Kittel
Chapter 9

Part 3

Wigner-Seitz Method

Wigner and Seitz showed that at least for the alkali metals there is no inconsistency between the electron wavefunctions of free atoms and the nearly free electron model of the band structure of a crystal. Over most of a band the energy may depend on the wavevector nearly as for a free electron. However, the Bloch wavefunction, unlike a plane wave, will pile up charge on the positive ion cores as in the atomic wavefunction.

A Bloch function satisfies the wave equation

$$\left(\frac{1}{2m}\mathbf{p}^2 + U(\mathbf{r})\right) e^{i\mathbf{k}\cdot\mathbf{r}} u_{\mathbf{k}}(\mathbf{r}) = \epsilon_{\mathbf{k}}\, e^{i\mathbf{k}\cdot\mathbf{r}} u_{\mathbf{k}}(\mathbf{r}) \ . \tag{16}$$

With $\mathbf{p} \equiv -i\hbar$ grad, we have

$$\mathbf{p}\, e^{i\mathbf{k}\cdot\mathbf{r}} u_{\mathbf{k}}(\mathbf{r}) = \hbar\mathbf{k}\, e^{i\mathbf{k}\cdot\mathbf{r}} u_{\mathbf{k}}(\mathbf{r}) + e^{i\mathbf{k}\cdot\mathbf{r}} \mathbf{p} u_{\mathbf{k}}(\mathbf{r}) \ ;$$

$$\mathbf{p}^2\, e^{i\mathbf{k}\cdot\mathbf{r}} u_{\mathbf{k}}(\mathbf{r}) = (\hbar k)^2\, e^{i\mathbf{k}\cdot\mathbf{r}} u_{\mathbf{k}}(\mathbf{r}) + e^{i\mathbf{k}\cdot\mathbf{r}} (2\hbar\mathbf{k}\cdot\mathbf{p}) u_{\mathbf{k}}(\mathbf{r}) + e^{i\mathbf{k}\cdot\mathbf{r}} \mathbf{p}^2 u_{\mathbf{k}}(\mathbf{r}) \ ;$$

thus (16) may be written as an equation for $u_{\mathbf{k}}$:

$$\left(\frac{1}{2m}(\mathbf{p}+\hbar\mathbf{k})^2 + U(\mathbf{r})\right) u_{\mathbf{k}}(\mathbf{r}) = \epsilon_{\mathbf{k}} u_{\mathbf{k}}(\mathbf{r}) \ . \tag{17}$$

At $\mathbf{k} = 0$ we have $\psi_0 = u_0(\mathbf{r})$, where $u_0(\mathbf{r})$ has the periodicity of the lattice, sees the ion cores, and near them will look like the wavefunction of the free atom.

It is much easier to find a solution at $\mathbf{k} = 0$ than for a general $\mathbf{k}$, because at $\mathbf{k} = 0$ a nondegenerate solution will have the full symmetry of the crystal. We can then use $u_0(\mathbf{r})$ to construct the approximate solution

$$\psi_{\mathbf{k}} = \exp(i\mathbf{k}\cdot\mathbf{r}) u_0(r) \ . \tag{18}$$

This is of the Bloch form, but u_0 is not an exact solution of (17): it is a solution only if we drop the term in $\mathbf{k}\cdot\mathbf{p}$. Often this term is treated as a perturbation, as in Problem 8. The $\mathbf{k}\cdot\mathbf{p}$ perturbation theory developed there is especially useful in finding the effective mass m^* at a band edge.

Because it takes account of the ion core potential, the function (18) is a much better approximation than a plane wave to the correct wavefunction. The energy of the approximate solution depends on $\mathbf{k}$ as $(\hbar k)^2/2m$, exactly as for the plane wave, even though the modulation represented by $u_0(\mathbf{r})$ may be very strong. Because u_0 is a solution of

$$\left(\frac{1}{2m}\mathbf{p}^2 + U(\mathbf{r})\right) u_0(\mathbf{r}) = \epsilon_0 u_0(\mathbf{r}) \tag{19}$$

the function (18) has the energy expectation value $\epsilon_0 + (\hbar^2 k^2/2m)$. The function $u_0(\mathbf{r})$ often will give us a good picture of the charge distribution within a cell.

Wigner and Seitz developed a simple and fairly accurate method of calculating $u_0(\mathbf{r})$. Figure 19 shows the Wigner-Seitz wavefunction for $\mathbf{k} = 0$ in the $3s$ conduction band of metallic sodium. The function is practically constant over 0.9 of the atomic volume. To the extent that the solutions for higher $\mathbf{k}$ may be approximated by $\exp(i\mathbf{k} \cdot \mathbf{r})u_0(\mathbf{r})$, the wavefunctions in the conduction band will be similar to plane waves over most of the atomic volume, but increase markedly and oscillate within the ion core.

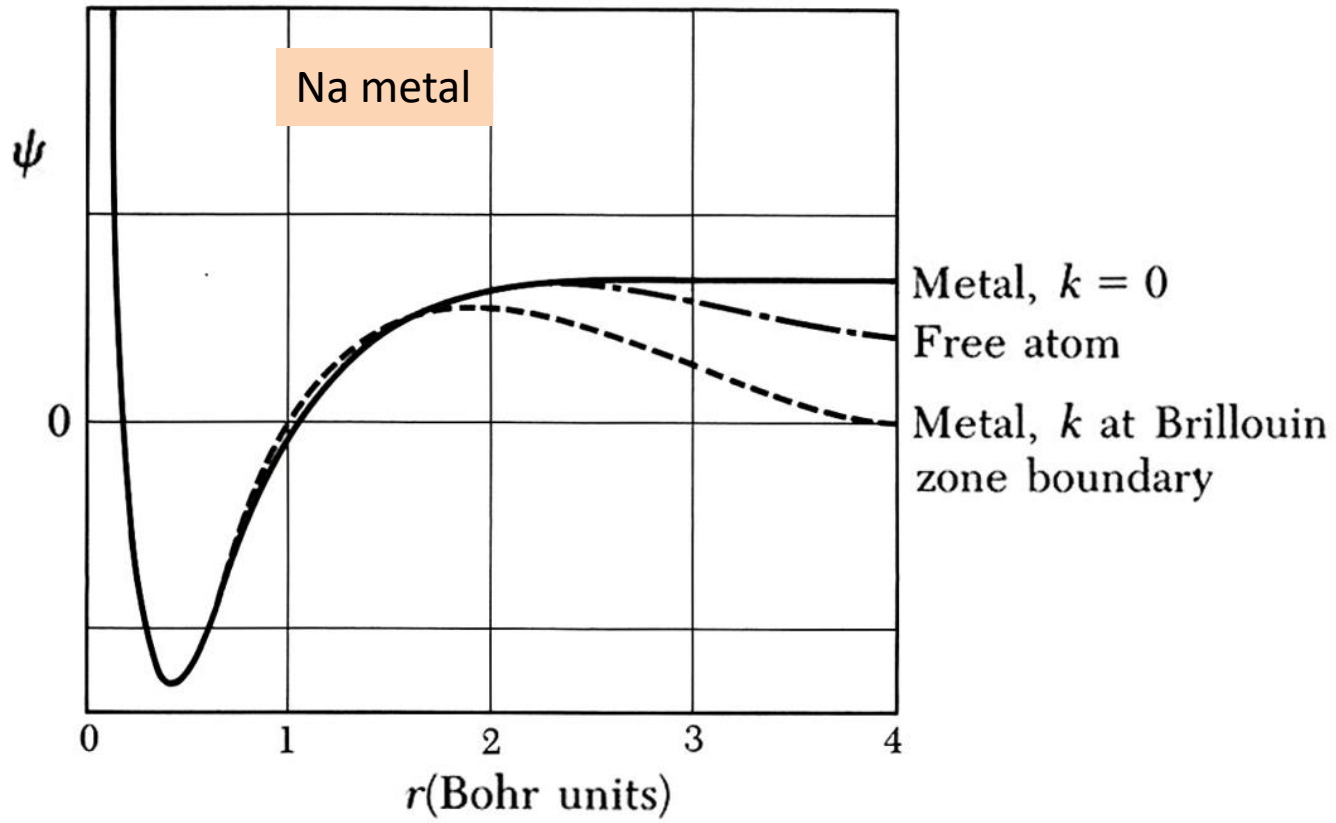

Figure 19 Radial wavefunctions for the 3*s* orbital of free sodium atom and for 3*s* conduction band in sodium metal. The wavefunctions, which are not normalized here, are found by integrating the Schrödinger equation for an electron in the potential well of an Na^+ ion core. For the free atom the wavefunction is integrated subject to the usual Schrödinger boundary condition $\psi(r) \rightarrow 0$ as $r \rightarrow \infty$; the energy eigenvalue is -5.15 eV. The wavefunction for wavevector $k = 0$ in the metal is subject to the Wigner-Seitz boundary condition that $d\psi/dr = 0$ when r is midway between neighboring atoms; the energy of this orbital is -8.2 eV, considerably lower than for the free atom. The orbitals at the zone boundary are not filled in sodium; their energy is $+2.7$ eV. (After E. Wigner and F. Seitz.)

See slide 10

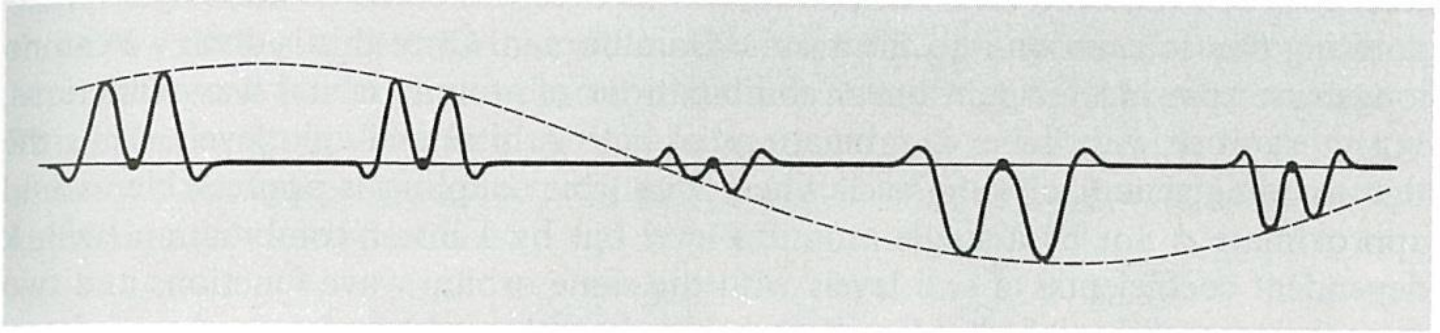

Figure 10.7
Characteristic spatial variation of the real (or imaginary) part of the tight-binding wave function (10.6).

Cohesive Energy. The stability of the simple metals with respect to free atoms is caused by the lowering of the energy of the Bloch orbital with $\mathbf{k} = 0$ in the crystal compared to the ground valence orbital of the free atom. The effect is illustrated in Fig. 19 for sodium and in Fig. 20 for a linear periodic potential of attractive square wells. The ground orbital energy is much lower at the actual spacing in the metal than for isolated atoms.

A decrease in ground orbital energy will increase the binding. The decrease in ground orbital energy is a consequence of the change in the boundary condition on the wavefunction: The Schrödinger boundary condition for the free atom is $\psi(\mathbf{r}) \rightarrow 0$ as $r \rightarrow \infty$. In the crystal the $\mathbf{k} = 0$ wavefunction $u_0(\mathbf{r})$ has the symmetry of the lattice and is symmetric about $\mathbf{r} = 0$. To have this, the normal derivative of ψ must vanish across every plane midway between adjacent atoms.

smaller b

Simple metals ⟵ Free atoms

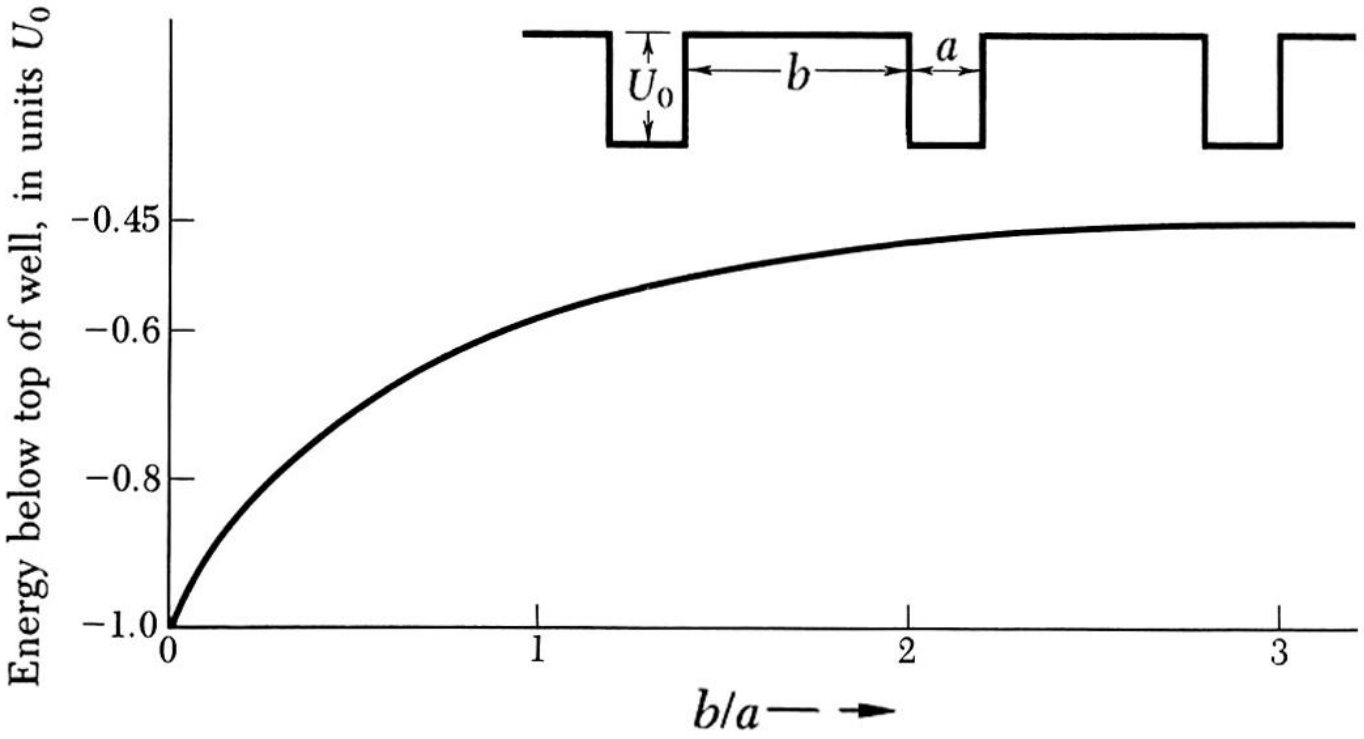

Figure 20 Ground orbital ($k = 0$) energy for an electron in a periodic square well potential of depth $|U_0| = 2\hbar^2/ma^2$. The energy is lowered as the wells come closer together. Here a is held constant and b is varied. Large b/a corresponds to separated atoms. (Courtesy of C. Y. Fong.)

In a spherical approximation to the shape of the smallest Wigner-Seitz cell we use the Wigner-Seitz boundary condition

$$(d\psi/dr)_{r_0} = 0 \ , \tag{20}$$

where r_0 is the radius of a sphere equal in volume to a primitive cell of the lattice. In sodium, $r_0 = 3.95$ Bohr units, or 2.08 Å; the half-distance to a nearest neighbor is 1.86 Å. The spherical approximation is not bad for fcc and bcc structures. The boundary condition allows the ground orbital wavefunction to have much less curvature than the free atom boundary condition. Much less curvature means much less kinetic energy.

In sodium the other filled orbitals in the conduction band can be represented in a rough approximation by wavefunctions of the form (18), with

$$\psi_{\mathbf{k}} = e^{i\mathbf{k}\cdot\mathbf{r}} u_0(\mathbf{r}) \ ; \qquad \epsilon_{\mathbf{k}} = \epsilon_0 + \frac{\hbar^2 k^2}{2m} \ .$$

The Fermi energy is 3.1 eV, from Table 6.1. The average kinetic energy per electron is 0.6 of the Fermi energy, or 1.9 eV. Because $\epsilon_0 = -8.2$ eV at $\mathbf{k} = 0$, the average electron energy is $\langle \epsilon_k \rangle = -8.2 + 1.9 = -6.3$ eV, compared with -5.15 eV for the valence electron of the free atom, Fig. 21.

We therefore estimate that sodium metal is stable by about 1.1 eV with respect to the free atom. This result agrees well with the experimental value 1.13 eV. We have neglected several corrections whose overall effect in sodium is small.

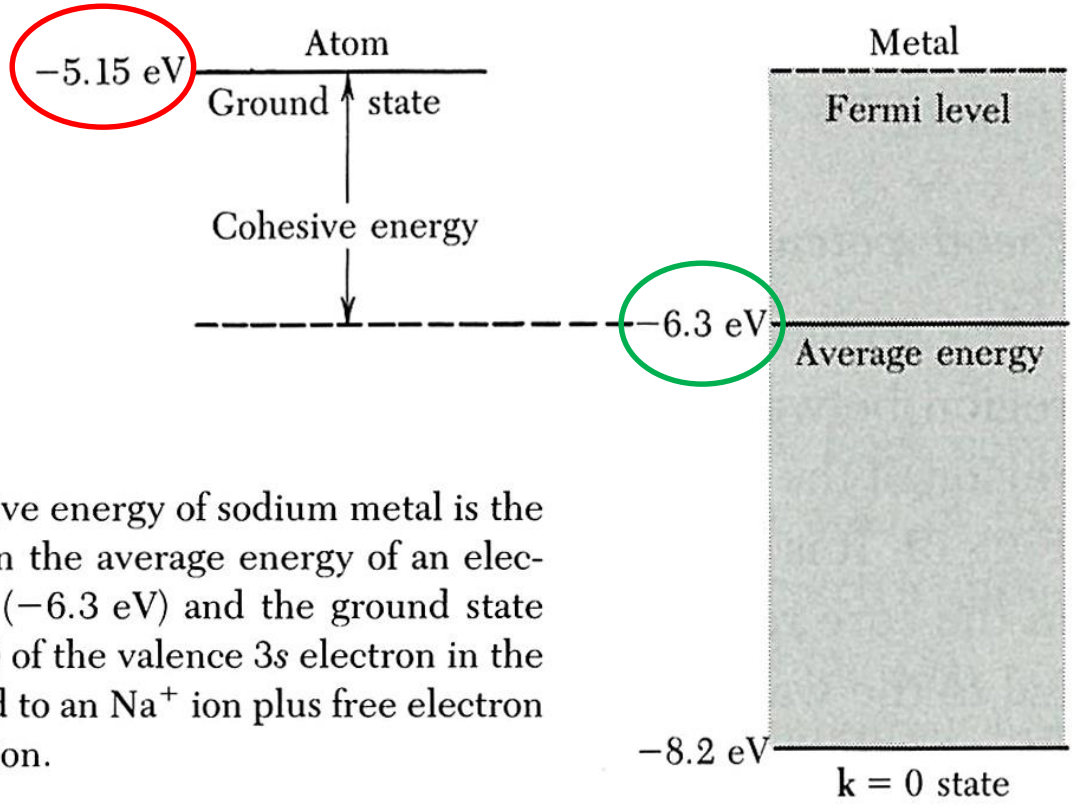

Figure 21 Cohesive energy of sodium metal is the difference between the average energy of an electron in the metal (−6.3 eV) and the ground state energy (−5.15 eV) of the valence 3*s* electron in the free atom, referred to an Na^+ ion plus free electron at infinite separation.

Pseudopotential Methods

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:

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

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

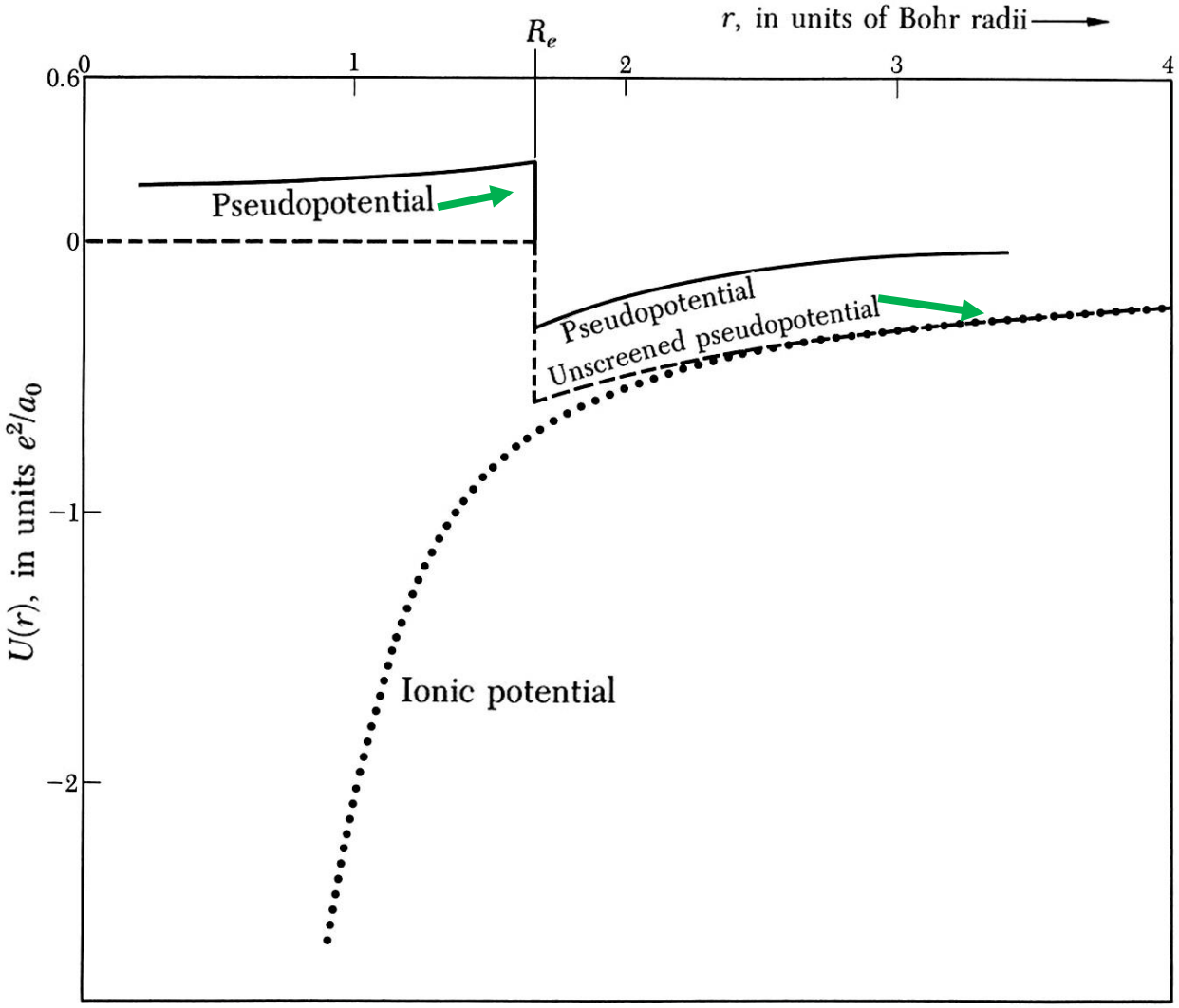

Figure 22a Pseudopotential for metallic sodium, based on the empty core model and screened by the Thomas-Fermi dielectric function. The calculations were made for an empty core radius $R_e = 1.66a_0$, where a_0 is the Bohr radius, and for a screening parameter $k_s a_0 = 0.79$. The dashed curve shows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

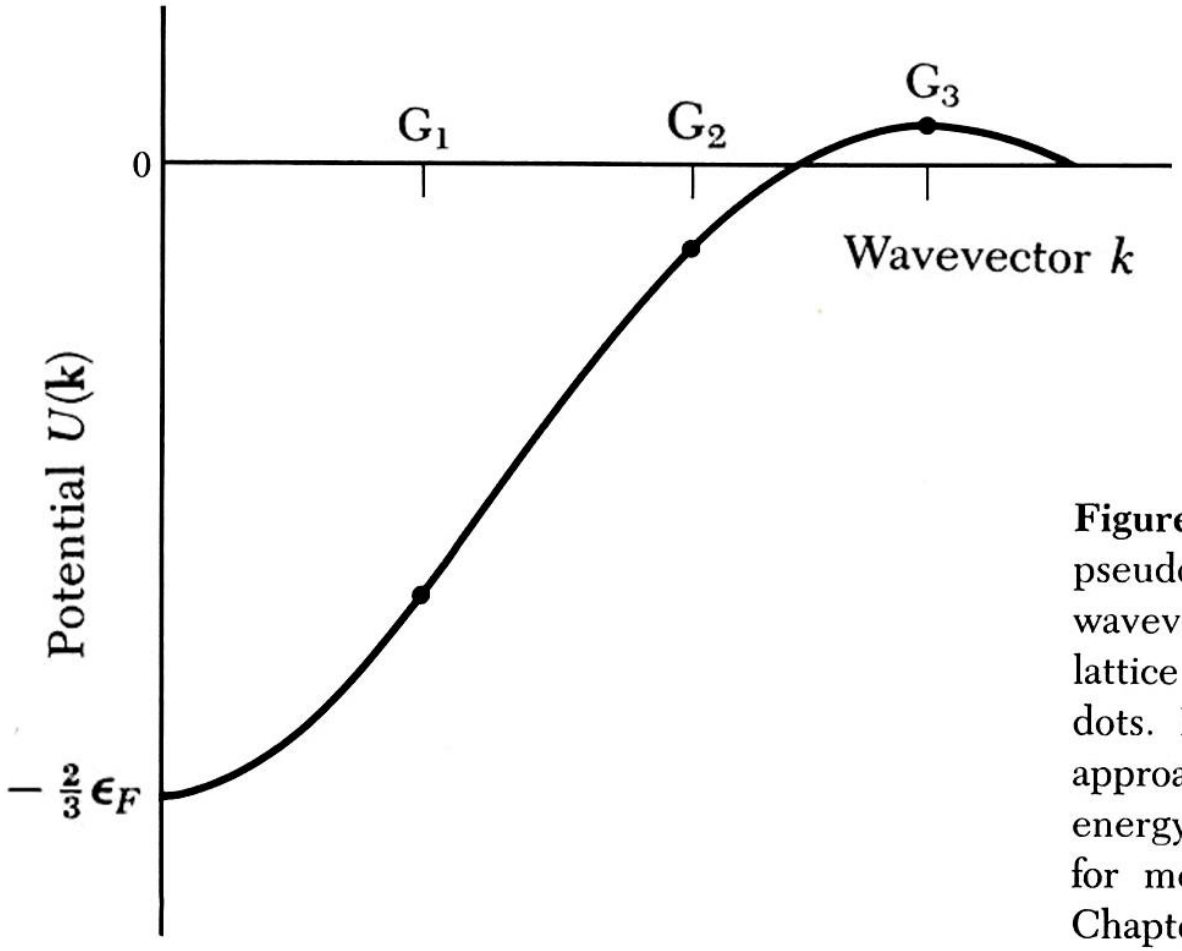

Figure 22b A typical reciprocal space pseudopotential. Values of $U(\mathbf{k})$ for wavevectors equal to the reciprocal lattice vectors, **G**, are indicated by the dots. For very small **k** the potential approaches $(-2/3)$ times the Fermi energy, which is the screened-ion limit for metals. This limit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