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CHAPTER 1

ELECTRONIC STRUCTURE OF METALS†

by VOLKER HEINE‡

1.1 PSEUDISM

‘Electronic structure’, interpreted widely, covers all that the outer conduction electrons in metals do, and with it practically all solid state properties, in the sense that the energy of a vacancy, for example, is given in terms of the energy of the whole electronic system. The present chapter is concerned with electronic structure that can be treated theoretically from a ‘fundamental’ point of view, i.e. based on the solution of the Schrödinger equation with more or less well-defined and justifiable approximations. The theories of magnetism and transport properties come within this definition, and form separate chapters. Otherwise, until recent years, it was only the band structure $\mathcal{E}(\mathbf{k})$ of an electron with wave-vector \mathbf{k} travelling through the periodic potential that could be discussed from fundamentals, together with a few immediately related properties such as the electronic specific heat. A phonon spectrum had to be analysed in terms of *ad hoc* force constants. Now, however, it can be calculated in favourable cases from the same basic potential set up for computing $\mathcal{E}(\mathbf{k})$. Other examples are stacking fault energies, phase transitions under pressure, and the resistivities of liquid metals. For simple metals, the area that can be treated ‘fundamentally’ is still centred on the band structure, but has begun to expand.

The concept unifying much of what we have to say is that of the *pseudo-potential*. While the term is relatively new in the present context, some of the ideas it draws together predate it qualitatively by twenty years. Recent developments sharpen and exploit them.

Figs. 1.1 and 1.2 show the results of measurements on the Fermi surface of lead (Anderson & Gold, 1965). The arcs of circles are what

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the Fermi surface would be for perfectly free electrons, namely, the Fermi sphere cut up by Brillouin zone planes (Fig. 1.1), the pieces being translated by appropriate reciprocal lattice vectors \mathbf{g} and re-assembled in successive bands $\mathcal{E}_n(\mathbf{k})$ inside the fundamental Brillouin zone (Fig. 1.2). The observed Fermi surface can be recognized as a modest distortion from the free-electron model, and the same is true of all other metals studied except the transition, rare earth and actinide

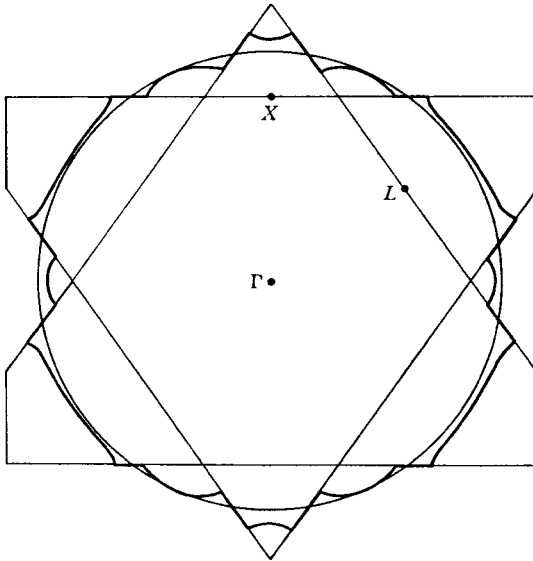


Fig. 1.1. The free electron Fermi sphere (light) and the observed Fermi surface of lead (heavy), shown with Brillouin zone planes in extended \mathbf{k} -space.

metals with incomplete inner d or/and f shells (see Chapter 2). Moreover, the distortions conform qualitatively, and sometimes quantitatively, to what would be expected on the basis of the nearly free electron (N.F.E.) approximation.† The band structures of the group IV semiconductors diamond, Si, Ge, gray Sn and the III–IV compounds have been probed by optical interband transitions, and the band structures inferred from the measurements also interpreted in N.F.E. terms (see, for example, Brust, 1964; Cohen & Bergstresser, 1966). Fermi surface measurements coupled with band structure calculations on the semimetals As, Sb, Bi indicate a N.F.E. situation there, too (Cohen, Falicov & Golin, 1964; Priestley *et al.* 1967; Lin & Falicov, 1966; Falicov & Lin, 1966). While the Fermi surface studies

† Throughout this chapter we shall not define terms that may easily be tracked down through the index of Ziman (1964*a*).

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and optical properties provide detailed information about a part of the band structure, the soft X-ray emission spectra give a rough overall picture which in bandwidth and shape conforms approximately to free electrons. Although most of the detailed evidence for the N.F.E. picture has been built up in the last ten years, the beginnings

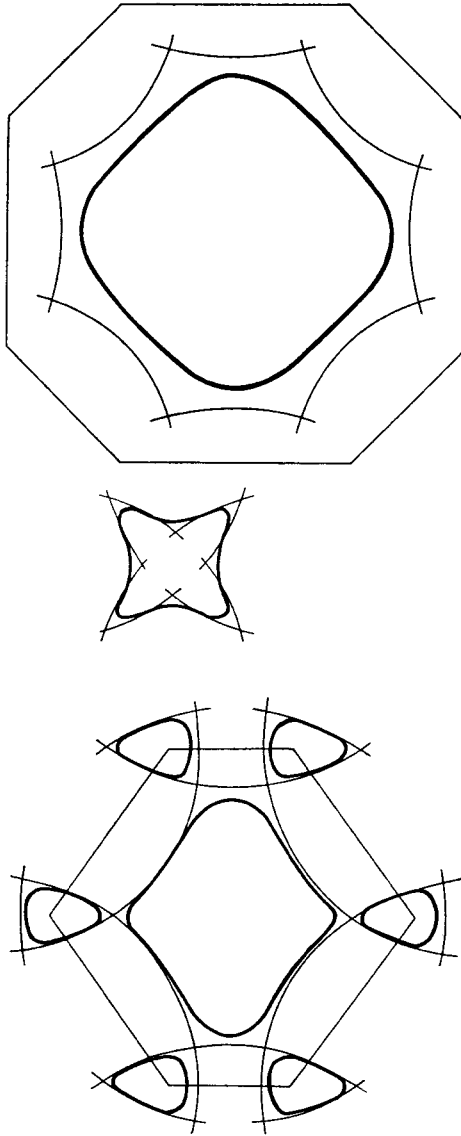


Fig. 1.2. Similar to Fig. 1.1, but with the various parts of the Fermi surface joined together inside the fundamental Brillouin zone.

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can already be seen in Mott & Jones' (1936) treatment of diamond and Bi, for example, in N.F.E. terms.

The success of the N.F.E. model for the band structure $\mathcal{E}(\mathbf{k})$ does not imply, however, that the potential $V(\mathbf{r})$ in the solid is weak or can be treated by perturbation theory, as assumed in most textbook presentations of the N.F.E. method. $V(\mathbf{r})$ becomes very strong near the atomic nuclei, much larger than the bandwidth of the conduction electrons and far too strong to be treated as a perturbation. Inside the ion core of the metal atom $V(\mathbf{r})$ is a sufficiently deep potential well to produce several atomic-like oscillations in the wave-function (Fig. 1.3).

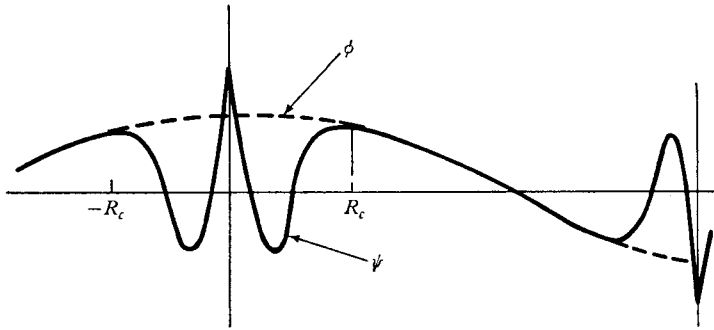


Fig. 1.3. Real wave-function ψ and pseudo-wave-function ϕ of an electron in a N.F.E. metal. R_c is the radius of the ion core.

In order to understand the success of the N.F.E. model, we have to take a broad view of how the electronic structure of a solid is formulated. First, there is the interaction of the electron wave with one atomic centre, and, secondly, there is the multiple scattering from the array of atoms taken together. This separation is present explicitly, for example, in the augmented plane wave (A.P.W.) and Korringa-Kohn-Rostoker (KKR) methods for calculating band structures, where each ion core is surrounded by a sphere of radius R (Fig. 1.4). $\mathcal{E}(\mathbf{k})$ is determined by solving the Schrödinger equation in the Swiss-cheese-like interstitial region, subject to a boundary condition on the spheres given by the radial derivative of the wave-function at R or by the phase shift (Ziman, 1964*a*, pp. 87–97). We may picture the atom as a black box (Fig. 1.5), and *the electronic structure is completely determined once we specify how strongly any incident wave from outside R , which we may decompose into plane waves $|\mathbf{k}\rangle$, is scattered into the direction $\mathbf{k} + \mathbf{q}$.*

The applicability of the N.F.E. model means that the *net scattering* by an atom can be *weak*, even though the potential is strong. How

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this is possible follows from considering the scattering expressed in terms of phase shifts η_l . These may be written

$$\eta_l = p_l\pi + \delta_l. \tag{1.1}$$

The integer p_l , chosen so that $|\delta_l| < \frac{1}{2}\pi$, counts the number of internal radial nodes. Since the usual phase shift formula for the scattering (Schiff, 1955, p. 105) only involves $\exp(2i\eta_l)$, any multiple of π in (1.1) does not contribute and the scattering is determined by δ_l , which is relatively small in those metals and semiconductors where the N.F.E. model holds.

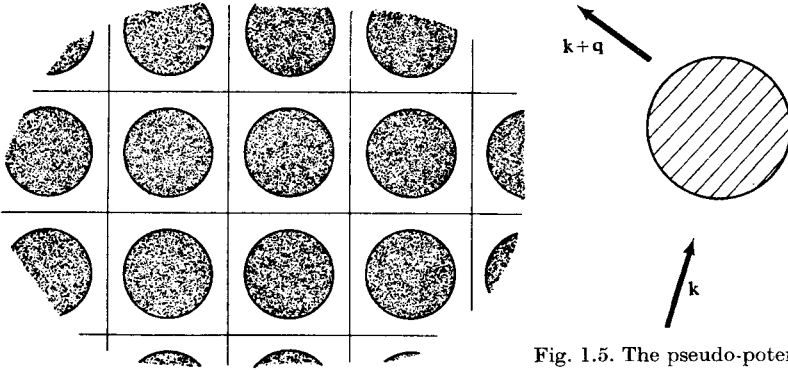


Fig. 1.4.

Fig. 1.5. The pseudo-potential $v(q)$ is defined in terms of the scattering amplitude of an atom, pictured as a black box, for scattering of electrons from \mathbf{k} to $\mathbf{k} + \mathbf{q}$.

In this case it is convenient to define a weak pseudo-potential V_{ps} with small phase shifts equal to δ_l (not to the η_l of the real potential) so that it gives just the correct amount of scattering. Alternatively we may demand that the pseudo Schrödinger equation†

$$(-\nabla^2 + V_{ps})\phi = \mathcal{E}\phi \tag{1.2}$$

has the same eigenvalues as the real Schrödinger equation. The V_{ps} is weak, the scattering amplitude of V_{ps} from \mathbf{k} to $\mathbf{k} + \mathbf{q}$ may then be expressed as a highly convergent perturbation series. Formally it is given by the element $\langle \mathbf{k} + \mathbf{q} | t | \mathbf{k} \rangle$ of the t -matrix (Messiah, 1961, pp. 807, 849)

$$t = V_{ps} + V_{ps}G_0V_{ps} + V_{ps}G_0V_{ps}G_0V_{ps} + \dots \tag{1.3}$$

† We use units with $2m = \hbar = e = 1$, except that energies will normally be given in Rydbergs where $1 \text{ Ry} = 13.6 \text{ eV}$.

where G_0 is the free propagating Green function. The scattering and hence the t -matrix derived from a given potential is of course unique, but the converse is certainly not true: there are many different V_{ps} which give the same scattering, at least over the limited energy range of interest for electronic structure. Indeed the whole possibility of defining a pseudo-potential rests on the fact that another potential can be found with identical scattering to the real potential V . From this point of view the transition from the real potential V to the pseudo-potential represents a partial transformation towards the t -matrix in which the strong inner core part of V giving the radial oscillations in ψ has been t -matrixed.

One explicit V_{ps} demonstrates the weakness of the pseudo-potential very clearly. It is (Austin *et al.* 1962)

$$V_{ps}\phi = V\phi - \sum_c \langle \psi_c, V\phi \rangle \psi_c, \quad (1.4a)$$

where the ψ_c are the $1s$, $2s$, $2p$, etc., orbitals in the ion core. (Strictly they are the $1s$, etc., solutions of the same Hamiltonian that operates on the valence electrons and so may differ slightly from the actual orbitals of the core.) It is not difficult to verify (Ziman, 1964*a*, p. 97) that (1.4*a*) gives the same valence eigenvalues in (1.2) as V itself does. Since the ψ_c have definite angular momenta l , the second term of (1.2) picks out and operates differently on the different l components of the pseudo-wave-function ϕ . If we consider for a moment only the $l = 0$ component, ϕ is approximately a constant inside the core because radial oscillations have been eliminated and an s -state has no angular nodes, and so ϕ may be taken outside the matrix element in (1.4)

$$V_{ps}\phi \approx [V - \sum_c \langle \psi_c, V \rangle \psi_c] \phi. \quad (1.4b)$$

The $\langle \psi_c, V \rangle$ are the expansion coefficients of V in terms of the set ψ_c . If we had a complete set, the bracket in (1.4*b*) would vanish identically. As it is, the ψ_c are a finite set of core orbitals which form quite a good expansion set inside the core. Thus the second term in (1.4*b*) cancels most of the strong potential V inside the core, as illustrated for a free Si^{4+} ion in Fig. 1.6. In fact, (1.4) is a special case of a more general cancellation theorem developed by Phillips & Kleinman (1959), Antoncik (1959), Cohen & Heine (1961), and Austin, Heine & Sham (1962).

The whole success of the pseudo-potential method, where it is

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applicable, depends on the perturbation series (1.3) being reasonably rapidly convergent. For many purposes the first term

$$v(q) \equiv \langle \mathbf{k} + \mathbf{q} | V_{ps} | \mathbf{k} \rangle \quad (1.5a)$$

may suffice, and we abbreviate it to $v(q)$. We may think of it as approximately the scattering amplitude, which is given precisely by (1.3), of the black box representing the atom. Part of the art of choosing pseudo-potentials is to reduce the corrections in (1.3) by making the high (large q) Fourier components $v(q)$ as small as possible. For

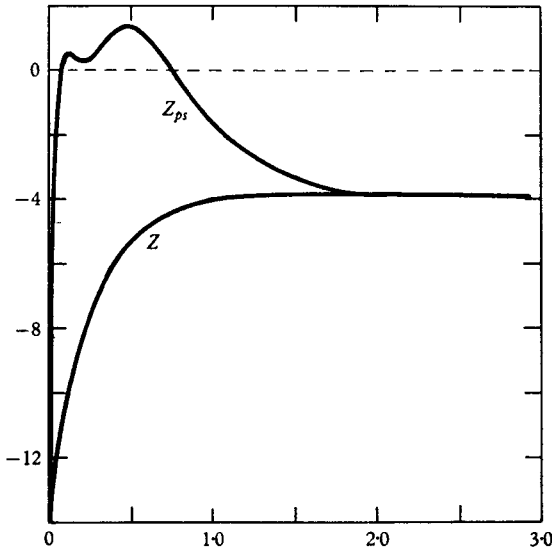


Fig. 1.6. The potential and pseudo-potential (for $l = 0$ states) of a Si^{4+} ion. The potential V is expressed in the form $V(r) = Z(r)/r$ and V_{ps} similarly in terms of $Z_{ps}(r)$. Note V and V_{ps} both become equal to the Coulomb potential $-4/r$ outside the core which has a radius of about one Bohr unit.

calculating band structures this is not too important: modern computers can handle large secular equations. But for calculating phonon spectra and electrical properties, for instance, the use of lowest-order Born approximation $v(q)$ can be a great help. In other problems, such as calculating the formation and migration energies of vacancies and interstitials in diamond-type semiconductors, Bennemann (1964, 1965) found the use of the full t -matrix essential. The degree of complication this causes is obvious from one glance at the papers! Finally, it should be emphasized that the scattering amplitude from \mathbf{k} to $\mathbf{k} + \mathbf{q}$ depends in general not only on q but also on k , $|\mathbf{k} + \mathbf{q}|$ and the energy \mathcal{E} .

The same applies to the pseudo-potential, for example, the non-local operator (1.4a), and what we just wrote as $v(q)$ should be written

$$v(q; k, |\mathbf{k} + \mathbf{q}|, \mathcal{E}). \quad (1.5b)$$

Actually (1.4) does not have an explicit energy dependence but some forms of V_{ps} do, in particular those involving the logarithmic derivative or phase shift which varies with energy.

We have been at pains to stress that electronic structure is a much wider field than calculating $\mathcal{E}(\mathbf{k})$. *Progress in science means unifying more and more experience through well-defined concepts which may be expressed in definite numbers. The scattering power of the atomic black box, or the pseudo-potential for N.F.E. solids, serves that purpose for electronic structure.* It remains the same, or nearly the same, whether we are calculating $\mathcal{E}(\mathbf{k})$ for a perfect metal or the frequency of a phonon in it. To a first approximation only the positions of the atoms change and the types of quantities one wishes to calculate depend largely on just these. This has one important consequence: it is not always necessary to calculate from first principles. Once the scattering power or pseudo-potential of an atom has been inferred from one set of experimental data, it may be applied to a study of other measurable properties. Although pseudo-potentials can be calculated with a gratifying accuracy, the precision needed for some applications goes beyond what can currently be achieved, and a pseudo-potential $v(q)$ matched to experiment, even at one or two values of q , is clearly superior. The pseudo-potential involves cancellation between large quantities, as seen in (1.4), and there are in addition many small effects of correlation and exchange. There may therefore be a natural limit, of the order of 0.01 Ry, to the accuracy with which pseudo-potentials will ever be calculated from first principles. After discussing band-structure calculations in §1.2, we therefore indicate in §1.3 how experimentally determined N.F.E. band structures may be analysed in terms of $v(q)$. In §1.5 we indicate how to calculate other properties of N.F.E. metals in terms of $v(q)$, applying this to a discussion of their crystal structures in §1.6.

The *transition metals* cannot of course be described in N.F.E. terms because of the narrow d -bands which have more of a tight binding character, but the general approach in terms of atomic scattering properties remains valid. We expect to be able to write the scattering in terms of a relatively weak pseudo-potential as far as the $l = 0$ and 1 components of the wave-function is concerned, but the $l = 2$

component reacts very strongly with the atomic potential as evidenced by the narrow bandwidth and its scattering has to be treated differently. The electronic structure of transition metals will be formulated in these terms in §1.4. The noble metals form a borderline case. If the whole band structure is being considered, then they must be treated as transition metals with their d -bands. If, on the other hand, only states near the Fermi level above the d -band are significant, then a relatively simple pseudo-potential including the indirect effects of the d -bands may suffice.

Section 1.7, which logically should come at the beginning of the whole chapter, discusses what meaning can be attached to the 'one-electron' band structure from the many-body point of view, taking into account all the interactions between the electrons.

1.2 BAND-STRUCTURE CALCULATIONS

The approach developed in §1.1, based on 'black box' atoms, depends partially on the fact that the potential in a metal or semiconductor is relatively flat in the interstitial region between the spheres (Fig. 4), at least when these are made large enough to touch the sides of the atomic polyhedron. Indeed, the potential is normally assumed to be a constant in this region in the Korringa-Kohn-Rostocker (KKR) and augmented plane wave (A.P.W.) methods for calculating the band structure $\mathcal{E}(\mathbf{k})$, though this simplification is not absolutely necessary for the latter. The electrons may be regarded as propagating approximately as plane waves between the atoms, and we expect $\mathcal{E}(\mathbf{k})$ to be defined by a secular equation of the form

$$\det \{ \{ (\mathbf{k} - \mathbf{g})^2 - \mathcal{E} \} \delta_{\mathbf{g}\mathbf{g}'} + \Gamma_{\mathbf{g}\mathbf{g}'} \} = 0, \quad (1.6)$$

where the \mathbf{g} 's are the reciprocal lattice vectors. $\Gamma_{\mathbf{g}\mathbf{g}'}$ represents the atomic scattering, plus that of the interstitial potential if any.

It is well known that the secular equation of the *orthogonalized plane wave* (O.P.W.) method is of the form (1.6), with $\Gamma_{\mathbf{g}\mathbf{g}'}$ (O.P.W.) the matrix element of the original O.P.W. form of the pseudo-potential

$$\Gamma_{\mathbf{g}\mathbf{g}'}(\text{O.P.W.}) = V_{\mathbf{g}-\mathbf{g}'} + \sum_c (\mathcal{E} - \mathcal{E}_c) \langle \mathbf{k} - \mathbf{g} | c \rangle \langle c | \mathbf{k} - \mathbf{g}' \rangle. \quad (1.7)$$

The details of this and other band-structure methods have been described well in several texts (see, e.g. Ziman, 1964*a*, chapter 3, and Callaway, 1964), and we will restrict ourselves to a few comments on the practical state of the art. In the orthogonalized plane wave (O.P.W.)

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method, convergence becomes very slow beyond about 0.01 Ry, because the representation of the inner oscillations of ψ in terms of plane waves and core functions ψ_c (Ziman, 1964*a*, p. 94) is only an *ad hoc* 'Ansatz' and it requires plane waves of very short wavelength to make the final corrections to ψ (Abarenkov & Heine, 1965). The success of the method depends on the fact that the Ansatz is remarkably good for atomic potentials which become progressively steeper near the origin. It does not work for a square well with infinitely high walls, for example. In a typical metal such as Al, the bandwidth is of the order of 1 Ry, the band gaps of order 0.1 Ry. An accuracy of 0.01 Ry in calculation is therefore often adequate. The virtue of the o.p.w. method is its relative simplicity, still falling as it does within the competence of an enthusiastic amateur. Its shortcoming, besides the question of convergence, is its unsuitability for transition metals and anything approaching an ionic compound. However, Deegan & Twose (1967) have successfully adapted the o.p.w. method to *d*-bands.

The *augmented plane wave* (A.P.W) method overcomes the convergence problem of o.p.w.s by an exact integration of the wave equation inside the atomic sphere, and gives eigenvalues to 10^{-3} Ry without difficulty. It also copes with *d*-bands and has been applied to a few compounds and stoichiometric alloys, e.g. TiC, V₃Si (Earn & Switendick, 1965; Mattheiss, 1965). Its secular equation has

$$\Gamma_{\mathbf{g}\mathbf{g}'}(\text{A.P.W.}) = (4\pi R^2/\Omega) \left\{ -[(\mathbf{k} - \mathbf{g}) \cdot (\mathbf{k} - \mathbf{g}') - \mathcal{E}] \frac{j_1(|\mathbf{g} - \mathbf{g}'|R')}{|\mathbf{g} - \mathbf{g}'|} \right. \\ \left. + \sum_{l=0}^{\infty} (2l+1) P_l(\cos \theta_{\mathbf{g}\mathbf{g}'}) j_l(|\mathbf{k} - \mathbf{g}|R) j_l(|\mathbf{k} - \mathbf{g}'|R) \frac{\mathcal{R}'_l(R, \mathcal{E})}{\mathcal{R}_l(R, \mathcal{E})} \right\} \quad (1.8)$$

(where $\theta_{\mathbf{g}\mathbf{g}'}$ is the angle between $\mathbf{k} - \mathbf{g}$ and $\mathbf{k} - \mathbf{g}'$, Ω the volume of the unit cell, and \mathcal{R}' the derivative of the radial wave-function \mathcal{R}). An A.P.W. calculation may take two years to develop from scratch. However, at least one experimentalist has learnt to use existing programmes to calculate a band structure as an aid in interpreting his data. The o.p.w. and A.P.W. methods have been extended to include spin-orbit coupling, and in the case of A.P.W. all other relativistic effects (Weisz, 1966; Loucks, 1965*a*).

In the *Korringa-Kohn-Rostocker* (KKR) method, the propagation of the electron wave between the inscribed spheres of Fig. 1.4 is