

Contents

Preface xi

Chapter 1	<i>Historical Development</i>	3
1.	Energy Quantization and Heat Capacities	4
2.	Blackbody Radiation	18
3.	Photons	22
4.	Spectra and Energy Quantization of Atoms	23
5.	Matter Waves	26
6.	Schrödinger's Equation	30
7.	Remarks on Motion in One Dimension	41
8.	Probability Interpretation	48
9.	Cold Fusion*	52
10.	Momentum	60
11.	Expectation Values and the Momentum Operator	70
12.	Many-Particle Systems	73
	<i>Problems</i>	82
Chapter 2	<i>Wave Mechanics</i>	91
13.	Linear Space of Wave Functions	91
14.	Principles of Quantum Mechanics	104

viii Contents

15. Parity	115
16. Linear Momentum	120
17. Orbital Angular Momentum	123
18. Single Particle in a Central Potential	139
19. Particle in an Electromagnetic Field*	146
<i>Problems</i>	159
Chapter 3 <i>Abstract Linear Space of State Vectors</i>	175
20. Bras, Kets, and Brackets	175
21. Principles of Quantum Mechanics	188
22. Recovering Wave Mechanics	192
23. Spin	196
24. Single Spin 1/2 System	204
25. Two Spin 1/2 Particles	214
<i>Problems</i>	223
Chapter 4 <i>Measurement Theory</i>	231
26. Quantum Measurement Theory	232
27. “Paradoxes” of Quantum Physics	242
28. Hidden Variables	252
29. Summary	255
Chapter 5 <i>Perturbation Theory</i>	259
30. Time-Independent Perturbation Theory	259
31. Zeeman Effect	264
32. Quadratic Stark Effect	266
33. Degenerate Perturbation Theory	271
34. Hyperfine Structure in Atomic Hydrogen	273
35. Time-Dependent Perturbation Theory	283
36. Induced Transitions between the Hyperfine Levels in Atomic Hydrogen	288

37. Spontaneous Transitions between the Hyperfine Levels in Atomic Hydrogen	291
<i>Problems</i>	304
Chapter 6 <i>Atomic and Molecular Structure</i>	323
38. Energy Variational Principle	323
39. The Ground State of Helium	326
40. The Lowest Excited States of Helium	329
41. Pauli Exclusion Principle	333
42. Lithium	337
43. Beryllium to Carbon*	343
44. Molecular Hydrogen	347
<i>Problems</i>	351
Chapter 7 <i>Scattering Theory</i>	359
45. Scattering Amplitude and Scattering Cross Section	360
46. Optical Theorem*	366
47. Born Approximation	369
48. Rutherford Scattering Cross Section	375
49. Partial Wave Expansion	377
50. Phase Shifts and Cross Sections	380
51. Resonant <i>s</i> -Wave Scattering	387
<i>Problems</i>	393
Chapter 8 <i>Dirac Theory of the Electron</i>	401
52. Electron Spin, Magnetic Dipole Moment, and Spin-Orbit Coupling*	401
Index	417

HISTORICAL DEVELOPMENT

The story of how people hit on the highly nonintuitive world picture of quantum mechanics, in which the physical state of a system is represented by an element in an abstract linear space and its observable properties by operators in the space, is fascinating and exceedingly complicated. The theory could not have been deduced from experiment, for the elements of the linear space are in principle not observable. It is also true that the theory did not arise from one person's great insight, as happened in Einstein's discovery of general relativity theory. The much greater change from the classical world picture of Newtonian mechanics and general relativity to the quantum world picture came in many steps taken by many people, often against the better judgment of participants.

The goal of this chapter is to show how classical physicists could have hit on wave mechanics. The strategy is to select topics that still are (or ought to be) part of the fundamental lore of any modern physicist. There are three major elements in the story. The first is the experimental evidence that the energy of an isolated system can only assume special discrete or quantized values. The second is the idea that the energy is proportional to the frequency of a wave function associated with the system. (This is the famous de Broglie relation $E = h\nu$, for energy E and frequency ν). The third is the connection between the de Broglie relation and energy quantization through the mathematical result that a wave equation with fixed boundary conditions allows only discrete quantized values of the frequency of oscillation of the wave function (as in the fundamental and harmonics of the vibration of a violin string). Some substantial computations are presented in this chapter, but the physics is introduced piecemeal, as needed. The principles of wave mechanics are collected in the next chapter, and are generalized to an abstract linear space in chapter 3.

1 Energy Quantization and Heat Capacities

The Boltzmann Distribution

Consider an object—an atom, molecule, rock—in a mechanically stable state and well isolated from its surroundings. In classical or quantum theory the object has a definite energy, E , that is conserved. Also, if the object consists of several weakly coupled parts E is the sum of the energies of the parts. In classical mechanics, E can assume any value from some minimum to the maximum allowed by stability. In quantum theory the possible values of the energy are discrete, or quantized,

$$E = E_i, \quad i = 0, 1, 2, \dots, \quad (1.1)$$

with E_0 the ground state energy, E_1 the energy in the first excited state, and so on. This remarkable quantization concept first appeared in 1900, in Planck's derivation of the blackbody radiation spectrum, as described in section 2. We will consider first the relevance of energy quantization to heat capacities of material objects, because the analysis is a little less lengthy.

To describe what happens when an object is heated to a given temperature T , let us imagine we have a statistical ensemble of $M \gg 1$ mechanically identical copies of the object, each of which has been placed in contact with a heat reservoir at temperature T , allowed to come to equilibrium, and then isolated. The reservoir is a macroscopic body much larger than the object. The ensemble might literally be a collection of objects, such as a large number of nearly free atoms, or we can think of the ensemble as representing one almost isolated object that is sampled at widely separated times.

The accidents of interaction of each object with the enormous number of atoms in the reservoir determine the probability distribution of final energies of the objects in the ensemble. Let N_i be the number of the M objects that are found to be in the i^{th} energy level. Then in the limit $M \rightarrow \infty$ the probability of finding that a randomly chosen object from the ensemble is in level i is defined to

$$P_i = N_i/M. \quad (1.2)$$

The value of M is required to suppress sampling fluctuations. If the ensemble represents one object sampled at many different times, P_i is

the probability that the object observed at a randomly chosen time is found to be in level i .

It will be assumed that the probability P_i in equation (1.2) depends only on the temperature T of the reservoir and on the energy E_i of the object (or more generally on the conserved quantities, which could include particle number), so at fixed temperature T the probability P_i is some function of energy,

$$P_i = F(E_i). \quad (1.3)$$

This assumption is justified below, in section 26 on measurement theory. For now the problem is to find the function $F(E_i)$.

Suppose the object consists of two weakly interacting parts, 1 and 2, so the allowed values of the energy of the object are of the form

$$E_i = E_a^1 + E_b^2, \quad (1.4)$$

for all combinations a, b of energy levels E_a^1 of part 1 and E_b^2 of part 2. The probability that part 1 is found to have energy E_a^1 is $P_a^1 = F(E_a^1)$, and part 2 has energy E_b^2 with probability $P_b^2 = F(E_b^2)$. Since the two parts are not interacting, the probability that one part has a given energy cannot depend on what the energy of the other part happens to be, that is, the parts are statistically independent. Since probabilities for independent events multiply, the probability that the object that consists of the two parts is in the energy level E_i in equation (1.4) is

$$P_i = P_a^1 P_b^2. \quad (1.5)$$

By equation (1.3) this is

$$F(E_a^1 + E_b^2) = F(E_a^1)F(E_b^2). \quad (1.6)$$

Since this equation is supposed to hold whatever the energies, we can write it as

$$F(E_a + E_b) = F(E_a)F(E_b), \quad (1.7)$$

for any values of E_a and E_b .

If it is not obvious that the solution to the functional equation (1.7) is an exponential, take the logarithm and differentiate with respect to E_a or E_b :

$$\frac{d}{dE_a} \log F(E) = \frac{1}{F(E)} \frac{dF}{dE} = \frac{1}{F(E_a)} \frac{dF}{dE_a} = \frac{1}{F(E_b)} \frac{dF}{dE_b} = -\beta, \quad (1.8)$$

6 Chapter 1

where $E = E_a + E_b$. Here and always the natural logarithm is written as $\log F$. The first step follows from the chain rule in calculus. The second step follows from equation (1.7), and the third step follows by differentiating with respect to E_b instead of E_a . The final step is to define the expression to be equal to the negative of β , the minus sign being chosen to make the solution (eq. [1.9]) look sensible.

We see from the third part of equation (1.8) that β cannot depend on E_b , and from the fourth part that it cannot depend on E_a . That means β is a constant. The solution to equation (1.8) therefore is

$$P = F(E) \propto e^{-\beta E}. \quad (1.9)$$

With β positive, the probability P in equations (1.3) and (1.9) approaches zero at $E \rightarrow \infty$, as is reasonable.

We will define the temperature T of the reservoir by the equation

$$\beta = \frac{1}{kT}, \quad (1.10)$$

where Boltzmann's constant is

$$k = 1.38 \times 10^{-16} \text{ erg deg}^{-1}, \quad (1.11)$$

and the temperature is measured in degrees Kelvin. (Recall that zero degrees Centigrade is 273°K .) This has the reasonable feature that the higher the temperature the higher the probable values of the energy. Equation (1.10) is equivalent to the more formal definition of temperature in statistical mechanics.

The definition of temperature in equation (1.10) brings equation (1.9) to

$$P \propto e^{-E/kT}. \quad (1.12)$$

This is the Boltzmann probability distribution for the energy E of an object prepared by allowing it to relax to thermal equilibrium with a heat reservoir at temperature T .

The normalization condition on the Boltzmann distribution is that the probabilities summed over all possible values of the energy have to add to unity:

$$\sum_i P_i = 1. \quad (1.13)$$

A useful symbol for expressing the normalization is the partition function,

$$Z = \sum_i e^{-\beta E_i} = \sum_i e^{-E_i/kT}, \quad (1.14)$$

in terms of which the form of the normalized Boltzmann distribution is

$$P_i = \frac{e^{-E_i/kT}}{Z}. \quad (1.15)$$

The mean thermal energy of the object is the result of averaging the energies across the ensemble. Thus, if N_i of the M objects in the ensemble have energy E_i , the arithmetic mean value or expectation value of the energies of the objects is

$$\langle E \rangle = U = \frac{\sum_i E_i N_i}{M}. \quad (1.16)$$

With $P_i = N_i/M$ (eq. [1.2]), the average is

$$U = \sum_i E_i P_i. \quad (1.17)$$

For the Boltzmann distribution (1.15), this is

$$U = \frac{\sum E_i e^{-\beta E_i}}{\sum e^{-\beta E_i}}, \quad (1.18)$$

where β always means $1/kT$ (eq. [1.10]). Finally, using the partition function (1.14), we can write this expression for the average energy in the handy form

$$U = -\frac{d}{d\beta} \log Z. \quad (1.19)$$

Here and always \log means the natural logarithm.

The Thermal Energy of a Simple Harmonic Oscillator

The Hamiltonian (the expression for the total energy) of a one-dimensional simple harmonic oscillator with displacement variable $x(t)$ is

$$H = \frac{p^2}{2m} + \frac{Kx^2}{2}, \quad (1.20)$$
$$\omega = 2\pi\nu = (K/m)^{1/2}.$$

8 Chapter 1

The momentum is $p = m\dot{x} = m dx/dt$, with m the mass, so the kinetic energy is $p^2/2m$. The spring constant is K , and the potential energy is $Kx^2/2$. As is readily checked, the natural frequency of the oscillator is $\omega = (K/m)^{1/2}$ (units of radians per second) or $\nu = \omega/(2\pi)$ (units of cycles per second = Hertz).

As discussed in the next section and in section 37, an electromagnetic radiation field can be described as a set of simple harmonic oscillators, one for each mode of oscillation. In working through the theory of thermal blackbody radiation, Planck introduced the constraint, as an intermediate step in the calculation, that the energy of each oscillator is only allowed to assume the discrete values

$$E_n = nh\nu = n\hbar\omega, \quad n = 0, 1, 2, \dots \quad (1.21)$$

(We will use h and $\hbar \equiv h/2\pi$, as convenient.) Planck's sensible plan was to take the limit $h \rightarrow 0$ at the end of the calculation, but he noticed that the predicted blackbody spectrum would agree with the measurements if instead he took h to be a nonzero constant,

$$\hbar = \frac{h}{2\pi} = 1.05457 \times 10^{-27} \text{ erg s.} \quad (1.22)$$

The value quoted here is the modern result. The only other improvement to the energy spectrum (allowed values of the energy) of a simple harmonic oscillator is to replace the integers n with $n + 1/2$. The additive constant of course does not affect a heat capacity (which is the rate of change of mean energy with temperature).

Einstein proposed that Planck's quantization rule might apply to a material oscillator such as an atom oscillating about its equilibrium position in a solid. Let us see how that would affect the heat capacity.

With Planck's quantization rule (1.21), the partition function (eq. [1.14]) for a one-dimensional simple harmonic oscillator is

$$Z = \sum_0^{\infty} e^{-nh\nu/kT} = \sum A^n, \quad (1.23)$$

with $A = e^{-h\nu/kT} = e^{-\beta h\nu}$. The trick for evaluating this sum is to note that we can write it

$$\begin{aligned} Z &= 1 + A + A^2 + A^3 + \dots \\ &= 1 + A[1 + A + A^2 + \dots] \\ &= 1 + AZ. \end{aligned} \quad (1.24)$$

Thus we see that the sum is

$$Z = \frac{1}{1 - A} = \frac{1}{1 - e^{-\beta h\nu}} = \frac{1}{1 - e^{-h\nu/kT}}. \quad (1.25)$$

Equation (1.19) gives the mean thermal energy,

$$U = \frac{d}{d\beta} \log(1 - e^{-\beta h\nu}). \quad (1.26)$$

On differentiating this expression out we get

$$U = \frac{h\nu}{e^{h\nu/kT} - 1}. \quad (1.27)$$

This is the wanted expression for the mean thermal energy of a one-dimensional simple harmonic oscillator with natural frequency ν at temperature T .

The classical limit is obtained at high temperature, $kT \gg h\nu$. When $h\nu/kT$ is small, the Taylor series expansion of the exponential in equation (1.27), keeping only the first nontrivial term, is

$$e^{h\nu/kT} \sim 1 + \frac{h\nu}{kT}. \quad (1.28)$$

This brings equation (1.27) to

$$U = kT. \quad (1.29)$$

The heat capacity in this limit is $C = dU/dT = k$. This is a special case of the classical energy equipartition theorem. The theorem says that for every quadratic term in position or momentum in the Hamiltonian there is a contribution $kT/2$ to the mean thermal energy of the system. There are two quadratic terms in equation (1.20), giving a net value of kT , which checks equation (1.29). Of course, a reasonable quantum theory must agree with classical physics in the high energy limit where we know classical physics works.

In the opposite low temperature limit, $kT \ll h\nu$, the mean energy in equation (1.27) is suppressed by the exponential in the denominator, as is the heat capacity. That is, Planck's energy quantization assumption in equation (1.21) leads to a characteristic temperature $T_c = h\nu/k$ for an oscillator with natural frequency ν . If the temperature is much

larger than T_c the energy quantization is scarcely noticeable, and we see classical behavior. If the temperature is well below T_c the situation is decidedly nonclassical: the oscillator is forced to the ground state that has the minimum allowed value of the energy. As discussed next, a similar effect applies to the kinetic energy of tumbling of a molecule in a gas.

Heat Capacity of Molecular Hydrogen

From the energy equipartition theorem of classical statistical mechanics we would have expected that the mean thermal energy of a gas of N hydrogen molecules is

$$\begin{aligned} U = & \frac{1}{2} NkT [3 \text{ (for the kinetic energy of translation in 3 dimensions)} \\ & + 2 \text{ (for rotation of the axis in two directions)} \\ & + 2 \text{ (for vibration along the axis)} \\ & + 1 \text{ (for rotation about the axis)}], \end{aligned} \tag{1.30}$$

plus maybe more for vibrations of the internal structures of the individual atoms.

At $T \lesssim 100$ K the measured heat capacity is $dU/dT \sim 3Nk/2$, so the hydrogen molecules act like a gas of pointlike particles, the only energy being the kinetic energy of translation. Following the discussion of the simple harmonic oscillator, we conclude that the energy levels corresponding to the kinetic energy of translation are close together compared to kT at $T \sim 100$ K, so classical energy equipartition applies to the motions of the molecules, and that the energy levels corresponding to the other modes of motion in equation (1.30) are more broadly separated, so these modes are not appreciably excited at $T \sim 100$ K.

At $T \sim 200$ to 400 K the heat capacity of molecular hydrogen gas is close to $dU/dT \sim 5Nk/2$, which is that of a classical gas of rigid dumbbells (the first two lines of eq. [1.30]). This means the energy of the first rotationally excited state of the molecule exceeds that of the ground state by the amount

$$E_1 - E_0 \sim kT_R, \quad T_R \sim 200 \text{ K.} \tag{1.31}$$

The allowed values of angular momentum in quantum mechanics will be computed in section 17. A useful order of magnitude approximation is Bohr's assumption, that the rotationally excited states are spaced at increments of angular momentum equal to \hbar . (This is discussed in section 4 below.) Let us check that these numbers make sense.

If the hydrogen molecule has angular momentum \hbar in the first rotationally excited state, and the moment of inertia of the molecule is I , then the kinetic energy of rotation in this state is

$$U_R = \frac{\hbar^2}{2I} \sim kT_R, \quad (1.32)$$

with $T_R \sim 200K$. The first equation is the classical expression for kinetic energy of rotation. The second equation with equation (1.11) for k and (1.22) for \hbar gives $I \sim 2 \times 10^{-41} \text{ g cm}^2$. We are only interested in checking the orders of magnitude, so let us approximate the moment of inertia of the molecule as $I \sim m_p r^2$, where

$$m_p = 1.67 \times 10^{-24} \text{ g} \quad (1.33)$$

is the proton mass and r is the separation of the two protons in the molecule. That gives $r \sim 3 \times 10^{-9} \text{ cm} = 0.3 \text{ \AA}$. The size of a hydrogen atom is set by the Bohr radius (eq. [4.9] below). Our result is about half a Bohr radius, reasonably close considering the rough approximations.

At $T \sim 2000 \text{ K}$ the heat capacity approaches that of a classical gas of dumbbells each of which can vibrate in length. This means the first vibrationally excited state of the molecule has energy roughly an order of magnitude above the first rotationally excited state. At $T \sim 3000 \text{ K}$ the gas dissociates into atomic hydrogen.

Einstein and Debye Solids

A solid stores energy in the vibrations of the atoms about their equilibrium positions. In the simplest approximation, which Einstein considered, each atom vibrates with the same frequency, ν , in each of three dimensions, so a solid containing N atoms can be thought of as $3N$ one-dimensional simple harmonic oscillators. The thermal energy of the solid is then, by equation (1.27),

$$U = \frac{3N\hbar\nu}{e^{\hbar\nu/kT} - 1}. \quad (1.34)$$

The high temperature limit is $U = 3NkT$, as in equations (1.28) and (1.29), so the heat capacity at high temperature is the classical energy equipartition expression

$$C = \frac{\partial U}{\partial T} = 3Nk. \quad (1.35)$$

By 1900 it was known that equation (1.35) is a good approximation to the heat capacities of solids at room temperature (this is the empirical law of Dulong and Petit), but Nernst had found that the heat capacity drops well below this value at low temperature, approaching zero at $T \rightarrow 0$. Einstein (1907) showed how the energy quantization assumption allows us to understand the decrease of heat capacity at low temperature: the heat capacity in equation (1.34) is strongly suppressed at $T \ll h\nu/k$.

Though the Einstein model gives the right qualitative picture, it says the heat capacity goes to zero at low temperature much faster than the measurements. It is easy to see why. When an atom moves it can bring its neighbors with it. This lowers the restoring force, which greatly lowers the frequency. That is, a solid acts like a collection of oscillators with a wide range of different frequencies. The lower frequency modes of oscillation are thermally excited at lower temperatures, so the heat capacity varies more slowly with temperature than it would if all the frequencies were the same. The Debye model to be discussed next approximates the low frequency modes of vibration of the solid as sound or pressure waves. The computation is lengthy but worth knowing, because it is used not only here but in the theory of blackbody radiation (section 2) and radiative transitions (section 37).

The low frequency modes that can be excited at low temperatures have long wavelengths and so are not much affected by the fact that the mass is in discrete lumps, in the atoms. For these long wavelength modes it is a good approximation to treat the solid as a continuous fluid, with smoothly varying mass density $\rho(\mathbf{r}, t)$ and velocity $\mathbf{v}(\mathbf{r}, t)$.

The mass and velocity functions obey two equations that express mass conservation and momentum conservation. The former is

$$\frac{\partial \rho}{\partial t} + \nabla \cdot \rho \mathbf{v} = 0, \quad (1.36)$$

while Newton's law $\mathbf{F} = m\mathbf{a}$ generalizes for a fluid to

$$\frac{\partial \mathbf{v}}{\partial t} + (\mathbf{v} \cdot \nabla) \mathbf{v} = -\nabla P / \rho. \quad (1.37)$$

The pressure is P , and $-\nabla P$ is the pressure force per unit volume. This force per unit volume divided by the mass per unit volume is the acceleration of a given fluid element. On the left-hand side of equation (1.37), $\partial \mathbf{v} / \partial t$ is the rate of change of the fluid velocity at a fixed point, and the second term converts this to the rate of change of velocity of a fixed fluid element. This combination is called the convective derivative. We see the same combination in the mass conservation equation (1.36) if we rewrite it as

$$\frac{\partial \rho}{\partial t} + \mathbf{v} \cdot \nabla \rho = -\rho \nabla \cdot \mathbf{v}. \quad (1.38)$$

Gauss's law can be used to rewrite the mass conservation equation as

$$\begin{aligned} \frac{dM}{dt} &= \frac{d}{dt} \int dV \rho = \int dV \frac{\partial \rho}{\partial t} = - \int dV \nabla \cdot \rho \mathbf{v} \\ &= - \oint dA \mathbf{n} \cdot \rho \mathbf{v}. \end{aligned} \quad (1.39)$$

The last integral is over a fixed surface that contains mass M . The last line says the time rate of change of M is fixed by the surface integral of the mass flux,

$$\mathbf{F} = \rho \mathbf{v}, \quad (1.40)$$

which is the rate at which mass is flowing through the surface.

We are interested in low amplitude vibrations, for which \mathbf{v} is small and ρ close to homogeneous, so we will write the mass density as

$$\rho(\mathbf{r}, t) = \rho_o(1 + \delta(\mathbf{r}, t)), \quad (1.41)$$

where ρ_o is the constant mean value, and keep only terms of first order in the perturbations δ or \mathbf{v} . In this approximation, we can write the pressure as

$$P = P(\rho) = P_o + c_s^2 \rho_o \delta, \quad c_s^2 = \frac{dP}{d\rho}. \quad (1.42)$$

As indicated, we are assuming the pressure P is a single valued function of density alone. The function has been expanded in a Taylor series, keeping only the constant part at $\delta = 0$ and the first order correction. In this order in perturbation theory, where we drop terms of order δ^2 , $\mathbf{v}\delta$, and v^2 , equations (1.37) and (1.38) become

$$\begin{aligned} \frac{\partial \delta}{\partial t} &= -\nabla \cdot \mathbf{v}, \\ \frac{\partial \mathbf{v}}{\partial t} &= -c_s^2 \nabla \delta. \end{aligned} \quad (1.43)$$

We can eliminate the velocity by taking the time derivative of the first equation and the divergence of the second, and exchanging order of differentiation. The result is

$$\frac{\partial^2 \delta}{\partial t^2} = c_s^2 \nabla^2 \delta. \quad (1.44)$$

To see why equation (1.44) is called a wave equation note that, as is readily checked, a solution is

$$\delta = F(x - c_s t), \quad (1.45)$$

where F is a differentiable function of the single variable $w = x - c_s t$, and x is the position along the x axis in a cartesian coordinate system. This solution represents a pressure wave moving without change of shape at the speed of sound, c_s , in the x direction.

The allowed frequencies of sound waves in an isolated solid depend on its shape. To simplify things, let us consider a cube of the solid with volume V , side $L = V^{1/3}$. The surface will be assumed to be free, meaning that the pressure at the surface vanishes. Therefore the constant P_o in equation (1.42) has to vanish, and δ has to vanish at the surface. A set of solutions of the wave equation that satisfy this boundary condition is

$$\delta = A \cos(\omega t - \phi) \sin(k_x x) \sin(k_y y) \sin(k_z z), \quad (1.46)$$

where A and ϕ are constants. This function satisfies the wave equation (1.44) if the frequency ω satisfies the relation

$$\omega = k c_s, \quad k^2 = k_x^2 + k_y^2 + k_z^2. \quad (1.47)$$

To assign the boundary condition $\delta = 0$, equation (1.46) places the sides of the cube at $x = 0$ and $x = L$; $y = 0$ and $y = L$; and $z = 0$ and $z = L$. Then we satisfy the boundary conditions if the constants k_x , k_y , and k_z are chosen so $k_x L$, $k_y L$, and $k_z L$ are integer multiples of π . We will write these conditions as

$$k_\alpha L = n_\alpha \pi, \quad n_\alpha = 0, 1, 2, \dots, \quad (1.48)$$

where the index $\alpha = 1, 2, 3$ refers to the x , y , and z components. (A word about notation: a vector may be specified by a boldface symbol,

as \mathbf{r} , or by its components, as $\mathbf{r} = (x, y, z)$, or by the index notation r_α with $r_1 = x$, $r_2 = y$, and $r_3 = z$.)

Equations (1.46) to (1.48) describe the normal modes of pressure oscillations of the solid in the fluid model, which we have noted is a good approximation at low temperatures where only the low frequency long wavelength modes are excited. (In a normal mode each mass element vibrates with the same frequency, as in eq. [1.46]. The word normal refers to the orthogonality relations discussed in section 12.) Since each mode behaves as a simple harmonic oscillator, we will follow Planck and Einstein in assuming that the allowed values of the energy of each mode are quantized, $E = h\nu = \hbar\omega$, where ω is the classical frequency of vibration of the mode (eq. [1.21]). (This assumption is justified in section 12 below.) Then at temperature T the mean thermal energy of the solid is given by equation (1.27):

$$U = \sum_{n_\alpha \geq 0} \frac{\hbar\omega_{\mathbf{n}}}{e^{\hbar\omega_{\mathbf{n}}/kT} - 1}. \quad (1.49)$$

The sum is over the triplets of nonnegative integers, with $\omega_{\mathbf{n}}$ given by equations (1.47) and (1.48),

$$\omega_{\mathbf{n}} = \frac{\pi c_s}{L} (n_x^2 + n_y^2 + n_z^2)^{1/2}. \quad (1.50)$$

The sum in equation (1.49) can be approximated by an integral, as follows. Let us write the change in k_α in equation (1.48) when n_α is incremented by unity, to $n_\alpha + 1$, as

$$\Delta k_\alpha = \frac{\pi}{L}. \quad (1.51)$$

Then we can write the sum over n_α as

$$\sum_{n_\alpha} = \frac{L}{\pi} \sum \Delta k_\alpha \sim \frac{L}{\pi} \int_0^\infty dk_\alpha. \quad (1.52)$$

The last step is a good approximation if the temperature is not exceedingly low, so that the sum extends to large n_α before the exponential in the denominator in equation (1.49) becomes large. In this case the fractional increment in k_α on each increment of n_α is small, so the sum is well approximated as an integral.

In three dimensions, equation (1.52) generalizes to

$$\sum = \frac{L^3}{\pi^3} \int_{k_\alpha > 0} d^3k. \quad (1.53)$$

At this point it is convenient to introduce new and even simpler boundary conditions. If the thermal energy is dominated by modes with wavelengths much shorter than the size of the solid, the heat capacity cannot depend on the shape of the object—we just have to specify some shape in order to fix definite boundary conditions for the wave equation. Mathematically convenient boundary conditions are that the solid fills a space periodic in a cube of width L , volume $V = L^3$, so the point (x, y, z) is the same as the point $(x + L, y, z)$ and so on for the other three directions. We can write solutions to the wave equation that satisfy these periodic boundary conditions as the real part of

$$\delta \propto e^{i\mathbf{k}\cdot\mathbf{r}-\omega t}, \quad \omega = kc_s. \quad (1.54)$$

The periodic boundary condition is that δ cannot change if x is shifted to $x + L$, so the propagation vector \mathbf{k} has to satisfy

$$k_\alpha = \frac{2\pi n_\alpha}{L} \quad \text{or} \quad \mathbf{k} = \frac{2\pi \mathbf{n}}{L}. \quad (1.55)$$

Here \mathbf{n} means the triplet of integers n_α of either sign,

$$n_\alpha = 0, \pm 1, \pm 2, \dots \quad (1.56)$$

Note that in the standing wave solution in equation (1.46) negative and positive integers (which means negative and positive k_α) are physically equivalent, the only difference being a change of sign which can be absorbed in the phase ϕ . Equation (1.54) represents a running wave, so a change of sign of n_α means a change in the direction the wave is running, which is a physical difference. Thus here we must sum over all eight octants of \mathbf{n} , while the sum in equation (1.53) is over the first octant only. A second difference is that here the increment in k_α for a unit increment of n_α is, by equation (1.55),

$$\Delta k_\alpha = \frac{2\pi}{L}, \quad (1.57)$$

twice the value in equation (1.51). Thus with periodic boundary conditions the sum over modes is approximated as the integral

$$\sum_{\mathbf{n}} = \frac{V}{(2\pi)^3} \int d^3k. \quad (1.58)$$

The integral is over all octants, 8 times the volume of the integral over the first octant in equation (1.53). This cancels the extra factor 2^3 in the denominator in equation (1.58).

Collecting equations (1.49) and (1.58), we see that the thermal energy of the solid is

$$U = \frac{V}{(2\pi)^3} \int d^3k \frac{\hbar\omega}{e^{\hbar\omega/kT} - 1}. \quad (1.59)$$

Because of the appearance of the factor V from the conversion of the sum to an integral, this equation says the energy per unit volume, U/V , is independent of the volume of the solid, which makes sense.

Since the integrand in equation (1.59) depends only on the magnitude of \mathbf{k} , we can write the volume element as $d^3k = 4\pi k^2 dk$. Then with $\omega = kc_s$ (eq. [1.54]) and the change of variables

$$y = \frac{\hbar\omega}{kT}, \quad (1.60)$$

(and taking care not to confuse Boltzmann's constant and the magnitude of the propagation vector) we get

$$U = \frac{V(kT)^4}{2\pi^2(\hbar c_s)^3} \int_0^\infty \frac{y^3 dy}{e^y - 1}. \quad (1.61)$$

The dimensionless integral is

$$\int_0^\infty \frac{y^3 dy}{e^y - 1} = \frac{\pi^4}{15}. \quad (1.62)$$

The final step is to note that energy can be stored also in shear waves, of which there are two for every pressure wave (shear in the two orthogonal directions perpendicular to the propagation vector \mathbf{k}), so we should multiply U by three and replace c_s with a mean velocity c_o

suitably averaged over pressure and shear modes. This gives the Debye equation,

$$\frac{U}{V} = \frac{\pi^2}{10} \frac{(kT)^4}{(\hbar c_0)^3}. \quad (1.63)$$

It will be recalled that this equation applies at low temperature where only long wavelength modes are excited. It gives a good approximation to the low temperature heat capacity of many solids. In others there are significant additional contributions, such as from thermal motions of electrons.

2 Blackbody Radiation

What Was Known in 1900

Consider a black cavity with walls at temperature T and a small hole to let us sample the radiation it contains. “Black” means that any light that enters the hole from outside is absorbed; any radiation coming out was emitted by the walls. At thermal equilibrium, the radiation energy with frequency in the range ω to $\omega + d\omega$ found in the volume element dV in the cavity is

$$du = u_\omega dV d\omega. \quad (2.1)$$

As indicated, the energy has to be proportional to the size dV of the volume element and to the bandwidth $d\omega$. The constant of proportionality, u_ω , is the spectral energy density, the energy per unit volume and unit bandwidth.

The second law of thermodynamics says u_ω can only depend on ω and on the wall temperature, T , independent of the nature of the wall. For we can imagine connecting two cavities made of different materials at the same temperature by a light pipe that passes only frequencies in the range ω to $\omega + d\omega$. If the radiation energy densities were different in the two cavities, we would find that heat is moving spontaneously from one reservoir to another at the same temperature, which alas is forbidden by the second law.

The net energy density is

$$u = \int_0^\infty u_\omega d\omega = aT^4. \quad (2.2)$$

This T^4 law was found empirically by Stefan (1879) and derived (apart from the value of Stefan's constant, a) by Boltzmann (1884) from thermodynamics.

A Quick Review of Electromagnetism

As a first step in the derivation of u_ω , let us write down Maxwell's equations. We will use Gaussian cgs units, where the electric and magnetic fields satisfy

$$\begin{aligned}\nabla \cdot \mathbf{E} &= 4\pi\rho, & \nabla \cdot \mathbf{B} &= 0, \\ \nabla \times \mathbf{E} + \frac{1}{c} \frac{\partial \mathbf{B}}{\partial t} &= 0, & (2.3) \\ \nabla \times \mathbf{B} - \frac{1}{c} \frac{\partial \mathbf{E}}{\partial t} &= \frac{4\pi}{c} \mathbf{j}.\end{aligned}$$

The charge density is ρ , and the charge conservation equation is

$$\frac{\partial \rho}{\partial t} + \nabla \cdot \mathbf{j} = 0, \quad (2.4)$$

where \mathbf{j} is the current density. This can be compared to equation (1.36) for mass conservation. The force on a charge q moving at velocity \mathbf{v} is

$$\mathbf{F} = q (\mathbf{E} + \mathbf{v} \times \mathbf{B}/c). \quad (2.5)$$

The charge is measured in electrostatic units, where the static electric field at position \mathbf{r} relative to a point charge q is

$$\mathbf{E} = \frac{q\mathbf{r}}{r^3}. \quad (2.6)$$

The electric and magnetic fields have the same units; for \mathbf{B} the unit is called a Gauss. The velocity of light is c .

To get the electromagnetic wave equation we need the identity

$$\mathbf{A} \times (\mathbf{B} \times \mathbf{C}) = \mathbf{B}(\mathbf{A} \cdot \mathbf{C}) - \mathbf{C}(\mathbf{A} \cdot \mathbf{B}). \quad (2.7)$$

This also applies to the gradient operator and a vector function of position, as long as we are careful not to change the order of differentiation. Thus we find from equation (2.7)

$$\nabla \times (\nabla \times \mathbf{E}) = \nabla(\nabla \cdot \mathbf{E}) - \nabla^2 \mathbf{E}. \quad (2.8)$$

In a pure radiation field there are no charges or currents: $\rho = 0$ and $\mathbf{j} = 0$. In this case the result of taking the curl of the third of Maxwell's equations (2.3), applying the identity (2.8), and then simplifying with the help of the other Maxwell equations is

$$\frac{\partial^2 \mathbf{E}}{\partial t^2} = c^2 \nabla^2 \mathbf{E}. \quad (2.9)$$

This is a wave equation for each component of the electric field, as in equation (1.44).

Just as for sound waves in a solid (eq. [1.54]), we can write a complete set of solutions to the vector wave equation (2.9) as the real part of

$$\mathbf{E} = \mathbf{E}_o e^{i\mathbf{k}\cdot\mathbf{r} - \omega t}, \quad (2.10)$$

where \mathbf{E}_o is a complex constant vector. This expression in the wave equation (2.9) gives the relation

$$\omega = kc. \quad (2.11)$$

To describe radiation in a cavity, let us adopt the periodic boundary conditions from the last section. Then the propagation vector \mathbf{k} has to satisfy (eq. [1.55])

$$k_\alpha = 2\pi n_\alpha / L, \quad n_\alpha = 0, \pm 1, \pm 2, \dots \quad (2.12)$$

There also is a transversality condition: on substituting equation (2.10) into the condition $\nabla \cdot \mathbf{E} = 0$ in the absence of charges we get

$$\mathbf{k} \cdot \mathbf{E}_o = 0. \quad (2.13)$$

This says the electric field \mathbf{E} has to be perpendicular to the direction \mathbf{k} of propagation of the wave.

It is left as an exercise to get the magnetic field \mathbf{B} in terms of \mathbf{E}_o and \mathbf{k} .

The Planck Spectrum

Planck's blackbody spectrum follows by the same procedure used in the last section to find the low temperature heat capacity of a solid. The increment of k_α per unit increment of the integer n_α is $dk_\alpha = 2\pi/L$

(eqs. [1.57], [2.12]), so the number of independent modes of oscillation of the electromagnetic field with wave number \mathbf{k} in the range d^3k is

$$dN = 2 \frac{V d^3k}{(2\pi)^3}. \quad (2.14)$$

This is a factor of two larger than in equation (1.58) because, by the transversality condition (2.13), there are two independent (orthogonal) directions for the electric field \mathbf{E} for given \mathbf{k} , so there are two independent modes of oscillation for given \mathbf{k} . Summing over directions gives $d^3k = 4\pi k^2 dk$. Using $k = \omega/c$ (eq. [2.11]), we find that the number of modes with frequency between ω and $\omega + d\omega$ is

$$dN = \frac{V \omega^2 d\omega}{\pi^2 c^3}. \quad (2.15)$$

On multiplying this by the mean energy per mode (eq. [1.27]), and dividing by the volume V , we arrive at the thermal energy per unit volume and per unit frequency interval,

$$u_\omega = \frac{du}{d\omega} = \frac{1}{\pi^2 c^3} \frac{\hbar \omega^3}{e^{\hbar\omega/kT} - 1}. \quad (2.16)$$

This is the Planck blackbody radiation spectrum.

In the classical limit, $\hbar\omega \ll kT$, we have as before $e^{\hbar\omega/kT} \sim 1 + \hbar\omega/kT$ (eq. [1.28]), so equation (2.16) becomes

$$u_\omega = \frac{kT\omega^2}{\pi^2 c^3}. \quad (2.17)$$

Planck's constant does not appear in this Rayleigh-Jeans law, as expected because the equation can be derived from classical statistical mechanics.

The net energy density is obtained by integrating equation (2.16) over all frequencies. On changing variables to $x = \hbar\omega/kT$ and using equation (1.62) we get

$$u = \int_0^\infty u_\omega d\omega = \frac{\pi^2 (kT)^4}{15 (\hbar c)^3}. \quad (2.18)$$

This is the Stefan-Boltzmann law. Using the measured values of Stefan's constant a , the frequency at the peak of the spectrum (2.16) at a given

temperature, and the velocity of light c , Planck could solve for Boltzmann's constant k and \hbar ; both were within 2 percent of the modern values.

Planck emphasized that, if his approach has any validity, \hbar ought to show up somewhere else in physics. Einstein gave the first two examples: heat capacities, as discussed in the last section, and the photoelectric effect to be discussed next.

3 Photons

Light shining on a metal knocks out electrons. Einstein (1905) proposed an interpretation of this effect based on Planck's prescription $E = n\hbar\omega$ (eq. [1.21]) for the energy of an oscillator. Planck's prescription indicates that light can only transfer energy in discrete units—photons, or quanta of the electromagnetic field—of amount $\hbar\omega$. If one of these units of energy is given to an electron in a metal, then the electron ought to leave the metal with energy

$$E \leq \hbar\omega - \Phi, \quad (3.1)$$

where Φ is the binding energy (the work required to pull an electron out of the metal). The inequality takes account of the fact that the electron may lose energy before reaching the surface. By 1917, Millikan had found that there is a linear relation between the maximum energy of the electrons released and the frequency of the incident light, consistent with equation (3.1), and had found that the slope \hbar of the relation agrees with Planck's value within the errors, again about 1 percent.

As discussed in chapter 8, the relativistic relation between the energy E of a particle, its momentum p , and its rest mass m is

$$E^2 = p^2c^2 + m^2c^4. \quad (3.2)$$

If the energy in light acts as discrete units, photons, perhaps the photons move as particles. Because these particles would have to move at the velocity of light, their rest mass would have to vanish, $m = 0$. The relativistic relation (3.2) indicates $E = pc$ for massless particles. Thus a photon with energy $E = \hbar\omega$ would be expected to have momentum

$$p = E/c = \hbar\omega/c. \quad (3.3)$$

Einstein was cautious about referring to the momentum of a photon; that it really has momentum in agreement with this equation was made clear by the Compton effect, that refers to the recoil of an electron that scatters a photon, as follows.

Imagine a photon of energy pc and momentum \mathbf{p} incident on an electron of mass m that initially is at rest. The net energy and momentum of the system are therefore $E = pc + mc^2$ and \mathbf{p} . If the photon scatters off the electron and leaves with momentum \mathbf{p}' , then to conserve momentum the electron must end up with momentum $\mathbf{P} = \mathbf{p} - \mathbf{p}'$. The final energy, which must be the same as the initial, is

$$E = pc + mc^2 = p'c + [(\mathbf{p} - \mathbf{p}')^2 c^2 + m^2 c^4]^{1/2}. \quad (3.4)$$

On subtracting $p'c$, squaring, and simplifying we get

$$p' = \frac{mcp}{mc + p - p \cos \theta}, \quad (3.5)$$

where θ is the angle between \mathbf{p} and \mathbf{p}' .

Using equation (3.3), we can write equation (3.5) as a relation between the initial and final frequencies ω and ω' of the photon,

$$\frac{1}{\omega'} = \frac{1}{\omega} + \frac{\hbar}{mc^2}(1 - \cos \theta). \quad (3.6)$$

Compton experimentally found this relation between the initial and final frequencies and the scattering angle, θ . This shows that light does scatter like a gas of massless particles, photons, with the usual relation (3.2) between energy and momentum.

4 Spectra and Energy Quantization of Atoms

The Combination Principle

A hot dilute gas of atoms or molecules emits light at sharply defined frequencies, ν_i . The set of values of these frequencies for a given material can be written as differences among a list of quantities called terms:

$$\nu_i = T_\alpha - T_\beta. \quad (4.1)$$

This provides a handy way to record the frequencies, because a list of terms gives a much longer list of term differences. But this combination principle also is telling us something about physics. If we multiply equation (4.1) by Planck's constant, we get

$$E_i = h\nu_i = h(T_\alpha - T_\beta). \quad (4.2)$$

Since $h\nu_i$ is the energy of the photon produced by the atom, this equation suggests the possible values of the energy of the atom are the discrete, or quantized, quantities $E_\alpha = hT_\alpha$. The atom would produce a photon with frequency ν_i when it makes a transition from the energy level α to the level β in equation (4.2). This is yet another example of energy quantization.

In atomic hydrogen, the terms have the particularly simple form

$$T_n = Rc/n^2, \quad n = 1, 2, 3, \dots, \quad (4.3)$$

where R is called the Rydberg constant. The frequencies corresponding to transitions from term $n > 2$ to term $n' = 2$ are the Balmer series,

$$\nu = Rc \left[\frac{1}{4} - \frac{1}{n^2} \right], \quad (4.4)$$

with $n = 3$ giving the prominent red line seen in the spectrum of atomic hydrogen. The next series to be discovered in atomic hydrogen were the Paschen series $n \rightarrow n' = 3$, in the infrared, and the Lyman series, $n \rightarrow n' = 1$, in the ultraviolet.

The Bohr Model

Equation (4.3) is so simple it ought to be understandable. Bohr found the first successful model. He started with the assumption that the angular momentum, L , of the electron in orbit around the proton in a hydrogen atom is quantized,

$$L = n\hbar, \quad n = 1, 2, 3, \dots \quad (4.5)$$

The original reasons for this assumption, adduced by Bohr and Ehrenfest, are not worth going into here.

Following Bohr, let us imagine the electron with charge $-e$ is moving in a circular orbit of radius a at speed v around a fixed proton in a hydrogen atom. (The proton is fixed because it is much more massive than the electron.) The proton has charge e . The balance of the electrostatic force of attraction of the electron to the proton and the acceleration of the electron moving in a circle is

$$\frac{e^2}{a^2} = \frac{mv^2}{a}, \quad (4.6)$$

where m is the mass of the electron. Bohr's condition (4.5) says the angular momentum of the electron

$$L = mav = n\hbar, \quad (4.7)$$

where n is a positive integer. The result of eliminating the velocity from these equations is

$$a = n^2 a_o, \quad (4.8)$$

where the Bohr radius is

$$a_o = \frac{\hbar^2}{me^2} = 5.3 \times 10^{-9} \text{ cm.} \quad (4.9)$$

The energy of the electron is the sum of its kinetic and potential energies,

$$E_n = \frac{mv^2}{2} - \frac{e^2}{a} = -\frac{e^2}{2a} = -\frac{e^4 m}{2\hbar^2 n^2}, \quad (4.10)$$

where the last steps follow from equations (4.6), (4.8), and (4.9).

We have argued that the energy $\Delta E = E_n - E_{n'}$ released in the transition of an atom from level n to level n' is given to a photon with frequency $\omega = \Delta E/\hbar$, so the frequencies of the radiation emitted by the atom are predicted from equation (4.10) to be

$$\omega = \frac{e^4 m}{2\hbar^3} \left(\frac{1}{(n')^2} - \frac{1}{n^2} \right). \quad (4.11)$$

With Planck's value for \hbar , Bohr found excellent agreement with the measured frequencies in the spectrum of atomic hydrogen. This was considered a great but certainly mysterious triumph.

5 Matter Waves

The de Broglie Relations

Since light, which clearly exhibits the properties of a wave (interference and all that), can also act like a gas of particles, as discussed in section 3, one might guess that material particles exhibit wave properties. The connection between the energy and momentum of a particle like an electron and the frequency and wavelength of the wave associated with the particle was introduced by de Broglie.

Let us begin with some definitions. Consider the plane wave function

$$\psi \propto e^{i\phi}, \quad \phi = \mathbf{k} \cdot \mathbf{r} - \omega t. \quad (5.1)$$

The propagation vector in this function is \mathbf{k} , the magnitude of \mathbf{k} is the wavenumber, and the angular frequency of the wave is ω . An example is the pressure wave discussed in section 1 (eq. [1.54]). We will assume here that ω depends on the magnitude of \mathbf{k} alone; the function $\omega = \omega(k)$ is called the dispersion relation.

As indicated in figure 5.1, the positions \mathbf{r} at which the phase ϕ at a fixed time t has a fixed value define a plane perpendicular to the propagation vector \mathbf{k} . (This is because a displacement of \mathbf{r} in a direction perpendicular to \mathbf{k} does not change the value of $\mathbf{k} \cdot \mathbf{r}$ in eq. [5.1]). The distance between planes with ϕ differing by 2π at a fixed instant of time is the wavelength,

$$\lambda = 2\pi/k. \quad (5.2)$$

A surface of fixed phase advances along the direction of \mathbf{k} at the phase velocity,

$$v_p = \omega/k, \quad (5.3)$$

as one sees by considering the displacement δr that would balance the time shift δt to hold ϕ in equation (5.1) constant.

We saw in section 2 that the dispersion relation for a photon is $\omega = kc$ (eq. [2.11]). According to the Planck relation (1.21), the photon has energy $E = \hbar\omega$, and equation (3.3) says the photon has momentum $p = E/c = \hbar\omega/c = \hbar k$. De Broglie proposed that electrons may exhibit the same wave-particle duality with the same de Broglie relations between

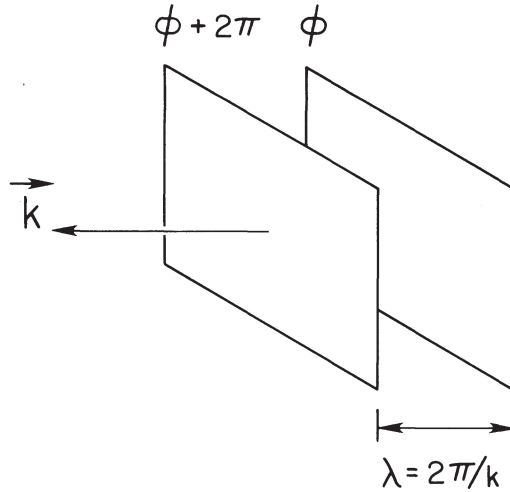


Fig. 5.1 The propagation vector for a plane wave is \mathbf{k} . The positions \mathbf{r} that lie in a plane of constant phase at a given instant of time satisfy $\mathbf{r} \cdot \mathbf{k} = \text{constant}$. The plane of constant phase is normal to the propagation vector \mathbf{k} . Two planes of constant phase with phase difference 2π are separated by the wavelength $\lambda = 2\pi/k$.

energy and frequency, and momentum and propagation vector,

$$\begin{aligned} E &= \hbar\omega, \\ \mathbf{p} &= \hbar\mathbf{k}. \end{aligned} \tag{5.4}$$

The wavelength (5.2) is then

$$\lambda = 2\pi/k = 2\pi\hbar/p = h/p. \tag{5.5}$$

This is equivalent to the second of the de Broglie relations (5.4).

The de Broglie momentum relation offers a way to understand the Bohr-Ehrenfest angular momentum condition in equation (4.5). Equation (4.6) refers to an electron moving around a circle of radius a . Imagine the electron is represented by a wave with wavelength $\lambda = h/p$ (eq. [5.5]) that runs around the circle. We want the wave to be continuous, so there has to be an integral number, n , of wavelengths around the circumference of the circle:

$$\text{circumference} = 2\pi a = n\lambda. \tag{5.6}$$

The de Broglie relation (5.5) thus says the angular momentum of the particle is

$$L = ap = ah/\lambda = nh/2\pi = n\hbar. \quad (5.7)$$

This is equation (4.5).

A nonrelativistic particle of mass m moving with momentum p has kinetic energy $E = p^2/2m$. Thus the dispersion relation derived from the de Broglie relations (5.4) is

$$\omega = \frac{E}{\hbar} = \frac{\hbar k^2}{2m}. \quad (5.8)$$

The phase velocity (eq. [5.3]) in this case is $v_p = \omega/k = \hbar k/2m = p/2m$. This differs from the usual relation between momentum and velocity by a factor of two. However, as we will now discuss, that is because we need another measure for the velocity.

Group Velocity of a Wave Packet

De Broglie assumed that the plane waves (5.1) can be superimposed (added together) to get more general wave functions, of the form

$$\psi(\mathbf{r}, t) = \int d^3k f(\mathbf{k}) e^{i\mathbf{k}\cdot\mathbf{r} - \omega(k)t}. \quad (5.9)$$

The factor $f(\mathbf{k})$ is the weight assigned to each plane wave. With periodic boundary conditions, the allowed values of \mathbf{k} are discrete, as discussed in section 1 (eq. [1.55]), so with periodic boundary conditions the integral (5.9) would be replaced with a sum.

Now let us choose the function $f(\mathbf{k})$ so ψ is a wave packet, which is to say ψ is fairly sharply peaked at one position. This is done by taking $f(\mathbf{k})$ to be bell-shaped, with its maximum at $\mathbf{k} = \mathbf{k}_o$, having a width Δk in all three directions, and with f rapidly approaching zero at $|\mathbf{k} - \mathbf{k}_o| > \Delta k$. To find the values of \mathbf{r} and t for which ψ is large, consider the phase

$$\phi = \mathbf{k} \cdot \mathbf{r} - \omega(k)t, \quad (5.10)$$

in the exponential in the integral in equation (5.9). For most choices of \mathbf{r} and t , the phase ϕ varies rapidly as \mathbf{k} varies over the range Δk around \mathbf{k}_o where f is appreciably large. This variation of ϕ makes $e^{i\phi}$ oscillate, and the oscillation makes the integral ψ small. But if ϕ as a function

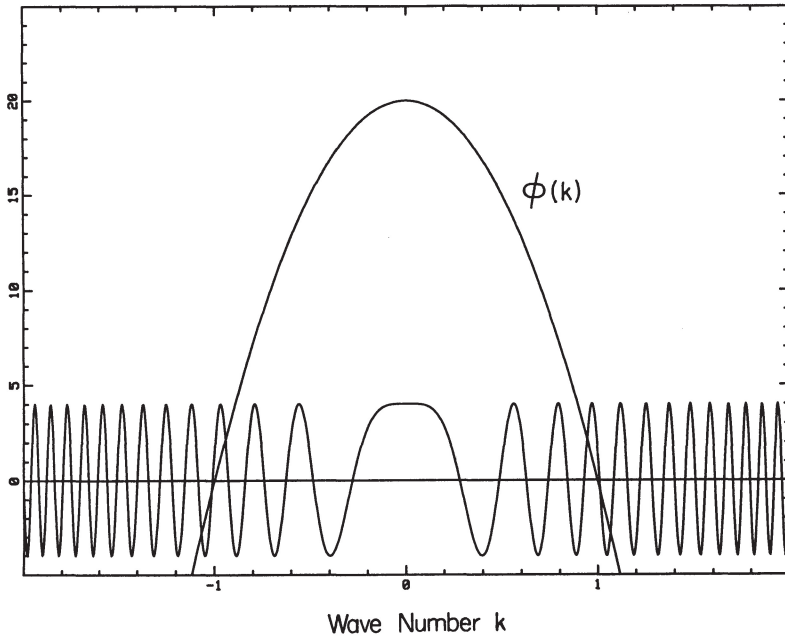


Fig. 5.2 Behavior of $e^{i\phi(k)}$ near an extremum of the function $\phi(k)$. The upper curve shows the parabola $\phi(k)$, in radians, as a function of wave number, k . The bottom curve shows the real part of $e^{i\phi(k)}$, in arbitrary units. This function oscillates rapidly except near the extremum of $\phi(k)$.

of \mathbf{k} happens to have an extremum at $\mathbf{k} = \mathbf{k}_o$, the oscillation of $e^{i\phi}$ near $\mathbf{k} = \mathbf{k}_o$ is suppressed, because ϕ varies only slowly with k near the extremum. This is illustrated in figure 5.2. When the oscillation of $e^{i\phi}$ is suppressed where $f(\mathbf{k})$ is large, the integral ψ is large.

The condition for a large value of $\psi(\mathbf{r}, t)$ is then that ϕ have an extremum at $\mathbf{k} \sim \mathbf{k}_o$. This means the first derivative of ϕ vanishes at $\mathbf{k} \sim \mathbf{k}_o$. Since we want ϕ to be an extremum with respect to variations of each component of \mathbf{k} , large ψ requires

$$\frac{\partial}{\partial k_\alpha} [\mathbf{k} \cdot \mathbf{r} - \omega(k)t] = 0 \quad \text{at} \quad \mathbf{k} = \mathbf{k}_o. \quad (5.11)$$

This is three equations, $\alpha = 1, 2, 3$ representing the three orthogonal components of \mathbf{k} . On differentiating out equation (5.11), we see that the peak of ψ is at

$$\mathbf{r} = \mathbf{v}_g t, \quad (5.12)$$

where the group velocity is

$$v_\alpha = \frac{\partial\omega}{\partial k_\alpha} = \frac{d\omega}{dk} \frac{\partial k}{\partial k_\alpha}. \quad (5.13)$$

The result of differentiating the expression $k^2 = \sum k_\beta^2$ with respect to the component k_α is

$$\frac{\partial k}{\partial k_\alpha} = \frac{k_\alpha}{k}. \quad (5.14)$$

This brings the group velocity (5.13) to

$$\mathbf{v}_g = \frac{d\omega}{dk} \frac{\mathbf{k}}{k}, \quad (5.15)$$

with $\mathbf{k} = \mathbf{k}_o$. The magnitude of this expression is

$$v_g = \frac{d\omega}{dk}. \quad (5.16)$$

The speed of motion of a wave packet thus is determined by the dispersion relation $\omega(k)$.

The group velocity (5.3) agrees with the phase velocity (5.16) if $\omega \propto k$, as in a pressure or electromagnetic wave (eq. [1.54]). For the nonrelativistic de Broglie dispersion relation in equation (5.8), the magnitude of the group velocity is

$$v_g = \frac{d\omega}{dk} = \frac{\hbar k}{m} = \frac{p}{m}. \quad (5.17)$$

This is the usual relation between velocity and momentum.

6 Schrödinger's Equation

Single-Particle Wave Equation

Schrödinger in 1926 wrote down the differential equation satisfied by the matter wave associated with a nonrelativistic particle moving in a potential well. He was guided by an analogy Hamilton had noted between the motion of a particle in classical mechanics and the short wavelength limit of the motion of a light wave in a medium with index of refraction that is a function of position. There is another clue. As we have seen in

sections 1 and 4, the allowed values of the energy of an isolated atom are quantized. According to de Broglie's relation $E = \hbar\omega$ (eq. [5.4]), that means the matter wave associated with the atom can only oscillate at discrete frequencies. One gets discrete frequencies from the solutions to a wave equation with fixed boundary conditions, as we saw in the normal mode analyses in sections 1 and 2 (eq. [1.50]). Thus a theory for the discrete energies might be based on a wave equation.

By de Broglie's relations, a wave with energy E oscillates with frequency $\omega = E/\hbar$,

$$\psi \propto e^{-i\omega t}. \quad (6.1)$$

The wave function therefore satisfies the differential equation

$$i\hbar \frac{\partial \psi}{\partial t} = E\psi. \quad (6.2)$$

If the wave has momentum \mathbf{p} , de Broglie's relations say it has wave number $\mathbf{k} = \mathbf{p}/\hbar$. That means the wave function varies with position as

$$\psi \propto e^{i\mathbf{k}\cdot\mathbf{r}}, \quad (6.3)$$

as in equation (5.1). Equation (6.3) satisfies the relation

$$-i\hbar \nabla \psi = \hbar \mathbf{k} \psi = \mathbf{p}\psi. \quad (6.4)$$

Applying this equation twice, and recalling that the kinetic energy is $E = p^2/2m$, one might guess that the wave equation for a free particle with energy E would be

$$E\psi = \frac{p^2}{2m}\psi = -\frac{\hbar^2}{2m}\nabla^2\psi. \quad (6.5)$$

A particle in a potential well, such as an electron in a hydrogen atom, has potential energy, $V(\mathbf{r})$, as well as kinetic energy. Schrödinger generalized the wave equation for the case of a particle with energy E and potential energy $V(\mathbf{r})$ by adding the potential energy to the kinetic energy in equation (6.5), to get

$$E\psi = -\frac{\hbar^2}{2m}\nabla^2\psi + V(\mathbf{r})\psi, \quad (6.6)$$

This is Schrödinger's equation for a single particle with definite energy E .

The more general time-dependent Schrödinger equation is obtained by eliminating E from equations (6.2) and (6.6), to get

$$i\hbar \frac{\partial \psi}{\partial t} = \left[-\frac{\hbar^2}{2m} \nabla^2 + V(\mathbf{r}) \right] \psi. \quad (6.7)$$

We arrived at equation (6.7) from equations (6.2) and (6.5), in which the system has a definite energy, E . We will assume that the more general solutions to this equation, where ψ does not vary with time as $e^{-iEt/\hbar}$, also are allowed. (Thus has the interesting consequence, that Schrödinger was reluctant to accept, that in states represented by such solutions the system does not have a definite energy.)

It is customary to write equation (6.7) in the form

$$i\hbar \frac{\partial \psi}{\partial t} = H\psi, \quad (6.8)$$

for the time-dependent case, and, when the energy is known to be E ,

$$H\psi = E\psi. \quad (6.9)$$

Here H is the derivative operator

$$H = -\frac{\hbar^2}{2m} \nabla^2 + V(\mathbf{r}). \quad (6.10)$$

In equation (6.9) it is understood that the wave function for the system is of the form $\psi(\mathbf{r})e^{-iEt/\hbar}$, where $\psi(\mathbf{r})$ is a time-independent solution to equation (6.9). This requires that V be a function of position alone; when V varies with time energy is not conserved, and one must use the more general equation (6.8).

The Schrödinger differential equation (6.8) has to be supplemented with boundary conditions. For a bounded system like a hydrogen atom it is reasonable to require that the ψ wave be bounded too, that is, that ψ go to zero at large distance from the proton. This will be formalized in section 8 in the condition that the wave function, ψ , for a physical system be square integrable, that is, that the integral of $|\psi|^2$ over all space be finite.

(continued...)

Index

- absorption cross section, 384
- adjoint, 93, 180; in polar coordinates, 172
- ammonia inversion oscillation, 86, 162
- Ångstrom, 82
- angular frequency, 26; positive, 290
- angular momentum, 11, 25, 123; addition of, 136, 165, 214, 312; commutation relations for, 124; conservation of, 134; eigenvalues of, 129; ladder operators for, 127, 165, 312; and rotations, 133, 197. *See also* orbital angular momentum; spin angular momentum
- annihilation operator, 295
- anticommutator, 117, 407

- barrier penetration. *See* tunneling
- basis, 102
- Bell's inequality, 252
- binding energy, 35
- blackbody radiation, 18
- Bohm-Aharonov effect, 155
- Bohr model, 24
- Bohr radius, 25
- Boltzmann constant, 6
- Boltzmann distribution, 7, 241
- Born approximation, 374, 394
- Born-Oppenheimer approximation, 348
- bracket, 178
- bra vector, 177
- Breit-Wigner resonance line shape, 391

- canonical momentum, 148; and velocity, 154
- canonical quantization, 152
- carbon, 344
- circular polarization, 290, 321
- cold fusion, 52
- collapse of the wave function, 51, 236
- combination principle, 23
- commutator, 37
- compatible observables, 109, 188
- complementarity principle, 246
- completeness, 101, 184
- Compton effect, 23
- Compton wavelength, 58, 283
- conservation of angular momentum, 134; of linear momentum, 121; of mass, 12; of parity, 119
- creation operator, 295

- de Broglie relations, 27, 404
- de Broglie wavelength, 27, 83, 404
- Debye heat capacity, 12, 77, 83
- decay from hyperfine state, 303; from resonance state, 393
- degenerate perturbation theory, 271
- density matrix, 239
- deuteron, 52, 87, 229; and neutron-proton scattering, 397; spin of, 315
- differential cross section, 365
- dipole electromagnetic field, 274
- Dirac delta function, 62
- Dirac equation, 406
- Dirac matrices, 408
- dispersion relation, 26
- double slit experiment, 243

- effective charge, 328
- effective potential for central force, 142
- Ehrenfest's theorem, 113
- eigenfunctions, 33, 95; simultaneous, 98
- eigenvalue, 33, 97; continuous, 106, 184
- eigenvalue equation, 33, 72, 78, 95, 182
- eigenvector, 181
- electric dipole moment, 266
- electric dipole radiation rate, 319
- electric dipole transition, 317; selection rules for, 320
- electron charge, 58; magnetic moment, 200; mass, 82; spin, 198
- electron configuration, 333
- electron volt, 82
- energy eigenvalue equation, 32, 192
- energy quantization, 4, 24, 31, 41
- energy variational principle, 323
- EPR effect, 246
- equipartition, 9
- exclusion principle, 333
- expectation value, 7, 70; time evolution of, 113. *See also* observable

418 Index

- fine-structure, 341
- fine-structure constant, 283
- first-order perturbation theory, 261
- flux density of mass, 12; of particles, 364; of probability, 50
- Fourier transform, 60; and Dirac delta function, 63
- four-vector, 403

- gauge transformation for the electromagnetic field, 149; for the wave function, 154
- Gaussian wave function, 84, 88
- generators for rotation, 133; for translation, 121
- group velocity, 30, 47
- gyromagnetic ratio, 200

- Hamiltonian, 110, 148, 192; for particle in magnetic field, 151
- heat capacity of Debye solid, 18; of Einstein solid, 11; of molecular hydrogen, 10
- Heisenberg representation, 112; for quantum field, 292
- helium, 326
- hermitian adjoint, 186
- hidden variables, 252
- hydrogen atom, 33, 143; wave functions of, 145; $2s$ state of, 310
- hydrogen molecule, 10, 82, 347, 357
- hyperfine structure, 228; in atomic hydrogen, 273; in deuterium, 315

- induced transition, 288, 299
- inner product, 71, 92

- ket vector, 177
- Kronecker delta function, 61

- Lagrangian, 147; for particle in magnetic field, 149
- Landé g -factor, 316
- Laplacian in polar coordinates, 141, 173
- Legendre polynomial, 161
- linear independence, 97
- linearity of probability amplitude, 234
- linear space, 91, 175
- lithium, 337
- Lorentz transformation, 402

- magnetic dipole interaction, 200, 275, 311
- magnetic dipole moment, 199; for deuteron, 315; in Dirac equation, 413; for electron, 200; for proton, 275
- magnetic resonance, 309
- many-particle system, 73, 196
- matrix eigenvalue equation, 78, 99
- matrix mechanics, 185
- Maxwell's equations, 19
- measurement theory, 231
- mixed state, 237
- momentum eigenfunction, 72; measurement, 64; operator, 71; wave function, 67, 195, 226

- normalization, 48, 106, 191; of continuous eigenvectors, 184
- normal modes, 15, 81

- observable, 105, 188; expectation value of, 71, 107, 190
- operator, 36, 92, 179; matrix element of, 185
- optical theorem, 366
- orbital angular momentum, 123; eigenfunctions for, 132
- orthogonality, 61, 182; of eigenvectors, 97
- oscillator, 36, 167; coherent states of, 169; and the electromagnetic field, 292; energy levels of, 40; ladder operators of, 39, 293; position matrix elements of, 294; squeezed states of, 170; thermal energy of, 9; wave function of, 84

- parity, 115; conservation of, 119
- partial wave, 362, 377; expansion of plane wave, 379, 386; phase shift of, 381, 387
- Pauli spin matrices, 207
- periodic boundary condition, 16
- permutation symbol, 125
- perturbation theory, 259
- phase velocity, 26
- phonon, 77
- photoionization, 22, 318
- photon, 22, 295; spin of, 291
- Planck constant, 8
- Planck spectrum, 21

- plane wave, 26; as momentum eigenstate, 72; as sum of spherical waves, 379, 386
- polar coordinates, 130
- polarizability tensor, 269
- position observable, 193
- position representation, 187
- position translation operator, 121
- precession, 167, 212, 227
- probability, 4; conservation of, 49, 191; distribution of, 67, 105, 189; flux of, 50
- probability amplitude, 189, 208; linearity of, 234
- probability in quantum mechanics, 48, 231
- propagation vector, 26
- proton magnetic moment, 275; mass, 11; spin, 198
- pure state, 232
- p -wave, 146
- radial wave function, 34, 142; and probability, 89
- Rayleigh-Jeans spectrum, 21
- reduced mass, 76
- resonant scattering, 391; and time delay, 393
- rotation operator, 134; for spin one-half, 209
- Rutherford cross section, 377
- Rydberg, 331
- scalar product. *See* inner product
- scattering, 359; boundary condition for, 361, 371
- scattering amplitude, 361
- scattering cross section, 365
- Schrödinger representation, 110, 191
- Schrödinger's cat, 248
- Schrödinger's equation, 32, 110, 192; radial form of, 34, 142
- selection rules, 291, 320
- self-adjoint operator, 93, 160, 181
- shadow scattering, 385
- singlet spin state, 217
- solid angle, 365
- spherical Bessel function, 378
- spherical harmonic, 132
- spherical wave. *See* partial wave
- spin angular momentum, 196; in Dirac equation, 410
- spin one matrices, 227
- spin one-half matrices, 207
- spin-orbit interaction, 339; in Dirac equation, 415
- spin wave function, 277, 334
- spontaneous transition, 299
- square potential well, 44, 85, 87
- standard deviation, 88
- Stark effect, 266
- state vector, 188; and measurements, 51, 232; time-dependence of, 111, 192
- Stefan-Boltzmann law, 21
- Stern-Gerlach effect, 202, 232
- stimulated transition. *See* induced transition
- sum over momentum states, 17, 21, 302
- s -wave, 146; part of plane wave, 381; phase shift, 381
- symmetries and conservation laws, 119
- term symbol, 335
- time-dependent perturbation theory, 283
- time translation operator, 111, 191
- transition probability, 287
- triangle rule for angular momentum, 137
- triplet spin state, 217
- tunneling, 54, 163, 393
- two-particle system, 74, 139
- uncertainty in energy and time, 287, 393
- uncertainty principle, 68, 224
- unitary transformation, 95, 191
- virial theorem, 353
- wave equation for radiation, 20; for sound, 14
- wave function, 91, 187; nodes of, 43; normalization of, 48, 106; radial, 34, 142
- wavelength, 26
- wave mechanics, 91, 187, 192
- wavenumber, 26
- wave packet, 28, 46, 65, 360, 392; for minimum energy-momentum uncertainty, 88
- Wigner-Eckart theorem, 316
- Wigner's friend, 248
- WKB approximation, 44
- Zeeman effect, 264; in hyperfine splitting in atomic hydrogen, 228
- zero point energy, 40, 357