Computational Methods in Solid State Physics

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Preface

The physics of metals is based on the fundamental laws of quantum mechanics. However, electrical conductivity, an important property of metals, came under study within the free-electron model before quantum mechanics was developed. In 1928 Sommerfeld [1] formulated a quantum-mechanical free-electron model and showed that electrical conductivity was a natural property of a quantum system obeying the Fermi statistics. The same year Bloch [2] proved the theorem on electrons moving in a periodic potential. The theorem allowed the classification of electron states by the wave vector $\mathbf{k}$ in the first Brillouin zone.

In 1931 Wilson [3] showed that the physical content of the Bloch theorem made it possible to divide crystals into metals, semiconductors, and insulators. Owing to this, the concept of band structure has gained recognition in solid state physics.

The first quantitative results on the ground state of metal were obtained by Wigner and Seitz [4] (1934) for sodium. Using the cellular method, they calculated the energy location of the bottom of the conduction band on the basis of experimental data on atomic potential.

In calculating the band structure, the crucial problem lies in choosing the crystal potential. Within the one-particle Hartree–Fock approximation the potential must be determined self-consistently. However, the exchange interaction leads to a non-local potential, which makes the calculations difficult. To avoid this difficulty Slater [5] (1934) proposed to use a simple expression, which is valid in the case of free-electron gas when the electron density ρ is constant. Slater suggested that the same expression for the local potential can also be used in the case of non-uniform density $\rho(\mathbf{r})$. Subsequently (1965), Slater [5] introduced a dimensionless parameter α, which may be determined by comparing the total energy of an atom, calculated with the local potential, to that obtained within the Hartree–Fock approximation. This method is known as the X_α-method, and has been widely used for several decades. A proper account of the electronic correlation became possible within the framework of the density functional theory (DFT). It has been proved by Hohenberg and Kohn [6] (1964) that all ground state properties of a many-electron system are described by a functional depending only on the density distribution. Kohn and Sham [7,8] (1965, 1966)

showed that the one-particle wave functions that determine the density $\rho(\mathbf{r})$ are solutions of a Schrödinger-like equation, the potential being the sum of the external potential and an effective local exchange–correlation potential V_{xc}.

It has turned out that in many cases of practical importance the exchange–correlation potential can be approximately derived from the energy of the electron–electron interaction in the homogenous electron gas ε_{xc} (the local density approximation, LDA). If ε_{xc} is taken to be the Hartree–Fock exchange energy, ε_x, the resulting potential is simply the X_α-potential with $\alpha = 2/3$. Thus, the DFT provides the necessary theoretical background to the self-consistent-field techniques developed by Hartree, Fock and Slater.

The density functional theory is only justified for ground state. In the case when the excited state is to be considered, an electron–hole pair is created, and the problem of taking into account two-particle correlations arises. Landau [9] has found that a common feature of the excitation spectrum of a macroscopic, many-fermion system is that the elementary excitations of the system show a quasiparticle behaviour.

In the Landau theory the fermi-liquid is characterized by the dispersion law of the quasi-particles, which is defined as a variational derivative of the total energy with respect to the distribution function, and the correlation function, which takes into account interaction between the quasiparticles. A one-particle approach proves to be valid if the inter-action is insignificant. Generally, to obtain the spectrum of elementary excitations of a many-fermion system one must determine the poles of Green's function. Green's function satisfies Dyson's equation, which involves a non-local self-energy operator describing the exchange–correlation effects. Hedin and Lundqvist [10] (1971) numerically showed that energy dependence of the self-energy operator in the valence band region can be ignored.

In this case Dyson's equation is reduced to an equation which can be obtained within the DFT, and which involves the same exchange–correlation potential V_{xc}. In other words, in many cases the Landau correlation function can be taken to be zero, i.e., the interaction between quasiparticles can be ignored. The one-particle approach is applicable if the energy bands are broad and interaction between the electrons at the same site is not too strong.

One can recognize three stages of evolution of theoretical methods of the band theory. In the first stage, from the mid-1930s to the mid-1950s, the basic methods of band theory were developed: the cellular method (Wigner and Seitz, [4] 1934), the APW method (augmented plane waves; Slater, [11] 1937), the OPW method (orthogonalized plane waves; Herring, [12] 1940), which played a crucial role in creating the concept of pseudopotential, and the KKR method (or the Green's function method; Korringa, [13] 1947; Kohn and Rostocker, [14] 1954). During this period there were no numerical calculations of the band structures of realistic crystals. During the second stage, which lasted up to the mid-1970s, elaborate computer codes were developed, and a great number of band structure calculations were performed. In addition, mathematical relationships between different methods were estab-lished. The third stage is due to the emergence of the concept of linear methods (Andersen, [15] 1975). During a short period a number of linear methods were developed: LMTO (linear method of MT-orbitals; Andersen, [15] 1975), linear APW (Andersen, [15] 1975; Koelling and Arbman, [16] 1975; Takeda and Kübler, [17] 1979), ASW (augmented spher-ical waves; Williams, Kübler, Gillat, [18] 1979), linear KKR (Pettifor, [19] 1972; Wonn et al., [20] 1974), TB-LMTO (Andersen and Jepsen, [21] 1984), and LASO (linear method

of augmented Slater orbitals; Davenport, [22] 1984). These methods made it possible to speed up the calculations by a factor of 100.

To gain a deeper insight into physical properties of complex materials it is necessary to establish relationships between the electronic structure and various physical effects. A way to do this is presented by linear methods of band theory.

It should be noted that for a long time solid state physics was developing independently of the efforts to perform band structure calculations. As a rule, to describe the electronic system an effective Hamiltonian was introduced which involved a number of fitting parameters. It was implied that to describe the properties of specific substance was a matter of selecting the parameters. The Heisenberg's Hamiltonian in the theory of the ferromagnetism in ionic crystals, the Andersen's Hamiltonian in the theory of lightly doped magnetic alloys, and the BCS Hamiltonian of the theory of superconductivity are examples. In the first case the effective Hamiltonian is determined by the exchange integral, in the second case the parameters are the energy of Coulomb repulsion of two electrons with antiparallel spins occupying the same d-orbital and the matrix element between the localized d-state and the conduction band state. The BCS Hamiltonian is determined by the density of states at the Fermi level and by electron–electron interaction. In recent years the gap between the traditional (constructing the effective Hamiltonians) and the band structure approaches has been narrowing. Owing to the progress in the many-body theory one can look forward to constructing a more precise effective crystal potential. On the other hand, a number of works have appeared, in which band structure calculations of realistic crystals are used to obtain the parameters of the effective Hamiltonian. Apart from this, the band structure calculations are necessary to understand the experimental data. The calculations are indispensable in interpreting, for example, optical and photoemission properties of crystals, as well as various effects determined by the behaviour of the electron on the Fermi surface in the presence of an electromagnetic field.

Nowadays, band theory holds a firm place in the physical picture of the world. However, there are technical problems in mastering the theory. The aim of this book is to remove some of these difficulties.

More than a decade has elapsed since the Russian edition of this book was published (V.V. Nemoshkalenko and V.N. Antonov, *Methods of Computational Physics in the Theory of Solid State. Band Theory of Metals*, Kiev, Naukova Dumka, 1985). We have introduced numerous changes to include recent achievements in band theory and to omit out-of-date results.

Chapter 1 of this book is of an introductory character and presents the theoretical foundations of band theory of solids, such as the Hartree–Fock–Slater self-consistent-field method and DFT for ground state properties of solids, and Green's function approach and Landau theory for description of elementary excitations in solids.

Chapter 2 describes the traditional methods of band theory such as the APW method, the KKR method, the OPW method and the pseudopotential method. The mathematical methods of interpolation and integration of the energy eigenvalues and wave functions in the Brillouin zone are also given.

Chapter 3 describes the present-day linear methods of band theory such as LMTO, TB-LMTO, LKKR, LAPW, ASW, and LASO methods.

In this book great attention is paid to the practical aspects of these methods. The book is structured in such a way that a reader can start using any method in practice without referring to other sources.

Contents

1 Electron States in Ideal Crystals

Determination of the energy band structure of solids is a many-body problem that requires the Schrödinger equation to be solved for an enormous number of nuclei and electrons. Even if we managed to solve the above equation and to find the complete wave function of a crystal depending on the positions of all nuclei and electrons, we face the complicated problem of how this function should be applied to the calculation of physically observable values. Thus, exact solution of the many-body problem is impossible and quite unnecessary. To theoretically describe the quantities of physical interest, it is required to know only the energy spectrum and several correlation functions (electron density, pair correlation function, etc.) which depend on a few variables.

Since only lower excitation branches of the crystal energy spectrum are important for our discussion, we can introduce the concept of quasiparticles as the elementary excitations of a system. Therefore, our problem reduces to defining the dispersion curves of the quasiparticles and analyzing their interactions. Two types of quasiparticles are known to exist, i.e., fermions and bosons. In a crystal, only electrons are fermions, while phonons and magnons are bosons.

The problem thus formulated is still rather complicated and needs further simplifications. The first simplification is to assume that the masses of ions M, forming the lattice, considerably exceed that of an electron, m. This great difference in masses gives rise to a large difference in their velocities and allows the following assumption: any concentration of nuclei (even a non-equilibrium one) may reasonably be associated with a quasi-equilibrium configuration of electrons which follows practically without inertia the motion of the nuclei. Hence, we can consider the electrons to be in a field of nearly at rest nuclei, that is, the energies of electrons and phonons are well separated. This approximation is the Born–Oppenheimer adiabatic approximation.

Although experience shows that the interactions between electrons and phonons have an insignificant effect on the electron energy and the shape of the Fermi surface, there exist many other properties which require that the electron–phonon interaction be accounted

for even in the first approximation. In fact, in some cases, the property under consideration would not exist if it were not for the above interaction. These properties include, for example, all the transport properties and the phenomenon of superconductivity.

In this book, we shall use the adiabatic approximation and consider only an electron subsystem. The reader interested in electron–phonon interaction in crystals may refer to [23].

We also use the approximation of an ideal lattice, meaning that the ions making the lattice are arranged in a rigorously periodic order. Hence, the problems related to electron states in crystals with impurities, disordered crystals, and surface phenomena fall beyond the scope of the present book.

In these approximations, the non-relativistic Hamiltonian of a many-electron system in a crystal is[1]

$$H = -\sum_i \nabla_i^2 + \sum_i V(\vec{r}_i) + \sum_{i,j}' \frac{2}{|\vec{r}_i - \vec{r}_j|},$$

where the first term is the sum of the kinetic energies of the individual electrons, the second defines the interaction of each of these electrons with the potential generated by the nuclei, and the final term contains the repulsive Coulomb interaction energy between pairs of electrons.

Two important properties of our electron subsystem should be pointed out. First, the electron density of all metals is such that the mean volume for one electron in the system is proportional to $r_e = [3/4\pi\rho]^{1/3} \approx 1 - 6$. It can be shown that this value agrees, by the order of magnitude, with the ratio of the potential energy of particles to their mean kinetic energy. Thus, the conduction electrons in metals are not an electron gas but rather a quantum Fermi liquid (the degeneracy temperature for these electrons at which quantum effects are appreciable is about 10^4 to 10^5 K).

Second, the electrons in a metal are screened at a radius smaller than the lattice constant. After the papers by *Bohm* and *Pines* [24,25], *Hubbard* [26], *Gell-Mann* and *Brueckner* [27] were published, it became clear that the long-range portion of the Coulomb interaction is responsible mainly for collective motions. Such collective motions (plasma oscillations) have an excitation energy high enough to prevent excitation of the plasma oscillations near the ground state of the system. As a result, individual motions of electrons may easily be determined from the screened Coulomb interaction with quite a small radius of action (in some cases as small as 1 Å). At larger interaction distances, only a certain average interaction between the electrons is observed.

The first of these properties does not allow us to introduce small parameters. Hence, we cannot use perturbation theory in its standard form. This makes theoretical analysis of an electron subsystem in metals more difficult and renders certain approximations poorly controllable. Thus, the comparison of theoretical estimations with experimental data is of prime importance.

The second property of the subsystem permits us to introduce the concept of weakly interacting quasiparticles and, thus, to use Landau's idea [28] that weak excitations of any

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[1]Unless otherwise specified, we use atomic units in which Planck's constant $\hbar$ is assumed to be equal to unity, the Bohr radius $a_0 = 0.529177$ Å is used as the unit of length, twice the electron mass m is used as the unit of mass, and the hydrogen atom ionization energy in Rydbergs (1 Ry = 13.6049 eV) is the unit of energy.

macroscopic many-fermion system exhibit one-particle behavior. Obviously, for other systems, the energy range where long-lived weakly interacting particles exist will be different. In metals this range is rather significant, reaching ~5–10 eV close to the Fermi level. This has enabled successful application of the band theory based on the one-particle concept to an analysis of the electronic properties of metals.

Section 1.1 of this chapter describes the ground state of an electron system in crystals. The properties of the ground state of any many-electron system are discussed in terms of the density functional theory (DFT). According to this theory [6–8], all properties of the ground state of such a system are well described by a certain functional depending on the electron density. Explicit definition of this functional is a difficult, unsolved problem so far. However, there exist good approximation methods for both homogeneous and inhomogeneous systems.

Section 1.1 also describes the approach to theoretical analysis of an electron system, proposed earlier by *Hartree* and *Fock* [5]. This approach uses a set of Hamiltonians, each of them a function of the coordinates of one electron. The variables in the Schrödinger equation are separated and the electrons analyzed independently. This one-electron approach results in the disappearance of the density of electron states in a metal at the Fermi level [29] which, surely, conflicts with the experimental data on the heat capacity of metals. *Slater* [5] found a way out of this controversy in his χ_α approximation for the exchange–correlation potential, now widely used in band theory.

In Section 1.2 we discuss the methods of calculating the elementary excitations in many-electron systems. The methods of constructing crystal potentials are given in Section 1.3 where different approximations of the exchange–correlation potential in the crystal energy band structure are described.

1.1 Ground State of a Many-Electron System

The motion of electrons in condensed media is highly correlated. At first glance, this leads to the conclusion that it is impossible to describe such a system in an approximation of independent particles. However, we can use a model system of non-interacting particles, where the total energy E and the electron density $\rho(\vec{r})$ match similar functions of the real system, and all the effects of interactions between electrons are described by an external field. This is the essence of the density functional theory (DFT). Before describing the DFT let us consider briefly the self-consistent field method developed by Hartree, Fock and Slater.

1.1.1 Hartree–Fock Equations

Hartree's fundamental contribution was to propose an approximation in which every electron moves independent of other electrons in the external nuclear field and the interaction between all the other electrons and the given electron may be replaced by the action of an electrostatic field induced by the charge density averaged over the states of these electrons. Here, every electron is assigned a separate function φ_i, that is, an orbital, while the complete wave function of a system of electrons is represented as the product of all the orbitals. Then the

one-electron equation for the orbital φ_i is [5]

$$\hat{F}_i \varphi_i(\vec{r}) = \varepsilon_i \varphi_i(\vec{r}), \tag{1.1}$$

$$\hat{F}_i = -\nabla^2 + V_C(\vec{r}) + V_i(\vec{r}). \tag{1.2}$$

Here, ∇^2 is the kinetic energy operator; $V_C(\vec{r})$ is the Coulomb potential energy of an electron at the point $\vec{r}$ resulting from the interaction with the nuclei and the total density of the charge of all the electrons of the given system. To compensate the self-interaction allowed for in $V_C(\vec{r})$ we need the energy

$$V_i(\vec{r}) = -n_i \int 2\frac{\varphi_i^*(\vec{r}')\varphi_i(\vec{r}')}{|\vec{r} - \vec{r}'|}\, d\vec{r}', \tag{1.3}$$

where n_i is the number of electrons in orbital i.

In the case of an atom with the nuclear charge Z, the Coulomb potential is

$$V_C(\vec{r}) = -\frac{2Z}{r} + \sum_j n_j \int 2\frac{\varphi_i^*(\vec{r}')\varphi_j(\vec{r}')}{|\vec{r} - \vec{r}'|}\, d\vec{r}'. \tag{1.4}$$

Thus, in a system containing N electrons, each electron is acted on by the field induced by the nuclei and $N - 1$ electrons.

The Hartree equations allow writing the energy functional determined using the functions φ_i. The functions φ_i, which are a self-consistent solution of (1.1), must minimize this functional. The above construction of the solution of (1.1) was used by Fock and independently by Slater to develop the so-called Hartree–Fock equations.

By the Pauli principle, the total wave function of a system should be antisymmetric with respect to the interchanging of electron pairs. The Hartree–Fock method takes into account the Pauli principle to approximate the total many-electron wave function by the determinant

$$\Psi(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \varphi_1(\vec{r}_1) & \varphi_1(\vec{r}_2) & \ldots & \varphi_1(\vec{r}_N) \\ \varphi_2(\vec{r}_1) & \varphi_2(\vec{r}_2) & \ldots & \varphi_2(\vec{r}_N) \\ \vdots & \vdots & \ddots & \vdots \\ \varphi_N(\vec{r}_1) & \varphi_N(\vec{r}_2) & \ldots & \varphi_N(\vec{r}_N) \end{vmatrix}. \tag{1.5}$$

When we substitute this many-electron wave function into the Schrödinger equation, using the Ritz variational principle,

$$\delta\left[\frac{\int \Psi^*(\mathbf{H} - E)\Psi\, dV}{\int \Psi^*\Psi\, dV}\right] = 0 \tag{1.6}$$

and allowing for all conditions of orthonormalization of the orbitals we obtain the Hartree–Fock equation [5]

$$[-\nabla^2 + V_C(\vec{r})]\varphi_i(\vec{r}) - \sum_j n_j \varphi_j(\vec{r}) \int 2\frac{\varphi_j^*(\vec{r}')\varphi_i(\vec{r}')}{|\vec{r} - \vec{r}'|}\, d\vec{r}' = \varepsilon_i \varphi_i(\vec{r}). \tag{1.7}$$

The summation in this equation is over the states of parallel-spin electrons. The first terms in (1.7) are identical to those in the Hartree equations (1.1, 1.2). The last term on the left-hand side of (1.7) describes the exchange interaction which is also a Coulomb interaction and related to the correlations in the motion of electrons resulting from the use of the

wave function in the form of (1.5). Note that if, instead of the summation over j, only the component with $j = i$ is left in the exchange term, then this term will be identical to $V_i(\vec{r})$ in the Hartree equation (1.3). This term describes the interaction of an electron with itself. Thus, it is clear that the exchange correction in the Hartree–Fock method includes the term describing the self-interaction and the terms with $j \neq i$, i.e., the exchange terms.

The Hartree–Fock equations are most convenient in the form of (1.1). Now, we obtain the operator [5]

$$\hat{F}_i = -\nabla^2 + V_C(\vec{r}) + V_{xi}(\vec{r}),\tag{1.8}$$

where

$$V_{xi}(\vec{r}) = -\frac{\sum_j n_j \int d\vec{r}'\, 2\varphi_i^*(\vec{r})\varphi_j^*(\vec{r}')\varphi_j(\vec{r})\varphi_i(\vec{r}')/|\vec{r} - \vec{r}'|}{\varphi_i^*(\vec{r})\varphi_i(\vec{r})}.\tag{1.9}$$

The exchange potential V_{xi} is the potential of the charge of one electron removed from the hole that surrounds it. Thus, the Hartree–Fock equations may be interpreted as the Hartree equations, that is, a separate electron moves in the field of the nucleus and the entire electron charge, and this field gets attenuated by the exchange charge field equal in magnitude to the electron charge localized in the Fermi hole surrounding the given electron.

The operator $\hat{F}_i$ (1.8) depends on orbitals, which complicates the solution of the Hartree–Fock equations. Therefore, the latter are related to nonlinear integrodifferential equations normally solved by iteration techniques. First, the initial set of orbitals $\varphi_i(\vec{r})$ is selected and substituted into (1.8). Then, solving the eigenvalue problem (1.1) another set of orbitals is defined and, thus, self-consistency is achieved.

At present, the Hartree–Fock method is the best one-electron method. However, it has also been most effective in calculating the electronic structure of finite many-particle systems, i.e., atoms.

However, application to macroscopic many-electron systems presents difficulties, even in the case of a free electron gas. It will be shown below that the exchange potential of a free electron gas is proportional to the function $F(k/k_F)$ which varies from unity at the bottom of the Fermi distribution to $1/2$ at its peak, and to zero in the region of excited states. Because the exchange energy is negative, when it is included the number of energy levels and the density of states at the bottom of the Fermi distribution are greatly reduced. Figure 1.1 shows the calculated density of states of a free electron system with the exchange correction included [30]. The density of states is no longer proportional to the square root of the energy as in the case when the exchange is not taken into account, but goes to zero on the Fermi sphere. This contradicts the experimental data on the low-temperature heat capacity of metals.

This effect has to do with the long-range effect of the Coulomb field. It has been mentioned above that the plasma excitations of metals lie at high energies, in the UV range, therefore they are not excited at normal temperatures. Due to the screening effect, the electron–electron interaction energy should be defined by the potential $V(r) \sim (1/r)e^{-\kappa r}$, where κ is the constant, rather than by the Coulomb potential. Thus, the potential decreases exponentially at distances smaller than the lattice constant. At larger inter-electron distances, there is only an average electron–electron interaction. Therefore, in the Hartree–Fock theory,
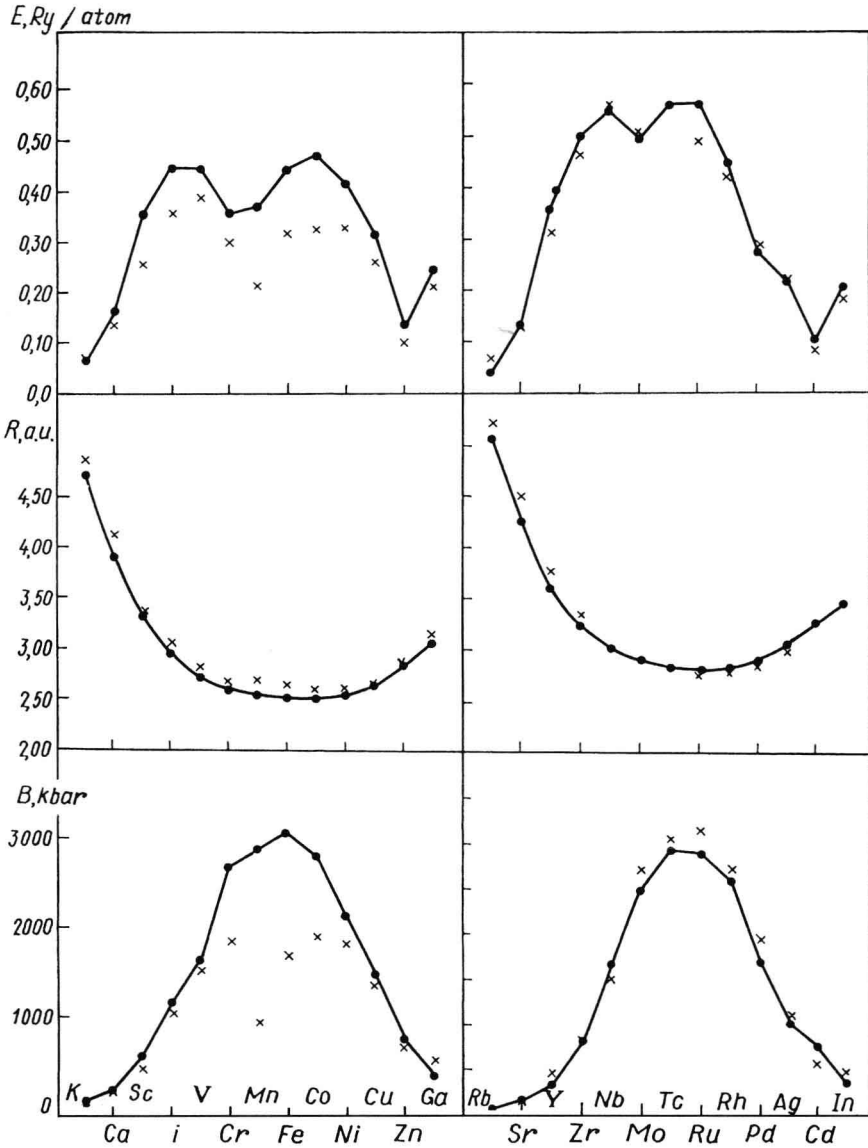
FIGURE 1.1. Density of states of the free electron gas [30]: 1 – Sommerfeld theory; 2 – Hartree–Fock theory.

when there is a strong dependence of the exchange energy on $\vec{k}$, the one-electron energies determined by Hartree–Fock are not correct for the Fermi statistics of macroscopic systems.

Yet, with the exchange term (1.9) replaced by the ordinary exchange correction depending solely on $\vec{r}$, better agreement between theory and experiment is observed in many cases. This is what is done in the χ_α method proposed by Slater.

1.1.2 Slater χ_α Approximation

To obtain an exchange potential which is identical for all the electron states, Slater proposed to replace the exchange term (1.9) by a weighted average with weighting corresponding to the probability of the existence of an electron described by the i-th orbital at the point $\vec{r}$ [31]. The charge density at the point $\vec{r}$ which is generated by the i-th orbital equals $n_i \varphi_i^*(\vec{r})\varphi_i(\vec{r})$, the total of the charge density of electrons at this point equals $\sum_k n_k \varphi_k^*(\vec{r})\varphi_k(\vec{r})$. Therefore, the probability for the electron at $\vec{r}$ to be in the state described by the i-th orbital is

$$\frac{n_i \varphi_i^*(\vec{r})\varphi_i(\vec{r})}{\sum_k n_k \varphi_k^*(\vec{r})\varphi_k(\vec{r})}. \tag{1.10}$$

Then, the required weighted average is

$$V_x = -\frac{\sum_i \sum_j n_i n_j \int \varphi_i^*(\vec{r})\varphi_i(\vec{r}')(2/|\vec{r}-\vec{r}'|)\varphi_j^*(\vec{r}')\varphi_j(\vec{r})\,d\vec{r}'}{\sum_k n_k \varphi_k^*(\vec{r})\varphi_k(\vec{r})}. \tag{1.11}$$

This potential is now identical for all the electron states. Therefore, (1.1, 1.8) become

$$[-\nabla^2 + V_C(\vec{r}) + V_x(\vec{r})]\varphi_i(\vec{r}) = \varepsilon_i \varphi_i(\vec{r}). \tag{1.12}$$

It should be noted again that the averaged exchange (1.11) has been introduced not only as a simplification of the Hartree–Fock method, but also to overcome the difficulties of the Hartree–Fock method in determining the band energies of solids. Thus, an important property of (1.12) is that its wave functions are mutually orthogonal and the electron moves in the average field generated by all other electrons. The exchange potentials (1.9, 1.11) may be accurately calculated for the free electron gas. In this case the Hartree–Fock wave functions are plane waves. The ground state of a gas of free electrons in momentum space is a Fermi sphere with radius k_F. The exchange potential for a state with the wave number k is defined by the equation [5]

$$V_x(k) = -8 \left(\frac{3}{8\pi}\rho\right)^{1/3} F(\eta), \tag{1.13}$$

where $\eta = k/k_F$ and

$$F(\eta) = \frac{1}{2} + \frac{1-\eta^2}{4\eta} \ln\left|\frac{1+\eta}{1-\eta}\right|. \tag{1.14}$$

The occurrence of the logarithmic singularity in $F(\eta)$ with $\eta = 1$ ($k = k_F$) is caused by the density of electron states equal to zero at the Fermi energy, which results, as shown above, in a disagreement between the Hartree–Fock theory and the experimental data for the electron heat capacity and magnetic susceptibility of crystals. To obtain the potential (1.11) for the free electron gas, we have to average it over all occupied states up to $k = k_F$. Since the number of electron states between η and $\eta + d\eta$ is proportional to $\eta^2 d\eta$, we have

$$F(\eta) = \frac{\int_0^1 \eta^2 F(\eta)\,d\eta}{\int_0^1 \eta^2\,d\eta} = \frac{3}{4}.$$

Now we obtain

$$V_x = -6\left(\frac{3}{8\pi}\rho\right)^{1/3}. \tag{1.15}$$

The averaged exchange potential depends on the electron charge density which, in the case of the free electron gas, is constant. It was proposed by *Slater* in [31] that, similar to the general case, when the charge density is inhomogeneous, the averaged exchange potential may be approximated by the potential for the free electron gas but with the local electron density $\rho(\vec{r}) = \sum_i \varphi_i^*(\vec{r})\varphi_i(\vec{r})$

$$V_{xs}(\vec{r}) = -6\left(\frac{3}{8\pi}\rho(\vec{r})\right)^{1/3}. \tag{1.16}$$

This is the so-called Slater exchange potential. Since Slater proposed using the exchange potential (1.16) in the band calculations, many calculations of the electron structure and physical properties of various systems have been performed. In most cases, good agreement was observed between theoretical and experimental data, especially for pure transition metals. Note that this potential is convenient for describing the properties of the ground state (distribution of electron density, total energy, parameters of the lattice, Fermi surface topology) and the excited states of metals (X-ray emission, optical spectra, etc.).

We should point out, however, that the exchange potential averaging used by Slater can hardly be considered to be rigorous. This is because in quantum mechanics the averaging, as an approximation, is physically meaningful only when a physically observable quantity is averaged. Therefore, Slater's approach is phenomenological, and (1.12) containing the exchange potential (1.16) should be considered as a one-particle equation rather than a one-electron equation.

Later, the density functional theory was developed, yielding the theoretical basis for the self-consistent field method developed by Hartree, Fock and Slater. The Slater approximation can be obtained as a particular case of the electron density functional with

$$E_{xc}[\rho] = \frac{3}{2}\int \rho(\vec{r})\varepsilon_x(\rho)\,d\vec{r}, \tag{1.17}$$

where $\varepsilon_x(\rho)$ is the exchange energy of a homogeneous system. Thus, if we use the DFT with only the exchange effect and omit the correlation, then we will obtain the Slater potential with the factor $2/3$. This is the exchange potential of Gaspar–Kohn–Sham [7,32]. This difference can be explained as follows. In deriving the Hartree–Fock equation, Slater proceeded from the determinant expression for the total energy. In this expression, the orbital φ_i was varied so as to minimize the total energy. This procedure leads to (1.8). Then, the exchange potential $V_{xi}(\vec{r})$ (1.9) was replaced by the averaged expression (1.11), and then by its statistical equivalent (1.16). In contrast to this, Gaspar, Kohn and Sham wrote the expression for the total energy in the statistical approximation and then varied over the functions φ_i to obtain a one-electron equation. Here, in (1.12), instead of $V_x(\vec{r})$ (1.16), only $2/3$ of this quantity has been obtained for the exchange component. In other words, the two operations of variation of the total energy and replacement of the exchange component by its statistical equivalent do not commute.

The results of Gaspar, Kohn and Sham may also be obtained from the Hartree–Fock exchange potential (1.13) by replacing it with its true value at $k = k_F$, i.e., on the Fermi