

Chapter 1

Condensed Matter Hamiltonian

1 NATURE OF CONDENSED MATTER

Structure of the Theory

Ultimately our goal is to understand, at the highest level of accuracy possible, the binding and the excitations of condensed matter systems. Condensed matter means solids and liquids, where solids can be crystalline or amorphous. The excitations consist of two classes, (a) motion of the nuclei, resolved into harmonic vibrational motion (phonons), plus corrections which are characteristic of solids, or of liquids, and (b) excitation of the electrons, modified through interaction with the nuclear motion. From the outset the complete theory is developed, to include metals and insulators, solids and liquids, within a single formulation. The accuracy and generality of theory is determined by comparisons with experimental data for real materials, and also by comparisons with computer simulations for model Hamiltonians. Only highly accurate experimental data are used, and those measurements which provide the most useful information in the present study are the phonon dispersion curves and elastic constants, and the thermodynamic entropy as function of temperature for solid and liquid phases.

Our study is limited to the elements, where the most extensive and reliable experimental data are available, and where the theory is as simple as possible. The nature of binding and excitations, and of the equilibrium statistical mechanical properties, is the same for alloys and compounds.

Our procedure is classic many-body physics. For a given material, all our information is coded into its Hamiltonian. All the equilibrium prop-

erties which can be compared with experiment follow in principle from the Hamiltonian. Indeed, nonequilibrium properties follow from the same Hamiltonian, but practical application of nonequilibrium statistical mechanics is not sufficiently developed to be helpful in our present study. On the other hand, precise information gained here, about the Hamiltonian and its equilibrium statistical properties, will help in developing the nonequilibrium theory. As we shall see in the following sections, the Hamiltonian for a condensed system of nuclei and electrons can be written

$$\mathcal{H} = \sum_K \frac{\mathbf{p}_K^2}{2M} + \Phi(\{\mathbf{r}_K\}) + \mathcal{H}_{EX}, \quad (1.1)$$

where the nuclei are labeled by the index K and have momenta and positions \mathbf{p}_K and \mathbf{r}_K respectively, and where M is the nuclear mass, $\Phi(\{\mathbf{r}_K\})$ is the potential for the nuclear motion, and \mathcal{H}_{EX} expresses electronic excited states. This form of \mathcal{H} covers our entire program, but its appearance is deceptively simple. It is necessary to use our deepest understanding of condensed matter to express (1.1) in a form which is tractable even in leading order. This is illustrated by the example of a crystal, where we know that the nuclei move only in the near vicinity of the lattice sites, so in leading approximation the potential Φ can be expanded to quadratic order in displacements from equilibrium, and the electronic states can be evaluated for the perfect crystal. In a similar way, a newly developed picture of the motion of nuclei in a monatomic liquid transforms the Hamiltonian of Eq. (1.1) into a tractable approximation for equilibrium liquid dynamics (Chapter 5).

A condensed matter system is composed of nuclei and electrons, point particles with only mutual Coulomb interactions. Fermi statistics is always important for the electrons, just as in free atoms, while the nuclear exchange statistics is almost always unimportant because, in most solids and liquids, the nuclei remain sufficiently well separated that exchange is virtually zero. Condensed matter systems where nuclear exchange is important, such as helium isotopes, are not covered by our presentation. It is also justified to treat condensed matter as a collection of rigid ions plus valence electrons, where each ion is a nucleus with a closed-shell core of electrons, and the valence electrons are those which participate in the binding and the excitations of the system. The core electrons remain nearly the same as the inner shells of a free atom, but the valence electrons occupy col-

lective states of the whole system, whose energies are spread into bands. Qualitatively, the binding of a condensed matter system is composed of an attractive term and a repulsive term, expressing the same physics as the binding of a molecule. The attractive term arises because, when a number of free atoms are brought together, so that their electrons begin to overlap, the electron density can move preferentially into spaces directly between nearest-neighbor nuclei, thus lowering the Coulomb energy of the system. The repulsion arises because, as a result of spin statistics, electron wavefunctions must be mutually orthogonal in real space, and this is achieved by wavefunction oscillations, producing (positive) kinetic energy. This term is also called Pauli repulsion. We shall now discuss how the various binding types of solid and liquid elements result from different ways in which the valence electrons can maximize the total binding energy.

Metals

For a metal, the valence band is broad and continuous in energy, and the groundstate energy is lowered with respect to free atoms by putting the valence electrons into the lower levels of the valence band (or bands). This means there are empty electronic states immediately above the highest occupied states, hence the electrons can move around easily, and this gives rise to the high conductivity of metals. For this reason the valence electrons, or sometimes the most mobile of them, are called conduction electrons. The high mobility of conduction electrons gives metals their strong screening capability, so that the effective internuclear forces, or interionic forces, are screened Coulomb forces. The presence of empty electronic states immediately above the Fermi energy also allows significant thermal excitation of electrons, at all temperatures of interest in condensed matter physics, and this gives rise to a free energy contribution present only in metals. These properties hold for all metallic systems, elements and alloys in solid and liquid phases.

An important subgroup of metals is the nearly-free-electron (NFE) metals, also called the simple metals. Their importance derives from two factors: (a) experimentally, these are the most thoroughly studied of all the elements in solid and liquid form, and accurate experimental data are available for many properties under widely varying conditions, and (b) we have a simple approximate electronic structure theory, and a corresponding Hamiltonian of the form of Eq. (1.1), which give good theoretical accounts

of the microscopic and macroscopic properties of the NFE metals. This theory, pseudopotential perturbation theory, is presented in Sec. 5. The corresponding interionic potential has the form

$$\Phi(\{\mathbf{r}_K\}) = \Omega(V) + \frac{1}{2} \sum_{KL} \phi(|\mathbf{r}_K - \mathbf{r}_L|; V) + \frac{1}{6} \sum_{KLM} \phi_{KLM} + \dots \quad (1.2)$$

Here $\Omega(V)$ is large and negative, is the main contribution to the binding energy, and depends on only the volume V , or more precisely on the volume per atom V_A . The pair potential $\phi(r; V)$ depends on the ion positions, hence controls the motion of the ions, and $\phi(r; V)$ also depends explicitly on V , because it works through the screening electrons. Three-ion interactions ϕ_{KLM} , and higher order interactions represented by $+\dots$ in Eq. (1.2), are present in the theory, but are formally small and usually neglected. Qualitatively for NFE metals at normal density, the magnitude $|\sum_{KL} \phi_{KL}|$ is small compared to $|\Omega(V)|$, and the depth of the attractive well in $\phi(r; V)$ is on the order of the melting temperature.

The theoretical pair potential for metallic Na is shown in Fig. 1.1. In pseudopotential perturbation theory, $\phi(r; V)$ has long range Friedel oscillations, but their magnitude is small compared to the accuracy of the theory. Hence it is justified to damp out the oscillations, to achieve a short range potential convenient for molecular dynamics simulations, as shown in the figure.

Among the well-studied elements in the periodic table, there are 22 NFE metals, 22 transition metals, 14 lanthanides, and a few actinides. Density functional theory does well for the electronic structure of all metals, except for the problem of localized f electrons (see the discussion at the end of Sec. 2). For non-NFE metals, there are no general theoretical forms for $\Phi(\{\mathbf{r}_K\})$, such as the NFE form given by Eq. (1.2), but much work is being done in this area. We are aware of no exceptions to the two rules, that solid metals melt to liquid metals, and that metals remain metals under compression. Whenever we study the physical properties of an elemental solid or liquid, we tend to compare them with the corresponding properties of a representative metal, that is to say, metals are our reference condensed-matter system.

The elements As, Sb, and Bi are metals with extremely small Fermi surfaces, corresponding to almost filled and almost empty bands, hence these elements have very small conductivities, and are called semimetals. These

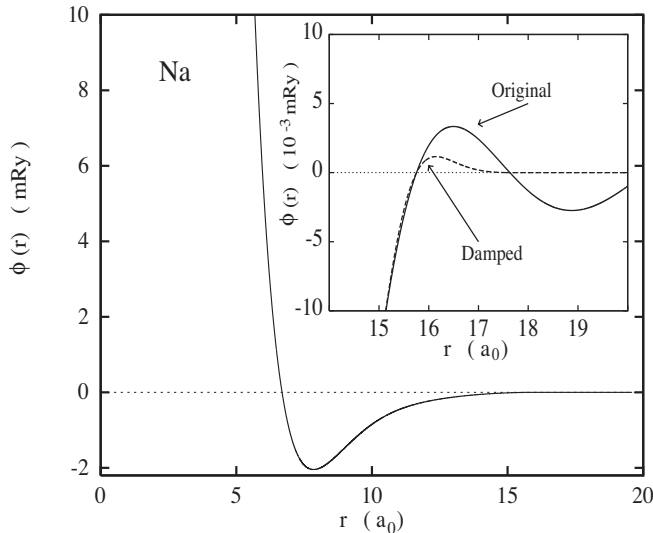


Figure 1.1. The ion-ion potential for pseudopotential sodium at $V_A = 278a_0^3$, the atomic volume of liquid sodium at melt. The original potential is from Wallace (1968), and the damped potential is from Wallace and Clements (1999).

elements melt to ordinary liquid metals, which in reasonable approximation are NFE metals, and as solids they are expected to become metallic upon sufficient compression.

Van der Waals Forces

In a free rare-gas atom, the electrons fill a closed shell. The atomic charge density, nucleus plus electrons, undergoes quantum fluctuations, all multipoles appear, but on average the charge density is spherically symmetric. When two such atoms are present, the fluctuating electrostatic multipole-multipole interaction can be treated in perturbation theory, and in second order, where the interactions are squared before they are averaged, a nonzero energy appears. The leading electrostatic energy is an attractive dipole-dipole interaction, proportional to r^{-6} , where r is the nuclear separation. This is the van der Waals interaction, and is responsible for most of the binding of a condensed system of rare-gas atoms. When two rare-gas atoms are far apart, such that the transit time of a photon between them is greater than the nominal charge-fluctuation time, then the electrostatic

potential becomes retarded, and the interatomic potential goes over to an r^{-7} dependence, and is a Casimir interaction (see Milonni, 1994, Chaps. 7 and 8; also Spruch, 1986).

When two rare-gas atoms are close enough that their electron densities overlap, the Pauli repulsion appears, and is especially strong because the electrons fill closed atomic shells. The *ab initio* theory of the forces between rare gas atoms, called dispersion forces, is under development still today. Density functional theory, in the form currently applied to condensed matter, is unable to account for dispersion forces. An empirical potential representing the interaction between two rare-gas atoms is the Lennard-Jones (LJ) potential,

$$\phi(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] , \quad (1.3)$$

where $\phi(r)$ passes through zero at $r = \sigma$, and has a minimum of $-\epsilon$ at slightly larger r . Parameters in the LJ potential are determined by fitting to experimental data (see Hirschfelder, Curtiss, and Bird, 1954; Guyer, 1969; Nardone *et al.*, 1996; and Suni, 1997). Parameters determined by fitting theoretical virial coefficients to experimental gas data are, from Hirschfelder *et al.* (1954),

$$\text{LJAr} : \quad \epsilon/k = 119.8K, \quad \sigma = 3.405 \overset{\circ}{\text{A}} . \quad (1.4)$$

We have used this potential in computer simulations, and it gives agreement at the few percent level with thermodynamic data for crystal and liquid Ar.

For a rare-gas solid or liquid, with the LJ potential, or with any central potential $\phi(r)$, the total nuclear-motion potential is

$$\Phi(\{\mathbf{r}_K\}) = \frac{1}{2} \sum_{KL} \phi(|\mathbf{r}_K - \mathbf{r}_L|) . \quad (1.5)$$

The system is weakly bound, hence has large compressibility and large thermal expansion. These properties are revealed in the scaled quantities listed in Table 1.1, where the volumes V_0 , V_{cm} , and V_{lm} are respectively the volume of the crystal at $T = 0$, the crystal at melt, and the liquid at melt. The relative expansion of the crystal from $T = 0$ to melt is larger for van der Waals than metallic forces, and the relative expansion from crystal

to liquid at melt is *much larger* for van der Waals than metallic forces. T_m and T_v are respectively the melting and vaporization temperature, and the last column shows that the van der Waals liquid at melt is *barely bound*. As a consequence, rare-gas liquids at melt are in fact halfway between a liquid and a gas (see Sec. 23 for a more precise characterization). On the other hand, the strong binding of metallic liquids, shown in the last column of Table 1.1, is due to the large contribution $\Omega(V)$, present in Eq. (1.2) but not in (1.5).

Table 1.1. Scaled quantities showing weakness of binding in van der Waals elements compared to metals, and showing the rigidity of covalent bonds relative to metals. There are no covalent liquids among the elements we have studied.

Bonding type	$\frac{V_{cm}-V_0}{V_0}$	$\frac{V_{lm}-V_{cm}}{V_{cm}}$	$\frac{T_v-T_m}{T_m}$
van der Waals	0.10	0.15	0.04
metal	0.07	0.04	1.5
covalent	0.02	—	—

The LJ model for Ar has been a paradigm for liquid theory for many years. The gaslike nature of this system was not recognized, and this inhibited development of a physically realistic theory of liquid dynamics. Fortunately, this problem does not appear when one studies liquid metals, which possess thoroughly liquid properties. Meanwhile it was found that modestly compressed Ar exhibits ordinary liquid behavior (see Fig. 23.1, and the compression dependence of melting in Sec. 26). We expect that all rare gases will be ordinary monatomic liquids when slightly compressed, and that all will become metals under sufficient compression.

Covalent Bonding and Other Types

Covalent electron wavefunctions consist (approximately) of linear combinations of atomic wavefunctions, split into bonding and antibonding orbitals. Covalent bonds are strongest when the bonding orbitals are completely filled, and the antibonding orbitals are completely empty. The hydrogen

molecule bond, formed with two electrons having antiparallel spins, is the prototype covalent bond. The diamond structure elements C, Si, Ge, and α -Sn are covalent. We shall omit C from our study, since dia-C at low pressure is metastable with respect to graphite, and graphite, also covalent, is strongly two-dimensional in character. Very little data are available for B, so the only covalent elements we can study are Si, Ge, and α -Sn.

Density functional theory does well for the electronic structure of the diamond crystals. A first approximation for the electronic structure is obtained from tight binding theory, with Bloch functions based on atomic sp^3 orbitals. There is a gap between bonding and antibonding valence bands, the lower band is filled, and the crystal is an insulator. The bonds are oriented toward the corners of a tetrahedron, and are quite rigid, i.e., are hard to stretch and hard to bend. The rigidity gives rise to very low compressibility and thermal expansion, and to high phonon frequencies. The extremely low relative expansion of the crystal from $T = 0$ to melt is shown in Table 1.1.

Aside from C, column IVA of the periodic table consists of Si, Ge, Sn, and Pb. Si and Ge are covalent to melt, α -Sn is covalent and transforms at around $0.6 T_m$ to metallic β -Sn, and Pb is metallic to melt. Liquid Si, Ge, Sn, and Pb are all NFE metals. Upon compression, α -Sn, Si, and Ge transform to the metallic phase with tetragonal (β -Sn) structure, and are expected to remain metals with further compression.

The elements H, N, O, and the halogens condense to diatomic molecular liquids and solids at low pressure. Also, P, S, Se, and Te have complicated bonding and very little experimental data. These systems are omitted from consideration in our study. All these elements are expected to become metallic under compression, and as metals, our present analysis will apply.

Condensed Matter Regime

We need to specify a criterion for condensed matter, consistent with the theoretical framework to be developed, and consistent with the conclusions to be drawn on the nature of solids and liquids. In all the work presented here, indeed in all our experience with solids and liquids, the essential character of condensed matter is that of collective nuclear motion within nearly-harmonic many-particle potential energy valleys. Correspondingly, the dominant term in the nuclear motion Hamiltonian is \mathcal{H}_{ph} , expressing resolution of this motion into a set of independent quasiharmonic phonons,

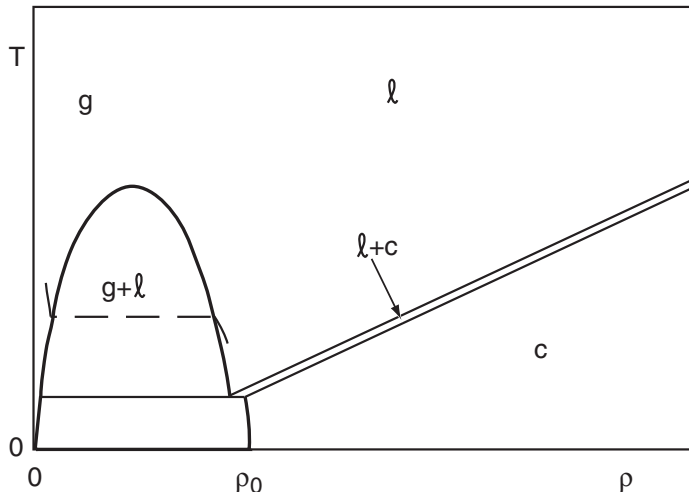


Figure 1.2. Generic phase diagram for an element in $T - \rho$ space, where g = gas, ℓ = liquid, and c = crystal. The dashed line through the gas + liquid region indicates vaporization (or condensation) at constant T and P .

and the nuclear motion entropy or specific heat is approximately that due to quasiharmonic phonons in quantum statistical mechanics. This property of the nuclear motion entropy or specific heat will be our criterion for condensed matter. When the nuclear motion is classical, which is usually the case at temperatures above a few tenths of T_m , the quasiharmonic specific heat is $3k$ per nucleus. In contrast, the nuclear motion specific heat for an ideal gas is $\frac{3}{2}k$ per nucleus.

Figure 1.2 shows a generic phase diagram for an element in temperature-density space. Several crystal phases are usually present, but only one is indicated. Density of the crystal at $T = 0$ and $P = 1$ bar is denoted ρ_0 , and the term *normal density* means any density in the vicinity of ρ_0 . At any temperature, if density is decreased from normal density, the system properties become more like a gas. When density is increased from normal density, the system should remain ordinary condensed matter, as indicated in the figure. At very high densities, our description will fail because the system will ultimately become relativistic, where particles are created out of the vacuum. This effect should be negligible to at least 10^3 or 10^4 g/cm³.

When the liquid is heated at 1 bar, thermal expansion carries it to lower densities, and eventually it arrives at the gas-liquid phase boundary,

where vaporization begins (see Fig. 1.2). The liquid might pass out of the condensed matter regime before it reaches the gas-liquid boundary. On the other hand, if the liquid is heated at constant density, it never vaporizes, and it changes only continuously and slowly to a gas. We estimate in Sec. 23 that the condensed matter criterion holds at temperatures up to around $5T_m$ at a given density. At higher temperatures, higher nuclear kinetic energy enables more gaslike motion. This effect, and other processes in condensed matter at very high temperatures, is discussed in Sec. 25.

This monograph carries the subtitle *A guide to accurate equations of state*. By equation of state, we mean the complete set of thermodynamic functions for a given material, which can be obtained from the Helmholtz free energy, which in turn is obtained from the canonical partition function. Through extensive comparison of theory and experiment, we shall demonstrate that the condensed matter Hamiltonian is sufficiently well understood, and the statistical mechanical procedures are sufficiently well tested, that we know in principle how to calculate *ab initio* the equation of state of an elemental solid or liquid, throughout the condensed matter regime, to an accuracy on the same order as the accuracy of experimental equation-of-state data. In addition, much has been learned about the errors associated with various simplifying approximations. Because it is physically based, our equation-of-state formulation provides functions of the correct form for fitting to experimental data, and provides the most reliable prediction of thermodynamic properties whenever experimental data are not available. Detailed discussions of the equation of state may be found in Secs. 20 and 25.

2 DENSITY FUNCTIONAL THEORY

Many-Electron Problem

The condensed matter system is composed of a large number of atoms, or in more detail, a collection of nuclei and electrons. The system is electrically neutral. The first step in solving for the motion is to fix the positions of the nuclei, and solve for the energy levels of the electronic system in the presence of the nuclear potential. There are Z electrons, labeled $\alpha = 1, \dots, Z$, and the position of electron α is \mathbf{r}_α . The total electronic kinetic energy

is \mathcal{T}_E ,

$$\mathcal{T}_E = - \sum_{\alpha} \frac{\hbar^2 \nabla_{\alpha}^2}{2m} , \quad (2.1)$$

and the total electron-electron Coulomb interaction is Ω_{EE} ,

$$\Omega_{EE} = \frac{1}{2} \sum'_{\alpha\beta} \frac{e^2}{|\mathbf{r}_{\alpha} - \mathbf{r}_{\beta}|} . \quad (2.2)$$

Each electron sees a potential $\mathcal{V}(\mathbf{r})$ due to the fixed set of nuclei, so that the total electronic Hamiltonian is

$$\mathcal{H}_E = \mathcal{T}_E + \Omega_{EE} + \sum_{\alpha} \mathcal{V}(\mathbf{r}_{\alpha}) . \quad (2.3)$$

Equation (2.3) is the customary Hamiltonian for the electronic structure problem. But notice there is a potential contribution that has not been mentioned, namely the Coulomb interaction among the nuclei. Common practice, followed here, is to include this interaction in $\sum_{\alpha} \mathcal{V}_{\alpha}$, though it does not actually depend on the electron positions. In this way, the Coulomb divergences present in Ω_{EE} and $\sum_{\alpha} \mathcal{V}_{\alpha}$ sum to zero. Exact composition of the total potential will be made explicit in the total Hamiltonian, Sec. 4. Since there is no spin dependence in \mathcal{H}_E , its eigenstates are spin degenerate. Spin dependent density functional theory describes magnetic states, and will not be treated in this monograph.

Let us briefly discuss the many-electron wavefunctions, for the purpose of defining electron correlation effects. It will be necessary to include spin, so that the spin states can be counted. An electron has position \mathbf{r} and spin σ , where $\sigma = 1, 2$. A normalized wavefunction is $\Phi(\mathbf{r}_1\sigma_1, \dots, \mathbf{r}_Z\sigma_Z)$ and satisfies

$$\sum_{\{\sigma\}} \int \dots \int \Phi^*(\mathbf{r}_1\sigma_1, \dots, \mathbf{r}_Z\sigma_Z) \Phi(\mathbf{r}_1\sigma_1, \dots, \mathbf{r}_Z\sigma_Z) d\mathbf{r}_1 \dots d\mathbf{r}_Z = 1 \quad (2.4)$$

where the specified sum is over both spin states for every electron. The one-electron density is $\rho(\mathbf{r})$, the probability per unit volume of having an electron at \mathbf{r} ,

$$\rho(\mathbf{r}_1) = Z \sum_{\{\sigma\}} \int \dots \int \Phi^* \Phi d\mathbf{r}_2 \dots d\mathbf{r}_Z . \quad (2.5)$$

The normalization is

$$\int \rho(\mathbf{r}) d\mathbf{r} = \mathcal{Z} \quad . \quad (2.6)$$

The two-electron density is $\rho(\mathbf{r}_1, \mathbf{r}_2)$,

$$\rho(\mathbf{r}_1, \mathbf{r}_2) = \mathcal{Z}(\mathcal{Z} - 1) \sum_{\{\sigma\}} \int \cdots \int \Phi^* \Phi d\mathbf{r}_3 \cdots d\mathbf{r}_Z \quad . \quad (2.7)$$

The normalization is

$$\int \rho(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_2 = (\mathcal{Z} - 1) \rho(\mathbf{r}_1) \quad . \quad (2.8)$$

This normalization is consistent with liquid theory (Hansen and McDonald, 1986, Sec. 2.5). Parr and Yang (1989, Eq. (2.4.3)) insert a factor of $\frac{1}{2}$ in $\rho(\mathbf{r}_1, \mathbf{r}_2)$. Positional correlations of the electrons are contained in $\rho(\mathbf{r}_1, \mathbf{r}_2)$. These correlations are isolated in the pair correlation function $g(\mathbf{r}_1, \mathbf{r}_2)$, defined by

$$\rho(\mathbf{r}_1, \mathbf{r}_2) = \rho(\mathbf{r}_1) \rho(\mathbf{r}_2) g(\mathbf{r}_1, \mathbf{r}_2) \quad . \quad (2.9)$$

The pair correlation function is a conditional probability: given an electron at \mathbf{r}_1 , the probability per unit volume of an electron at \mathbf{r}_2 is $\rho(\mathbf{r}_2)g(\mathbf{r}_1, \mathbf{r}_2)$. At large separations, there is no correlation, so $g(\mathbf{r}_1, \mathbf{r}_2) \rightarrow 1$ at large separations, and the *local* correlation is contained in the function $h(\mathbf{r}_1, \mathbf{r}_2) = g(\mathbf{r}_1, \mathbf{r}_2) - 1$. The density $\rho(\mathbf{r}_2)h(\mathbf{r}_1, \mathbf{r}_2)$ is the exchange-correlation hole around an electron at \mathbf{r}_1 , and from the above equations it follows

$$\int \rho(\mathbf{r}_2) h(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_2 = -1 \quad . \quad (2.10)$$

In words, if an electron is located at \mathbf{r}_1 , then in the vicinity of \mathbf{r}_1 the density of the *remaining* electrons is deficient by one.

When the electronic system is in the state with wavefunction Φ , the total Coulomb energy (2.2) can be written with the aid of (2.7),

$$\Omega_{EE} = \frac{e^2}{2} \iint \frac{\rho(\mathbf{r}_1, \mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 \quad . \quad (2.11)$$

This can be separated into the uncorrelated and correlated parts respectively, as

$$\frac{e^2}{2} \iint \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 + \frac{e^2}{2} \iint \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)h(\mathbf{r}_1, \mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 . \quad (2.12)$$

The second term contains the positional correlations, and is the exchange-correlation energy. This term *reduces* the total Coulomb energy, since the electrons are always able to avoid one another to some degree, as indicated by the minus sign in (2.10).

Many-Electron Groundstate

This monograph is written primarily for individuals who are interested in the elementary excitations in condensed matter, the phonons and electrons, and the statistical mechanics of those excitations. The electronic structure community is currently able to calculate the parameters of the elementary excitations, through density functional theory. Here we shall give a brief but rigorous outline of density functional theory of the many-electron groundstate. Our intention is to assist communication between the electronic structure community, and those who need to use the calculated results of electronic structure theory. Thorough presentations of density functional theory are provided by Parr and Yang (1989), and Dreizler and Gross (1990).

The Rayleigh-Ritz variational principle tells us that the groundstate energy \mathcal{E}_g is given by the minimum value of $\langle \Psi | \mathcal{H}_E | \Psi \rangle$, where the minimization is over the space of normalized antisymmetric Z -electron functions. The minimizing function is the groundstate wavefunction Ψ_g , and this wavefunction gives the groundstate multielectron densities, among them the one-electron density $\rho_g(\mathbf{r})$. To convert this variational principle into density functional theory, it is only necessary to organize the variational process into the constrained search described by Levy (1979), and discussed further by Lieb (1982). Let Ψ_ρ be a normalized many-electron function which integrates to a specified one-electron density $\rho(\mathbf{r})$. Then $\mathcal{E}[\rho]$ is a functional of $\rho(\mathbf{r})$, defined by

$$\mathcal{E}[\rho] = \min \langle \Psi_\rho | \mathcal{H}_E | \Psi_\rho \rangle , \quad (2.13)$$

where the minimization is over all Ψ_ρ for the given $\rho(\mathbf{r})$. Then from the

Rayleigh-Ritz principle,

$$\mathcal{E}_g = \min \mathcal{E}[\rho] \quad , \quad (2.14)$$

where the minimization is over all $\rho(\mathbf{r})$. The minimizing one-electron density is the groundstate density $\rho_g(\mathbf{r})$. For applications in the present monograph, the electronic system will have a nondegenerate groundstate. In this case, (2.14) establishes a one-to-one correspondence between \mathcal{E}_g and $\rho_g(\mathbf{r})$. In the derivation leading to (2.14), the only restriction on the one-electron density is that it be obtained from a normalized antisymmetric \mathcal{Z} -electron function. Such a density is called *\mathcal{Z} -representable* (Levy 1979).

In Eq. (2.3), \mathcal{H}_E is written as the sum of three terms. Each term contributes to the right side of (2.13), hence each term corresponds to a functional contributing to $\mathcal{E}[\rho]$. Let $\Psi_\rho(\min)$ be the function which minimizes $\langle \Psi_\rho | \mathcal{H}_E | \Psi_\rho \rangle$. We then have the functionals

$$\mathcal{T}_E[\rho] = \langle \Psi_\rho(\min) | \mathcal{T}_E | \Psi_\rho(\min) \rangle \quad , \quad (2.15)$$

$$\Omega_{EE}[\rho] = \langle \Psi_\rho(\min) | \Omega_{EE} | \Psi_\rho(\min) \rangle \quad , \quad (2.16)$$

and the total energy functional is

$$\mathcal{E}[\rho] = \mathcal{T}_E[\rho] + \Omega_{EE}[\rho] + \int \rho(\mathbf{r}) \mathcal{V}(\mathbf{r}) d\mathbf{r} \quad . \quad (2.17)$$

Now in the minimization of $\langle \Psi_\rho | \mathcal{H}_E | \Psi_\rho \rangle$, Eq. (2.13), $\rho(\mathbf{r})$ is held constant, hence the contribution $\int \rho(\mathbf{r}) \mathcal{V}(\mathbf{r}) d\mathbf{r}$ is also constant, so that the minimizing function $\Psi_\rho(\min)$ is independent of the potential $\mathcal{V}(\mathbf{r})$. Hence $\mathcal{T}_E[\rho]$ and $\Omega_{EE}[\rho]$ are universal functionals, independent of $\mathcal{V}(\mathbf{r})$. An important early step in the development of density functional theory was the proof of the existence of the universal functional $F[\rho] = \mathcal{T}_E[\rho] + \Omega_{EE}[\rho]$, by Hohenberg and Kohn (1964). Through the Levy constrained search outlined above, we now have equations for the universal functionals, albeit complicated equations, namely Eqs. (2.15) and (2.16).

Kohn-Sham Formulation

Kohn and Sham (1965) presented a formulation for the groundstate energy of an interacting many-electron system, where the only restriction in principle is that $\rho(\mathbf{r})$ be *noninteracting V -representable* (explained below). They

first consider a noninteracting \mathcal{Z} -electron system with Hamiltonian $\Sigma_\alpha \mathcal{H}_\alpha^s$, where \mathcal{H}_α^s is the single-electron Hamiltonian

$$\mathcal{H}_\alpha^s = -\frac{\hbar^2 \nabla_\alpha^2}{2m} + V^s(\mathbf{r}_\alpha) \quad , \quad (2.18)$$

and where $V^s(\mathbf{r})$ is a fixed potential acting on an electron at \mathbf{r} , with $V^s(\mathbf{r})$ to be determined so as to facilitate the many-electron solution. The single-electron Hamiltonian has a complete set of eigenfunctions $\psi_\lambda(\mathbf{r})$, with eigenvalues E_λ , $\lambda = 1, 2, \dots$, which satisfy

$$\mathcal{H}^s \psi_\lambda(\mathbf{r}) = E_\lambda \psi_\lambda(\mathbf{r}) \quad , \quad (2.19)$$

$$\int \psi_\lambda^*(\mathbf{r}) \psi_{\lambda'}(\mathbf{r}) d\mathbf{r} = \delta_{\lambda\lambda'} \quad . \quad (2.20)$$

In the groundstate, the \mathcal{Z} lowest single-electron states are occupied. The groundstate wavefunction is a Slater determinant of the occupied ψ_λ , and the groundstate energy \mathcal{E}_g^s and one-electron density $\rho_g^s(\mathbf{r})$ are respectively

$$\mathcal{E}_g^s = \sum_{\lambda=1}^{\mathcal{Z}} E_\lambda \quad , \quad (2.21)$$

$$\rho_g^s(\mathbf{r}) = \sum_{\lambda=1}^{\mathcal{Z}} \psi_\lambda^*(\mathbf{r}) \psi_\lambda(\mathbf{r}) \quad . \quad (2.22)$$

In sums such as these, it is understood that the $\psi_\lambda(\mathbf{r})$ are present in degenerate pairs, corresponding to the two spin states for each electron.

The next step is to forget the Schrödinger solution just presented, and apply density functional theory to the noninteracting system. The constrained search program is the same as defined in Eqs. (2.13) and (2.14), but now the variational set of system functions is a single Slater determinant, made up from \mathcal{Z} orthonormal variational functions $\phi_\lambda(\mathbf{r})$, $\lambda = 1, \dots, \mathcal{Z}$. This means that the one-electron density, and the various energy functionals, are less general than in the interacting electron system, because they are defined on a restricted class of functions. The one-electron density is

$$\rho^s(\mathbf{r}) = \sum_{\lambda=1}^{\mathcal{Z}} |\phi_\lambda(\mathbf{r})|^2 \quad , \quad (2.23)$$

and the energy functional (2.17) becomes

$$\mathcal{E}^s[\rho^s] = \mathcal{T}^s[\rho^s] + \int \rho^s(\mathbf{r})V^s(\mathbf{r})d\mathbf{r} \quad , \quad (2.24)$$

where

$$\mathcal{T}^s[\rho^s] = \sum_{\lambda=1}^Z \left\langle \phi_\lambda \left| -\frac{\hbar^2 \nabla^2}{2m} \right| \phi_\lambda \right\rangle \quad . \quad (2.25)$$

Density functional theory now tells us that the groundstate energy is $\mathcal{E}_g^s = \min \mathcal{E}^s[\rho^s]$, and the minimizing $\rho^s(\mathbf{r})$ is the groundstate density $\rho_g^s(\mathbf{r})$.

Kohn and Sham now assume that the groundstate density $\rho_g(\mathbf{r})$ for an interacting system is *noninteracting V-representable*, which means $\rho_g(\mathbf{r})$ is identical to the density $\rho_g^s(\mathbf{r})$ for a noninteracting system with *some* $V^s(\mathbf{r})$. To appreciate the importance of this step, notice that the form written in (2.23) is a very weak restriction on the one-electron density, but if we were trying to solve the Schrödinger equation for the electronic groundstate, limiting the wavefunction to a Slater determinant would be a very serious restriction. The condition $\rho_g(\mathbf{r}) = \rho_g^s(\mathbf{r})$ implies that the functional variations of both $\mathcal{E}[\rho]$ and $\mathcal{E}^s[\rho]$ are zero at the same density:

$$\frac{\delta \mathcal{E}[\rho]}{\delta \rho} = \frac{\delta \mathcal{E}^s[\rho]}{\delta \rho} = 0, \quad \text{at } \rho(\mathbf{r}) = \rho_g(\mathbf{r}) \quad . \quad (2.26)$$

With $\mathcal{E}[\rho]$ and $\mathcal{E}^s[\rho]$ from (2.17) and (2.24) respectively, the above variation leads to the equation for $V^s(\mathbf{r})$,

$$V^s(\mathbf{r}) = \mathcal{V}(\mathbf{r}) + e^2 \int \frac{\rho_g(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + V_{xc}(\mathbf{r}) \quad , \quad (2.27)$$

where $V_{xc}(\mathbf{r})$ is the exchange-correlation potential, given by

$$V_{xc}(\mathbf{r}) = \left. \frac{\delta \mathcal{E}_{xc}[\rho]}{\delta \rho(\mathbf{r})} \right|_{\rho_g} \quad , \quad (2.28)$$

with (see problem 2.1)

$$\mathcal{E}_{xc}[\rho] = \mathcal{E}_E[\rho] - \mathcal{T}^s[\rho] + \frac{e^2}{2} \iint \frac{\rho(\mathbf{r})\rho(\mathbf{r}')h(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' \quad . \quad (2.29)$$

The groundstate energy of the interacting system is given by Eq. (2.17), as $\mathcal{E}_g = \mathcal{E}[\rho_g]$. Likewise the groundstate energy of the noninteracting system

is given by Eq. (2.24), as $\mathcal{E}_g^s = \mathcal{E}^s[\rho_g]$. By writing $\mathcal{E}_g = \mathcal{E}_g^s + (\mathcal{E}_g - \mathcal{E}_g^s)$, it follows (see problem 2.2)

$$\mathcal{E}_g = \sum_{\lambda=1}^Z E_{\lambda} - \frac{e^2}{2} \iint \frac{\rho_g(\mathbf{r})\rho_g(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' + \mathcal{E}_{xc}[\rho_g] - \int \rho_g(\mathbf{r})V_{xc}(\mathbf{r})d\mathbf{r} . \quad (2.30)$$

This expresses the groundstate energy of the interacting system in terms of the Schrödinger solution (2.21) and (2.22) for the noninteracting system, plus two small terms representing exchange and correlation effects. Notice $\mathcal{E}_{xc}[\rho]$, Eq. (2.29), which is commonly referred to as the exchange-correlation energy, contains the configurational exchange-correlation energy from Eq. (2.12), and contains also a kinetic energy term specific to the Kohn-Sham formulation.

Operationally, the Kohn-Sham procedure for calculating \mathcal{E}_g is as follows. Initial information consists of the potential $\mathcal{V}(\mathbf{r})$ due to the nuclei, and some approximation for the universal functional $\mathcal{E}_{xc}[\rho]$, Eq. (2.29). A guess is made for the groundstate density, $\rho_g^s(\mathbf{r})$, then $V^s(\mathbf{r})$ is calculated from (2.27), the noninteracting-system equations (2.19) and (2.20) are solved, and $\rho_g^s(\mathbf{r})$ is calculated from Eq. (2.22). The process is iterated to self-consistency in $\rho_g^s(\mathbf{r})$, and then \mathcal{E}_g is evaluated from (2.30).

The equations which define $\mathcal{E}_{xc}[\rho]$, starting with Eq. (2.13) for $\mathcal{E}[\rho]$, are hopelessly complicated. The utility of the Kohn-Sham formulation is that the exchange-correlation terms in \mathcal{E}_g , Eq. (2.30), are small, so an approximation is acceptable. The *local density* approximation consists of writing the exchange-correlation energy in the form

$$\mathcal{E}_{xc}[\rho] = \int \rho(\mathbf{r})X(\rho(\mathbf{r}))d\mathbf{r} , \quad (2.31)$$

where $X(\rho(\mathbf{r}))$ is a function of $\rho(\mathbf{r})$, not a functional. Then from (2.28), the exchange-correlation potential $V_{xc}(\mathbf{r})$ also becomes a function of the local density $\rho(\mathbf{r})$,

$$V_{xc}(\mathbf{r}) = \frac{d[\rho(\mathbf{r})X(\rho(\mathbf{r}))]}{d\rho(\mathbf{r})} . \quad (2.32)$$

Kohn and Sham (1965) pointed out that the local density approximation is correct for a uniform electron gas, and in fact they limited their original derivation to the local density approximation.

Current Applications of Density Functional Theory

Density functional theory for the electronic groundstate of condensed matter systems has been under active development since the papers of Hohenberg and Kohn (1964), and Kohn and Sham (1965). The focus has been to find a reliable approximation for the exchange-correlation functional, and the work has been done through a great many studies in which theory and experiment are compared for a wide variety of crystal properties. The Kohn-Sham formulation in local density approximation (LDA) has become the standard technique for band structure calculations, and currently provides respectable *ab initio* results for most crystals. The word “respectable” here means that calculations agree with experiment to within a few times the experimental error. In recent years, the theory has been extended beyond LDA, by means of the generalized gradient approximation (GGA), which includes gradients of the local one-electron density. Often but not always, GGA results are in better agreement with experiment than LDA results.

The current status of density functional theory is illustrated by examples from the recent literature. Calculations of cohesive energies, equilibrium lattice parameters, and bulk moduli are common. Calculations for various crystal structures of a given element almost always confirm the experimentally observed stable crystal structure, and similar calculations for elements under compression almost always confirm experimentally observed phase transitions as function of pressure. Elastic constants and phonon frequencies are calculated, as well as vacancy formation energies and pressure-induced changes in c/a ratios. Spin-dependent density functional theory is able to account for the crystal structures of Fe, Co, and Ni. A current frontier in electronic structure theory is the f-electron metals, the lanthanides and actinides, which are characterized by complicated crystal structures, temperature-induced phase transitions, and the availability of both localized and delocalized f-electron states. Calculations account for the observed crystal structures and equilibrium volumes of the light actinides (Th, Pa, U, Np, and Pu), while the high-temperature phases of Pu, and all crystal phases of the heavy actinides, are influenced by f-electron localization, a process whose physical origin is currently under study. Many results of density functional theory will be presented at appropriate places in this monograph.

Work has also proceeded to extend density functional theory to excited

electronic states. Mermin (1965) gave a formal density functional theory for the free energy of a system of interacting electrons in the presence of a fixed external potential. Individual excited states have been studied by Theophilou (1979), Görling (1999), and Levy and Nagy (1999). These papers make use of the stationary property of an excited state eigenfunction, when it is restricted to be orthogonal to all lower lying eigenfunctions. But the problem is extremely complicated, and we shall have to take an alternate approach in the following sections, in order to construct a practically useful condensed matter Hamiltonian.

The development of density functional theory was recognized by the award of the Nobel Prize in Chemistry to Walter Kohn in 1998.

Problems

2.1 Starting from Eq. (2.26), derive (2.27) – (2.29).

2.2 Derive Eq. (2.30). Notice the first term on the right expresses \mathcal{E}_g^s .

3 ELECTRONIC EXCITED STATES IN METALS

What Kind of Theory is Needed

The essential characteristic of a metal is its unfilled conduction band. In the electronic groundstate, one-electron states are filled up to the Fermi energy, and are empty above the Fermi energy, hence there are many low-lying excited states available to the electronic system. At finite temperatures, thermal excitation of the electrons will contribute to the thermal energy and the entropy of a metal. This electronic-excitation contribution dominates the energy and entropy at very low temperatures, and continues to make a small to moderate contribution at higher temperatures, so that it is almost always larger than experimental error in the measured thermal energy and entropy. Therefore, we require a theory for the thermal excitation of electrons in metals. The same theory will also apply to semimetals, the main difference being that a semimetal has an unusually small density of electronic states at the Fermi energy. On the other hand, in an insulator, the lowest excited electronic states lie above the groundstate by a gap, of an eV or so, hence the electronic excitations give a negligible contribution to the thermal energy and entropy. Qualitatively, the same is true in a semiconductor. Nevertheless, one can use the same formal theory as we shall

develop for metals, to calculate electronic excitation effects in insulators and semiconductors, should it become of interest to do so.

If one could calculate the electronic groundstate, and the excited states as well, for the nuclei located at a fixed configuration, one could then evaluate the electronic free energy with the nuclei at that configuration. The free energy density functional theory of Mermin (1965) offers a technique for doing this in principle. However, such an electronic free energy, even if it could be evaluated for *any* configuration of the nuclei, and even if it could be averaged over the nuclear configurations, does not in principle give us the excitation free energy of a condensed matter system. This is because, in a complete treatment of the system, one has to allow the nuclei to move, that is to have kinetic energy, and this kinetic energy induces transitions among the electronic states. In other words, the nuclear kinetic energy perturbs the electronic states, and this perturbation is not present in any calculation of electronic states where the nuclei are at fixed positions. The process just described, of inducing electronic transitions by the nuclear motion, constitutes the nonadiabatic part of the system motion. To treat the nonadiabatic part, one requires the complete system Hamiltonian, expressing *simultaneous coupled motion* of the nuclei and electrons.

In this section, a tractable approximation is constructed for the electronic excited states in metals, when the nuclei are at arbitrary fixed locations. In Sec. 4, the coupled nuclear and electronic motion will be analyzed.

One-Electron Approximation: The Groundstate

The term *one-electron approximation* generally indicates a model in which the system wavefunctions are constructed from single-electron functions. It is applied to the electronic groundstate, by minimizing $\langle \Psi | \mathcal{H}_E | \Psi \rangle$, where Ψ is some variational representation of the total wavefunction. The Hartree approximation results when Ψ is a product of single-electron functions, and exhibits kinetic energy, potential energy due to the external potential $\mathcal{V}(\mathbf{r})$, and uncorrelated electron Coulomb energy. Hartree-Fock results when Ψ is a Slater determinant, and exhibits one additional term, the exchange Coulomb energy. But the Hartree-Fock equations are complicated to solve for condensed matter systems, so Slater proposed to replace the exchange terms in the Hartree-Fock equations by a one-electron potential depending on the local one-electron density. Later, the local exchange potential was modified with the intention of including correlation energy as well.

The latter procedure, with an arbitrary form for the exchange-correlation potential, is presented in *Thermodynamics of Crystals*, Sec. 22, and will be followed here. Excellent discussions of the one-electron approximations may be found in Kittel (1963, Ch. 5), Slater (1974), and Harrison (1989, App. A).

The starting point is an orthonormal set of one-electron variational functions $\psi_\lambda(\mathbf{r})$, $\lambda = 1, \dots, \mathcal{Z}$. The groundstate energy is supposed to be

$$\begin{aligned} \mathcal{E}_g &= \sum_\lambda \int \psi_\lambda^*(\mathbf{r}) \left[-\frac{\hbar^2 \nabla^2}{2m} + \mathcal{V}(\mathbf{r}) \right] \psi_\lambda(\mathbf{r}) d\mathbf{r} \\ &+ \frac{1}{2} \sum_{\lambda\lambda'} \iint \psi_\lambda^*(\mathbf{r}) \psi_{\lambda'}^*(\mathbf{r}') \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} \psi_\lambda(\mathbf{r}) \psi_{\lambda'}(\mathbf{r}') d\mathbf{r} d\mathbf{r}' \\ &+ \sum_\lambda \int \psi_\lambda^*(\mathbf{r}) X(\rho_g(\mathbf{r})) \psi_\lambda(\mathbf{r}) d\mathbf{r} \quad , \end{aligned} \quad (3.1)$$

where the groundstate one-electron density is

$$\rho_g(\mathbf{r}) = \sum_\lambda \psi_\lambda^*(\mathbf{r}) \psi_\lambda(\mathbf{r}) \quad . \quad (3.2)$$

In (3.1), the first term is kinetic energy, and $\mathcal{V}(\mathbf{r})$ is the potential each electron sees due to the nuclei at fixed positions. The double sum is the uncorrelated Coulomb energy, the same as the first term in (2.12), and the last term is the exchange-correlation energy, where the function $X(\rho(\mathbf{r}))$ will eventually be calibrated to get the result of density functional theory for \mathcal{E}_g . Now the variation of \mathcal{E}_g is set to zero,

$$\delta \mathcal{E}_g = \sum_\lambda \int \left[\frac{\partial \mathcal{E}_g}{\partial \psi_\lambda^*(\mathbf{r})} \delta \psi_\lambda^*(\mathbf{r}) + \frac{\partial \mathcal{E}_g}{\partial \psi_\lambda(\mathbf{r})} \delta \psi_\lambda(\mathbf{r}) \right] d\mathbf{r} = 0 \quad , \quad (3.3)$$

subject to the condition that the variational functions remain normalized,

$$\delta \int \psi_\lambda^*(\mathbf{r}) \psi_\lambda(\mathbf{r}) d\mathbf{r} = \int [\delta \psi_\lambda^*(\mathbf{r}) \psi_\lambda(\mathbf{r}) + \psi_\lambda^*(\mathbf{r}) \delta \psi_\lambda(\mathbf{r})] d\mathbf{r} = 0 \quad . \quad (3.4)$$

The last equation is multiplied by the real Lagrange multiplier E_λ , and is summed over λ and subtracted from Eq. (3.3), to give

$$\sum_\lambda \int \left[\frac{\partial \mathcal{E}_g}{\partial \psi_\lambda^*(\mathbf{r})} - E_\lambda \psi_\lambda(\mathbf{r}) \right] \delta \psi_\lambda^*(\mathbf{r}) d\mathbf{r} + \text{complex conjugate} = 0 \quad . \quad (3.5)$$

Since $\delta\psi_\lambda(\mathbf{r})$ is an arbitrary complex function, then in (3.5) the coefficients of both $\delta\psi_\lambda(\mathbf{r})$ and $\delta\psi_\lambda^*(\mathbf{r})$ must vanish everywhere, and this gives the one-electron wave equations,

$$\frac{\partial \mathcal{E}_g}{\partial \psi_\lambda^*(\mathbf{r})} - E_\lambda \psi_\lambda(\mathbf{r}) = 0 \quad . \quad (3.6)$$

Since \mathcal{E}_g and E_λ are real, the complex conjugate equations contain the same information.

Equations (3.6) are transformed to the one-electron Schrödinger equation with Hamiltonian h (see problem 3.1),

$$h\psi_\lambda(\mathbf{r}) = \left[-\frac{\hbar^2 \nabla^2}{2m} + V_g(\mathbf{r}) \right] \psi_\lambda(\mathbf{r}) = E_\lambda \psi_\lambda(\mathbf{r}) \quad , \quad (3.7)$$

where $V_g(\mathbf{r})$ is the self consistent one-electron potential,

$$V_g(\mathbf{r}) = \mathcal{V}(\mathbf{r}) + e^2 \int \frac{\rho_g(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + \frac{d\rho_g(\mathbf{r})X(\rho_g(\mathbf{r}))}{d\rho_g(\mathbf{r})} \quad . \quad (3.8)$$

The system of equations (3.2), (3.7), and (3.8) have to be solved self consistently. The total groundstate energy (3.1) can now be expressed in terms of the one-electron eigenvalues E_λ (see problem 3.2),

$$\begin{aligned} \mathcal{E}_g &= \sum_\lambda E_\lambda - \frac{e^2}{2} \iint \frac{\rho_g(\mathbf{r})\rho_g(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}d\mathbf{r}' \\ &+ \sum_\lambda \int \psi_\lambda^*(\mathbf{r}) \left[X(\rho_g(\mathbf{r})) - \frac{d\rho_g(\mathbf{r})X(\rho_g(\mathbf{r}))}{d\rho_g(\mathbf{r})} \right] \psi_\lambda(\mathbf{r}) d\mathbf{r} \quad . \quad (3.9) \end{aligned}$$

The second and third terms on the right are corrections of the Coulomb energy and the exchange-correlation energy, respectively, for multiple counting which appears in $\sum_\lambda E_\lambda$. The above equations prescribe the groundstate in the one-electron approximation, where the function $X(\rho_g(\mathbf{r}))$ is still arbitrary.

One-Electron Approximation: Excited States

For crystal and liquid metals in the condensed matter regime, thermal energy constitutes only a small perturbation in the electronic structure problem. In particular, for any set of nuclear positions, the electronic charge density at all temperatures of interest remains close to its value at zero temperature. Hence the potential an electron sees, due to the nuclei *and*

due to the the other electrons as well, is to first approximation independent of temperature, and equal to its evaluation in the electronic groundstate. This is the approximation we shall make, in treating the electronic excited states in metals.

Suppose the self consistent one-electron groundstate has been obtained, for a given external potential $\mathcal{V}(\mathbf{r})$, and for appropriate boundary conditions. The process has given us a one-electron Hamiltonian h , defined in (3.7), based on the potential $V_g(\mathbf{r})$ defined in (3.8). We shall assume that the excited electronic states are given in this one-electron approximation, with $V_g(\mathbf{r})$ fixed. Then h has a complete set of wavefunctions $\psi_\lambda(\mathbf{r})$, $\lambda = 0, 1 \dots$, which satisfy

$$h\psi_\lambda(\mathbf{r}) = E_\lambda\psi_\lambda(\mathbf{r}) \quad , \quad (3.10)$$

$$\int \psi_\lambda^*(\mathbf{r})\psi_{\lambda'}(\mathbf{r}) = \delta_{\lambda\lambda'} \quad . \quad (3.11)$$

To enumerate the states of the \mathcal{Z} -electron system, let us introduce the occupation numbers $f_\lambda = 0, 1$. For any system state, the set of occupied ψ_λ have $f_\lambda = 1$, the set of unoccupied ψ_λ have $f_\lambda = 0$, and the number of occupied states is always \mathcal{Z} , so that

$$\sum_\lambda f_\lambda = \mathcal{Z} \quad . \quad (3.12)$$

The \mathcal{Z} -electron system now has energy levels $\mathcal{E} = \sum_\lambda f_\lambda E_\lambda$. But we want to apply this description to the excited states only, and not to the groundstate. Let us use a different symbol, namely $g_\lambda = 0, 1$, for the occupation numbers when the system is in its groundstate. Then the system excited states have excitation energies given by

$$\mathcal{E} - \mathcal{E}_g = \sum_\lambda (f_\lambda - g_\lambda) E_\lambda \quad . \quad (3.13)$$

The operator equivalent to (3.13), *i.e.* the Hamiltonian which has the same energy levels, is the *electronic excitation* Hamiltonian \mathcal{H}_{EX} , given by

$$\mathcal{H}_{EX} = \sum_\alpha h(\mathbf{r}_\alpha) - \sum_\lambda g_\lambda E_\lambda \quad , \quad (3.14)$$

where $h(\mathbf{r})$ is given by Eq. (3.7). For a prescribed set of nuclear positions, \mathcal{H}_{EX} has a complete set of \mathcal{Z} -electron states, each wavefunction is a Slater

determinant, and the lowest lying state has zero energy. While \mathcal{H}_{EX} is expressed entirely in the one-electron approximation, the groundstate energy \mathcal{E}_g of the many-electron system is independent of \mathcal{H}_{EX} , hence we are free to find \mathcal{E}_g from the best theory available, or even from experimental data.

Calibration from Density Functional Theory

Through the introduction of the function $X(\rho_g(\mathbf{r}))$ in Eq. (3.1), the groundstate energy in the one-electron approximation has been rendered an uncontrolled approximation, since it is no longer in the form $\langle \Psi | \mathcal{H}_E | \Psi \rangle$ for some wavefunction Ψ . Hence \mathcal{E}_g is no longer an upper bound for the true groundstate energy. The same property holds for the Kohn-Sham formulation of density functional theory, whenever an approximation is made for the unknown functional $\mathcal{E}_{xc}[\rho]$ of Eq. (2.29). In fact, the common result of Kohn-Sham calculations for a real material is to place the groundstate energy *below* the experimental value. It is possible to calibrate the one-electron approximation so that its groundstate energy, Eq. (3.1), is the same as the energy obtained from density functional theory. Let us do this here for the Kohn-Sham formulation in the local density approximation. The calibration is accomplished merely by setting the function $X(\rho_g(\mathbf{r}))$ in (3.1) equal to the function $X(\rho(\mathbf{r}))$ in (2.31) (see problem 3.3). Under this condition, the one-electron Hamiltonian in (3.7), with potential given by (3.8), is the same as the Kohn-Sham Hamiltonian (2.18), with potential given by (2.27). Hence a Kohn-Sham calculation in local density approximation provides all the parameters, namely the groundstate potential $V_g(\mathbf{r})$ and the set of E_λ , which appear in the electronic excitation Hamiltonian of (3.14). We shall assume that these parameters are available for any metallic system of interest, and will use them to construct the total system Hamiltonian, including both adiabatic and nonadiabatic contributions, in Sec. 4 below.

Regarding numerical aspects of electronic structure calculations, note that one ordinarily uses a set of basis functions sufficient for a good representation of the $\psi_\lambda(\mathbf{r})$ which are occupied in the groundstate. This basis set will normally give low-lying excited states accurately for a metal, but at some level of excitation, the groundstate basis set will not be sufficient, because every higher lying $\psi_\lambda(\mathbf{r})$ has to be orthogonal to all lower $\psi_\lambda(\mathbf{r})$. Hence to find accurate values for the excited energies E_λ , or what is equivalent, for the electronic density of states above the Fermi energy, the basis

set has to be augmented from that used for an ordinary groundstate calculation. The same problem is encountered, and presumably solved, when wavefunctions of electronic excited states are used to calculate optical properties of a crystal.

Problems

3.1 Derive Eqs. (3.7) and (3.8) from (3.6). Note $\partial\rho_g(\mathbf{r})/\partial\psi_\lambda^*(\mathbf{r}) = \psi_\lambda(\mathbf{r})$, from Eq. (3.2).

3.2 Derive Eq. (3.9) from (3.1).

3.3 When $X(\rho_g(\mathbf{r}))$ in (3.1) is the same as $X(\rho(\mathbf{r}))$ in (2.31), show that the two expressions (3.1) and (2.30) for \mathcal{E}_g are the same.

4 TOTAL HAMILTONIAN

Nuclear Motion Hamiltonian

Our condensed matter system is composed of N similar nuclei and \mathcal{Z} electrons. The nuclei have mass M , charge ze , and positions \mathbf{r}_K , with $K = 1, \dots, N$, while the electrons have positions \mathbf{r}_α , with $\alpha = 1, \dots, \mathcal{Z}$, and $\mathcal{Z} = zN$. The Hamiltonian is the sum of kinetic energies and Coulomb potentials:

$$\mathcal{H} = \mathcal{T}_N + \mathcal{T}_E + \Omega + NI \quad , \quad (4.1)$$

where

$$\mathcal{T}_N = - \sum_K \frac{\hbar^2 \nabla_K^2}{2M} \quad , \quad (4.2)$$

$$\mathcal{T}_E = - \sum_\alpha \frac{\hbar^2 \nabla_\alpha^2}{2M} \quad , \quad (4.3)$$

$$\Omega = \frac{1}{2} \sum'_{KL} \frac{z^2 e^2}{|\mathbf{r}_K - \mathbf{r}_L|} - \sum_{\alpha K} \frac{ze^2}{|\mathbf{r}_\alpha - \mathbf{r}_K|} + \frac{1}{2} \sum'_{\alpha\beta} \frac{e^2}{|\mathbf{r}_\alpha - \mathbf{r}_\beta|} \quad , \quad (4.4)$$

and where I is the total ionization energy of a single atom. The term NI is included in \mathcal{H} so that the system energy levels are measured with respect to a set of infinitely separated neutral atoms. Though the above

Hamiltonian explicitly represents an elemental material, the derivations can be done as well for a mixture of atoms representing an alloy or a compound. Finally, while one usually thinks of a system in a box with periodic boundary conditions, other geometries and boundary conditions are equally permissible.

For the electronic problem, discussed in Secs. 2 and 3, the nuclei are fixed at their positions \mathbf{r}_K , making $\mathcal{T}_N = 0$, and reducing \mathcal{H} to $\mathcal{H}_E = \mathcal{T}_E + \Omega$. The Coulomb terms in (4.4) for Ω are respectively nuclear-nuclear, electron-nuclear, and electron-electron. The first two terms in Ω combine to form the potential $\Sigma_\alpha \mathcal{V}(\mathbf{r}_\alpha)$ written in (2.3), and the last term in Ω is Ω_{EE} of (2.2). Now the point of the whole exercise of trying to solve for the electronic groundstate is this: the groundstate energy $\mathcal{E}_g(\{\mathbf{r}_K\})$, the energy of the entire system when the nuclei are fixed and the electrons are in their groundstate, is an excellent approximation for the potential which governs the motion of the nuclei. To this approximation, the nuclear motion is described by the Hamiltonian

$$\mathcal{H}_N = \mathcal{T}_N + \Phi(\{\mathbf{r}_K\}) \quad , \quad (4.5)$$

$$\Phi(\{\mathbf{r}_K\}) = \mathcal{E}_g(\{\mathbf{r}_K\}) + NI \quad . \quad (4.6)$$

This is the nuclear motion Hamiltonian, where $\Phi(\{\mathbf{r}_K\})$ is called the groundstate adiabatic potential, or simply the adiabatic potential.

Suppose we have an exact solution for the many-electron groundstate energy $\mathcal{E}_g(\{\mathbf{r}_K\})$. By adding and subtracting \mathcal{E}_g to the total Hamiltonian (4.1), and by using (4.5) and (4.6), it follows

$$\mathcal{H} = \mathcal{H}_N + (\mathcal{H}_E - \mathcal{E}_g) \quad . \quad (4.7)$$

Obviously, the electronic part $\mathcal{H}_E - \mathcal{E}_g$ expresses only *excitation* of the electronic system from its groundstate. At this point, let us replace $\mathcal{H}_E - \mathcal{E}_g$ by its one-electron approximation \mathcal{H}_{EX} , Eq. (3.14), so that

$$\mathcal{H} \doteq \mathcal{H}_N + \mathcal{H}_{EX} \quad . \quad (4.8)$$

Now the nuclear motion Hamiltonian \mathcal{H}_N contains in principle the exact adiabatic potential $\Phi = \mathcal{E}_g + NI$. From all of our experience in studying nuclear motion, illustrated by the evidence to be presented in the following chapters, \mathcal{H}_N is the most accurate nuclear-motion Hamiltonian we know

how to make. On the other hand, the electronic excitation Hamiltonian \mathcal{H}_{EX} is intrinsically approximate, through its formulation in terms of the one-electron approximation. Nevertheless, the evidence so far, also to be reported in the following chapters, indicates that \mathcal{H}_{EX} is accurate to the same level as the overall experimental error in the thermal excitation properties of metals.

Electrons at the Reference Structure

A nuclear configuration is specified by the set of nuclear positions $\{\mathbf{r}_K\}$. In the nuclear configuration space, the potential surface is $\Phi(\{\mathbf{r}_K\})$, and the forces are gradients of $\Phi(\{\mathbf{r}_K\})$. An equilibrium configuration is one where the force on each nucleus vanishes, and a *structure* is a locally stable equilibrium configuration, *i.e.* the configuration at the bottom of a many-particle valley. Structures are representative of the configurations found in condensed matter systems. In a crystal the nuclei move in the vicinity of a single crystal structure, while in an amorphous solid the nuclei move in the vicinity of a single random structure. In a liquid the nuclei move among many random valleys, but these valleys are all equivalent, and are represented by a single random structure. Hence for a given state of condensed matter, one can choose a *reference structure*, where the electronic excitations are representative of the excitations in all the most popular nuclear configurations found in that state of matter. It will then be very useful to split the electronic excitation Hamiltonian into a part evaluated at the reference structure, and the remaining part which sees the motion of the nuclei.

Positions of the nuclei in the reference structure are denoted \mathbf{R}_K , $K = 1, \dots, N$. The potential of an electron at \mathbf{r} , due to the nuclei in configuration $\{\mathbf{r}_K\}$, has been denoted $\mathcal{V}(\mathbf{r})$, and is more completely specified as $\mathcal{V}(\mathbf{r}; \{\mathbf{r}_K\})$. Let us write $\mathcal{V}^\sigma(\mathbf{r})$ to denote evaluation at the nuclear reference structure, so that $\mathcal{V}^\sigma(\mathbf{r}) = \mathcal{V}(\mathbf{r}; \{\mathbf{R}_K\})$. Then $\mathcal{V}(\mathbf{r})$ can be expanded about the reference structure,

$$\mathcal{V}(\mathbf{r}) = \mathcal{V}^\sigma(\mathbf{r}) + \delta\mathcal{V}(\mathbf{r}) \quad , \quad (4.9)$$

where this equation defines $\delta\mathcal{V}(\mathbf{r})$, *i.e.*

$$\delta\mathcal{V}(\mathbf{r}) = \mathcal{V}(\mathbf{r}; \{\mathbf{r}_K\}) - \mathcal{V}(\mathbf{r}; \{\mathbf{R}_K\}) \quad . \quad (4.10)$$

In the same way the one-electron potential $V_g(\mathbf{r})$, which depends explicitly

and implicitly on the nuclear configuration, can be expanded about the reference structure,

$$V_g(\mathbf{r}) = V_g^\sigma(\mathbf{r}) + \delta V_g(\mathbf{r}) . \quad (4.11)$$

Then in Eq. (3.7), the one-electron Hamiltonian becomes $h = h^\sigma + \delta V_g$, and the one-electron energies become $E_\lambda = E_\lambda^\sigma + \delta E_\lambda$. Let us finally expand \mathcal{H}_{EX} , Eq. (3.14), about the reference structure:

$$\mathcal{H}_{EX} = \mathcal{H}_{EX}^\sigma + \delta \mathcal{H}_{EX} , \quad (4.12)$$

where

$$\mathcal{H}_{EX}^\sigma = \sum_{\alpha} h^\sigma(\mathbf{r}_\alpha) - \sum_{\lambda} g_\lambda E_\lambda^\sigma , \quad (4.13)$$

$$\delta \mathcal{H}_{EX} = \sum_{\alpha} \delta V_g(\mathbf{r}_\alpha) - \sum_{\lambda} g_\lambda \delta E_\lambda . \quad (4.14)$$

At the reference structure, the one-electron wavefunctions are $\psi_\lambda^\sigma(\mathbf{r})$, and each system wavefunction is a Slater determinant of the occupied $\psi_\lambda^\sigma(\mathbf{r})$. Determinantal matrix elements can be used to express \mathcal{H}_{EX} in the basis of reference structure electrons. The result for \mathcal{H}_{EX}^σ is

$$\mathcal{H}_{EX}^\sigma = \sum_{\lambda} E_\lambda^\sigma (C_\lambda^+ C_\lambda - g_\lambda) , \quad (4.15)$$

where C_λ^+ and C_λ are respectively the creation and annihilation operators for electrons at the reference structure. The eigenvalues of $C_\lambda^+ C_\lambda$ are f_λ , and the condition (3.12) that the total number of electrons is \mathcal{Z} becomes

$$\sum_{\lambda} C_\lambda^+ C_\lambda = \mathcal{Z} . \quad (4.16)$$

The result for $\delta \mathcal{H}_{EX}$ is

$$\delta \mathcal{H}_{EX} = \sum_{\lambda\lambda'} \delta V_{\lambda\lambda'} C_\lambda^+ C_{\lambda'} - \sum_{\lambda} g_\lambda \delta E_\lambda , \quad (4.17)$$

where

$$\delta V_{\lambda\lambda'} = \langle \psi_\lambda^\sigma | \delta V_g | \psi_{\lambda'}^\sigma \rangle . \quad (4.18)$$

Notice once again that both $\delta V_{\lambda\lambda'}$ and δE_λ depend parametrically on the nuclear positions, and they also have an implicit dependence on the reference structure itself.

The total Hamiltonian (4.8) can now be written

$$\mathcal{H} \doteq \mathcal{H}_N + \mathcal{H}_{EX}^\sigma + \delta\mathcal{H}_{EX} \quad . \quad (4.19)$$

This is a valuable result. First, since the nuclear positions do not appear *as variables* in \mathcal{H}_{EX}^σ , then \mathcal{H}_N and \mathcal{H}_{EX}^σ commute, which means there is no interaction between the motion of the nuclei and the excitation of reference structure electrons. Hence \mathcal{H}_N and \mathcal{H}_{EX}^σ represent two *independent* systems, and this simplifies the dynamics and statistical mechanics. Second, speaking generally of condensed matter systems, the three terms on the right of (4.19) are ordered in strongly decreasing importance. Hence the interaction between nuclear motion and electronic excitation is isolated in the smallest term in (4.19), and in the dynamics and statistical mechanics of metals, this term can ordinarily be treated as a perturbation.

Notes on the Resolution of the Total Hamiltonian

The total Hamiltonian expressed in Eq. (4.19) will be the starting point for all subsequent developments in this monograph. We need to discuss some subtle points associated with this Hamiltonian, and for this purpose we can limit our consideration to a metal crystal. The general idea is contained in this observation: electron-phonon interactions are not defined until the electrons and phonons are defined, and then, electron-phonon interactions are uniquely defined, through the (unique) total Hamiltonian.

The smallest Hamiltonian contribution, $\delta\mathcal{H}_{EX}$, expresses the interaction between motion of the nuclei and excitation of the electrons. In a crystal, the nuclear motion is analyzed into phonons, and $\delta\mathcal{H}_{EX}$ constitutes the electron-phonon interaction. In Eq. (4.17), $\delta\mathcal{H}_{EX}$ is expressed in terms of reference structure electrons, for which the total electronic wavefunctions are $\Psi(\{\mathbf{r}_\alpha\}, \{\mathbf{R}_K\})$. In the total system Schrödinger equation, the nuclear motion will give rise to terms which do not mix these electronic states, and terms which do mix them. Let us define these terms respectively as *adiabatic* and *nonadiabatic*. Their contributions to the free energy of a metallic crystal will be studied in Sec. 18. A formal separation of adiabatic and nonadiabatic effects for nonmetallic crystals, applicable in principle to metallic crystals as well, is given by Born and Huang (1954, Appendix VIII). Born

and Huang work with the electronic wavefunctions $\Psi(\{\mathbf{r}_\alpha\}, \{\mathbf{r}_K\})$, which are valid for arbitrary positions of the nuclei, and they define adiabatic (nonadiabatic) nuclear motion as that which does not mix (does mix) these electronic states. Obviously the present definition of adiabatic and nonadiabatic effects, in terms of the wavefunctions $\Psi(\{\mathbf{r}_\alpha\}, \{\mathbf{R}_K\})$, is nontrivially different from the definition of Born and Huang. As a practical note, working in the basis of reference structure electrons gives us the ability to evaluate matrix elements of the electron-phonon interaction, which would be virtually impossible in the representation of Born and Huang.

A still more subtle point arises. The “adiabatic” potential $\Phi(\{\mathbf{r}_K\})$ is $\mathcal{E}_g(\{\mathbf{r}_K\}) + NI$, and $\mathcal{E}_g(\{\mathbf{r}_K\})$ is the electronic groundstate energy when the nuclei are fixed at $\{\mathbf{r}_K\}$. But when the nuclei are *moving*, as they are in all quantum states of the total system, $\delta\mathcal{H}_{EX}$ becomes an *operator* in phonon space, hence $\delta\mathcal{H}_{EX}$ gives a small correction to the groundstate energy, say $\delta\mathcal{E}_g(\{\mathbf{r}_K\})$. So the true groundstate energy is $\mathcal{E}_g + \delta\mathcal{E}_g$, and is by definition adiabatic. Born and Huang (1954) recognize $\mathcal{E}_g + \delta\mathcal{E}_g$ as the true adiabatic groundstate potential. However, we do not include $\delta\mathcal{E}_g$ in our nuclear motion potential Φ , because $\delta\mathcal{E}_g$ is extremely small and is virtually impossible to calculate or to measure. Instead we keep all components of the electron-phonon interaction, present in all electronic states including the groundstate, in the Hamiltonian $\delta\mathcal{H}_{EX}$. Our procedure has the advantage, both practical and aesthetic, of treating all contributions to $\delta\mathcal{H}_{EX}$ on the same footing.

Since the electrons, phonons, and all interactions among them are described by one global Hamiltonian, there is a consistency condition among them, namely that all their separate energy operators must add up to the total Hamiltonian of Eq. (4.1), or Eq. (4.7). But in condensed matter research, various excitations are almost always studied separately, and consistency conditions implied by the global Hamiltonian are rarely observed. Electron-phonon interactions are usually studied through \mathcal{H}_E , but according to Eq. (4.7) these interactions are contained in the operator $\mathcal{H}_E - \mathcal{E}_g$, not \mathcal{H}_E . The fact that the electron-phonon Hamiltonian must contain only *excited* electronic states, and not the electronic groundstate, is sometimes crucial, but is almost always overlooked.

It is quite satisfactory to be able to present such a simple derivation as that going from (4.1) to (4.19). The result here is identical to that obtained from a much more tortuous procedure in *Thermodynamics of Cryst-*

tals. Present equations are the same as those in Sec. 24 of *Thermodynamics of Crystals*, as follows: (4.7) is (24.13), (4.15) is (24.20), and (4.19) expressed specifically for crystals is (24.22).

5 NEARLY-FREE-ELECTRON METALS

Pseudopotential Perturbation Theory

The nearly-free-electron metals can be represented approximately by a collection of rigid closed-shell ions, plus their valence electrons, which interact weakly with one another and with the ions. If these interactions were *not* weak, the electronic structure problem would be intractable, and could only be solved by computer. On the other hand, if the interactions were neglected entirely, the valence electrons would be a free electron system, possessing kinetic energy and Fermi statistics, and missing all the remaining interesting properties of real metals. But by treating the interactions in perturbation theory, the electronic structure problem is tractable, yet exhibits all the important properties of real metals within a single unified theoretical framework. Further, when properly calibrated, this theory will give an accurate account of a wide range of experimental properties of metals. Extensive treatments may be found in Harrison (1989, Chaps. 15–17), and in *Thermodynamics of Crystals* (Chap. 6 and Sec. 34).

The theory starts with the interaction of a valence electron with an ion core. In an accurate electronic structure calculation, the complications within the core, namely the deep Coulomb well and the orthogonalization of valence electrons to core electrons, are handled numerically. Here these complications are replaced by a weak local *pseudopotential*, allowing the valence electrons to have the right energies, and to have wavefunctions which are correct *outside* the core, but not *inside* the core. The interaction of an electron at \mathbf{r} with a spherically symmetric ion core centered at the origin is represented by the bare pseudopotential $w_b(|\mathbf{r}|)$. The interaction of an electron at \mathbf{r} with all the ion cores, located at \mathbf{r}_K , is

$$W_b(\mathbf{r}) = \sum_K w_b(|\mathbf{r} - \mathbf{r}_K|) \quad . \quad (5.1)$$

The total potential seen by one electron is then

$$W(\mathbf{r}) = W_b(\mathbf{r}) + W_s(\mathbf{r}) + W_{xc}(\mathbf{r}) \quad , \quad (5.2)$$

where the screening potential $W_s(\mathbf{r})$ is due to the Coulomb interaction with all the other valence electrons, and where the potential $W_{xc}(\mathbf{r})$ is an approximation for exchange and correlation effects among the valence electrons. The one-electron Hamiltonian is

$$h = -\frac{\hbar^2 \nabla^2}{2m} + W(\mathbf{r}) \quad , \quad (5.3)$$

and $W(\mathbf{r})$ is considered a perturbation. $W(\mathbf{r})$ will be evaluated self-consistently in the electronic groundstate, so that $W(\mathbf{r}) = W_g(\mathbf{r})$, and the subscript g will not be needed. Henceforth we shall refer to the valence electrons simply as “the electrons”, and to $W(\mathbf{r})$ as “the pseudopotential”.

The system is composed of N ion cores, each with charge ze , together with $\mathcal{Z} = zN$ electrons, all in a cubical box of volume V , with periodic boundary conditions at the box surface. A plane wave which satisfies the boundary conditions is $|\mathbf{p}\rangle$,

$$|\mathbf{p}\rangle = \frac{1}{\sqrt{V}} e^{i\mathbf{p}\cdot\mathbf{r}} \quad , \quad (5.4)$$

where the wavevectors \mathbf{p} form a discrete infinite set. The plane waves are orthonormal,

$$\langle \mathbf{p}' | \mathbf{p} \rangle = \frac{1}{V} \int e^{i(\mathbf{p}-\mathbf{p}')\cdot\mathbf{r}} d\mathbf{r} = \delta_{\mathbf{p}\mathbf{p}'} \quad , \quad (5.5)$$

and they are complete in the space of functions which satisfy the boundary conditions,

$$\sum_{\mathbf{p}} |\mathbf{p}\rangle \langle \mathbf{p}| = \frac{1}{V} \sum_{\mathbf{p}} e^{i\mathbf{p}\cdot(\mathbf{r}-\mathbf{r}')} = \delta(\mathbf{r}-\mathbf{r}') \quad . \quad (5.6)$$

Planewave matrix elements of a function $f(\mathbf{r})$ yield the Fourier transform,

$$f(\mathbf{q}) = \langle \mathbf{p} + \mathbf{q} | f | \mathbf{p} \rangle = \frac{1}{V} \int f(\mathbf{r}) e^{-i\mathbf{q}\cdot\mathbf{r}} d\mathbf{r} \quad . \quad (5.7)$$

The inverse transform is obtained by applying the completeness relation (5.6), to find

$$f(\mathbf{r}) = \sum_{\mathbf{q}} f(\mathbf{q}) e^{i\mathbf{q}\cdot\mathbf{r}} \xrightarrow{V \rightarrow \infty} \frac{V}{(2\pi)^3} \int f(\mathbf{q}) e^{i\mathbf{q}\cdot\mathbf{r}} d\mathbf{q} \quad . \quad (5.8)$$

The transformation to the integral uses that $V/(2\pi)^3$ is the density of vectors in \mathbf{q} -space. Note the transformation between (5.7) and (5.8) is asymmetric in the factors of 2π . Finally, the convolution formula works out to be

$$\frac{1}{V} \int f(\mathbf{r})g(\mathbf{r})d\mathbf{r} = \sum_{\mathbf{q}} f(\mathbf{q})g(-\mathbf{q}) . \quad (5.9)$$

Let us return to the electronic structure problem, defined by the Hamiltonian (5.3) and the periodic boundary condition. In zeroth order, the solutions are free electrons,

$$-\frac{\hbar^2 \nabla^2}{2m} |\mathbf{p}\rangle = e_{\mathbf{p}} |\mathbf{p}\rangle , \quad e_{\mathbf{p}} = \frac{\hbar^2 p^2}{2m} . \quad (5.10)$$

With $W(\mathbf{r})$ treated as a perturbation, the solutions are still indexed by the wavevectors \mathbf{p} , and they satisfy

$$h\psi_{\mathbf{p}} = E_{\mathbf{p}}\psi_{\mathbf{p}} , \quad \langle \psi_{\mathbf{p}'} | \psi_{\mathbf{p}} \rangle = \delta_{\mathbf{p}\mathbf{p}'} . \quad (5.11)$$

The wavefunctions to first order, and the energies to second order, are

$$\psi_{\mathbf{p}} = |\mathbf{p}\rangle + \sum_{\mathbf{q}}' \frac{W(\mathbf{q})|\mathbf{p} + \mathbf{q}\rangle}{(e_{\mathbf{p}} - e_{\mathbf{p}+\mathbf{q}})} , \quad (5.12)$$

$$E_{\mathbf{p}} = e_{\mathbf{p}} + W(\mathbf{q}=0) + \sum_{\mathbf{q}}' \frac{|W(\mathbf{q})|^2}{(e_{\mathbf{p}} - e_{\mathbf{p}+\mathbf{q}})} , \quad (5.13)$$

where the prime on $\sum_{\mathbf{q}}'$ means to omit the $\mathbf{q} = 0$ term. Since $W(\mathbf{r})$ is real, then $W(\mathbf{q})^* = W(-\mathbf{q})$.

Groundstate Electron Density

In the groundstate, the electrons occupy the one-electron states up to the Fermi energy E_F . The Fermi energy specifies a constant-energy surface in \mathbf{p} -space, the Fermi surface. In zeroth order, the constant-energy surfaces are spheres, and the Fermi energy is

$$e_F = \frac{\hbar^2 f^2}{2m} , \quad (5.14)$$

where f is the zeroth-order (free electron) Fermi wave vector. The Fermi surface is at $|\mathbf{p}| = f$. The Fermi sphere must contain exactly zN electrons, and this determines f , according to

$$zN = \frac{2V}{8\pi^3} \int_0^f d\mathbf{p} = \frac{Vf^3}{3\pi^2} \quad , \quad (5.15)$$

where the factor 2 in the integral expression accounts for spin degeneracy. The volume per atom is $V_A = V/N$, the average electron density is $\rho_0 = z/V_A$, and in these terms f is given by

$$f^3 = \frac{3\pi^2 z}{V_A} = 3\pi^2 \rho_0 \quad . \quad (5.16)$$

The total kinetic energy in zeroth order is the total free-electron energy, given by

$$\frac{2V}{8\pi^3} \int_0^f d\mathbf{p} \frac{\hbar^2 p^2}{2m} = zN \left(\frac{3\hbar^2 f^2}{10m} \right) = zN \left(\frac{3}{5} e_F \right) \quad . \quad (5.17)$$

The electron density at \mathbf{r} is $\rho(\mathbf{r})$,

$$\rho(\mathbf{r}) = \sum_{\mathbf{p}} g_{\mathbf{p}} \psi_{\mathbf{p}}^*(\mathbf{r}) \psi_{\mathbf{p}}(\mathbf{r}) \quad , \quad (5.18)$$

where as usual $g_{\mathbf{p}}$ are the groundstate occupation numbers, and $\sum_{\mathbf{p}} g_{\mathbf{p}} = zN$. When a sum is restricted to the occupied one-electron states, as indicated by the presence of $g_{\mathbf{p}}$ in $\sum_{\mathbf{p}}$, it is understood that a factor 2 for spin is implicit in the sum. From Eq. (5.12) for the wavefunctions, $\rho(\mathbf{r})$ to first order is

$$\rho(\mathbf{r}) = \frac{1}{V} \sum_{\mathbf{p}} g_{\mathbf{p}} \left\{ 1 + \sum_{\mathbf{q}}' \left[\frac{W(-\mathbf{q})e^{-i\mathbf{q}\cdot\mathbf{r}}}{(e_{\mathbf{p}} - e_{\mathbf{p}-\mathbf{q}})} + \frac{W(\mathbf{q})e^{i\mathbf{q}\cdot\mathbf{r}}}{(e_{\mathbf{p}} - e_{\mathbf{p}+\mathbf{q}})} \right] \right\} \quad . \quad (5.19)$$

The $\mathbf{q} = 0$ component is just the average electron density,

$$\rho(\mathbf{q} = 0) = \rho_0 = \frac{z}{V_A} \quad . \quad (5.20)$$

For the $\mathbf{q} \neq 0$ components, the two terms in (5.19) can be combined by interchanging \mathbf{q} with $-\mathbf{q}$ inside the sum, to obtain

$$\rho(\mathbf{q}) = \frac{2}{V} \sum_{\mathbf{p}} g_{\mathbf{p}} \frac{W(\mathbf{q})}{(e_{\mathbf{p}} - e_{\mathbf{p}+\mathbf{q}})} \quad , \quad \mathbf{q} \neq 0 \quad . \quad (5.21)$$

We only want to evaluate this to leading order, which means the $\Sigma_{\mathbf{p}}$, after transforming to an integral, needs to be evaluated only over the zeroth-order Fermi sphere. The result is

$$\rho(\mathbf{q}) = \frac{q^2}{4\pi e^2} W(\mathbf{q}) [1 - H(q)] \quad , \quad \mathbf{q} \neq 0 \quad , \quad (5.22)$$

where $H(q)$ is the static Hartree dielectric function, given by

$$H(q) - 1 = \frac{2me^2 f}{\pi \hbar^2 q^2} \left[\frac{1 - (q/2f)^2}{2(q/2f)} \ln \left| \frac{1 + (q/2f)}{1 - (q/2f)} \right| + 1 \right] \quad . \quad (5.23)$$

Equation (5.22) begins to reveal how the electrons respond to the potential field, represented by $W(\mathbf{q})$. The next step is to calculate the field self consistently.

Screening and Exchange-Correlation Potentials

The screening potential is the Coulomb potential arising from the electron density $\rho(\mathbf{r})$,

$$W_s(\mathbf{r}) = e^2 \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \quad , \quad (5.24)$$

and this function obeys Poisson's equation, so that

$$W_s(\mathbf{q}) = \frac{4\pi e^2}{q^2} \rho(\mathbf{q}) \quad , \quad \mathbf{q} \neq 0 \quad . \quad (5.25)$$

In the present formulation, the $\mathbf{q} = 0$ component of $W_s(\mathbf{q})$ is not defined, and it need not be defined, since all ‘‘Coulomb divergences’’ sum to zero. The theory could otherwise be constructed by replacing the Coulomb interaction $1/r$ with $e^{-\kappa r}/r$, with κ small and positive, and then the denominator in (5.25) would be $q^2 + \kappa^2$, and the $\mathbf{q} = 0$ term is defined. In physically meaningful quantities, the $\mathbf{q} = 0$ terms will cancel and the limit $\kappa \rightarrow 0$ will exist. Notice also that the nonphysical Coulomb interaction of each electron with itself will be contained here in the total Coulomb energy $\int \rho(\mathbf{r}) W_s(\mathbf{r}) d\mathbf{r}$. In a theory where the electrons are approximately plane waves, this self energy is of relative order N^{-1} in the total energy, hence is negligible.

By eliminating $\rho(\mathbf{q})$ between (5.22) and (5.25), the screening potential is simply related to the total potential,

$$W_s(\mathbf{q}) = W(\mathbf{q})[1 - H(q)] \quad . \quad (5.26)$$

This constitutes a solution for the screening potential, and is a key result of electron response theory.

Let us write the exchange-correlation potential $W_{xc}(\mathbf{r})$, which appears in Eq. (5.2), through its Fourier components, as a local field correction to the screening potential,

$$W_{xc}(\mathbf{q}) = -W_s(\mathbf{q})Y(\mathbf{q}) = -\frac{4\pi e^2}{q^2}\rho(\mathbf{q})Y(\mathbf{q}) \quad . \quad (5.27)$$

As usual, all the intractable many-electron effects are represented by the unknown function $Y(\mathbf{q})$. Here we shall take a simple model for $Y(\mathbf{q})$, which will serve to illustrate the construction of the complete theory,

$$Y(\mathbf{q}) = Y(q) = \frac{q^2}{2(q^2 + \xi f^2)} \quad , \quad (5.28)$$

where ξ is a positive density-dependent parameter. Arguments for this form are as follows. Since exchange and correlation operate to keep electrons apart, they reduce the (positive) Coulomb energy, so that $W_s + W_{xc}$ must be less than W_s . This accounts for the minus sign in (5.27). Further, W_{xc} should go to a finite function of density as $\mathbf{q} \rightarrow 0$, and, as observed by Hubbard (1958), exchange alone should make $Y(q)$ approach $\frac{1}{2}$ at large q . From Eqs. (5.27) and (5.28), it is apparent that $W_{xc}(q)$ represents a screened Coulomb potential. In fact \mathcal{E}_{xc} , the total exchange-correlation energy corresponding to W_{xc} , is a functional of the electron density $\rho(\mathbf{r})$,

$$\mathcal{E}_{xc} = \int \rho(\mathbf{r})X(\mathbf{r})d\mathbf{r} \quad , \quad (5.29)$$

where $X(\mathbf{r})$ is *also* a functional of $\rho(\mathbf{r})$,

$$X(\mathbf{r}) = -\frac{e^2}{4} \int \rho(\mathbf{r}') \frac{e^{-\kappa|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' \quad . \quad (5.30)$$

Because \mathcal{E}_{xc} is quadratic in $\rho(\mathbf{r})$, the exchange-correlation potential becomes (see Eq. (2.28))

$$W_{xc}(\mathbf{r}) = 2X(\mathbf{r}) \quad . \quad (5.31)$$

The Fourier transform of $W_{xc}(\mathbf{r})$ is given by Eqs. (5.27) and (5.28), with $\kappa = \xi f^2$.

There are various ways to calibrate ξ . As $\mathbf{q} \rightarrow 0$, the above equations reduce to a local density approximation for a homogeneous electron system at density ρ_0 . If we set $\mathcal{E}_{xc}[\rho_0]$ equal to the exchange energy of the uniform electron gas, then $\xi = 4/9$. Instead, one can use the compressibility sum rule, which expresses that the system compressibility must be the same whether calculated from the velocities of long wavelength acoustic phonons, or from homogeneous deformation (the derivation is given in Chap. 3). From the compressibility of the uniform electron gas, one finds $\xi = 2$ for exchange only, minus a small density-dependent correction for correlation (see *e.g.* Wallace, 1968). On the other hand, the compressibility calculated from density functional theory gives $\xi = 1.2$ in a pseudopotential model for Al (Straub *et al.*, 1994). More sophisticated models for the exchange-correlation contribution to electron response are discussed by Singwi and Tosi (1981, Secs. 5 and 6), and by Mahan (1981, Sec. 5.5).

The total pseudopotential $W(\mathbf{q})$ is now determined. From (5.26) and (5.27), the screening and exchange-correlation contribution amount to

$$W_s(\mathbf{q}) + W_{xc}(\mathbf{q}) = W(\mathbf{q})[1 - H(q)][1 - Y(q)] \quad . \quad (5.32)$$

Now since $W = W_b + W_s + W_{xc}$, the screening and exchange-correlation contributions can be eliminated to find

$$W(\mathbf{q}) = \frac{W_b(\mathbf{q})}{1 + [H(q) - 1][1 - Y(q)]} \quad . \quad (5.33)$$

So the total potential seen by any single electron is the bare potential from all the ions, screened collectively by all the electrons, where the screening function is controlled by the Coulomb interaction and the exchange-correlation effects among the electrons. If $Y(q)$ is set zero, then $W(\mathbf{q})$ reduces to $W_b(\mathbf{q})/H(q)$, exhibiting the meaning of $H(q)$ as a dielectric function.

Electron-Ion Interaction

The heart of our theory is the bare pseudopotential $w_b(r)$, representing the interaction of one electron with one ion. The ion has charge $+ze$, so that outside the ion core $w_b(r)$ is $-ze^2/r$. Then the bare interaction can be

written

$$w_b(r) = -\frac{ze^2}{r} + w_c(r) \quad , \quad (5.34)$$

where the core potential $w_c(r)$ is localized to the core region. Inside the core, an electron sees a strong negative Coulomb potential from the nucleus, but the electron also has a large positive kinetic energy due to its orthogonalization to core electrons. The sum of these energies is represented by a relatively weak local potential, hence the name pseudopotential. In this monograph, $w_c(r)$ is viewed as a function to be modeled so as to achieve a good overall theory for nearly-free-electron metals. The Harrison model takes $w_c(r)$ proportional to a $1s$ electron density, so that $w_c(r) = \beta e^{-r/r_c}$, where β and r_c are positive parameters. The Heine-Abarenkov model is a well of depth β inside the core, plus the ion Coulomb potential outside the core:

$$w_b(r) = -\beta \text{ for } r \leq r_c \quad , \quad w_b(r) = -\frac{ze^2}{r} \text{ for } r > r_c \quad . \quad (5.35)$$

The Ashcroft empty core model results from setting $\beta = 0$ in the Heine-Abarenkov model.

Since $W_b(\mathbf{r})$ is a sum of single ion pseudopotentials, then $W_b(\mathbf{q})$ factors in an important way:

$$\begin{aligned} W_b(\mathbf{q}) &= \frac{1}{V} \int W_b(\mathbf{r}) e^{-i\mathbf{q}\cdot\mathbf{r}} d\mathbf{r} \\ &= \frac{1}{V} \sum_K e^{-i\mathbf{q}\cdot\mathbf{r}_K} \int w_b(|\mathbf{r} - \mathbf{r}_K|) e^{-i\mathbf{q}\cdot(\mathbf{r} - \mathbf{r}_K)} d\mathbf{r} \\ &= S(\mathbf{q}) w_b(q) \quad , \end{aligned} \quad (5.36)$$

where $S(\mathbf{q})$ is the structure factor,

$$S(\mathbf{q}) = \frac{1}{N} \sum_K e^{-i\mathbf{q}\cdot\mathbf{r}_K} \quad , \quad (5.37)$$

and $w_b(q)$ is the single-ion bare pseudopotential,

$$w_b(q) = \frac{1}{V_A} \int w_b(r) e^{-i\mathbf{q}\cdot\mathbf{r}} d\mathbf{r} \quad . \quad (5.38)$$

Notice that $S(\mathbf{q})$ is normalized to 1 at $\mathbf{q} = 0$, and also that $w_b(q)$ is normalized by the volume per atom V_A , which is appropriate since $w_b(r)$ belongs to a single ion. The importance of the decomposition (5.36) is that all

dependence of $W_b(\mathbf{q})$ on the ion positions \mathbf{r}_K is contained in the structure factor $S(\mathbf{q})$. Further, since $W(\mathbf{q})$ is proportional to $W_b(\mathbf{q})$, from Eq. (5.33), then the factorization of $W_b(\mathbf{q})$ carries over to the total potential, so that

$$W(\mathbf{q}) = S(\mathbf{q})w(q) \quad , \quad (5.39)$$

where $w(q)$ is called the screened-ion form factor, or simply the form factor,

$$w(q) = \frac{w_b(q)}{1 + [H(q) - 1][1 - Y(q)]} \quad . \quad (5.40)$$

With the last two equations, it becomes apparent why pseudopotential perturbation theory can treat a wide variety of properties in a simple unified formulation. First, the dependence on ion positions is reduced to $S(\mathbf{q})$ in the wavefunctions to first order, and to $|S(\mathbf{q})|^2$ in the energies to second order. Hence the theory is ideal for calculating what happens when the ions move around, and it easily handles configurations appearing in crystal, amorphous solid, and liquid states. Second, again in the electron wavefunctions and energies, the effect of all interactions appears in the form factor $w(q)$. And since screening and exchange-correlation effects are evaluated in zeroth order, *i.e.* in the free-electron approximation, the functions $H(q)$ and $Y(q)$ in Eq. (5.40) depend only on the mean electron density, through the parameters f and ξ .

A characteristic property of metals, resulting from the long-range divergence of electron Coulomb interactions, is that the dielectric function diverges as $q \rightarrow 0$. This property is contained in $H(q)$, Eq. (5.23), whose small- q expansion is

$$H(q) - 1 = \frac{4me^2f}{\pi\hbar^2q^2} - \frac{me^2}{3\pi\hbar^2f} + \dots \quad . \quad (5.41)$$

But $w_b(q)$ has the same divergence with opposite sign, because $w_b(r)$ has an attractive Coulomb potential at large r , so that $w(q)$, Eq. (5.40), has the finite limit

$$\lim_{q \rightarrow 0} w(q) = -\frac{2}{3}e_F = -\frac{\hbar^2f^2}{3m} \quad . \quad (5.42)$$

Electronic Groundstate Energy

The electronic groundstate energy in the one-electron approximation is written in Eq. (3.9), specifically with exchange-correlation effects given by

a local density approximation. The corresponding equation in pseudopotential perturbation theory reads

$$\mathcal{E}_g = \sum_{\mathbf{p}} g_{\mathbf{p}} E_{\mathbf{p}} - \frac{1}{2} \int \rho(\mathbf{r}) W_s(\mathbf{r}) d\mathbf{r} + \int \rho(\mathbf{r}) [X(\mathbf{r}) - W_{xc}(\mathbf{r})] d\mathbf{r} . \quad (5.43)$$

On the right side, the two integrals correct for what is “over counted” in the sum of one-electron energies. We shall continue to use the exchange-correlation model outlined in Eqs. (5.27) to (5.31), so that

$$\int \rho(\mathbf{r}) [X(\mathbf{r}) - W_{xc}(\mathbf{r})] d\mathbf{r} = -\frac{1}{2} \int \rho(\mathbf{r}) W_{xc}(\mathbf{r}) d\mathbf{r} . \quad (5.44)$$

Notice that the direct ion-ion interaction energy is still not contained in Eq. (5.43), but will be added when the effective ion-ion potential is constructed below. With the aid of Eq. (5.13) for $E_{\mathbf{p}}$, the sum of one-electron energies is

$$\sum_{\mathbf{p}} g_{\mathbf{p}} E_{\mathbf{p}} = \sum_{\mathbf{p}} g_{\mathbf{p}} e_{\mathbf{p}} + zN W(\mathbf{q} = 0) + \sum'_{\mathbf{q}} \sum_{\mathbf{p}} g_{\mathbf{p}} \frac{W(\mathbf{q})W(-\mathbf{q})}{(e_{\mathbf{p}} - e_{\mathbf{p}+\mathbf{q}})} . \quad (5.45)$$

The first term on the right is the sum of free electron energies, given by Eq. (5.17) (see problem 5.1). In view of Eq. (5.21) for $\rho(\mathbf{q})$, the last term in (5.45) is

$$\frac{1}{2} V \sum_{\mathbf{q}} \rho(\mathbf{q}) W(-\mathbf{q}) - \frac{1}{2} V \rho(\mathbf{q} = 0) W(\mathbf{q} = 0) , \quad (5.46)$$

where the $\mathbf{q} = 0$ term has been added and subtracted. With Eq. (5.44), the two integrals in (5.43) combine to yield

$$-\frac{1}{2} V \sum_{\mathbf{q}} \rho(\mathbf{q}) [W_s(-\mathbf{q}) + W_{xc}(-\mathbf{q})] . \quad (5.47)$$

Then since $W = W_b + W_s + W_{xc}$, the above contributions to \mathcal{E}_g become

$$\mathcal{E}_g = zN \left[\frac{3}{5} e_F + \frac{1}{2} W(\mathbf{q} = 0) \right] + \frac{1}{2} V \sum_{\mathbf{q}} \rho(\mathbf{q}) W_b(-\mathbf{q}) , \quad (5.48)$$

where we used $\rho(\mathbf{q} = 0) = \rho_0$, and $V\rho_0 = zN$.

The only term in Eq. (5.48) which depends on the ion positions is the last term, and that dependence can be made explicit through the structure

factor $S(\mathbf{q})$. This is done by using successively Eqs. (5.22), (5.33), and (5.36), to find

$$\frac{1}{2}V \sum_{\mathbf{q}} \rho(\mathbf{q})W_b(-\mathbf{q}) = N \sum_{\mathbf{q}} S(\mathbf{q})S(-\mathbf{q})F(q) \quad , \quad (5.49)$$

where $F(q)$ is the energy-wavenumber characteristic, given by

$$F(q) = \frac{q^2 V_A}{8\pi e^2} \frac{[w_b(q)]^2 [1 - H(q)]}{1 + [H(q) - 1][1 - Y(q)]} \quad . \quad (5.50)$$

Putting in for $S(\mathbf{q})$, from (5.37), the right side of (5.49) is transformed to

$$\frac{1}{2} \sum'_{KL} v_{ind}(|\mathbf{r}_K - \mathbf{r}_L|) + \sum_{\mathbf{q}} F(q) \quad , \quad (5.51)$$

where

$$v_{ind}(|\mathbf{r}|) = \frac{2}{N} \sum_{\mathbf{q}} F(q) e^{i\mathbf{q}\cdot\mathbf{r}} \quad . \quad (5.52)$$

Here v_{ind} is the *indirect* ion-ion interaction, arising from ion-electron-ion interactions summed over intermediate electrons in the electronic ground-state.

The above equations for \mathcal{E}_g , and for $v_{ind}(r)$, were derived in *Thermodynamics of Crystals*, at a time when computer limitations required us to split these functions into real-space and Fourier-space contributions. It is now possible for computers to calculate all our functions entirely in real space, or in Fourier space, and the new formulation is enormously simpler. In the new algebra, the Coulomb divergences are handled differently from before. The undefined (infinite) terms in the above equations are the $\mathbf{q} = 0$ component of W_s in (5.47), and the $\mathbf{q} = 0$ component of W_b in (5.48) and (5.49). But these undefined components all appear inside sums, and the sums can be transformed to integrals, which are finite. There remains the bare Coulomb behavior $1/r$ at large r , present in $v_{ind}(r)$, but this will be canceled by the direct ion-ion interactions. It is possible to show that Eq. (5.48) for \mathcal{E}_g is the same as Eq. (27.14) for E_G in *Thermodynamics of Crystals*.

Adiabatic Potential

The groundstate energy contribution still missing from Eq. (5.48) is the sum of direct interactions among the ions. The ion cores are still considered rigid, in particular nonpolarizable, so the Coulomb energy between two nonoverlapping ions separated by r is $z^2 e^2/r$. The *effective* ion-ion potential $\phi(r)$ is therefore $z^2 e^2/r + v_{ind}(r)$. Transforming (5.52) to an integral over \mathbf{q} , we have

$$\phi(r; V) = \frac{z^2 e^2}{r} + \frac{V_A}{\pi^2} \int_0^\infty F(q) \frac{\sin qr}{qr} q^2 dq . \quad (5.53)$$

At large r , the leading dependence of the integral is $-z^2 e^2/r$, hence $\phi(r)$ does not exhibit bare Coulomb behavior at large r . The volume dependence of $\phi(r; V)$ comes from the explicit appearance of V_A , and also from the volume dependences of ξ , f , and the parameters in $w_c(r)$.

The adiabatic potential Φ is defined in Eq. (4.6), and for N rigid ions whose ionization energy is I_z , it follows $\Phi = \mathcal{E}_g + NI_z$. From Eqs. (5.48) to (5.53), we can write

$$\Phi(\{\mathbf{r}_K\}) = \Omega(V) + \frac{1}{2} \sum'_{KL} \phi(|\mathbf{r}_K - \mathbf{r}_L|; V) , \quad (5.54)$$

correct to second order in the pseudopotential, where

$$\Omega(V) = NI_z + zN \left[\frac{3}{5} e_F + \frac{1}{2} W(\mathbf{q} = 0) \right] + \frac{V}{2\pi^2} \int_0^\infty F(q) q^2 dq . \quad (5.55)$$

According to Eq. (5.42), $\frac{1}{2} W(\mathbf{q} = 0) = -\frac{1}{3} e_F$. Except for the constant NI_z , the indicated volume dependence of $\Omega(V)$ is present in every term on the right of (5.55), and includes the volume dependences of ξ , f , and the parameters in $w_c(r)$. The ionization energy is positive and large, the term in square brackets is positive and relatively small, while the major contribution to $\Omega(V)$ is the integral, which is negative and expresses the metallic binding, dominated by the ion-electron Coulomb attraction. As pointed out in Sec. 1, in connection with Eq. (1.2), the sum of effective ion-ion potentials makes a relatively small contribution to $\Phi(\{\mathbf{r}_K\})$ in Eq. (5.54).

The leading dependence of $\phi(r)$ at large r turns out to be (see *e.g.* Harrison, 1989, Eq. (17–12))

$$\phi(r) \propto \frac{\cos 2fr}{r^3} , \quad \text{at large } r . \quad (5.56)$$

The cosine factor produces the Friedel oscillations, and results from the discontinuity in the groundstate occupation of the electron states, at the Fermi energy. The convergence of $\phi(r)$ is sufficient to make the energy $\frac{1}{2}\Sigma_{KL}\phi(|\mathbf{r}_K - \mathbf{r}_L|)$ finite, that is, the energy $\phi_K = \frac{1}{2}\Sigma_L\phi(|\mathbf{r}_K - \mathbf{r}_L|)$ is finite for every ion K . But if we take strain and volume derivatives of the total energy, as in the calculation of stresses and elastic constants, and if we take those derivatives *inside the sum*, as we do in Secs. 10 and 14, then the derivative contributions arising from ϕ_K no longer converge in an infinite system. This is a spurious effect, since the energy itself is always finite, hence has finite strain derivatives. The problem is cured by cutting off $\phi(r)$ at some large r , such that the total energy is unaffected at the level of accuracy of the theory. Friedel oscillations in nearly-free-electron metals are generally smaller than a few μRy , or say $1K$, and the whole theoretical construction cannot be meaningful at this energy. Original and damped forms of $\phi(r)$ for Na are shown in Fig. 1.1.

Electronic Excited States

When we extend pseudopotential perturbation theory to electronic states above the groundstate, we make the same “weak excitation” approximation as in Sec. 3, namely that the potential seen by an electron, in this case the complete screened pseudopotential $W(\mathbf{r})$, will retain its groundstate evaluation, even as some electrons are excited out of the groundstate. This is accomplished by using the groundstate evaluations of the response functions $H(q)$ and $Y(q)$.

Let us consider the excitation of reference structure electrons. As we shall see in Sec. 7, the contribution to a thermodynamic function arising from excitation of reference structure electrons is expressed in terms of the electronic density of states, $n(E^\sigma)$. In pseudopotential perturbation theory, all the dependence on ion positions is in $W(\mathbf{r}) = W(\mathbf{r}; \{\mathbf{r}_K\})$. At the reference structure this is $W^\sigma(\mathbf{r}) = W(\mathbf{r}; \{\mathbf{R}_K\})$. Since W is a perturbation, $n(E^\sigma)$ will be the free electron value $n(e)$, plus something small. In fact, whenever pseudopotential perturbation theory is a good description to begin with, then we expect the accurate $n(E^\sigma)$ from density functional theory to be reasonably well approximated by the free electron model. This turns out to be the case. The situation is illustrated, and the computational details are described, in Sec. 18.

When it comes to calculating *interactions* involving reference structure

electrons, the situation is different, because here the electron wavefunctions are needed. In some matrix elements, the perturbation part of the wavefunction can be as important as the free electron part. The Hamiltonian $\delta\mathcal{H}_{EX}$, describing interaction of the excited reference structure electrons with the motion of the ions, and the corresponding contribution to the free energy, are derived in pseudopotential perturbation theory in Sec. 18.

Finally, pseudopotential perturbation theory provides a conceptual simplification in the resolution of the total Hamiltonian. The exact electron excitation Hamiltonian is $\mathcal{H}_E - \mathcal{E}_g$, in Eq. (4.7), and this is approximated in Eq. (4.8), when it is replaced by its one-electron approximation \mathcal{H}_{EX} . But in pseudopotential perturbation theory, the one-electron description is exact in zeroth order, hence no separate one-electron approximation is required.

Calibration of Pseudopotential Models

Pseudopotential perturbation theory is an approximate electronic structure theory, and is most useful when calibrated, either to more accurate theoretical results, or to experimental data. The general result for a real metal is that a calibrated pseudopotential model accounts for physical properties far beyond the data to which it is calibrated. The adiabatic potential expressed in Eqs. (5.53) to (5.55) produces an excellent total Hamiltonian for the alkali metals, when the exchange-correlation parameter ξ is determined from the compressibility of the uniform electron gas, and when the core potential $w_c(r)$ is calibrated to experimental data. This is the pseudopotential model for Na whose effective ion-ion potential is shown in Fig. 1.1, and which is utilized throughout this monograph to illustrate what is achievable with a highly accurate Hamiltonian. The list of properties accurately accounted for by this model for Na includes the binding energy, the compressibility and elastic constants, thermal expansion, the phonon spectrum, the melting temperature, quasiharmonic and anharmonic contributions to thermodynamic functions from $T = 0$ to melt, electron-phonon interactions, and corresponding properties of the liquid as well.

In the old days, to test sensitivity to the form of $w_c(r)$, the parameters were adjusted on Harrison and Heine-Abarenkov models to obtain a good overall fit to the experimental phonon dispersion curves of Al (Wallace, 1969b). The best Heine-Abarenkov potential turned out to be an Ashcroft empty core potential. Dispersion curves are virtually identical for the two

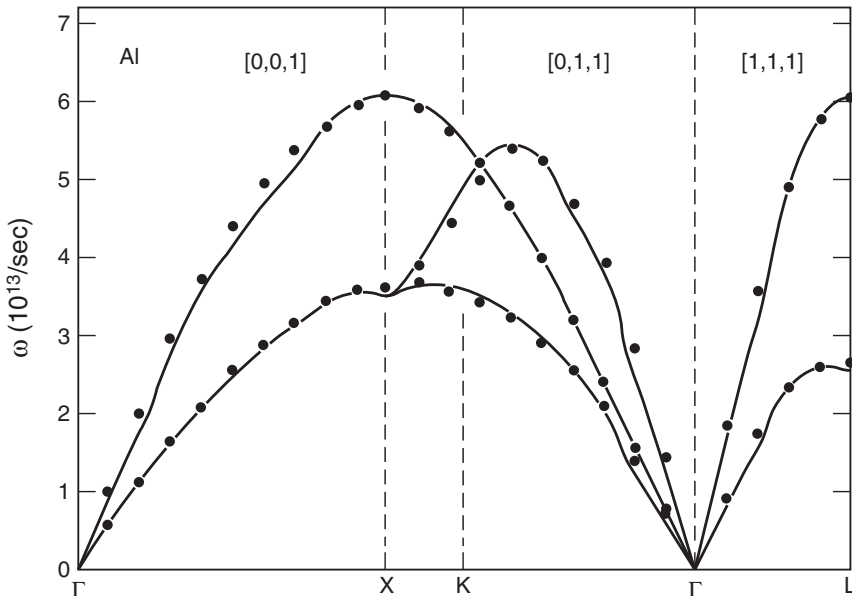


Figure 5.1. Calculated phonon dispersion curves (lines) for fcc Al, compared with experiment at 80K (points). In the theoretical curves, Kohn anomalies are artificially sharpened to make them clearly visible.

models, and are compared with experiment in Fig. 5.1. The form factors for the two models are compared in Fig. 5.2, and are seen to differ only at $q \gtrsim 2f$. We conclude that the phonon frequencies are only weakly dependent on $w(q)$ at large q . Values of $w(q)$ at the first two inverse lattice vectors, extracted from experimental Fermi surface data by Ashcroft (1963), are also shown in Fig. 5.2, and are in good agreement with our model form factors. These models for Al also give good results for quantities related to phonon-phonon and electron-phonon interactions.

However, these Al pseudopotential models give only qualitatively correct results for the binding energy and compressibility. This discrepancy was recognized by Ashcroft and Langreth (1967), as a general property of the theory, and was accounted for by adding another term into $\Omega(V)$, proportional to V_A^{-1} and representing the $\mathbf{q} = 0$ component of contributions from higher order perturbation theory. In a more recent study of Al, Straub *et al.* (1994) calibrated a complete pseudopotential model, namely the core potential $w_c(r)$, the exchange-correlation parameter ξ , and the total $\Omega(V)$

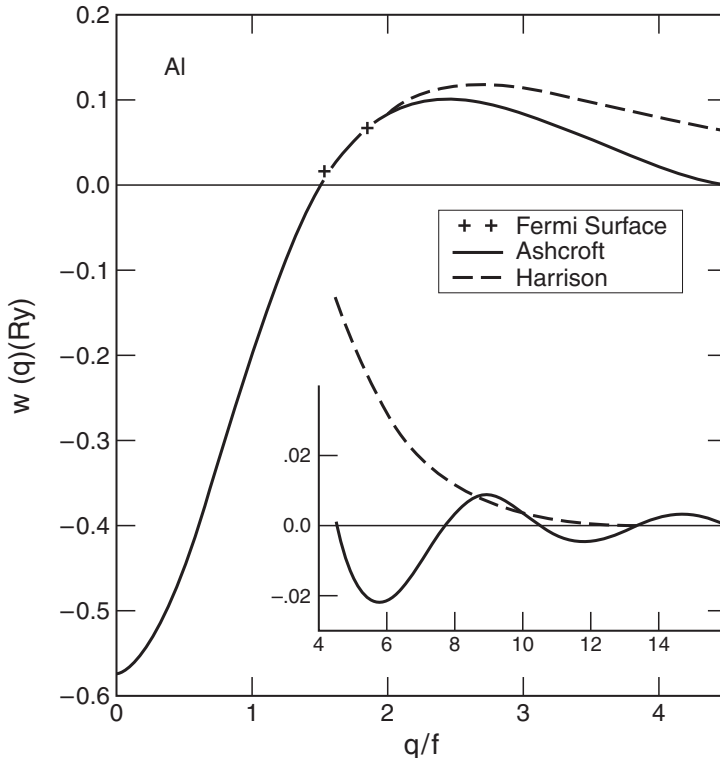


Figure 5.2. Screened form factors for the two pseudopotential models whose parameters were determined to give the best overall fit to the measured phonon frequencies for Al.

function, to density functional calculations of the static lattice potential and a small number of zone-boundary phonon frequencies. In this way, the pseudopotential perturbation theory serves as an interpolation formula for the entire $\Phi(\{\mathbf{r}_K\})$ surface, from just a few points on that surface calculated from a much more accurate theory.

Since we are interested in the equation of state of condensed matter, the theory developed here is supposed to apply to metals under compression, even under extreme compression. Considering the various effects which are represented by the local core potential $w_c(r)$, mentioned in connection with Eq. (5.34), and considering that the valence electrons are increasingly forced into the core region as a metal is compressed, the parameters of $w_c(r)$ must in principle vary with the system volume V . This property was

accounted for in the Al model mentioned above (Straub *et al.*, 1994), since that model was independently calibrated to results of density functional theory at a series of volumes. However, in our models for the alkali metals (Wallace, 1968), we added an empirical Born-Mayer repulsion to $\phi(r)$, of the form $\alpha e^{-\gamma r}$, intended to account for the Pauli repulsion when the ion cores begin to overlap. As it turns out, the Born-Mayer term gives only a small contribution to the physical properties, in all the comparisons of theory and experiment presented in this monograph. Moreover, since the whole model was calibrated to experimental data, the Born-Mayer repulsion gives a proper *empirical* account of compression effects. Nevertheless, Born-Mayer repulsion is not consistent with the physical basis of pseudopotential perturbation theory. Instead, the pseudopotential parameters themselves should vary with V , and when a metal is compressed to the point where ion cores begin to overlap, the outer shell of core electrons should be removed and included with the valence electrons.

Pseudopotential perturbation theory is still being developed as a description from first principles of the electronic structure of nearly-free-electron metals. Ashcroft (1990) discussed effects in liquid metals, associated with nonrigid ion cores, and with transient clustering of the ions. Pollack *et al.* (1997) compared experiment and theory for zone-boundary phonons and elastic constants from a local pseudopotential in second order, and they also examined nonlocal and nonperturbative effects.

Problem

5.1 In arriving at Eq. (5.48), the sum of free electron energies in (5.45) is evaluated over the zeroth order Fermi sphere. Is this the correct procedure? Show that the true Fermi surface differs from the free electron surface in second order in $W(\mathbf{q})$, and both surfaces enclose the same volume. Hence show the sum of free electron energies is the same to second order when evaluated over either volume.