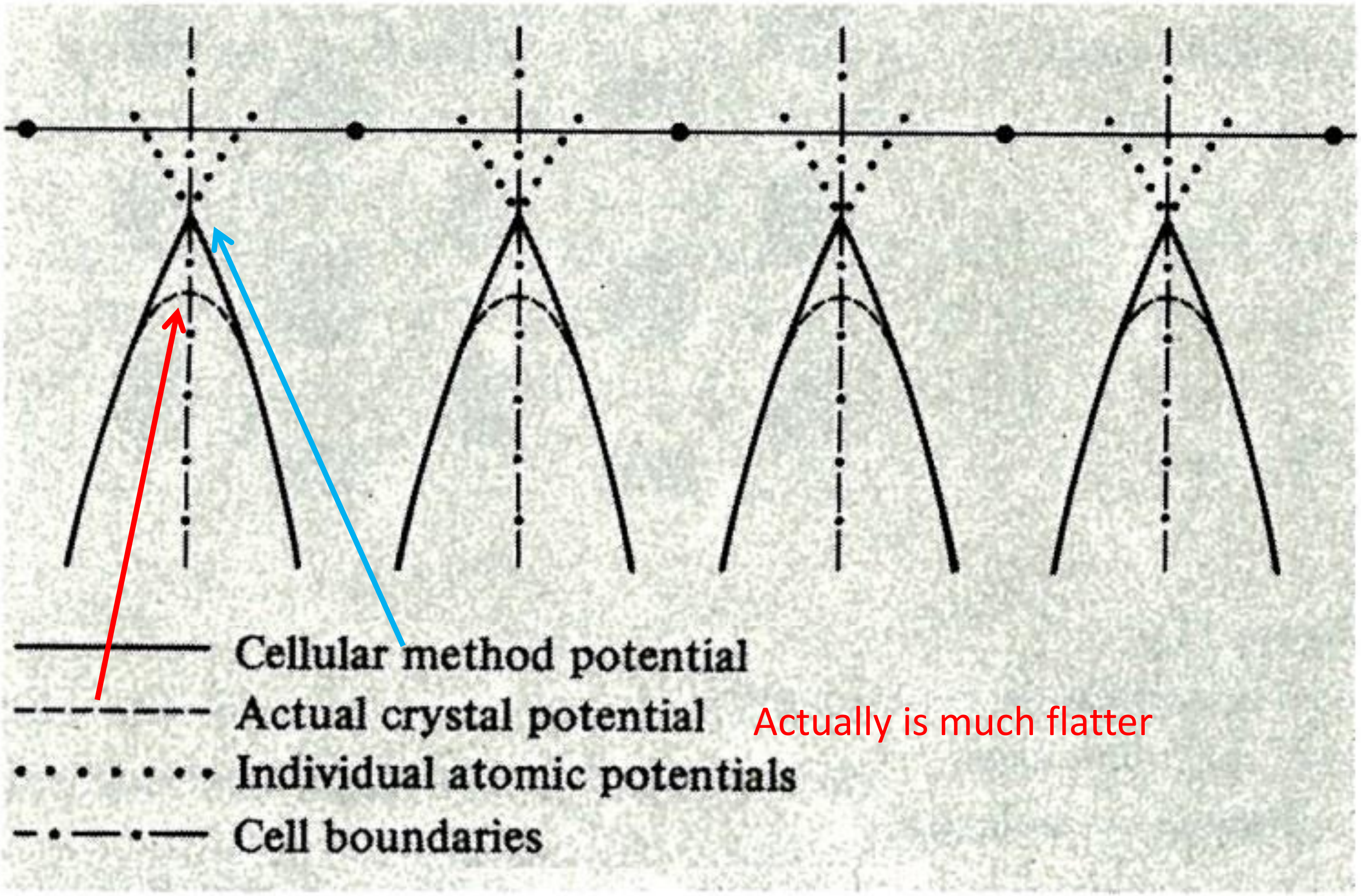
Chapter 11

Other Methods for Calculating Band Structure

Part II



Actually is much flatter

Figure 11.5
The cellular method potential has a discontinuous derivative midway between lattice points, but the actual potential is quite flat there.

A potential that overcomes both objections is the *muffin-tin potential*, which is taken to represent an isolated ion within a sphere of specified radius r_0 about each lattice point, and taken to be zero (i.e., constant) elsewhere (with r_0 chosen small enough that the spheres do not overlap). (See Figure 11.6.) The muffin-tin potential mitigates both problems, being flat in the interstitial regions, and leading to matching conditions on a spherical rather than a polyhedral surface.

Formally, the muffin-tin potential can be defined (for all **R**) by:

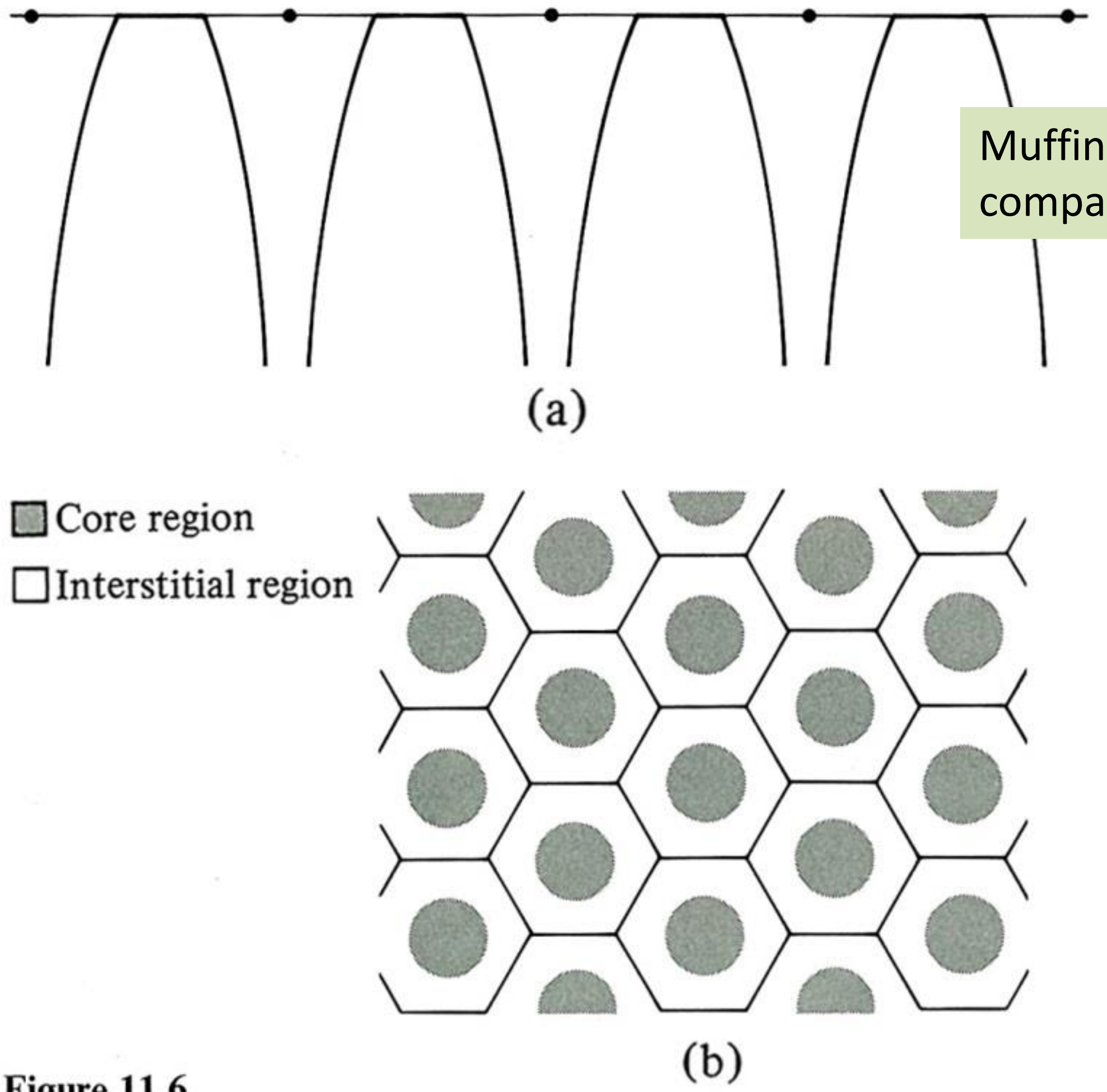
$$\begin{aligned} U(\mathbf{r}) &= V(|\mathbf{r}-\mathbf{R}|), \quad && \text{when } |\mathbf{r}-\mathbf{R}| < r_0 \quad && \text{(the \textit{core} or \textit{atomic region}),} \\ &= V(r_0) = 0, && \text{when } |\mathbf{r}-\mathbf{R}| > r_0 && \text{(the \textit{interstitial region}),} \end{aligned} \qquad \textbf{(11.13)}$$

where r_0 is less than half the nearest-neighbor distance.[13]

If we agree that the function $V(r)$ is zero when its argument exceeds r_0, then we can write $U(\mathbf{r})$ very simply as

$$U(\mathbf{r}) = \sum_{\mathbf{R}} V(|\mathbf{r}-\mathbf{R}|). \qquad \textbf{(11.14)}$$

Two methods are in wide use for computing the bands in a muffin-tin potential: the augmented plane-wave (APW) method and the method of Korringa, Kohn, and Rostoker (KKR).



Muffin tin potential, compare with Fig. 11.5

Figure 11.6

(a) The muffin-tin potential, plotted along a line of ions. (b) The muffin-tin potential is constant (zero) in the interstitial regions and represents an isolated ion in each core region.

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, $\varepsilon = \hbar^2 k^2/2m$). 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:

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

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 $\phi_{\mathbf{k},\mathcal{E}}$ for all $\mathbf{k}$ and $\mathcal{E}$. Note that in the interstitial region the APW satisfies not (11.15) but $H\phi_{\mathbf{k},\mathcal{E}} = (\hbar^2 k^2/2m)\phi_{\mathbf{k},\mathcal{E}}$. Note also that, in general, $\phi_{\mathbf{k},\mathcal{E}}$ will have a discontinuous derivative on the boundary between interstitial and atomic regions, so that $\nabla^2\phi_{\mathbf{k},\mathcal{E}}$ 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 $\phi_{\mathbf{k}+\mathbf{K},\mathcal{E}}$ 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

$$\boxed{\psi_{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{K}} c_{\mathbf{K}}\phi_{\mathbf{k}+\mathbf{K},\mathcal{E}(\mathbf{k})}(\mathbf{r}),} \qquad \textbf{(11.16)}$$

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, $\mathcal{E}(\mathbf{k})$ 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.

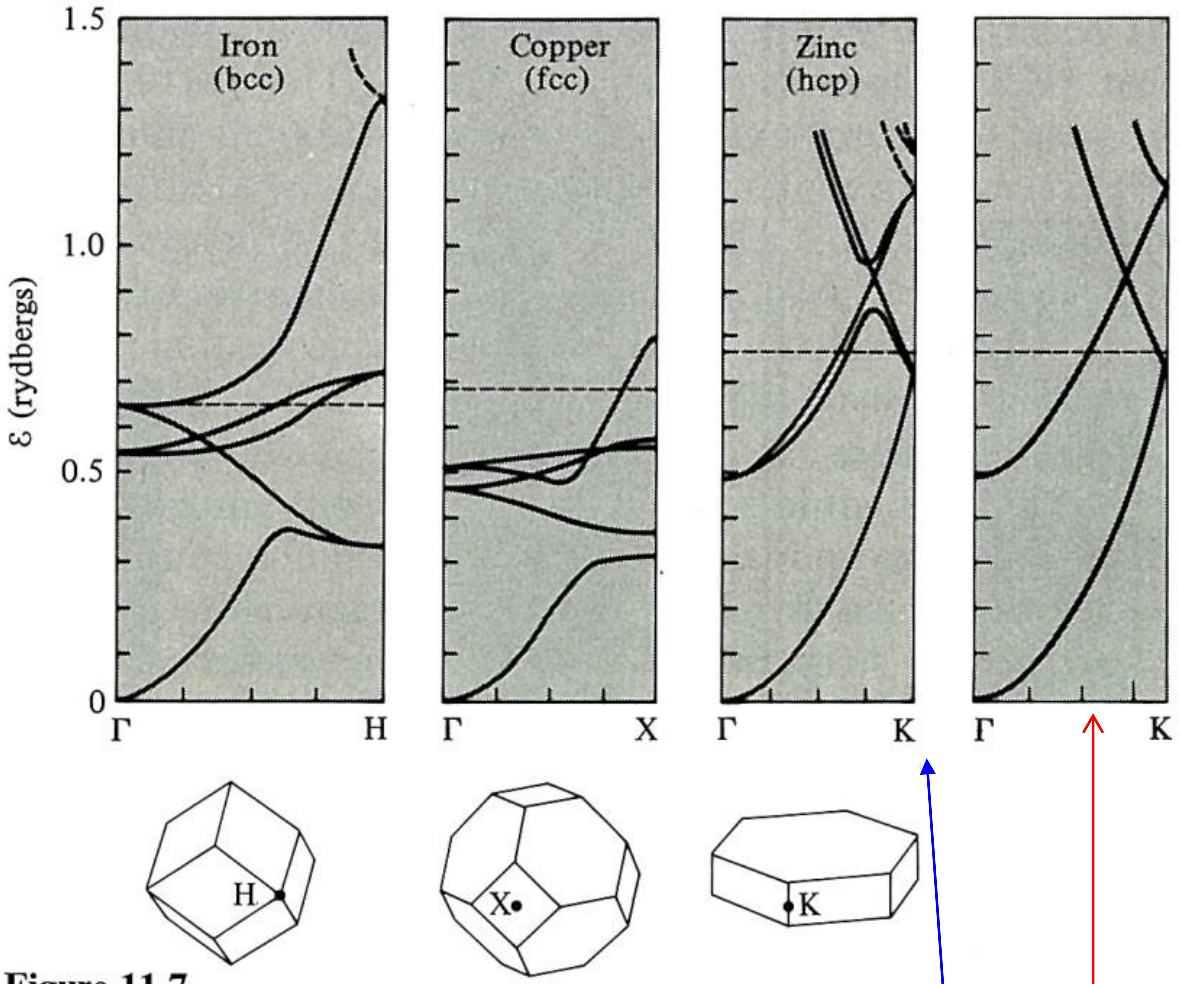


Figure 11.7

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.

Ti, Cellular method

Ti, APW

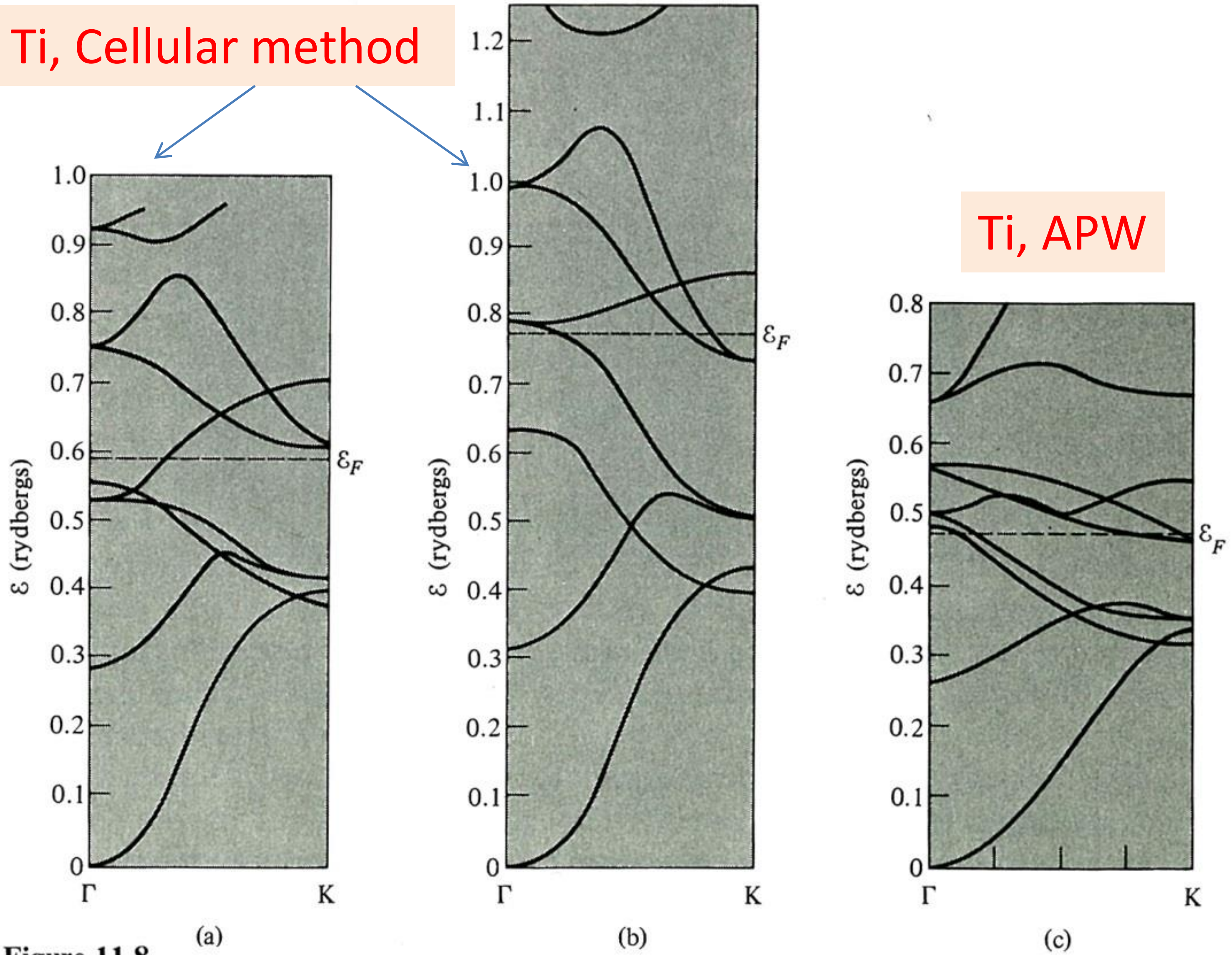


Figure 11.8
Three calculated band structures for titanium. Curves (a) and (b) were calculated by the cellular method for two possible potentials. They are taken from S. L. Altmann, in *Soft X-Ray Band Spectra*, D. Fabian (ed.), Academic Press—London, 1968. Curve (c) is from the APW calculation of Mattheis.

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:

OPW Valence wave function

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

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]

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

which implies that

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

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 **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:

$$\psi_{\mathbf{k}} = \sum_{\mathbf{K}} c_{\mathbf{K}} \phi_{\mathbf{k}+\mathbf{K}}. \qquad \textbf{(11.27)}$$

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.

Pseudopotential Methods

(Kittel Chapter 9)

Conduction electron wavefunctions are usually smoothly varying in the region between the ion cores, but have a complicated nodal structure in the region of the cores. This behavior is illustrated by the ground orbital of sodium, Fig. 19. It is helpful to view the nodes in the conduction electron wavefunction in the core region as created by the requirement that the function be orthogonal to the wavefunctions of the core electrons. This all comes out of the Schrödinger equation, but we can see that we need the flexibility of two nodes in the 3*s* conduction orbital of Na in order to be orthogonal both to the 1*s* core orbital with no nodes and the 2*s* core orbital with one node.

Outside the core the potential energy that acts on the conduction electron is relatively weak: the potential energy is only the coulomb potential of the singly-charged positive ion cores and is reduced markedly by the electrostatic screening of the other conduction electrons, Chapter 10. In this outer region the conduction electron wavefunctions are as smoothly varying as plane waves.

If the conduction orbitals in this outer region are approximately plane waves, the energy must depend on the wavevector approximately as $\epsilon_{\mathbf{k}} = \hbar^2 k^2/2m$ as for free electrons. But how do we treat the conduction orbitals in the core region where the orbitals are not at all like plane waves?

What goes on in the core is largely irrelevant to the dependence of ϵ on $\mathbf{k}$. Recall that we can calculate the energy by applying the hamiltonian operator to an orbital at any point in space. Applied in the outer region, this operation will give an energy nearly equal to the free electron energy.

This argument leads naturally to the idea that we might replace the actual potential energy (and filled shells) in the core region by an effective potential energy[1] that gives the same wavefunctions outside the core as are given by the actual ion cores. It is startling to find that the effective potential or pseudopotential that satisfies this requirement is nearly zero. This conclusion about pseudopotentials is supported by a large amount of empirical experience as well as by theoretical arguments. The result is referred to as the **cancellation theorem**.

Empty Core Model

The pseudopotential for a problem is not unique nor exact, but it may be very good. On the Empty Core Model (ECM) we can even take the unscreened pseudopotential to be zero inside some radius R_e:

$$\boxed{U(r) = \begin{cases} 0 \quad , & \text{for } r < R_e \ ; \\ -e^2/r \ , & \text{for } r > R_e \ . \end{cases}} \tag{21}$$

This potential should now be screened as described in Chapter 10. Each component $U(\mathbf{K})$ of $U(r)$ is to be divided by the dielectric constant $\epsilon(\mathbf{K})$ of the electron gas. If, just as an example, we use the Thomas-Fermi dielectric function (10.33), we obtain the screened pseudopotential plotted in Fig. 22a.

The pseudopotential as drawn is much weaker than the true potential, but the pseudopotential was adjusted so that the wavefunction in the outer region is nearly identical to that for the true potential. In the language of scattering theory, we adjust the phase shifts of the pseudopotential to match those of the true potential.

Calculation of the band structure depends only on the Fourier components of the pseudopotential at the reciprocal lattice vectors. Usually only a few values of the coefficients $U(\mathbf{G})$ are needed to get a good band structure: see the $U(\mathbf{G})$ in Fig. 22b. These coefficients are sometimes calculated from model potentials, and sometimes they are obtained from fits of tentative band structures to the results of optical measurements. Good values of $U(0)$ can be estimated from first principles; it is shown in (10.43) that for a screened Coulomb potential $U(0) = -\frac{2}{3}\epsilon_F$.

In the remarkably successful Empirical Pseudopotential Method (EPM) the band structure is calculated using a few coefficients $U(\mathbf{G})$ deduced from theoretical fits to measurements of the optical reflectance and absorption of crystals, as discussed in Chapter 11. Tables of values of $U(\mathbf{G})$ are given in the review by M. L. Cohen and V. Heine.

Charge density maps can be plotted from the wavefunctions generated by the EPM—see Fig. 3.11. The results are in excellent agreement with x-ray diffraction determinations; such maps give an understanding of the bonding and have great predictive value for proposed new structures and compounds.

The EPM values of the coefficients $U(\mathbf{G})$ often are additive in the contributions of the several types of ions that are present. Thus it may be possible to construct the $U(\mathbf{G})$ for entirely new structures, starting from results on known structures. Further, the pressure dependence of a band structure may be determined when it is possible to estimate from the form of the $U(r)$ curve the dependence of $U(\mathbf{G})$ on small variations of $\mathbf{G}$.

It is often possible to calculate band structures, cohesive energy, lattice constants, and bulk moduli from first principles. In such *ab initio* pseudopotential calculations the basic inputs are the crystal structure type and the atomic number, along with well-tested theoretical approximations to exchange energy terms. This is not the same as calculating from atomic number alone, but it is the most reasonable basis for a first-principles calculation. The results of M. T. Yin and M. L. Cohen, Phys. Rev. B **26**, 5668 (1982), are compared with experiment in the table that follows.

	Lattice constant (Å)	Cohesive energy (eV)	Bulk modulus (Mbar)
Silicon			
Calculated	5.45	4.84	0.98
Experimental	5.43	4.63	0.99
Germanium			
Calculated	5.66	4.26	0.73
Experimental	5.65	3.85	0.77
Diamond			
Calculated	3.60	8.10	4.33
Experimental	3.57	7.35	4.43

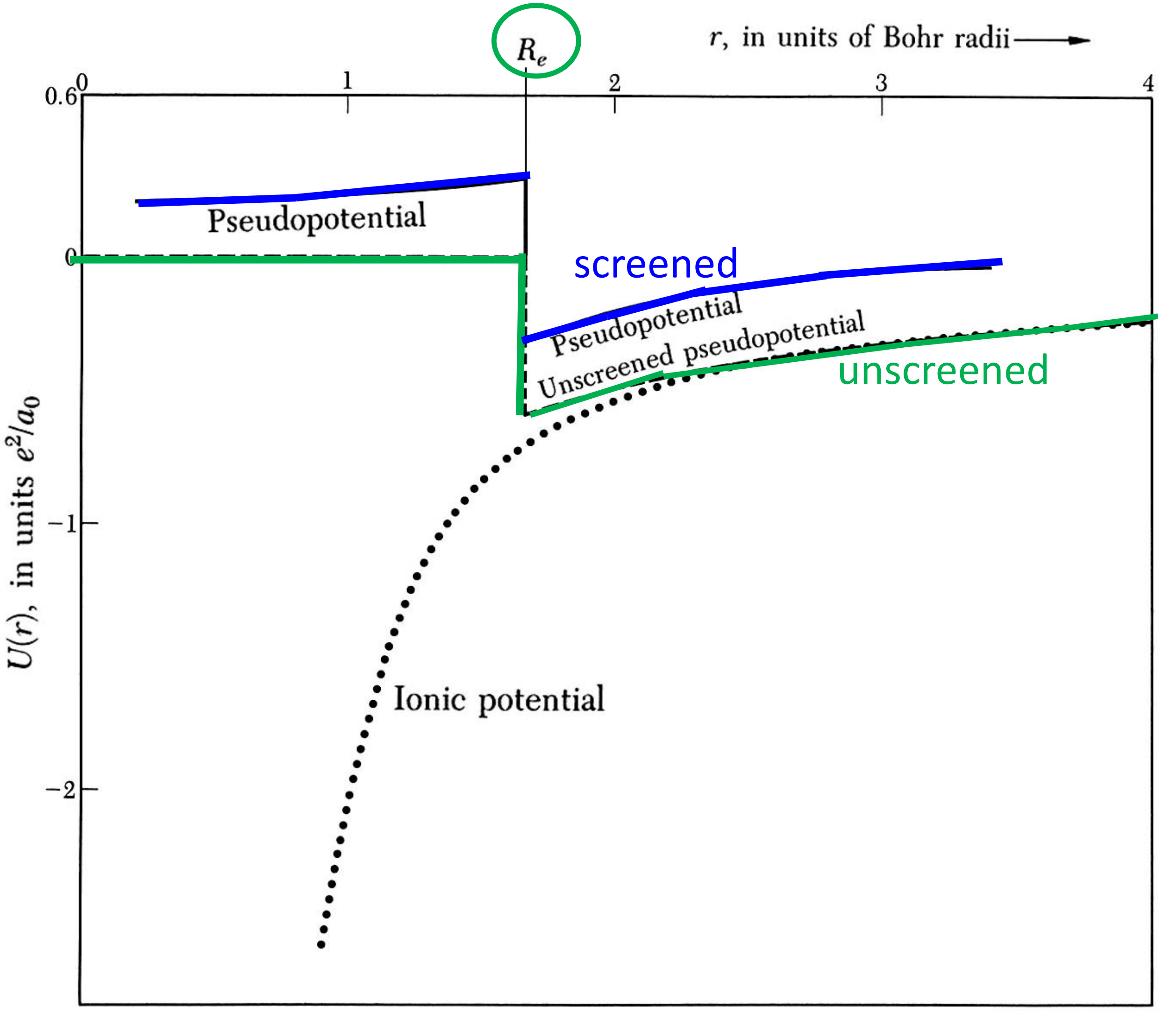


Figure 22a Pseudopotential for metallic sodium, based on the empty core model and screened by the Thomas-Fermi dielectric function. The calculations were made for an empty core radius $R_e = 1.66a_0$, where a_0 is the Bohr radius, and for a screening parameter $k_s a_0 = 0.79$. The dashed curve shows 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 $r = 0.15$.

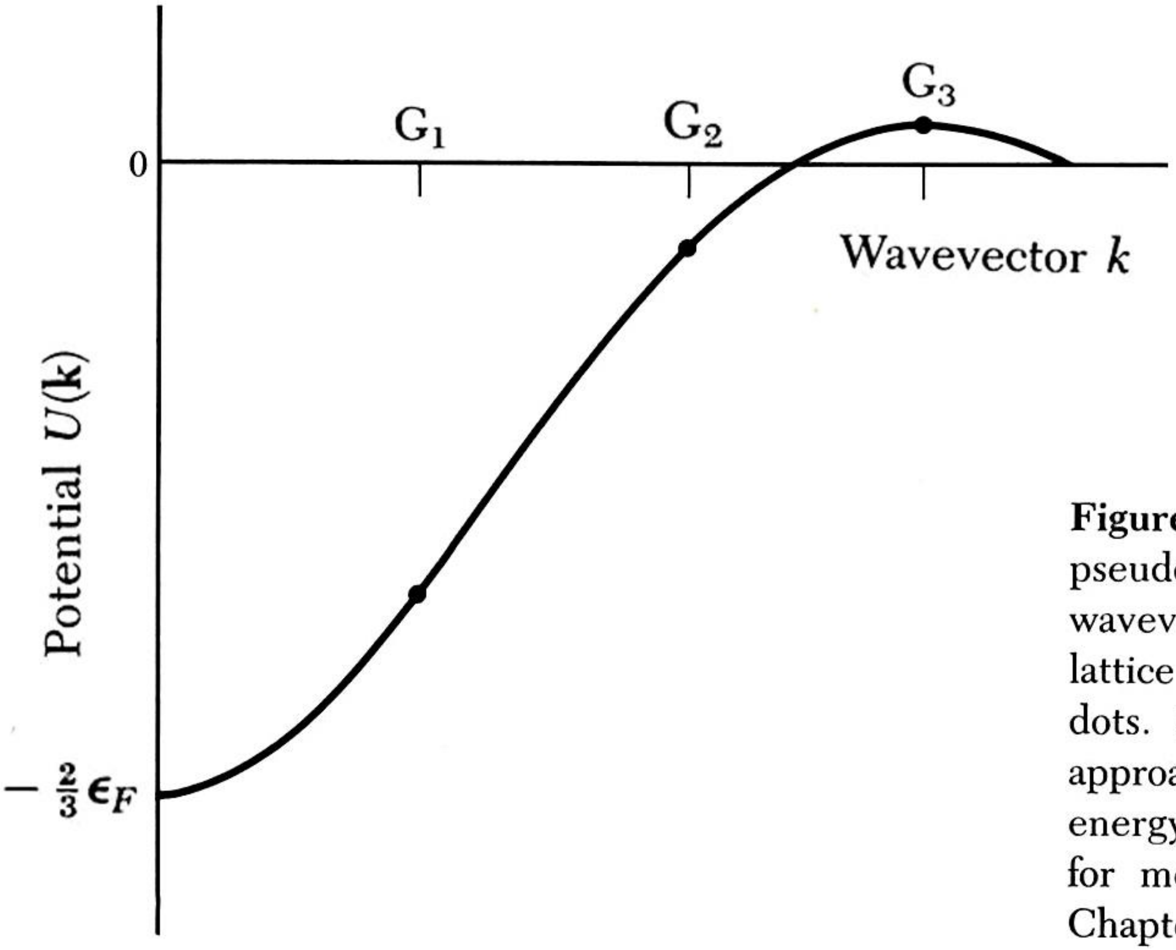


Figure 22b A typical reciprocal space pseudopotential. Values of $U(\mathbf{k})$ for wavevectors equal to the reciprocal lattice vectors, $\mathbf{G}$, are indicated by the dots. For very small $\mathbf{k}$ the potential approaches $(-2/3)$ times the Fermi energy, which is the screened-ion limit for metals. This limit is derived in Chapter 10. (After M. L. Cohen.)

THE PSEUDOPOTENTIAL

(AM Chapter 11)

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:

$\phi_k{}^v$: the plane-wave part of the exact valence wave function $\psi_k{}^v$

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

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

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

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

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

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 $H + \mathrm{V}_R$. 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:

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

$$V^{pseudo} = \underset{<0}{\underset{\downarrow}{U}} + \underset{>0}{\underset{\downarrow}{V^R}}$$

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, $\mathcal{E}_{\mathbf{k}}^{v}$, 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 $\mathcal{E}_{\mathbf{k}}^{v}$ 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 $\mathcal{E}_{\mathbf{k}}^{v} = \mathcal{E}_F$, 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]

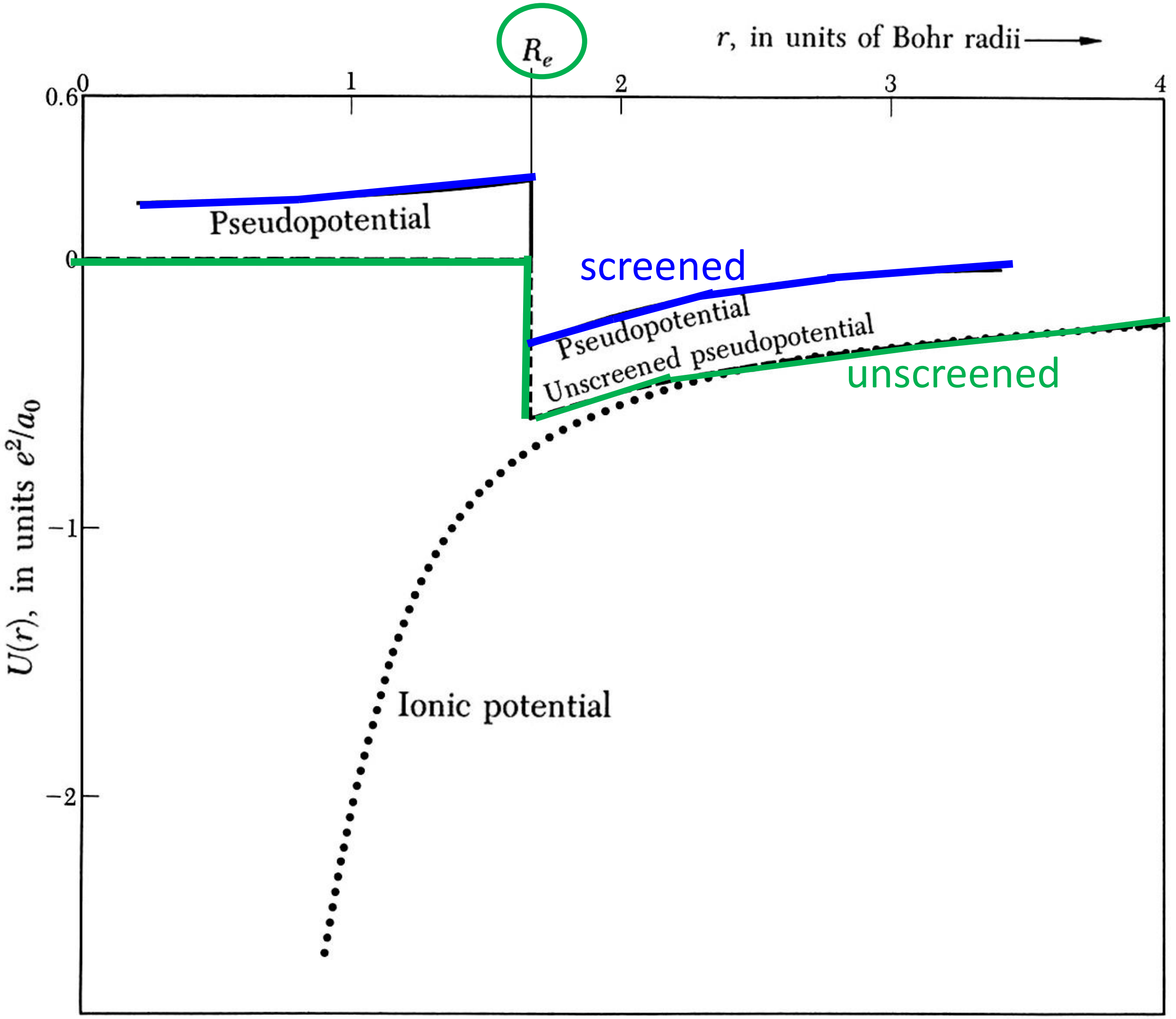


Figure 22a Pseudopotential for metallic sodium, based on the empty core model and screened by the Thomas-Fermi dielectric function. The calculations were made for an empty core radius $R_e = 1.66a_0$, where a_0 is the Bohr radius, and for a screening parameter $k_s a_0 = 0.79$. The dashed curve shows 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 $r = 0.15$.