Chapter 11

Other Methods for Calculating Band Structure

Part II

THE AUGMENTED PLANE-WAVE METHOD (APW)

This approach, due to J. C. Slater,[14] represents $\psi_{\mathbf{k}}(\mathbf{r})$ as a superposition of a finite number of plane waves in the flat interstitial region, while forcing it to have a more rapid oscillatory atomic behavior in the core region. This is achieved by expanding $\psi_{\mathbf{k},\varepsilon}$ in a set of *augmented plane waves.*[15] The APW $\phi_{\mathbf{k},\varepsilon}$ is defined as follows:

1. $\phi_{\mathbf{k},\varepsilon} = e^{i\mathbf{k}\cdot\mathbf{r}}$ in the interstitial region. It is important to note that there is no constraint relating ε and $\mathbf{k}$ (such as, for example, $\varepsilon = \hbar^2k^2/2m$). One can define an APW for any energy ε and any wave vector $\mathbf{k}$. *Thus any single APW does not satisfy the crystal Schrödinger equation for energy ε in the interstitial region.*
2. $\phi_{\mathbf{k},\varepsilon}$ is *continuous* at the boundary between atomic and interstitial regions.
3. In the atomic region about $\mathbf{R}$, $\phi_{\mathbf{k},\varepsilon}$ does satisfy the atomic Schrödinger equation:

$$-\frac{\hbar^2}{2m}\nabla^2\phi_{\mathbf{k},\varepsilon}(\mathbf{r}) + V(|\mathbf{r}-\mathbf{R}|)\phi_{\mathbf{k},\varepsilon}(\mathbf{r}) = \varepsilon\phi_{\mathbf{k},\varepsilon}(\mathbf{r}), \qquad |\mathbf{r}-\mathbf{R}| < r_0. \quad \textbf{(11.15)}$$

Since $\mathbf{k}$ does not appear in this equation, $\phi_{\mathbf{k},\varepsilon}$ gets its $\mathbf{k}$ dependence only via the boundary condition (2) and the $\mathbf{k}$ dependence determined by (1) in the interstitial region.

It can be shown that these conditions determine a unique APW $\phi_{\mathbf{k},\varepsilon}$ for all $\mathbf{k}$ and ε. Note that in the interstitial region the APW satisfies not (11.15) but $H\phi_{\mathbf{k},\varepsilon} = (\hbar^2 k^2/2m)\phi_{\mathbf{k},\varepsilon}$. Note also that, in general, $\phi_{\mathbf{k},\varepsilon}$ will have a discontinuous derivative on the boundary between interstitial and atomic regions, so that $\nabla^2\phi_{\mathbf{k},\varepsilon}$ will have delta-function singularities there.

The APW method tries to approximate the correct solution to the crystal Schrödinger equation (11.1) by a superposition of APW's, all with the same energy. For any reciprocal lattice vector $\mathbf{K}$ the APW $\phi_{\mathbf{k}+\mathbf{K},\varepsilon}$ satisfies the Bloch condition with wave vector $\mathbf{k}$ (Problem 2), and therefore the expansion of $\psi_{\mathbf{k}}(\mathbf{r})$ will be of the form

$$\psi_{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{K}} c_{\mathbf{K}}\phi_{\mathbf{k}+\mathbf{K},\varepsilon(\mathbf{k})}(\mathbf{r}), \tag{11.16}$$

where the sum is over reciprocal lattice vectors.

By taking the energy of the APW to be the actual energy of the Bloch level, we guarantee that $\psi_{\mathbf{k}}(\mathbf{r})$ satisfies the crystal Schrödinger equation in the atomic regions. The hope is that not too many augmented plane waves will suffice to approximate the solutions to the full Schrödinger equation in the interstitial region[16] and at the boundary. In practice, as many as a hundred APW's can be used; by the time this stage is reached, $\varepsilon(\mathbf{k})$ does not change appreciably when more APW's are added, and one feels with some confidence that good convergence has been achieved.

Because each APW has a discontinuous derivative at the boundary of the atomic and interstitial regions, it is best to work not with the Schrödinger equation but with an equivalent variational principle:

Given any *differentiable* (but not necessarily twice differentiable)[17] function $\psi(\mathbf{r})$, define the energy functional:

$$E[\psi] = \frac{\int \left(\frac{\hbar^2}{2m} |\nabla \psi(\mathbf{r})|^2 + U(\mathbf{r}) |\psi(\mathbf{r})|^2 \right) d\mathbf{r}}{\int |\psi(\mathbf{r})|^2 \, d\mathbf{r}}. \tag{11.17}$$

It can be shown[18] that a solution to the Schrödinger equation (11.1) satisfying the Bloch condition with wave vector $\mathbf{k}$ and energy $\mathcal{E}(\mathbf{k})$ makes (11.17) stationary with respect to differentiable functions $\psi(\mathbf{r})$ that satisfy the Bloch condition with wave vector $\mathbf{k}$. The value of $E[\psi_\mathbf{k}]$ is just the energy $\mathcal{E}(\mathbf{k})$ of the level $\psi_\mathbf{k}$.

The variational principle is exploited by using the APW expansion (11.16) to calculate $E[\psi_\mathbf{k}]$. This leads to an approximation to $\mathcal{E}(\mathbf{k}) = E[\psi_\mathbf{k}]$ that depends on the coefficients $c_\mathbf{K}$. The demand that $E[\psi_\mathbf{k}]$ be stationary leads to the conditions $\partial E/\partial c_\mathbf{K} = 0$, which are a set of homogeneous equations in the $c_\mathbf{K}$. The coefficients in this set of equations depend on the sought for energy $\mathcal{E}(\mathbf{k})$, both through the $\mathcal{E}(\mathbf{k})$ dependence of the APW's and because the value of $E[\psi_\mathbf{k}]$ at the stationary point is $\mathcal{E}(\mathbf{k})$. Setting the determinant of these coefficients equal to zero gives an equation whose roots determine the $\mathcal{E}(\mathbf{k})$.

As in the cellular case, it is often preferable to work with a set of APW's of definite energy and search for the **k** at which the secular determinant vanishes, thereby mapping out the constant energy surfaces in **k**-space. With modern computing techniques it appears possible to include enough augmented plane waves to achieve excellent convergence,[19] and the APW method is one of the more successful schemes for calculating band structure.[20]

In Figure 11.7 we show portions of the energy bands for a few metallic elements, as calculated by L. F. Mattheiss using the APW method. One of the interesting results of this analysis is the extent to which the bands in zinc, which has a filled atomic *d*-shell, resemble the free electron bands. A comparison of Mattheiss' curves for titanium with the cellular calculations by Altmann (Figure 11.8) should, however, instill a healthy sense of caution: Although there are recognizable similarities, there are quite noticeable differences. These are probably due more to the differences in choice of potential than to the validity of the calculation methods, but they serve to indicate that one should be wary in using the results of first principles band-structure calculations.

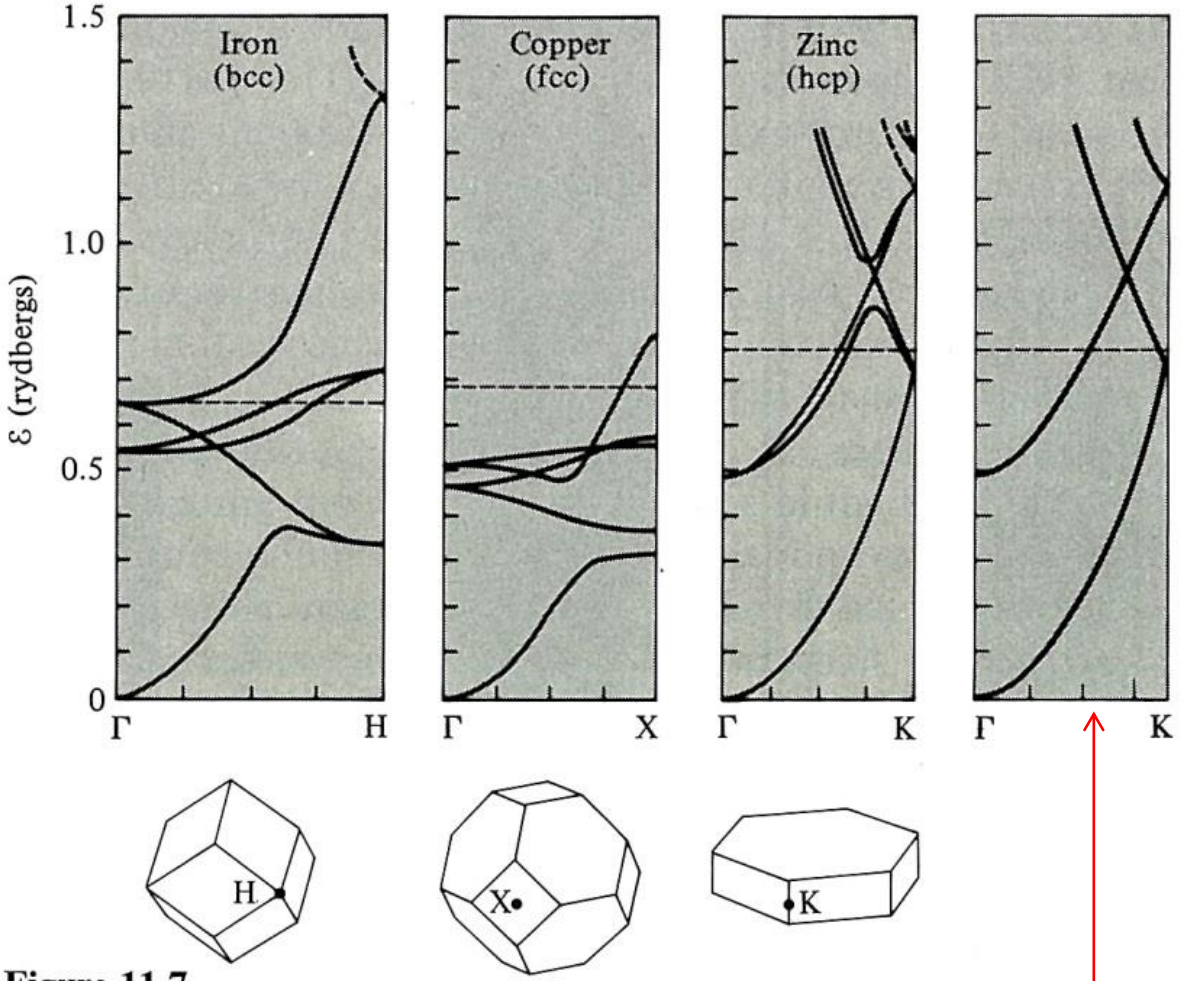


Figure 11.7

APW energy bands for iron, copper, and zinc, calculated by L. F. Mattheis, *Phys. Rev.* **134**, A970 (1964). The bands are plotted from the origin of **k**-space to the points indicated on the zone surfaces. Note the striking resemblance between the calculated bands of zinc and the free electron bands (pictured to the right). Zinc has two *s*-electrons outside of a closed-shell configuration. The horizontal dashed lines mark the Fermi energy.

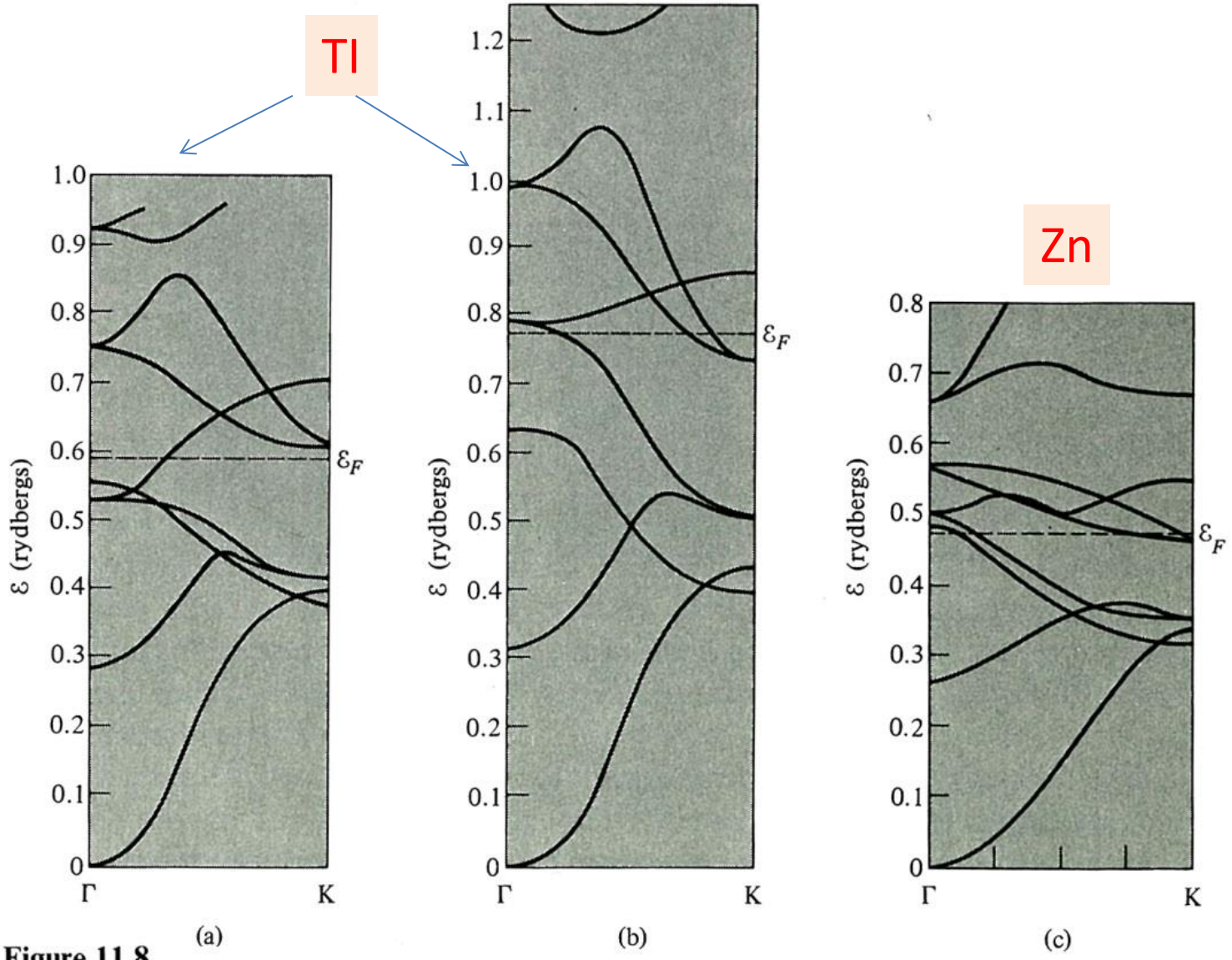


Figure 11.8
Three calculated band structures for titanium. Curves (a) and (b) were calculated by the cellular method for two possible potentials. They are taken from S. L. Altmann, in *Soft X-Ray Band Spectra*, D. Fabian (ed.), Academic Press—London, 1968. Curve (c) is from the APW calculation of Mattheis.

THE ORTHOGONALIZED PLANE-WAVE METHOD (OPW)

An alternative method of combining rapid oscillations in the ion core region with plane-wavelike behavior interstitially, is the method of orthogonalized plane waves, due to Herring.[25] The OPW method does *not* require a muffin-tin potential to make calculations feasible, and is therefore of particular value if one insists on using an undoctored potential. In addition, the method affords some insight into why the nearly free electron approximation does so remarkably well in predicting the band structures of a variety of metals.

We begin by explicitly distinguishing between the core electrons and the valence electrons. The core wave functions are well localized about the lattice sites. The valence electrons, on the other hand, can be found with appreciable probability in the interstitial regions, where our hope is that their wave functions will be well approximated be a very small number of plane waves. Throughout this and the next section we shall affix superscripts c or v to wave functions to indicate whether they describe core or valence levels.

The difficulty with approximating a valence wave function by a few plane waves *everywhere* in space (as in the nearly free electron method) is that this hopelessly fails to produce the rapid oscillatory behavior required in the core region. Herring noted that this could be taken care of by using not simple plane waves, but plane waves orthogonalized to the core levels right from the start. Thus we define the *orthogonalized* plane wave (OPW) $\phi_{\mathbf{k}}$ by:

$$\phi_{\mathbf{k}} = e^{i\mathbf{k}\cdot\mathbf{r}} + \sum_c b_c \psi_{\mathbf{k}}^c(\mathbf{r}), \tag{11.24}$$

where the sum is over *all* core levels with Bloch wave vector $\mathbf{k}$. The core wave functions are assumed to be known (generally they are taken to be tight-binding combinations of calculated atomic levels), and the constants b_c are determined by requiring that $\phi_{\mathbf{k}}$ be orthogonal to every core level:[26]

$$\int d\mathbf{r}\ \psi_{\mathbf{k}}^{c*}(\mathbf{r})\phi_{\mathbf{k}}(\mathbf{r}) = 0, \tag{11.25}$$

which implies that

$$b_c = -\int d\mathbf{r}\ \psi_{\mathbf{k}}^{c*}(\mathbf{r})e^{i\mathbf{k}\cdot\mathbf{r}}. \tag{11.26}$$

The OPW $\phi_{\mathbf{k}}$ has the following properties characteristic of valence level wave functions:

1. By explicit construction it is orthogonal to all the core levels. It therefore also has the required rapid oscillations in the core region. This is particularly evident from (11.24), since the core wave functions $\psi_{\mathbf{k}}^{c}(\mathbf{r})$ appearing in $\phi_{\mathbf{k}}$ themselves oscillate in the core region.
2. Because the core levels are localized about lattice points, the second term in (11.24) is small in the interstitial region, where $\phi_{\mathbf{k}}$ is very close to the single plane wave $e^{i\mathbf{k}\cdot\mathbf{r}}$.

Since the plane wave $e^{i\mathbf{k}\cdot\mathbf{r}}$ and the core wave functions $\psi_{\mathbf{k}}^{c}(\mathbf{r})$ satisfy the Bloch condition with wave vector $\mathbf{k}$, so will the OPW $\phi_{\mathbf{k}}$. We may therefore, as in the APW method, seek an expansion of the actual electronic eigenstates of the Schrödinger equation as linear combinations of OPW's:

$$\psi_{\mathbf{k}} = \sum_{\mathbf{K}} c_{\mathbf{K}} \phi_{\mathbf{k}+\mathbf{K}}. \tag{11.27}$$

As in the APW method, we can determine the coefficients $c_{\mathbf{K}}$ in (11.27) and the energies $\mathcal{E}(\mathbf{k})$ by inserting (11.27) into the variational principle (11.17), and requiring that the derivatives of the resulting expression with respect to all the $c_{\mathbf{K}}$'s vanish. The crystal potential $U(\mathbf{r})$ will enter into the resulting secular problem only through its OPW matrix elements:

$$\int \phi^*_{\mathbf{k}+\mathbf{K}}(\mathbf{r}) U(\mathbf{r}) \phi_{\mathbf{k}+\mathbf{K}'}(\mathbf{r})\, d\mathbf{r}. \tag{11.28}$$

The OPW method owes its success to the fact that although the plane-wave matrix elements of U are large, its OPW matrix elements turn out to be much smaller. Therefore, although it is hopeless to try to get convergence by expanding $\psi_{\mathbf{k}}$ in plane waves, the convergence of the expansion in OPW's is very much faster.

THE PSEUDOPOTENTIAL

The theory of the pseudopotential began as an extension of the OPW method. Aside from the possibility it offers of refining OPW calculations, it also provides at least a partial explanation for the success of nearly free electron calculations in fitting actual band structures.

We describe the pseudopotential method only in its earliest formulation,[28] which is basically a recasting of the OPW approach. Suppose that we write the exact wave function for a valence level as a linear combination of OPW's, as in (11.27). Let $\phi_{\mathbf{k}}^{v}$ be the plane-wave part of this expansion:

Pseudo-potential function

$$\phi_{\mathbf{k}}^{v}(\mathbf{r}) = \sum_{\mathbf{K}} c_{\mathbf{K}} e^{i(\mathbf{k}+\mathbf{K})\cdot\mathbf{r}}. \tag{11.29}$$

Then we can rewrite the expansions (11.27) and (11.24) as

$$\psi_{\mathbf{k}}^{v}(\mathbf{r}) = \phi_{\mathbf{k}}^{v}(\mathbf{r}) - \sum_{c} \left(\int d\mathbf{r}'\, \psi_{\mathbf{k}}^{c*}(\mathbf{r}')\phi_{\mathbf{k}}^{v}(\mathbf{r}') \right) \psi_{\mathbf{k}}^{c}(\mathbf{r}). \tag{11.30}$$

Since $\psi_{\mathbf{k}}^{v}$ is an exact valence wave function, it satisfies Schrödinger's equation with eigenvalue $\mathcal{E}_{\mathbf{k}}^{v}$:

$$H\psi_{\mathbf{k}}^{v} = \mathcal{E}_{\mathbf{k}}^{v}\psi_{\mathbf{k}}^{v}. \tag{11.31}$$

Substitution of (11.30) into (11.31) gives

$$H\phi_{\mathbf{k}}^{v} - \sum_{c} \left(\int d\mathbf{r}'\, \psi_{\mathbf{k}}^{c*}\phi_{\mathbf{k}}^{v} \right) H\psi_{\mathbf{k}}^{c} = \mathcal{E}_{\mathbf{k}}^{v} \left(\phi_{\mathbf{k}}^{v} - \sum_{c} \left(\int d\mathbf{r}'\, \psi_{\mathbf{k}}^{c*}\phi_{\mathbf{k}}^{v} \right) \psi_{\mathbf{k}}^{c} \right). \tag{11.32}$$

If we note that $H\psi_{\mathbf{k}}{}^{c} = \mathcal{E}_{\mathbf{k}}{}^{c}\psi_{\mathbf{k}}{}^{c}$ for the exact core levels, then we can rewrite (11.32) as

$$(H + V^R)\phi_{\mathbf{k}}{}^{v} = \mathcal{E}_{\mathbf{k}}{}^{v}\phi_{\mathbf{k}}{}^{v}, \tag{11.33}$$

where we have buried some rather cumbersome terms in the operator V^R, which is defined by

$$V^R\psi = \sum_c (\mathcal{E}_{\mathbf{k}}{}^{v} - \mathcal{E}_c)\left(\int d\mathbf{r}'\, \psi_{\mathbf{k}}^{c*}\psi\right)\psi_{\mathbf{k}}{}^{c}. \tag{11.34}$$

We have therefore arrived at an effective Schrödinger equation (11.33) satisfied by $\phi_{\mathbf{k}}{}^{v}$, the smooth part of the Bloch function. Since experience with the OPW method suggests that $\phi_{\mathbf{k}}{}^{v}$ can be approximated by a linear combination of a small number of plane waves, we might expect that the nearly free electron theory of Chapter 9 could be applied to finding the valence levels of $H + V_R$. This is the starting point for pseudopotential calculation and analysis.

The *pseudopotential* is defined to be the sum of the actual periodic potential U, and V^R:

$V^{pseudo} = U + V^R$

$$H + V^R = -\frac{\hbar^2}{2m}\nabla^2 + V^{\text{pseudo}}. \tag{11.35}$$

The hope is that the pseudopotential is sufficiently small to justify a nearly free electron calculation of the valence levels. One can see a hint that this might be so from the fact that although the actual periodic potential is attractive near the ion cores, and thus $(\psi, U\psi) = \int d\mathbf{r}\, \psi^*(\mathbf{r})U(\mathbf{r})\psi(\mathbf{r})$ is negative, the corresponding matrix element of the potential V^R is, according to (11.34),

$$(\psi, V^R\psi) = \sum_c (\mathcal{E}_{\mathbf{k}}^v - \mathcal{E}_{\mathbf{k}}^c) \left| \int d\mathbf{r}\, \psi_{\mathbf{k}}^{c*}\psi \right|^2. \tag{11.36}$$

Since the valence energies lie above the core energies, this is always positive. Thus adding V^R to U provides at least a partial cancellation, and one might optimistically hope for it to lead to a potential weak enough to do nearly free electron calculations for $\phi_{\mathbf{k}}^v$ (the so-called pseudo wave function), treating the pseudopotential as a weak perturbation.

There are some peculiar features to the pseudopotential. Equation (11.34) implies that V^R (and hence the pseudopotential) is nonlocal; i.e., its effect on a wave function $\psi(\mathbf{r})$ is not merely to multiply it by some function of $\mathbf{r}$. In addition, the pseudopotential depends on the energy of the level being sought, $\varepsilon_{\mathbf{k}}^{v}$, which means that many of the basic theorems one is used to applying without further thought (such as the orthogonality of eigenfunctions belonging to different eigenvalues) are no longer applicable to H^{pseudo}.

The second difficulty can be removed by setting $\varepsilon_{\mathbf{k}}^{v}$ in (11.34) and in V^{pseudo} equal to the energy of the levels one is most interested in—generally the Fermi energy. Of course, once this replacement has been made, the eigenvalues of $H + V^R$ are no longer exactly those of the original Hamiltonian, except for the levels at the Fermi energy. Since these are frequently the levels of greatest interest, this need not be too great a price to pay. For example, one can, in this way, find the set of $\mathbf{k}$ for which $\varepsilon_{\mathbf{k}}^{v} = \varepsilon_F$, thereby mapping out the Fermi surface.

There turn out to be many ways other than (11.34) to define a V^R such that $H + V^R$ has the same *valence* eigenvalues as the actual crystal Hamiltonian H. From such choices has arisen a wealth of pseudopotential lore, whose usefulness for anything other than justifying the nearly free electron Fermi surfaces has yet to be convincingly established.[29]

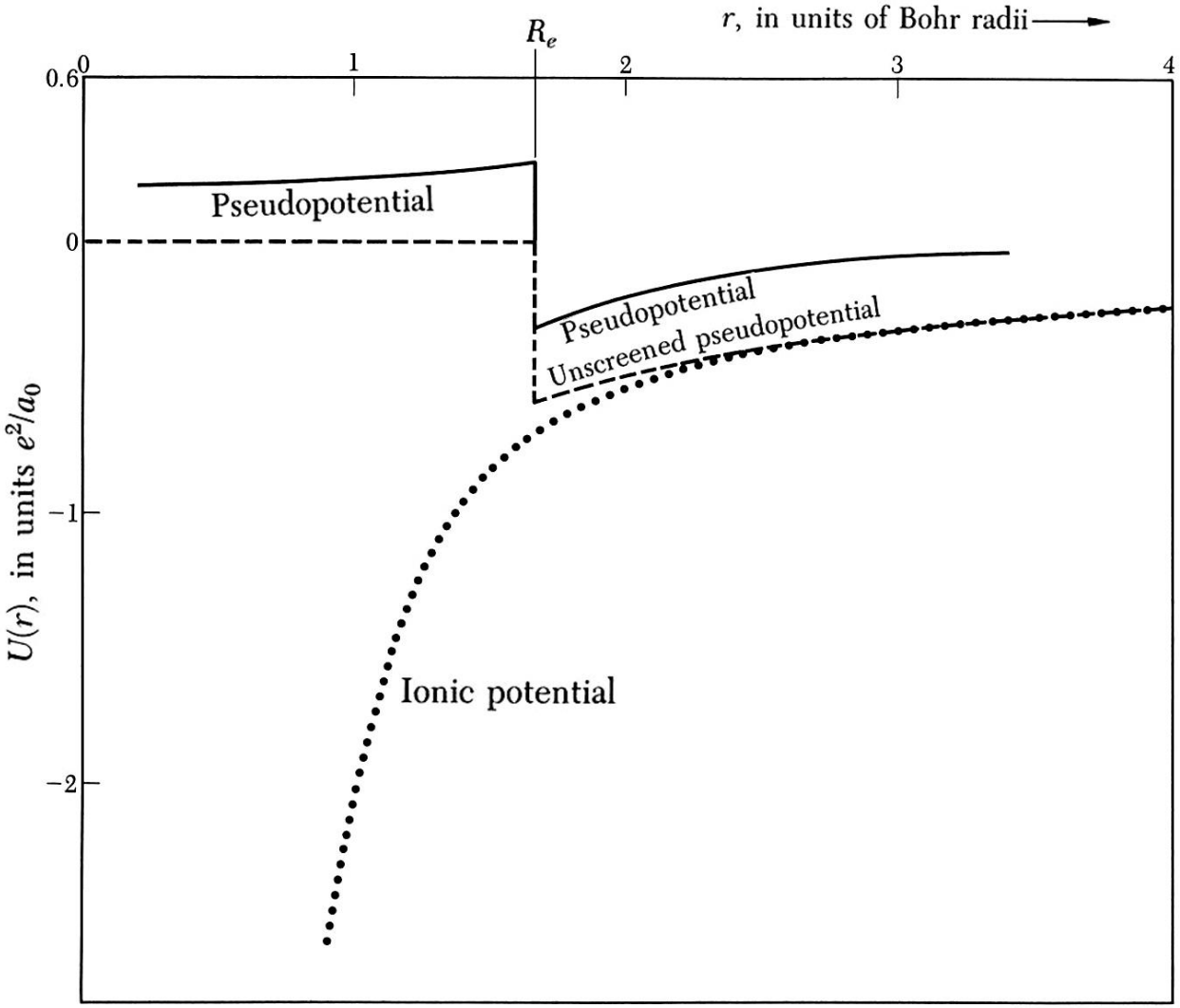


Figure 22a Pseudopotential for metallic sodium, based on the empty core model and screened by the Thomas-Fermi dielectric function. The calculations were made for an empty core radius $R_e = 1.66a_0$, where a_0 is the Bohr radius, and for a screening parameter $k_s a_0 = 0.79$. The dashed curve shows the assumed unscreened potential, as from (21). The dotted curve is the actual potential of the ion core; other values of $U(r)$ are -50.4, -11.6, and -4.6, for $r = 0.15$, 0.4, and 0.7, respectively. Thus the actual potential of the ion (chosen to fit the energy levels of the free atom) is very much larger than the pseudopotential, over 200 times larger at $r = 0.15$.

THE GREEN'S FUNCTION METHOD OF KORRINGA, KOHN, AND ROSTOKER (KKR)

An alternative approach to the muffin-tin potential is provided by a method due to Korringa and to Kohn and Rostoker.[21] This starts from the integral form of the Schrödinger equation[22]

$$\psi_{\mathbf{k}}(\mathbf{r}) = \int d\mathbf{r}'\, G_{\varepsilon(\mathbf{k})}(\mathbf{r} - \mathbf{r}')U(\mathbf{r}')\psi_{\mathbf{k}}(\mathbf{r}'), \tag{11.18}$$

where the integral is over all space and

$$\begin{aligned} G_{\varepsilon}(\mathbf{r} - \mathbf{r}') &= -\frac{2m}{\hbar^2}\frac{e^{iK|\mathbf{r}-\mathbf{r}'|}}{4\pi|\mathbf{r} - \mathbf{r}'|}, \\ K &= \sqrt{2m\varepsilon/\hbar^2}, \qquad \varepsilon > 0, \\ &= i\sqrt{2m(-\varepsilon)/\hbar^2}, \qquad \varepsilon < 0. \end{aligned} \tag{11.19}$$

Substituting the form (11.14) for the muffin-tin potential into (11.18), and making the change of variables $\mathbf{r}'' = \mathbf{r}' - \mathbf{R}$ in each term of the resulting sum, we can rewrite (11.18) as

$$\psi_{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{R}} \int d\mathbf{r}''\, G_{\varepsilon(\mathbf{k})}(\mathbf{r} - \mathbf{r}'' - \mathbf{R})V(r'')\psi_{\mathbf{k}}(\mathbf{r}'' + \mathbf{R}). \tag{11.20}$$

The Bloch condition gives $\psi_{\mathbf{k}}(\mathbf{r}'' + \mathbf{R}) = e^{i\mathbf{k}\cdot\mathbf{R}}\psi_{\mathbf{k}}(\mathbf{r}'')$, and we can therefore rewrite (11.20) (replacing $\mathbf{r}''$ by $\mathbf{r}'$):

$$\psi_{\mathbf{k}}(\mathbf{r}) = \int d\mathbf{r}'\, \mathcal{G}_{\mathbf{k},\mathcal{E}(\mathbf{k})}(\mathbf{r} - \mathbf{r}')V(r')\psi_{\mathbf{k}}(\mathbf{r}'), \tag{11.21}$$

where

$$\mathcal{G}_{\mathbf{k},\mathcal{E}}(\mathbf{r} - \mathbf{r}') = \sum_{\mathbf{R}} G_{\mathcal{E}}(\mathbf{r} - \mathbf{r}' - \mathbf{R})e^{i\mathbf{k}\cdot\mathbf{R}}. \tag{11.22}$$

Equation (11.21) has the pleasing feature that *all* of the dependence on both wave vector $\mathbf{k}$ and crystal structure is contained in the function $\mathcal{G}_{\mathbf{k},\mathcal{E}}$, which can be calculated, once and for all, for a variety of crystal structures for specified values of $\mathcal{E}$ and $\mathbf{k}$.[23] It is shown in Problem 3 that Eq. (11.21) implies that on the sphere of radius r_0, the values of $\psi_{\mathbf{k}}$ are constrained to satisfy the following integral equation:

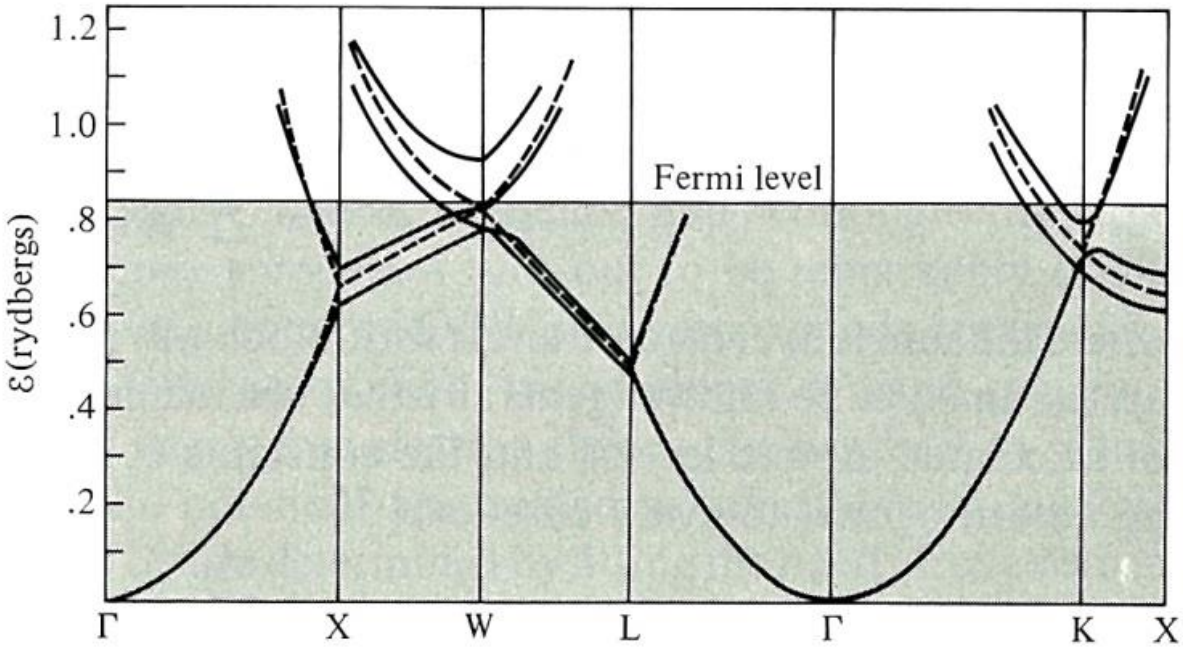
$$0 = \int d\Omega' \left[\mathcal{G}_{\mathbf{k},\mathcal{E}(\mathbf{k})}(r_0\theta\phi, r_0\theta'\phi') \frac{\partial}{\partial r} \psi(r\theta'\phi') \Big|_{r=r_0} - \psi(r_0\theta'\phi') \frac{\partial}{\partial r} \mathcal{G}_{\mathbf{k},\mathcal{E}(\mathbf{k})}(r_0\theta\phi, r\theta'\phi') \Big|_{r=r_0} \right]. \tag{11.23}$$

Since the function $\psi_{\mathbf{k}}$ is continuous, it retains the form determined by the atomic problem (Eqs. (11.9) to (11.11)) at r_0. The approximation of the KKR method (which is exact for the muffin-tin potential up to this point) is to assume that $\psi_{\mathbf{k}}$ will be given to a reasonable degree of accuracy by keeping only a finite number (say N) of spherical harmonics in the expansion (11.11). By placing this truncated expansion in (11.23), multiplying by $Y_{lm}(\theta, \phi)$, and integrating the result over the solid angle $d\theta\, d\phi$ for all l and m appearing in the truncated expansion, we obtain a set of N linear equations for the A_{lm} appearing in the expansion (11.11). The coefficients in these equations depend on $\mathcal{E}(\mathbf{k})$ and $\mathbf{k}$ through $\mathcal{G}_{\mathbf{k},\mathcal{E}(\mathbf{k})}$ and through the radial wave function $\chi_{l,\mathcal{E}}$ and its derivative $\chi'_{l,\mathcal{E}}$. Setting the $N \times N$ determinant of the coefficients equal to zero once again gives an equation determining the relation between $\mathcal{E}$ and $\mathbf{k}$. As in the methods described earlier, one can either search for values of $\mathcal{E}$ giving a solution for fixed $\mathbf{k}$, or fix $\mathcal{E}$ and map out the surface in $\mathbf{k}$-space at which the determinant vanishes, which will then give the constant-energy surface $\mathcal{E}(\mathbf{k}) = \mathcal{E}$.

Both the KKR and APW methods can be regarded as techniques which, if carried out exactly for the muffin-tin potential, would lead to infinite-order determinantal conditions. These are then approximated by taking only a finite subdeterminant. In the APW method the truncation is in **K**; the wave function is approximated in the interstitial region. In KKR, on the other hand, the sum over all **K** is effectively performed when $\mathcal{G}_{\mathbf{k},\varepsilon}$ is computed.[24] Instead, the approximation is in the form of the wave function in the atomic region. In both cases the procedure converges well if sufficiently many terms are retained; in practice the KKR method appears to require fewer terms in the spherical harmonic expansion than the APW technique requires in the **K** expansion. When the APW and KKR methods are applied to the same muffin-tin potential, they give results in substantial agreement.

The results of a KKR calculation for the $3s^2$ and $3p^1$ derived bands of aluminum are displayed in Figure 11.9. Note the extraordinary resemblance of the calculated bands to the free electron levels, plotted as dashed lines in the same figure. The only discernible effects of the interaction between electrons and ions are, as predicted by nearly free electron theory, to split the band degeneracies. This is a striking illustration of our observation (see page 152) that metals whose atomic configuration consists of a small number of *s* and *p* electrons outside of a rare-gas configuration have band structures that can be reproduced very well by the nearly free electron bands. The next two methods to be discussed attempt to shed some light on this remarkable fact.

Figure 11.9
Calculated valence bands for aluminum (three electrons outside of a closed-shell neon configuration) compared with *free* electron bands (dashed lines). The bands are computed by the KKR method. (B. Segall, *Phys. Rev.* **124**, 1797 (1961).)



On the other hand, one frequently encounters "calculations" of band structure that appear to be nothing but the nearly free electron theory of Chapter 9, in which the Fourier components $U_{\mathbf{K}}$ of the potential are treated as adjustable parameters rather than known quantities. The $U_{\mathbf{K}}$ are determined by fitting the nearly free electron bands either to empirical data or to the bands calculated in detail by one of the more realistic methods. As an example of this, the KKR bands for aluminum, shown in Figure 11.9, can be reproduced with remarkable precision throughout the zone by a nearly free electron calculation that uses only four plane waves and requires only two parameters[27]: U_{111} and U_{200}.

Since nearly free electron theory surely cannot work so well, it must be that the apparently nearly free electron secular problem is actually the final stage of a much more complicated analysis, such as that of the OPW method, the Fourier components $U_{\mathbf{K}}$ being OPW rather than plane-wave matrix elements of the potential. One therefore refers to such a calculation as an OPW calculation. In this context, however, such a designation is little more than a reminder that although the analysis is formally identical to nearly free electron theory, it can be placed on a more secure theoretical footing.

It is not at all clear, however, that the OPW approach is the best way to reduce the actual problem of an electron in a periodic potential to an effectively "nearly free" electron calculation. A more systematic way of studying this problem, as well as a variety of additional calculational approaches, is offered by the *pseudopotential methods.*