PHYSICAL REVIEW VOLUME 124, NUMBER 6 DECEMBER 15, 1961

Dielectric Screening and Self-Consistent Crystal Fields*

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(Received July 25, 1961)

The construction of self-consistent Hartree crystal potentials is discussed in terms of screening of "external" ionic potentials by a nearly-free valence-electron gas. An essential preliminary is the introduction of a repulsive potential which replaces the requirement of orthogonality of one-electron valence and core wave functions. Because of the excellent cancellation of core and repulsive potentials, the resulting effective ionic potential V_{eff} is weak. Using an approximate dielectric constant to screen V_{eff}, we obtain a prescription for estimating *a priori* self-consistent Hartree potentials in metals and semiconductors. The dielectric screening can be extended to include exchange and correlation. Comparison with detailed band calculations for diamond, silicon, and cubic boron nitride reveals the accuracy and limitations of the method. The screening of the longest wavelength Fourier component of V_{eff} is predicted quite satisfactorily. By studying bonding and charge transfer effects we find that nonlinear local field corrections (crystal hybridization) are important in screening of shorter wavelength Fourier components of V_{eff}.

1. INTRODUCTION

RECENTLY the connection between Hartree screening of weak external potentials and the dielectric properties of an electron gas has been discussed by several authors. Silverman and Weiss[1] have treated the screening to first order in the potential of a point-ion impurity in a high-density electron gas. They found that the result of a self-consistent Hartree calculation is the same as that of a many-body treatment including electron-electron correlation in the random phase approximation of Sawada.[2] Ehrenreich and Cohen[3] have shown in general that the screening to first order of an arbitrary external potential is the same in the Sawada approximation as it is for self-consistent Hartree fields. Because the response is linear in the external field, the screening in both cases is determined by the dielectric constant, or better, dielectric function of a free electron gas.

These results suggest a general approach to the problem of estimating an initial conduction- or valence-electron crystal charge density for self-consistent energy-band calculations in metals or semiconductors. Hitherto, conduction-electron charge densities in metals have generally been taken to be constant outside the core regions, and no attempt has been made at self-consistency, with the exception of Heine's work on Al.[4] We shall see, however, that even in the alkali metals significant corrections to the conduction-electron potential are expected as a result of self-consistent screening. For many polyvalent metals the corrections may be quite large.

Again, in the case of nonmetals, only one attempt has been made at self-consistency, that of Kleinman and Phillips for several semiconductors.[5–7] Here, in contrast to Al, the perturbation of the electron gas outside the cores is large. To calculate the "covalent" screening charge they made a laborious sampling of the charge densities associated with states at the various symmetry points of the Brillouin zone. The object of this paper is to present a simple *a priori* method for estimating such charge densities for metals or semiconductors of arbitrary crystal structures.

Our approach extends the perturbation treatment of dielectric screening to crystal potentials which contain strong, short-range core parts. Before we treat such potentials by perturbation theory, we must first remove the effects of the strong core potential. Herring[8] accomplished this by orthogonalizing plane waves to core eigenfunctions. Phillips and Kleinman[9] rewrote the orthogonalization terms as an effective repulsive potential. Numerical calculations showed that the repulsive potential almost cancelled the original potential in the core region, leaving only a weak, long-range effective potential. More generally, Cohen and Heine[10] have shown that the cancellation is always expected because the repulsive potential is just the original potential expanded in the basis of core eigenfunctions except for small correction terms.

In Sec. 2 the self-consistent Hartree problem is formulated using Herring's basis functions (orthogonalized plane waves or OPW's), and the utility of dielectric screening of the effective potential for *a priori* estimates is indicated. In Sec. 3 the results are extended to include exchange and correlation, while Sec. 4 contains a comparison with the results of a detailed band calculation. The limitations and further applications of the method are discussed in Sec. 5.

2. SCREENING OF THE EFFECTIVE POTENTIAL

It was Herring who first pointed out[8] that the expansion of Bloch wave functions in plane waves could be made rapidly convergent in spite of the strong,

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* Research supported in part by the Office of Naval Research.

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[7] L. Kleinman and J. C. Phillips, Phys. Rev. **118**, 1153 (1960).

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short-range core potentials by augmenting the basis set with core eigenfunctions ϕ_t of the valence Hamiltonian $\mathcal{H}_0$. The OPW basis functions are then

$$\chi_{\mathbf{k}}=(\mathrm{OPW})=[1/(1-\sum|a_{t\mathbf{k}}|^2)^{\frac{1}{2}}]\times[e^{i\mathbf{k}\cdot\mathbf{r}}-\textstyle\sum_t a_{t\mathbf{k}}\phi_t], \quad (2.1)$$

where $a_{t\mathbf{k}}=(\phi_t,e^{i\mathbf{k}\cdot\mathbf{r}})$. A more convenient form of (2.1) proposed by Phillips and Kleinman[9] is

$$\psi=[1/(1-\sum|b_t|^2)^{\frac{1}{2}}][\phi-\textstyle\sum_t b_t\phi_t], \quad (2.2)$$

where $b_t=(\phi_t,\phi)$ and ϕ is a normalized "smooth" wave function. The latter is determined from the wave equation

$$(T+V+V_R)\phi=E\phi, \quad (2.3)$$

$$V_R\phi=\textstyle\sum_t(E-E_t)(\phi_t,\phi)\phi_t, \quad (2.4)$$

which is obtained by substituting (2.2) into $H\psi=E\psi$. The potential V is the sum of V_i, the ionic potential, and V_s, the self-consistent screening potential of the valence electrons.

The utility of the ϕ representation results from the cancellation of V_i and V_R in the core region, so that in

$$V_{\mathrm{eff}}=V_i+V_R, \quad (2.5)$$

the short-range part of the potential is nearly zero. This means that if ϕ is expanded in plane waves, rapid convergence will be obtained, as anticipated by Herring.

The cancellation of the core part of V_i by V_R has been discussed by Cohen and Heine.[10] Their equation (23) can be rewritten to good approximation as

$$V_{\mathrm{eff}}\phi=[V\phi-\textstyle\sum_t(\phi_tV\phi)\phi_t][1+\sum_t|(\phi_t,\phi)|^2]. \quad (2.6)$$

Because the ϕ_t form a good basis set in the core region, the cancellation of the short-range potential is evident. The correction term in the second bracket in (2.6) is typically of order 0.1.

If the potential were entirely cancelled, ϕ would be a single plane wave and the wave function ψ a single OPW, $\chi_{\mathbf{k}}$. These one-electron states would be occupied within a Fermi sphere containing the correct number of valence electrons per atom. The corresponding charge density would be

$$\begin{aligned}\rho_s^0&=\sum_{k'<k_F}\chi_{\mathbf{k}'}^*\chi_{\mathbf{k}'}\\&=\sum_{k'<k_F}\frac{1}{1-\sum|a_{t\mathbf{k}'}|^2}\Big[1-2\,\mathrm{Re}\sum_t a_{t\mathbf{k}'}e^{-i\mathbf{k}'\cdot\mathbf{r}}\phi_t\\&\qquad+\sum_{t',t''}a_{t''\mathbf{k}'}^*a_{t'\mathbf{k}'}\phi_{t''}^*\phi_{t'}\Big]. \quad (2.7)\end{aligned}$$

When the cancellation in (2.6) is imperfect, we should calculate self-consistently the change in ρ_s^0 induced by V_{eff}. Because V_{eff} is small, first-order perturbation theory now suffices to determine this change, $\rho_s^1-\rho_s^0$.

From (2.7), the potential associated with ρ_s^0 (aside from a constant) is restricted to the core region where ϕ_t is large, and it is natural to add it to the ionic potential V_i. We expect that V_{eff} perturbs the valence charge density primarily outside the cores, so that V_i remains essentially unchanged in the course of making the valence charge density self-consistent.

Since we are concerned here with Hartree screening, we will take the ϕ_t in (2.1) to be eigenfunctions of the Hartree potential V. The modifications necessary to include the effects of exchange and correlation are discussed in Sec. 3. The repulsive potential is also in general an operator, not a true potential. For small cores it behaves as a potential, and we will treat it as such in the calculations below. This point is illustrated by an example in Sec. 4.

We now wish to determine the screening potential V_s produced by the valence electrons when we solve the equation

$$H\phi_{\mathbf{k}}=(T+V_{\mathrm{eff}}+V_s)\phi_{\mathbf{k}}=E_{\mathbf{k}}\phi_{\mathbf{k}} \quad (2.8)$$

self-consistently to first order in V_{eff}. Here V_s is the potential produced by the charge density

$$\begin{aligned}\delta\rho_s=\rho_s^1-\rho_s^0&=\sum_{k'<k_F}(\psi_{\mathbf{k}'}^*\psi_{\mathbf{k}'}-\chi_{\mathbf{k}'}^*\chi_{\mathbf{k}'})\\&\simeq\sum_{k'<k_F}\frac{1}{1-\sum|b_t|^2}(\phi_{\mathbf{k}'}^*\phi_{\mathbf{k}'}-1). \quad (2.9)\end{aligned}$$

We have neglected in (2.9) the change in the conduction electron charge density in the core region associated with the change in orthogonalization coefficients; it can be shown that the corresponding change in V_s is of second order in V_{eff}. A small core approximation, which makes an error of about 10% in first order in $V_s^{\mathbf{K}}$, is

$$\begin{aligned}\delta\rho_s&\simeq\sum_{k'<k_F}(\phi_{\mathbf{k}'}^*\phi_{\mathbf{k}'}-1)(1+\sum_t|b_t|^2)\\&\simeq\sum_{k'<k_F}(\phi_{\mathbf{k}'}^*\phi_{\mathbf{k}'}-1). \quad (2.10)\end{aligned}$$

For small cores the problem thus reduces to that of an electron gas in a weak external potential. Note the similarity between (2.10) and (2.6).

Both $\delta\rho_s$ and the potentials in (2.7) have the periodicity of the lattice:

$$\begin{aligned}&\delta\rho_s(\mathbf{r})=\sum_{\mathbf{K}\neq0}\rho_s^{\mathbf{K}}e^{i\mathbf{K}\cdot\mathbf{r}}, \qquad V^{\mathbf{K}}=V_{\mathrm{eff}}^{\mathbf{K}}+V_s^{\mathbf{K}},\\&V_{\mathrm{eff}}(\mathbf{r})=\sum_{\mathbf{K}}V_{\mathrm{eff}}^{\mathbf{K}}e^{i\mathbf{K}\cdot\mathbf{r}}, \quad V_s(\mathbf{r})=\sum_{\mathbf{K}\neq0}V_s^{\mathbf{K}}e^{i\mathbf{K}\cdot\mathbf{r}},\end{aligned} \quad (2.11)$$

where $\mathbf{K}$ is a reciprocal lattice vector. We now solve (2.8) to first order in V for the occupied states $\mathbf{k}$:

$$\phi_{\mathbf{k}}=\phi_{\mathbf{k}}^0+\sum_{\mathbf{K}}\frac{V^{\mathbf{K}}}{E_{\mathbf{k}}-E_{\mathbf{k}+\mathbf{K}}}\phi_{\mathbf{k}+\mathbf{K}}^0, \quad (2.12)$$

and compute the screening charge density ρ_s to first order in V:

$$\delta\rho_s = e\sum_{\mathbf{k}'} N_{k'}(\phi_{\mathbf{k}'}{}^*\phi_{\mathbf{k}'} - \phi_{\mathbf{k}'}{}^{0*}\phi_{\mathbf{k}'}{}^0)$$

$$= e\sum_{\mathbf{k}',\mathbf{K}} \frac{N_{\mathbf{k}'} - N_{\mathbf{k}'+\mathbf{K}}}{E_{\mathbf{k}'} - E_{\mathbf{k}'+\mathbf{K}}} V^{\mathbf{K}} e^{i\mathbf{K}\cdot\mathbf{r}}. \quad (2.13)$$

In (2.13), $N_{\mathbf{k}}$ is the occupation number of the unperturbed state $\phi_{\mathbf{k}}{}^0 = e^{i\mathbf{k}\cdot\mathbf{r}}$. From (2.13), it follows that

$$\delta\rho_s{}^{\mathbf{K}} = eV^{\mathbf{K}} \sum_{\mathbf{k}'} \frac{N_{\mathbf{k}'} - N_{\mathbf{k}'+\mathbf{K}}}{E_{\mathbf{k}'} - E_{\mathbf{k}'+\mathbf{K}}}, \quad (2.14)$$

and from Poisson's equation, which is

$$K^2 V_s{}^{\mathbf{K}} = 4\pi e\delta\rho_s{}^{\mathbf{K}}, \quad (2.15)$$

we find that

$$V_s{}^{\mathbf{K}} = \frac{4\pi e^2}{K^2}(V_{\text{eff}}{}^{\mathbf{K}} + V_s{}^{\mathbf{K}}) \sum_{\mathbf{k}'} \frac{N_{\mathbf{k}'} - N_{\mathbf{k}'+\mathbf{K}}}{E_{\mathbf{k}'} - E_{\mathbf{k}'+\mathbf{K}}}. \quad (2.16)$$

Equation (2.16) can be written

$$V^{\mathbf{K}}\left[1 + \frac{4\pi e^2}{K^2} \sum_{\mathbf{k}'} \frac{N_{\mathbf{k}'} - N_{\mathbf{k}'+\mathbf{K}}}{E_{\mathbf{k}'+\mathbf{K}} - E_{\mathbf{k}'}}\right] = V_{\text{eff}}{}^{\mathbf{K}}. \quad (2.17)$$

Now the bracket on the left in (2.17) is just the static dielectric function $\epsilon(K,0)$ in the Hartree approximation for free electrons as first calculated by Lindhard.[11] Our self-consistent Hartree potential is thus

$$V(\mathbf{r}) = \sum{}'_{\mathbf{K}} [V_{\text{eff}}{}^{\mathbf{K}}/\epsilon(K,0)] e^{i\mathbf{K}\cdot\mathbf{r}}. \quad (2.18)$$

Note that (2.18) can be calculated from atomic wave functions and energy levels and a property of the free electron gas. Thus, with little labor, the crystal potential can be made approximately self-consistent at the beginning of a detailed band calculation.

3. EXCHANGE AND CORRELATION

For accurate band calculations, the effect of exchange and correlation must be added to the one-electron Hamiltonian. A prescription for doing this has been described by one of us in terms of a generalized Koopman's theory[12] based on Hubbard's formulation[13] of the many-electron correlation problem. It is found that, neglecting local-field corrections, the one-electron potential for valence electrons is

$$V = V_i + V_s + A_{iv} + B_0 + \mathcal{B}_{vv}, \quad (3.1)$$

where V_i and V_s are the Hartree Coulomb potentials defined in Sec. 2. The exchange and correlation interaction between valence and core electrons is written as A_{iv}. In the "small core" case, core energies are separated from valence energies by much more than the plasma energy, so that core-valence exchange is essentially unscreened.[12] In addition, the spherical symmetry of the core enables one to write the exchange operator $\mathcal{A}_{iv}$ as an exchange potential A_{iv}.[14]

The quantity B_0 in (3.11) is a constant potential[12] associated with the zero-point Coulomb energy of the plasma oscillations. It has no effect on the self-consistent problem except through the modification of V_R because of the shift of core levels relative to valence levels.

Spatially dependent valence-valence exchange and correlation are described by the screened exchange operator $\mathcal{B}_{vv}$, which, like V_s, is to be calculated self-consistently. Hubbard has shown[15] that when local potentials are treated self-consistently a large class of self-energy corrections vanish, and Pratt[16] has extended Hubbard's treatment to include nonlocal potentials such as screened exchange. Pratt has also emphasized that Hubbard's theory, like all other quantitative treatments of correlation, is based on perturbation theory, not the variational principle (as in the Hartree and Hartree-Fock methods). By treating first-order exchange and correlation self-consistently we minimize higher order corrections, so that the largest of these is, for example, screened second-order exchange. The latter has been shown[12] to be quite small, indeed probably negligible in practice.

We have seen in Sec. 2 that an external potential $V_i{}^{\mathbf{K}}e^{i\mathbf{K}\cdot\mathbf{r}}$ perturbs the free-electron gas, inducing a charge density $\rho_s{}^{\mathbf{K}}e^{i\mathbf{K}\cdot\mathbf{r}}$, which in turn produces a screening potential $V_s{}^{\mathbf{K}}e^{i\mathbf{K}\cdot\mathbf{r}}$. When exchange and correlation are included in our one-electron Hamiltonian, we expect similar oscillations in the exchange and correlation "potential." In general, $\mathcal{B}_{vv}$ is an operator, so that it cannot be represented as a potential B_{vv}. However, if we take advantage of the fact that the screened exchange interaction $\text{Re}\{[\epsilon(q)q^2]^{-1}\}$ is almost constant for $q \lesssim 2k_F$, and work only to first order in $V^{\mathbf{K}}$, as in Sec. 2, we find that $\mathcal{B}_{vv}$ can be put in potential form. More accurate methods which should be used to calculate $\mathcal{B}_{vv}$ in practice have been illustrated for Si.[17] Here we explore the formal results for a nearly free electron gas which should be useful in making *a priori* estimates not only of $V_s{}^{\mathbf{K}}$ but of $B_{vv}{}^{\mathbf{K}}$ as well.

The general expression for $\mathcal{B}_{vv}$ is[12]

$$\mathcal{B}_{vv}\psi_{\mathbf{k}}(\mathbf{r}_1) = -e^2 \sum_{\mathbf{k}'} \int \frac{\psi_{\mathbf{k}'}{}^*(\mathbf{r}_2)\psi_{\mathbf{k}}(\mathbf{r}_2)}{r_{12}} \times \text{Re}\frac{1}{\sigma(r_{12},\omega_{\mathbf{k}'\mathbf{k}})} d^3r_2 \psi_{\mathbf{k}'}(\mathbf{r}_1). \quad (3.2)$$

Here σ is the complex wave-number and frequency-dependent screening function of the free-electron gas[15]

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[14] See, e.g., reference 4 or reference 7.

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[17] J. C. Phillips and L. Kleinman, Phys. Rev. (to be published).

in a spatial representation.[12] In order to simplify the self-consistency problem obtained when (3.2) is added to the Hamiltonian, we replace $\sigma(r_{12},\omega_{\mathbf{k}'\mathbf{k}})$ in (3.2) by $\sigma(r_{12},0)$. In Si this approximation[17] changed B_{vv} by only 5%. In (3.2) we must evaluate the density matrix

$$\rho_s(\mathbf{r}_1,\mathbf{r}_2)=\sum_{\mathbf{k}'}\psi_{\mathbf{k}'}{}^*(\mathbf{r}_2)\psi_{\mathbf{k}'}(\mathbf{r}_1). \tag{3.3}$$

We proceed as in Sec. 2 to divide $\rho_s(\mathbf{r}_1,\mathbf{r}_2)$ into its "one OPW" part and a perturbed part:

$$\rho_s(\mathbf{r}_1,\mathbf{r}_2)=\rho_s{}^0(\mathbf{r}_1,\mathbf{r}_2)+\delta\rho_s(\mathbf{r}_1,\mathbf{r}_2), \tag{3.4}$$

$$\rho_s{}^0(\mathbf{r}_1,\mathbf{r}_2)=\sum_{k'<k_F}\chi_{\mathbf{k}'}{}^*(\mathbf{r}_2)\chi_{\mathbf{k}'}(\mathbf{r}_1), \tag{3.5}$$

$$\begin{aligned}\rho_s{}^0=\sum_{k'<k_F}\frac{1}{1-\sum_t|a_{t\mathbf{k}'}|^2}\Big[&e^{i\mathbf{k}'\cdot(\mathbf{r}_1-\mathbf{r}_2)}\\ &-\sum_t a_{t\mathbf{k}'}\phi_t(r_1)e^{-i\mathbf{k}'\cdot\mathbf{r}_2}-\sum_t a_{t\mathbf{k}'}{}^*\phi_t{}^*(\mathbf{r}_2)e^{i\mathbf{k}'\cdot\mathbf{r}_1}\\ &+\sum_{t',t''}a_{t''\mathbf{k}'}{}^*a_{t'\mathbf{k}'}\phi_{t''}{}^*(\mathbf{r}_2)\phi_{t'}(\mathbf{r}_1)\Big].\end{aligned} \tag{3.6}$$

In the brackets in (3.6) the last three terms involve core orbitals. The screened exchange interaction in (3.2) is short-range, so that the contribution to the screened exchange operator of the last three terms in (3.6) is confined to the spherically symmetric core region. As was the case with the core-valence exchange operator $\mathcal{A}_{iv}$, advantage can be taken of the spherical symmetry to represent these terms as a potential. They can then be added to the core-valence exchange potential A_{iv}.

The treatment of $\delta\rho_s(\mathbf{r}_1,\mathbf{r}_2)$ also parallels that of $\delta\rho_s(\mathbf{r})$ in Sec. 2. Thus $\rho_s(\mathbf{r}_1,\mathbf{r}_2)$ is the same as $\rho_s{}^0(\mathbf{r}_1,\mathbf{r}_2)$ except that in (3.6) $e^{i\mathbf{k}'\cdot(\mathbf{r}_1-\mathbf{r}_2)}$ is replaced by $\phi_{\mathbf{k}'}{}^*(\mathbf{r}_2)\times\phi_{\mathbf{k}'}(\mathbf{r}_1)$ and $a_{t\mathbf{k}}$ is replaced by $b_{t\mathbf{k}}$. As before, the latter change leads to core corrections of at least second order in V_{eff}, which we neglect. Thus, we have, as in (2.10),

$$\begin{aligned}\delta\rho_s(\mathbf{r}_1,\mathbf{r}_2)&=\sum_{k'<k_F}[\phi_{\mathbf{k}'}{}^*(\mathbf{r}_2)\phi_{\mathbf{k}'}(\mathbf{r}_1)-e^{i\mathbf{k}'\cdot(\mathbf{r}_1-\mathbf{r}_2)}][1+\sum_t|b_{t\mathbf{k}'}|^2]\\ &\simeq\sum_{k'<k_F}[\phi_{\mathbf{k}'}{}^*(\mathbf{r}_2)\phi_{\mathbf{k}'}(\mathbf{r}_1)-e^{i\mathbf{k}'\cdot(\mathbf{r}_1-\mathbf{r}_2)}]\end{aligned} \tag{3.7}$$

to lowest order in $|b_{t\mathbf{k}'}|^2$.

Using (3.4) we can now define

$$\mathcal{B}_{vv}\phi_{\mathbf{k}}=B_{vv}{}^0\phi_{\mathbf{k}}+\delta\mathcal{B}_{vv}\phi_{\mathbf{k}}, \tag{3.8}$$

where $\mathcal{B}_{vv}{}^0$ is the "free electron" part of the screened exchange potential from the first term in the brackets in (3.6). $B_{vv}{}^0$ is spatially constant, while $\delta\mathcal{B}_{vv}$, which is associated with $\delta\rho_s$, contains spatial oscillations when written in potential form. We now investigate the effect of $\delta\mathcal{B}_{vv}$ on the basis functions $\phi_{\mathbf{k}}$.

Our single-particle Hamiltonian, including exchange and correlation operations, is

$$\mathcal{H}\phi_{\mathbf{k}}=[T+V_{\mathrm{eff}}+B_0+B_{vv}{}^0+V_s+\delta\mathcal{B}_{vv}]\phi_{\mathbf{k}}, \tag{3.9}$$

$$V_{\mathrm{eff}}=V_i+V_R+A_{iv}. \tag{3.10}$$

[In (3.10), V_i and A_{iv} include orthogonalization terms.] Our Hamiltonian is divided into zeroth- and first-order parts $\mathcal{H}=\mathcal{H}_0+\mathcal{H}_1$,

$$\mathcal{H}_0=T+B_0+B_{vv}{}^0+V_{\mathrm{eff}}{}^{\mathbf{K}=0}, \tag{3.11}$$

$$\mathcal{H}_1=V_{\mathrm{eff}}{}^{\mathbf{K}\neq0}+V_s+\delta\mathcal{B}_{vv}. \tag{3.12}$$

The last two terms are to be calculated self-consistently to first order. Writing $\phi_{\mathbf{k}}=\phi_{\mathbf{k}}{}^0+\phi_{\mathbf{k}}{}'$, we have

$$\mathcal{H}_0\phi_{\mathbf{k}}{}^0=E_{\mathbf{k}}{}^0\phi_{\mathbf{k}}{}^0, \tag{3.13}$$

$$E_{\mathbf{k}}{}^0=\hbar^2k^2/2m+B_0+V_{\mathrm{eff}}{}^{\mathbf{K}=0}+\langle B_{vv}{}^0\rangle. \tag{3.14}$$

The last term in (3.14) is the screened exchange energy $\beta(\mathbf{k})$ in the free electron gas. Because of translational invariance we have

$$\phi_{\mathbf{k}}{}^1=\sum_{\mathbf{K}\neq0}c_{\mathbf{K}}(k)e^{i(\mathbf{k}+\mathbf{K})\cdot\mathbf{r}}, \tag{3.15}$$

so that from first-order perturbation theory

$$c_{\mathbf{K}}(k)=\frac{\langle\mathbf{k}+\mathbf{K}|\mathcal{H}_1|\mathbf{k}\rangle}{E_{\mathbf{k}}{}^0-E_{\mathbf{k}+\mathbf{K}}{}^0}=\frac{\int d^3r_1e^{-i(\mathbf{k}+\mathbf{K})\cdot\mathbf{r}_1}\mathcal{H}_1e^{i\mathbf{k}\cdot\mathbf{r}_1}}{E_{\mathbf{k}}{}^0-E_{\mathbf{k}+\mathbf{K}}{}^0}. \tag{3.16}$$

By substituting (3.15) in (3.7) we obtain

$$\begin{aligned}\delta\rho_s(\mathbf{r}_1,\mathbf{r}_2)\\ =\sum_{k'<k_F}e^{i\mathbf{k}'\cdot(\mathbf{r}_1-\mathbf{r}_2)}\sum_{\mathbf{K}\neq0}[c_{\mathbf{k}}{}^*e^{-i\mathbf{K}\cdot\mathbf{r}_2}+c_{\mathbf{K}}e^{i\mathbf{K}\cdot\mathbf{r}_1}],\end{aligned} \tag{3.17}$$

which, from (3.12), gives

$$\begin{aligned}&\langle\mathbf{k}+\mathbf{K}|\mathcal{H}_1|\mathbf{k}\rangle\\ &=V_{\mathrm{eff}}{}^{\mathbf{K}}+\sum_{k'<k_F}\frac{4\pi e^2}{K^2}(c_{\mathbf{K}}(\mathbf{k}')+c_{-\mathbf{K}}{}^*(\mathbf{k}'))\\ &\quad+\sum_{k'<k_F}\sum_{\mathbf{K}'\neq0}\int d^3r_1d^3r_2\frac{1}{\sigma(r_{12},0)r_{12}}\{c_{\mathbf{K}'}\exp i\\ &\quad\times[-(\mathbf{k}+\mathbf{K})\cdot\mathbf{r}_1+\mathbf{k}\cdot\mathbf{r}_2+\mathbf{k}'\cdot(\mathbf{r}_1-\mathbf{r}_2)+\mathbf{K}'\cdot\mathbf{r}_1]\\ &\quad+c_{-\mathbf{K}'}{}^*\exp i[-(\mathbf{k}+\mathbf{K})\cdot\mathbf{r}_1+\mathbf{k}\cdot\mathbf{r}_2+\mathbf{k}'\cdot(\mathbf{r}_1-\mathbf{r}_2)\\ &\qquad+\mathbf{K}'\cdot\mathbf{r}_2]\}.\end{aligned} \tag{3.18}$$

The effective interaction $[\sigma(r_{12},0)r_{12}]^{-1}$ in (3.2) is defined as the Fourier transform of $[\epsilon(q,0)q^2]^{-1}$. Thus the last term in (3.18) reduces to

$$\sum_{k'<k_F}\left[\frac{4\pi e^2}{(\mathbf{k}-\mathbf{k}')^2\epsilon(\mathbf{k}-\mathbf{k}',0)}c_{\mathbf{K}}(\mathbf{k}')+\frac{4\pi e^2}{(\mathbf{k}+\mathbf{K}-\mathbf{k}')^2\epsilon(\mathbf{k}-\mathbf{k}'+\mathbf{K},0)}c_{-\mathbf{K}}{}^*(\mathbf{k}')\right],\quad(3.19)$$

where $c_{\mathbf{K}}(\mathbf{k}')$ is given self-consistently by (3.16), (3.18), and (3.19). We see that $c_{\mathbf{K}}(\mathbf{k})$ depends only on $c_{\mathbf{K}}(\mathbf{k}')$ and $c_{-\mathbf{K}}{}^*(\mathbf{k}')$. Because $c_{\mathbf{K}}$ and $c_{\mathbf{K}'}$ are independent, in the linear approximation the screened exchange operator has been reduced to (nonlocal) potential form. However, we still have to deal with an integral equation for $c_{\mathbf{K}}(\mathbf{k})$ in terms of $c_{\mathbf{K}}(\mathbf{k}')$. Now $\epsilon(q)q^2$ is almost constant for $q\lesssim k_F$, and the $\mathbf{k}'$ dependence of δB is small compared to that of the nonlocal repulsive potential itself. For our *a priori* estimates, we simplify the integral equation by assuming that the average effective interaction $(\mathbf{k}-\mathbf{k}')^2\epsilon(\mathbf{k}-\mathbf{k}',0)$ is that of $\mathbf{k}'=0$. Then from (3.18) and (3.19)

$$\langle\mathbf{k}+\mathbf{K}|\mathcal{H}_1|\mathbf{K}\rangle=V_{\text{eff}}{}^{\mathbf{K}}+\sum_{k'<k_F}\frac{4\pi e^2}{K^2}(c_{\mathbf{K}}+c_{-\mathbf{K}}{}^*)+\frac{\beta(\mathbf{k})}{N}\sum_{k'<k_F}c_{\mathbf{K}}(k')+\frac{\beta(\mathbf{k}+\mathbf{K})}{N}\sum_{k'<k_F}c_{-\mathbf{K}}{}^*(\mathbf{k}'),\quad(3.20)$$

where N is the number of electrons per unit volume. According to (3.16) we have

$$\sum_{k'<k_F}c_{-\mathbf{K}}{}^*(\mathbf{k}')=\sum_{k'<k_F}\frac{\langle\mathbf{k}'|\mathcal{H}_1|\mathbf{k}'-\mathbf{K}\rangle}{E_{\mathbf{k}'}{}^0-E_{\mathbf{k}'-\mathbf{K}}{}^0}=\sum_{k'<k_F}\frac{\langle-\mathbf{k}'|\mathcal{H}_1|-\mathbf{k}'-\mathbf{K}\rangle}{E_{\mathbf{k}'}{}^0-E_{\mathbf{k}'+\mathbf{K}}{}^0}$$
$$=\sum_{k'<k_F}\frac{\langle\mathbf{k}'+\mathbf{K}|\mathcal{H}_1|\mathbf{k}'\rangle}{E_{\mathbf{k}'}{}^0-E_{\mathbf{k}'+\mathbf{K}}{}^0}=\sum_{k'<k_F}c_{\mathbf{K}}(\mathbf{k}'),\quad(3.21)$$

so that (3.20) simplifies to

$$\langle\mathbf{k}+\mathbf{K}|\mathcal{H}_1|\mathbf{k}\rangle=V_{\text{eff}}{}^{\mathbf{K}}+\frac{8\pi e^2}{K^2}\sum_{k'<k_F}c_{\mathbf{K}}(\mathbf{k}')+\frac{\beta(\mathbf{k})+\beta(\mathbf{k}+\mathbf{K})}{N}\sum_{k'<k_F}c_{\mathbf{K}}(\mathbf{k}').\quad(3.22)$$

By summing (3.16) and using (3.22) to compute $F_{\mathbf{K}}=\sum_{\mathbf{k}'}c_{\mathbf{K}}(\mathbf{k}')$ self-consistently, we find

$$F_{\mathbf{K}}\left[1-\frac{4\pi e^2}{K^2}\sum_{\mathbf{k}'}\frac{N_{\mathbf{k}'}-N_{\mathbf{k}'+\mathbf{K}}}{E_{\mathbf{k}'}{}^0-E_{\mathbf{k}'+\mathbf{K}}}-\frac{1}{2N}\sum_{\mathbf{k}'}\frac{(N_{\mathbf{k}'}-N_{\mathbf{k}'+\mathbf{K}})(\beta_{\mathbf{k}'}+\beta_{\mathbf{k}'+\mathbf{K}})}{E_{\mathbf{k}'}{}^0-E_{\mathbf{k}'+\mathbf{K}}{}^0}\right]=\sum_{k'<k_F}\frac{V_{\text{eff}}{}^{\mathbf{K}}}{E_{\mathbf{k}'}{}^0-E_{\mathbf{k}'+\mathbf{K}}{}^0},\quad(3.23)$$

in close analogy with (2.17). The complete perturbing potential is V_{eff} divided by the brackets on the left side of (3.23), so that

$$V(\mathbf{r})=\sum_{\mathbf{K}\neq0}\frac{V_{\text{eff}}{}^{\mathbf{K}}e^{i\mathbf{K}\cdot\mathbf{r}}}{\epsilon_{\text{ex}}(\mathbf{K},0)},\quad(3.24)$$

$$\epsilon_{\text{ex}}(\mathbf{K},0)=1-\frac{4\pi e^2}{K^2}\sum_{\mathbf{k}'}\frac{N_{\mathbf{k}'}-N_{\mathbf{k}'+\mathbf{K}}}{E_{\mathbf{k}'}{}^0-E_{\mathbf{k}'+\mathbf{K}}{}^0}\times\left\{1+\frac{\hbar^2K^2}{2m\hbar\omega_p}\frac{(\beta_{\mathbf{k}'}+\beta_{\mathbf{k}'+\mathbf{K}})}{2\hbar\omega_p}\right\}.\quad(3.25)$$

The extra term in the brackets in (3.25) is the screened exchange correction to the dielectric function which screens the driving potential V_{eff}. In Si, $\beta_{k'}\simeq-2.5$ ev, $\hbar\omega_p\simeq17$ ev, and for $\mathbf{K}=2\pi a^{-1}(1,1,1)$, $\hbar^2K^2/2m\simeq14$ ev. Thus the extra term is about -0.13.

4. COMPARISON WITH BAND CALCULATIONS

The results of Secs. 2 and 3 enable us to make *a priori* estimates of self-consistent Coulomb potentials without having carried out a band calculation. On the other hand, approximately self-consistent band calculations have been carried out for diamond and silicon.[5,7] In these calculations the secular equation was solved exactly (instead of to first order in $V_{\mathbf{K}}$), but the sum over $\mathbf{k}'$ (which we have been able to evaluate analytically because of our nearly free electron approximation) was replaced by a sampling of 32 states of the valence band. It is therefore of interest to compare the *a priori* estimates with the results of references 5 and 7 as well as the x-ray data for diamond.[18]

To do so we must first estimate $V_R{}^{\mathbf{K}}$ in diamond and silicon. According to Cohen and Heine[10] V_R, as given by (2.4), can be grouped as

$$V_R=V_{Rs}+V_{Rp}+\cdots,\quad(4.1)$$

where only V_{Rp} operates on functions with p symmetry, etc. Because of the l dependence of V_R, a suitable average of (4.1) must be made.

Our chief concern in estimating ρ_s is to represent $\langle\mathbf{k}'|V_R|\mathbf{k}'+\mathbf{K}\rangle$ correctly, where $\mathbf{k}'$ refers to the valence band and $\mathbf{K}$ to one of the first few reciprocal lattice vectors. We recall that V_R is a local approximation to the orthogonalized plane wave terms which for this matrix element is

$$\textstyle\sum_{nl}[E(\mathbf{k}')-E_{nl}]a_{nl}{}^*(\mathbf{k}'+\mathbf{K})a_{nl}(\mathbf{k}').\quad(4.2)$$

In the small-core approximation, $a_{ns}(\mathbf{k}')$ is approximately constant and $a_{np}(\mathbf{k}')\sim\mathbf{k}'$. Thus the s repulsive potential is that for the state $\mathbf{k}'$,

$$\textstyle\sum_n[E(\mathbf{k}')-E_{ns}]a_{ns}{}^*(\mathbf{k}'+\mathbf{K})a_{ns}(\mathbf{k}')\simeq\sum_n[E(\mathbf{k}')-E_{ns}]a_{ns}{}^*(\mathbf{k}')a_{ns}(\mathbf{k}'),\quad(4.3)$$

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[18] L. Kleinman and J. C. Phillips, Phys. Rev. (to be published).

while the p apparently is not:

$$\sum_n [E(\mathbf{k}')-E_{np}]a_{np}^*(\mathbf{k}'+\mathbf{K})a_{ns}(\mathbf{k}') \sim (\mathbf{k}'+\mathbf{K})\cdot\mathbf{k}'. \quad (4.4)$$

However, inversion symmetry makes $\sum_{\mathbf{k}'} \mathbf{k}'\cdot\mathbf{K}=0$, so that the correct p repulsive potential is again that for the state $\mathbf{k}'$.

In diamond and silicon, Kleinman and Phillips[5,7] have found that the valence band is about half s and half p in atomic character. In Tables I and II we list V_{eff} in diamond and silicon, calculated from

$$V_{\text{eff}}^{\mathbf{K}} = V_i^{\mathbf{K}} + \tfrac{1}{2}(V_{Rs}^{\mathbf{K}} + V_{Rp}^{\mathbf{K}}). \quad (4.5)$$

From Tables I and II we see that $V_{\text{eff}}^{\mathbf{K}_1}$, where $K_1^2=3(2\pi a^{-1})^2$, is much greater than $V_{\text{eff}}^{\mathbf{K}_n}$, $\mathbf{K}_n \neq \mathbf{K}_1$. According to the linear theory developed in Secs. 2 and 3, each component $V_{\text{eff}}^{\mathbf{K}_i}$ is independently screened by $\epsilon(K_i)$. A detailed study of the valence screening charge density in diamond[18] has shown that because $V_{\text{eff}}^{\mathbf{K}_1}$ is so large ($V_{\text{eff}}^{\mathbf{K}_1} \simeq E_F/2$), our linear theory gives $V_s^{\mathbf{K}_i}$ correctly only for $\mathbf{K}_i = \mathbf{K}_1$. The higher Fourier coefficients are strongly modified by nonlinear hybridizing of $\rho_s^{\mathbf{K}_n}$ with $\rho_s^{\mathbf{K}_1}$. A detailed discussion of nonlinear screening, which may be called local-field corrections or crystal hybridization, is given in reference 18. Here we are concerned with linear dielectric effects, so that we consider only $V^{\mathbf{K}_1}$.

TABLE I. Fourier coefficients of ionic, repulsive, and effective potentials, per unit cell, in rydbergs, for diamond. Also listed are V_s, the valence Coulomb potential, and V_{ex}, a Thomas-Fermi exchange potential which gives a good approximation to the screened exchange potential.

K^2	$V_i^{\mathbf{K}}$	$V_{Rs}^{\mathbf{K}}$	$\frac{1}{2}(V_{Rs}^{\mathbf{K}}+V_{Rp}^{\mathbf{K}})$	$V_{\text{eff}}^{\mathbf{K}}$
3	−1.05	0.57	0.28	−0.77
8	−0.42	0.43	0.22	−0.20
11	−0.32	0.37	0.19	−0.13
16	−0.19	0.30	0.15	−0.04
K^2	$V_{\text{eff}}^{\mathbf{K}}$	$V_s^{\mathbf{K}}$	$V_{\text{ex}}^{\mathbf{K}}$	$V^{\mathbf{K}}$
3	−0.77	0.32	−0.16	−0.61

According to (2.18) and (3.25) we have two choices for the screening factor $\epsilon(K_1)$. These are:

1. The Hartree dielectric function for the free-electron gas, $\epsilon^0(K_1)$, as in (2.17).
2. The free-electron dielectric function $\epsilon_{\text{ex}}^0(K_1)$ with screened exchange included, as in (3.25).

The screened potential corresponding to the first choice, $V_{\text{eff}}^{\mathbf{K}_1}/\epsilon^0(K_1)$, does not include valence-valence exchange. To it, therefore, we must add the screened exchange potential to get the total potential to be used in band-structure calculations. The results for diamond and Si obtained by taking the exchange potential from Tables I and II are compared in Table III (line 1) with the results of the detailed sample of the charge density; the agreement is excellent. The screened potential corresponding to the second choice already incorporates exchange, $V_{\text{eff}}^{\mathbf{K}_1}/\epsilon_{\text{ex}}^0(K_1)$ is also given in Table III (line 2); the agreement with the sampling calculation is noticeably poorer. Thus the approximations in Sec. 3 significantly underestimate the decrease in ϵ^0 caused by exchange.

TABLE II. Fourier coefficients of potential in rydbergs, for silicon. The notation is the same as in Table I.

K^2	$V_i^{\mathbf{K}}$	$V_{Rs}^{\mathbf{K}}$	$V_{Rp}^{\mathbf{K}}$	$\frac{1}{2}(V_{Rs}^{\mathbf{K}}+V_{Rp}^{\mathbf{K}})$	$V_{\text{eff}}^{\mathbf{K}}$
3	−0.79	0.62	0.39	0.50	−0.29
8	−0.37	0.43	0.26	0.34	−0.07
11	−0.29	0.36	0.22	0.29	0.00
16	−0.23	0.27	0.17	0.22	−0.01
	$V_{\text{eff}}^{\mathbf{K}}$	$V_s^{\mathbf{K}}$	$V_{\text{ex}}^{\mathbf{K}}$	$V^{\mathbf{K}}$	
3	−0.29	0.15	−0.07	−0.21	

5. FURTHER APPLICATIONS AND LIMITATIONS

From the quantitative success of linear screening (choice 1) for semiconductors we conclude that *a fortiori* linear screening can be used to estimate self-consistent charge densities in metals. Many band calculations have assumed that ρ_s was given by ρ_s^0, as in (2.7). Also the Wigner-Seitz spherical approximation has often been made. (For a discussion of the errors introduced by the latter approximation, see Heine[4] or Callaway and Glasser.[19]) From (2.18) or (3.24) we can see that most of these calculations were not self-consistent, since large band gaps ($V_{\text{eff}}^{\mathbf{K}} \neq 0$) were often found. The screening we have discussed tends to reduce band gaps and make the $E(\mathbf{k})$ curves more closely resemble those of a nearly free electron gas.

The principle limitation of our method lies in the linear dielectric approximation. Nonlinear hybridization effects contribute to the formation of the covalent band in diamond.[18] We may also consider hybridization corrections in heteropolar (partially ionic) semiconductors such as boron nitride.[6] Here again we find that only the first Fourier coefficient of charge transfer (V_{111}^a in the notation of reference 6) is given correctly by the linear theory. Further explorations of hybridization corrections by detailed self-consistent band calculations are

TABLE III. Dielectric constants and Fourier coefficient $[\mathbf{K}_1 = 2\pi a^{-1}(1,1,1)]$ of total potential (in rydbergs) for diamond and silicon. The first and second lines correspond to the approximations 1 and 2 for dielectric screening described in Sec. 4. The third line gives the value obtained from sampling crystal charge densities at 32 points in the valence band, in self-consistent calculations including screened exchange.

	$\epsilon(K_1)_{\text{C}}$	$\epsilon(K_1)_{\text{Si}}$	$V_{\text{C}}^{\mathbf{K}_1}$	$V_{\text{Si}}^{\mathbf{K}_1}$
Hartree free electron	1.66	1.96	−0.62	−0.22
Screened-exchange free electron	1.55	1.83	−0.51	−0.16
Band value			−0.61	−0.21

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[19] J. Callaway and M. L. Glasser, Phys. Rev. 112, 73 (1958).

desirable. Nevertheless, we may conjecture that this is a general result, namely: linear dielectric screening (choice 1) gives quantitatively correct results for the valence response to the longest and strongest wavelength component of the effective potential. An improvement of the theory of Sec. 3 would permit quantitatively accurate *a priori* estimate of the screened exchange potential as well.

PHYSICAL REVIEW VOLUME 124, NUMBER 6 DECEMBER 15, 1961

Energy Bands in Lithium

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(Received July 31, 1961)

A previous calculation of energy bands in lithium which employed the orthogonalized plane wave method, has been extended with the determination of the energies of states along the [100], [110], and [111] axes in the Brillouin zone. The Fermi energy has been determined. The Fermi surface predicted by these calculations is not in contact with the Brillouin zone, and is only slightly distorted from the sphere characteristic of free electrons.

INTRODUCTION

THE work reported here is an extension of a previous calculation of energy bands in lithium[1] based on the method of orthogonalized plane waves (OPW).[2] The earlier work considered only states at the four principal symmetry points in the Brillouin zone of the body-centered cubic lattice: Γ, H, P, and N (see Fig. 1). This calculation revealed the existence of a large energy gap (about 3.1 ev) between the two lowest states at the face center N. Since the Fermi surface of the electron distribution in a monovalent, body-centered cubic metal (considering the electrons to be free) approaches the boundary of the Brillouin zone most closely in the vicinity of the face center N, the question of possible contact between the Fermi surface and the zone became important. Cohen and Heine[3] concluded that existing experimental information suggested a large area of contact between the surface and the zone boundary. The experimental data which they considered are not, however, definitive in this regard since the crucial cyclotron resonance, de Haas-van Alphen effect, and ultrasonic attenuation measurements have not been reported. It seemed desirable to extend the energy band study to include enough points in the interior of the zone to make possible a determination of the Fermi energy and, hence, to make a definite prediction concerning contact.

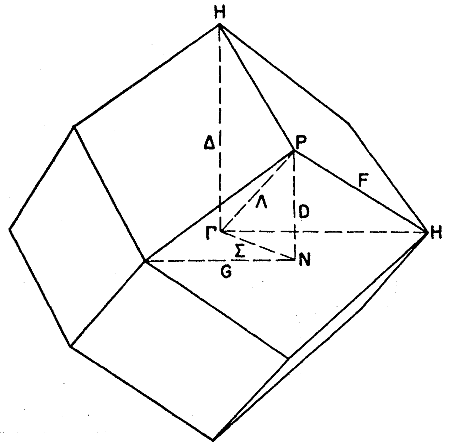

FIG. 1. The Brillouin zone for the body-centered cubic lattice. Points and lines of symmetry are shown.

The extension was made in the following way. The Fourier coefficients of the crystal potential (derived from the semi-empirical potential of Seitz[4] as quoted by Kohn and Rostoker[5]) were modified to take account of the fact that the normal component of the gradient of the crystal potential must vanish at many points on the surface of the atomic polyhedron. Energy levels were determined at twenty-one points on the surface and in the interior of the zone, including the four symmetry points previously mentioned and seventeen other points located along the [100], [110], and [111] axes (Δ, Σ, and Λ, respectively, in Fig. 1). These energy values were used to determine the seven lowest coefficients in the expansion of the energy in Kubic harmonics, and from these, the Fermi energy was determined according to a method proposed by de Launay[6] in a different problem.

While this work was in progress, other calculations of energy bands in lithium have been reported by Ham[7]

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[7] F. S. Ham, in *The Fermi Surface*, edited by W. A. Harrison and M. B. Webb (John Wiley & Sons, Inc., New York, 1960), p. 9.