the momentum-frequency variables,

$$p=(p_0,\mathbf{p}).$$

Expanding $\mathbf{G}(p)$ in terms of the Pauli matrices, $\boldsymbol{\tau}_i$, $\mathbf{1}$ in the 2×2 spin space leads to the expression (16) for $\mathbf{G}$ in lowest approximation. The trace is over the spin space. The propagator $\mathbf{G}$ may be diagonalized by means of the unitary Bogoliubov transformation:

$$\mathbf{U}(\mathbf{p})\mathbf{G}(p)\mathbf{U}(p)=i/[p_0-\boldsymbol{\tau}_3(E(p)-i\eta)],$$

where $\mathbf{U}(\mathbf{p})=u(\mathbf{p})\boldsymbol{\tau}_3-v(p)\boldsymbol{\tau}_1$. Here u, v, and E are defined by

$$E(p)=[(p^2/2m-\mu)^2+\phi^2]^{1/2},$$

$$[u(p)]^2=\frac{1}{2}\left(1+\frac{p^2/2m-\mu}{E(p)}\right),$$

$$[v(p)]^2=1-[u(p)]^2.$$

PHYSICAL REVIEW VOLUME 129, NUMBER 6 15 MARCH 1963

Electronic Structure and the Properties of Metals. I. Formulation

Walter A. Harrison
General Electric Research Laboratory, Schenectady, New York

(Received 22 October 1962)

A method is formulated for the calculation from first principles of a variety of electronic and atomic properties of metals. The method depends upon three approximations: (1) the self-consistent-field approximation; (2) the assumption that the core states are the same as in the free atom; and (3) a perturbation solution, carried to second order, of the Hamiltonian matrix based upon orthogonalized plane waves. Only the last approximation distinguishes the method from more traditional band calculations; it is regarded as appropriate for the treatment of most polyvalent metals. The only experimental parameters which enter for a given metal are the atomic number and the atomic volume.

It is found that many electronic properties, including the Fermi surface and scattering by defects or phonons, may be calculated as for free electrons with an effective perturbing potential. The matrix elements of this potential may be written as the product of a structure factor, depending only on the ion positions, and a form factor depending only on the Hartree-Fock field of the ion and upon the atomic volume. The form factor is found to be a function only of the magnitude of the change in wave number.

It is found that for a given ion density the energy of the system may be written in terms of a central-force, two-body interaction between ions or in terms of a sum over wave number space of the Fourier transform of this interaction (the energy-wave number characteristic). The procedure for computing these functions from the Hartree-Fock field of the corresponding ion is given.

I. INTRODUCTION

EXISTING *a priori* calculations of metallic properties based on the full Hartree or Hartree-Fock treatment of the crystal potential have been, for the most part, restricted to computations of the energy bands. There are exceptions, notably calculations of the lattice distance and attempts at calculation of the cohesive energy, but for the most part properties which depend upon the details of the lattice potential and the electronic structure have been beyond the reach of available techniques.

Recent developments have given hope of going beyond these limitations in treating polyvalent metals. This hope is based on the surprising fact that the Fermi surfaces of these metals differ very little from free-electron spheres,[1] indicating a relatively weak influence of the lattice potential. This suggests that we might regard this potential as a perturbation and sufficiently simplify the analysis, in comparison to traditional band calculations, that many new aspects of the behavior of metals could be treated in some detail.

The work to be described here is part of such a program. There are two classes of properties which we wish to attack: first, atomic properties which depend upon the variation of the total energy as the atoms are rearranged; and second, electronic properties which depend on the scattering of electrons when the crystal is not perfectly ordered. For both classes of properties the computations can be carried out without the explicit determination of the energy bands. We propose to carry out a rather complete Hartree calculation (exchange is also included where it is felt to be important) for a general arrangement of the metal ions.

Certainly the most crucial approximation to be made is the self-consistent-field approximation. Because of this approximation we regard the cohesive energy, which has a large contribution from the correlation energy, as beyond our reach. Further, we might expect the change in energy associated with change in volume to have a large contribution from correlations. On the other hand, it is hoped that changes in energy when the

---

[1] Extensive discussion of this point appears in the article, W. A. Harrison, Phys. Rev. **118**, 1190 (1960), and in several articles appearing in *The Fermi Surface*, edited by W. A. Harrison and M. B. Webb (John Wiley & Sons, Inc., New York, 1960).

ions are rearranged at constant volume may be rather insensitive to many-particle effects. Detailed calculations of the type described here should give a test to the hypothesis that the Hartree approximation suffices for treating such properties.

The second major approximation which is made is the treatment of the crystal potential as a perturbation, and the use of second-order perturbation theory. In most of the polyvalent metals the band gaps, as determined from band calculations, are of the order of a tenth the Fermi energy and the perturbation treatment should be justified. In cases where degenerate, or nearly degenerate, electron states are coupled by the lattice potential, degenerate perturbation theory must be used. This corresponds to taking principal values at singularities which occur when energies of all occupied states are added. There is, of course, no hope of treating the noble metals in this manner since the band gaps are comparable to the Fermi energy. In the polyvalent metals, on the other hand, the errors involved in using the perturbation treatment should be small compared to those in determining the potential. Thus, considered as a band calculation, the accuracy should not be appreciably less than for more refined methods of computing the band energies from a computed potential. Such a treatment of the band energies has been used by Bassani and Celli[2] previously. It should also be added that the use of perturbation theory allows a self-consistent treatment, and therefore favors this treatment over methods which are not done self-consistently.

A third approximation is made in assuming that the core states are the same as in the free atom. This should be quite good in most polyvalent metals, moderately good in a metal like zinc, and of course totally inadequate in a noble or transition metal. This assumption is essential not only in allowing us to neglect the banding of the core states and their corresponding energy change but also in assuring that the first-order, self-consistent crystal potential can be written as a sum of spherically symmetric terms which do not change when the ions are rearranged.

Some further numerical approximations may be made in any detailed analysis, but those mentioned above are the significant and essential ones.

The procedure may be outlined as follows: We take as a starting approximation to the conduction-band wave function, single plane waves orthogonalized to the core states on each ion (wherever it may lie). The expectation value of the energy, based upon this wave function is found to be independent of the arrangement of the ions. These approximate wave functions are then improved (and orthogonalized to each other) by taking linear combinations (time-dependent linear combinations in the case of scattering) of orthogonalized plane waves, and the improvement in the energy expectation value (the time dependence of the linear combinations in scattering) is found to depend on the ion arrangement. It is the structure-dependent terms which we seek in our analysis. The above calculation is facilitated by transforming to a pseudopotential formalism, which is then carried out self-consistently in a perturbation expansion.

A prominent feature of the method is the factorization of matrix elements of the Hamiltonian into a structure-dependent factor and an ion-potential-dependent factor (form factor) as one does in diffraction theory. Once this set of form factors is computed, the scattering by any defect of interest involves simply a computation of the geometrical structure factors which multiply the appropriate form factors, and the application of ordinary free-electron scattering theory. When the effect of the band structure is important, it appears in the second-order scattering calculation.

A second feature of the method derives from this same factorization. In the energy computation these structure factors, which are functions of wave number, are separated out and all other summations performed first. Thus, the total energy is written as a sum over wave number space of the square of the structure factor times an energy wave number characteristic. This characteristic may be computed for a particular type of ion at a given density and then the energy of any arrangement of ions is readily computed from the simple structure factors and this single characteristic.

We may alternatively make a Fourier transform of this characteristic and derive an entirely equivalent two-body central force between ions which allows the calculation of the total energy change when the atoms are rearranged at constant volume. It is rather striking that there exists such a two-body central force interaction (for rearrangements at constant volume) in this nearly-free-electron limit. Such an interaction (for general rearrangements) exists also in the tight-binding limit, but in the intermediate case it appears that multibody forces are required.

Because it is possible to separate out the factors which depend upon the ion positions, it is perhaps more descriptive of the method to say we calculate the Hamiltonian of the ions rather than the energy of the metal. We may, for example, introduce a vacancy and minimize this Hamiltonian with respect to the positions of the neighboring ions. Thus, we obtain rather easily the structure of the vacancy with a calculation which has the validity of a full band calculation.

A third feature which we might mention is the complete independence of the method on any long-range periodic structure. We precede just as directly with a defect present, with a stacking fault, or even with a liquid metal. We need simply compute, or determine from diffraction experiments, the structure factors and use our previously computed energy wave number characteristic. The method is also directly applicable to

---

[2] F. Bassani and V. Celli, Nuovo Cimento **11**, 805 (1959); J. Phys. Chem. Solids **20**, 64 (1961).

alloys and should lose nothing in reliability, though the computations are complicated somewhat.

A fourth feature of the method is that it is a working method which can be applied in detail to a real metal with a moderate amount of computation. The author has, in fact, applied it to zinc and obtained form factors and the energy wave number characteristic and considered several properties in terms of them. These are to be described in the adjoining communication.

II. DERIVATION OF THE EFFECTIVE HAMILTONIAN

In an independent-particle approximation the electronic behavior is derivable from a one-electron Schrödinger equation,

$$(T+V_{\mathrm{op}})\Psi_k=i\hbar\partial\Psi_k/\partial t. \qquad (2.1)$$

T is the kinetic energy operator, V_{op} contains the crystal field and is written as an operator since it will include some exchange terms. We distinguish between conduction-band states Ψ_k and core states, $\Psi_\alpha=\psi_\alpha \times\exp(-iE_\alpha t/\hbar)$. The core states are the free-atom core states computed in the Hartree-Fock approximation. The index α, therefore, specifies the ion position as well as the angular momentum and energy quantum numbers. The conduction-band states are to be computed in the Hartree approximation but including exchange with the core states; that is, we use a hybrid system.

By utilizing a pseudopotential formalism based on the orthogonalized-plane-wave (OPW) method, we will convert Eq. (2.1) into a form which allows for a perturbation expansion. Following Phillips and Kleinman[3] we write the conduction-band wave functions as two terms

$$\Psi_k=[\varphi_k-\textstyle\sum_\alpha(\psi_\alpha,\varphi_k)\psi_\alpha]e^{-i\omega_k t}, \qquad (2.2)$$

where φ_k is to be made smooth in some sense. $\hbar\omega_k$ will, of course, be taken equal to the appropriate electron energy, but at this point φ_k may depend upon time. Such a form is always valid and simply makes explicit the orthogonality between the Ψ_k and the ψ_α.

Equation (2.2) may be substituted into Eq. (2.1) to obtain an equation satisfied by φ_k,

$$\begin{aligned}T\varphi_k+V_{\mathrm{op}}\varphi_k-\textstyle\sum_\alpha(\psi_\alpha,\varphi_k)(E_\alpha-\hbar\omega_k)\psi_\alpha\\ =\hbar\omega_k\varphi_k+i\hbar(\partial/\partial t)[\varphi_k-\textstyle\sum_\alpha(\psi_\alpha,\varphi_k)\psi_\alpha]. \qquad (2.3)\end{aligned}$$

We define the pseudopotential, W, by

$$W\varphi_k=V_{\mathrm{op}}\varphi_k-\textstyle\sum_\alpha(\psi_\alpha,\varphi_k)(E_\alpha-\hbar\omega_k)\psi_\alpha, \qquad (2.4)$$

so that (2.3) may be written in the form,

$$T\varphi_k+W\varphi_k=\hbar\omega_k\varphi_k+i\hbar\partial/\partial t[\varphi_k-\textstyle\sum_\alpha(\psi_\alpha,\varphi_k)\psi_\alpha]. \qquad (2.5)$$

The term in W will be regarded as a perturbation in all of our analysis.

Cohen and Heine[4] have pointed out that there are many choices of the φ_k which correspond to the same Ψ_k derived by Eq. (2.2). We wish to pick a particular set of φ_k which gives speedy convergence to the perturbation expansion and which puts the pseudopotential, W, in convenient form. Cohen and Heine sought rapid convergence by minimizing $-(\varphi_k,\nabla^2\varphi_k)/(\varphi_k,\varphi_k)$. If φ_k is an energy eigenstate, this is equivalent to maximizing $(\varphi_k,W\varphi_k)/(\varphi_k,\varphi_k)$, as may be seen from Eq. (2.3). This was also the procedure used by the author[5] in his earlier treatment of zinc. Such an approach leads to difficulties if the potential is written as a sum of localized, but overlapping, potentials; the resulting expression involves overlap integrals between local potentials and neighboring cores. These difficulties are avoided by defining an approximate potential V_{op}' which *can* be written as a sum of nonoverlapping potentials and maximizing the corresponding $(\varphi_k,W'\varphi_k)/(\varphi_k,\varphi_k)$. We include the strongest part of the potential near the ion cores in V_{op}' so that we do not expect to lose appreciable speed of convergence. Furthermore, when we compute matrix elements, we use W rather than only W', so the accuracy of the method should not be affected and our result is almost independent of the precise manner in which V_{op}' is constructed.

The optimization proceeds just as in our earlier treatment of zinc[5] and we obtain

$$W'\varphi_k=U\varphi_k+\frac{(\varphi_k,U\varphi_k)\sum_\alpha(\psi_\alpha,\varphi_k)\psi_\alpha}{(\varphi_k,\varphi_k)-\sum_\beta(\psi_\beta,\varphi_k)(\varphi_k,\psi_\beta)},$$

with

$$U\varphi_k=V_{\mathrm{op}}'\varphi_k-\textstyle\sum_\alpha(\psi_\alpha,V_{\mathrm{op}}'\varphi_k)\psi_\alpha. \qquad (2.6)$$

We may note that the operator W' is not Hermitian, nor is it linear; these difficulties derive from the nonorthogonality between the orthogonalized plane waves. We may avoid associated ambiguities by defining a more general operator, $W'(\kappa)$:

$$W'(\kappa)\varphi_k=U\varphi_k+\frac{(\varphi_\kappa,U\varphi_\kappa)\sum_\alpha(\psi_\alpha,\varphi_k)\psi_\alpha}{(\varphi_\kappa,\varphi_\kappa)-\sum_\beta(\varphi_\kappa,\psi_\beta)(\psi_\beta,\varphi_\kappa)}. \qquad (2.7)$$

The difference between W and W' is a simple potential, which we write as $V(\mathbf{r})$. Thus, the total pseudopotential which enters our calculations is given by

$$W(k)\varphi_k=W'(k)\varphi_k+V(\mathbf{r})\varphi_k. \qquad (2.8)$$

We have found a special form[6] for the pseudopotential, $W(k)$. This has been achieved without approximation and should be distinguished from treatments in which W is assumed to have the form of a simple potential.[7,8] Such an assumption is frequently called a

---

[3] J. C. Phillips and L. Kleinman, Phys. Rev. **116**, 287, 880 (1959).

[4] M. H. Cohen and V. Heine, Phys. Rev. **122**, 1821 (1961).

[5] W. A. Harrison, Phys. Rev. **126**, 497 (1962).

[6] B. J. Austin, V. Heine, and L. J. Sham [Phys. Rev. **127**, 276 (1962)], have discussed the relationship between various forms of the pseudopotential.

[7] J. M. Ziman, Phil Mag. **6**, 1013 (1961).

[8] M. H. Cohen and J. C. Phillips, Phys. Rev. **124**, 1818 (1961).

pseudopotential approximation though it would more appropriately be called a wave-number-independent pseudopotential approximation. In our detailed treatment of zinc, we find such an approximation totally inadequate.

In our subsequent analysis, we will regard off-diagonal matrix elements of W, W', and V as small. We may readily see that this assertion requires also that we regard expressions of the form $\sum_\alpha(\varphi_{k'},\psi_\alpha)(\psi_\alpha,\varphi_k)$ (which we call OPW overlaps) as small and of the same order. This follows from Eq. (2.4), from which we see that different matrix elements will differ by terms of order $(E_{k'}-E_k)\sum_\alpha(\varphi_{k'},\psi_\alpha)(\psi_\alpha,\varphi_k)$. In our detailed treatment of zinc we find, in fact, that $\sum_\alpha(\varphi_k,\psi_\alpha)(\psi_\alpha,\varphi_k)$ is of the order of the matrix elements divided by the Fermi energy (near 10%) so this is consistent in practice.

III. THE PERTURBATION EXPANSION

A. The Energy Eigenstates

We seek first the time-independent perturbation expansion. Writing the energy-eigenvalue $\hbar\omega_k=E_k$, Eq. (2.5) becomes

$$T\varphi_k+V\varphi_k+U\varphi_k+\frac{(\varphi_k,U\varphi_k)\sum_\alpha(\psi_\alpha,\varphi_k)\psi_\alpha}{(\varphi_k,\varphi_k)-\sum_\alpha(\varphi_k,\psi_\alpha)(\psi_\alpha,\varphi_k)}=E_k\varphi_k. \qquad (3.1)$$

The zero-order solutions are plane waves. φ_k is expanded in the form,

$$\varphi_k=\Omega^{-1/2}e^{i\mathbf{k}\cdot\mathbf{r}}\sum_{\mathbf{q}}a(\mathbf{k})_{\mathbf{q}}e^{i\mathbf{q}\cdot\mathbf{r}}, \qquad (3.2)$$

where Ω is the volume of the crystal. $a(\mathbf{k})_0$ is of zero order; the remaining $a(\mathbf{k})_{\mathbf{q}}$ are first or higher order. Equation (3.2) is substituted in (3.1) and the resulting equation solved in zero, first, and second order. Particular care must be taken in this analysis because of the nonlinearity of W. We obtain finally the first-order coefficients in the wave function,

$$a(\mathbf{k})_{\mathbf{q}}=\frac{\langle\mathbf{k}+\mathbf{q}|W(k)|\mathbf{k}\rangle}{T_k-T_{k+q}}a(\mathbf{k})_0, \qquad (3.3)$$

and the energy to second order,

$$E_k=T_k+\langle\mathbf{k}|W(k)|\mathbf{k}\rangle+\sum_{\mathbf{q}}\frac{\langle\mathbf{k}|W(k)|\mathbf{k}+\mathbf{q}\rangle\langle\mathbf{k}+\mathbf{q}|W(k)|\mathbf{k}\rangle}{T_k-T_{k+q}}. \qquad (3.4)$$

Here T_k is the kinetic energy, $\hbar^2k^2/2m$. The matrix elements are all between plane waves and are given by

$$\langle\mathbf{k}'|W(\kappa)|\mathbf{k}\rangle=\langle\mathbf{k}'|V|\mathbf{k}\rangle+\langle\mathbf{k}'|U|\mathbf{k}\rangle+\frac{\langle\boldsymbol{\kappa}|U|\boldsymbol{\kappa}\rangle\sum_\alpha\langle\mathbf{k}'|\alpha\rangle\langle\alpha|\mathbf{k}\rangle}{1-\sum_\beta\langle\boldsymbol{\kappa}|\beta\rangle\langle\beta|\boldsymbol{\kappa}\rangle}, \qquad (3.5)$$

with

$$\langle\mathbf{k}'|U|\mathbf{k}\rangle=\Omega^{-1}\int e^{-i\mathbf{k}'\cdot\mathbf{r}}Ue^{i\mathbf{k}\cdot\mathbf{r}}d\tau, \qquad (3.6)$$

and

$$\langle\alpha|\mathbf{k}\rangle=\Omega^{-1/2}\int\psi_\alpha^*e^{i\mathbf{k}\cdot\mathbf{r}}d\tau. \qquad (3.7)$$

For purposes of calculation, it is conveneint to rewrite the matrix element $\langle\mathbf{k}|W(k)|\mathbf{k}+\mathbf{q}\rangle$ such that the state $|\mathbf{k}\rangle$ lies to the right. This interchange is not immediate because of the non-Hermiticity of $W(k)$ arising from the non-Hermiticity of U. Taking the form of U from Eq. (2.6) ,we see that

$$\langle\mathbf{k}'|U|\mathbf{k}\rangle^*=\langle\mathbf{k}|V_{\text{op}}'|\mathbf{k}'\rangle-\sum_\alpha\langle\mathbf{k}|V_{\text{op}}'|\alpha\rangle\langle\alpha|\mathbf{k}'\rangle. \qquad (3.8)$$

Furthermore, since V_{op}' is a good approximation to the ionic potential in the region of the core, we may write

$$\langle\mathbf{k}|V_{\text{op}}'|\alpha\rangle=\langle\mathbf{k}|E_\alpha-T|\alpha\rangle=(E_\alpha-T_k)\langle\mathbf{k}|\alpha\rangle.$$

When this is substituted into Eq. (3.8), we obtain

$$\langle\mathbf{k}'|U|\mathbf{k}\rangle^*-\langle\mathbf{k}|U|\mathbf{k}'\rangle=(T_k-T_{k'})\sum_\alpha\langle\mathbf{k}|\alpha\rangle\langle\alpha|\mathbf{k}'\rangle.$$

Finally, we combine this result with Eq. (3.5) to obtain the non-Hermiticity of $W(\kappa)$ explicitly:

$$\langle\mathbf{k}+\mathbf{q}|W(\kappa)|\mathbf{k}\rangle^*-\langle\mathbf{k}|W(\kappa)|\mathbf{k}+\mathbf{q}\rangle=(T_k-T_{k+q})\sum_\alpha\langle\mathbf{k}|\alpha\rangle\langle\alpha|\mathbf{k}+\mathbf{q}\rangle. \qquad (3.9)$$

The energy, (3.4) becomes

$$E_k=T_k+\langle\mathbf{k}|W(k)|\mathbf{k}\rangle-\sum_{\mathbf{q}}\langle\mathbf{k}+\mathbf{q}|W(k)|\mathbf{k}\rangle\sum_\alpha\langle\mathbf{k}|\alpha\rangle\langle\alpha|\mathbf{k}+\mathbf{q}\rangle+\sum_{\mathbf{q}}|\langle\mathbf{k}+\mathbf{q}|W(k)|\mathbf{k}\rangle|^2/(T_k-T_{k+q}). \qquad (3.10)$$

B. Scattering

We also find the time-dependent perturbation result. We regard W as the perturbation giving rise to the scattering. It may be noted that in proceeding in this way we include in the scattering, terms which are customarily regarded as band structure; that is, W includes the periodic lattice potential as well as the potential arising from the defect of interest. It is readily seen, however, that the periodic potential does not contribute to the resistivity in that the set of electrons involved is of measure zero and our result will be proportional to the number of defects as it should be.

When scattering occurs in first order, the band structure (or periodic potential) does not enter at all. When it occurs in second order, we obtain cross terms so that the band structure does enter and again the resistivity is proportional to the number of defects. This is distinct from Umklapp, which is still only first order in the pseudopotential.

This inclusion of the periodic potential to just the same order as the defect potential seems totally appropriate; the strength of the potential of an ion in the periodic array is ordinarily comparable to that of the defect. The analysis is immensely simpler than analyzing the band structure to all orders before introducing the defect, and the formulation is much more straightforward.

The formulation given here was developed in conjunction with Smith Freeman, Jr. It is similar to, but more direct than, a formulation given by Austin, Heine, and Sham.[9] We expand φ_k in the form

$$\varphi_k=\Omega^{-1/2}\sum_{\mathbf{q}} a(t)_{\mathbf{q}}e^{i(\mathbf{k}+\mathbf{q})\cdot\mathbf{r}-i\omega_q t}.$$

This is substituted into the time-dependent Schrödinger equation, (3.5), and again solved by orders. The derivation proceeds as in the usual time-dependent case except that we must insert the explicit form for W from Eqs. (2.7) and (2.8) and keep track of the additional terms arising from the nonlinearity of W. At time zero we take only a_0 to be nonzero; we take

$$\hbar\omega_q=\langle\mathbf{k}+\mathbf{q}|T+W(k)|\mathbf{k}+\mathbf{q}\rangle-\langle\mathbf{k}|T+W(k)|\mathbf{k}\rangle.$$

We find finally that if there is a nonvanishing matrix element of W connecting the initial state $\mathbf{k}$ and the final state $\mathbf{k}'$ that

$$i\hbar\dot{a}_{k'-k}=a_0\langle\mathbf{k}'|W(k)|\mathbf{k}\rangle\exp(i\omega_{k'-k}t),$$

from which we may proceed to the transition rate as if we were treating free electrons:

$$P_{k'k}=(2\pi/\hbar)|\langle\mathbf{k}'|W(k)|\mathbf{k}\rangle|^2\delta(\hbar\omega_{k'-k}). \tag{3.11}$$

We may note that this transition rate gives us the correct decay of the current since the wave function between cores is directly proportional to φ. Therefore, the current in these regions may be evaluated as if the wave function were for free electrons.

If there is no matrix element connecting the states $\mathbf{k}$ and $\mathbf{k}'$, we must go to second order from which we obtain

$$P_{k'k}=\frac{2\pi}{\hbar}\left|\frac{\sum_{\mathbf{q}}\langle\mathbf{k}+\mathbf{q}|W(k)|\mathbf{k}'\rangle^*\langle\mathbf{k}+\mathbf{q}|W(k)|\mathbf{k}\rangle}{\hbar\omega_{\mathbf{q}}}\right|^2\delta(\hbar\omega_{k'-k}). \tag{3.12}$$

It is interesting to note that in the scattering problem we do not obtain any terms, such as the next to last term in Eq. (3.10) for the energy, which arise directly from the non-orthogonality of the OPW's.

IV. THE SELF-CONSISTENT POTENTIAL

We wish to write the potential operator as a sum of spherically symmetric operators centered on the individual ion sites. The bare ion potentials can be written this way, and since only first-order screening enters, the screening field for each ion may be computed separately and will also be spherically symmetric. Thus each crystal field operator, O, which enters our computation may be written as a sum of local operators, o, entered on the ion sites, $\mathbf{r}_j$,

$$O(\mathbf{r})=\sum_j o(\mathbf{r}-\mathbf{r}_j), \tag{4.1}$$

This allows us to separate the matrix elements into two factors,

$$\langle\mathbf{k}+\mathbf{q}|O(\mathbf{r})|\mathbf{k}\rangle=S(\mathbf{q})\langle\mathbf{k}+\mathbf{q}|o|\mathbf{k}\rangle, \tag{4.2}$$

with

$$S(\mathbf{q})=\sum_j e^{-i\mathbf{q}\cdot\mathbf{r}_j}/N, \tag{4.3}$$

and

$$\langle\mathbf{k}+\mathbf{q}|o|\mathbf{k}\rangle=\Omega_0^{-1}\int e^{-i(\mathbf{k}+\mathbf{q})\cdot\mathbf{r}}o(\mathbf{r})e^{i\mathbf{k}\cdot\mathbf{r}}d\tau. \tag{4.4}$$

Ω_0 is the atomic volume, Ω/N. $S(\mathbf{q})$ is the structure factor which appears in diffraction theory; it depends only upon the positions of the ions and not on the ionic potentials. $\langle\mathbf{k}+\mathbf{q}|o|\mathbf{k}\rangle$ is analogous to the atomic form factor in diffraction theory; it depends upon the ionic potential, but not on the positions of the ions. We may note that, in contrast to diffraction theory, $o(\mathbf{r})$ may not commute with $\exp(i\mathbf{k}\cdot\mathbf{r})$ and therefore this form factor may depend upon $\mathbf{k}$ as well as $\mathbf{q}$.

The index α specifying the core states is replaced by a double index (j,t), with j specifying the position of the ion and t specifying the quantum numbers of the atomic state. Then matrix elements between core states and conduction-band states may also be written in convenient form,

$$\langle\alpha|O|\mathbf{k}\rangle=(e^{i\mathbf{k}\cdot\mathbf{r}_j}/N^{1/2})\langle t|o|\mathbf{k}\rangle, \tag{4.5}$$

with

$$\langle t|o|\mathbf{k}\rangle=\Omega_0^{-1/2}\int\psi_t(\mathbf{r})o(\mathbf{r})e^{i\mathbf{k}\cdot\mathbf{r}}d\tau. \tag{4.6}$$

The orthogonality coefficients are of this form with O replaced by unity. This separation of matrix elements into structure-dependent and potential-dependent factors not only gives an immense computational simplification, but also gives us hope of realistically computing the changes in energy when the ions are rearranged.

Since $S(0)$ is equal to one and is thus independent of the arrangement of the ions, the diagonal matrix elements are independent of the arrangement of the ions. We are only interested in the changes in energy and in matrix elements as the ions are rearranged at constant volume; therefore, we may disregard diagonal elements throughout our analysis. We may now proceed to an explicit discussion of the potential.

In our derivation of the effective Hamiltonian we divided the potential into a nonoverlapping part, v_{op}' and an overlapping part, v. We require that v_{op}' include the strong portion of the potential near the ion core. In our calculations we take v_{op}' to be the Hartree-Fock field of the bare ion, cut off at a sphere with volume

---

[9] See reference 6.

equal to the cell volume. Then v includes the tails of the ion potential beyond the cutoff sphere and the potential due to the conduction electrons. The results appear to be quite insensitive to the details of the splitting of the potential.

With this definition of v_{op}', and with the definition of localized operators given above, the form factors associated with U and W become, respectively,

$$\langle\mathbf{k}+\mathbf{q}|u|\mathbf{k}\rangle=\langle\mathbf{k}+\mathbf{q}|v_{\text{op}}'|\mathbf{k}\rangle -\sum_t\langle t|v_{\text{op}}'|\mathbf{k}\rangle\langle\mathbf{k}+\mathbf{q}|t\rangle, \quad (4.7)$$

and

$$\langle\mathbf{k}+\mathbf{q}|w(\kappa)|\mathbf{k}\rangle =\langle\mathbf{k}+\mathbf{q}|v|\mathbf{k}\rangle+\langle\mathbf{k}+\mathbf{q}|u|\mathbf{k}\rangle +\frac{\langle\boldsymbol{\kappa}|u|\boldsymbol{\kappa}\rangle}{1-\sum_t\langle\boldsymbol{\kappa}|t\rangle\langle t|\boldsymbol{\kappa}\rangle}\sum_t\langle\mathbf{k}+\mathbf{q}|t\rangle\langle t|\mathbf{k}\rangle. \quad (4.8)$$

The form factor associated with W is called the OPW form factor. It enters directly in the computation of energy states and in scattering.

The potential v_{op}' is obtained directly from a Hartree or Hartree-Fock analysis of the ion or atom in question by truncating at the equivalent sphere. The potential v contains the tail of the ion field beyond the equivalent sphere and the field due to the conduction electrons. This latter requires further calculation.

We develop the field due to the conduction electrons by orders, noting again that terms of order $\sum_t\langle k'|t\rangle\langle t|k\rangle$, as well as terms of order w, are first order. The charge distribution due to individual OPW's contains a zero-order uniform charge density, $-Ze/\Omega_0$, and a first-order charge density which derives from the orthogonalization of the plane waves to the core states and their renormalization. This first-order charge density contributes to off-diagonal matrix elements, $\langle\mathbf{k}+\mathbf{q}|W(k)|\mathbf{k}\rangle$ for $\mathbf{q}\neq0$, while the zero-order charge density contributes only to diagonal elements.

The replacement of individual OPW's by linear combinations of OPW's to first order in W gives an additional first-order charge distribution corresponding to a linear combination of plane waves and an additional second-order contribution due to the orthogonalization terms. Such a second-order contribution to the matrix elements does not enter our second-order energy calculation nor our scattering calculation.

The off-diagonal matrix elements of v, then, derive from the tails of the ionic potential, from the charge distribution associated with orthogonalization of the plane waves to the core states, and finally from the self-consistent charge density, ρ_{sc}, which we may compute from the first-order φ_k's[10];

$$\rho_{\text{sc}}=-e\sum_{k<k_F}\varphi_k{}^*\varphi_k.$$

Cohen and Phillips[7] have also made this replacement of the OPW's by plane waves in computing the screening without, however, indicating that this is consistent to the order to which the computation is made. Our treatment of screening differs from theirs primarily in that they also replace $W(k)$ by a simple potential. For our purposes this is quite inadequate. Where they find the matrix elements are simply divided by the Hartree dielectric function, we find a more complicated expression.

The first-order screening charge density is readily obtained from the first-order φ_k's given by Eq. (3.2).

$$\rho_{\text{sc}}=-(e/\Omega)\sum_q\sum_{k<k_F}\left[a(\mathbf{k})_q e^{i\mathbf{q}\cdot\mathbf{r}}+a(\mathbf{k})_q{}^* e^{-i\mathbf{q}\cdot\mathbf{r}}\right].$$

Using Poisson's equation, we obtain the screening potential, V^{sc}, and obtain for the corresponding form factor,

$$v_q{}^{\text{sc}}=\langle\mathbf{k}+\mathbf{q}|v^{\text{sc}}|\mathbf{k}\rangle =(4\pi e^2/q^2\Omega)\sum_{k<k_F}\left[a(\mathbf{k})_q+a(\mathbf{k})_{-q}{}^*\right].$$

Finally we may substitute for the $a(\mathbf{k})_q$ from Eq. (3.3), write $w(k)$ as a sum of the unscreened value, $w(k)^0$ and the screening potential, v^{sc}, snd solve for v^{sc}. We obtain

$$v_q{}^{\text{sc}}=\frac{\dfrac{4\pi e^2}{q^2\Omega}\displaystyle\sum_{k<k_F}\left\{\frac{\langle\mathbf{k}+\mathbf{q}|w(k)^0|\mathbf{k}\rangle}{T_k-T_{k+q}}+\frac{\langle\mathbf{k}-\mathbf{q}|w(k)^0|\mathbf{k}\rangle^*}{T_k-T_{k-q}}\right\}}{1-\dfrac{4\pi e^2}{q^2\Omega}\displaystyle\sum_{k<k_F}\left\{\frac{1}{T_k-T_{k+q}}+\frac{1}{T_k-T_{k-q}}\right\}}. \quad (4.9)$$

If $\langle\mathbf{k}+\mathbf{q}|w(k)^0|\mathbf{k}\rangle$ and $\langle\mathbf{k}-\mathbf{q}|w(k)^0|\mathbf{k}\rangle^*$ were independent of $\mathbf{k}$ they could be taken outside the summation to obtain the Cohen-Phillips result,

$$v_q{}^{\text{sc}}=\langle\mathbf{k}+\mathbf{q}|w(k)^0|\mathbf{k}\rangle(1-\epsilon_q)/\epsilon_q,$$

where ϵ_q is the Hartree dielectric function. This, however, is not the case and the rather laborious summations of Eq. (4.9) must be performed to obtain the self-consistent potential.

V. COMPUTATION OF THE MATRIX ELEMENTS

We will follow and extend the method which we developed for the computation of matrix elements for zinc.[5] In that treatment we took for the potential (called the unscreened potential in that treatment) simply the v_{op}' described above (with a slightly different cutoff

---

[10] Summation over k here, and throughout the analysis, should be regarded as sums over states; i.e., they include a sum over spin as well as a sum over wave number.

procedure). That appears to have been reasonably reliable for computation of the Fermi surface, but not for the more general problems we wish to consider. In the earlier treatment, we considered only matrix elements between states lying on the Fermi surface; we now need more general matrix elements. We proceed by computing the form factors associated with the potential v_{op}'; we then include additional terms in the potential to obtain the unscreened form factors $\langle \mathbf{k}+\mathbf{q}|w(k)^0|\mathbf{k}\rangle$, and finally compute and add the screening terms to obtain the final OPW form factor from which matrix elements are to be determined.

v_{op}' contains exchange between conduction and core electrons and is, therefore, an l-dependent potential. It is appropriate in computing these terms to expand the plane waves in spherical harmonics and spherical Bessel functions. We then follow the procedure described earlier,[5] but generalized such that the magnitude of the final wavenumber, $\mathbf{k}'=\mathbf{k}+\mathbf{q}$, may differ from the magnitude of the initial wave number, $\mathbf{k}$. We obtain for the form factor associated with $\boldsymbol{u}$,

$$\begin{aligned}\langle \mathbf{k}+\mathbf{q}|u|\mathbf{k}\rangle &\\ = (4\pi/\Omega_0)\textstyle\sum_l(2l+1)P_l(\cos 2\Theta) &\\ \times\Big[\int r^2 j_l(k'r)v_{\mathrm{op}}' j_l(kr)dr &\\ -\textstyle\sum_n \int rP_{nl}(r)v_{\mathrm{op}}' j_l(kr)dr &\\ \times\int xj_l(k'x)P_{nl}(x)dx\Big]. &\quad (5.1)\end{aligned}$$

The $P_l(\cos 2\Theta)$ are Legendre polynomials of

$$\cos 2\Theta = \mathbf{k}\cdot\mathbf{k}'/kk';$$

i.e., 2Θ is the angle between $\mathbf{k}$ and $\mathbf{k}'=\mathbf{k}+\mathbf{q}$. The $P_{nl}(r)$ are the radial core functions,

$$\psi_t = r^{-1}P_{nl}(r)Y_l^m(\theta,\varphi).$$

We may write the sum of overlap integrals which also appears in the expression for $\langle \mathbf{k}+\mathbf{q}|w(k)|\mathbf{k}\rangle$ in similar form,

$$\begin{aligned}\textstyle\sum_t\langle \mathbf{k}+\mathbf{q}|t\rangle\langle t|\mathbf{k}\rangle &= (4\pi/\Omega_0)\textstyle\sum_l(2l+1)P_l(\cos 2\Theta)\\ &\times\textstyle\sum_n \int rj_l(k'r)P_{nl}(r)dr\int xP_{nl}(x)j_l(kx)dx. \quad (5.2)\end{aligned}$$

In computing the form factors associated with the tails of the core potential, the potential due to replacement of plane waves by OPW's, and actually some parts of v_{op}' which are not l dependent it is convenient to expand the product of the initial and final states rather than the two individually. Then since the potentials are spherically symmetric, only the $l=0$ term contributes; this procedure was followed previously.[5]

We have again achieved a sizable reduction in numerical work in that only the small number of integrals appearing in (5.1) need be evaluated to obtain all of the matrix elements between any initial state with magnitude of wave number k and any final state with magnitude of wave number k'. In scattering calculations the right-hand state in any matrix element which enters has the Fermi wave number. In energy calculations, it has always a wave number equal to or less than the Fermi wavenumber.

If we have the Hartree-Fock fields and wave functions for the ion in question, we evaluate the above integrals for a set of wave numbers of interest and can then write down the $\langle \mathbf{k}+\mathbf{q}|u|\mathbf{k}\rangle$. We then compute the additional potential $v-v^{\mathrm{sc}}$ from the tail and orthogonalization terms and find $\langle \mathbf{k}+\mathbf{q}|w(k)^0|\mathbf{k}\rangle$ for each q of interest and for various $k<k_F$. These are then substituted into (4.9) to obtain the v_q^{sc} for the q of interest. This is added on and we obtain the final OPW form factor which enters directly in the perturbation calculations of Sec. III.

This completes the bulk of the computation required for a scattering calculation. For a particular type of defect we determine the geometrical structure factors $S(\mathbf{q})$. These, in conjunction with the OPW form factors computed as above, give us the matrix elements entering (3.11) or (3.12) and we need simply sum over final states to obtain a scattering time.

We are somewhat further from the end of the energy calculations. The form factors above enable us to obtain matrix elements and Hartree energies by Eq. (3.10), but we require the total energy of the system and we proceed to that calculation.

VI. THE TOTAL ENERGY

There are three contributions to this energy: First, the sum of the band energies of the occupied conduction-band states. This is a sum of the E_k of Eq. (3.10) over all $k\le k_F$. Second, we must subtract an energy equal to the electron-electron Coulomb energy since this is counted twice in the Hartree approximation. Finally, we add the interaction between ions. This is simply the Coulomb interaction since we have taken the core states to be the atomic core states. The last two contributions are individually infinite, but their sum is not.

It will be convenient to regroup these contributions into three terms which we call the "free-electron energy," the "electrostatic energy," and the "band-structure energy." The division is somewhat arbitrary, but the one we select seems rather natural and is convenient for the calculations. Only the last two depend upon the arrangement of the ions and need to be computed explicitly.

Before defining our separation of terms, it is necessary to develop the various electrostatic contributions in detail. We define four charge densities:

ρ_0 is the average charge density of the electrons (the charge density of all normalized plane waves with $k<k_F$).

ρ_{opw} is the change in conduction-electron charge density due to orthogonalization with the core states and the subsequent renormalization.

ρ_{sc} is the change in conduction-electron charge density arising from the use of multiple-OPW wave functions (as a result of the perturbation calculation) rather than single OPW's.

ρ_{ion} is the charge density of point ions with charge equal to the valence.

We also define the four potentials, Φ^0, Φ^{opw}, Φ^{sc}, and Φ^{ion} which may be derived from the corresponding charge densities with Poisson's equation.

In terms of these quantities, the self-energy of the electrons which we wish to subtract is $\frac{1}{2}\int(\rho_0+\rho_{\mathrm{opw}}+\rho_{\mathrm{sc}})\times(\Phi^0+\Phi^{\mathrm{opw}}+\Phi^{\mathrm{sc}})d\tau$. The ion-ion self-energy which must be added is $\frac{1}{2}\int\rho_{\mathrm{ion}}\Phi^{\mathrm{ion}}d\tau$. (This integral should exclude the infinite self-energy of the individual ions.) It is convenient also to extract one contribution from the sum over diagonal matrix elements from (3.10), the contribution from the potential of the point ions and the compensating uniform negative background, $\int\rho_0(\Phi^0+\Phi^{\mathrm{ion}})d\tau$. These contributions may be collected, noting that in any term ρ and Φ may be interchanged. Further, we note that ρ_{opw} and ρ_{sc} have vanishing average values, while ρ_0 is constant. The resulting energy is

$$\frac{1}{2}\int(\rho_0+\rho_{\mathrm{ion}})(\Phi^0+\Phi^{\mathrm{ion}})d\tau-\frac{1}{2}\int\rho_{\mathrm{opw}}\Phi^{\mathrm{opw}}d\tau$$
$$-\int\rho_{\mathrm{opw}}\Phi^{\mathrm{sc}}d\tau-\frac{1}{2}\int\rho_{\mathrm{sc}}\Phi^{\mathrm{sc}}d\tau. \qquad (6.1)$$

The first integral is simply the electrostatic energy of positive point ions, with charge equal to the valence, and a compensating uniform negative background. The second integral is a similar self-energy of localized positive distributions arising from the orthogonalization and a compensating uniform negative distribution due to renormalization. If we define $e\delta Z$ to be the total charge localized at each ion by the orthogonalization (about $0.28e$ in zinc) then the sum of the two first terms is simply the electrostatic energy (within a constant term independent of arrangement) of point ions with effective valence Z^*, given by

$$Z^{*2}=Z^2-(\delta Z)^2, \qquad (6.2)$$

imbedded in a compensating uniform background. We define this to be the "electrostatic energy." It is customarily computed by methods due to Ewald.

The last two terms in (6.1) and the sum over off-diagonal ($\mathbf{q}\neq0$) terms in Eq. (3.10) are to be included in the "band-structure energy." The remaining diagonal terms in (3.10) and the kinetic energy are included in the "free-electron energy," which is independent of the positions of the ions and not considered further.

The third term in (6.1) may be written in more convenient form by noting that $\Phi^{\mathrm{sc}}=\sum_q(1/e)V_q^{\mathrm{sc}}e^{i\mathbf{q}\cdot\mathbf{r}}$. [See Eq. (4.9) for the corresponding form factor.] We obtain ρ_{opw} explicitly and obtain finally

$$-\int\rho_{\mathrm{opw}}\Phi^{\mathrm{sc}}d\tau=\sum_q V_q^{\mathrm{sc}}\sum_{\alpha,k}\Big\{\langle\mathbf{k}-\mathbf{q}|\alpha\rangle\langle\alpha|\mathbf{k}\rangle$$
$$+\langle\mathbf{k}|\alpha\rangle\langle\alpha|\mathbf{k}+\mathbf{q}\rangle-\langle\mathbf{k}|\alpha\rangle\langle\alpha|\mathbf{k}\rangle\int\psi_\alpha{}^*\psi_\alpha e^{i\mathbf{q}\cdot\mathbf{r}}d\tau\Big\}.$$

The integral on the right has not appeared before; it may be evaluated explicitly or might be estimated as $e^{i\mathbf{q}\cdot\mathbf{r}_i}$. It can then be seen that the first and last terms in the curly brackets very nearly cancel. The final term in Eq. (6.1) may also be written more conveniently as

$$-(1/2)\int\rho_{\mathrm{sc}}\Phi^{\mathrm{sc}}d\tau=-\tfrac{1}{2}\sum_q(\Omega q^2/4\pi e^2)|V_q^{\mathrm{sc}}|^2.$$

The total band-structure energy per electron is, then

$$E_{\mathrm{bs}}=(1/NZ)\sum_{q,k}\Big\{-[\langle\mathbf{k}+\mathbf{q}|W(k)|\mathbf{k}\rangle-V_q^{\mathrm{sc}}]$$
$$\times\sum_\alpha\langle\mathbf{k}|\alpha\rangle\langle\alpha|\mathbf{k}+\mathbf{q}\rangle$$
$$+|\langle\mathbf{k}+\mathbf{q}|W(k)|\mathbf{k}\rangle|^2/(T_k-T_{k+q})$$
$$+V_q^{\mathrm{sc}}\sum_\alpha(\langle\mathbf{k}-\mathbf{q}|\alpha\rangle\langle\alpha|\mathbf{k}\rangle$$
$$-\langle\mathbf{k}|\alpha\rangle\langle\alpha|\mathbf{k}\rangle\int\psi_\alpha{}^*\psi_\alpha e^{i\mathbf{q}\cdot\mathbf{r}}d\tau)\Big\}$$
$$-(1/2Z)\sum_q(\Omega_0q^2/4\pi e^2)|V_q^{\mathrm{sc}}|^2.$$

The matrix elements and orthogonality coefficients may be separated into structure factors and form factors and the energy per electron written in the final convenient form,

$$E_{\mathrm{bs}}=\sum_{\mathbf{q}}S^*(\mathbf{q})S(\mathbf{q})E(q), \qquad (6.3)$$

where $E(q)$ is defined as the energy wave number characteristic and is given by

$$E(q)=(1/NZ)\sum_k\Big\{-\langle\mathbf{k}+\mathbf{q}|w(k)^0|\mathbf{k}\rangle\sum_t\langle\mathbf{k}|t\rangle\langle t|\mathbf{k}+\mathbf{q}\rangle$$
$$+|\langle\mathbf{k}+\mathbf{q}|w(k)|\mathbf{k}\rangle|^2/(T_k-T_{k+q})$$
$$+v_q^{\mathrm{sc}}\sum_t(\langle\mathbf{k}+\mathbf{q}|t\rangle\langle t|\mathbf{k}\rangle$$
$$-\langle\mathbf{k}|t\rangle\langle t|\mathbf{k}\rangle\int\psi_t{}^*\psi_t e^{i\mathbf{q}\cdot\mathbf{r}}d\tau)\Big\}$$
$$-(\Omega_0q^2/8\pi Ze^2)|v_q^{\mathrm{sc}}|^2. \qquad (6.4)$$

Here again $w(k)^0$ is the unscreened pseudopotential and the summation over k implies a sum over wave number and spin of the occupied states.

We may compute this $E(q)$ by the methods described above for a given ion type and given ion density. The computation of the energy for a given arrangement of ions then involves first the computation of the structure factors $S(\mathbf{q})$; for a perfect crystal these will be delta functions at the reciprocal lattice points. We then multiply the square of each by the $E(q)$ value calculated and sum over wave number space to obtain the band structure energy. To this we add the electrostatic energy computed with the effective charge given by Eq. (6.2) and obtain all of the energy which depends upon the ion arrangement. The convergence of the computation of band-structure energy at large q seems to be quite rapid.

VII. THE EFFECTIVE ION-ION INTERACTION

For many problems, the above formulation is very convenient. Furthermore, it is of some interest physically to separate the band-structure and electrostatic contributions. For some purposes it may be preferable to transform the formulation into an ion-ion interaction which includes both the electrostatic and band-structure terms. This approach has been suggested by Cohen.[11] Such a formulation converges badly at large distances for either contribution by itself, but appears to converge quite well for the sum; this is because of the screening of the long range Coulomb interaction by the self-consistent field.

This form may be derived directly by adding the band-structure and electrostatic energy, writing the structure factors out explicitly in Eq. (6.3), and interchanging the summations to obtain the energy per ion

$$E=(Z/N^2)\sum_{ij}\sum_q E(q)e^{i\mathbf{q}\cdot(\mathbf{r}_i-\mathbf{r}_j)}+ \\ +(1/2N)\sum_{ij} Z^{*2}e^2/|\mathbf{r}_i-\mathbf{r}_j|.$$

This is to be equated to the energy per ion written in terms of the effective ion-ion interaction $\mathcal{V}(r)$,

$$E=(1/2N)\sum_{ij}\mathcal{V}(\mathbf{r}_i-\mathbf{r}_j).$$

From these two expressions for the energy, it follows that

$$\begin{aligned}\mathcal{V}(r)&=(2Z/N)\sum_q E(q)e^{i\mathbf{q}\cdot\mathbf{r}}+Z^{*2}e^2/r\\&=\frac{3Z^2}{k_Fr}\int x\sin(k_Frx)E(k_Fx)dx+Z^{*2}e^2/r,\end{aligned} \tag{7.1}$$

with $x=q/k_F$.

This transformation may be made explicitly once $E(q)$ has been computed. We may note the limiting behavior at large and small distance. The short-range limit has little meaning in that we have assumed that the cores do not overlap and we cannot bring ions very close without violating this condition. Under the approximations we have made, the first term in (7.1) goes to a constant as r goes to zero and the second term dominates. The appearance of an effective charge of Z^* rather than Z or than the total atomic number is of no great significance. At large distance the Coulomb field is screened in any case. At small distances the appropriate effective charge depends upon the conditions and assumptions with respect to overlap.

At large distance we can show that the first term approaches $-Z^{*2}e^2/r$, just cancelling the second. We may expect oscillating terms falling off as $1/r^3$ to arise from irrgularities in $E(q)$ at $q=2k_F$. However, these are not important in the total energy unless there is an accidental matching of a lattice distance and the Fermi wavelength. The remaining terms are expected to drop exponentially because of the screening.

---

[11] M. H. Cohen, paper contributed to Colloqium on The Structure of Metallic Solid Solutions, Orsay, France, July 9–11, 1962 in the Proceedings of the Colloquim (to be published).