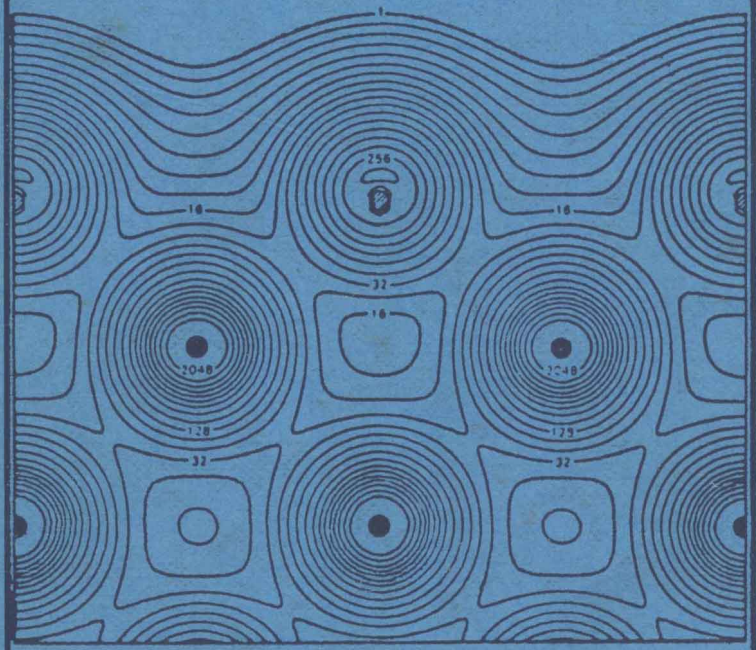
ELECTRONS IN METALS AND ALLOYS



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Electrons in Metals and Alloys

To my parents
(J.A.A.)

Preface

In this volume, the behaviour of electrons in pure metals, both crystalline and disordered, and in metallic alloys will be discussed, especially in relation to the way in which they govern the thermodynamics, and other properties, of these conducting assemblies.

From the outset, attention will focus on the simplest wave-mechanically well-defined quantities that govern the properties of metals and alloys. Paramount among these is the ground-state electron density.

By thereby moving attention away from many complex details of electronic structure that are found to differ, apparently considerably, between individual metals built even from chemically similar atoms, we believe that this volume, although predominantly about theory and concepts, should be particularly appropriate to the needs of a wide spectrum of workers within the general area of materials science, and including specifically physical metallurgy.

To further this end, we have avoided using advanced techniques in the body of the text; occasionally density matrices and Green functions will be encountered. The basic introductory material with which we have assumed all readers to be acquainted is: (i) a first course in the properties of matter; (ii) an introductory course in quantum mechanics; and (iii) some modest knowledge of classical and quantum statistics.

For the reader lacking this background, much of it could be derived from Kittel's *Introduction to Solid State Physics.*[1] Elementary properties of liquids are covered in the book by Temperley and Trevena, *Liquids and their Properties,*[2] while an introduction to quantum mechanics with a flavour useful for reading our book can still be obtained from the now old work of Pauling and Wilson *Introduction to Quantum Mechanics.*[3] Coulson's *Valence*[4] and Pauling's *The Nature of the Chemical Bond*[5] also provide very valuable background.

The final point we must make concerns decisions as to the coverage of our book. Although it is fundamentally about electrons, we have felt it essential, in one chapter, to discuss electron–phonon interaction in relation to electrical transport in normal metals. Owing to the present excitement about high-T_c superconductors, we have briefly treated superconductivity in Chapter 8. This, of course, is a topic that remains of great importance in

metal physics, but to do justice to it would have meant increasing our work by at least one third of its present size. This, we felt, was undesirable, and as numerous excellent specialist books have been written on superconductivity (e.g. Schrieffer's *Superconductivity*[6]), we refer the reader to these.

Of course, it is hardly possible in a work of this kind to avoid some errors creeping in. We trust these will be solely, and then only occasionally, of detail, but we should be most grateful to hear from readers who find our book useful as to how to improve it in the future: either by removing errors or by clarifying arguments.

Inevitably, we have drawn extensively on the work, and the writings, of other authors. We trust that we have made explicit and appropriate references in all cases, but again if we have not in an occasional case then we should appreciate being told.

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Contents

1 Background and outline

The many-electron wavefunction $\Psi(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_N)$ of an N-electron system, with $N \approx 10^{23}$ as in a macroscopic piece of metal, is obviously of utterly impossible complexity to work with. Therefore it is essential to reduce the amount of information one must handle, and two approaches to this problem have emerged historically:

(i) to ascribe to each electron its own personal wavefunction, as in the self-consistent-field approach initiated by Hartree;[1] or
(ii) to integrate out of the probability density $\Psi\Psi^*$ as much information as is feasible to still leave a useful tool from which to construct a theory.

Both of the ideas (i) and (ii) above will play an essential role in this volume. As far as (i) is concerned, once each electron is given its own wavefunction, the remaining question centres round the way to construct a many-electron wavefunction—but now, of course, approximately—from the wavefunctions of the individual electrons. Hartree simply formed Ψ as the product of the N one-electron wavefunctions, but this does not satisfy the requirement of a correct wavefunction for a system of Fermions, namely that the total wavefunction, now including spin, should be antisymmetric in the interchange of the coordinates, space and spin, of any pair of electrons. Hartree's theory was therefore generalized to the so-called Hartree–Fock theory, in which the Hartree product wavefunction is properly antisymmetrized. This corresponds to building Ψ from a single Slater determinant[2] of one-electron 'spin-orbitals', which are constructed as the space wavefunction for a particular electron times its spin function, i.e. either α for upward spin or β for downward spin.

While such an extension of the Hartree method (provided that the one-electron wavefunctions are chosen optimally, to include the Fock–Slater antisymmetrization described above) leads to a significant advance over Hartree theory for atoms, say, it has proved as a result of long experience to lead to objectionable results for metals, in that there are major contradictions between the original Hartree–Fock theory and experiment. Thus the observed linear electronic specific heat at low temperatures is nicely accounted for by the original Hartree method, but a wrong prediction involving a $\ln T$

dependence is found from Hartree-Fock theory. And there are other, equally objectionable, predictions.

In the pioneering work of Bohm and Pines,[3] it was clearly recognized for the first time that the long-range Coulomb interaction e^2/r_{ij} between electrons at separation r_{ij} had to be screened out in a conducting medium such as a metal. The essential point they made was that the long-range Coulomb interactions led to a collective oscillation of the electron density, with a frequency that had been calculated much earlier by Langmuir in a classical plasma: namely[4]

$$\omega_{\text{plasma}} = \omega_{\text{p}} = \left(\frac{4\pi n_0 e^2}{m}\right)^{1/2}, \tag{1.1}$$

where n_0 is the average conduction electron density in the metal and m is the electron mass. For densities appropriate to metals, this is a very high frequency, $\omega_{\text{p}} \approx 10^{16}\,\text{s}^{-1}$, to be compared with a characteristic vibrational frequency of ions, say the Debye frequency which is of the order of $10^{13}\,\text{s}^{-1}$.

When the period $2\pi/\omega_{\text{p}}$ of the plasma oscillations is multiplied by a characteristic electron velocity, called the Fermi velocity (cf. Chapter 2) to obtain a characteristic length, l say, this turns out for a good conductor like Cu to correspond to a length of about 1 Å. The physical interpretation of this result, as stressed by Bohm and Pines,[3] is that, once the collective plasma effects induced by the long-range Coulomb interaction are accounted for, the bare Coulomb interaction e^2/r_{ij} is very effectively screened:

$$\frac{e^2}{r_{ij}} \to \frac{e^2}{r_{ij}} \exp\left(\frac{-r_{ij}}{l}\right). \tag{1.2}$$

Although a result such as (1.2) was already known from the work of Debye and Hückel in the theory of strong electrolytes, their theory was classical, whereas Bohm and Pines were dealing with the completely degenerate electron assembly formed by the conduction electrons in a metal.

It should be cautioned that (1.2) is a little primitive for such an electron assembly, as discussed elsewhere in this volume, but the essential idea of Bohm and Pines is built into the basic approach used throughout this book. Essentially, when one calculates the expectation value of the total Hamiltonian H of the metal with respect to the single Slater determinant of one-electron orbitals, which represents the antisymmetrized Hartree product discussed above, this leads, beyond the Hartree energy, to energy from the antisymmetrization; this is the so-called exchange energy. What the work of Bohm and Pines showed was that, in essence, calculating the exchange energy with the bare interaction e^2/r_{ij} is physically incorrect; the interaction must be screened. Then the objectionable features of the original Hartree–Fock

theory when applied to a metal can be completely avoided. In the technical language of many-electron theory, one should in all essentials treat exchange (which is a manifestation of Pauli-Principle correlations between parallel-spin electrons) together with the electronic correlations induced by Coulomb repulsions, and then one is led back much closer to the predictions of the original Hartree theory.

Having described the development of Hartree's idea of personal electron wavefunctions, referred to as (i) above, how its generalization by Fock and Slater, while valuable in some contexts, was not useful for metals, and how Bohm and Pines led the way to the resolution of these difficulties, we return to the idea (ii).

In its simplest form, one integrates $\Psi^*\Psi$ over the coordinates of $N-1$ electrons, to obtain, with suitable normalization $\int n(\boldsymbol{r})\,\mathrm{d}^3r = N$, the electron density $n(\boldsymbol{r})$. In a perfect metal crystal, not only is this a useful theoretical tool, as we shall see in Chapter 2, but it is also, at least in principle, an observable, accessible to experiment by measuring the intensity of X-ray scattering at the Bragg reflections.

While this theory, in terms of the electron density $n(\boldsymbol{r})$, was pioneered by Thomas[5] and independently by Fermi[6] in the late 1920s, it was not formally proved until 1964 by Hohenberg and Kohn[7] that the ground-state energy, E say, of an N-electron system is indeed uniquely determined (formally rather than explicitly, however, to date) by the electron density. This formally completes the Thomas–Fermi theory, as is discussed at length in Chapter 2.

Slater[8] recognized in 1951 that the link between the electron-density description and the Hartree one-electron wavefunction theory would be fruitful, leading to the so-called Dirac–Slater exchange potential, discussed in Section 2.3. Again, this description of the link was formally completed, some 15 years after Slater's work, by Kohn and Sham.[9]

Of course, it remains true that such a theory has 'forced' the N-electron problem into a one-body mould or framework. This reflects itself in a whole variety of ways. Thus, while single-particle Schrödinger equations, with a local Hartree-like potential $V(\boldsymbol{r})$, can, at least in principle, generate the ground-state density $n(\boldsymbol{r})$ of the fully interacting N-electron assembly, the electron dynamics are not properly treated. For these, one must generalize the density $n(\boldsymbol{r})$ to the first-order density matrix $\gamma(\boldsymbol{r},\boldsymbol{r}')$, which is such that its diagonal element $\gamma(\boldsymbol{r},\boldsymbol{r}) = n(\boldsymbol{r})$; for the precise definition of γ from Ψ, see Appendix 2.2. The dynamics, such as is required to interpret Compton scattering of X-rays from a metal, is in the off-diagonal elements of $\gamma(\boldsymbol{r},\boldsymbol{r}')$, and these are not accessible via single-electron Schrödinger equations.

However, as we shall see in this book, many properties of metals and alloys turn out to be correctly characterized either by the ground-state electron density $n(\boldsymbol{r})$ or by single-particle equations of the Hartree type, but with

a local potential energy $V(\boldsymbol{r})$ that includes a Hartree term, plus a term in which exchange and correlation are subsumed together into a 'correction' $V_{\text{exchange+correlation}}(\boldsymbol{r}) = V_{\text{xc}}(\boldsymbol{r})$ to the Hartree potential energy. This, in a sense that will be clear to the reader, embodies the essence of the Bohm–Pines arguments.

However, as has already been anticipated, collective effects manifest themselves in certain circumstances, as in the energy losses of fast electrons fired through metal films, the plasmon losses associated with the quanta of the electron density or plasma oscillations.[10] Therefore many-electron effects remain of great interest, and some of these require a genuine many-electron theory, not merely an exchange-plus-correlation correction to a one-body potential.

Until we reach the topic of magnetism (Chapter 9), however, it is true to say that a great deal of understanding of many properties of crystalline metals and alloys can be gained from the study of electron states generated by such a local one-body potential energy $V(\boldsymbol{r})$. This is the electronic energy band theory of metals, pioneered by Bloch, Brillouin and Wilson.[11] But already this involves a great deal of detail, and for many purposes, especially relating to physical metallurgy and materials science, much less detail is required. Again, one can appeal to the electron-density description. When one writes the ground-state density $n(\boldsymbol{r})$, the arguments above show, when developed as in Chapter 2, that

$$n(\boldsymbol{r}) = \sum_{i=1}^{N} \psi_i^*(\boldsymbol{r})\psi_i(\boldsymbol{r}). \tag{1.3}$$

But, if one wished, one could sum in (1.3) not up to the highest occupied single-particle energy level (the Fermi energy E_{F}) but only up to energy E:

$$n(\boldsymbol{r}, E) = \sum_{\varepsilon_i < E} \psi_i^*(\boldsymbol{r})\psi_i(\boldsymbol{r}), \tag{1.4}$$

where ε_i are the single-particle energy levels associated with the one-electron wavefunctions $\psi_i(\boldsymbol{r})$. Of course, it has not been proved from electron-density theory that $n(\boldsymbol{r}, E)$ defined in (1.4) has direct physical significance except at the Fermi level when $E = E_{\text{F}}$. Nevertheless, since in a metal there are occupied states infinitesimally close to the Fermi level, it seems entirely plausible that for E near to E_{F}, $n(\boldsymbol{r}, E)$ will be physically significant. In particular, the local density of states

$$N(\boldsymbol{r}, E) = \frac{\partial n(\boldsymbol{r}, E)}{\partial E} \tag{1.5}$$

is an especially useful quantity in an alloy, whereas in a pure metal the average

of $N(\boldsymbol{r}, E)$ over the unit cell Ω (the electronic density of states)

$$N(E) = \int_{\Omega} N(\boldsymbol{r}, E)\, \mathrm{d}^3 r, \tag{1.6}$$

is of great value in giving insight into the behaviour of different metals.

The other major area, beyond those already touched on, that is given some prominence in this volume is that of disordered metals: i.e. metals in the liquid or the amorphous phase.

We shall see that—though this may seem surprising in that the electron theory of metals pioneered by Bloch, Brillouin and Wilson was crucially dependent on the lattice periodicity of the one-body potential $V(\boldsymbol{r})$—in fact many properties of metals are more dependent on the short-range order than on the long-range crystallinity. Then a lot of the theory developed for crystalline solids can be reformulated to shift the emphasis away from periodicity, and this leaves results that, at very least, are relevant to disordered metals. However, a new feature, Anderson localization[12,13] of electron states, does follow as a consequence of disorder.

As well as discussing the above aspects of electron theory, we have not hesitated to treat semi-empirical theories when these theories lead to insight, and in particular when they relate to the basic language of the theory of metals. In Chapter 3, therefore, Miedema's very successful semi-empirical treatment of heats of formation of alloys is dealt with. Miedema's theory,[14] although semi-empirical, is based on the use of parameters deeply rooted in the theory of metals, namely the electronegativity and the electron density at the boundary of the atomic cells in the metal. First, the electron density is the basic tool in the development based on idea (ii) above. On the other hand, as elaborated in Chapter 3, electronegativity is a chemical concept introduced by Pauling[15] as the power of an atom to attract electrons to itself in a molecule or compound. Extensive use of this concept has been made in chemistry to allow the correlation of a substantial number of electronic properties. On the theoretical side, it will be seen in Chapter 2 that electron-density theory provides a sound quantum-mechanical foundation for electronegativity, by identifying this with the negative of the chemical potential, which is a well-defined quantity entering electron-density theory.

One of the goals of the theory of alloys is to predict the stable phases observed in the equilibrium phase diagram. This has important implications in materials science, but it is a formidable task. First-principles theories to date are not sufficiently accurate for this purpose, although there have been important advances in recent years, which will be reviewed in Chapter 6. Consequently, semi-empirical theories are of great value, since simple models allow one to focus on the few important factors believed to be primarily