

# Electron–Electron Interaction

# 7

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## 7.1 INTRODUCTION

In the nearly free electron model, we assumed that the motion of the electrons is independent of each other. The independent electron was assumed to obey the one-electron Schrodinger equation, and the lattice potential was considered to be due to the motion of the electron in a background of static positive charges in the lattice. In this approximation, we neglect the electron–electron interaction as well as the motion of the ions at a finite temperature.

However, in a rigorous solution of the underlying quantum mechanical problem, the Hamiltonian of the solid should include the motion of the interacting  $N$  electrons as well as the motion of the nuclei of which the mass is much heavier than that of the electrons. Because the nuclei are much more massive than the electrons and the interaction between the conduction electrons and the lattice waves is a complex problem, as a first step in solving the Hamiltonian, we will apply the Born–Oppenheimer approximation. According to this approximation, the electronic problem is first solved by assuming that the nuclei are static, classical potentials. The motion of the nuclei gradually increases around their equilibrium positions in the lattice when the temperature increases. As we saw in Chapter 2, the quanta of these lattice vibrations are called phonons. In the Born–Oppenheimer approximation, it is assumed that the cloud of negative charge of the electrons follow the nuclei in their motion. Because this motion is followed by charge redistribution, the energies involved in moving the nuclei also depend on the electron energy. This interaction between the conduction electrons and lattice waves is a dynamical problem that can be treated by perturbation theory. In the adiabatic approximation of Born and Oppenheimer, the eigenfunction of the Hamiltonian can be written as a product of the  $N$ -electron wave function  $\Psi(\mathbf{r}_1 s_1, \mathbf{r}_2 s_2, \dots, \mathbf{r}_N s_N)$  and  $\Phi(\mathbf{u})$ , where  $\Phi(\mathbf{u})$  satisfies a Schrodinger equation for the wave functions of the ions and  $\Psi(\mathbf{r}_1 s_1, \mathbf{r}_2 s_2, \dots, \mathbf{r}_N s_N)$  is the wave function of the  $N$  electrons in a static lattice, frozen with the  $l$ th ion at the point  $\mathbf{R}_l$  of the Bravais lattice. Here, the instantaneous positions of the  $N$  electrons are  $\mathbf{r}_i (i = 1, 2, \dots, N)$  and the corresponding spins are  $s_i$ . We will consider the ionic motion in a later section, where we will show that we would need to add an additional term  $\varepsilon_e(\mathbf{u})$ , which is the total energy of the electrons as a function of the ions, in the Schrodinger equation for the ions.

If we include the electron–electron interactions, the Schrodinger equation for the  $N$ -electron wave function can be written as

$$H\Psi = \sum_{i=1}^N \left( -\frac{\hbar^2}{2m} \nabla_i^2 \Psi - ze^2 \sum_l \frac{1}{|\mathbf{r}_i - \mathbf{R}_l|} \Psi \right) + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} \Psi. \quad (7.1)$$

It is impossible to solve Eq. (7.1), even with the fastest computer available to physicists, because the total number of electrons is of the order of  $10^{23}$ . The only possible way to solve Eq. (7.1) is by making drastic approximations. We will start with the simplest approximation, known as the Hartree approximation.

## 7.2 HARTREE APPROXIMATION

There are two alternate methods to derive the Hartree approximation. We will first consider the simplest method. We proceed with the basic idea of “deriving” from Eq. (7.1) the one-electron Schrodinger equation for the electrons in a lattice potential of the form

$$-\frac{\hbar^2}{2m} \nabla^2 \psi(\mathbf{r}) + U(\mathbf{r})\psi(\mathbf{r}) = \varepsilon\psi(\mathbf{r}), \quad (7.2)$$

by obviously making suitable (and drastic) approximations in Eq. (7.1). The potential due to the static ions in the lattice is

$$U_{ion}(\mathbf{r}) = -ze^2 \sum_l \frac{1}{|\mathbf{r} - \mathbf{R}_l|}. \quad (7.3)$$

The effective electron–electron potential  $U_{ee}(\mathbf{r})$  can be approximated as an electron moving in a field produced by the sum of all other electrons. If the electrons are considered as a smooth distribution of negative charge of charge density  $-en(\mathbf{r})$ , where  $n(\mathbf{r})$  is the number density of electrons,

$$n(\mathbf{r}) = \sum_j |\psi_j(\mathbf{r})|^2, \quad (7.4)$$

the potential energy of the electron in this field would be

$$U_{ee}(\mathbf{r}) = \int d\mathbf{r}' \frac{e^2 n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}. \quad (7.5)$$

The one-electron Schrodinger equation is obtained by adding  $U = U_{ion} + U_{ee}$ ,

$$-\frac{\hbar^2}{2m} \nabla^2 \psi_i(\mathbf{r}) - Ze^2 \sum_l \frac{1}{|\mathbf{r} - \mathbf{R}_l|} \psi_i(\mathbf{r}) + \left[ e^2 \sum_j \int d\mathbf{r}' |\psi_j(\mathbf{r}')|^2 \frac{1}{|\mathbf{r} - \mathbf{r}'|} \right] \psi_i(\mathbf{r}) = \varepsilon_i \psi_i(\mathbf{r}). \quad (7.6)$$

Eq. (7.6) is known as the Hartree equation. The Hartree equation can also be derived from Eq. (7.1) by following a variational method as follows. We write the  $N$ -electron wave function as

$$\Psi(\mathbf{r}_1 s_1, \mathbf{r}_2 s_2, \dots, \mathbf{r}_N s_N) = \psi_1(\mathbf{r}_1 s_1) \psi_2(\mathbf{r}_2 s_2) \dots \psi_N(\mathbf{r}_N s_N), \quad (7.7)$$

where  $\psi_i(\mathbf{r}_i s_i)$  are a set of orthonormal one-electron wave functions. We have to consider  $\Psi$  as a trial wave function for a variational calculation and find the equation that is satisfied by the single-particle functions  $\psi_i(\mathbf{r}_i s_i)$  so that the trial function (Eq. 7.7) minimizes

$$\langle H \rangle = \sum_{s_1} \sum_{s_2} \dots \sum_{s_N} \int d\mathbf{r}_1 d\mathbf{r}_2 \dots d\mathbf{r}_N \Psi^* H \Psi. \quad (7.8)$$

Here,  $\Psi$  is normalized because the set  $\psi_i(\mathbf{r}_i s_i)$  is orthonormal. If we rewrite the Hamiltonian in Eq. (7.1) as

$$H = \sum_i H_i + \frac{1}{2} \sum_{i \neq j} V_{ij}, \quad (7.9)$$

we note that  $H_i$  operates only on the coordinate of the  $i$ th electron and  $V_{ij}$  operates on the two-body coordinates of both  $i$  and  $j$ . From Eqs. (7.7) through (7.9), we obtain

$$\langle H \rangle = \sum_i \int \psi_i^* H_i \psi_i d\mathbf{r} + \frac{1}{2} \sum_{i \neq j} \iint d\mathbf{r}_i d\mathbf{r}_j \psi_i^* \psi_j^* V_{ij} \psi_i \psi_j. \quad (7.10)$$

If we minimize  $\langle H \rangle$  with respect to variation of  $\psi_i^*$ , we obtain

$$\delta \langle H \rangle = \sum_i \int \delta \psi_i^* \left[ H_i + \sum_{j \neq i} \int \psi_j^* V_{ij} \psi_j d\mathbf{r}_j \right] \psi_i d\mathbf{r}_i = 0, \quad (7.11)$$

where the variations  $\delta \psi_i^*$  satisfy the equation

$$\int \delta \psi_i^* \psi_i d\mathbf{r}_i = 0, \quad (7.12)$$

because of their normalization conditions. Eq. (7.12) acts as a constraint on the variation of  $\langle H \rangle$ . We follow the method of Lagrangian multipliers by multiplying Eq. (7.12) by a multiplier  $\epsilon_i$  and subtract the sum from Eq. (7.11). We obtain

$$\sum_i \int \delta\psi_i^* \left[ H_i + \sum_{j \neq i} \int \psi_j^* V_{ij} \psi_j d\mathbf{r}_j - \epsilon_i \right] \psi_i d\mathbf{r}_i = 0. \quad (7.13)$$

Because the variations  $\delta\psi_i^*$  are independent, the coefficient of each  $\delta\psi_i^*$  must vanish; i.e., we must have

$$\left( H_i + \sum_{j \neq i} \int \psi_j^* V_{ij} \psi_j d\mathbf{r}_j \right) \psi_i = \epsilon_i \psi_i, \quad (7.14)$$

which, along with Eqs. (7.1) and (7.9), leads to the Hartree equation,

$$-\frac{\hbar^2}{2m} \nabla^2 \psi_i(\mathbf{r}_i) - Ze^2 \sum_l \frac{1}{|\mathbf{r}_i - \mathbf{R}_l|} \psi_i(\mathbf{r}_i) + \left[ e^2 \sum_{j \neq i} \int d\mathbf{r}_j |\psi_j(\mathbf{r}_j)|^2 \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \right] \psi_i(\mathbf{r}_i) = \epsilon_i \psi_i(\mathbf{r}_i). \quad (7.15)$$

Comparing Eqs. (7.6) and (7.15), we note that the result of the formal derivation of the Hartree equation (Eq. 7.15) is almost identical to that derived earlier (Eq. 7.6) by using a qualitative argument except that each electron interacts not with the full charge density of the system (Eq. 7.6), but with the charge density minus the density of the electron itself. However, in general, the set of equations in Eq. (7.6) is known as the Hartree equations and is easier to solve. In what follows, we will assume that Eq. (7.6) is the Hartree equation even though it fails to represent the way in which a particular configuration of the  $N - 1$  electrons affects the electron under consideration.

The nonlinear Hartree equations (Eq. 7.6) for one-electron wave functions and energies are usually solved by first guessing a form for  $U_{ee}$  (the term in the square bracket in Eq. 7.6) and the one-particle Schrodinger equation is solved. The value of  $U_{ee}$  is again computed from the new wave functions  $\psi_i(\mathbf{r})$ , and the Schrodinger equation is again solved using these values. This iteration procedure is continued until there is no significant change in the potential. In fact, for this reason, the Hartree approximation is also known as the “self-consistent field approximation.”

The major failure of the Hartree approximation is that in the formal derivation (by using the variational principle), we started with Eq. (7.7) in which the basic approximation is that the full  $N$ -electron wave function  $\Psi$  is a product of the one-electron levels. However, this simple assumption is not compatible with the Pauli principle according to which the  $N$ -electron wave function is antisymmetric; that is, the sign of  $\Psi$  changes when two of its arguments are interchanged, i.e.,

$$\Psi(\mathbf{r}_1 s_1, \dots, \mathbf{r}_i s_i, \dots, \mathbf{r}_l s_l, \dots, \mathbf{r}_N s_N) = -\Psi(\mathbf{r}_1 s_1, \dots, \mathbf{r}_l s_l, \dots, \mathbf{r}_i s_i, \dots, \mathbf{r}_N s_N). \quad (7.16)$$

Eq. (7.7) does not satisfy the constraints imposed by Eq. (7.16) unless  $\Psi = 0$  identically.

In addition to the noncompliance of the Pauli principle, the other failure of the Hartree approximation is that it does not include the well-known effects such as “exchange,” “correlation,” and “screening.” In what follows, we will discuss “exchange” by deriving the Hartree–Fock equations and “screening” by discussing “Thomas–Fermi theory” and “Lindhard theory,” but we will ignore “correlation” because it is much harder to discuss and is in the realm of “many-body problems,” which requires the use of “field theory,” a subject beyond the scope of this book.

## 7.3 HARTREE–FOCK APPROXIMATION

### 7.3.1 General Formulation

Fock and Slater showed that the simplest way to ensure that the  $N$ -electron wave function obeys the Pauli principle is to construct a Slater determinant of orthonormal one-electron wave functions that is antisymmetric:

$$\Psi(\mathbf{r}_1 s_1, \mathbf{r}_2 s_2, \dots, \mathbf{r}_N s_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(\mathbf{r}_1 s_1) & \psi_1(\mathbf{r}_2 s_2) & \dots & \psi_1(\mathbf{r}_N s_N) \\ \vdots & \vdots & & \vdots \\ \psi_N(\mathbf{r}_1 s_1) & \psi_N(\mathbf{r}_2 s_2) & \dots & \psi_N(\mathbf{r}_N s_N) \end{vmatrix}. \quad (7.17)$$

The Slater determinant can be rewritten in the alternate form,

$$\Psi(\mathbf{r}_1 s_1, \mathbf{r}_2 s_2, \dots, \mathbf{r}_N s_N) = \frac{1}{\sqrt{N!}} \sum_n (-1)^n \psi_{n_1}(\mathbf{r}_1 s_1) \psi_{n_2}(\mathbf{r}_2 s_2) \dots \psi_{n_N}(\mathbf{r}_N s_N), \quad (7.18)$$

where the sum is over all permutations  $n$  of  $1 \dots N$ . Eq. (7.18) can be rewritten in the alternate form

$$\Psi(\mathbf{r}_1 s_1 \dots \mathbf{r}_N s_N) = \frac{1}{\sqrt{N!}} \sum_n (-1)^n \prod_j \psi_{n_j}(\mathbf{r}_j s_j). \quad (7.19)$$

Here, if the Hamiltonian does not involve the spin explicitly,  $\psi_i(\mathbf{r}_j s_j)$  has the simple form

$$\psi_i(\mathbf{r}_j s_j) = \phi_i(\mathbf{r}_j) \chi_i(s_j), \quad (7.20)$$

where  $\chi_i(s_j) = \delta_{s_j,1}$  for “spin-up” functions and  $\chi_i(s_j) = \delta_{s_j,-1}$  for “spin-down” functions.

It can be shown, by using the Slater determinant (Eq. 7.19) for the wave function  $\Psi(\mathbf{r}_1 s_1, \mathbf{r}_2 s_2, \dots, \mathbf{r}_N s_N)$  in Eq. (7.1) and a variational technique, very similar to that used for the Hartree approximation but involving much more tedious algebra, that the Hartree–Fock equation can be rewritten as (Problem 7.1)

$$\begin{aligned} \frac{-\hbar^2}{2m} \nabla^2 \phi_i(\mathbf{r}) - z e^2 \sum_l \frac{1}{|\mathbf{r} - \mathbf{R}_l|} \phi_i(\mathbf{r}) + \left[ e^2 \sum_j \int d\mathbf{r}' |\phi_j(\mathbf{r}')|^2 \frac{1}{|\mathbf{r} - \mathbf{r}'|} \right] \phi_i(\mathbf{r}) \\ - \sum_j \int d\mathbf{r}' \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} \phi_j^*(\mathbf{r}') \phi_i(\mathbf{r}') \phi_j(\mathbf{r}) \delta_{\chi_i, \chi_j} = \varepsilon_i \phi_i(\mathbf{r}). \end{aligned} \quad (7.21)$$

Eq. (7.21) can also be expressed as

$$-\frac{\hbar^2}{2m} \nabla^2 \phi_i(\mathbf{r}) + U^{\text{ion}}(\mathbf{r}) \phi_i(\mathbf{r}) + U^{\text{el}}(\mathbf{r}) \phi_i(\mathbf{r}) + U^{\text{ex}}(\mathbf{r}) \phi_i(\mathbf{r}) = \varepsilon_i \phi_i(\mathbf{r}). \quad (7.22)$$

The Hartree–Fock equation derived in Eq. (7.21) differs from the Hartree equation derived in Eq. (7.15) in the sense that there is an additional term (the last term) on the left side of the equation known as the exchange term. It can be interpreted by stating that particles 1 and 2 flip places during the course of interaction and the negative sign in the exchange integral is due to the antisymmetry

of the wave function. The exchange term is in fact an integral operator of the type  $U^{ex}(\mathbf{r})\phi(\mathbf{r}) = \int U(\mathbf{r}, \mathbf{r}')\phi(\mathbf{r}')d\mathbf{r}'$ . Thus, the Hartree–Fock equations are a complicated set of nonlinear equations that can only be solved numerically.

### 7.3.2 Hartree–Fock Theory for Jellium

The only case in which the Hartree–Fock equations can be solved exactly is the jellium model where the electrons in a metal are considered to be a set of free electrons of which the solutions are the familiar plane waves. In the jellium model, the positively charged ions are represented by a uniform distribution of positive charge with the same density as the electronic charge.

If there are  $N$  electrons in a volume  $V$ , the wave function of the free electrons is the plane waves

$$\phi_i(\mathbf{r}) = \frac{e^{i\mathbf{k}_i \cdot \mathbf{r}}}{\sqrt{V}}. \quad (7.23)$$

The kinetic energy term is

$$-\frac{\hbar^2}{2m} \nabla^2 \left( \frac{1}{\sqrt{V}} e^{i\mathbf{k}_i \cdot \mathbf{r}} \right) = \frac{1}{\sqrt{V}} \frac{\hbar^2 k_i^2}{2m} e^{i\mathbf{k}_i \cdot \mathbf{r}} = \frac{\hbar^2 k_i^2}{2m} \phi_i(\mathbf{r}). \quad (7.24)$$

The potential due to the interaction of the ions with the electrons in Eq. (7.22) in the jellium model can be expressed from Eq. (7.21) as

$$U^{ion}(\mathbf{r}) = -\frac{N}{V} \int d\mathbf{r}' \frac{e^2}{|\mathbf{r} - \mathbf{r}'|}. \quad (7.25)$$

The potential due to the Coulomb interaction in Eq. (7.22) in the jellium model can be expressed from Eq. (7.21) as

$$U^{el}(\mathbf{r}) = \int d\mathbf{r}' \sum_{j=1}^N \frac{e^2 |\phi_j(\mathbf{r})|^2}{|\mathbf{r} - \mathbf{r}'|}. \quad (7.26)$$

For plane waves,

$$\sum_{j=1}^N |\phi_j(\mathbf{r})|^2 = \frac{N}{V}. \quad (7.27)$$

From Eqs. (7.26) and (7.27),

$$U^{el}(\mathbf{r}) = \frac{N}{V} \int d\mathbf{r}' \frac{e^2}{|\mathbf{r} - \mathbf{r}'|}. \quad (7.28)$$

From Eqs. (7.25) and (7.28), we obtain

$$U^{ion} + U^{el} = 0. \quad (7.29)$$

We note that this type of cancellation is true only for the jellium model. We will now discuss the exchange term that arises due to the antisymmetry of the wave function and distinguishes the Hartree approximation from the Hartree–Fock approximation. The exchange term can be written as

$$U^{ex}\phi_i(\mathbf{r}) = -\sum_{j=1}^N \left[ \int d\mathbf{r}' \frac{e^2}{|\mathbf{r}-\mathbf{r}'|} \phi_j^*(\mathbf{r}') \phi_i(\mathbf{r}') \right] \phi_j(\mathbf{r}) \delta_{\chi_i, \chi_j}. \quad (7.30)$$

From Eqs. (7.23) and (7.30), we obtain

$$U^{ex}\phi_i(\mathbf{r}) = -\frac{e^2}{V^{3/2}} \sum_{j=1}^N \left[ \int d\mathbf{r}' \frac{e^{i(\mathbf{k}_i-\mathbf{k}_j)\cdot\mathbf{r}'} e^{i\mathbf{k}_j\cdot\mathbf{r}}}{|\mathbf{r}-\mathbf{r}'|} \right] \delta_{\chi_i, \chi_j}. \quad (7.31)$$

Changing the variable of integration  $\mathbf{r}'' = \mathbf{r}' - \mathbf{r}$ , we can rewrite Eq. (7.31) as

$$U^{ex}\phi_i(\mathbf{r}) = -\frac{e^2}{V^{3/2}} \sum_{j=1}^N \left[ \int d\mathbf{r}'' \frac{e^{i(\mathbf{k}_i-\mathbf{k}_j)\cdot\mathbf{r}''}}{r''} \right] e^{i\mathbf{k}_j\cdot\mathbf{r}} \delta_{\chi_i, \chi_j}. \quad (7.32)$$

Using the relation

$$\phi_i(\mathbf{r}) = \frac{1}{\sqrt{V}} e^{i\mathbf{k}\cdot\mathbf{r}}, \quad (7.33)$$

and the Fourier transformation

$$\int d\mathbf{r}'' \frac{e^{i(\mathbf{k}_i-\mathbf{k}_j)\cdot\mathbf{r}''}}{r''} = \frac{4\pi}{|\mathbf{k}_i-\mathbf{k}_j|^2}, \quad (7.34)$$

Eq. (7.32) can be rewritten as

$$U^{ex}\phi_i(\mathbf{r}) = -e^2 \phi_i(\mathbf{r}) \sum_{j=1}^N \frac{1}{V} \frac{4\pi}{|\mathbf{k}_i-\mathbf{k}_j|^2} \delta_{\chi_i, \chi_j}. \quad (7.35)$$

Before we proceed further, it is appropriate to mention that there is a divergence when  $\mathbf{k}_i \rightarrow \mathbf{k}_j$ . This divergence arises due to the unphysical assumption in the Hartree–Fock approximation, which treats only two electrons at a time, that the Coulomb interaction  $\frac{e^2}{|\mathbf{r}-\mathbf{r}'|}$  decays very slowly at long distances. In practice, the effective interaction between two electrons falls off much more rapidly due to the effect of screening, i.e., where the rest of the electrons play a role in reducing this interaction. We will treat the effect of screening in a subsequent section.

The sum over  $\mathbf{k}_j$  can be converted to an integration over  $\mathbf{k}$  space as outlined in Chapter 3:

$$\sum_{\mathbf{k}} F(\mathbf{k}) = \frac{V}{8\pi^3} \int d\mathbf{k} F(\mathbf{k}). \quad (7.36)$$

The density of states is usually multiplied by a factor of 2 because each  $\mathbf{k}$  state can have two electrons of opposite spin. However, the Kronecker delta function  $\delta_{\chi_i, \chi_j}$  reduces the density of states by a factor of  $\frac{1}{2}$ . Thus, Eq. (7.35) can be rewritten as

$$U^{ex}\phi_i(\mathbf{r}) = -e^2\phi_i(\mathbf{r}) \int \frac{d\mathbf{k}}{8\pi^3} \frac{4\pi}{(k^2 + k_i^2 - 2kk_i \cos \theta)}. \quad (7.37)$$

Because  $d\mathbf{k} = k^2 dk \sin \theta d\theta d\phi$ , integrating Eq. (7.37) over  $d\phi$  yields a factor of  $2\pi$ . Then integrating over  $d(\cos \theta)d\theta$  and subsequently over  $d\mathbf{k}$  (Problem 7.2), we can easily show that

$$U^{ex}\phi_i(\mathbf{r}) = -e^2\phi_i(\mathbf{r}) \frac{1}{2\pi k_i} \left[ (k_F^2 - k_i^2) \ln \left( \frac{k_F + k_i}{k_F - k_i} \right) + 2k_i k_F \right]. \quad (7.38)$$

We define a Lindhard dielectric function as

$$F(x) = \frac{1}{2} + \frac{(1-x^2)}{4x} \ln \left| \frac{1+x}{1-x} \right| \quad (7.39)$$

and express Eq. (7.38) as

$$U^{ex}\phi_i(\mathbf{r}) = -\frac{2e^2}{\pi} k_F F\left(\frac{k_i}{k_F}\right) \phi_i(\mathbf{r}). \quad (7.40)$$

From Eqs. (7.22), (7.24), (7.29), and (7.40), we obtain

$$\epsilon_i(\mathbf{k}) = \frac{\hbar^2 k_i^2}{2m} - \frac{2e^2}{\pi} k_F F\left(\frac{k_i}{k_F}\right). \quad (7.41)$$

We note that the group velocity of the electrons at the Fermi surface,  $\frac{1}{\hbar} \left( \frac{\partial \epsilon}{\partial k_i} \right) \Big|_{k_i=k_F}$ , is infinite, an unphysical result due to the fact that screening has been neglected in deriving the Hartree–Fock results.

The total energy of the  $N$ -electron system is obtained by summing over  $\epsilon_i(\mathbf{k})$ , multiplying the first term in Eq. (7.41) by 2 (because each  $\mathbf{k}$  has two spin levels), and then dividing the second term by 2 (to avoid counting each electron pair twice while summing the interaction energy of an electron with all electrons). We obtain

$$E = 2 \sum_{k \leq k_F} \frac{\hbar^2 k^2}{2m} - \frac{e^2 k_F}{\pi} \sum_{k \leq k_F} \left[ 1 + \frac{k_F^2 - k^2}{2kk_F} \ln \left| \frac{k_F + k}{k_F - k} \right| \right]. \quad (7.42)$$

The first term was evaluated in Chapter 1, and the second term is evaluated in Problem 7.3. We obtain

$$E = N \left[ \frac{3}{5} \epsilon_F - \frac{3}{4} \frac{e^2 k_F}{\pi} \right]. \quad (7.43)$$



Eq. (7.43) can also be rewritten as (Problem 7.4)

$$\begin{aligned}\frac{E}{N} &= \frac{e^2}{2a_0} \left[ \frac{3}{5} (k_F a_0)^2 - \frac{3}{2\pi} (k_F a_0) \right] \\ &= \left[ \frac{2.21}{(r_s/a_0)^2} - \frac{0.916}{(r_s/a_0)} \right] \text{Ry},\end{aligned}\tag{7.44}$$

where  $a_0$  is the Bohr radius and  $r_s$  is the radius of the average free space (sphere) for each electron (Chapter 1). It may be noted that the second term in Eq. (7.44) is comparable to the first term for simple metals, and hence, the electron–electron interaction term cannot be ignored in the theory of metals.

However, as we indicated earlier, there is a logarithmic singularity in the expression for energy when  $k = k_F$ . The singularity arises due to the fact that we have ignored the presence of other electrons when considering the effect of electron–electron interaction in the Hartree–Fock approximation. One has to consider the effect of screening to eliminate this divergence. There are two theories to include the effect of screening. We will first discuss the general effect of screening and then discuss both the Thomas–Fermi and Lindhard theories of screening.

## 7.4 EFFECT OF SCREENING

### 7.4.1 General Formulation

It is shown in Problem 7.5 that the Fourier transform of the external potential due to an external positive charge (for example, substituting a Zn ion for a Cu ion),  $\phi^e(\mathbf{q})$ , is related to the Fourier transform of the total potential (external plus induced charge),  $\phi(\mathbf{q})$ , by the relation

$$\phi(\mathbf{q}) = \frac{\phi^e(\mathbf{q})}{\epsilon(\mathbf{q})},\tag{7.45}$$

where  $\epsilon(\mathbf{q})$  is the wave-vector-dependent dielectric constant. This type of relation is normally used in dielectric materials where the wave vector dependence is not considered because the fields are uniform.

The induced charge density  $\rho^i(\mathbf{r})$  is linearly related to the total potential  $\phi(\mathbf{r}) = \phi^e(\mathbf{r}) + \phi^i(\mathbf{r})$ , provided  $\phi(\mathbf{r})$  is sufficiently weak. Here,  $\phi^e(\mathbf{r})$  is the potential due to the extra positively charged particle introduced in the metal, and  $\phi^i(\mathbf{r})$  is the potential due to the cloud of screening electrons induced by it. In such a case, one can write Fourier transforms as

$$\rho^i(\mathbf{q}) = \chi(\mathbf{q})\phi(\mathbf{q}).\tag{7.46}$$

We will now derive a relation between  $\chi(\mathbf{q})$  and  $\epsilon(\mathbf{q})$ , the dielectric constant. The Poisson's equations for the particle's charge density  $\rho^e(\mathbf{r})$  can be written as

$$-\nabla^2 \phi^e(\mathbf{r}) = 4\pi \rho^e(\mathbf{r}),\tag{7.47}$$

the Fourier transform of which is

$$q^2 \phi^e(\mathbf{q}) = 4\pi \rho^e(\mathbf{q}).\tag{7.48}$$

If the total charge density  $\rho(\mathbf{r}) = \rho^e(\mathbf{r}) + \rho^i(\mathbf{r})$ , the Poisson's equation is

$$-\nabla^2 \phi(\mathbf{r}) = 4\pi\rho(\mathbf{r}), \quad (7.49)$$

the Fourier transform of which is

$$q^2 \phi(q) = 4\pi\rho(q). \quad (7.50)$$

From Eqs. (7.46), (7.48), and (7.50), we obtain

$$\phi(q) = \frac{\phi^e(q)}{\left(1 - \frac{4\pi}{q^2}\chi(q)\right)}. \quad (7.51)$$

Comparing Eqs. (7.45) and (7.51), we derive the relation between  $\epsilon(q)$  and  $\chi(q)$ ,

$$\epsilon(q) = 1 - \frac{4\pi}{q^2}\chi(q). \quad (7.52)$$

### 7.4.2 Thomas–Fermi Approximation

Thomas and Fermi argued that if the total local potential  $\phi(\mathbf{r})$  is slowly varying, the energy of an electron,  $\epsilon(\mathbf{k})$ , will be modified from the free electron value. Treating this modification in a classical approximation, we obtain

$$\epsilon(\mathbf{k}) = \frac{\hbar^2 k^2}{2m} - e\phi(\mathbf{r}). \quad (7.53)$$

The induced charge density is

$$\rho^i(\mathbf{r}) = -e[n(\mathbf{r}) - n_0], \quad (7.54)$$

where  $-en(\mathbf{r})$  is the charge density when there is a local potential  $\phi(\mathbf{r})$ , and  $en_0$  is the charge density of the positive background ( $\phi(\mathbf{r}) = 0$ ). We can rewrite Eq. (7.54) in the alternate form

$$\rho^i(\mathbf{r}) = -e[n_0(\mu + e\phi(\mathbf{r})) - n_0(\mu)], \quad (7.55)$$

where

$$n_0(\mu) = \frac{1}{4\pi^3} \int d\mathbf{k} \frac{1}{e^{[\beta(\hbar^2 k^2/2m) - \mu]} + 1}. \quad (7.56)$$

Because  $\phi(\mathbf{r})$  is small, we make a Taylor expansion of the first term in Eq. (7.55). The leading terms cancel, and Eq. (7.55) can be rewritten in the alternate form

$$\rho^i(\mathbf{r}) \approx -e^2 \frac{\partial n_0}{\partial \mu} \phi(\mathbf{r}). \quad (7.57)$$

We make a Fourier transformation of  $\rho^i(\mathbf{r})$  and  $\phi(\mathbf{r})$ , and from Eqs. (7.46) and (7.57), we obtain

$$\chi_{TF}(\mathbf{q}) = -e^2 \frac{\partial n_0}{\partial \mu}. \quad (7.58)$$

From Eqs. (7.52) and (7.58), we obtain

$$\epsilon_{TF}(\mathbf{q}) = 1 + \frac{4\pi e^2}{q^2} \frac{\partial n_0}{\partial \mu}, \quad (7.59)$$

where  $\epsilon_{TF}(\mathbf{q})$  is the dielectric constant in the Thomas–Fermi approximation. If we define a screening factor

$$\lambda_{TF}^2 = 4\pi e^2 \frac{\partial n_0}{\partial \mu}, \quad (7.60)$$

Eq. (7.60) can be rewritten as

$$\epsilon_{TF}(\mathbf{q}) = 1 + \frac{\lambda_{TF}^2}{q^2}. \quad (7.61)$$

As an example, if there is a point charge  $Q$  at  $\mathbf{r}$ , it can be shown that (Problem 7.6)

$$\phi(\mathbf{r}) = \phi_e(\mathbf{r}) e^{-\lambda_{TF} r}. \quad (7.62)$$

This is known as the screened Coulomb potential because there is an exponential damping factor  $\lambda_{TF}$ .

### 7.4.3 Lindhard Theory of Screening

In a quantum mechanical treatment of Eq. (7.53), the one-electron Schrodinger equation can be written as

$$-\frac{\hbar^2}{2m} \nabla^2 \psi_{\mathbf{k}}(\mathbf{r}) - e\phi(\mathbf{r}) \psi_{\mathbf{k}}(\mathbf{r}) = \epsilon_{\mathbf{k}} \psi_{\mathbf{k}}(\mathbf{r}), \quad (7.63)$$

where  $-e\phi(\mathbf{r})$  is the potential energy. In the absence of the potential, the one-electron wave function is a plane wave that we denote by  $|\mathbf{k}\rangle$ . Using first-order perturbation theory, we obtain

$$\psi_{\mathbf{k}}(\mathbf{r}) = |\mathbf{k}\rangle + \sum_{\mathbf{q}} b_{\mathbf{k}+\mathbf{q}} |\mathbf{k}+\mathbf{q}\rangle, \quad (7.64)$$

where

$$b_{\mathbf{k}+\mathbf{q}} = \frac{\langle \mathbf{k}+\mathbf{q} | -e\phi(\mathbf{r}) | \mathbf{k} \rangle}{\epsilon^0(\mathbf{k}) - \epsilon^0(\mathbf{k}+\mathbf{q})} \quad (7.65)$$

and

$$|\mathbf{k}\rangle = e^{i\mathbf{k}\cdot\mathbf{r}}. \quad (7.66)$$

The charge density is

$$\rho(\mathbf{r}) = -e \sum_{\mathbf{k}} f^0(\mathbf{k}) |\psi_{\mathbf{k}}(\mathbf{r})|^2 = \rho^0(\mathbf{r}) + \rho^i(\mathbf{r}), \quad (7.67)$$

where  $f^0(\mathbf{k})$  is the equilibrium Fermi distribution. We can write the charge density as

$$\rho(\mathbf{r}) = -e \sum_{\mathbf{k}} [f^0(\mathbf{k}) |\psi_{\mathbf{k}}(\mathbf{r})|^2] \quad (7.68)$$

$$= -e \sum_{\mathbf{k}} f^0(\mathbf{k}) \left[ \left\{ e^{-i\mathbf{k}\cdot\mathbf{r}} + \sum_{\mathbf{q}} b_{\mathbf{k}+\mathbf{q}}^* e^{-i(\mathbf{k}+\mathbf{q})\cdot\mathbf{r}} \right\} \left\{ e^{i\mathbf{k}\cdot\mathbf{r}} + \sum_{\mathbf{q}} b_{\mathbf{k}+\mathbf{q}} e^{i(\mathbf{k}+\mathbf{q})\cdot\mathbf{r}} \right\} \right]. \quad (7.69)$$

Eq. (7.69) can be approximated as

$$\rho(\mathbf{r}) \approx -e \sum_{\mathbf{k}} f_0(\mathbf{k}) \left[ 1 + \sum_{\mathbf{q}} b_{\mathbf{k}+\mathbf{q}} e^{i\mathbf{q}\cdot\mathbf{r}} + \sum_{\mathbf{q}} b_{\mathbf{k}+\mathbf{q}}^* e^{-i\mathbf{q}\cdot\mathbf{r}} \right] \quad (7.70)$$

or

$$\rho(\mathbf{r}) \approx \rho^0(\mathbf{r}) + \sum_{\mathbf{k}} \sum_{\mathbf{q}} \left\{ \frac{e^2 \phi(\mathbf{q}) [f^0(\mathbf{k}) - f^0(\mathbf{k} + \mathbf{q})] e^{i\mathbf{q}\cdot\mathbf{r}}}{\varepsilon(\mathbf{k}) - \varepsilon(\mathbf{k} + \mathbf{q})} \right\}, \quad (7.71)$$

where we have written  $\mathbf{k}$  for  $\mathbf{k} - \mathbf{q}$ ,  $\mathbf{k} + \mathbf{q}$  for  $\mathbf{k}$ , and  $e^{i\mathbf{q}\cdot\mathbf{r}}$  for  $e^{-i\mathbf{q}\cdot\mathbf{r}}$  as the labels for the second term.

Because

$$\rho(\mathbf{r}) = \rho^0(\mathbf{r}) + \rho^i(\mathbf{r}), \quad (7.72)$$

$$\rho^i(\mathbf{r}) = \sum_{\mathbf{q}} \rho^i(\mathbf{q}) e^{i\mathbf{q}\cdot\mathbf{r}}, \quad (7.73)$$

from Eqs. (7.71) through (7.73), we obtain

$$\rho^i(\mathbf{q}) = e^2 \sum_{\mathbf{k}} \frac{f^0(\mathbf{k}) - f^0(\mathbf{k} + \mathbf{q})}{\varepsilon(\mathbf{k}) - \varepsilon(\mathbf{k} + \mathbf{q})} \phi(\mathbf{q}). \quad (7.74)$$

From Eqs. (7.46) and (7.74), we obtain

$$\chi_L(\mathbf{q}) = e^2 \sum_{\mathbf{k}} \frac{f^0(\mathbf{k}) - f^0(\mathbf{k} + \mathbf{q})}{\varepsilon(\mathbf{k}) - \varepsilon(\mathbf{k} + \mathbf{q})}, \quad (7.75)$$

where  $\chi_L(\mathbf{q})$  is the expression derived from Lindhard theory. From Eqs. (7.52) and (7.75), we obtain the expression for the dielectric constant for static screening in the Lindhard theory:

$$\epsilon_L(\mathbf{q}) = 1 - \frac{4\pi e^2}{q^2} \sum_{\mathbf{k}} \frac{f^0(\mathbf{k}) - f^0(\mathbf{k} + \mathbf{q})}{\varepsilon(\mathbf{k}) - \varepsilon(\mathbf{k} + \mathbf{q})}. \quad (7.76)$$

We first consider the dielectric constant when  $\mathbf{q} \rightarrow 0$ . We can write

$$\varepsilon(\mathbf{k}) - \varepsilon(\mathbf{k} + \mathbf{q}) \approx -\mathbf{q} \cdot \nabla_{\mathbf{k}} \varepsilon(\mathbf{k}) \quad (7.77)$$

and

$$f^0(\mathbf{k}) - f^0(\mathbf{k} + \mathbf{q}) \approx -\mathbf{q} \cdot \frac{\partial f^0(\mathbf{k})}{\partial \varepsilon} \nabla_{\mathbf{k}} \varepsilon(\mathbf{k}). \quad (7.78)$$

From Eqs. (7.76) through (7.78), we obtain

$$\varepsilon_L(\mathbf{q}) \approx 1 - \frac{4\pi e^2}{q^2} \sum_{\mathbf{k}} \frac{\partial f^0(\mathbf{k})}{\partial \varepsilon}, \quad (7.79)$$

which can be rewritten in the alternate form,

$$\varepsilon_L(\mathbf{q}) \approx 1 + \frac{4\pi e^2}{q^2} \int \left( -\frac{\partial f^0(\mathbf{k})}{\partial \varepsilon} \right) g(\varepsilon) d\varepsilon, \quad (7.80)$$

where  $g(\varepsilon)$  is the density of states. Because, at very low temperatures,

$$\left( -\frac{\partial f^0(\mathbf{k})}{\partial \varepsilon} \right) \approx \delta(\varepsilon - \varepsilon_F), \quad (7.81)$$

Eq. (7.80) can be rewritten in the alternate form

$$\varepsilon_L(\mathbf{q}) \approx 1 + \frac{4\pi^2}{q^2} g(\varepsilon_F). \quad (7.82)$$

From Eq. (7.82), we obtain  $\varepsilon \rightarrow \infty$  as  $q \rightarrow 0$ . Thus, an external field of long wavelength is almost entirely screened due to the flow of electrons. We can show that the same results are obtained through a simpler method by using the Thomas–Fermi approximation.

We can also write

$$\varepsilon(\mathbf{k}) - \varepsilon(\mathbf{k} + \mathbf{q}) \approx -\hbar^2(\mathbf{k} \cdot \mathbf{q}/m) \quad (7.83)$$

and

$$\sum_{\mathbf{k}} F(\mathbf{k}) = \int \frac{d\mathbf{k}}{4\pi^3} F(\mathbf{k}). \quad (7.84)$$

We note that Eq. (7.84) is different from Eq. (7.34) because we have considered  $V=1$  and multiplied the density of states by a factor of 2 to be able to accommodate two electrons of opposite spin in each  $\mathbf{k}$  state.

We obtain from Eqs. (7.71) through (7.73) and (7.83) through (7.84),

$$\rho^i(\mathbf{q}) = -e^2 \int \frac{d\mathbf{k}}{4\pi^3} \frac{f_0(\mathbf{k}) - f_0(\mathbf{k} + \mathbf{q})}{\hbar^2(\mathbf{k} \cdot \mathbf{q}/m)} \phi(\mathbf{q}). \quad (7.85)$$

Comparing with the definition of  $\rho^i(\mathbf{q}) = \chi(\mathbf{q})\phi(\mathbf{q})$ , in Eq. (7.46), we obtain

$$\chi_L(\mathbf{q}) = -e^2 \int \frac{d\mathbf{k}}{4\pi^3} \frac{f_0(\mathbf{k}) - f_0(\mathbf{k} + \mathbf{q})}{\hbar^2(\mathbf{k} \cdot \mathbf{q})/m}. \quad (7.86)$$

We note that the equilibrium Fermi function for free electrons is

$$f_0(\mathbf{k}) = \frac{1}{e^{\beta(\hbar^2 k^2/2m - \mu)} + 1}, \quad (7.87)$$

$$f_0(\mathbf{k}) - f_0(\mathbf{k} + \mathbf{q}) \approx \frac{\hbar^2}{m} \mathbf{k} \cdot \mathbf{q} \frac{\partial}{\partial \mu} f_0(\mathbf{k}) + O(q^2). \quad (7.88)$$

From Eqs. (7.86) and (7.88), we obtain

$$\chi_L(\mathbf{q}) \approx -e^2 \frac{\partial n_0}{\partial \mu} = \chi_{TF}(\mathbf{q}), \quad (7.89)$$

which is identical to the Thomas–Fermi result derived in Eq. (7.58).

However, the general result for  $\chi_L(\mathbf{q})$  in Lindhard theory can be obtained by integrating Eq. (7.86) at  $T=0$ . It can be shown that (Problem 7.7)

$$\chi_L(\mathbf{q}) = -e^2 \left( \frac{mk_F}{\hbar^2 \pi^2} \right) \left[ \frac{1}{2} + \frac{1-x^2}{4x} \ln \left| \frac{1+x}{1-x} \right| \right], \quad (7.90)$$

where  $x = \frac{q}{2k_F}$ . We note that when  $T \ll T_F$ ,

$$\frac{\partial n_0}{\partial \mu} = g(\varepsilon_F) = \frac{mk_F}{\hbar^2 \pi^2}. \quad (7.91)$$

From Eqs. (7.90) through (7.91), we obtain

$$\chi_L(\mathbf{q}) = \chi_{TF}(\mathbf{q})F(x). \quad (7.92)$$

We have shown that the function in the square bracket, which is 1 at  $x=0$  and is equal to the function  $F(x)$  appearing in the Hartree–Fock energy, is the Lindhard correction to the Thomas–Fermi result. Thus, the dielectric constant  $\epsilon_L = 1 - 4\pi\chi_L/q^2$  is not analytic at  $q = 2k_F$ . In fact, the static dielectric constant in the Lindhard theory can be written as (Problem 7.8)

$$\epsilon_L(\mathbf{q}) = 1 + \frac{4\pi e^2}{q^2} \frac{mk_F}{\hbar^2 \pi^2} \left[ \frac{1}{2} + \frac{4k_F^2 - q^2}{8k_F q} \ln \left| \frac{2k_F + q}{2k_F - q} \right| \right]. \quad (7.93)$$

It can also be shown that at large distances and at  $T=0$ , the screened potential  $\phi(\mathbf{r})$  of a point charge is of the form

$$\phi(\mathbf{r}) \sim \frac{1}{r^3} \cos 2k_F r. \quad (7.94)$$

If we write

$$\epsilon_L(\mathbf{q}) = 1 + \frac{\lambda_L^2}{q^2}, \quad (7.95)$$

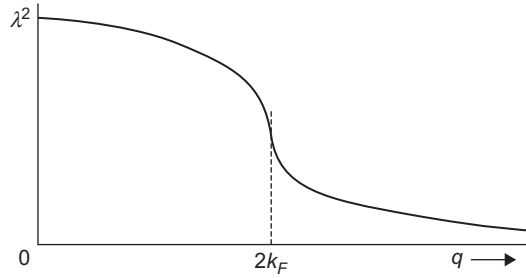
where  $\lambda_L$  is the screening parameter, we obtain

$$\lambda_L^2 = 4\pi e^2 \frac{mk_F}{\hbar^2 \pi^2} \left[ \frac{1}{2} + \frac{4k_F^2 - q^2}{8k_F q} \ln \left| \frac{2k_F + q}{2k_F - q} \right| \right]. \quad (7.96)$$

The variation of  $\lambda_L^2$  as a function of  $q$  is shown in Figure 7.1.

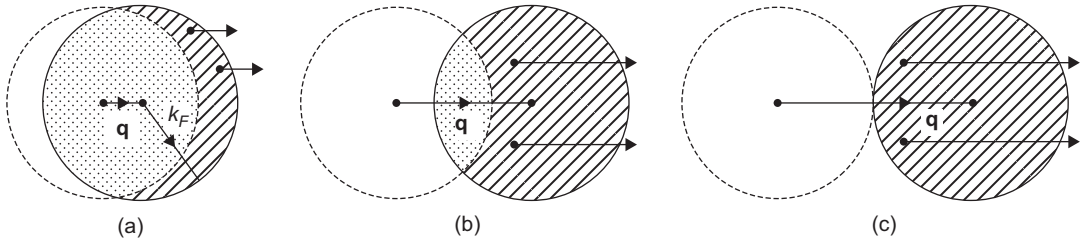
We note from Eqs. (7.60) and (7.96) that as  $q \rightarrow 0$ ,  $\lambda_L \rightarrow \lambda_{TF}$ . The effective screening length  $1/\lambda_L$  increases as  $q$  increases, and it becomes increasingly difficult to screen out the potentials of short wavelength.

When  $q = q_c = 2k_F$ , there is a logarithmic singularity in the expression for  $\lambda_L^2$ . This singularity arises due to the term  $f^0(\mathbf{k}) - f^0(\mathbf{k} + \mathbf{q})$  occurring in the summation over  $\mathbf{k}$  in the expression for  $\epsilon_L(\mathbf{q})$  in Eq. (7.76). If we consider the values of  $\mathbf{k}$ , where either  $|\mathbf{k}| > k_F$  is occupied and  $|\mathbf{k} + \mathbf{q}| > k_F$  is empty or vice versa, these lie in two regions covering the surface of the Fermi sphere. Figure 7.2 shows these regions of the Fermi sphere.



**FIGURE 7.1**

Variation of Lindhard screening parameter with  $q$ .



**FIGURE 7.2**

Contribution to the dielectric constant from different regions of the Fermi sphere.

These regions gradually expand as  $q$  increases. Thus, the sum over  $\mathbf{k}$  increases until a value of  $q = q_c = 2k_F$  is reached and the whole Fermi sphere contributes to the sum. Because there are no additional terms in the sum over  $\mathbf{k}$ , the functional form of the sum changes. However, each term remains a continuous function of  $\mathbf{q}$ . The singularity is not serious because the contribution from the last few points on the sphere before reaching  $q = q_c = 2k_F$  is small. However, at  $q = 2k_F$ ,  $\partial \epsilon_L / \partial q \rightarrow \infty$ .

If we consider the effect of an extra positive point charge in the jellium model, the “external field” is

$$V(\mathbf{r}) = e^2/r, \quad (7.97)$$

and the Fourier transform in a three-dimensional box is

$$V(\mathbf{q}) = 4\pi e^2/q^2. \quad (7.98)$$

The “screened” potential is

$$U(\mathbf{q}) = V(\mathbf{q})/\epsilon_L(\mathbf{q}) \quad (7.99)$$

and

$$U(\mathbf{r}) = \int U(\mathbf{q}) e^{-i\mathbf{q}\cdot\mathbf{r}} d\mathbf{q}. \quad (7.100)$$

From Eqs. (7.93) and (7.98) through (7.100), we obtain

$$U(\mathbf{r}) = 4\pi e^2 \int \left\{ q^2 + \frac{4me^2 k_F}{\hbar^2 \pi} \left[ \frac{1}{2} + \frac{4k_F^2 - q^2}{8k_F q} \ln \left| \frac{2k_F + q}{2k_F - q} \right| \right] \right\}^{-1} e^{-i\mathbf{q}\cdot\mathbf{r}} d\mathbf{q}. \quad (7.101)$$

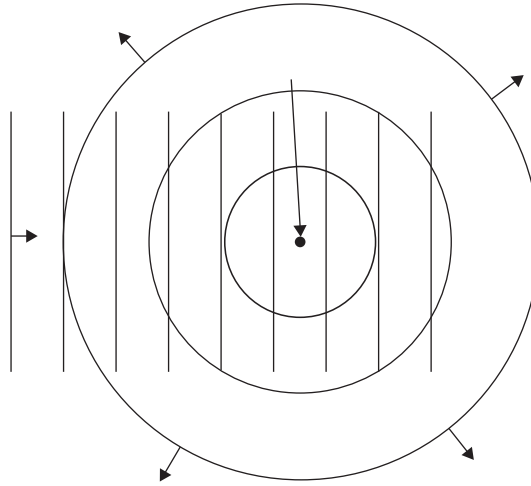
Due to the singularity at  $q = 2k_F$ , there will be a special contribution to  $U(\mathbf{r})$  that will contain oscillations of wave number  $2k_F$ . These oscillations are known as Friedel oscillations or Ruderman–Kittel oscillations depending on the context. We will now derive the Friedel oscillations using a much simpler approach.

## 7.5 FRIEDEL SUM RULE AND OSCILLATIONS

Friedel derived an equivalent formula for the oscillations by considering the effect of a spherically symmetric potential  $U(\mathbf{r})$  (impurity) placed in the electron gas. First, he derived a sum rule for the valence difference between the impurity and the solvent metal. Then he derived an expression for the oscillating charge density associated with the singularity in Eq. (7.101). It is well known in quantum mechanics<sup>14</sup> that when an incident plane wave (for convenience, we consider it moving in the  $z$  direction) is scattered by a spherically symmetric potential (see Figure 7.3), the wave function at a distance far from the scattering target ( $r \rightarrow \infty$ ) can be expressed as

$$\psi_k(r, \theta) = e^{ikz} + \frac{f(\theta)e^{ikr}}{r}. \quad (7.102)$$



**FIGURE 7.3**

Plane wave is incident in the  $z$  direction on spherically symmetric potential at the center. The scattered outgoing wave is spherical.

It has been shown in Liboff—Eqs. (14.11) through (14.13)—that at large distances,

$$\psi_k(r, \theta) = \sum_{l=0}^{\infty} i^l (2l+1) e^{i\delta_l} \frac{1}{kr} \sin(kr - \frac{l\pi}{2} + \delta_l) P_l(\cos \theta). \quad (7.103)$$

Here,  $P_l(\cos \theta)$  is a Legendre polynomial, and  $\delta_l$  is a phase shift for the  $l$ th partial wave

$$\psi_{k,l}(r, \theta) = A_{k,l} \frac{1}{r} \sin(kr - \frac{l\pi}{2} + \delta_l) P_l(\cos \theta). \quad (7.104)$$

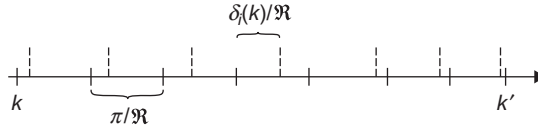
Friedel used the boundary condition that  $\psi_k = 0$  at  $r = \mathfrak{R}$ , as if the spherically symmetric potential was placed at the center of a sphere of radius  $\mathfrak{R}$ . Thus, the values of  $k$  that are appropriate are

$$k\mathfrak{R} - \frac{l\pi}{2} + \delta_l = m\pi, \quad (7.105)$$

where  $m$  is an integer. We note that the phase shift  $\delta_l$  would have been zero if the sphere had been empty. In that case, the “allowed” values of  $k$  would be

$$k_m = \frac{\left(m + \frac{l}{2}\right)\pi}{\mathfrak{R}}. \quad (7.106)$$

There are many values of  $l$  for each value of  $m$ , and there are  $(2l+1)$  values of  $\psi$  for each  $l$ . However, the total number of states with  $\varepsilon \leq \varepsilon_F$ , i.e., states of which the wave vector is less than  $k_F$ ,

**FIGURE 7.4**

New “allowed” values between  $k$  and  $k'$ .

would be the same as that for the cubic lattice considered in Chapter 1. When the impurity with the spherically symmetric potential is at the center of the sphere,  $\delta_l \neq 0$  and the “allowed” values of  $k$  do not become equal to  $k_m$ . They will be shifted by  $\delta_l/\mathfrak{R}$ . In addition,  $\delta_l$  varies with  $k$ . This is shown schematically in Figure 7.4.

Thus, between  $k$  and  $k'$ , the set will have  $[\delta_l(k) - \delta_l(k')]/\pi$  new “allowed” values. Because  $\delta_l(k=0) = 0$ , counting a factor of 2 for spin states of an electron and the fact that for each  $l$  there are  $(2l+1)$  states, the total number of extra electrons needed to fill up to the Fermi wave vector  $k_F$  is

$$\xi = \frac{2}{\pi} \sum_l (2l+1) \delta_l(k_F). \quad (7.107)$$

Here,  $\xi$  is the difference between the valence of the spherically symmetric impurity and the metal, which is the number of electrons necessary to neutralize the charge of the impurity. Eq. (7.107) is the Friedel sum rule, which was derived with two basic assumptions that the charge of a spherically symmetric impurity must be neutralized by extra electrons within a finite distance, and at large distances,  $k_F$  is the same as in the crystal without any impurity.

At large distances from the spherical potential at the center of the sphere  $\mathfrak{R}$ , the change in the electron charge density associated with the phase-shifted waves in Eq. (7.104) is given by  $\delta\rho = -e\delta n$ , where  $\delta n$  is the change in electron density,

$$\delta\rho = -e \sum_l (2l+1) \int_0^{k_F} \left[ |\psi_{k,l}(\delta_l)|^2 - |\psi_{k,l}(0)|^2 \right] \frac{2\mathfrak{R}}{\pi} dk. \quad (7.108)$$

Here, we have used the expression from Eq. (7.106),

$$k_m - k_{m-1} = \frac{\pi}{\mathfrak{R}}, \quad (7.109)$$

and there are two spin states for each  $k$ .

The wave function in Eq. (7.104) has been normalized in a sphere of radius  $\mathfrak{R}$  in which the terms going to zero more rapidly at large values of  $r$  have been neglected,

$$\int |\psi_{k,l}(r, \delta_l)|^2 r^2 dr \sin\theta d\theta d\phi = A_l^2 \int_0^{\mathfrak{R}} \int_0^{\pi} \int_0^{2\pi} dr \sin^2(kr - \frac{l\pi}{2} + \delta_l) P_l^2(\cos\theta) \sin\theta d\theta d\phi. \quad (7.110)$$

Because  $\int_{-1}^1 P_l^2(x) dx = \frac{2}{2l+1}$  and  $\sin^2 \varphi = \frac{1}{2}(1 - \cos 2\varphi)$ , neglecting the oscillatory terms, we obtain

$$A_l \approx \frac{(2l+1)^{1/2}}{(2\pi\mathfrak{R})^{1/2}}. \quad (7.111)$$

From Eqs. (7.104) and (7.111), we obtain

$$\psi_{k,l}(r, \delta_l) \approx \frac{(2l+1)^{1/2}}{(2\pi\mathfrak{R})^{1/2}} \frac{1}{r} \sin\left(kr - \frac{l\pi}{2} + \delta_l\right). \quad (7.112)$$

From Eqs. (7.108) and (7.112), we obtain

$$\delta\rho = -\frac{e}{\pi^2} \sum_l (2l+1) \int_0^{k_F} \left[ \sin^2\left(kr - \frac{l\pi}{2} + \delta_l\right) - \sin^2\left(kr - \frac{l\pi}{2}\right) \right] \frac{1}{r^2} dk. \quad (7.113)$$

Using the formula

$$\sin^2(\alpha) - \sin^2(\beta) = \sin(\alpha + \beta) \sin(\alpha - \beta), \quad (7.114)$$

we obtain from Eq. (7.113)

$$\delta\rho = -\frac{e}{2\pi^2} \sum_l (2l+1) \int_0^{k_F} \sin(2kr - l\pi + \delta_l) \sin \delta_l \frac{1}{r^3} d(2kr). \quad (7.115)$$

By integrating Eq. (7.115), we obtain

$$\delta\rho \approx \frac{-e}{2\pi^2} \sum_l (2l+1) (-1)^l \sin \delta_l \frac{\cos(2k_F r + \delta_l)}{r^3}. \quad (7.116)$$

Here, the terms going to zero more rapidly at  $r$  (the limit of the integral at  $k=0$ ) have been dropped. Eq. (7.116) gives the oscillating charge density that arises due to the singularity obtained earlier in Eq. (7.101). The oscillating charge is not a negligible effect because it varies as  $1/r^3$ . Further, the electrons are driven away by the spherically symmetric impurity in some regions because  $\delta\rho$  becomes negative.

## 7.6 FREQUENCY AND WAVE-NUMBER-DEPENDENT DIELECTRIC CONSTANT

We consider a homogeneous electron gas that has a number density  $n = N/v$ , where  $v$  is the volume of the crystal. When an external perturbation  $\phi_e(\mathbf{r}, t)$  is applied, fluctuations in the electron gas are induced such that

$$n = n_0 + \delta n. \quad (7.117)$$

The fluctuations give rise to an internal potential  $\phi_i(\mathbf{r}, t)$ , which essentially describes the screening effect of the electron gas on an electron at  $\mathbf{r}$ . These fluctuations are obtained by the Poisson equation

$$\nabla^2 \phi_i(\mathbf{r}, t) = -4\pi e^2 \delta n(\mathbf{r}, t). \quad (7.118)$$

The total potential acting on the electron is

$$\phi(\mathbf{r}, t) = \phi_i(\mathbf{r}, t) + \phi_e(\mathbf{r}, t). \quad (7.119)$$

The statistical mean values of any physical quantity  $G$  are determined through the statistical operator  $\langle \hat{G} \rangle = \text{tr}(\hat{\rho} \hat{G})$  (Eq. 3.14) where  $\hat{\rho}_k$  is defined in Eq. (3.24) as

$$\hat{\rho}_k = Z_k^{-1} e^{-\beta(\varepsilon(\mathbf{k}) - \mu)}, \quad (7.120)$$

where  $Z_k$  is the grand partition function defined in Eq. (3.23) as

$$\hat{Z}_k = 1 + e^{-\beta(\varepsilon(\mathbf{k}) - \mu)}, \quad (7.121)$$

where the spin has been omitted in both Eqs. (7.120) and (7.121).

It can be easily shown that the equilibrium state of the electron gas (index 0) is given by

$$\hat{H}_0 |\mathbf{k}\rangle = \varepsilon(\mathbf{k}) |\mathbf{k}\rangle, \quad (7.122)$$

and

$$\hat{\rho}_0 |\mathbf{k}\rangle = f_0(\mathbf{k}) |\mathbf{k}\rangle, \quad (7.123)$$

where  $f_0(\mathbf{k})$  is the Fermi distribution function. In the presence of the time-dependent external perturbation,

$$\hat{H} = \hat{H}_0 + \hat{\phi}(\mathbf{r}, t) \quad (7.124)$$

and

$$\hat{\rho} = \hat{\rho}_0 + \delta\hat{\rho}(\mathbf{r}, t). \quad (7.125)$$

We have

$$i\hbar \delta\dot{\hat{\rho}} |\mathbf{k}\rangle = [\hat{H}, \hat{\rho}] |\mathbf{k}\rangle = [\hat{H}_0, \delta\hat{\rho}] |\mathbf{k}\rangle + [\hat{\phi}, \hat{\rho}_0] |\mathbf{k}\rangle. \quad (7.126)$$

Here, we have neglected the term  $[\hat{\phi}, \delta\hat{\rho}] |\mathbf{k}\rangle$  in Eq. (7.126). We note that  $\hat{H}_0$  commutes with  $\hat{\rho}_0$ . We can rewrite Eq. (7.126) as

$$i\hbar \langle \mathbf{k}' | \delta\dot{\hat{\rho}} | \mathbf{k} \rangle = [\varepsilon(\mathbf{k}') - \varepsilon(\mathbf{k})] \langle \mathbf{k}' | \delta\hat{\rho} | \mathbf{k} \rangle - [f_0(\mathbf{k}') - f_0(\mathbf{k})] \langle \mathbf{k}' | \hat{\phi} | \mathbf{k} \rangle. \quad (7.127)$$

The  $\mathbf{q}$ th Fourier component of  $\phi$  is given by

$$\phi_{\mathbf{q}}(t) = \frac{1}{v} \int e^{-i\mathbf{q}\cdot\mathbf{r}} \phi(\mathbf{r}, t) d\mathbf{r}, \quad (7.128)$$

where

$$\mathbf{q} = \mathbf{k}' - \mathbf{k}. \quad (7.129)$$

We can express

$$\phi(\mathbf{r}, t) = \iint \phi(\mathbf{q}, \omega) e^{i\mathbf{q}\cdot\mathbf{r}} e^{i\omega t} e^{\alpha t} d\mathbf{q} d\omega, \quad (7.130)$$

where the term  $e^{\alpha t}$  has been multiplied so that the oscillation of frequency  $\omega$  and wave vector  $\mathbf{q} \equiv \mathbf{k}' - \mathbf{k}$  grows slowly with a time constant  $\alpha$ . In the final result,  $\alpha \rightarrow 0$ . Because  $\delta\rho$  has the same time dependence as  $\phi(\mathbf{r}, t)$ , from Eqs. (7.127) and (7.128), we obtain for each Fourier component (Problem 7.10)

$$[\varepsilon(\mathbf{k} + \mathbf{q}) - \varepsilon(\mathbf{k}) - i\hbar(i\omega + \alpha)] \langle \mathbf{k} + \mathbf{q} | \delta\hat{\rho} | \mathbf{k} \rangle = [f_0(\mathbf{k} + \mathbf{q}) - f_0(\mathbf{k})] \phi_{\mathbf{q}}(t), \quad (7.131)$$

where

$$\phi_{\mathbf{q}}(t) = \phi_{e\mathbf{q}}(t) + \phi_{i\mathbf{q}}(t) = [\phi_e(\mathbf{q}, \omega) + \phi_i(\mathbf{q}, \omega)] e^{(i\omega t + \alpha t)}. \quad (7.132)$$

From Eqs. (7.118), (7.128), and (7.132), we obtain

$$q^2 \phi_{i\mathbf{q}}(t) = 4\pi e^2 \delta n_{\mathbf{q}}. \quad (7.133)$$

It can be easily shown that the particle concentration  $\delta n(\mathbf{r}_0, t)$  is given by

$$\delta n(\mathbf{r}_0, t) = \sum_{\mathbf{q}} e^{i\mathbf{q}\cdot\mathbf{r}_0} \delta n_{\mathbf{q}}. \quad (7.134)$$

We can also express from Eqs. (7.121) and (7.125)

$$\begin{aligned} \delta n(\mathbf{r}_0, t) &= \text{tr}[\delta(\mathbf{r} - \mathbf{r}_0) \delta\rho] = \sum_{\mathbf{k}\mathbf{k}'} \langle \mathbf{k} | \delta(\mathbf{r} - \mathbf{r}_0) | \mathbf{k}' \rangle \langle \mathbf{k}' | \delta\rho | \mathbf{k} \rangle \\ &= \frac{1}{v} \sum_{\mathbf{k}\mathbf{k}'} e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}_0} \langle \mathbf{k}' | \delta\rho | \mathbf{k} \rangle \\ &= \frac{1}{v} \sum_{\mathbf{q}} e^{i\mathbf{q}\cdot\mathbf{r}_0} \sum_{\mathbf{k}} \langle \mathbf{k} + \mathbf{q} | \delta\rho | \mathbf{k} \rangle. \end{aligned} \quad (7.135)$$

From Eqs. (7.133) through (7.135), we obtain (taking  $v = 1$ )

$$\phi_{i\mathbf{q}}(t) = \frac{4\pi e^2}{q^2} \sum_{\mathbf{k}} \langle \mathbf{k} + \mathbf{q} | \delta\rho | \mathbf{k} \rangle. \quad (7.136)$$

From Eqs. (7.131), (7.132), and (7.136), we obtain

$$\begin{aligned} \phi_i(\mathbf{q}, \omega) &= \phi(\mathbf{q}, \omega) - \phi_e(\mathbf{q}, \omega) \\ &= \frac{4\pi e^2}{q^2} \sum_{\mathbf{k}} \frac{f_0(\mathbf{k} + \mathbf{q}) - f_0(\mathbf{k})}{\varepsilon(\mathbf{k} + \mathbf{q}) - \varepsilon(\mathbf{k}) + \hbar\omega - i\hbar\alpha} \phi(\mathbf{q}, \omega). \end{aligned} \quad (7.137)$$

We obtain from Eq. (7.137),

$$\phi_e(\mathbf{q}, \omega) = \phi(\mathbf{q}, \omega) \left[ 1 - \frac{4\pi e^2}{q^2} \sum_{\mathbf{k}} \frac{f_0(\mathbf{k} + \mathbf{q}) - f_0(\mathbf{k})}{\varepsilon(\mathbf{k} + \mathbf{q}) - \varepsilon(\mathbf{k}) + \hbar\omega - i\hbar\alpha} \right]. \quad (7.138)$$

If we define the dielectric constant as

$$\epsilon(\mathbf{q}, \omega) = \frac{\phi_e(\mathbf{q}, \omega)}{\phi(\mathbf{q}, \omega)}, \quad (7.139)$$

we obtain from Eqs. (7.138) and (7.139)

$$\epsilon(\mathbf{q}, \omega) = 1 - \frac{4\pi e^2}{q^2} \sum_{\mathbf{k}} \frac{f^0(\mathbf{k} + \mathbf{q}) - f^0(\mathbf{k})}{\varepsilon(\mathbf{k} + \mathbf{q}) - \varepsilon(\mathbf{k}) + \hbar\omega - i\hbar\alpha}. \quad (7.140)$$

Eq. (7.140) is the Lindhard equation for the dielectric constant of the electron gas. We note that for the case of static screening ( $\omega = 0, \alpha = 0$ ), Eq. (7.140) becomes identical to Eq. (7.76) derived by using time-independent perturbation theory.

We can write

$$\lim_{\alpha \rightarrow 0} \frac{1}{z - i\alpha} = P\left(\frac{1}{z}\right) + i\pi\delta(z). \quad (7.141)$$

Thus, we obtain

$$\epsilon(\mathbf{q}, \omega) = \epsilon_1(\mathbf{q}, \omega) + i\epsilon_2(\mathbf{q}, \omega), \quad (7.142)$$

where

$$\epsilon_1(\mathbf{q}, \omega) = 1 - \frac{4\pi e^2}{q^2} P \left[ \sum_{\mathbf{k}} \frac{f^0(\mathbf{k} + \mathbf{q}) - f^0(\mathbf{k})}{\varepsilon(\mathbf{k} + \mathbf{q}) - \varepsilon(\mathbf{k}) + \hbar\omega} \right] \quad (7.143)$$

and

$$\epsilon_2(\mathbf{q}, \omega) = \frac{4\pi^2 e^2}{q^2} \sum_{\mathbf{k}} [f^0(\mathbf{k} + \mathbf{q}) - f^0(\mathbf{k})] \delta(\varepsilon(\mathbf{k} + \mathbf{q}) - \varepsilon(\mathbf{k}) - \hbar\omega). \quad (7.144)$$

The imaginary part  $\epsilon_2(\mathbf{q}, \omega)$  is related to the absorption constant of the electron gas and pair excitations are involved in this absorption. The conservation of energy indicated by the  $\delta$ -function indicates that in Eq. (7.143), the denominator always has

$$\hbar\omega > [\varepsilon(\mathbf{k} + \mathbf{q}) - \varepsilon(\mathbf{k})] \quad (7.145)$$

for each term. We divide the summation over  $\mathbf{k}$  into two parts and introduce new summation indices  $\mathbf{k} + \mathbf{q}$  and  $-\mathbf{k}$  into the first and second part, respectively. We bring the two parts together and neglect all energy differences between states  $\mathbf{k} + \mathbf{q}$  and  $\mathbf{k}$ .

We obtain

$$\epsilon_1(\mathbf{q}, \omega) = 1 - \left\{ \frac{4\pi e^2}{q^2} \sum_{\mathbf{k}} \frac{f^0(\mathbf{k})}{\epsilon(\mathbf{k}) - \epsilon(\mathbf{k} - \mathbf{q}) + \hbar\omega} - \sum_{-\mathbf{k}} \frac{f^0(-\mathbf{k})}{\epsilon(-\mathbf{k}) - \epsilon(-\mathbf{k} + \mathbf{q}) - \hbar\omega} \right\}, \quad (7.146)$$

$$= 1 + \frac{4\pi e^2}{q^2} \sum_{\mathbf{k}} \frac{2f^0(\mathbf{k}) \{ \epsilon(\mathbf{k}) - \epsilon(\mathbf{k} - \mathbf{q}) \}}{\hbar^2 \omega^2}. \quad (7.147)$$

Here, we have rearranged the sum over  $\mathbf{k}$  and neglected the energy differences in the denominator because  $\hbar\omega \gg [\epsilon(\mathbf{k}) - \epsilon(\mathbf{k} - \mathbf{q})]$  in the plasma oscillation region.

Expanding  $\epsilon(\mathbf{k}) - \epsilon(\mathbf{k} - \mathbf{q})$  in powers of  $\mathbf{q}$ , the first term vanishes. We obtain

$$\epsilon(\mathbf{q}) - \epsilon(\mathbf{k} - \mathbf{q}) \approx -\frac{\hbar^2 q^2}{2m} \quad (7.148)$$

and

$$\sum_{\mathbf{k}} f^0(\mathbf{k}) = n. \quad (7.149)$$

Substituting Eqs. (7.147) and (7.148) in Eq. (7.149), we obtain

$$\epsilon_1(\omega) = 1 - \frac{4\pi n e^2}{m\omega^2} = 1 - \frac{\omega_p^2}{\omega^2}, \quad (7.150)$$

where  $\omega_p$  is the plasma frequency. Eq. (7.150) shows that when  $\omega \rightarrow \omega_p$ ,  $\epsilon_1 \rightarrow 0$ . However, from Eq. (7.138),

$$\phi(\mathbf{q}, \omega) = \frac{\phi_e(\mathbf{q}, \omega)}{\epsilon(\mathbf{q}, \omega)} \rightarrow \infty. \quad (7.151)$$

An infinitesimal external field  $\phi_e(\mathbf{q}, \omega)$  gives rise to an extremely large effective field. Thus, the system is self-exciting.  $\omega_p$  is a natural mode of oscillation of the electron gas. It is called a plasma mode.

We note that Eq. (7.140) is also known as Lindhard dielectric susceptibility.

Thus, if  $\phi_e(\mathbf{r}, t)$  is the actual external potential, the Fourier transformation is given by

$$\phi_e(\mathbf{r}, t) = \iint \phi_e(\mathbf{q}, \omega) e^{i\mathbf{q}\cdot\mathbf{r}} e^{i\omega t} d\mathbf{q} d\omega. \quad (7.152)$$

The effective potential  $U(\mathbf{r}, t)$  seen by the electrons is given by

$$U(\mathbf{r}, t) = \iint \frac{\phi_e(\mathbf{q}, \omega)}{\epsilon_L(\mathbf{q}, \omega)} e^{i\mathbf{q}\cdot\mathbf{r}} e^{i\omega t} d\mathbf{q} d\omega. \quad (7.153)$$

## 7.7 MOTT TRANSITION

The Mott transition is an example of a metal-insulator transition that has been actually observed in transition metal oxides. This involves discussion of the Hubbard model, which we will consider later. However, we will consider the basic argument for metal-insulator transition first proposed by Mott. He argued that if one has a collection of hydrogen or other monovalent atoms, it is unlikely that they will form a conductor even if they are far apart from each other. Individual hydrogen atoms are insulators because the electron is bound to the parent atom. If, through some process, an electron is taken out from one of the array of hydrogen (or any other group of monovalent) atoms, it will leave behind a positively charged ion. However, the electron will still be attracted to the positively charged ion and might even form a bound state. Thus, it would not be able to carry current. The solid would still be an insulator. There has to be a certain criterion when such types of insulators would become conductors (metals).

When many electrons are excited, the electron gas would screen the electron–ion interaction. The potential is of the form (because of screening of the ion)

$$V(r) = -\frac{e^2}{r} e^{-\lambda r}. \quad (7.154)$$

If the density of ionized electrons is  $n$ , we have derived in Eq. (7.96) an expression for the screening parameter  $\lambda_L$ , which can be written for small  $q$  values as

$$\lambda^2 \approx \frac{4e^2 m k_F}{\hbar^2 \pi}. \quad (7.155)$$

Because  $k_F = (3\pi^2 n)^{1/3}$ ,

$$\lambda^2 \approx \frac{4me^2 n^{1/3}}{\hbar^2}. \quad (7.156)$$

The radius of the ground state of a hydrogen atom is given by

$$a_o = \frac{\hbar^2}{me^2}. \quad (7.157)$$

There cannot be any bound state if  $1/\lambda < a_o$ . The criterion that the ionized atom, of which the potential is expressed in Eq. (7.154), is capable of recapturing the electron that has been removed from it is

$$\lambda < a_o^{-1}. \quad (7.158)$$

From Eqs. (7.156) through (7.158), this condition can be expressed as

$$n^{-1/3} > 4a_o. \quad (7.159)$$

Thus, if the average spacing of the atoms is greater than 4 atomic units, the system would be an insulator. As the atoms come closer, the transition from insulator to metal would be quite sharp. This is known as a Mott transition.



## 7.8 DENSITY FUNCTIONAL THEORY

### 7.8.1 General Formulation

Hohenberg and Kohn hypothesized that the electron density  $n(\mathbf{r})$  of a many-electron system at point  $\mathbf{r}$  has all the information about the many-electron wave function. In this case,  $n(\mathbf{r})$  is defined as

$$n(\mathbf{r}) = \langle \Psi | \sum_{l=1}^N \delta(\mathbf{r} - \mathbf{r}_l) | \Psi \rangle. \quad (7.160)$$

Here,  $\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$  is the many-electron wave function defined earlier both in the context of the Hartree and Hartree–Fock approximations. Eq. (7.160) can be rewritten in the alternate form

$$n(\mathbf{r}) = N \int d\mathbf{r}_1 d\mathbf{r}_2 \dots d\mathbf{r}_N \Psi^*(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) \delta(\mathbf{r} - \mathbf{r}_1) \Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N). \quad (7.161)$$

According to Hohenberg and Kohn, the electronic density  $n(\mathbf{r})$  determines the external potentials  $U(\mathbf{r})$  and the number of electrons that are inside these potentials. If the kinetic energy of the electrons is  $T$ , the ground-state energy is  $\varepsilon$ , the electrons that obey Schrodinger's equation interact via the Coulomb potentials  $U_{ee}$ , and the potential due to the ions is  $U$ , one can write an expression for the functional for the ground-state energy  $\varepsilon[n]$ ,

$$\varepsilon[n] = T[n] + U[n] + U_{ee}[n]. \quad (7.162)$$

If the functional  $\varepsilon[n]$  is found, the ground-state energy density  $n(\mathbf{r})$  minimizes it. However, there is a constraint that the total number of electrons is

$$N = \int d\mathbf{r} n(\mathbf{r}). \quad (7.163)$$

Because  $U[n]$  depends only on the density, one can also write

$$U[n] = \int d\mathbf{r} n(\mathbf{r}) U(\mathbf{r}). \quad (7.164)$$

If we write

$$F_{HK}[n] = T[n] + U_{ee}[n], \quad (7.165)$$

it is a universal function for all systems of  $N$  particles. We obtain from Eqs. (7.162) and (7.165),

$$\varepsilon[n] = F_{HK}[n] + U[n]. \quad (7.166)$$

We can also define a functional  $F[n]$ , which is the minimum over all wave functions producing density  $n(\mathbf{r})$  of  $F$ :

$$F[n] \equiv \min_{\Psi \rightarrow n} \langle \Psi | T + U_{ee} | \Psi \rangle. \quad (7.167)$$

In theory, after the universal function  $F[n]$  is found, any set of nuclei can be added to the many-particle system through the potential  $U(\mathbf{r})$ . Then one has to find the function  $n(\mathbf{r})$ , which minimizes

it to solve the Schrodinger equation. In practice,  $F[n]$  can be obtained by making appropriate approximations such that the results would agree with the experimental results, and hence, the form of  $F[n]$  varies with the nature of the experiment.

### 7.8.2 Local Density Approximation

Kohn and Sham introduced the local density approximation (LDA), in which they proposed to express the electron density as a function of a set of  $N$  single-electron wave functions  $\psi_i(\mathbf{r})$  instead of a function of all material properties,

$$n(\mathbf{r}) = \sum_{i=1}^N |\psi_i(\mathbf{r})|^2. \quad (7.168)$$

The kinetic energy term of the energy functional is written as

$$T[n] = \sum_i \frac{\hbar^2}{2m} |\nabla \psi_i|^2. \quad (7.169)$$

The rest of the quantities (including exchange) are obtained from the results of a homogeneous electron gas. We derived (the second term in Eq. 7.43) that

$$\varepsilon_{ex} = -\frac{3}{4}N \frac{e^2 k_F}{\pi}, \quad (7.170)$$

and we derived in Chapter 1 that

$$n = \frac{k_F^3}{3\pi^2}, \quad (7.171)$$

from which we obtain

$$\varepsilon_{ex}[n] = -\frac{3e^2}{4} \left(\frac{3}{\pi}\right)^{1/3} \int n^{4/3}(\mathbf{r}) d\mathbf{r}. \quad (7.172)$$

From Eqs. (7.169) and (7.172) and using standard expressions for  $U_{ee}[n]$  and  $U[n]$ , we obtain

$$\varepsilon[n] = \sum_{i=1}^N \frac{\hbar^2}{2m} |\nabla \psi_i|^2 + \int d\mathbf{r} n(\mathbf{r}) U(\mathbf{r}) + \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \frac{e^2 n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} - \frac{3e^2}{4} \left(\frac{3}{\pi}\right)^{1/3} \int d\mathbf{r} n^{4/3}(\mathbf{r}). \quad (7.173)$$

If we vary Eq. (7.173) with respect to  $\psi_i^*$  (because we know the density as a functional of the wave function from Eq. 7.168), we obtain

$$\frac{-\hbar^2}{2m} \nabla^2 \psi_i(\mathbf{r}) + \left\{ U(\mathbf{r}) + \int d\mathbf{r}' \frac{e^2 n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} - e^2 \left(\frac{3}{\pi} n(\mathbf{r})\right)^{1/3} \right\} \psi_i(\mathbf{r}) = \varepsilon_i \psi_i(\mathbf{r}). \quad (7.174)$$

In general, if one wants to add the correlation terms (any corrections to the exchange terms because of the many-body nature of the  $N$ -electron system), one can rewrite Eq. (7.174) in the alternate form

$$\frac{-\hbar^2}{2m} \nabla^2 \psi_i(\mathbf{r}) + \left\{ U(\mathbf{r}) + \int d\mathbf{r}' \frac{e^2 n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + \frac{\partial \epsilon_{xc}(n)}{\partial n} \right\} \psi_i(\mathbf{r}) = \epsilon_i \psi_i(\mathbf{r}). \quad (7.175)$$

Here,  $\epsilon_{xc}(n)$  is the exchange-correlation energy of the electron gas.

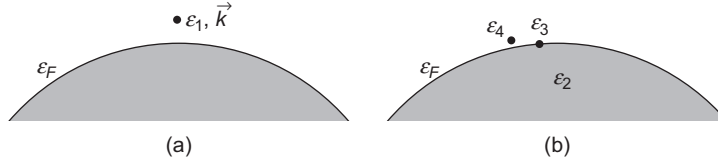
The approximation of the form (Eq. 7.175) is known as the local density approximation (LDA). A variety of band calculations are based on the density functional theory in general and the LDA in particular. The success of these band calculations primarily depends on the use of appropriate exchange-correlation functions. In fact, the correlation functions are a consequence of many-body theory and can be calculated only by using field-theoretical methods. In band calculations, one can only make intelligent guesses of these functions depending on the available experimental results. However, a variety of first principles calculations of the exchange functionals are available to calculate the total energies of atoms. It has been shown that the recent calculations using these functionals yield more accurate results for the energy of atoms than the results obtained by using the Hartree–Fock approximation. In fact, Kohn was awarded the Nobel prize in chemistry for his pioneering work on density functional theory.

## 7.9 FERMI LIQUID THEORY

### 7.9.1 Quasiparticles

The Fermi liquid theory was originally developed by Landau to explain the properties of liquid  $^3\text{He}$ . However, it has also been applied to the theory of electron–electron interactions in metals. In particular, the Fermi liquid theory explains the success of the independent electron approximation even though the electron–electron interactions are significant. The Fermi liquid theory also indicates how the effect of electron–electron interactions can be qualitatively taken into account in the study of the properties of metals in general and transport properties in particular.

In Landau’s argument, if one starts with a set of noninteracting electrons and gradually turns on the interactions between electrons, there would be two types of effects. The energy of the one-electron level would be modified, and it can be treated by the Hartree–Fock and other types of approximations described earlier in this chapter. However, in the Hartree–Fock approximation, the one-electron levels are stationary in spite of the interacting system. In contrast, when the interactions between the electrons are turned on, the electrons would be scattered in and out of the single-electron levels, which are no longer stationary. If the scattering is sufficiently low, one can introduce a relaxation time and try to solve the problem by using a relaxation-time mechanism used to treat transport theories. However, the electron–electron relaxation time is usually much larger than those used in other transport theories. The basic idea of the Landau Fermi Liquid theory is to consider the excitations of the strongly interacting system instead of concentrating on the nature of the ground state. The scattering rate of the fermions is considerably reduced due to the Pauli exclusion principle. In addition, Landau termed the elementary excitations, which act like particles, as quasiparticles. These quasiparticles interact with each other, but not as strongly as the particles from which they are constructed.

**FIGURE 7.5**

(a) An excited state  $\varepsilon_1 > \varepsilon_F$  of wave vector  $\mathbf{k}$ . (b)  $\varepsilon_2 < \varepsilon_F, \varepsilon_3 > \varepsilon_F, \varepsilon_4 > \varepsilon_F$ .

To highlight Landau's theory, we consider an  $N$ -electron state at  $T=0$  filling a Fermi sphere of radius  $k_F$  and energy  $\varepsilon_F$ . In addition, there is a single excited electron (quasiparticle) in a level  $\varepsilon_1 > \varepsilon_F$ . To be scattered, this electron can interact with an electron of energy  $\varepsilon_2$ , but because only electron levels of energy less than  $\varepsilon_F$  are occupied,  $\varepsilon_2 < \varepsilon_F$ . Both of these electrons can scatter only into energy states  $\varepsilon_3$  and  $\varepsilon_4$ , which are unoccupied; i.e., these states are above the Fermi sphere. Thus,  $\varepsilon_3 > \varepsilon_F$  and  $\varepsilon_4 > \varepsilon_F$ . These are schematically shown in Figure 7.5.

The law of conservation of energy requires that

$$\varepsilon_1 + \varepsilon_2 = \varepsilon_3 + \varepsilon_4. \quad (7.176)$$

Because  $\varepsilon_1 > \varepsilon_F$  at  $T=0$ , some phase space is available for scattering, and  $\varepsilon_2, \varepsilon_3$ , and  $\varepsilon_4$  can vary within a shell of which the thickness is on the order of  $|\varepsilon_1 - \varepsilon_F|$  near the Fermi surface. After  $\varepsilon_2$  and  $\varepsilon_3$  are fixed within the shell  $|\varepsilon_1 - \varepsilon_F|$ , there cannot be any new choice for the value of  $\varepsilon_4$  because of Eq. (7.176). Thus, at  $T \rightarrow 0$ , the scattering rate is given by

$$\frac{1}{\tau} \Big|_{T=0} \approx a_1(\varepsilon_1 - \varepsilon_F)^2. \quad (7.177)$$

If we consider the scattering at a temperature  $T$ , there would be partially occupied levels of width  $k_B T$  around  $\varepsilon_F$ . Thus, there will be an additional scattering rate proportional to  $(k_B T)^2$ . The scattering rate near the Fermi surface at temperature  $T$  is given by

$$\frac{1}{\tau} \approx a_1(\varepsilon_1 - \varepsilon_F)^2 + a_2(k_B T)^2. \quad (7.178)$$

These derivations are the same as that for an independent  $N$ -electron system. However, we will discuss Landau's formulation of quasiparticles and his arguments that lead to a one-to-one correspondence with the fermions in the  $N$ -electron system. We will first derive an approximate formula for the temperature-dependent part of the relaxation time in Eq. (7.178). If  $\varepsilon_1 \sim \varepsilon_F$ , the first term in Eq. (7.178) can be neglected compared to the second term;  $\tau$  will essentially be proportional to  $1/T^2$ . We further assume that the dependence of  $\tau$  on the electron–electron interaction is through the Fourier transform of the interaction potential, which can be estimated by the Thomas–Fermi screened potential defined in Eq. (7.61). Because  $\frac{\partial n_0}{\partial \mu} > 1$ , according to Eq. (7.61), the Thomas–Fermi screened potential is everywhere less than  $\left(\frac{4\pi e^2}{\lambda_{TF}^2}\right)$ . Thus, neglecting the first term in Eq. (7.178), we assume that

$$\frac{1}{\tau} \propto \left(\frac{4\pi e^2}{\lambda_{TF}^2}\right)(k_B T)^2. \quad (7.179)$$

From Eqs. (7.60), (7.91), and (7.179), we obtain

$$\frac{1}{\tau} \propto \left( \frac{\hbar^2 \pi^2}{mk_F} \right)^2 (k_B T)^2. \quad (7.180)$$

The proportionality constant ‘ $a$ ’ in Eq. (7.180) can be written as a dimensionless number by multiplying Eq. (7.180) by  $m^3/\hbar^7$  such that  $\frac{1}{\tau}$  has the dimensions of inverse time,

$$\frac{1}{\tau} = \frac{a(k_B T)^2}{\hbar \epsilon_F}. \quad (7.181)$$

It has been estimated that the range of the dimensionless number ‘ $a$ ’ is between 1 and 100.

The empirical formula for scattering in the presence of electron–electron interaction, using the Thomas–Fermi theory for screening, was derived essentially by turning on electron–electron interaction on an  $N$ -particle independent electron system. Landau validated these arguments by using the concept of quasiparticles, according to which the low-lying states of the strongly interacting  $N$ -electron system evolve in a continuous way such that there is a one-to-one correspondence with the noninteracting electron system. In a noninteracting electron system, if  $n$  electrons of wave vectors  $\mathbf{k}_1, \dots, \mathbf{k}_n$  above  $k_F$  have been excited from the states  $\mathbf{k}'_1, \dots, \mathbf{k}'_n$  below  $k_F$ , the energy of the excited state is

$$E = E_g + \epsilon(\mathbf{k}_1) + \dots + \epsilon(\mathbf{k}_n) - \epsilon(\mathbf{k}'_1) - \dots - \epsilon(\mathbf{k}'_n), \quad (7.182)$$

where  $E_g$  is the ground-state energy, and for free electrons,  $\epsilon(\mathbf{k}_i) = \hbar^2 k_i^2/2m$ . The quasiparticles are the states of the interacting system where  $n$  quasiparticles have been excited out of levels with wave vectors  $\mathbf{k}'_1, \dots, \mathbf{k}'_n$  below  $k_F$  and the same number of excited quasiparticles with wave vectors  $\mathbf{k}_1, \dots, \mathbf{k}_n$  are present above  $k_F$ . In this case, we have the relation

$$E = E_g + \epsilon(\mathbf{k}_1) + \dots + \epsilon(\mathbf{k}_n) - \epsilon(\mathbf{k}'_1) - \dots - \epsilon(\mathbf{k}'_n), \quad (7.183)$$

but  $\epsilon(\mathbf{k}_i)$  are very different from the free electron energies. In fact, the quasiparticle relation  $\epsilon(\mathbf{k}_i)$  versus  $\mathbf{k}_i$  is very difficult to determine because particles with the same spin have an interaction that differs from the interaction between particles with a different spin. However, there is indeed a one-to-one correspondence between the free electrons and quasiparticles. Landau showed, by using Green’s function methods, that for all orders of perturbation theory, every interacting Fermi system is normal in the sense that the quasiparticle representation is valid. Landau’s argument is very complex, and we will not discuss his theory any further here.

The summary of Landau’s model of quasiparticles is that there exists a set of wave functions that are in one-to-one correspondence with low-lying excited states of the noninteracting Fermi gas. They behave under translations like noninteracting particles with index  $\mathbf{k}$ . Similarly, states that correspond to low-energy holes of the noninteracting electron gas can be constructed. Although these states are not true eigenfunctions, they decay very slowly near the Fermi surface.

## 7.9.2 Energy Functional

Landau proposed a phenomenological description of a quantum state with a large number of quasiparticles. Let  $n_{\mathbf{k}\sigma}$  describe the occupation number of state  $\mathbf{k}$ . In the ground state,  $n_{\mathbf{k}\sigma} = 1$  below the

Fermi surface and  $n_{\mathbf{k}\sigma} = 0$  above it. The difference between the occupation of the state  $\mathbf{k}\sigma$  and its occupation in the ground state is given by  $\delta n_{\mathbf{k}\sigma}$ . Suppose that the energy of the quantum state can be expanded in terms of the occupation number  $\delta n_{\mathbf{k}\sigma}$  by

$$\varepsilon[\delta n] = \varepsilon_0 + \sum_{\mathbf{k}\sigma} \varepsilon_{\mathbf{k}}^{(0)} \delta n_{\mathbf{k}\sigma} + \frac{1}{2} \sum_{\mathbf{k}\sigma, \mathbf{k}'\sigma'} \delta n_{\mathbf{k}\sigma} f(\mathbf{k}\sigma, \mathbf{k}'\sigma') \delta n_{\mathbf{k}'\sigma'} + \dots, \quad (7.184)$$

where  $\delta n_{\mathbf{k}\sigma}$  is the change in the occupation number of the quasiparticle mode of wave vector  $\mathbf{k}$  and spin  $\sigma$  in the ground state, and  $\delta n_{\mathbf{k}'\sigma'}$  corresponds to the higher energy level. The function  $\varepsilon_{\mathbf{k}}^{(0)}$  is the energy of the noninteracting particles. For a metal, it is the energy of the Bloch electrons. The  $f$ -function, which depends on the mutual spins of the two quasiparticles, describes interactions between the quasiparticles. The exchange force favors parallel alignment of spin because the Pauli exclusion principle keeps two electrons with the same spin away from the same point in space. Thus, the correlation effect is enhanced while the mutual electrostatic potential energy is reduced. However, in general, it is difficult to compute the  $f$ -function.

At zero temperature, the energy needed to add one quasiparticle  $\delta n_{\mathbf{k}\sigma}$  above the Fermi surface is

$$\varepsilon_{\mathbf{k}\sigma} \equiv \varepsilon_{\mathbf{k}\sigma}^{(0)} + \sum_{\mathbf{k}'\sigma'} f(\mathbf{k}\sigma, \mathbf{k}'\sigma') \delta n_{\mathbf{k}'\sigma'}. \quad (7.185)$$

Because the chemical potential  $\mu$  increases when a quasiparticle is added, the system will be filled with quasiparticles until the cost of adding them rises above  $\mu$ . Similarly, the quasiparticle states will empty out until  $\mu = \varepsilon_{\mathbf{k}\sigma}$ . At  $T = 0$ ,  $\mu = \varepsilon_F$  and the occupation numbers  $n_{\mathbf{k}\sigma}$  are

$$n_{\mathbf{k}\sigma}^{(0)} \equiv \theta(\varepsilon_F - \varepsilon_{\mathbf{k}\sigma}). \quad (7.186)$$

The Fermi wave vector is defined by  $\varepsilon_{\mathbf{k}_F} = \varepsilon_F$  for an isotropic system. Because there is a one-to-one correspondence between the quasiparticles and the free particles,

$$n = \frac{N}{V} = \frac{1}{V} \sum_{\mathbf{k}\sigma} f_{\mathbf{k}\sigma} = \frac{k_F^3}{3\pi^2}. \quad (7.187)$$

It can also be shown after some algebra that

$$\delta n_{\mathbf{k}\sigma} = n_{\mathbf{k}\sigma} - n_{\mathbf{k}\sigma}^{(0)} = \frac{1}{e^{\beta(\varepsilon_{\mathbf{k}\sigma} - \mu)} + 1} - n_{\mathbf{k}\sigma}^{(0)}. \quad (7.188)$$

Eq. (7.188) indicates the probability that the quasiparticle states are occupied is given by an implicit expression for the Fermi function with the value of energy given in Eq. (7.185).

The effective mass of the quasiparticles can be obtained from the relation

$$v_F \equiv \left| \frac{1}{\hbar} \frac{\partial \varepsilon_{\mathbf{k}}}{\partial \mathbf{k}} \right|_{k_F} \equiv \frac{\hbar k_F}{m^*}, \quad (7.189)$$

where  $\varepsilon_{\mathbf{k}}$  was defined in Eq. (7.185), from which it becomes obvious that the effective mass  $m^*$  is different from the free electron mass.

The effective mass can be computed by calculating the particle current of quasiparticles in two different ways and then by equating them.

Because the quasiparticle states are eigenfunctions of the momentum, the total flow of particles  $\mathbf{J}_N$  is given by

$$\mathbf{J}_N = \sum_{\mathbf{k}\sigma} \frac{\hbar \mathbf{k}_\sigma}{m} n_{\mathbf{k}\sigma}, \quad (7.190)$$

which can be rewritten in the alternate form

$$\mathbf{J}_N = \sum_{\mathbf{k}\sigma} \frac{\hbar \mathbf{k}_\sigma}{m} \delta n_{\mathbf{k}\sigma} \quad (7.191)$$

because  $n_{\mathbf{k}\sigma}^{(0)}$  is spherically symmetric. The particle current can also be calculated by calculating the change in energy when their momenta change by a small amount. It can be shown that

$$\mathbf{J}_N = \sum_{\mathbf{k}\sigma} \mathbf{v}_{\mathbf{k}\sigma} n_{\mathbf{k}\sigma}, \quad (7.192)$$

where

$$\mathbf{v}_{\mathbf{k}\sigma} = \frac{1}{\hbar} \frac{\partial \varepsilon_{\mathbf{k}\sigma}}{\partial \mathbf{k}}. \quad (7.193)$$

From Eqs. (7.185), (7.192), and (7.193), we obtain

$$\mathbf{J}_N = \frac{1}{\hbar} \sum_{\mathbf{k}\sigma} \frac{\partial \varepsilon_{\mathbf{k}\sigma}^{(0)}}{\partial \mathbf{k}} n_{\mathbf{k}\sigma} + \frac{1}{\hbar} \sum_{\mathbf{k}\mathbf{k}'\sigma\sigma'} n_{\mathbf{k}\sigma} \frac{\partial}{\partial \mathbf{k}} [f(\mathbf{k}\sigma, \mathbf{k}'\sigma') \delta n_{\mathbf{k}'\sigma'}]. \quad (7.194)$$

We can write Eq. (7.194) by using Eq. (7.188) in the alternate form

$$\mathbf{J}_N = \frac{1}{\hbar} \sum_{\mathbf{k}\sigma} \frac{\partial \varepsilon_{\mathbf{k}\sigma}^{(0)}}{\partial \mathbf{k}} \delta n_{\mathbf{k}\sigma} + \frac{1}{\hbar} \sum_{\mathbf{k}\mathbf{k}'\sigma\sigma'} [\delta n_{\mathbf{k}\sigma} + n_{\mathbf{k}\sigma}^0] \frac{\partial}{\partial \mathbf{k}} [f(\mathbf{k}\sigma, \mathbf{k}'\sigma') \delta n_{\mathbf{k}'\sigma'}]. \quad (7.195)$$

Eq. (7.195) can be rewritten with the help of Eq. (7.185),

$$\mathbf{J}_N = \sum_{\mathbf{k}\sigma} \mathbf{v}_{\mathbf{k}\sigma} \delta n_{\mathbf{k}\sigma} + \frac{1}{\hbar} \sum_{\mathbf{k}\mathbf{k}'\sigma\sigma'} n_{\mathbf{k}\sigma}^0 \frac{\partial}{\partial \mathbf{k}} [f(\mathbf{k}\sigma, \mathbf{k}'\sigma') \delta n_{\mathbf{k}'\sigma'}]. \quad (7.196)$$

Integrating the second term by parts, we obtain

$$\mathbf{J}_N = \sum_{\mathbf{k}\sigma} \mathbf{v}_{\mathbf{k}\sigma} \delta n_{\mathbf{k}\sigma} - \frac{1}{\hbar} \sum_{\mathbf{k}\mathbf{k}'\sigma\sigma'} \frac{\partial n_{\mathbf{k}\sigma}^{(0)}}{\partial \mathbf{k}} f(\mathbf{k}\sigma, \mathbf{k}'\sigma') \delta n_{\mathbf{k}'\sigma'}, \quad (7.197)$$

which can be rewritten in the alternate form by interchanging  $\mathbf{k}\sigma$  and  $\mathbf{k}'\sigma'$ ,

$$\mathbf{J}_N = \sum_{\mathbf{k}\sigma} \mathbf{v}_{\mathbf{k}\sigma} \delta n_{\mathbf{k}\sigma} + \sum_{\mathbf{k}\mathbf{k}'\sigma\sigma'} f(\mathbf{k}\sigma, \mathbf{k}'\sigma') \mathbf{v}_{\mathbf{k}'\sigma'} \delta (\varepsilon_{\mathbf{k}'\sigma'}^{(0)} - \varepsilon_F) \delta n_{\mathbf{k}\sigma}. \quad (7.198)$$

Comparing Eqs. (7.190) and (7.198) for the case when one  $\delta n_{\mathbf{k}\sigma}$  is nonzero, we obtain

$$\frac{\hbar \mathbf{k}}{m} = \mathbf{v}_{\mathbf{k}} + \sum_{\mathbf{k}'\sigma'} f(\mathbf{k}\sigma, \mathbf{k}'\sigma') \mathbf{v}_{\mathbf{k}'\sigma'} \delta(\varepsilon_{\mathbf{k}'\sigma'}^{(0)} - \varepsilon_F). \quad (7.199)$$

Using the definition of the effective mass from Eq. (7.189), we obtain

$$\frac{\hbar \mathbf{k}}{m} = \frac{\hbar \mathbf{k}}{m^*} + \sum_{\mathbf{k}'\sigma'} f(\mathbf{k}\sigma, \mathbf{k}'\sigma') \frac{\hbar \mathbf{k}'}{m^*} \delta(\varepsilon_{\mathbf{k}'\sigma'}^{(0)} - \varepsilon_F). \quad (7.200)$$

We take dot products on both sides with  $\mathbf{k}$  and assume that the Fermi surface is spherical. In addition, because the Fermi liquid theory is valid near the Fermi surface, the magnitudes of both  $\mathbf{k}$  and  $\mathbf{k}'$  are approximately  $k_F$ . Thus, we can rewrite Eq. (7.200) in the alternate form

$$\frac{m^*}{m} \approx 1 + \sum_{\mathbf{k}'\sigma'} f(\mathbf{k}\sigma, \mathbf{k}'\sigma') \frac{\mathbf{k} \cdot \mathbf{k}'}{k_F^2} \delta(\varepsilon_{\mathbf{k}'\sigma'}^{(0)} - \varepsilon_F). \quad (7.201)$$

The summation over  $\mathbf{k}'$  can be converted as an integration, and we can write

$$\frac{m}{m^*} = 1 + V \int dk' k'^2 g(\mathbf{k}') \delta(\varepsilon_{\mathbf{k}'\sigma'}^{(0)} - \varepsilon_F) \iint_{00}^{\theta 2\pi} d\theta \sin \theta d\phi f(\mathbf{k}\sigma, \mathbf{k}'\sigma') \cos \theta, \quad (7.202)$$

where  $\theta$  is the angle between  $\hat{\mathbf{k}}$  and  $\hat{\mathbf{k}}'$ . Because the density of states  $g(\varepsilon)$  normally includes the angular integral, dividing  $g(\varepsilon)$  by  $4\pi$ , we obtain

$$\int g(\mathbf{k}') k'^2 \delta(\varepsilon_{\mathbf{k}'}^{(0)} - \varepsilon_F) dk' = \frac{1}{4\pi} \int g(\varepsilon_{k'}^{(0)}) \delta(\varepsilon_{k'}^{(0)} - \varepsilon_F) d\varepsilon = \frac{g(\varepsilon_F)}{4\pi}. \quad (7.203)$$

Further, because  $f(\mathbf{k}\sigma, \mathbf{k}'\sigma')$  depends on the angle between  $\mathbf{k}$  and  $\mathbf{k}'$  near the Fermi surface, we obtain from Eqs. (7.202) and (7.203)

$$\frac{m^*}{m} = 1 + \frac{1}{2} V g(\varepsilon_F) \int_{-1}^1 d(\cos \theta) f(\mathbf{k}\sigma, \mathbf{k}'\sigma') \cos \theta. \quad (7.204)$$

We note that the effective mass depends on the weighted average of the interactions over the Fermi surface, but the latter is not known for strongly correlated systems. We will now derive an expression for the effective mass from Eq. (7.204) and the Fermi liquid parameters.

### 7.9.3 Fermi Liquid Parameters

If we assume that the particles with the same spin have the possibility of a different interaction compared to the particles with different spin, we define

$$f(\mathbf{k}\uparrow, \mathbf{k}'\uparrow) = f(\mathbf{k}\downarrow, \mathbf{k}'\downarrow) = f_{\mathbf{k}\mathbf{k}'}^s + f_{\mathbf{k}\mathbf{k}'}^a, \quad (7.205)$$

$$f(\mathbf{k}\uparrow, \mathbf{k}'\downarrow) = f(\mathbf{k}\downarrow, \mathbf{k}'\uparrow) = f_{\mathbf{k}\mathbf{k}'}^s - f_{\mathbf{k}\mathbf{k}'}^a, \quad (7.206)$$



where the symmetric and antisymmetric functions are represented by  $s$  and  $a$ . These formulae may be inverted,

$$f_{\mathbf{k}\mathbf{k}'}^s = \sum_{l=0}^{\infty} f_l^s P_l(\cos \theta) \quad (7.207)$$

and

$$f_{\mathbf{k}\mathbf{k}'}^a = \sum_{l=0}^{\infty} f_l^a P_l(\cos \theta), \quad (7.208)$$

where  $P_l(\cos \theta)$  is the Legendre polynomial. We can invert Eqs. (7.207) and (7.208) to write

$$f_l^s = \frac{2l+1}{2} \int_{-1}^1 d(\cos \theta) P_l(\cos \theta) f_{\mathbf{k}\mathbf{k}'}^s \quad (7.209)$$

and

$$f_l^a = \frac{2l+1}{2} \int_{-1}^1 d(\cos \theta) P_l(\cos \theta) f_{\mathbf{k}\mathbf{k}'}^a. \quad (7.210)$$

We define the dimensionless Fermi liquid parameters

$$F_l^s \equiv Vg(\varepsilon_F) f_l^s \quad (7.211)$$

and

$$F_l^a \equiv Vg(\varepsilon_F) f_l^a. \quad (7.212)$$

Here,  $Vg(\varepsilon_F)$  is the density of energy states at the Fermi surface.  $F_l^s$  and  $F_l^a$  are known as Fermi liquid parameters. For example, it can be shown that the effective mass defined in Eq. (7.204) and the Fermi liquid parameters defined in Eqs. (7.205) and (7.206) have the form

$$\frac{m^*}{m} = 1 + \frac{1}{2} Vg(\varepsilon_F) \int_{-1}^1 d(\cos \theta) P_1(\cos \theta) \left[ \frac{f(\mathbf{k}\uparrow, \mathbf{k}'\uparrow) + f(\mathbf{k}\uparrow, \mathbf{k}'\downarrow)}{2} \right]. \quad (7.213)$$

From Eqs. (7.209), (7.211), and (7.212), we obtain

$$\frac{m^*}{m} = 1 + \frac{1}{3} F_1^s. \quad (7.214)$$

The effective mass equation is widely used in Fermi liquid theory, especially in highly correlated systems.

## 7.10 GREEN'S FUNCTION METHOD

### 7.10.1 General Formulation

The Green's function method has been widely used in solving many-body problems that go beyond the electron–electron interactions. It starts with the idea that amplitude for finding a particle at site  $|\mathbf{R}\rangle$  at time  $t$ , when it was at site  $|0\rangle$  at time 0, is given by

$$\langle \mathbf{R} | \hat{G}(t) | 0 \rangle = \langle \mathbf{R} | e^{-i\hat{H}t/\hbar} | 0 \rangle. \quad (7.215)$$

The Fourier transformation of  $\hat{G}(t)$  is given by

$$\hat{G}(\xi) = \frac{1}{i\hbar} \int_0^\infty dt e^{i\xi t/\hbar} \hat{G}(t). \quad (7.216)$$

Eq. (7.216) converges if  $\xi$  has a positive imaginary part, and hence,  $\xi$  varies in a complex plane. In fact, the physical significance of the Green's functions depends on the complex part of the energy. From Eqs. (7.125) and (7.126), we obtain

$$\hat{G}(\xi) = (\xi - \hat{H})^{-1}. \quad (7.217)$$

If the Hamiltonian is perturbed, we can write

$$\hat{H} = \hat{H}_0 + \hat{H}_1. \quad (7.218)$$

If we define

$$\hat{G}_0 = (\xi - \hat{H}_0)^{-1}, \quad (7.219)$$

we obtain from Eqs. (7.217) and (7.219)

$$\hat{G} = (\xi - \hat{H}_0 - \hat{H}_1)^{-1} \quad (7.220)$$

$$= ((\xi - \hat{H}_0)(1 - (\xi - \hat{H}_0)^{-1} \hat{H}_1))^{-1} \quad (7.221)$$

$$= (1 - \hat{G}_0 \hat{H}_1)^{-1} \hat{G}_0 \quad (7.222)$$

$$= \hat{G}_0 + \hat{G}_0 \hat{H}_1 \hat{G}_0 + \hat{G}_0 \hat{H}_1 \hat{G}_0 \hat{H}_1 \hat{G}_0 + \cdots \quad (7.223)$$

$$= \hat{G}_0 + \hat{G}_0 \hat{H}_1 \hat{G} = \hat{G} \hat{H}_1 \hat{G}_0 \equiv \hat{G}_0 + \hat{G}_0 \hat{T} \hat{G}_0. \quad (7.224)$$

Here, the  $\hat{T}$  matrix is the operator that satisfies the equality in Eq. (7.224).

### 7.10.2 Finite-Temperature Green's Function Formalism for Interacting Bloch Electrons

In the finite-temperature Green's function formalism for an interacting system of Bloch electrons in the presence of a periodic potential  $V(\mathbf{r})$ , the one-particle propagator  $G$  satisfies the equation

$$(\xi_l - H)G(\mathbf{r}, \mathbf{r}', \xi_l) + \int d\mathbf{r}'' \Sigma(\mathbf{r}, \mathbf{r}', \xi_l) G(\mathbf{r}'', \mathbf{r}', \xi_l) = \delta(\mathbf{r} - \mathbf{r}'), \quad (7.225)$$

where  $\Sigma$  is the exact proper self-energy operator,  $\xi_l$  is the complex energy,

$$\xi_l = (2l + 1)i\pi/\beta + \mu, \quad (7.226)$$

$\mu$  is the chemical potential,  $l = 0, \pm 1, \pm 2, \dots$ , and  $\hat{H}$  is the one-particle Hamiltonian,

$$\hat{H} = \frac{p^2}{2m} + V(\mathbf{r}). \quad (7.227)$$

Both  $G$  and  $\Sigma$  have the symmetry

$$G(\mathbf{r} + \mathbf{R}, \mathbf{r}' + \mathbf{R}, \xi_l) = G(\mathbf{r}, \mathbf{r}', \xi_l) \quad (7.228)$$

and

$$\Sigma(\mathbf{r} + \mathbf{R}, \mathbf{r}' + \mathbf{R}, \xi_l) = \Sigma(\mathbf{r}, \mathbf{r}', \xi_l). \quad (7.229)$$

We can write the equation of motion in the Bloch representation, i.e., in terms of the basis functions,

$$\phi_{n\mathbf{k}\rho}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} U_{n\mathbf{k}\rho}(\mathbf{r}), \quad (7.230)$$

where  $U_{n\mathbf{k}\rho}(\mathbf{r})$  is a periodic two-component function,  $n$  is the band index,  $\mathbf{k}$  is the reduced wave vector, and  $\rho$  is the spin index. Using the Bloch representation, we can rewrite Eq. (7.225) as

$$\begin{aligned} & \sum_{n'', \rho'', \mathbf{k}', \mathbf{k}''} \int d\mathbf{r} d\mathbf{r}' d\mathbf{r}'' e^{-i\mathbf{k}\cdot\mathbf{r}} U_{n\mathbf{k}\rho}^*(\mathbf{r}) \left( \xi_l - \frac{p^2}{2m} - V(\mathbf{r}) \right) e^{i\mathbf{k}''\cdot(\mathbf{r}-\mathbf{r}'')} U_{n''\mathbf{k}''\rho''}(\mathbf{r}) U_{n''\mathbf{k}'\rho''}^*(\mathbf{r}'') \\ & \quad \times G(\mathbf{r}'', \mathbf{r}', \xi_l) U_{n'\mathbf{k}'\rho'}(\mathbf{r}') e^{i\mathbf{k}'\cdot\mathbf{r}'} \\ & + \sum_{n'', \rho'', \mathbf{k}', \mathbf{k}''} \int d\mathbf{r} d\mathbf{r}' d\mathbf{r}'' e^{-i\mathbf{k}\cdot\mathbf{r}} U_{n\mathbf{k}\rho}^*(\mathbf{r}) \Sigma(\mathbf{r}, \mathbf{r}'', \xi_l) e^{i\mathbf{k}''\cdot(\mathbf{r}''-\mathbf{r}')} U_{n''\mathbf{k}''\rho''}(\mathbf{r}'') U_{n''\mathbf{k}'\rho''}^*(\mathbf{r}') \\ & \quad \times G(\mathbf{r}', \mathbf{r}', \xi_l) U_{n'\mathbf{k}'\rho'}(\mathbf{r}') e^{i\mathbf{k}'\cdot\mathbf{r}'} = \delta_{nn'} \delta_{\rho\rho'}. \end{aligned} \quad (7.231)$$

Eq. (7.231) can be rewritten in the alternate form (Problem 7.11)

$$\sum_{n'', \rho''} [\xi_l - H(\mathbf{k}', \xi_l)]_{n\mathbf{k}\rho, n''\mathbf{k}\rho''} G_{n''\mathbf{k}\rho'', n'\mathbf{k}\rho'}(\mathbf{k}', \xi_l) |_{\mathbf{k}'=\mathbf{k}} = \delta_{nn'} \delta_{\rho\rho'}, \quad (7.232)$$

where

$$H(\mathbf{k}', \xi_l) = \frac{1}{2m} (\mathbf{p} + \hbar \mathbf{k}')^2 + V(\mathbf{r}) + \Sigma(\mathbf{k}', \xi_l), \quad (7.233)$$

$$\Sigma_{n\mathbf{k}\rho, n'\mathbf{k}\rho'}(\mathbf{k}', \xi_l) = \int d\mathbf{r} d\mathbf{r}' U_{n\mathbf{k}\rho}^*(\mathbf{r}) e^{-i\mathbf{k}' \cdot (\mathbf{r} - \mathbf{r}')} \Sigma(\mathbf{r}, \mathbf{r}', \xi_l) U_{n'\mathbf{k}\rho'}(\mathbf{r}'), \quad (7.234)$$

and

$$G_{n'\mathbf{k}\rho', n\mathbf{k}\rho}(\mathbf{k}', \xi_l) = \int d\mathbf{r} d\mathbf{r}' U_{n'\mathbf{k}\rho'}^*(\mathbf{r}) G(\mathbf{r}, \mathbf{r}', \xi_l) e^{-i\mathbf{k}' \cdot (\mathbf{r} - \mathbf{r}')} U_{n\mathbf{k}\rho}(\mathbf{r}'). \quad (7.235)$$

Because the  $U_{n\mathbf{k}\rho}$ 's form a complete set of periodic functions, Eq. (7.232) can be rewritten in the alternate form

$$[\xi_l - H(\mathbf{k}, \xi_l)] G(\mathbf{k}, \xi_l) = I. \quad (7.236)$$

Eq. (2.236) can also be rewritten as

$$G(\mathbf{k}, \xi_l) = \frac{1}{\xi_l - H(\mathbf{k}, \xi_l)}. \quad (7.237)$$

### 7.10.3 Exchange Self-Energy in the Band Model

The exchange contribution to the self-energy is nonlocal in  $\mathbf{r}$  space,

$$\Sigma(\mathbf{r}, \mathbf{r}', \xi_l) = -\frac{1}{\beta} \sum_{\xi_l} v_{eff}(\mathbf{r}, \mathbf{r}') G(\mathbf{r}, \mathbf{r}', \xi_l - \xi_l'), \quad (7.238)$$

where a simple static screening approximation is made in obtaining  $v_{eff}(\mathbf{r}, \mathbf{r}')$  from  $v(\mathbf{r}, \mathbf{r}')$ . In this approximation, the self-energy is independent of  $\xi_l$ , and one can write

$$\Sigma(\mathbf{r}, \mathbf{r}') = -\frac{1}{\beta} \sum_{\xi_l} v_{eff}(\mathbf{r}, \mathbf{r}') G(\mathbf{r}, \mathbf{r}', \xi_l). \quad (7.239)$$

$\Sigma$  and  $G$  can be expanded in terms of Bloch states as follows:

$$\Sigma(\mathbf{r}, \mathbf{r}') = \sum_{n,m,\mathbf{k},\rho,\rho'} \Sigma_{n\rho,m\rho'}(\mathbf{k}) \psi_{n\mathbf{k}\rho}(\mathbf{r}) \psi_{m\mathbf{k}\rho'}^*(\mathbf{r}') \quad (7.240)$$

and

$$G(\mathbf{r}, \mathbf{r}') = \sum_{n,m,\mathbf{k},\rho,\rho'} G_{n\rho,m\rho'}(\mathbf{k}) \psi_{n\mathbf{k}\rho}(\mathbf{r}) \psi_{m\mathbf{k}\rho'}^*(\mathbf{r}'). \quad (7.241)$$

Substituting Eqs. (7.240) and (7.241) in Eq. (7.239), we obtain

$$\begin{aligned} \sum_{n,m,\rho,\rho'} \Sigma_{n\rho,m\rho'}(\mathbf{k}) \psi_{n\mathbf{k}\rho}(\mathbf{r}) \psi_{m\mathbf{k}\rho'}^*(\mathbf{r}') \\ = -\frac{1}{\beta} \sum_{\xi_i} \sum_{p,q,\mathbf{k}',\bar{\rho},\bar{\rho}'} v_{eff}(\mathbf{r}, \mathbf{r}') G_{p\bar{\rho},q\bar{\rho}'}(\mathbf{k}') \psi_{p\mathbf{k}'\bar{\rho}}(\mathbf{r}) \psi_{q\mathbf{k}'\bar{\rho}'}(\mathbf{r}'). \end{aligned} \quad (7.242)$$

If the effective electron–electron interaction is spin independent, then  $\rho = \bar{\rho}$ ,  $\rho' = \bar{\rho}'$ , and we have

$$\Sigma_{n\rho,m\rho'}(\mathbf{k}) = -\frac{1}{\beta} \sum_{\mathbf{k}', \xi_i, p, q} \langle nm | v_{eff}(\mathbf{k}, \mathbf{k}') | pq \rangle_{\rho\rho'} G_{p\rho,q\rho'}(\mathbf{k}, \xi_i), \quad (7.243)$$

where

$$\langle nm | v_{eff}(\mathbf{k}, \mathbf{k}') | pq \rangle_{\rho\rho'} = \int \psi_{n\mathbf{k}\rho}^*(\mathbf{r}) \psi_{m\mathbf{k}\rho'}(\mathbf{r}') v_{eff}(\mathbf{r}, \mathbf{r}') \psi_{p\mathbf{k}'\rho}(\mathbf{r}) \psi_{q\mathbf{k}'\rho'}^*(\mathbf{r}') d\mathbf{r} d\mathbf{r}'. \quad (7.244)$$

Equation (7.243) is the expression for exchange self-energy in the band model. The problem of exchange self-energy in the band model, which includes the effect of a magnetic field where the self-energy has been expanded in different orders in the magnetic field, is discussed in more detail in Chapter 12 (Section 12.4.5).

## PROBLEMS

7.1. In Eq. (7.1), we obtained

$$H\Psi = \sum_{i=1}^N \left( -\frac{\hbar^2}{2m_e} \nabla_i^2 \Psi - ze^2 \sum_l \frac{1}{|\mathbf{r}_i - \mathbf{R}_l|} \Psi \right) + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} \Psi. \quad (1)$$

The Hamiltonian can be written as

$$H = \sum_i H_i + \frac{1}{2} \sum_{i \neq j} V_{ij}, \quad (2)$$

where  $H_i$  operates on the coordinate of the  $i$ th electron, and  $V_{ij}$  operates on the two-body coordinates of both  $i$  and  $j$ .

In Eq. (7.19), we showed that

$$\Psi(\mathbf{r}_1 s_1 \dots \mathbf{r}_N) = \frac{1}{\sqrt{N!}} \sum_n (-1)^n \prod_k \psi_{n_k}(\mathbf{r}_k s_k). \quad (3)$$

Show that the expectation value of the one-electron terms in the Hamiltonian  $\langle H_i \rangle$  is

$$\sum_{s_1 \dots s_N} \int d^N \mathbf{r} \frac{1}{N!} \sum_{n n'} (-1)^{n+n'} \left[ \prod_k \psi_{n_k}^*(\mathbf{r}_k s_k) \right] \sum_i \left( -\frac{\hbar^2 \nabla_i^2}{2m} - \sum_l \frac{ze^2}{|\mathbf{r}_i - \mathbf{R}_l|} \right) \left[ \prod_{k'} \psi_{n_{k'}}(\mathbf{r}_{k'} s_{k'}) \right]. \quad (4)$$

Because the  $\psi$ 's are orthonormal, only  $n = n'$  terms survive the summation and

integration  $\sum_{s_1 \dots s_N} \int d^N \mathbf{r}$ . The sum over  $n$  results in a factor  $(N-1)!$  for all indices other than  $i$ .

Hence, show that Eq. (4) can be rewritten as

$$\sum_i \sum_{s_i} \int d\mathbf{r}_i \frac{1}{N!} \sum_n \psi_{n_i}^*(\mathbf{r}_i s_i) \left( \frac{-\hbar^2 \nabla_i^2}{2m} - \sum_l \frac{ze^2}{|\mathbf{r}_i - \mathbf{R}_l|} \right) \psi_{n_i}(\mathbf{r}_i s_i). \quad (5)$$

The sum over  $n$  results in a factor  $(N-1)!$  for all indices other than  $i$ . However,  $s_i$  ranges over all values that can be written as a sum over  $i'$ , and one can drop the dummy index  $i$  when integrating over  $\mathbf{r}_i s_i$ . Show that Eq. (5) can be rewritten as

$$\sum_i \sum_s \int d\mathbf{r} \frac{1}{N} \sum_{i'} \psi_{i'}^*(\mathbf{r} s) \left( \frac{-\hbar^2 \nabla^2}{2m} - \sum_l \frac{ze^2}{|\mathbf{r} - \mathbf{R}_l|} \right) \psi_{i'}(\mathbf{r} s). \quad (6)$$

Because  $\psi_i(\mathbf{r}_i s_i) = \phi_i(\mathbf{r}_i) \chi_i(s_i)$ , the sum over the spin index can be eliminated. The sum over  $i$  yields a factor of  $N$ , and the sum over  $i'$  can be rewritten as a sum over  $i$ . Show that Eq. (6) can be expressed as

$$\sum_{i=1}^N \int d\mathbf{r} \phi_i^*(\mathbf{r}) \left( \frac{-\hbar^2 \nabla^2}{2m} - \sum_l \frac{-ze^2}{|\mathbf{r} - \mathbf{R}_l|} \right) \phi_i(\mathbf{r}). \quad (7)$$

The expectation value of the Coulomb interaction term in the Hamiltonian is obtained from Eqs. (2) and (3) as

$$\sum_{s_1 \dots s_N} \int d^N \mathbf{r} \sum_{n, n'} \frac{1}{N!} \frac{1}{2} \sum_{i \neq j} \frac{e^2 (-1)^{n+n'}}{|\mathbf{r}_i - \mathbf{r}_j|} \prod_{k, k'} \psi_{n_k}^*(\mathbf{r}_k s_k) \psi_{n'_k}(\mathbf{r}_k s'_k). \quad (8)$$

Show that Eq. (8) can be rewritten in the alternate form

$$\sum_{s_1 \dots s_N} \int d^N \mathbf{r} \sum_{n, n'} \frac{1}{N!} \frac{1}{2} \sum_{i \neq j} \frac{e^2 (-1)^{n+n'}}{|\mathbf{r}_i - \mathbf{r}_j|} \left[ \psi_{n_i}^*(\mathbf{r}_i) \psi_{n_j}^*(\mathbf{r}_j) \psi_{n'_i}(\mathbf{r}_i) \psi_{n'_j}(\mathbf{r}_j) \prod_{k, k' \neq i, j} \psi_{n_k}^*(\mathbf{r}_k) \psi_{n'_k}(\mathbf{r}_k) \right], \quad (9)$$

where  $\psi_{n_i}(\mathbf{r}_i) \equiv \psi_{n_i}(\mathbf{r}_i, s_i)$  etc. for brevity. Integrating over all the terms except  $\mathbf{r}_i$  and  $\mathbf{r}_j$  (which leaves two permutations  $n'$  for given  $n$ ), show that Eq. (9) can be rewritten as

$$\frac{1}{2} \sum_{i \neq j} \sum_{s_i s_j} \int d\mathbf{r}_i d\mathbf{r}_j \sum_n \frac{1}{N!} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} \left[ |\psi_{n_i}(\mathbf{r}_i)|^2 |\psi_{n_j}(\mathbf{r}_j)|^2 - \psi_{n_i}^*(\mathbf{r}_i) \psi_{n_j}^*(\mathbf{r}_j) \psi_{n_i}(\mathbf{r}_j) \psi_{n_j}(\mathbf{r}_i) \right]. \quad (10)$$

Show that because the integrations can be performed over the dummy variables 1 and 2, the sum over  $i \neq j$  yields a factor of  $N(N-1)$ . Hence, show that Eq. (10) can be rewritten as

$$\sum_{s_1 s_2} \int \frac{d\mathbf{r}_1 d\mathbf{r}_2}{2(N-2)!} \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} \sum_n \left[ |\psi_{n_1}(\mathbf{r}_1)|^2 |\psi_{n_2}(\mathbf{r}_2)|^2 - \psi_{n_1}^*(\mathbf{r}_1) \psi_{n_2}^*(\mathbf{r}_2) \psi_{n_1}(\mathbf{r}_2) \psi_{n_2}(\mathbf{r}_1) \right]. \quad (11)$$

Summing over the permutations over  $n$ , show that Eq. (11) can be rewritten as

$$\sum_{s_1 s_2} \frac{1}{2} \int \frac{e^2 d\mathbf{r}_1 d\mathbf{r}_2}{|\mathbf{r}_1 - \mathbf{r}_2|} \sum_{i \neq j} \left[ |\psi_i(\mathbf{r}_1)|^2 |\psi_j(\mathbf{r}_2)|^2 - \psi_i^*(\mathbf{r}_1) \psi_j^*(\mathbf{r}_2) \psi_i(\mathbf{r}_2) \psi_j(\mathbf{r}_1) \right]. \quad (12)$$

Using Eq. (7.20), show that Eq. (12) can be rewritten as

$$\frac{1}{2} \int \frac{e^2 d\mathbf{r}_1 d\mathbf{r}_2}{|\mathbf{r}_1 - \mathbf{r}_2|} \sum_{i \neq j} \left[ |\phi_i(\mathbf{r}_1)|^2 |\phi_j(\mathbf{r}_2)|^2 - \phi_i^*(\mathbf{r}_1) \phi_j^*(\mathbf{r}_2) \phi_i(\mathbf{r}_2) \phi_j(\mathbf{r}_1) \delta_{\chi_i, \chi_j} \right]. \quad (13)$$

From Eqs. (7) and (13), we obtain

$$\begin{aligned} \langle H \rangle &= \sum_{i=1}^N \int d\mathbf{r} \phi_i^*(\mathbf{r}) \left( \frac{-\hbar^2 \nabla^2}{2m} - \sum_l \frac{ze^2}{|\mathbf{r} - \mathbf{R}_l|} \right) \phi_i(\mathbf{r}) \\ &\quad + \frac{1}{2} \iint \frac{e^2 d\mathbf{r}_1 d\mathbf{r}_2}{|\mathbf{r}_1 - \mathbf{r}_2|} \sum_{i \neq j} \left[ |\phi_i(\mathbf{r}_1)|^2 |\phi_j(\mathbf{r}_2)|^2 - \phi_i^*(\mathbf{r}_1) \phi_j^*(\mathbf{r}_2) \phi_i(\mathbf{r}_2) \phi_j(\mathbf{r}_1) \delta_{\chi_i, \chi_j} \right] \\ &= \sum_i \int \phi_i^* H_1 \phi_i d\mathbf{r} + \frac{1}{2} \sum_{i \neq j} \iint d\mathbf{r}_1 d\mathbf{r}_2 \phi_i^*(\mathbf{r}_1) \phi_j^*(\mathbf{r}_2) H_{12} \phi_i(\mathbf{r}_2) \phi_j(\mathbf{r}_1) \\ &\quad - \frac{1}{2} \sum_{i \neq j} \iint d\mathbf{r}_1 d\mathbf{r}_2 \phi_i^*(\mathbf{r}_1) \phi_j^*(\mathbf{r}_2) H_{12} \phi_i(\mathbf{r}_2) \phi_j(\mathbf{r}_1) \delta_{\chi_i, \chi_j}, \end{aligned}$$

where

$$H_1 \equiv \left( \frac{-\hbar^2 \nabla^2}{2m} - \sum_l \frac{ze^2}{|\mathbf{r} - \mathbf{R}_l|} \right)$$

and

$$H_{12} \equiv \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|}.$$

Following a variational technique similar to that adopted in Eqs. (7.11) through (7.15), derive the Hartree-Fock equation in Eq. (7.21).

**7.2.** We derived

$$\begin{aligned} U^{ex} \phi_i(\mathbf{r}) &= -e^2 \phi_i(\mathbf{r}) \int_{k_F} \frac{d\mathbf{k}}{8\pi^3} \frac{4\pi}{(k^2 + k_i^2 - 2kk_i \cos \theta)} \\ &= -e^2 \phi_i(\mathbf{r}) \int_0^{k_F} \int_0^\pi \frac{k^2 dk \sin \theta d\theta}{\pi(k_i^2 + k^2 - 2kk_i \cos \theta)}. \end{aligned} \quad (1)$$

First, integrate over  $d\theta$  and then integrate over  $dk$  to obtain

$$U^{ex} \phi_i(\mathbf{r}) = -e^2 \phi_i(\mathbf{r}) \frac{1}{2\pi k_i} \left[ (k_F^2 - k_i^2) \ln \left( \frac{k_F + k_i}{k_F - k_i} \right) + 2k_i k_F \right]. \quad (2)$$

7.3. Show, by integration, that the total energy of  $N$  electrons

$$E = 2 \sum_{k \leq k_F} \frac{\hbar^2 k^2}{2m} - \frac{e^2 k_F}{\pi} \sum_{k \leq k_F} \left[ 1 + \frac{k_F^2 - k^2}{2kk_F} \ln \left| \frac{k_F + k}{k_F - k} \right| \right] \quad (1)$$

$$= N \left[ \frac{3}{5} \varepsilon_F - \frac{3}{4} \frac{e^2 k_F}{\pi} \right]. \quad (2)$$

The first term was evaluated in Chapter 1.

7.4. We derived in Eq. (7.43),

$$E = N \left[ \frac{3}{5} \varepsilon_F - \frac{3}{4} \frac{e^2 k_F}{\pi} \right]. \quad (1)$$

Show that Eq. (1) can also be rewritten as

$$\begin{aligned} \frac{E}{N} &= \frac{e^2}{2a_0} \left[ \frac{3}{5} (k_F a_0)^2 - \frac{3}{2\pi} (k_F a_0) \right] \\ &= \left[ \frac{2.21}{(r_s/a_0)^2} - \frac{0.916}{(r_s/a_0)} \right] \text{Ry}. \end{aligned} \quad (2)$$

$$(1 \text{ Ry} = e^2/2a_0 = 13.6 \text{ eV}).$$

7.5. Assume that a positively charged particle is placed at position  $\mathbf{r}$  (an example is the substitution of a Zn ion for a copper ion in a metal lattice), which creates a surplus of negative charge, thereby screening its field. The electrostatic potential can be written as

$$\phi(\mathbf{r}) = \phi^e(\mathbf{r}) + \phi^i(\mathbf{r}). \quad (1)$$

Here,  $\phi^e(\mathbf{r})$  is potential due to the positively charged particle, and  $\phi^i(\mathbf{r})$  arises due to the induced charge density because of the presence of the positively charged particle. The Poisson's equation can be written as

$$-\nabla^2 \phi(\mathbf{r}) = 4\pi \rho(\mathbf{r}), \quad (2)$$

where the total charge density  $\rho(\mathbf{r})$  can be expressed as

$$\rho(\mathbf{r}) = \rho^e(\mathbf{r}) + \rho^i(\mathbf{r}). \quad (3)$$

Here,  $\rho^e(\mathbf{r})$  and  $\rho^i(\mathbf{r})$  are the external and induced charge densities, respectively.

Show that in a spatially uniform electron gas,  $\phi^e(\mathbf{r})$  and  $\phi(\mathbf{r})$  are linearly related through the difference between their position, in an equation of the form

$$\phi^e(\mathbf{r}) = \int d\mathbf{r}' \epsilon(\mathbf{r} - \mathbf{r}') \phi(\mathbf{r}'). \quad (4)$$



By making appropriate Fourier transformations,

$$\epsilon(\mathbf{q}) = \int d\mathbf{r} e^{-i\mathbf{q}\cdot\mathbf{r}} \epsilon(\mathbf{r}), \quad (5)$$

$$\phi^e(\mathbf{q}) = \int d\mathbf{r} e^{-i\mathbf{q}\cdot\mathbf{r}} \phi^e(\mathbf{r}), \quad (6)$$

and

$$\phi(\mathbf{r}') = \int \frac{d\mathbf{q}}{(2\pi)^3} e^{i\mathbf{q}\cdot\mathbf{r}'} \phi(\mathbf{q}), \quad (7)$$

show that

$$\phi^e(\mathbf{q}) = \phi(\mathbf{q})\epsilon(\mathbf{q}). \quad (8)$$

Eq. (8) can be rewritten in the alternate form

$$\phi(\mathbf{q}) = \frac{\phi^e(\mathbf{q})}{\epsilon(\mathbf{q})}, \quad (9)$$

where  $\epsilon(\mathbf{q})$  is the dielectric constant of the metal.

**7.6.** If the external potential in a metal (in the jellium model) is due to a positive point charge  $Q$  located at  $\mathbf{r}$ , show that

$$\phi^e(\mathbf{q}) = \frac{4\pi Q}{q^2} \quad (1)$$

Hence, show from Eq. (7.61) that

$$\phi(\mathbf{q}) = \frac{\phi^e(\mathbf{q})}{\epsilon(\mathbf{q})} = \frac{4\pi Q}{q^2 + \lambda^2}. \quad (2)$$

Using Fourier transformation, show that

$$\phi(\mathbf{r}) = \int \frac{d\mathbf{q}}{(2\pi)^3} \phi(\mathbf{q}) e^{i\mathbf{q}\cdot\mathbf{r}} = \frac{Q}{r} e^{-\lambda r}. \quad (3)$$

**7.7.** Show that at  $T=0$ , the integral

$$\chi(\mathbf{q}) = -e^2 \int \frac{d\mathbf{k}}{4\pi^3} \frac{f_0(\mathbf{k}) - f_0(\mathbf{k} + \mathbf{q})}{\hbar^2(\mathbf{k} \cdot \mathbf{q})/m} \quad (1)$$

can be performed explicitly to give

$$\chi(\mathbf{q}) = -e^2 \left( \frac{mk_F}{\hbar^2 \pi^2} \right) \left[ \frac{1}{2} + \frac{1-x^2}{4x} \ln \left| \frac{1+x}{1-x} \right| \right], \quad (2)$$

where

$$x = \frac{q}{2k_F}.$$

**7.8.** The expression for the dielectric constant for static screening in the Lindhard theory, derived in Eq. (7.76), is given by

$$\epsilon_L(\mathbf{q}) = 1 - \frac{4\pi e^2}{q^2} \sum_{\mathbf{k}} \frac{f^0(\mathbf{k}) - f^0(\mathbf{k} + \mathbf{q})}{\epsilon(\mathbf{k}) - \epsilon(\mathbf{k} + \mathbf{q})}. \quad (1)$$

By adjusting the summation over  $f^0(\mathbf{k} + \mathbf{q})$  to  $f^0(\mathbf{k})$  and converting the summation over  $\mathbf{k}$  to an integration by using polar coordinates, show that (Eq. 7.93)

$$\epsilon_L(\mathbf{q}) = 1 + \frac{4\pi e^2}{q^2} \frac{mk_F}{\hbar^2 \pi^2} \left[ \frac{1}{2} + \frac{4k_F^2 - q^2}{8k_F q} \ln \left| \frac{2k_F + q}{2k_F - q} \right| \right]. \quad (2)$$

**7.9.** If we define

$$f_{\mathbf{k}\mathbf{k}'}^s = \sum_{l=0}^{\infty} f_l^s P_l(\cos \theta) \quad (1)$$

and

$$f_{\mathbf{k}\mathbf{k}'}^a = \sum_{l=0}^{\infty} f_l^a P_l(\cos \theta), \quad (2)$$

by using the properties of the Legendre polynomial, show that

$$f_l^s = \frac{2l+1}{2} \int_{-1}^1 d(\cos \theta) P_l(\cos \theta) f_{\mathbf{k}\mathbf{k}'}^s \quad (3)$$

and

$$f_l^a = \frac{2l+1}{2} \int_{-1}^1 d(\cos \theta) P_l(\cos \theta) f_{\mathbf{k}\mathbf{k}'}^a. \quad (4)$$

**7.10.** Derive from Eq. (7.127)

$$i\hbar \langle \mathbf{k}' | \delta \dot{\rho} | \mathbf{k} \rangle = [\epsilon(\mathbf{k}') - \epsilon(\mathbf{k})] \langle \mathbf{k}' | \delta \rho | \mathbf{k} \rangle - [f_0(\mathbf{k}') - f_0(\mathbf{k})] \langle \mathbf{k}' | \phi | \mathbf{k} \rangle, \quad (1)$$

and the fact that  $\delta \rho$  has the same time dependence as  $\phi(\mathbf{r}, t)$  in Eq. (7.130), show that

$$[\epsilon(\mathbf{k} + \mathbf{q}) - \epsilon(\mathbf{k}) - i\hbar(i\omega + \alpha)] \langle \mathbf{k} + \mathbf{q} | \delta \rho | \mathbf{k} \rangle = [f_0(\mathbf{k} + \mathbf{q}) - f_0(\mathbf{k})] \phi_{\mathbf{q}}(t), \quad (2)$$

where

$$\phi_{\mathbf{q}}(t) = \phi_{e\mathbf{q}}(t) + \phi_{i\mathbf{q}}(t) = [\phi_e(\mathbf{q}, \omega) + \phi_i(\mathbf{q}, \omega)]e^{(i\omega t + at)}. \quad (3)$$

7.11. We derived in Eq. (7.231)

$$\begin{aligned} & \sum_{n'', \rho'', \mathbf{k}', \mathbf{k}''} \int d\mathbf{r} d\mathbf{r}' d\mathbf{r}'' e^{-i\mathbf{k} \cdot \mathbf{r}} U_{n\mathbf{k}\rho}^*(\mathbf{r}) \left( \xi_l - \frac{p^2}{2m} - V(\mathbf{r}) \right) e^{i\mathbf{k}'' \cdot (\mathbf{r} - \mathbf{r}'')} U_{n''\mathbf{k}''\rho''}(\mathbf{r}) U_{n''\mathbf{k}''\rho''}^*(\mathbf{r}'') \\ & \quad \times G(\mathbf{r}'', \mathbf{r}', \xi_l) U_{n'\mathbf{k}'\rho'}(\mathbf{r}') e^{i\mathbf{k}' \cdot \mathbf{r}'} \\ & + \sum_{n'', \rho'', \mathbf{k}', \mathbf{k}''} \int d\mathbf{r} d\mathbf{r}' d\mathbf{r}'' d\mathbf{r}''' e^{-i\mathbf{k} \cdot \mathbf{r}} U_{n\mathbf{k}\rho}^*(\mathbf{r}) \Sigma(\mathbf{r}, \mathbf{r}'', \xi_l) e^{i\mathbf{k}'' \cdot (\mathbf{r}'' - \mathbf{r}''')} U_{n''\mathbf{k}''\rho''}(\mathbf{r}'') U_{n''\mathbf{k}''\rho''}^*(\mathbf{r}''') \\ & \quad \times G(\mathbf{r}''', \mathbf{r}', \xi_l) U_{n'\mathbf{k}'\rho'}(\mathbf{r}') e^{i\mathbf{k}' \cdot \mathbf{r}'} = \delta_{nn'} \delta_{\rho\rho'}. \end{aligned} \quad (1)$$

Show that Eq. (1) can be rewritten in the alternate form

$$\sum_{n'', \rho''} [\xi_l - H(\mathbf{k}', \xi_l)]_{n\mathbf{k}\rho, n''\mathbf{k}\rho''} G_{n''\mathbf{k}\rho'', n'\mathbf{k}\rho'}(\mathbf{k}', \xi_l) \big|_{\mathbf{k}'=\mathbf{k}} = \delta_{nn'} \delta_{\rho\rho'}, \quad (2)$$

where

$$H(\mathbf{k}', \xi_l) = \frac{1}{2m} (\mathbf{p} + \hbar \mathbf{k}')^2 + V(\mathbf{r}) + \Sigma(\mathbf{k}', \xi_l), \quad (3)$$

$$\Sigma_{n\mathbf{k}\rho, n''\mathbf{k}\rho''}(\mathbf{k}', \xi_l) = \int d\mathbf{r} d\mathbf{r}' U_{n\mathbf{k}\rho}^*(\mathbf{r}) e^{-i\mathbf{k}' \cdot (\mathbf{r} - \mathbf{r}')} \Sigma(\mathbf{r}, \mathbf{r}', \xi_l) U_{n''\mathbf{k}\rho''}(\mathbf{r}'), \quad (4)$$

and

$$G_{n''\mathbf{k}\rho'', n'\mathbf{k}\rho'}(\mathbf{k}', \xi_l) = \int d\mathbf{r} d\mathbf{r}' U_{n''\mathbf{k}\rho''}^*(\mathbf{r}) G(\mathbf{r}, \mathbf{r}', \xi_l) e^{-i\mathbf{k}' \cdot (\mathbf{r} - \mathbf{r}')} U_{n'\mathbf{k}\rho'}(\mathbf{r}'). \quad (5)$$

Because the  $U_{n\mathbf{k}\rho}$ 's form a complete set of periodic functions, show that Eq. (5) can be rewritten in the alternate form

$$[\xi_l - H(\mathbf{k}, \xi_l)] G(\mathbf{k}, \xi_l) = I. \quad (6)$$

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