

ELEMENTARY EXCITATIONS IN SOLIDS



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ELEMENTARY EXCITATIONS IN SOLIDS

LECTURES ON PROTONS, ELECTRONS,
AND PLASMONS

DAVID PINES

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Editor's Foreword

Perseus Books's *Frontiers in Physics* series has, since 1961, made it possible for leading physicists to communicate in coherent fashion their views of recent developments in the most exciting and active fields of physics—without having to devote the time and energy required to prepare a formal review or monograph. Indeed, throughout its nearly forty-year existence, the series has emphasized informality in both style and content, as well as pedagogical clarity. Over time, it was expected that these informal accounts would be replaced by more formal counterparts—textbooks or monographs—as the cutting-edge topics they treated gradually became integrated into the body of physics knowledge and reader interest dwindled. However, this has not proven to be the case for a number of the volumes in the series: Many works have remained in-print on an on-demand basis, while others have such intrinsic value that the physics community has urged us to extend their life span.

The *Advanced Book Classics* series has been designed to meet this demand. It will keep in-print those volumes in *Frontiers in Physics* or its sister series, *Lecture Notes and Supplements in Physics*, that continue to provide a unique account of a topic of lasting interest. And through a sizable printing, these classics will be made available at a comparatively modest cost to the reader.

In the 1950s, thanks to the development of experimental probes such as nuclear magnetic resonance and inelastic neutron scattering, and the development of field-theoretic methods for dealing with coupled systems of electrons and ions, and the strong interactions between helium atoms in the helium liquids, a significant paradigm shift took place in the physics of condensed matter. No longer did one have to ignore the influence of strong particle interactions on the excited states of condensed matter systems; rather one could view these excited states as a collection of interacting elementary excitations whose behavior and

effective interactions could be determined directly through experiment and described theoretically, often in quantitative fashion. In the lecture note volume *Elementary Excitations in Solids*, based on lectures given at the University of Illinois in 1961, I tried to introduce graduate students and advanced undergraduate students to this new way of thinking about excited states in solids. To my surprise—and pleasure—both students and instructors find that thirty-five years later these lectures continue to provide a useful pedagogical introduction to the basic concepts we use in our description of the solid state, and I am pleased that their inclusion in the *Advanced Book Classics* series will make the volume readily accessible to new generations of readers.

David Pines
Tesuque, NM
January 1999

PREFACE

This book has grown from lectures given in an advanced course in the theory of solids at the University of Illinois during the fall semester 1961-1962. It was assumed that the student possessed a knowledge of quantum mechanics equivalent to a year's course in that topic; no prior knowledge of field theory was assumed. The course was designed to follow one in the one-electron or band theory of solids. However, in the view of the wide applicability (to plasma physics, nuclear physics, low-temperature physics) of many of the physical ideas and techniques developed in the course, a prior knowledge of solid-state physics was not regarded as a *sine qua non*. For this reason, both Chapter 2 on phonons and Chapter 3 on electrons contain a certain amount of material which is usually included in an introductory solid-state physics course.

The course was a new one. It was prompted by the need to communicate to the graduate student at an early stage in his career our present view of a solid as a system of interacting particles which, under suitable circumstances, behaves like a collection of nearly independent elementary excitations. Such a view has emerged from the work of many people during the past decade; its development has been greatly influenced by the many exciting discoveries in the closely related field of the many-body problem. Just as the "one-electron" problem in solid-state physics has long served as a proving ground for the ideas of elementary quantum mechanics, so now the theory of elementary excitations in solids serves as a proving ground for the application of general quantum mechanical techniques developed for the study of many-particle systems.

Many of these techniques and concepts are essentially field-theoretic in nature, and there is little doubt that the present-day solid-state physicist will have need of them. However, a detailed exposition of the Green's

function approach to many-particle systems is essentially a matter for a course in itself. It would seem that until the appropriate field-theoretic techniques become part of a standard course in quantum mechanics it is not likely to prove easy to draw upon them extensively for an exposition of solid-state physics. The writer has attempted an uneasy compromise in this respect. Two of the most important developments on the many-body side have been the solution of certain model problems (problems for which the solution is valid in a certain range of densities, temperature, etc., ...) and the formal but exact theory of the response of a system to a weakly coupled external probe. Examples of both developments are considered in Chapter 3, which deals with the interacting electron gas; the random phase approximation is described in detail, as is the response of an electron system to an external longitudinal probe. In addition, the equation-of-motion is introduced and applied to both the Hartree-Fock approximation and the random phase approximation. On the other hand, Feynman diagrams are introduced for essentially pictorial purposes only (no rules for calculations being given) and Green's functions are mentioned only very briefly. The interested reader may find an elementary introduction to these techniques in the following books: L. P. Kadanoff and G. Baym, *Quantum Statistical Mechanics*, W. A. Benjamin, Inc., 1962; P. Nozières, *Theory of Interacting Fermi Systems*, Dunod-Benjamin, 1963; D. Pines, *The Many-Body Problem*, W. A. Benjamin, Inc., 1962.

In addition to introducing a certain number of basic concepts, the writer has endeavored to refer to experiment as frequently as possible. For the most part, both the basic theory and the applications discussed deal with the behavior of "simple" metals, such as the alkali metals, in contrast to "complicated" metals, such as the transition metals and the rare earths. Insulators are scarcely discussed; there is some consideration of the consequences of electron interaction in semiconductors in Chapter 4.

There are a number of different elementary excitations of importance in solids; these are described briefly in Chapter 1. Of these only three are discussed in any detail in this book. The choice was a deliberate one; the writer felt it was better to discuss a few examples in some detail, rather than giving a broader, but less detailed survey of the field. The general methods and points of view developed for the excitations described herein may be applied equally well to the other excitations of interest; it is the writer's hope to return to this question at a subsequent date. For the excitations not considered in detail, an attempt has been made to provide the reader with a list of some recent relevant references. To these should be added the following lecture-note volume which is, in many respects, a companion volume to this one: P. W. Anderson, *Concepts in Solids*, W. A. Benjamin, Inc., 1963.

Chapter 3, which deals with the interacting electron gas, omits one

major development of importance, the application of the Landau Fermi liquid theory to this system. The Landau theory represents a powerful tool for the discussion of the behavior of an almost-free-electron-like system in the limit of long wavelengths and low excitation frequencies. For example, it tells one which properties of the system are unaffected by electron-electron interaction; where it is applicable it also specifies the minimum number of parameters required to describe a given system property. On the other hand, it offers no explicit method for the calculation of the quasi-particle properties of interest. Methods, approximate though they may be, do exist for calculating various properties of an electron gas at metallic densities. It therefore seemed better to concentrate on the microscopic, albeit approximate, approach to quantities like the specific heat and spin susceptibility in lieu of the exact, but phenomenological application of the Landau theory. It may be added that the Landau theory applies not at all to many of the problems discussed in this book (e.g., the correlation energy of an electron gas, plasmons, optical properties of solids, etc., ...).

The introduction of a frequency and wave-vector-dependent dielectric constant offers a way to discuss a number of properties of an electron gas in simple compact fashion. The method is described and applied to the discussion of the random phase approximation in Chapter 3. Nevertheless, it seemed useful from a pedagogical point of view to present first a historical survey of the earlier methods for treating the electron gas. It is hoped that the survey will enable the reader to place the more recent developments in their proper perspective, as well as to indicate some of the existing interrelationships between the many apparently different approaches developed for this problem.

In Chapter 5, which deals with electron-phonon interactions, considerable emphasis is placed on the development of a unified theory in which both electron-electron *and* electron-phonon interactions are considered at the outset. Particular attention is paid to phonon frequencies, the effective electron-electron interaction, and the effective electron-phonon interaction in simple metals. Calculations of the conductivity of the alkali metals are presented, but no detailed derivation of transport properties is given. This restricted view of the field has been adopted for two reasons: First, it is now possible to give an elementary discussion of the combined effects of electron-electron and electron-phonon interactions; second, there now exist a number of good discussions of transport properties in the scientific literature.

Problems have been included with all chapters but the first. It is hoped that the problems will enable the reader to fill in some of the missing steps in derivations quoted in the book, and serve as well to assist him in applying some of the concepts he has learned to physical situations not discussed explicitly herein.

I should like to thank Dr. Setsuo Ichimaru for his very considerable assistance in the preparation of this book. Dr. Ichimaru's notes on the lectures were of great value in the writing of the present manuscript. He is, in addition, in large part responsible for the preparation of the Appendixes. I am greatly indebted to Dr. Henry Ehrenreich, who read carefully the entire manuscript, and made a number of extremely useful suggestions. It is a pleasure to acknowledge helpful comments and discussions with my colleagues, Professors John Bardeen and Philippe Nozières on the matters discussed herein. I should like also to thank the John Simon Guggenheim Memorial Foundation for their support during the preparation of the book, and to thank Mrs. Ann Wells, Mme R. Chadon, and Mme O. Jancovici for their assistance with the typing of the manuscript.

DAVID PINES

Paris, France
February 25, 1963

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Chapter 1

INTRODUCTORY SURVEY

1-1 GENERAL CONSIDERATIONS

Whenever we deal with solids we are dealing with a many-body problem. Thus we ask what happens when we bring together some 10^{23} atoms/per cubic centimeter to make a crystal. This has certain important consequences. For instance, it means that we cannot expect exact solutions—that instead we must be continually developing approximate models to fit the situation at hand. Thus in making a theory it is usually essential that we be aware of the experimental work on the phenomenon under consideration and vice versa. Many of the important present-day developments arise out of such a close collaboration between the theoretical and the experimental physicist.

It is this use of approximate models which lends solid-state physics much of its fascination. Indeed, we may regard it as a marvelous proving ground for quantum mechanics and the ingenuity of the theoretical and experimental physicist. For unlike the nuclear or elementary particle physicist we know what our particles are, and what are the forces between them, but we must use all our intelligence and insight to understand the consequences of this interaction. Thanks to the work of many people, particularly during the last decade, it is now possible to view much of solid-state physics in terms of certain *elementary excitations* which interact only weakly with one another.

The use of an elementary excitation to describe the complicated interrelated motion of many particles has turned out to be an extraordinarily useful device in contemporary physics, and it is this view of a solid which we wish to adopt in this book.

Under what circumstances is it useful to regard a solid as a collection of essentially independent elementary excitations? First of

all, it is necessary that the excitations possess a well-defined energy. Let us suppose that the excitations are labeled by their momenta, which will be the case for a translationally invariant system. We shall see that the energy of a given excitation of momentum p will be of the form

$$\tilde{\xi}_p = \xi_p - i\gamma_p \quad (1-1)$$

where γ_p , the imaginary part of the energy, is inversely proportional to the lifetime of the excitation. In order that the excitation be well defined, it must be long-lived. This means that one must have

$$\gamma_p \ll \xi_p \quad (1-2)$$

the real part of the energy of the excitation.

One may well ask how it is possible that in a system, which, like a solid, is composed of strongly interacting particles, it is possible to find elementary excitations which satisfy the requirement (1-2). To answer this question let us consider the ways in which an excitation may decay. There are essentially two: (1) scattering against another excitation, and (2) scattering against the "ground-state particles."

The first mode of decay is negligible if one confines one's attention to temperatures sufficiently low that only a comparatively small number of excitations are present. The second mode of decay is less easily inhibited; it turns out for the various systems of interest there exist *coherence* factors which limit the phase space available for the decay of an excitation of low momentum or long wavelength. (An obvious example is the limit placed by the Pauli principle on the scattering of an electron in the immediate vicinity of Fermi surface.)

The requirement, (1-2), usually limits one to comparatively low temperatures and often, as well, to phenomena that involve comparatively low frequencies and long wavelengths. Where it is not satisfied, it may still be useful to describe a given physical process in terms of the excitations involved, but it becomes essential to take into account the fact that the excitations possess a finite lifetime.

Where (1-2) is satisfied, in thermal equilibrium one may characterize the excitation by a distribution function,

$$f_p(T) = \frac{1}{e^{\beta \xi_p} \pm 1} \quad (1-3)$$

where $\beta = 1/kT$; the plus sign applies if the excitation obeys Fermi-Dirac statistics, the minus sign for Bose-Einstein statistics. $f_p(T)$ gives the probability of finding an excitation of momentum p , energy ξ_p , at the temperature T ; from a knowledge of all the $f_p(T)$, one can

determine in straightforward fashion the various thermodynamic properties of the system.

These remarks are quite general; to see what they mean, it is necessary that one consider some specific examples. But before doing that let us specify clearly the basic model we shall take to describe a solid throughout this book.

1-2 BASIC HAMILTONIAN

The basic Hamiltonian which describes our model of the solid is of the form

$$H = H_{\text{ion}} + H_{\text{electron}} + H_{\text{electron-ion}} \quad (1-4)$$

where

$$H_{\text{ion}} = \sum_i \frac{P_i^2}{2M} + 1/2 \sum_{i \neq j} V(R_i - R_j) \quad (1-5)$$

$$H_{\text{electron}} = \sum_i \frac{p_i^2}{2m} + 1/2 \sum_{i \neq j} \frac{e^2}{|r_i - r_j|} \quad (1-6)$$

$$H_{\text{electron-ion}} = \sum_{i,j} v(r_i - R_j) \quad (1-7)$$

H_{ion} describes a collection of ions (of a single species) which interact through a potential $V(R_i - R_j)$ which depends only on the distance between the ions. By ion we mean a nucleus plus the closed-shell, or core, electrons, that is, those electrons which are essentially unchanged when the atoms are brought together to make a solid.

H_{electron} describes the valence electrons (the electrons outside the last closed shell), which are assumed to interact via a Coulomb interaction. Finally, $H_{\text{electron-ion}}$ describes the interaction between the electrons and the ions, which is again assumed to be represented by a suitably chosen potential.

In adopting (1-4) as our basic Hamiltonian, we have already made a number of approximations in our treatment of a solid. Thus, in general the interaction between ions is not well-represented by a potential, $V(R)$, when the coupling between the closed-shell electrons on different ions begins to play an important role. Again, in using a potential to represent electron-ion interaction, we have neglected the fact that the ions possess a structure (the core electrons); again, where the Pauli principle plays an important role in the interaction between the valence electrons and the core electrons, that interaction may no

longer be represented by a simple potential. It is desirable to consider the validity of these approximations in detail, but such a study lies beyond the scope of this book; we shall therefore simply regard them as valid for the problems we study here. (It may be added that compared to the approximations which of necessity we shall have to make later, the present approximations look very good indeed.)

In general one studies only selected parts of the Hamiltonian, (1-4). Thus, for example, the band theory of solids is based upon the model Hamiltonian,

$$H_B = \sum_i \frac{p_i^2}{2m} + \sum_{i,j} v(\mathbf{r}_i - \mathbf{R}_{j0}) + V_H(\mathbf{r}_i) \quad (1-8)$$

where the \mathbf{R}_{j0} represents the fixed equilibrium positions of the ions and the potential V_H represents the (periodic) Hartree potential of the electrons. One studies the motion of a single electron in the periodic field of the ions and the Hartree potential, and takes the Pauli principle into account in the assignment of one-electron states. In so doing one neglects aspects other than the Hartree potential of the interaction between the electrons. On the other hand, where one is primarily interested in understanding the interaction between electrons in metals, it is useful to consider only H_{electron} , (1-5), replacing the effect of the ion cores by a uniform distribution of positive charge. In this way one can approximate the role that electron interaction plays without having present the additional complications introduced by the periodic ion potential. Of course one wants finally to keep both the periodic ion potential and the electron interactions, and to include as well the effects associated with the departure of the ions from the equilibrium positions, since only in this way does one arrive at a generally adequate description of the solid.

1-3 ELEMENTARY EXCITATIONS

We have built up our knowledge about the elementary excitations in solids by first considering various different parts of the Hamiltonian (1-4), and then taking into account the remaining terms which act to couple different excitations together. Let us adopt this approach in carrying out a preliminary survey of some of the excitations of importance in solids.

Phonons

It is well known that the motions of a crystal lattice, in which each atom vibrates about an equilibrium point, may be resolved into normal modes, each mode generally representing a wave moving through the lattice. The system, from this viewpoint, is simply a collection of harmonic oscillators, with one oscillator for each of the lattice waves;

if we impose the quantum commutation rules on the canonical momenta, the familiar harmonic-oscillator energy spectrum is obtained. These elementary units of lattice excitation are given the name *phonon*; phonons are bosons, and represent perhaps the simplest elementary excitation in a solid.

One arrives at a description in terms of completely independent phonons if one takes the ion Hamiltonian as (1-5) and keeps only the terms which are quadratic in the displacement of the ions from their equilibrium positions. If, however, one includes as well the third-order, or anharmonic, terms in the expansion of the potential energy, one finds a *phonon-phonon interaction*; this interaction gives rise to a scattering between phonons of different wavevectors which acts to limit the lifetime of a given phonon; it acts also to shift the phonon energy.

Another term which influences phonon motion is the *electron-phonon interaction*, which one obtains on keeping the first-order term (in the displacement of the ions from their equilibrium positions) in the expansion of the electron-ion Hamiltonian, (1-7). In metals this term acts to change the phonon frequencies markedly from those obtained using only H_{ion} , (1-5); it also offers an additional mechanism by which the phonons may be damped.

Despite the phonon-phonon and phonon-electron interactions, both long-wavelength and short-wavelength phonons turn out to be well-defined excitations up to the melting point of a solid; in the liquid state, only the comparatively long-wavelength longitudinal phonons continue to represent a well-defined excitation.

Quasi-Particles

In the absence of electron-electron or electron-ion interaction, it is well known that we can describe the excitations of an electron system in terms of single-particle excitations, of energy

$$\varepsilon_p = \frac{p^2}{2m} - \mu_0 \quad (1-9)$$

measured relative to the chemical potential, μ_0 , for the noninteracting system. At $T = 0$, all the momentum states $p \leq p_0$ are occupied, while those for $p \geq p_0$ are empty; p_0 , the radius of the filled Fermi sphere, is simply related to the electron density. At finite temperatures, the distribution function for an excitation of momentum p is

$$f_p^0(T) = \frac{1}{e^{\beta \varepsilon_p} + 1} \quad (1-10)$$

Suppose one now considers the electron-electron interaction, that is, assumes that the system Hamiltonian is given by (1-6). It is not

obvious that there is a well-defined elementary excitation, which resembles (1-9), for this Hamiltonian, since coupling between the electrons is far from weak. Nevertheless, as Landau, Silin, and Luttinger and Nozières¹ have shown, in the presence of electron-electron interaction one can introduce a distribution function for *quasi-particles*, of energy ξ_p measured relative to the Fermi energy (or chemical potential) for the interacting system, which takes the form

$$f_p(T) = \frac{1}{e^{\beta \xi_p} + 1} \quad (1-11)$$

at low-enough temperatures. From (1-11) one obtains, for example, the familiar linear dependence on temperature of the electronic contribution to the specific heat.

One may picture the quasi-particle as a particle accompanied by a co-moving cloud of other particles. As a particle moves along, it pushes other particles out of its way, drags other particles along with it, and the like; it is this co-moving cloud which acts to alter the energy-momentum relation from (1-9) to ξ_p .

The quasi-particle description applies only to excitations in the immediate vicinity of the surface of the filled Fermi sphere; only these excitations possess a lifetime sufficiently long to satisfy the criterion (1-3). The long lifetime of quasi-particle excitations in the immediate vicinity of the Fermi surface is a simple consequence of the Pauli principle, which limits the amount of phase space available for single-particle collisions in such a way that

$$\gamma_p \sim \frac{(p - p_0)^2}{p^2} \xi_p \quad (1-12)$$

(for a quasi-particle above the Fermi surface). At a temperature T , one sees directly from (1-11) that the quasi-particles which are excited will be those lying within the shell $p_0 - \delta p \leq p \leq p_0 + \delta p$, where $(\delta p/p_0) \sim \kappa T/\mu$. The lifetime of such an excited quasi-particle will therefore be

$$\gamma_p(T) \sim \left(\frac{\delta p}{p_0} \right)^2 \xi_p \approx \left(\frac{\kappa T}{\mu} \right)^2 \xi_p$$

so that the use of the distribution function (1-11) to describe the thermodynamic properties of the system is consistent as long as $\kappa T \ll \mu$.

When one considers the static electron-ion interaction, $\sum_{ij} v(\mathbf{r}_i - \mathbf{R}_{j0})$, the above picture changes somewhat. It is then preferable to begin with the model Hamiltonian, (1-8), representing electrons moving in a

periodic potential; and to put in the electron-electron interaction subsequently. Thus one has, in the absence of electron-electron interaction, the well-known band theory of solids, according to which the electrons are labeled by their Bloch wave energies; $\varepsilon_{p\mu}^0$, where p is the momentum within a band and μ refers to the band under consideration. (We are using the extended zone scheme.) The general properties of the quasi-particle excitations (in the presence of electron interactions) have yet to be developed in any detail for this case. However, on the basis of the electron gas discussed above, it is clear that for metals the conduction-band quasi-particles in the immediate vicinity of the Fermi surface will be well-defined elementary excitations. Moreover, one can estimate the validity of a quasi-particle picture for a given band state by considering the phase-space restrictions imposed by the Pauli principle (and perhaps symmetry considerations as well) on the possibility of decay of that state as a consequence of electron-electron interaction.

Finally, we must consider the influence of *electron-phonon interaction* on the properties of our quasi-particles in solids. For metals that influence can be profound in some cases, since it gives rise to the phenomenon of superconductivity. As Bardeen, Cooper, and Schrieffer² have shown, superconductivity can arise in metals as a consequence of an attractive phonon-induced, electron-electron interaction. For superconductors, the quasi-particle spectrum takes the form

$$\xi_p^s = \left[\xi_p^2 + \Delta^2 \right]^{1/2} \quad (1-13)$$

where ξ_p is the usual quasi-particle energy measured relative to the Fermi surface and Δ is a constant. The distribution function for the quasi-particles in a superconductor is given by

$$f_p^s(T) = \frac{1}{e^{\beta \xi_p^s} + 1} \quad (1-14)$$

Because of the energy gap, Δ , in the quasi-particle spectrum, the specific heat of a superconductor is proportional to $\exp -(\beta \Delta)$ at sufficiently low temperatures.

It should be added that for normal metals (as distinct from superconductors) the electron-phonon interaction acts to change the quasi-particle energy and the specific heat. It also provides an additional quasi-particle damping mechanism and acts to limit the conductivity of metals at all temperatures. However, it does not alter the concept of the quasi-particle as a well-defined elementary excitation of the system in the immediate vicinity of the Fermi surface.

Plasmons

Yet another kind of elementary excitation is possible for an interacting electron gas, as described by the Hamiltonian (1-6). In such a

system, as a consequence of the Coulomb interaction, one can have a collective oscillation of the electron particle density, the plasma oscillation. In the limit of long wavelengths, the frequency of the oscillation is given by the plasma frequency;

$$\omega_p = \left(\frac{4\pi N e^2}{m} \right)^{1/2} \quad (1-15)$$

where N is the electron density. The plasma oscillation has no counterpart in the noninteracting electron system; it corresponds directly to the oscillations studied by Langmuir and Tonks in classical gaseous discharges, or plasmas. The quantum of plasma oscillation is the plasmon; plasmons are bosons, and have a distribution function of the characteristic boson form at finite temperatures. A low-momentum plasmon has an energy $\hbar\omega_p$; according to (1-15) plasmon energies range from about 5 to 30 eV for electron systems of metallic densities; consequently plasmons play no role in determining the thermodynamic properties of an electron system.

The plasmon is not a completely well-defined elementary excitation, in that it can decay into pairs of quasi-particles: however, at long wavelengths, the imaginary part of the energy of a plasmon of momentum p is proportional to $(p/p_F)^2\omega_p$, so that the excitation easily satisfies the criterion, (1-3).

When one takes into account the influence of the periodic ion potential on the plasmon spectrum, one finds that the plasmon lifetime depends on the strength of the electron interband transition of energy in the vicinity of $\hbar\omega_p$. For many solids, $\hbar\omega_p$ is large compared to the interband excitations of importance (the latter often being only a few electron volts). Consequently, the valence-electron plasmon is a well-defined excitation for a wide group of metals, semiconductors, semimetals, and insulators.

Other Elementary Excitations

We mention briefly certain other elementary excitations which one encounters in solids, and which we shall not have an opportunity to consider in detail in this book. In insulating polar crystals, an electron in the conduction band is strongly coupled to the optical mode of the lattice vibrations. As a result, when the electron moves, it is accompanied by a co-moving cloud of phonons, which may act to change its mass appreciably. The resultant quasi-particle is known as a *polaron*.³

In insulators, or in certain semiconductors, in consequence of electron-electron interaction, there may exist well-defined elementary excitations within the energy gap which separates the valence-electron band from the conduction-electron band. The excitations are

known as *excitons*³: they correspond to a bound electron-hole pair state. The energy of an exciton lies within the gap as a consequence of the attractive Coulomb interaction between an electron excited from the valence band and the hole it has left behind there. Excitons, like plasmons, are bosons.

In a ferromagnet, the low-lying excitations correspond to oscillations in the electron-spin-density fluctuations, and are known as spin waves. The quantized spin waves are called magnons⁴; these obey Bose statistics, and may be used to treat the thermodynamic properties of a ferromagnetic system.

1-4 THE MEASUREMENT OF THE ELEMENTARY EXCITATION SPECTRUM

One measures directly the spectrum of elementary excitations in a solid by means of various kinds of external probes. The ideal external probe is one which is only very weakly coupled to the solid, so that the system response can be expressed in terms of the properties of the excitations in the absence of the probe. The great strides which have been made in the purification of solids have enabled the experimentalist to use more and more sophisticated external probes, often involving a combination of both static and time-dependent magnetic and electric fields. A high degree of purity is required because even quite small amounts of impurity may tend to mask the subtle resonance effects under investigation. One of the major consequences of the development of better probes and "better" solids is our vastly improved and by now quite detailed knowledge of the Fermi surface of a number of metals.⁵

Great advances have been made too in the development of external probes which do not depend on an applied magnetic field. Here we may mention three such, which we shall consider in some detail in the course of this book:

1. The direct measurement of the phonon spectrum in solids by means of the inelastic scattering of slow neutrons.
2. The direct measurement of the valence-electron excitation spectrum, and particularly the plasmons, by means of the inelastic scattering of fast electrons.
3. The extension of optical measurements of the electronic excitation spectrum to the region between 5 and 25 ev.

Both neutron scattering and fast electron scattering represent examples of longitudinal probes of the elementary excitations. In both cases, the external probe couples directly to a longitudinal excitation, the density fluctuation of the solid. On the other hand, measurements of the optical reflectivity of a solid constitute a transverse probe of the solid, in that the electromagnetic wave couples directly to the transverse current-density fluctuations of the electrons.

Concurrent with the experimental advances has been the realization on the part of theorists that for a weakly coupled external probe one can specify the system response in terms of the exact eigenstates of the many-particle system under consideration. Such a description may serve as a starting point for detailed theoretical calculations based on a specific model for the system. Moreover, one can, for example, relate the measurements of the density-fluctuation spectrum directly to the space-time particle-particle correlations and fluctuations in the solid, and so obtain a more detailed understanding of the system behavior.

1-5 SCOPE OF THE BOOK

As is clear from the title, the elementary excitations on which we shall focus our attention are electrons, phonons, and plasmons. Although some of our treatment will be comparatively general, for the most part the specific applications which are developed in the course of the book have to do with "simple" metals, that is, metals which display essentially free-electron-like behavior. Thus we shall often have in mind the alkali metals (the favorite metals of the theorist); we shall steer clear of the transition metals and rare earths. It should also be emphasized that it is not possible to treat the properties of even alkali metals with an accuracy of, say, 1 per cent. There are simply too many variables, too many approximations that one is forced to make along the way, to hope to arrive at this sort of accuracy for a calculation of solid-state properties from first principles. One therefore speaks of a "good" agreement between theory and experiment for the alkali metals if the agreement approaches, say 10 to 15 per cent. Such a close correspondence between theory and experiment is not to be hoped for, in general, when one is comparing theory and experiment for a given solid-state property.

Our general plan is to present the excitations, and their mutual interaction, in what might be regarded as an order of increasing complexity. Thus we begin with phonons, since these represent in many ways the simplest of the elementary excitations in solids. In Chapter 2 we review some general features of phonons in solids and discuss briefly the phonon dispersion relation in simple metals. We consider the phonon contribution to the specific heat and the stability of a solid against melting as simple examples of quantum statistical calculations based on the notion of independent elementary excitations. The use of slow neutrons as a probe of phonon spectra in solids is described in some detail, and a sketch is given of some of the general features of phonon-phonon interaction.

Following a review of the Sommerfeld-Hartree free electron model in Chapter 3, the Hartree-Fock approximation is discussed. There follows a preliminary and essentially historical survey of electron

interactions in a dense electron gas. The approach of Wigner, Bohm, and Pines, and Gell-Mann and Brueckner, are described; the important physical concepts of screening and collective oscillation (plasmons) are presented in elementary fashion. There follows a somewhat formal section on the definition of the frequency and wave-vector-dependent dielectric constant, and of the dynamic form factor, and the way these concepts permit one to obtain in simple fashion a number of interrelated physical properties of an electron system. These include time-dependent density correlations, the scattering of a fast charged particle, the pair-distribution function, and the ground-state energy. Emphasis is placed here on the *exact* specification of the system response to longitudinal fields which vary in space and time. The dielectric constant is then derived in the random phase approximation, and the aforementioned physical properties in this approximation are derived and discussed. The concluding section of this chapter is devoted to a consideration of electron interactions in simple metals. Following a discussion of the inapplicability of the random phase approximation, the calculations that have been carried out for the correlation energy, the specific heat, and the spin susceptibility of the alkali metals are presented.

The first part of Chapter 4 is devoted to the way electron interaction in solids differs from that in a free-electron gas; in particular, the changes in screening behavior and the plasmon spectra are considered. The experimental observation of plasmon spectra in solids by means of fast-electron-scattering experiments is then presented in some detail. There follows a discussion of the optical properties of solids, in which considerable use is made of the formalism developed to treat the dielectric response of an electron system. A selected group of recent optical experiments on metals and semiconductors is then described; the emphasis is here placed on the high-frequency (5 to 25 eV) behavior of the electron systems in question.

Perhaps the principle emphasis in Chapter 5 is to sort out the consequences of dealing simultaneously with electron-electron and electron-phonon interaction in simple metals. The alteration in phonon frequencies arising from electron-phonon *and* electron-electron interaction is discussed in some detail, as is the phonon-induced electron-electron interaction, which plays such an important role in the theory of superconductivity. As a typical example of a nonequilibrium calculation involving large quantum systems described by coupled excitations, the way in which a system of coupled electrons and phonons approaches equilibrium is considered. The high-temperature conductivity of simple metals is discussed; the chapter concludes with a brief description of the low-temperature conductivity, and of quasi-particle properties in simple metals.

References

1. For review of the Landau Fermi liquid theory, and its application to the electron gas, see P. Nozières, "Interacting Fermi Systems," Dunod-Benjamin, 1963, Chapter 1.
2. For an excellent recent review of the BCS theory, see the article by J. Bardeen and J. R. Schrieffer, in "Progress in Low Temperature Physics," Vol. 3 (ed. by C. J. Gorter), North-Holland, Amsterdam, 1961.
3. See, for example, "Polarons and Excitons" (the Proceedings of the Scottish University Summer School in Theoretical Physics), 1962.
4. See, for example, the lectures by C. Kittel, in "Low Temperature Physics," edited by C. DeWitt, B. Dreyfus, and P. G. de Gennes, Gordon and Breach, New York, 1962.
5. See, for example, the lectures by A. B. Pippard in "Low Temperature Physics," op. cit.

Chapter 2

PHONONS

2-1 LATTICE DYNAMICS IN ONE DIMENSION

Lattice-Wave Dispersion Relation

We begin our study of phonons with a brief review of lattice dynamics and the quantization of the phonon field. It is recommended to the reader who is unfamiliar with these topics that he consult one of the standard texts (Peierls¹ or Ziman,² for example) where more of the mathematical details and physical discussion may be found.

Because we are here interested primarily in lattice motion, we shall restrict our attention to that part of the general Hamiltonian, (1-4), which involves ion motion only, H_{ion} . We return later (in Chapter 5) to a discussion of the coupled motion of ions and electrons in metals.

Most of the salient features of phonons may be understood from a study of a one-dimensional solid, i.e., a linear atomic array. For that reason, we begin our review there, and consider the appropriate three-dimensional generalization in a subsequent section.

The simplest linear crystal structure for similar ions is one of equal spacing. The equilibrium position of the n^{th} ion is denoted by R_{no} . Obviously, we have $R_{no} = na$, where a is the interionic spacing. The actual position (under vibrations) of the n^{th} ion is R_n . Defining δR_n as the departure from equilibrium of the n^{th} ion, we obtain

$$R_n = R_{no} + \delta R_n \quad (2-1)$$

For our one-dimensional solid, the Hamiltonian of the system is

$$H = \sum_i \frac{P_i^2}{2M} + \frac{1}{2} \sum_{i \neq j} V(R_i - R_j) \quad (2-2)$$

where R_i and P_i are the position and momentum of the i^{th} ion.

One assumes that the displacement from equilibrium of the ions is small, so that one can expand any quantity involving R_n , say, as a Taylor series in δR_n . Thus one expands $V(R_i - R_j)$ in a Taylor series about the equilibrium separation $R_{i0} - R_{j0}$. Retaining up to the quadratic terms in δR_i , we may write (2-2) as

$$H = \sum_i \frac{P_i^2}{2M} + \frac{1}{2} \sum_{i \neq j} V(R_{i0} - R_{j0}) + \sum_{i,j} \frac{A_{ij}}{2} \delta R_i \delta R_j \quad (2-3)$$

where

$$A_{ij} = \frac{\partial^2 V(R_i - R_j)}{\partial R_i \partial R_j} \quad i \neq j \quad (2-4)$$

$$A_{ii} = \sum_{j \neq i} \frac{\partial^2 V(R_i - R_j)}{\partial R_i^2} \quad (2-5)$$

The terms linear in δR_i do not contribute to (2-4) because of the equilibrium condition, $\partial V(R_i - R_j)/\partial R_i = 0$ (the force on any atom vanishes in equilibrium). The second term in the right-hand side of (2-4) is a constant and may be neglected hereafter.

The equation of motion for the i^{th} ion is

$$\dot{P}_i = - \frac{\partial H}{\partial R_i} = M \ddot{\delta R}_i$$

or

$$M \ddot{\delta R}_i = - \sum_j A_{ij} \delta R_j \quad (2-6)$$

Focussing our attention on oscillatory solutions we let

$$\delta R_i(t) = e^{-i\omega t} \delta R_i \quad (2-7)$$

(The use of the same symbol for the time-dependent and time-independent displacement should not cause confusion.) This substitution gives for (2-6)

$$M\omega^2 \delta R_i = \sum_j A_{ij} \delta R_j \quad (2-8)$$

There are certain limitations placed on the solutions of (2-8), limitations which arise because of the periodic character of the equilibrium ionic array. Clearly the physical properties of the system are unaltered by the displacement,

$$R_n \rightarrow R_n + na$$

where n is an integral number. Put another way, there is nothing which distinguishes the motion of the i^{th} atom from that of its neighbors. As a result, the solutions for R_i and R_{i+1} can differ at most by a phase factor. We therefore write

$$\delta R_{n+1} = e^{ika} \delta R_n \quad (2-9)$$

A solution of (2-9) is obtained if we write

$$\delta R_n = q_k e^{ikR_n} = q_k e^{ikna} \quad (2-10)$$

with q_k independent of n , as direct substitution of (2-10) into (2-9) shows. The mathematical proof that (2-9) and (2-10) are a direct consequence of periodicity is known as Floquet's theorem,^{2a} and is given as a problem at the end of this chapter.

We see that the different solutions of (2-8) may be labeled by the wave vector k . So far no mention has been made as to what values of k we might expect. The exact specification of k depends on the boundary conditions. The most convenient choice is a periodic boundary condition as, for one thing, it provides a simple way to count available states. In our one-dimensional study we use a long "chain." We require, then, that if we go a distance $L = Na$, we obtain the same result for any physical property, such as the lattice displacement. Inspection of (2-10) shows that $kL = 2\pi n$, where n is an integer; that is,

$$k = \frac{2\pi n}{L} = \frac{2\pi}{a} \frac{n}{N} \quad (2-11)$$

We can write down the density in k space, i.e., the number of normal modes per unit k . This becomes

$$\frac{dn}{dk} = \frac{L}{2\pi} \quad (2-12)$$

More often, one is interested in the number of states per unit frequency, i.e.,

$$dn/d\omega = (dn/dk) [1/(\partial\omega/\partial k)] = L/2\pi [1/(\partial\omega/\partial k)]$$

We remark that not all values of k are independent; only a finite number are unique. Inspection of either (2-9) or (2-10) shows that the equation for δR_n is invariant if one changes k to $k + 2\pi a$. Thus only those values of k which lie in the range 0 to $2\pi/a$ constitute a unique set. However, it is often more convenient to let k be in the range defined by

$$-\pi/a \leq k \leq \pi/a \quad (2-13)$$

The number of independent k values is obtained with the aid of (2-12) as

$$\frac{dn}{dk} \Delta k = (L/2\pi)(2\pi/a) = L/a = N \quad (2-14)$$

The number of independent values of k is thus the same as the number of ions (in a chain of length L).

The dispersion relation which determines ω as a function of k is obtained by substituting (2-10) into (2-8). One finds

$$M \omega_k^2 = \sum_j A_{ij} e^{ik(R_{j0} - R_{i0})} \quad (2-15)$$

a result which involves only the distance between the atoms, as it should.

Equation (2-15) is the dispersion relation that determines ω^2 (or ω) as a function of k . There are several quite general properties which this dispersion relation possesses. First, for $k = 0$,

$$M \omega^2(0) = \sum_j A_{ij} = 0 \quad (2-16)$$

That (2-12) is true may be seen either from the translational invariance of the system or by a direct substitution of (2-4) and (2-5) into (2-15) and the use of $\partial/\partial R_i = -\partial/\partial R_j$ in those equations. Hence, ω_k starts out at the value 0. The second observation is that ω^2 is an even function of k . This is easily obtained from the symmetry of the coefficients, A_{ij} . Hence it follows for small k that

$$\omega^2 = s^2 k^2 + \dots \quad (2-17)$$

Here s represents the speed of sound.

It is instructive to solve the dispersion relation (2-15) for the case of atoms interacting via nearest neighbor interactions only; the calculation is given as a problem for the reader.

Transformation to Normal Modes

We now consider the transformation from the N coordinates, R_i , which represent the positions of the atoms, to N new coordinates, q_k , which describe the normal modes of oscillation of the ions about their equilibrium positions. The transformation is given by

$$P_i = \left(\frac{M}{N}\right)^{1/2} \sum_k p_k e^{ikR_i} \quad (2-18a)$$

$$\delta R_i = \frac{1}{(NM)^{1/2}} \sum_k q_k e^{ikR_i} \quad (2-18b)$$

where p_k is the momentum conjugate to q_k . Here all the dynamical variables are time-dependent and from the reality condition for P_i and δR_i , we obtain $2N$ relations:

$$\begin{aligned} p_k^+ &= p_{-k} \\ q_k^+ &= q_{-k} \end{aligned} \quad (2-19)$$

These relations reduce the number of independent variables from $4N$ (real and imaginary parts of p_k and q_k) to $2N$, as one would expect.

With the aid of the dispersion relation (2-15), the Hamiltonian (2-3) can be rewritten in terms of the new coordinates as

$$H = \sum_k \frac{p_k^+ p_k}{2} + \omega_k^2 \frac{q_k^+ q_k}{2} \quad (2-20)$$

where ω_k is determined by the dispersion relation (2-15). The Hamiltonian (2-20) describes a harmonic-oscillator field decomposed into independent normal modes.

Quantization of the Lattice Waves

Because the Hamiltonian for the lattice waves resembles a collection of independent harmonic oscillators, the quantization of the lattice waves proceeds along the well-known route followed for the harmonic oscillator.³ We first remark that the commutation rules for the lattice coordinates, p_k and q_k , follow directly from those for individual ion coordinates, which read:

$$\begin{aligned} [P_i, \delta R_j] &= (\hbar/i) \delta_{ij} \\ [P_i, P_j] &= [R_i, R_j] = 0 \end{aligned} \quad (2-21)$$

It is an elementary exercise to show that because of (2-18a) and (2-18b), one finds

$$\begin{aligned} [p_k, q_{k'}] &= (\hbar/i) \delta_{kk'} \\ [p_k, p_{k'}] &= [q_k, q_{k'}] = 0 \end{aligned} \quad (2-22)$$

One could, if one liked, discuss the properties of the quantized lattice waves in terms of the representation specified by the Hamiltonian (2-20) and the commutation rules (2-22). It is, however, far more convenient to transform to a different representation, in which the lattice-wave function describes only the number of quantized lattice waves present under given conditions. A quantized lattice wave is known as a *phonon*. In this representation the operators of interest are no longer the coordinates or momentum of a given lattice wave, but rather correspond to operators which change the number of phonons.

The transformation is specified by the equations

$$\begin{aligned} p_k &= [\hbar\omega_k/2]^{1/2} i (a_k^\dagger - a_{-k}) \\ q_k &= [\hbar/2\omega_k]^{1/2} (a_k + a_{-k}^\dagger) \end{aligned} \quad (2-23)$$

The a_k and a_k^\dagger act to destroy, and create, a phonon of wave vector k , energy $\hbar\omega_k$, respectively. Their properties may be obtained directly from their commutation rules, which are a simple consequence of the transformation (2-23), and (2-22),

$$\begin{aligned} [a_k, a_{k'}^\dagger] &= \delta_{kk'} \\ [a_k, a_{k'}] &= [a_k^\dagger, a_{k'}^\dagger] = 0 \end{aligned} \quad (2-24)$$

The transformed Hamiltonian reads

$$H = \sum_k \hbar\omega_k [a_k^\dagger a_k + 1/2] \quad (2-25)$$

The various properties of the operators and eigenstates of the Hamiltonian, (2-25), may be found in any standard textbook on quantum mechanics.³ Here we summarize those which are most essential for what follows, namely,

$$N_k^{\text{op}} = a_k^\dagger a_k \quad (2-26)$$

$$N_k^{\text{op}} |n_k\rangle = n_k |n_k\rangle \quad (2-27)$$

$$a_k |n_k\rangle = \sqrt{n_k} |n_k - 1\rangle \quad (2-28)$$

$$a_k^\dagger |n_k\rangle = \sqrt{n_k + 1} |n_k + 1\rangle \quad (2-29)$$

$$a_k |0\rangle = 0 \quad (2-30)$$

In (2-26), N_k^{op} is the number operator; it commutes with the Hamiltonian, (2-25); according to (2-27) its eigenvalues, n_k , specify the number of phonons present of wave vector k . $|n_k\rangle$ denotes the system wave function in which there are n phonons of wave vector k present [the number of other phonons present not being relevant for equations (2-26) through (2-29)]. Equations (2-28) and (2-29) tell us that a_k and a_k^\dagger do play the role of destruction and creation operators, while in (2-30) $|0\rangle$ is the ground-state wave function, in which there are no phonons present.

Finally one has

$$E_o = \sum_k \frac{\hbar \omega_k}{2} \quad (2-31)$$

so that the ground-state energy is a sum of the zero-point energies of the phonons, and

$$H |n_k\rangle = (E_o + n_k \hbar \omega_k) |n_k\rangle \quad (2-32)$$

so that each phonon may be regarded as possessing an energy $\hbar \omega_k$.

Phonon "Pseudomomentum"

It is tempting to assume that a phonon of wave vector k possesses a momentum $\hbar k$. This is not however true, as we may see most directly if we recall that there are only N independent values of k , lying between $-\pi/a < k < \pi/a$. The "momentum" of a phonon is thus not defined to within an integral multiple of $2\pi/a$. To put the matter another way, if one considers a momentum transfer $\hbar q$ to the ions, in a process in which only a single phonon is involved, the momentum conservation condition reads

$$\hbar q = \hbar k + \hbar K_n \quad (2-33)$$

where K_n is the reciprocal lattice wave vector, defined by

$$K_n = \pm n \frac{2\pi}{a} \quad (2-34)$$