\omega$. Then the energy is

$$U = \int d\omega D_\lambda(\omega) \frac{\hbar\omega}{\exp(\hbar\omega/\tau) - 1}. \quad (9)$$

The lattice heat capacity is found by differentiation with respect to temperature. Let $x = \hbar\omega/\tau = \hbar\omega/k_B T$; then $\partial U/\partial T$ gives

$$C_{\text{lat}} = k_B \sum_\lambda \int d\omega D_\lambda(\omega) \frac{x^2 \exp x}{(\exp x - 1)^2}. \quad (10)$$

The central problem is to find $D(\omega)$, the number of modes per unit frequency range. This function is called the density of modes or, more often,

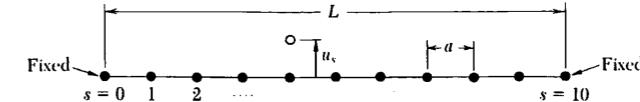


Figure 2 Elastic line of $N + 1$ atoms, with $N = 10$, for boundary conditions that the end atoms $s = 0$ and $s = 10$ are fixed. The particle displacements in the normal modes for either longitudinal or transverse displacements are of the form, $u_s \propto \sin sKa$. This form is automatically zero at the atom at the end $s = 0$, and we choose K to make the displacement zero at the end $s = 10$.

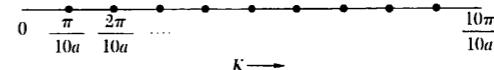


Figure 3 The boundary condition $\sin sKa = 0$ for $s = 10$ can be satisfied by choosing $K = \pi/10a, 2\pi/10a, \dots, 9\pi/10a$, where $10a$ is the length L of the line. The present figure is in K space. The dots are not atoms but are the allowed values of K . Of the $N + 1$ particles on the line, only $N - 1$ are allowed to move, and their most general motion can be expressed in terms of the $N - 1$ allowed values of K . This quantization of K has nothing to do with quantum mechanics but follows classically from the boundary conditions that the end atoms be fixed.

density of states. The best practical way to obtain the density of states is to measure the dispersion relation ω versus K in selected crystal directions by inelastic neutron scattering and then to make a theoretical analytic fit to give the dispersion relation in a general direction, from which $D(\omega)$ may be calculated.

Density of States in One Dimension

Consider the boundary value problem for vibrations of a one-dimensional line (Fig. 2) of length L carrying $N + 1$ particles at separation a . We suppose that the particles $s = 0$ and $s = N$ at the ends of the line are held fixed. Each normal vibrational mode of polarization p has the form of a standing wave, where u_s is the displacement of the particle s :

$$u_s = u(0) \exp(-i\omega_{K,p}t) \sin sKa, \quad (11)$$

where $\omega_{K,p}$ is related to K by the appropriate dispersion relation.

As in Fig. 3, the wavevector K is restricted by the fixed-end boundary conditions to the values

$$K = \frac{\pi}{L}, \quad \frac{2\pi}{L}, \quad \frac{3\pi}{L}, \quad \dots, \quad \frac{(N-1)\pi}{L}. \quad (12)$$

The solution for $K = \pi/L$ has

$$u_s \propto \sin(s\pi a/L) \quad (13)$$

and vanishes for $s = 0$ and $s = N$ as required.

The solution for $K = N\pi/L = \pi/a = K_{\max}$ has $u_s \propto \sin s\pi$; this permits no motion of any atom, because $\sin s\pi$ vanishes at each atom. Thus there are $N - 1$ allowed independent values of K in (12). This number is equal to the

number of particles allowed to move. Each allowed value of K is associated with a standing wave. For the one-dimensional line there is one mode for each interval $\Delta K = \pi/L$, so that the number of modes per unit range of K is L/π for $K \leq \pi/a$, and 0 for $K > \pi/a$.

There are three polarizations p for each value of K : in one dimension two of these are transverse and one longitudinal. In three dimensions the polarizations are this simple only for wavevectors in certain special crystal directions.

Another device for enumerating modes is often used that is equally valid. We consider the medium as unbounded, but require that the solutions be periodic over a large distance L , so that $u(sa) = u(sa + L)$. The method of **periodic boundary conditions** (Figs. 4 and 5) does not change the physics of the problem in any essential respect for a large system. In the running wave solution $u_s = u(0) \exp[i(sKa - \omega_K t)]$ the allowed values of K are

$$K = 0, \pm \frac{2\pi}{L}, \pm \frac{4\pi}{L}, \pm \frac{6\pi}{L}, \dots, \frac{N\pi}{L}. \quad (14)$$

This method of enumeration gives the same number of modes (one per mobile atom) as given by (12), but we have now both plus and minus values of K , with the interval $\Delta K = 2\pi/L$ between successive values of K . For periodic boundary conditions the number of modes per unit range of K is $L/2\pi$ for $-\pi/a \leq K \leq \pi/a$, and 0 otherwise. The situation in a two-dimensional lattice is portrayed in Fig. 6.

We need to know $D(\omega)$, the number of modes per unit frequency range. The number of modes $D(\omega) d\omega$ in $d\omega$ at ω is given in one dimension by

$$D(\omega) d\omega = \frac{L}{\pi} \frac{dK}{d\omega} d\omega = \frac{L}{\pi} \cdot \frac{d\omega}{d\omega/dK}. \quad (15)$$

We can obtain the group velocity $d\omega/dK$ from the dispersion relation ω versus K . There is a singularity in $D(\omega)$ whenever the dispersion relation $\omega(K)$ is horizontal; that is, whenever the group velocity is zero.

Density of States in Three Dimensions

We apply periodic boundary conditions over N^3 primitive cells within a cube of side L , so that \mathbf{K} is determined by the condition

$$\exp[i(K_x x + K_y y + K_z z)] \equiv \exp[i(K_x(x+L) + K_y(y+L) + K_z(z+L))], \quad (16)$$

whence

$$K_x, K_y, K_z = 0; \pm \frac{2\pi}{L}; \pm \frac{4\pi}{L}; \dots; \frac{N\pi}{L}. \quad (17)$$

Therefore there is one allowed value of \mathbf{K} per volume $(2\pi/L)^3$ in \mathbf{K} space, or

$$\left(\frac{L}{2\pi}\right)^3 = \frac{V}{8\pi^3} \quad (18)$$

Figure 4 Consider N particles constrained to slide on a circular ring. The particles can oscillate if connected by elastic springs. In a normal mode the displacement u_s of atom s will be of the form $\sin sKa$ or $\cos sKa$; these are independent modes. By the geometrical periodicity of the ring the boundary condition is that $u_{N+s} = u_s$ for all s , so that NKa must be an integral multiple of 2π . For $N = 8$ the allowed independent values of K are 0, $2\pi/8a$, $4\pi/8a$, $6\pi/8a$, and $8\pi/8a$. The value $K = 0$ is meaningless for the sine form, because $\sin s0a = 0$. The value $8\pi/8a$ has a meaning only for the cosine form, because $\sin (s8\pi a/8a) = \sin s\pi = 0$. The three other values of K are allowed for both the sine and cosine modes, giving a total of eight allowed modes for the eight particles. Thus the periodic boundary condition leads to one allowed mode per particle, exactly as for the fixed-end boundary condition of Fig. 3. If we had taken the modes in the complex form $\exp(isKa)$, the periodic boundary condition would lead to the eight modes with $K = 0, \pm 2\pi/Na, \pm 4\pi/Na, \pm 6\pi/Na$, and $8\pi/Na$, as in Eq. (14).

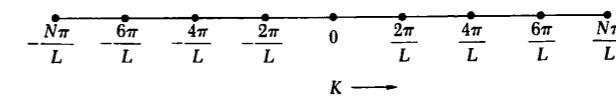


Figure 5 Allowed values of wavevector K for periodic boundary conditions applied to a linear lattice of periodicity $N = 8$ atoms on a line of length L . The $K = 0$ solution is the uniform mode. The special points $\pm N\pi/L$ represent only a single solution because $\exp(i\pi s)$ is identical to $\exp(-i\pi s)$; thus there are eight allowed modes, with displacements of the s th atom proportional to $1, \exp(\pm i\pi s/4), \exp(\pm i\pi s/2), \exp(\pm i3\pi s/4), \exp(i\pi s)$.

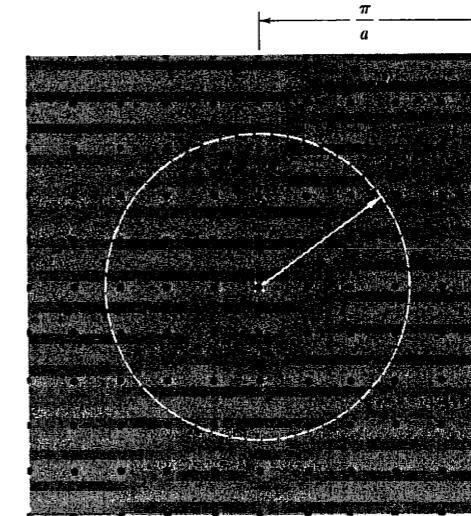


Figure 6 Allowed values in Fourier space of the phonon wavevector K for a square lattice of lattice constant a , with periodic boundary conditions applied over a square of side $L = 10a$. The uniform mode is marked with a cross. There is one allowed value of K per area $(2\pi/10a)^2 = (2\pi/L)^2$, so that within the circle of area πK^2 the smoothed number of allowed points is $\pi K^2(L/2\pi)^2$.

allowed values of \mathbf{K} per unit volume of \mathbf{K} space, for each polarization and for each branch. The volume of the specimen is $V = L^3$.

The total number of modes with wavevector less than K is found from (18) to be $(L/2\pi)^3$ times the volume of a sphere of radius K . Thus

$$N = (L/2\pi)^3 (4\pi K^3/3) \quad (19)$$

for each polarization type. The density of states for each polarization is

$$D(\omega) = dN/d\omega = (VK^2/2\pi^2)(dK/d\omega) . \quad (20)$$

Debye Model for Density of States

In the Debye approximation the velocity of sound is taken as constant for each polarization type, as it would be for a classical elastic continuum. The dispersion relation is written as

$$\omega = vK , \quad (21)$$

with v the constant velocity of sound.

The density of states (20) becomes

$$D(\omega) = V\omega^2/2\pi^2v^3 . \quad (22)$$

If there are N primitive cells in the specimen, the total number of acoustic phonon modes is N . A cutoff frequency ω_D is determined by (19) as

$$\omega_D^3 = 6\pi^2v^3N/V . \quad (23)$$

To this frequency there corresponds a cutoff wavevector in \mathbf{K} space:

$$K_D = \omega_D/v = (6\pi^2N/V)^{1/3} . \quad (24)$$

On the Debye model we do not allow modes of wavevector larger than K_D . The number of modes with $K \leq K_D$ exhausts the number of degrees of freedom of a monatomic lattice.

The thermal energy (9) is given by

$$U = \int d\omega D(\omega) \langle n(\omega) \rangle \hbar\omega = \int_0^{\omega_D} d\omega \left(\frac{V\omega^2}{2\pi^2v^3} \right) \left(\frac{\hbar\omega}{e^{\hbar\omega/\tau} - 1} \right) , \quad (25)$$

for each polarization type. For brevity we assume that the phonon velocity is independent of the polarization, so that we multiply by the factor 3 to obtain

$$U = \frac{3V\hbar}{2\pi^2v^3} \int_0^{\omega_D} d\omega \frac{\omega^3}{e^{\hbar\omega/\tau} - 1} = \frac{3Vk_B^4 T^4}{2\pi^2v^3\hbar^3} \int_0^{x_D} dx \frac{x^3}{e^x - 1} , \quad (26)$$

where $x \equiv \hbar\omega/\tau \equiv \hbar\omega/k_B T$ and

$$x_D \equiv \hbar\omega_D/k_B T \equiv \theta/T . \quad (27)$$

This defines the **Debye temperature** θ in terms of ω_D defined by (23). We may express θ as

$$\theta = \frac{\hbar v}{k_B} \cdot \left(\frac{6\pi^2 N}{V} \right)^{1/3} , \quad (28)$$

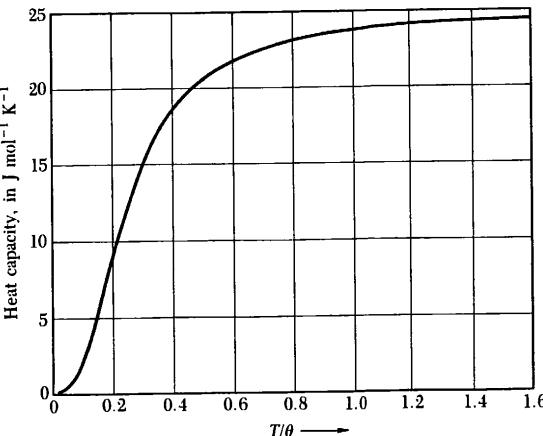


Figure 7 Heat capacity C_V of a solid, according to the Debye approximation. The vertical scale is in $J \text{ mol}^{-1} \text{ K}^{-1}$. The horizontal scale is the temperature normalized to the Debye temperature θ . The region of the T^3 law is below 0.1θ . The asymptotic value at high values of T/θ is $24.943 \text{ J mol}^{-1} \text{ deg}^{-1}$.

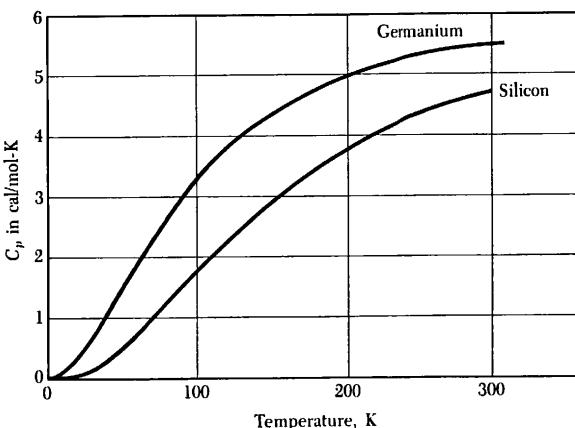


Figure 8 Heat capacity of silicon and germanium. Note the decrease at low temperatures. To convert a value in cal/mol-K to J/mol-K, multiply by 4.186.

so that the total phonon energy is

$$U = 9Nk_B T \left(\frac{T}{\theta} \right)^3 \int_0^{x_D} dx \frac{x^3}{e^x - 1} , \quad (29)$$

where N is the number of atoms in the specimen and $x_D = \theta/T$.

The heat capacity is found most easily by differentiating the middle expression of (26) with respect to temperature. Then

$$C_V = \frac{3V\hbar^2}{2\pi^2v^3k_B T^2} \int_0^{\omega_D} d\omega \frac{\omega^4 e^{\hbar\omega/\tau}}{(e^{\hbar\omega/\tau} - 1)^2} = 9Nk_B \left(\frac{T}{\theta} \right)^3 \int_0^{x_D} dx \frac{x^4 e^x}{(e^x - 1)^2} . \quad (30)$$

The Debye heat capacity is plotted in Fig. 7. At $T \gg \theta$ the heat capacity approaches the classical value of $3Nk_B$. Measured values for silicon and germanium are plotted in Fig. 8.

Debye T^3 Law

At very low temperatures we may approximate (29) by letting the upper limit go to infinity. We have

$$\int_0^\infty dx \frac{x^3}{e^x - 1} = \int_0^\infty dx x^3 \sum_{s=1}^{\infty} \exp(-sx) = 6 \sum_1^{\infty} \frac{1}{s^4} = \frac{\pi^4}{15}, \quad (31)$$

where the sum over s^{-4} is found in standard tables. Thus $U \cong 3\pi^4 N k_B T^4 / 5\theta^3$ for $T \ll \theta$, and

$$C_V \cong \frac{12\pi^4}{5} N k_B \left(\frac{T}{\theta}\right)^3 \cong 234 N k_B \left(\frac{T}{\theta}\right)^3, \quad (32)$$

which is the Debye T^3 approximation. Experimental results for argon are plotted in Fig. 9.

At sufficiently low temperatures the T^3 approximation is quite good; that is, when only long wavelength acoustic modes are thermally excited. These are just the modes that may be treated as an elastic continuum with macroscopic elastic constants. The energy of the short wavelength modes (for which this approximation fails) is too high for them to be populated significantly at low temperatures.

We understand the T^3 result by a simple argument (Fig. 10). Only those lattice modes having $\hbar\omega < k_B T$ will be excited to any appreciable extent at a low temperature T . The excitation of these modes will be approximately classical, each with an energy close to $k_B T$, according to Fig. 1.

Of the allowed volume in \mathbf{K} space, the fraction occupied by the excited modes is of the order of $(\omega_T/\omega_D)^3$ or $(K_T/K_D)^3$, where K_T is a “thermal” wavevector defined such that $\hbar v K_T = k_B T$ and K_D is the Debye cutoff wavevector. Thus the fraction occupied is $(T/\theta)^3$ of the total volume in \mathbf{K} space. There are of the order of $3N(T/\theta)^3$ excited modes, each having energy $k_B T$. The energy is $\sim 3Nk_B T(T/\theta)^3$, and the heat capacity is $\sim 12Nk_B(T/\theta)^3$.

For actual crystals the temperatures at which the T^3 approximation holds are quite low. It may be necessary to be below $T = \theta/50$ to get reasonably pure T^3 behavior.

Selected values of θ are given in Table 1. Note, for example, in the alkali metals that the heavier atoms have the lowest θ 's, because the velocity of sound decreases as the density increases.

Einstein Model of the Density of States

Consider N oscillators of the same frequency ω_0 and in one dimension. The Einstein density of states is $D(\omega) = N\delta(\omega - \omega_0)$, where the delta function is centered at ω_0 . The thermal energy of the system is

$$U = N\langle n \rangle \hbar\omega = \frac{N\hbar\omega}{e^{\hbar\omega/\tau} - 1}, \quad (33)$$

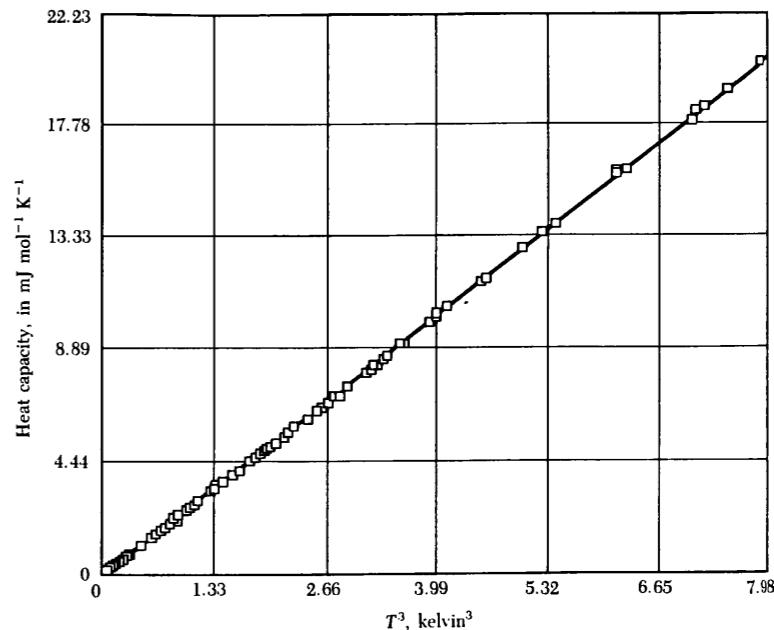


Figure 9 Low temperature heat capacity of solid argon, plotted against T^3 . In this temperature region the experimental results are in excellent agreement with the Debye T^3 law with $\theta = 92.0$ K. (Courtesy of L. Finegold and N. E. Phillips.)

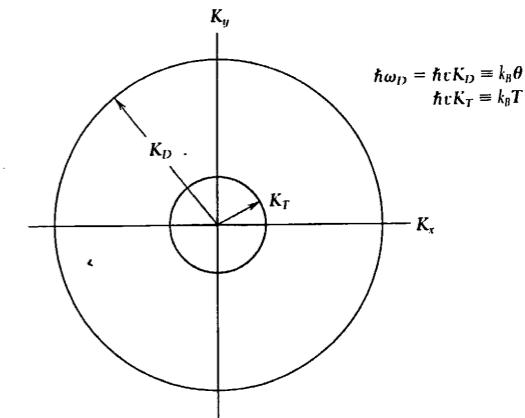


Figure 10 To obtain a qualitative explanation of the Debye T^3 law, we suppose that all phonon modes of wavevector less than K_T have the classical thermal energy $k_B T$ and that modes between K_T and the Debye cutoff K_D are not excited at all. Of the $3N$ possible modes, the fraction excited is $(K_T/K_D)^3 = (T/\theta)^3$, because this is the ratio of the volume of the inner sphere to the outer sphere. The energy is $U \approx k_B T \cdot 3N(T/\theta)^3$, and the heat capacity is $C_V = \partial U / \partial T \approx 12Nk_B(T/\theta)^3$.

Table 1 Debye temperature and thermal conductivity^a

Li	Be	Debye temperature and thermal conductivity											
		Low temperature limit of θ , in Kelvin											
		Thermal conductivity at 300 K, in $\text{W cm}^{-1}\text{K}^{-1}$											
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge
91	230	360.	420	380	630	410	470	445	450	343	327	320	374
1.02	0.16	0.22	0.31	0.94	0.94	0.08	0.80	1.00	0.91	4.01	1.16	0.41	0.60
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn w
56	147	280	291	275	450	1.38	0.51	1.17	1.50	480	274	225	209
0.58	0.17	0.23	0.54	0.51	0.51	0.72	0.72	0.72	0.72	0.97	4.29	0.97	0.82
Cs	Ba	La β	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb
38	110	142	252	240	400	430	500	420	240	165	71.9	78.5	105
0.36	0.14	0.23	0.58	1.74	0.48	0.48	0.88	1.47	0.72	0.72	3.17	0.46	0.35
Fr	Ra	Ac	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er
			0.11	0.12	0.16		0.13		0.11	0.11	0.11	0.14	0.17
Th	Pa	U		Np	Pu	Am		Cm	Bk	Cf	Es	Fm	Md
			163		207	0.28	0.06	0.07					
			0.54										

^aMost of the θ values were supplied by N. Pearlman; references are given the A.I.P. Handbook, 3rd ed.; the thermal conductivity values are from R. W. Powell and Y. S. Touloukian, Science 181, 999 (1973).

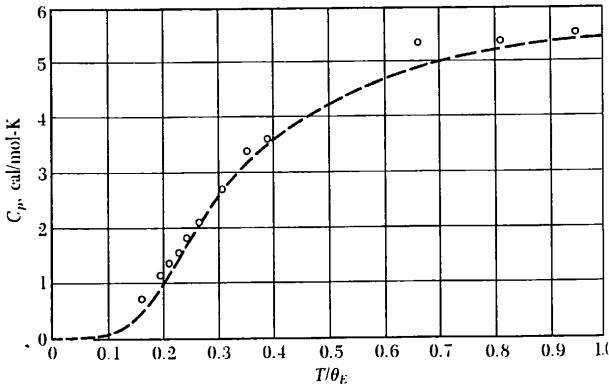


Figure 11 Comparison of experimental values of the heat capacity of diamond with values calculated on the Einstein model, using the characteristic temperature $\theta_E = \hbar\omega/k_B = 1320$ K. To convert to J/mol-deg, multiply by 4.186.

with ω now written in place of ω_0 , for convenience.

The heat capacity of the oscillators is

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V = N k_B \left(\frac{\hbar\omega}{\tau} \right)^2 \frac{e^{\hbar\omega/\tau}}{(e^{\hbar\omega/\tau} - 1)^2}, \quad (34)$$

as plotted in Fig. 11. This expresses the Einstein result for the contribution of N identical oscillators to the heat capacity of a solid.

In three dimensions N is replaced by $3N$. The high temperature limit of C_V becomes $3Nk_B$, which is known as the Dulong and Petit value.

At low temperatures (34) decreases as $\exp(-\hbar\omega/\tau)$, whereas the experimental form of the phonon contribution is known to be T^3 as accounted for by the Debye model treated above. The Einstein model is often used to approximate the optical phonon part of the phonon spectrum.

General Result for $D(\omega)$

We want to find a general expression for $D(\omega)$, the number of states per unit frequency range, given the phonon dispersion relation $\omega(\mathbf{k})$. The number of allowed values of \mathbf{k} for which the phonon frequency is between ω and $\omega + d\omega$ is

$$D(\omega) d\omega = \left(\frac{L}{2\pi} \right)^3 \int_{\text{shell}} d^3 K, \quad (35)$$

where the integral is extended over the volume of the shell in \mathbf{k} space bounded by the two surfaces on which the phonon frequency is constant, one surface on which the frequency is ω and the other on which the frequency is $\omega + d\omega$.

The real problem is to evaluate the volume of this shell. We let dS_ω denote an element of area (Fig. 12) on the surface in \mathbf{k} space of the selected constant

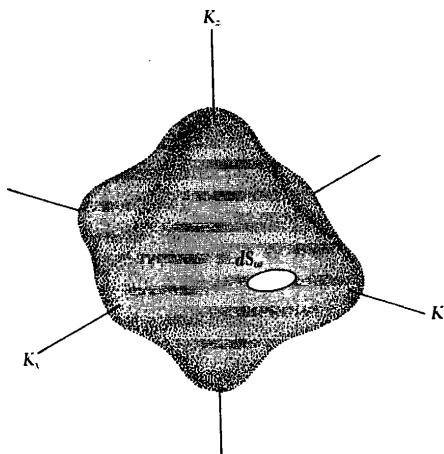


Figure 12 Element of area dS_ω on a constant frequency surface in \mathbf{K} space. The volume between two surfaces of constant frequency at ω and $\omega + d\omega$ is equal to $\int dS_\omega d\omega / |\nabla_{\mathbf{K}}\omega|$.

frequency ω . The element of volume between the constant frequency surfaces ω and $\omega + d\omega$ is a right cylinder of base dS_ω and altitude dK_\perp , so that

$$\int_{\text{shell}} d^3K = \int dS_\omega dK_\perp. \quad (36)$$

Here dK_\perp is the perpendicular distance (Fig. 13) between the surface ω constant and the surface $\omega + d\omega$ constant. The value of dK_\perp will vary from one point to another on the surface.

The gradient of ω , which is $\nabla_{\mathbf{K}}\omega$, is also normal to the surface ω constant, and the quantity

$$|\nabla_{\mathbf{K}}\omega| dK_\perp = d\omega,$$

is the difference in frequency between the two surfaces connected by dK_\perp . Thus the element of the volume is

$$dS_\omega dK_\perp = dS_\omega \frac{d\omega}{|\nabla_{\mathbf{K}}\omega|} = dS_\omega \frac{d\omega}{v_g},$$

where $v_g = |\nabla_{\mathbf{K}}\omega|$ is the magnitude of the group velocity of a phonon. For (35) we have

$$D(\omega) d\omega = \left(\frac{L}{2\pi} \right)^3 \int \frac{dS_\omega}{v_g} d\omega.$$

We divide both sides by $d\omega$ and write $V = L^3$ for the volume of the crystal: the result for the density of states is

$$D(\omega) = \frac{V}{(2\pi)^3} \int \frac{dS_\omega}{v_g}. \quad (37)$$

Figure 13 The quantity dK_\perp is the perpendicular distance between two constant frequency surfaces in \mathbf{K} space, one at frequency ω and the other at frequency $\omega + d\omega$.

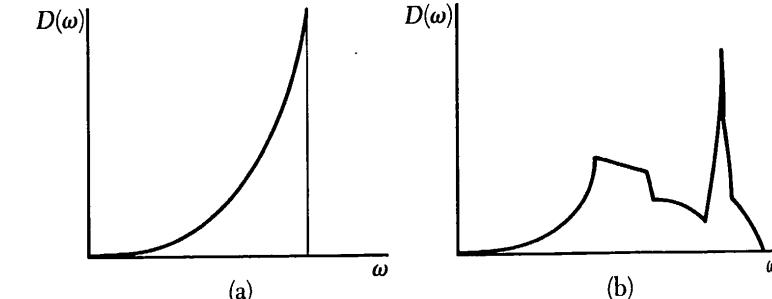
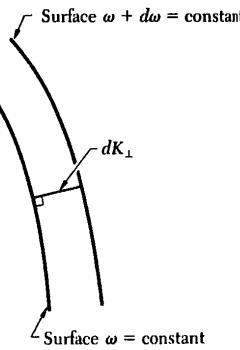


Figure 14 Density of states as a function of frequency for (a) the Debye solid and (b) an actual crystal structure. The spectrum for the crystal starts as ω^2 for small ω , but discontinuities develop at singular points.

The integral is taken over the area of the surface ω constant, in \mathbf{K} space. The result refers to a single branch of the dispersion relation. We can use this result also in electron band theory.

There is a special interest in the contribution to $D(\omega)$ from points at which the group velocity is zero. Such critical points produce singularities (known as Van Hove singularities) in the distribution function (Fig. 14).

ANHARMONIC CRYSTAL INTERACTIONS

The theory of lattice vibrations discussed thus far has been limited in the potential energy to terms quadratic in the interatomic displacements. This is the harmonic theory; among its consequences are:

- Two lattice waves do not interact; a single wave does not decay or change form with time.
- There is no thermal expansion.
- Adiabatic and isothermal elastic constants are equal.
- The elastic constants are independent of pressure and temperature.
- The heat capacity becomes constant at high temperatures $T > \theta$.

In real crystals none of these consequences is satisfied accurately. The deviations may be attributed to the neglect of anharmonic (higher than quadratic) terms in the interatomic displacements. We discuss some of the simpler aspects of anharmonic effects.

Beautiful demonstrations of anharmonic effects are the experiments on the interaction of two phonons to produce a third phonon at a frequency $\omega_3 = \omega_1 + \omega_2$. Shiren described an experiment in which a beam of longitudinal phonons of frequency 9.20 GHz interacts in an MgO crystal with a parallel beam of longitudinal phonons at 9.18 GHz. The interaction of the two beams produced a third beam of longitudinal phonons at $9.20 + 9.18 = 18.38$ GHz.

Three-phonon processes are caused by third-order terms in the lattice potential energy. A typical term might be $U_3 = Ae_{xx}e_{yy}e_{zz}$, where the e 's are strain components and A is a constant. The A 's have the same dimensions as elastic stiffness constants but may have values perhaps an order of magnitude larger. The physics of the phonon interaction can be stated simply: the presence of one phonon causes a periodic elastic strain which (through the anharmonic interaction) modulates in space and time the elastic constant of the crystal. A second phonon perceives the modulation of the elastic constant and thereupon is scattered to produce a third phonon, just as from a moving three-dimensional grating.

Thermal Expansion

We may understand thermal expansion by considering for a classical oscillator the effect of anharmonic terms in the potential energy on the mean separation of a pair of atoms at a temperature T . We take the potential energy of the atoms at a displacement x from their equilibrium separation at absolute zero as

$$U(x) = cx^2 - gx^3 - fx^4, \quad (38)$$

with c , g , and f all positive. The term in x^3 represents the asymmetry of the mutual repulsion of the atoms and the term in x^4 represents the softening of the vibration at large amplitudes. The minimum at $x = 0$ is not an absolute minimum, but for small oscillations the form is an adequate representation of an interatomic potential.

We calculate the average displacement by using the Boltzmann distribution function, which weights the possible values of x according to their thermodynamic probability:

$$\langle x \rangle = \frac{\int_{-\infty}^{\infty} dx x \exp[-\beta U(x)]}{\int_{-\infty}^{\infty} dx \exp[-\beta U(x)]},$$

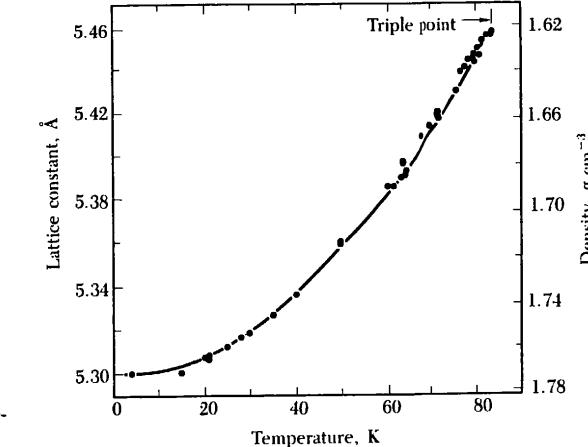


Figure 15 Lattice constant of solid argon as a function of temperature.

with $\beta \equiv 1/k_B T$. For displacements such that the anharmonic terms in the energy are small in comparison with $k_B T$, we may expand the integrands as
 $\int dx x \exp(-\beta U) \approx \int dx \exp(-\beta cx^2)(x + \beta gx^4 + \beta fx^5) = (3\pi^{1/2}/4)(g/c^{5/2})\beta^{-3/2};$
 $\int dx \exp(-\beta U) \approx \int dx \exp(-\beta cx^2) = (\pi/\beta c)^{1/2}, \quad (39)$

whence the thermal expansion is

$$\langle x \rangle = \frac{3g}{4c^2} k_B T \quad (40)$$

in the classical region. Note that in (39) we have left cx^2 in the exponential, but we have expanded $\exp(\beta gx^3 + \beta fx^4) \approx 1 + \beta gx^3 + \beta fx^4 + \dots$

Measurements of the lattice constant of solid argon are shown in Fig. 15. The slope of the curve is proportional to the thermal expansion coefficient. The expansion coefficient vanishes as $T \rightarrow 0$, as we expect from Problem 5. In lowest order the thermal expansion does not involve the symmetric term fx^4 in $U(x)$, but only the antisymmetric term gx^3 .

THERMAL CONDUCTIVITY

The thermal conductivity coefficient K of a solid is defined with respect to the steady-state flow of heat down a long rod with a temperature gradient dT/dx :

$$j_U = -K \frac{dT}{dx}, \quad (41)$$

where j_U is the flux of thermal energy, or the energy transmitted across unit area per unit time.

This form implies that the process of thermal energy transfer is a random process. The energy does not simply enter one end of the specimen and proceed directly in a straight path to the other end, but diffuses through the specimen, suffering frequent collisions. If the energy were propagated directly through the specimen without deflection, then the expression for the thermal flux would not depend on the temperature gradient, but only on the difference in temperature ΔT between the ends of the specimen, regardless of the length of the specimen. The random nature of the conductivity process brings the temperature gradient and, as we shall see, a mean free path into the expression for the thermal flux.

From the kinetic theory of gases we find below in a certain approximation the following expression for the thermal conductivity:

$$K = \frac{1}{3} C v \ell , \quad (42)$$

where C is the heat capacity per unit volume, v is the average particle velocity, and ℓ is the mean free path of a particle between collisions. This result was applied first by Debye to describe thermal conductivity in dielectric solids, with C as the heat capacity of the phonons, v the phonon velocity, and ℓ the phonon mean free path. Several representative values of the mean free path are given in Table 2.

We give the elementary kinetic theory which leads to (42). The flux of particles in the x direction is $\frac{1}{2}n\langle|v_x|\rangle$, where n is the concentration of molecules; in equilibrium there is a flux of equal magnitude in the opposite direction. The $\langle \dots \rangle$ denote average value.

If c is the heat capacity of a particle, then in moving from a region at local temperature $T + \Delta T$ to a region at local temperature T a particle will give up energy $c \Delta T$. Now ΔT between the ends of a free path of the particle is given by

$$\Delta T = \frac{dT}{dx} \ell_x = \frac{dT}{dx} v_x \tau ,$$

where τ is the average time between collisions.

The net flux of energy (from both senses of the particle flux) is therefore

$$j_U = -n\langle v_x^2 \rangle c \tau \frac{dT}{dx} = -\frac{1}{3}n\langle v^2 \rangle c \tau \frac{dT}{dx} . \quad (43)$$

If, as for phonons, v is constant, we may write (43) as

$$j_U = -\frac{1}{3}Cv\ell \frac{dT}{dx} , \quad (44)$$

with $\ell \equiv v\tau$ and $C \equiv nc$. Thus $K = \frac{1}{3}Cv\ell$.

Table 2 Phonon mean free paths

[Calculated from (44), taking $v = 5 \times 10^5$ cm/sec as a representative sound velocity. The ℓ 's obtained in this way refer to umklapp processes.]

Crystal	$T, ^\circ\text{C}$	$C, \text{in } \text{J cm}^{-3}\text{deg}^{-1}$	$K, \text{in } \text{W cm}^{-1}\text{deg}^{-1}$	$\ell, \text{in } \text{\AA}$
Quartz ^a	0	2.00	0.13	40
	-190	0.55	0.50	540
NaCl	0	1.88	0.07	23
	-190	1.00	0.27	100

^a Parallel to optic axis.

Thermal Resistivity of Phonon Gas

The phonon mean free path ℓ is determined principally by two processes, geometrical scattering and scattering by other phonons. If the forces between atoms were purely harmonic, there would be no mechanism for collisions between different phonons, and the mean free path would be limited solely by collisions of a phonon with the crystal boundary, and by lattice imperfections. There are situations where these effects are dominant.

With anharmonic lattice interactions, there is a coupling between different phonons which limits the value of the mean free path. The exact states of the anharmonic system are no longer like pure phonons.

The theory of the effect of anharmonic coupling on thermal resistivity predicts that ℓ is proportional to $1/T$ at high temperatures,² in agreement with many experiments. We can understand this dependence in terms of the number of phonons with which a given phonon can interact: at high temperature the total number of excited phonons is proportional to T . The collision frequency of a given phonon should be proportional to the number of phonons with which it can collide, whence $\ell \propto 1/T$.

To define a thermal conductivity there must exist mechanisms in the crystal whereby the distribution of phonons may be brought locally into thermal equilibrium. Without such mechanisms we may not speak of the phonons at one end of the crystal as being in thermal equilibrium at a temperature T_2 and those at the other end in equilibrium at T_1 .

It is not sufficient to have only a way of limiting the mean free path, but there must also be a way of establishing a local thermal equilibrium distribution of phonons. Phonon collisions with a static imperfection or a crystal boundary

²See J. M. Ziman, *Electrons and phonons*, Oxford, 1960; R. Berman, "Heat conductivity of non-metallic crystals," *Contemp. Phys.* 14, 101 (1973).

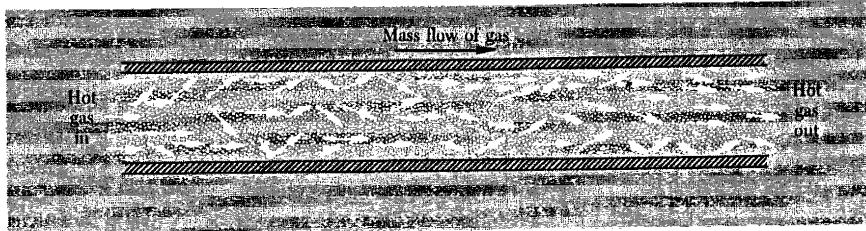


Figure 16a Flow of gas molecules in a state of drifting equilibrium down a long open tube with frictionless walls. Elastic collision processes among the gas molecules do not change the momentum or energy flux of the gas because in each collision the velocity of the center of mass of the colliding particles and their energy remain unchanged. Thus energy is transported from left to right without being driven by a temperature gradient. Therefore the thermal resistivity is zero and the thermal conductivity is infinite.

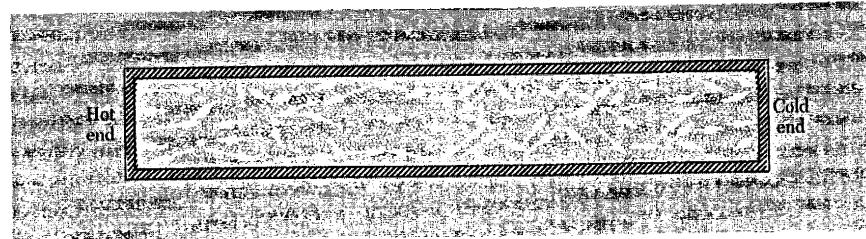


Figure 16b The usual definition of thermal conductivity in a gas refers to a situation where no mass flow is permitted. Here the tube is closed at both ends, preventing the escape or entrance of molecules. With a temperature gradient the colliding pairs with above-average center of mass velocities will tend to be directed to the right, those with below-average velocities will tend to be directed to the left. A slight concentration gradient, high on the right, will be set up to enable the net mass transport to be zero while allowing a net energy transport from the hot to the cold end.

will not by themselves establish thermal equilibrium, because such collisions do not change the energy of individual phonons: the frequency ω_2 of the scattered phonon is equal to the frequency ω_1 of the incident phonon.

It is rather remarkable also that a three-phonon collision process

$$\mathbf{K}_1 + \mathbf{K}_2 = \mathbf{K}_3 \quad (45)$$

will not establish equilibrium, but for a subtle reason: the total momentum of the phonon gas is not changed by such a collision. An equilibrium distribution of phonons at a temperature T can move down the crystal with a drift velocity which is not disturbed by three-phonon collisions of the form (45). For such collisions the phonon momentum

$$\mathbf{J} = \sum_{\mathbf{K}} n_{\mathbf{K}} \hbar \mathbf{K} \quad (46)$$

is conserved, because on collision the change in \mathbf{J} is $\mathbf{K}_3 - \mathbf{K}_2 - \mathbf{K}_1 = 0$. Here $n_{\mathbf{K}}$ is the number of phonons having wavevector \mathbf{K} .

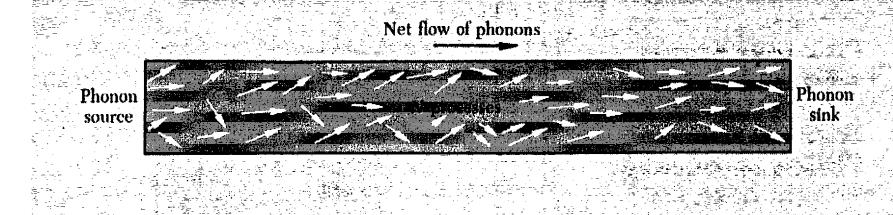


Figure 16c In a crystal we may arrange to create phonons chiefly at one end, as by illuminating the left end with a lamp. From that end there will be a net flux of phonons toward the right end of the crystal. If only N processes ($\mathbf{K}_1 + \mathbf{K}_2 = \mathbf{K}_3$) occur, the phonon flux is unchanged in momentum on collision and some phonon flux will persist down the length of the crystal. On arrival of phonons at the right end we can arrange in principle to convert most of their energy to radiation, thereby creating a sink for the phonons. Just as in (a) the thermal resistivity is zero.

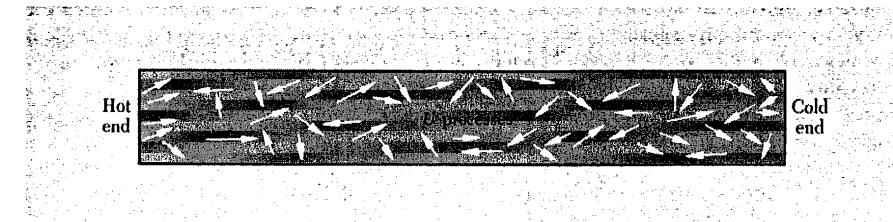


Figure 16d In U processes there is a large net change in phonon momentum in each collision event. An initial net phonon flux will rapidly decay as we move to the right. The ends may act as sources and sinks. Net energy transport under a temperature gradient occurs as in (b).

For a distribution with $\mathbf{J} \neq 0$, collisions such as (45) are incapable of establishing complete thermal equilibrium because they leave \mathbf{J} unchanged. If we start a distribution of hot phonons down a rod with $\mathbf{J} \neq 0$, the distribution will propagate down the rod with \mathbf{J} unchanged. Therefore there is no thermal resistance. The problem as illustrated in Fig. 16 is like that of the collisions between molecules of a gas in a straight tube with frictionless walls.

Umklapp Processes

The important three-phonon processes that cause thermal resistivity are not of the form $\mathbf{K}_1 + \mathbf{K}_2 = \mathbf{K}_3$ in which \mathbf{K} is conserved, but are of the form

$$\mathbf{K}_1 + \mathbf{K}_2 = \mathbf{K}_3 + \mathbf{G}, \quad (47)$$

where \mathbf{G} is a reciprocal lattice vector (Fig. 17). These processes, discovered by Peierls, are called **umklapp processes**. We recall that \mathbf{G} may occur in all momentum conservation laws in crystals.

We have seen examples of wave interaction processes in crystals for which the total wavevector change need not be zero, but may be a reciprocal lattice

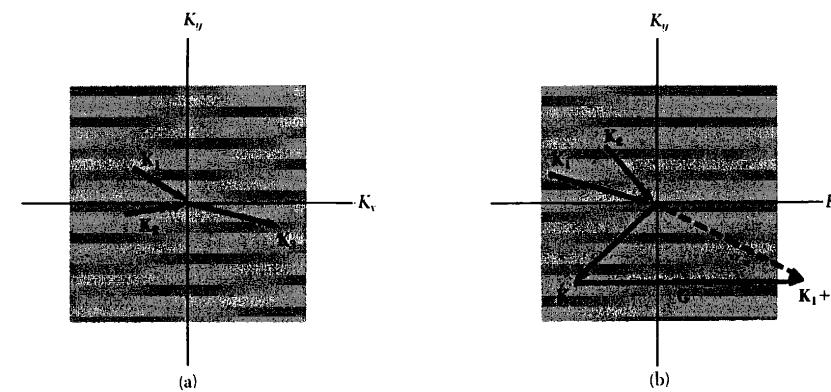


Figure 17 (a) Normal $\mathbf{K}_1 + \mathbf{K}_2 = \mathbf{K}_3$ and (b) umklapp $\mathbf{K}_1 + \mathbf{K}_2 = \mathbf{K}_3 + \mathbf{G}$ phonon collision processes in a two-dimensional square lattice. The square in each figure represents the first Brillouin zone in the phonon \mathbf{K} space; this zone contains all the possible independent values of the phonon wavevector. Vectors \mathbf{K} with arrowheads at the center of the zone represent phonons absorbed in the collision process; those with arrowheads away from the center of the zone represent phonons emitted in the collision. We see in (b) that in the umklapp process the direction of the x -component of the phonon flux has been reversed. The reciprocal lattice vector \mathbf{G} as shown is of length $2\pi/a$, where a is the lattice constant of the crystal lattice, and is parallel to the K_x axis. For all processes, N or U , energy must be conserved, so that $\omega_1 + \omega_2 = \omega_3$.

vector. Such processes are always possible in periodic lattices. The argument is particularly strong for phonons: the only meaningful phonon \mathbf{K} 's lie in the first Brillouin zone, so that any longer \mathbf{K} produced in a collision must be brought back into the first zone by addition of a \mathbf{G} . A collision of two phonons both with a negative value of K_x can by an umklapp process ($G \neq 0$) create a phonon with positive K_x . Umklapp processes are also called U processes.

Collisions in which $\mathbf{G} = 0$ are called **normal processes** or N processes. At high temperatures $T > \theta$ all phonon modes are excited because $k_B T > \hbar\omega_{\max}$. A substantial proportion of all phonon collisions will then be U processes, with the attendant high momentum change in the collision. In this regime we can estimate the thermal resistivity without particular distinction between N and U processes; by the earlier argument about nonlinear effects we expect to find a lattice thermal resistivity $\propto T$ at high temperatures.

The energy of phonons $\mathbf{K}_1, \mathbf{K}_2$ suitable for umklapp to occur is of the order of $\frac{1}{2}k_B\theta$, because each of the phonons 1 and 2 must have wavevectors of the order of $\frac{1}{2}\mathbf{G}$ in order for the collision (47) to be possible. If both phonons have low K , and therefore low energy, there is no way to get from their collision a phonon of wavevector outside the first zone. The umklapp process must conserve energy, just as for the normal process. At low temperatures the number of suitable phonons of the high energy $\frac{1}{2}k_B\theta$ required may be expected to vary roughly as $\exp(-\theta/2T)$, according to the Boltzmann factor. The exponential form is in good agreement with experiment. In summary, the phonon mean

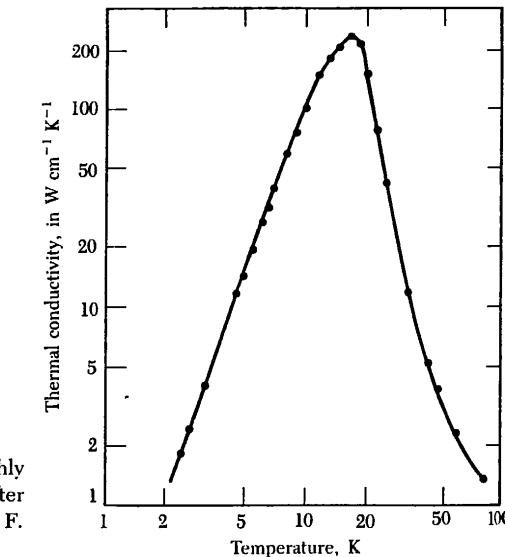


Figure 18 Thermal conductivity of a highly purified crystal of sodium fluoride, after H. E. Jackson, C. T. Walker, and T. F. McNelly.

free path which enters (42) is the mean free path for umklapp collisions between phonons and not for all collisions between phonons.

Imperfections

Geometrical effects may also be important in limiting the mean free path. We must consider scattering by crystal boundaries, the distribution of isotopic masses in natural chemical elements, chemical impurities, lattice imperfections, and amorphous structures.

When at low temperatures the mean free path ℓ becomes comparable with the width of the test specimen, the value of ℓ is limited by the width, and the thermal conductivity becomes a function of the dimensions of the specimen. This effect was discovered by de Haas and Biermasz.^a The abrupt decrease in thermal conductivity of pure crystals at low temperatures is caused by the size effect.

At low temperatures the umklapp process becomes ineffective in limiting the thermal conductivity, and the size effect becomes dominant, as shown in Fig. 18. One would expect then that the phonon mean free path would be constant and of the order of the diameter D of the specimen, so that

$$K \approx CvD . \quad (48)$$

The only temperature-dependent term on the right is C , the heat capacity, which varies as T^3 at low temperatures. We expect the thermal conductivity to vary as T^3 at low temperatures. The size effect enters whenever the phonon mean free path becomes comparable with the diameter of the specimen.

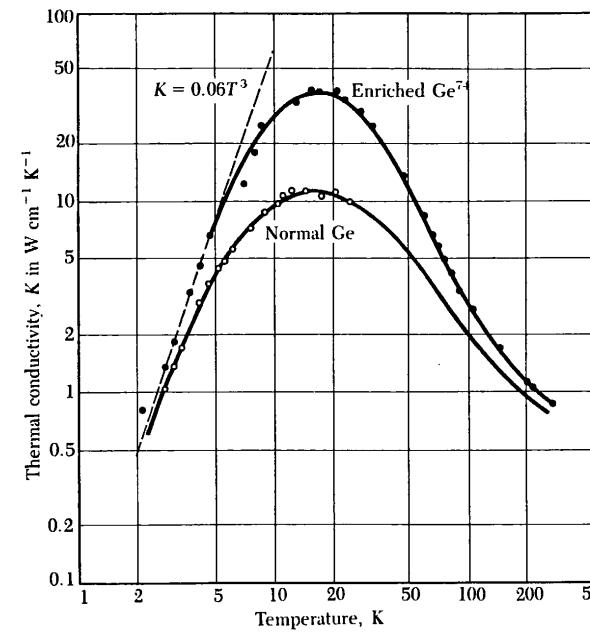


Figure 19 Isotope effect on thermal conduction in germanium, amounting to a factor of three at the conductivity maximum. The enriched specimen is 96 percent Ge⁷⁴; natural germanium is 20 percent Ge⁷⁰, 27 percent Ge⁷², 8 percent Ge⁷³, 37 percent Ge⁷⁴, and 8 percent Ge⁷⁶. Below 5 K the enriched specimen has $K = 0.060 T^3$, which agrees well with Casimir's theory for thermal resistance caused by boundary scattering. (After T. H. Geballe and G. W. Hull.)

Dielectric crystals may have thermal conductivities as high as metals. Synthetic sapphire (Al_2O_3) has one of the highest values of the conductivity: nearly $200 \text{ W cm}^{-1} \text{ K}^{-1}$ at 30 K. The maximum of the thermal conductivity in sapphire is greater than the maximum of $100 \text{ W cm}^{-1} \text{ K}^{-1}$ in copper. Metallic gallium, however, has a conductivity of $845 \text{ W cm}^{-1} \text{ K}^{-1}$ at 1.8 K. The electronic contribution to the thermal conductivity of metals is treated in Chapter 6.

In an otherwise perfect crystal the distribution of isotopes of the chemical elements often provides an important mechanism for phonon scattering. The random distribution of isotopes disturbs the periodicity of the density as seen by an elastic wave. In some substances scattering of phonons by isotopes is comparable in importance to scattering by other phonons. Results for germanium are shown in Fig. 19.

Problems

- 1. Singularity in density of states.** (a) From the dispersion relation derived in Chapter 4 for a monatomic linear lattice of N atoms with nearest neighbor interactions, show that the density of modes is

$$D(\omega) = \frac{2N}{\pi} \cdot \frac{1}{(\omega_m^2 - \omega^2)^{1/2}},$$

where ω_m is the maximum frequency. (b) Suppose that an optical phonon branch has the form $\omega(K) = \omega_0 - AK^2$, near $K = 0$ in three dimensions. Show that $D(\omega) = (L/2\pi)^3(2\pi/A^{3/2})(\omega_0 - \omega)^{1/2}$ for $\omega < \omega_0$ and $D(\omega) = 0$ for $\omega > \omega_0$. Here the density of modes is discontinuous.

- 2. Rms thermal dilation of crystal cell.** (a) Estimate for 300 K the root mean square thermal dilation $\Delta V/V$ for a primitive cell of sodium. Take the bulk modulus as $7 \times 10^{10} \text{ erg cm}^{-3}$. Note that the Debye temperature 158 K is less than 300 K, so that the thermal energy is of the order of $k_B T$. (b) Use this result to estimate the root mean square thermal fluctuation $\Delta a/a$ of the lattice parameter.

- 3. Zero point lattice displacement and strain.** (a) In the Debye approximation, show that the mean square displacement of an atom at absolute zero is $\langle R^2 \rangle = 3\hbar\omega_D^2/8\pi^2pv^3$, where v is the velocity of sound. Start from the result (4.29) summed over the independent lattice modes: $\langle R^2 \rangle = (\hbar/2\rho V)\sum\omega^{-1}$. We have included a factor of $\frac{1}{2}$ to go from square amplitude to square displacement. (b) Show that $\sum\omega^{-1}$ and $\langle R^2 \rangle$ diverge for a one-dimensional lattice, but that the mean square strain is finite. Consider $\langle (\partial R/\partial x)^2 \rangle = \frac{1}{2}\sum K^2 u_0^2$ as the mean square strain, and show that it is equal to $\hbar\omega_D^2 L/4\pi MNv^3$ for a line of N atoms each of mass M , counting longitudinal modes only. The divergence of R^2 is not significant for any physical measurement.

- 4. Heat capacity of layer lattice.** (a) Consider a dielectric crystal made up of layers of atoms, with rigid coupling between layers so that the motion of the atoms is restricted to the plane of the layer. Show that the phonon heat capacity in the Debye approximation in the low temperature limit is proportional to T^2 . (b) Suppose instead, as in many layer structures, that adjacent layers are very weakly bound to each other. What form would you expect the phonon heat capacity to approach at extremely low temperatures?

- *5. Grüneisen constant.** (a) Show that the free energy of a phonon mode of frequency ω is $k_B T \ln [2 \sinh (\hbar\omega/2k_B T)]$. It is necessary to retain the zero-point energy $\frac{1}{2}\hbar\omega$ to obtain this result. (b) If Δ is the fractional volume change, then the free energy of the crystal may be written as

$$F(\Delta, T) = \frac{1}{2}B\Delta^2 + k_B T \sum \ln [2 \sinh (\hbar\omega_K/2k_B T)],$$

where B is the bulk modulus. Assume that the volume dependence of ω_K is $\delta\omega/\omega = -\gamma\Delta$, where γ is known as the Grüneisen constant. If γ is taken as independent of the

*This problem is somewhat difficult.