

## 1

## Concept of a solid: qualitative introduction and overview

### 1.1 Classification of solids

Condensed matter physics and solid state physics usually refer to the same area of physics, but in principle the former title is broader. Condensed matter is meant to include solids, liquids, liquid crystals, and some plasmas in or near solids. This is the largest branch of physics at this time, and it covers a broad scope of physical phenomena. Topics range from studies of the most fundamental aspects of physics to applied problems related to technology.

The focus of this book will be primarily on the quantum theory of solids. To begin, it is useful to start with the concept of a solid and then describe the two commonly used models that form the basis for modern research in this area. The word “solid” evokes a familiar visual picture well described by the definition in the Oxford Dictionary: “Of stable shape, not liquid or fluid, having some rigidity.” It is the property of rigidity that is basic to the early studies of solids. These studies focused on the mechanical properties of solids. As a result, until the nineteenth century the most common classification of solids involved their rigidity or mechanical properties. The Mohs hardness scale (talc – 1; calcite – 3; quartz – 7; diamond – 10) is a typical example. This is a useful but limited approach for classifying solids.

The advent of atomic theory brought more microscopic concepts about solids. Solids were viewed as collections of more or less strongly interacting atoms. From the point of view of atomic theory, a gas is described in terms of a collection of almost independent atoms, while a liquid is formed by atoms that are weakly interacting. This picture leads to a description of the formation of solids, under pressure or by freezing, in which the distances between atoms are reduced and, in turn, this causes them to interact more strongly. Molecular solids are formed by condensing molecular gases.

Hence, the development of atomic physics and chemical analysis led to a more detailed classification of solids according to chemical composition. Although for most studies of solids it is necessary to establish the identity of the constituent atoms, such a scheme provides limited insight into many of the basic concepts of condensed matter physics.

Solids can also be classified according to their crystalline structure. This monumental feat has occupied crystallographers and applied mathematicians for over a hundred years. The discovery of X-ray crystallography added an important component to the atomic model. The chemical view of a crystalline solid as a collection of strongly interacting atoms can be expanded by adding that the atoms arrange themselves in a periodic structure. This

**Table 1.1** Classification of solids using resistivity.

Class	Typical resistivity ( $\Omega$ cm)	Example
metal	$10^{-6}$	copper
semimetal	$10^{-3}$	bismuth
semiconductor	$10^{-2}$ – $10^9$	silicon
insulator	$10^{14}$ – $10^{22}$	diamond

would not be true for non-crystalline solids such as window glass. For most modern studies of solids, it is usually assumed that the structure and chemical composition are known and that information of this kind is the starting point for most investigations. When new materials are discovered, chemical and structural analyses are often the first steps in the characterization process.

Properties other than mechanical, chemical, and structural can be used to classify solids. Electromagnetic and thermal characteristics are commonly used. In particular, the resistivity  $\rho$  is the most used property, since it involves a single scalar quantity or a symmetric tensor with a range of values for different substances that varies at room temperature by about 28 orders of magnitude. For many materials  $\rho$  can be measured with great precision. Even though this approach focuses on a macroscopic property, with some theoretical analysis, it provides considerable insight into the microscopic nature of solids. Table 1.1 lists the classification according to resistivity of the four classes of solids: metals, semimetals, semiconductors, and insulators. Typical resistivities and examples for each class are also given. Although the divisions between classes are approximate, this classification of solids is extremely useful for a wide variety of studies and applications.

The chemical and structural classifications lead naturally to a model of crystalline solids based on interacting atoms. This is a fruitful approach and suggests that it may be possible to explain and predict the properties of solids through an adjustment or perturbation of the properties of atoms. The use of the resistivity for the classification of types of solids suggests another view, where the responses of a solid to external probes are used to classify solids. Electromagnetic, thermal, or mechanical probes can give rise to responses that may arise from the collective nature of the interacting particles in solids. However, viewing the solid as perturbed atoms may not lead naturally to an interpretation of its properties in terms of collective or cooperative effects. The interacting atoms approach is convenient for describing ground-state properties, whereas collective effects are best explained in terms of a model based on the excitations of the solid. Both models are discussed in more detail below.

## 1.2 A first model of a solid: interacting atoms

Consider aluminum metal. It is a relatively soft solid with hardness between 2 and 2.9 on the Mohs scale and it is composed of a single element. It crystallizes in the face-centered

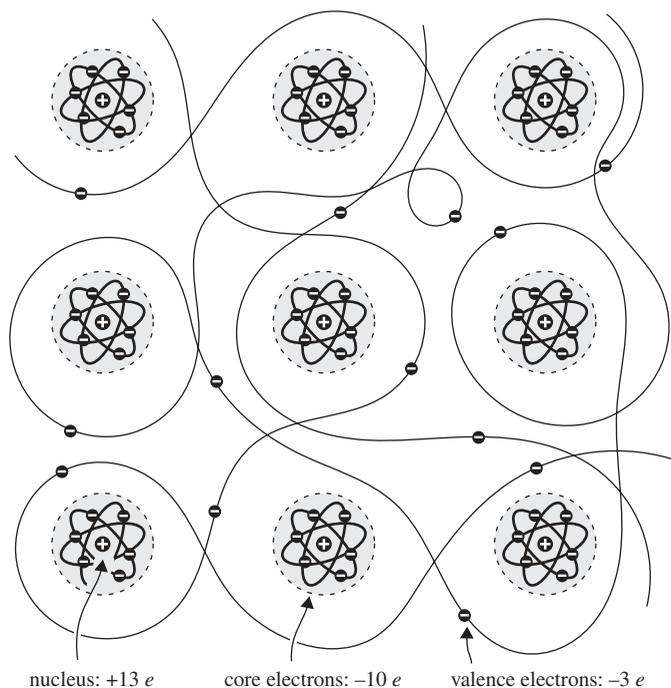


Figure 1.1

Schematic drawing of a solid consisting of atoms with atomic number  $z = 13$  containing cores and valence electrons. Here  $e$  denotes the charge of a proton.

cubic structure with cubic lattice constant  $a = 4.5 \text{ \AA}$ , it is a reasonably good conductor ( $\rho = 2.8 \times 10^{-6} \text{ } \Omega \text{ cm}$  at  $20^\circ\text{C}$ ), and it becomes a superconductor at  $T_c = 1.19 \text{ K}$ .

What model can be used as a basis for explaining these properties? Why is aluminum different from copper, solid argon, solid oxygen, silicon, sodium chloride, or anthracene?

The most straightforward approach is to start from the chemical and atomic descriptions and to consider aluminum metal as a collection of interacting aluminum atoms. Each aluminum atom is composed of a nucleus with atomic number  $Z = 13$ . Hence in the neutral atom, there are 13 protons and 13 electrons. The electronic configuration can be easily divided into 10 core electrons, denoted by principal and angular momentum quantum labels as  $[(1s)^2(2s)^2(2p)^6]$ , and three outer valence electrons  $[(3s)^2(3p)^1]$ .

One picture of solid aluminum is a collection of cores with each core composed of a nucleus plus the tightly bound core electrons. Because of the cancellation of charge of 10 protons by the core electrons, the core has an effective charge  $Z_{\text{eff}} = 3$ . Moving around the cores and between them is a collection of itinerant, nearly-free electrons; there are three per core. A schematic drawing is given in Fig. 1.1. Cores and valence electrons move in a potential set by their mutual interactions. The laws of motion are well known and are described by quantum mechanics. The Schrödinger equation is sufficient in most cases; however, the Dirac equation may be necessary if relativistic effects are to be incorporated. The forces are also known; only electromagnetism plays a role. Gravity and weak

interactions are too feeble, and strong interactions are too short-ranged. However, the problem is not an easily solvable one since there are of the order of  $10^{23}$  interacting particles in solids per  $\text{cm}^3$ . Approximate methods must be used and simpler models developed. These will be discussed in Chapter 2.

### 1.3 A second model: elementary excitations

A drastically different approach to studying condensed matter systems is also in common use. In quantum mechanics and quantum field theory, it is often convenient to change the description of a system when discussing its excited states. This picture is based on the excitations that can emerge when a system is not in its ground state. A standard example is a harmonic oscillator of mass  $m$  moving in a quadratic potential  $\frac{1}{2}m\omega^2x^2$ . This system has an energy spectrum defined by a quantum number  $n$ ,  $E_n = (n + \frac{1}{2})\hbar\omega$ , which can be viewed as a ground state having energy  $E_0 = \frac{1}{2}\hbar\omega$ , and higher-energy states in which quanta of excitation energy  $\hbar\omega$  can be created and subsequently destroyed in any non-negative integral number  $n$ . Another example is the electromagnetic field, which can be viewed as a collection of quantized particle-like excitations, the photons, each one characterized by a wavevector  $\mathbf{k}$ , a polarization direction  $\hat{\mathbf{e}}$ , and energy  $\hbar\omega = \hbar c|\mathbf{k}|$ , where  $c$  is the velocity of light.

The examples above give an operational definition of a quantum system that is described by its excitations, each one defined by its energy and other specific physical characteristics. Once the excitations are identified, the next task is to study the interactions between various excitations and the manner in which these excitations appear, disappear, or are modified when the external conditions of the quantum system change. In the end, the quantum system will be characterized by its elementary excitations when probes are used to study its properties.

The elementary excitations of a solid can often be divided into two classes: quasiparticles and collective excitations. Quasiparticles are usually fermions and resemble well-defined excited states of the non-interacting real particles of the solid. Collective excitations are usually bosons and do not resemble their constituent real particles. In the majority of cases, collective excitations are associated with macroscopic collective motions of the system, which in turn are described by quanta of generalized harmonic oscillators that can be created or destroyed in an integral number  $n$ . Each quantum provides an excitation energy  $\hbar\omega$ .

The language of second quantization is the natural one to use for this model. Since elementary excitations can be created and destroyed, and since symmetric (Bose–Einstein) or antisymmetric (Fermi–Dirac) conditions must be satisfied, creation and destruction operators, with their attendant commutation and anticommutation rules, are among the fundamental descriptive tools of this approach.

To explain the properties of a solid, it is advantageous to define the elementary excitations of the solid, to describe their properties and characteristics, to evaluate their interactions, and to determine how they respond to external probes.

## 1.4 Elementary excitations associated with solids and liquids

**Quasielectrons.** Quasielectrons (or electrons for short) are quasiparticles that behave like non-interacting electrons in low-lying excited states. They are fermions that are characterized by energy and quantum numbers, such as their wavevectors and spin orientations. Their properties include the effects of the environment in which they move. An important example is that of an electron experiencing the interaction with other electrons that can change its free electron mass  $m$  to an effective mass  $m^* > m$ . The resultant quasielectron can be described by one-particle states of spin  $\frac{1}{2}$  and charge  $-|e|$ . Typical excitation energies for quasielectrons are of the order of the Coulomb interaction energy between two electrons separated by a crystal lattice parameter  $a$ :  $\frac{e^2}{a} \cong 5$  eV. Typical velocities associated with quasielectrons are  $v \cong (\frac{e^2}{am})^{1/2} \cong 10^8$  cm/s.

**Hole.** The removal of an electron from an orbital that is normally occupied in the ground state is called a hole. The analogy is made with the Dirac theory of positrons. A hole is a quasiparticle that has charge  $+|e|$ , spin  $\frac{1}{2}$ , and energies and velocities similar to quasielectrons. When electrons are injected into or removed from a solid in processes such as those associated with quantum tunneling phenomena and electron emission, they are often treated as single particles without any reference to the holes left behind. The holes are usually studied separately.

**Phonon.** A phonon is a collective excitation (boson) associated with lattice vibrations or sound waves. It is defined by a wavevector  $\mathbf{q}$ , a branch or polarization mode index  $\alpha$ , and an energy  $\hbar\omega$ . Typical energies are of the order of  $k_B T_D$ , where  $k_B$  is Boltzmann's constant and  $T_D$  is the Debye temperature. Since  $T_D$  is of the order of room temperature ( $\sim 300$  K), a typical phonon energy is  $\hbar\omega \cong 0.025$  eV.

**Plasmon.** A plasmon is a collective excitation (boson) associated with the collective motion of the electronic charge density. It is characterized by a wavevector  $\mathbf{q}$  and an energy of the order of the classical plasma energy (in three dimensions)

$$\hbar\omega_p = \hbar \left( \frac{4\pi n e^2}{m} \right)^{\frac{1}{2}}, \quad (1.1)$$

where  $n$  is the density of valence electrons per unit volume. For typical solids,  $\hbar\omega_p \cong 10$  eV. This value can be smaller by an order of magnitude or more in low-density electron or hole systems such as those found in semimetals and degenerate semiconductors.

**Magnon.** A magnon is the collective excitation (boson) associated with spin waves or spin excitations, resulting from the occurrence of spin reversals in an ordered magnetic system. Typical energies are of the order of the ordering temperatures (Curie or Néel). These can be as high as  $10^{-1}$  eV, but are usually much lower ( $\sim 4 \times 10^{-5}$  eV).

**Polaron.** A polaron is a special type of quasielectron that exists in crystals. It can be regarded as an electron or a hole moving through a crystal and carrying a lattice deformation or strain with it. If the strain is expressed in terms of excitations of phonons, this leads to the view of a polaron as an electron accompanied by a cloud of phonons. The terms

“polaron” and “polaron effects” are often used to describe changes in electron properties arising from electron–phonon interactions in general.

**Exciton.** An exciton is a bound or quasibound state of a quasidelectron and a hole. This elementary excitation is similar to positronium, and it often behaves as a boson which can be decomposed into its two component fermions or radiatively annihilated. Excitons are usually observed in insulators and semiconductors. Typical binding energies are  $\sim 0.025$  eV in three-dimensional systems.

**Superconducting quasiparticles.** Superconducting quasiparticles are fermions that describe the electronic excited states of a superconductor. They are sometimes called Cooper particles (not Cooper pairs) or Bogoliubons. Because of the physics inherent in the description of the superconducting ground state, these quasiparticles are viewed as a linear combination of quasidelectrons and holes. Typical energies are of the order of the superconducting transition temperature between  $10^{-5}$  eV and  $10^{-2}$  eV, depending on the material.

**Roton.** A roton can be viewed as a special phonon associated with a local energy minimum in the dispersion relation at a finite wavevector. This description usually applies to liquid  $\text{He}^4$ . Typical roton energies in helium are of the order of  $10^{-3}$  eV.

## 1.5 External probes

Knowledge about the properties of solids is obtained from measurements done under well-defined conditions. These are either equilibrium situations, in which the temperature and externally applied static electric and magnetic fields are predetermined, or dynamical situations in which energy, momentum, angular momentum, and other dynamical quantities are exchanged with the environment. In the latter case, the agents that effect this exchange are also microscopic quanta, the so-called test or probe particles. Some of these are listed below.

**Photons.** Electromagnetic probes are the most commonly used probes in solids, for example, they are used in absorption spectra, reflectivity spectra, and photoemission spectra. The energy range of the useful photons spans the available electromagnetic spectrum, from radio frequency studies of metals ( $\hbar\omega \cong 2 \times 10^{-8}$  eV) to  $\gamma$ -radiation studies of the Mössbauer effect ( $\hbar\omega \cong 2 \times 10^6$  eV).

**Electrons.** Electrons are used to probe solids in a variety of ways. They are injected and extracted through electrical contacts and tunneling junctions, or used as scattering particles in electron beams. Typical energies vary with the experiment:  $\sim 1$  meV for superconductive tunneling;  $\sim 1$  eV for semiconductor tunneling;  $\sim 10^{-2}$  to 2 eV for scanning tunneling microscope investigations of surfaces;  $\sim 10$  to 100 eV for low-energy electron diffraction at solid surfaces; and  $\sim 100$  keV to 1 MeV for high-energy electron microscopy.

**Positrons.** Positron annihilation in solids arising from electron–positron interactions provides useful information for investigating the electronic properties of solids – primarily metals. Photons are emitted when the annihilation occurs and studies of the emitted radiation give information about the electronic structure.

**Neutrons.** Neutron scattering has become the standard and preferred technique to study magnetic structural properties and properties of phonons, magnons, and other collective excitations in solids, owing to the fact that a neutron is a neutral particle with a magnetic moment.

**Muons and pions.** Muons and pions are used as probes, but they are not as commonly used as most of the other particles discussed here. Muons are more versatile than pions because of their similarity to heavy electrons. Their magnetic moments and decay modes can give information not obtained with other methods.

**Protons.** Protons can be used to study the structures of crystalline solids, primarily by examining their trajectories in solids.

**Atoms.** Light atoms and ions are usually employed to study surfaces; sometimes they can be used to probe deeper into solids. Their role is often similar to that of electrons in scattering experiments.

## 1.6 Dispersion curves

All the probe particles can be characterized by a momentum (or wavevector or wavelength) and an energy (or frequency). The particles are assumed to exist in free space or vacuum. For massive particles with mass  $m$ , the dispersion curve, which is the functional relation between the energy  $E$  and the momentum  $\mathbf{p}$  or wavevector  $\mathbf{k}$ , is given by

$$E = \frac{\mathbf{p}^2}{2m} = \frac{\hbar^2 \mathbf{k}^2}{2m}, \quad (1.2)$$

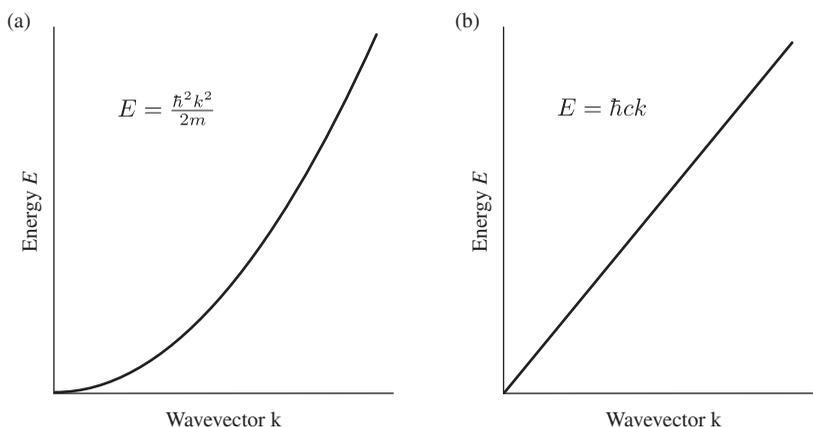
or, in the relativistic limit, by

$$E = (\hbar^2 \mathbf{k}^2 c^2 + m^2 c^4)^{1/2} - mc^2, \quad (1.3)$$

where  $c$  is the speed of light. The probing photon in free space (a massless particle) is described by the dispersion curve, connecting the frequency  $\omega$  and wavevector  $\mathbf{k}$ ,  $\omega = c\mathbf{k}$ . These dispersion curves are illustrated in Fig. 1.2. In a solid or liquid, most elementary excitations are also defined by a wavevector and an energy or frequency. The functional dependence of the energy on the wavevector, that is, the dispersion curve, constitutes one of the most fundamental properties of the excitations to be determined.

The quasidelectron dispersion curve can be used to distinguish the various types of solids: metals – no gap in the spectrum and the existence of a Fermi surface; semiconductors and insulators – an electronic energy gap of order 0.1 to 10 eV, caused by the ion core potential and uniquely related to specific  $\mathbf{k}$ -space locations; and superconductors – an energy gap for creating a quasidelectron and quasihole pair of order  $2\Delta < 10^{-1}$  eV caused by dynamic interactions of the electrons.

Some examples of dispersion curves for quasiparticles are shown in Fig. 1.3. The quasidelectrons and holes in metals (Fig. 1.3(a)) have excitation energies which start from zero. Excitations with zero energy define a surface in  $\mathbf{k}$ -space known as the Fermi surface. For



**Figure 1.2** Dispersion curves for probe particles. (a) Free particle of mass  $m$ . (b) Photons in vacuum.

semiconductors, the excitation spectrum has a different starting value for electrons and holes, which depends on the chemical potential  $\mu$  (or  $E_F$ ) of the system. Silicon is used as an example in Fig. 1.3(b). The lowest-energy electron excitation is at a well-defined  $k$ -vector,  $\mathbf{k} = \mathbf{k}_{cb}$ , and the lowest-energy hole state is at  $\mathbf{k} = \mathbf{k}_{vb}$ . For the silicon example,  $\mathbf{k}_{vb} = 0$ , while  $\mathbf{k}_{cb}$  has a finite value along the (100) direction of  $k$ -space, and the minimum energy required to create a quasielectron and a hole is 1.1 eV. This is the minimum bandgap  $E_g$  for silicon.

Superconducting quasiparticle spectra also exhibit an energy gap. The minimum energy for creating both a superconducting quasielectron and quasihole requires an energy of  $2\Delta$ . This is usually a much smaller gap than in semiconductors ( $2\Delta = 0.3$  meV in aluminum), and it appears at what, in the normal state, was the Fermi surface of the metal. The semiconducting and superconducting gaps are of very different natures; their characteristics are discussed in subsequent chapters.

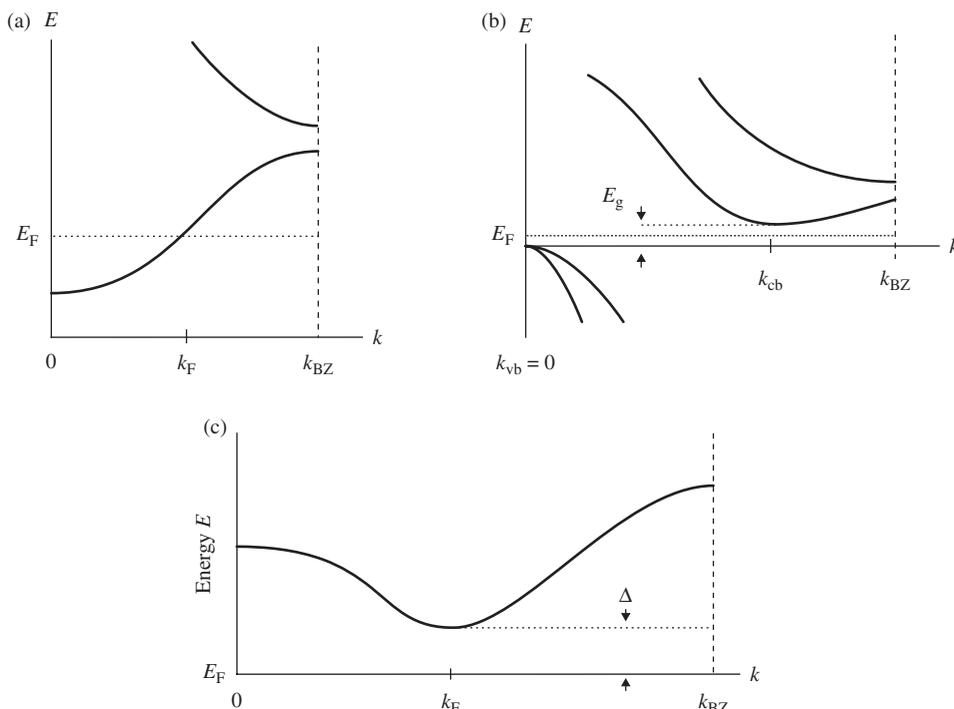
It is often convenient to choose a specific form for the dispersion curve near local minima or maxima and in other regions where quadratic approximations are appropriate. For example, in the case of an electron or hole at a band minimum with wavevector  $\mathbf{k}_0$ , it is convenient to write

$$E(\mathbf{k}) = \frac{1}{2}\hbar^2(\mathbf{k} - \mathbf{k}_0) \cdot \mathbf{A} \cdot (\mathbf{k} - \mathbf{k}_0), \quad (1.4)$$

where the tensor  $A_{ij} \equiv 1/m_{ij}^*$  can be interpreted as an inverse effective mass tensor. For a free electron, the relation (Eq. (1.4)) holds exactly with

$$A_{ij} = m^{-1}\delta_{ij}, \quad (1.5)$$

where  $m$  is the free electron mass (see Eq. (1.2) and Fig. 1.2). In solids, effective masses may differ substantially from the free electron mass. For example,  $m^* \cong 0.01m$  for quasielectrons near the conduction band minimum in InSb. This small  $m^*$  value is caused by the static crystal potential, which is also responsible for the existence of the energy gap. In sodium metal, where the Fermi surface is, to a very good approximation, a sphere of radius



**Figure 1.3**

Dispersion curves. (a) Quasielectrons and holes in a simple metal, for example, an alkali metal. Quasielectrons are excited into states  $E > E_F, k > k_F$ , where  $E_F$  and  $k_F$  are the Fermi energy and wavevector and  $k_{BZ}$  is the wavevector for the Brillouin zone edge. Hole states are by convention often plotted by the dispersion curve for  $E < E_F$  and  $k < k_F$ . However, since it costs energy to remove an electron to create a hole, the hole branch of the dispersion curve should be inverted and the energies measured positively with hole energies between zero and  $E_F$ . (b) Quasielectrons and holes in a semiconductor. For the case illustrated, the lowest-energy quasielectron wavevector is centered at  $k_{cb}$  at the conduction band minimum, while the lowest-energy hole wavevector is at the valence band maximum centered near  $k_{vb} = 0$ . These two kinds of states are separated by energy gap  $E_g$ . As in (a), the hole branch of the dispersion curve should be inverted, with the energies measured positively. (c) Quasiparticles in a superconductor. Here the quasielectron and hole branches of (a) are combined. The superconducting gap  $\Delta$  for creating a single quasiparticle appears at  $k_F$ .

$k_F$ , the quasiparticle dispersion curve is given by

$$E(\mathbf{k}) = \frac{\hbar^2}{2m^*} |k^2 - k_F^2|. \tag{1.6}$$

Equation (1.6) is valid for both quasielectrons ( $|\mathbf{k}| > k_F$ ) and holes ( $|\mathbf{k}| < k_F$ ) with an effective mass of  $m^* \cong 1.25m$ . This enhancement of 25% over the free electron value is not caused by the static crystal potential. It arises from the dynamic interactions between electrons and phonons and interactions among the electrons.

In Fig. 1.4, examples of dispersion curves for collective excitations are given. The specific properties related to features of particular curves are discussed in later chapters.

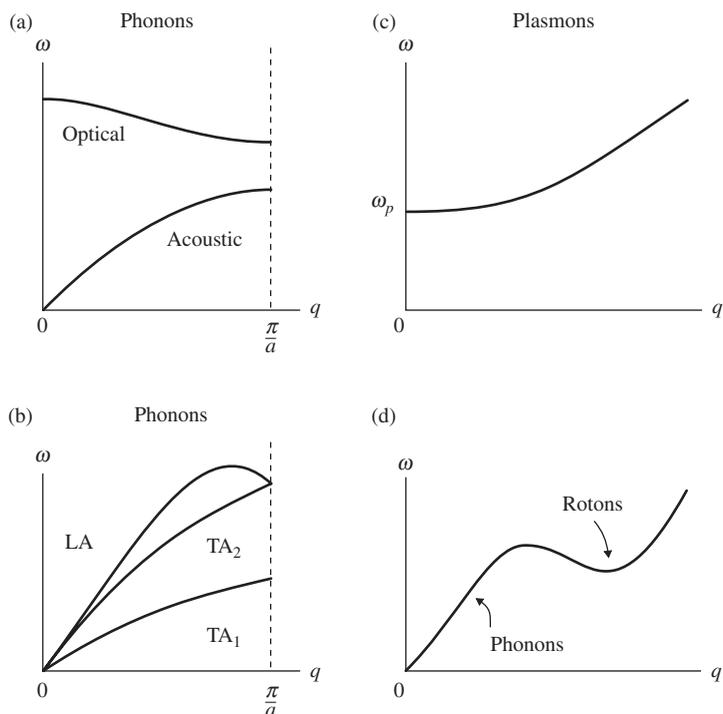


Figure 1.4

Dispersion curves (schematic) for collective excitations. (a) Phonons in a one-dimensional solid with lattice constant  $a$  and two masses per unit cell. (b) Phonons in a three-dimensional solid with one atom/cell. LA, TA<sub>1</sub>, and TA<sub>2</sub> refer to the longitudinal acoustic mode and the two transverse acoustic modes, respectively. (c) Plasmons in a three-dimensional metal where  $\omega_p$  is the classical plasma frequency. (d) Phonons and rotons in liquid He-4.

In restricted regions of given spectra, useful analytic approximations are commonly made. For instance, for each mode  $\alpha$  of the acoustic phonon dispersion relation near  $\mathbf{q} = 0$ , it is possible to write

$$\hbar\omega_\alpha = \hbar v_\alpha |\mathbf{q}|, \quad (1.7)$$

where  $v_\alpha$  is the speed of sound propagation for mode  $\alpha$ .

The determination and interpretation of the dispersion curves for the elementary excitations can be complex. However, a scheme or investigational approach can be outlined. This approach consists of: (1) defining the bare elementary excitation by means of a Hamiltonian formalism; (2) solving the equations of motion to determine the dispersion curves for the “bare” elementary excitations; (3) solving for the “final” spectrum of the excitations after including the necessary interactions among the excitations; (4) including the effects of the external probes and their interactions with the excitations; and (5) solving the new coupled equations to determine the response functions for the condensed matter system.

In the above scheme, steps (1) and (2) are usually handled by ordinary quantum mechanical methods, using the Schrödinger equation appropriate for one body in an external potential. Steps (3), (4), and (5) are concerned with the many-body aspects that can be