Transition-Metal Pseudopotentials

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The pseudopotential method is reformulated and directly generalized to transition metals. The Schrödinger equation, in the self-consistent field approximation, is transformed without approximation into a transition-metal pseudopotential equation. The usual simple-metal pseudopotential appears in a modified form, but is nevertheless weak. An additional term appears which plays a role akin to *s-d* hybridization. Eigenstates and eigenvalues are then sought in a perturbation expansion in the pseudopotential and hybridization terms. It is possible, as with simple-metal pseudopotentials, to sum over states to obtain both the screening field and the total energy, though this summation is simple only when we neglect the partial filling or partial emptying of *d* bands. This is appropriate for the noble metals, the alkaline earths, and perhaps some transition metals between. For such cases there exists a pseudopotential form factor, just as in the simple metals, and an energy–wave-number characteristic from which a two-body central-force interaction may be derived. The form factor is evaluated for copper (using a semilocal approximation); it yields a good estimate of the *s-p* gap at *L* and of the resistivity of liquid copper.

I. INTRODUCTION

THE essence of the pseudopotential method,[1] as applied to simple metals, is the use of perturbation theory in treating the effects of the periodic potential. Rather than seeking the energy-band structure *per se*, we may directly treat properties of the metal such as electron scattering and may in fact sum the energy of all states in the crystal to obtain the total energy as a function of the configuration of the atoms.

In this application to the simple metals there are three essential approximations. First, we make a self-consistent field approximation, assuming the existence of a one-electron Hamiltonian in terms of which the eigenstates are calculable. Second, we divide the eigenstates into core states and conduction-band states and assume that the core eigenstates are the same in the metal as in the free atom. This is equivalent to an assumption of small cores and that approximation enters at a number of points in the treatment. We then seek the conduction-band states and make use of their known orthogonality to the core states to transform the Schrödinger equation to an exactly equivalent pseudopotential equation. In this equation the true wave function is replaced by a pseudo-wave-function which must be orthogonalized to the core states in order to obtain the true wave function. Finally, we assume that the pseudo-wave-function is sufficiently smooth, and correspondingly the pseudopotential is sufficiently weak, that we may solve this equation in perturbation theory going only to low orders.

Because of these assumptions the method is inapplicable to the transition metals, among which we include the noble metals as the last members of the series. (For similar reasons it may also be inaccurate for the neighboring metals—for example, calcium below and zinc above.) The failure, of course, arises from the *d* states. They are not sufficiently tightly bound (nor sufficiently localized) that we may validly treat them as the same

in the metal as in the free atom. At the same time they retain enough of their atomic character that if they are treated as conduction-band states, the pseudo-wave-function is not smooth, the pseudopotential is very large, and perturbation theory is inapplicable.

This has, of course, not prevented the calculation of the energy bands themselves[2,3] using methods which are *not* based upon low-order perturbation theory. In addition, there have been approximate methods of treating the *d*-state resonance.[4] These have, however, been directed at determining the energy spectrum itself and have not allowed the direct calculation of properties which the pseudopotential method has made possible for the simple metals.

We seek here a more direct generalization of the simple-metal pseudopotentials to the case of atomic *d* states. This is achieved by reformulating the pseudopotential method as an expansion of the conduction-band eigenstates in an overcomplete set made up of plane waves and atomic core states; this is entirely equivalent to the more usual formulation. This form may be directly generalized to the treatment of transition metals by seeking an expansion of the conduction-band states in an overcomplete set composed of plane waves, atomic core states, *and atomic d states*. This point of view is very close to that used by Deegan and Twose[3] in extending the orthogonalized-plane-wave (OPW) method to transition metals. In the use of the atomic *d*-wave functions, however, we must note that they are not eigenstates of the Hamiltonian of the metal. We write the difference in potential in a free atom and the potential in the neighborhood of an atom in the metal (except for a constant term) as Δ, and this, as well as

[1] W. A. Harrison, *Pseudopotentials in the Theory of Metals* (W. A. Benjamin, Inc., New York, 1966).

[2] Copper, for example, by B. Segall, Phys. Rev. **125**, 109 (1962); G. A. Burdick, *ibid.* **129**, 138 (1963).

[3] R. A. Deegan and W. D. Twose, Phys. Rev. **164**, 993 (1967).

[4] M. Saffren, *The Fermi Surface*, edited by W. A. Harrison and M. B. Webb (Wiley-Interscience, Inc., New York, 1960); L. Hodges and H. Ehrenreich, Phys. Letters **16**, 203 (1965); F. M. Mueller, Phys. Rev. **153**, 659 (1967); V. Heine, *ibid.* **153** 673 (1967); P. W. Anderson and W. McMillen, Estratto Rend. Scuola Intern. Fis. (Enrico Fermi) **37**, 50 (1967).

the pseudopotential itself, becomes an expansion parameter.

As in the pseudopotential method for simple metals, we first derive a pseudopotential equation that is exactly equivalent to the original Schrödinger equation. We then seek the eigenstates and eigenvalues by perturbation theory. This enables us to sum the total charge density and obtain a screening potential. It also enables us to sum the total energy of the system, leading to the structure-dependent energy in terms of an effective two-body central-force interaction.

Although the formulation itself is applicable to metals with partially filled d bands, analysis is simple only in cases in which the partial filling of any d bands can be neglected. Thus, when we sum over states, we will sum over entire d bands and partially filled s-p bands. Our expressions will be directly applicable to the noble metals and to the alkaline earths. (In the latter, the d resonance is close to the Fermi energy but above it.) It may also be applicable to some transition metals in which the major portion of the Fermi surface is free-electron-like with only small pockets of electrons or holes in d bands.

The analysis itself is extremely intricate. We may see the origin of this in terms of the transformations made on the Hermitian Hamiltonian matrix which may be constructed from the original Schrödinger equation. In going to the simple-metal pseudopotential we change from a basis set of plane waves by a nonunitary transformation to the nonorthogonal set of orthogonalized plane waves. The complexity of rigorous pseudopotential theory, the non-Hermiticity of the pseudo-Hamiltonian matrix, and the operator nature of the pseudopotential all arise from this nonunitary transformation. However, the transformation may be thought of as square, since there exists one orthogonalized plane wave for each plane-wave basis state and one conduction-band eigenstate for each orthogonalized plane wave In adding the atomic d states to the basis set, the transformation is not even square, since we have increased the number of basis states. This is the ultimate origin of the complexity that will arise. We will find it necessary to construct by perturbation theory states which in zero order are linear combinations of atomic d states, as well as states which in zero order are single orthogonalized plane waves. It seems apparent now[5] that the same essential results can be obtained more simply in terms of a pseudo-Green's function. That analysis is currently in progress. Nonetheless, it seems very desirable to first carry through the direct perturbation-theoretic approach which exposes in detail each step and each approximation. Only then can we be certain of the validity of the results. In particular, we can see the precise nature of the treatment of Δ as a perturbation parameter, and the nature of the divergence occurring at resonance.

As in the pseudopotential method as applied to simple metals, we can very simply state the only important approximations at the beginning. We have made a self-consistent field approximation and a small core approximation with respect to the core states. At some stages we also treat the atomic d states as small; in particular, we assume that the screening field does not vary greatly over the diameter of an atomic d state. Finally, we assume that the potential Δ defined above, as well as the pseudopotential, is small enough to allow their treatment in perturbation theory. In particular, we will see that Δ^2 must be treated as of the same order as the pseudopotential W. The rapid convergence of the OPW method as used by Deegan and Twose[3] supports the contention that this will be true.

Also, as in the case of the pseudopotential method for simple metals, we will be able to define a pseudopotential form factor to be used directly in the calculation of electronic properties involving electrons at the Fermi surface, and we will be able to define an energy–wave-number characteristic in terms of which atomic properties may be calculated. Thus, once these characteristic curves are computed for a particular metal, we may proceed with the treatment of properties in a very simple and direct fashion equivalent to nearly-free-electron theory.

In spite of the simple beginning and end points of the formulation, the algebra itself is quite complicated. For that reason, we will return in Sec. VIII to summarize briefly the major steps and major results. We also give, in Sec. VII, a cursory application of the method to copper.

Aside from allowing the extension of the pseudopotential method to a wider range of metals, there may be a second very useful feature. In transforming the Schrödinger equation without approximation to the transition-metal pseudopotential equation, we obtain a form very close to a commonly used model for resonant states. The pseudo-Hamiltonian contains a kinetic energy, a weak transition-metal pseudopotential, and a term strongly reminiscent of a phenomenological hybridization between free and localized states. In this term, the operator $\Delta\,|\,d\rangle\langle d\,|\,\Delta$ plays the role of the square of the hybridization parameter. However, because this equation is obtained from the Schrödinger equation without approximation, it provides a firmer foundation for such theories and allows a first-principles calculation of the parameters that enter the model.

Finally, the method that is used to treat the d states appears to be directly generalizable (and becomes, in fact, somewhat simpler) to filled bands in insulators, semiconductors, and molecules. In essence, this approach begins with the method of linear combination of atomic orbitals (LCAO) as a zero-order approximation and computes corrections by perturbation theory. Hopefully, this will provide a reliable framework for the discussion of bonding in these other systems. We are currently exploring this possibility.

[5] J. Moriarty (private communication).

II. PSEUDOPOTENTIAL EQUATION

We begin by reformulating the pseudopotential of simple metals in a form which is directly generalizable to transition metals. In both cases we begin with a self-consistent field approximation, assuming that there exists a self-consistent potential $V(\mathbf{r})$ in terms of which the eigenstates are obtainable;

$$(T+V)|\psi\rangle=E|\psi\rangle. \tag{1}$$

T is, of course, the kinetic-energy operator, and $|\psi\rangle$ is the true electronic eigenstate (not the pseudo-wave-function). In all metals there exist deep core eigenstates $|\alpha\rangle$ of Eq. (1) which are virtually unchanged when the atoms are combined to form the metal. Each has an eigenvalue E_α which in the metal may be slightly shifted from that in the atom, but the shift is rather easily calculable. Our interest then is in computing the valence states which are appreciably changed in the formation of the metal. In doing this we take advantage of the fact that valence-band states $|\psi\rangle$ must be orthogonal to the known core states. We make this orthogonality explicit by writing the true wave function in terms of a pseudo-wave-function $|\phi\rangle$, that is,

$$|\psi\rangle=(1-\sum_\alpha|\alpha\rangle\langle\alpha|)|\phi\rangle.$$

Substituting this into Eq. (1), we obtain a differential equation for $|\phi\rangle$, which is called the pseudopotential equation, and which can be solved by perturbation methods.

Up to the point at which perturbation theory is used, there is no important approximation in the method. Exact solution of the pseudopotential equation will give exact eigenvalues of the initial problem. However, the utility of the method derives from the fact that the pseudopotential is weak and perturbation theory is applicable. If we use this method for treating transition metals, the utility is lost. The atomic d states of the free atom are appreciably modified in going to the solid and cannot, therefore, be regarded as core states but, like the valence states in the simple metals, must be computed from the pseudopotential equation. At the same time, these d states retain much of their atomic character and, in particular, are rather well localized. Thus, an expansion of the d states in plane waves is very slowly convergent and perturbation theory is quite inadequate.

We will make an alternative formulation of the pseudopotential method which is equivalent to that given above for the simple metals, but which is directly applicable to transition metals. We first restate the pseudopotential method from a different point of view. We again are seeking solutions of Eq. (1) and, in particular, a rapidly convergent expansion for the wave function. An expansion of the wave function in terms of plane waves alone is poorly convergent because of the atomic like structure near the metallic cores. However,

we may supplement our plane-wave expansion by including also free-atom core states. We know, from the rapid convergence of the OPW method, that such an expansion can be rapidly converging. In the case of transition metals we include also in our basis set the atomic d functions. In contrast to the case of simple metals, then, we are including in our basis set local functions which are not eigenstates of the Hamiltonian. In either case we are expanding in an overcomplete set which need not entail any approxmation. We are now writing the true wave function in the form

$$\psi=\sum_k a_k|\mathbf{k}\rangle+\sum_\alpha a_\alpha|\alpha\rangle+\sum_d a_d|d\rangle; \tag{2}$$

the states $|d\rangle$ are, of course, atomic d states. Let us examine these states more carefully. They are eigenstates of Eq. (1) with the true potential V in the metal replaced by the free-atom potential V^a. Thus,

$$(T+V^a)|d\rangle=E_d{}^a|d\rangle, \tag{3}$$

where $E_d{}^a$ is the atomic eigenvalue. We write the difference between the atomic potential and the true potential in the neighborhood of the single ion as δV; that is, in the neighborhood of one atom $V^a=V+\delta V$. We see that operation upon a d state with the crystal Hamiltonian yields

$$(T+V)|d\rangle=E_d{}^a|d\rangle-\delta V|d\rangle. \tag{4}$$

It will be more convenient to use as a parameter the expectation value of the energy of an atomic d state in the presence of the crystal Hamiltonian:

$$E_d=\langle d|T+V|d\rangle=E_d{}^a-\langle d|\delta V|d\rangle. \tag{5}$$

Equation (4) may be rewritten in the form

$$(T+V)|d\rangle=E_d|d\rangle-\Delta|d\rangle, \tag{6}$$

where Δ is given by

$$\Delta|d\rangle=\delta V|d\rangle-\langle d|\delta V|d\rangle|d\rangle. \tag{7}$$

We note that the operation of the Hamiltonian on the core states $|\alpha\rangle$ could be formulated similarly, but in assuming that the core states are unchanged in going to the crystal, we explicitly take the corresponding Δ equal to zero. This is entirely equivalent to the assumption that δV does not vary appreciably over the core states $|\alpha\rangle$.

We may now substitute our expansion [Eq. (2)] into Eq. (1). Writing the result in terms of the pseudo-wave-function,

$$|\varphi\rangle=\sum_k a_k|\mathbf{k}\rangle,$$

and collecting all terms in the core and d states on the left, we obtain

$$T|\varphi\rangle+V|\varphi\rangle+\sum_\alpha(E_\alpha-E)a_\alpha|\alpha\rangle$$
$$+\sum_d a_d(E_d-E-\Delta)|d\rangle=E|\varphi\rangle. \tag{8}$$

We may evaluate the a_α immediately by operating on the left side with a particular core state $\langle\alpha|$, using the Hermiticity of the Hamiltonian to write $\langle\alpha|T+V|\varphi\rangle = E_\alpha\langle\alpha|\varphi\rangle$. We further note that the atomic core states are orthogonal to the atomic d states, and also that, since δV (and therefore Δ) does not vary appreciably over the core state, $\langle\alpha|\Delta|d\rangle = 0$. We obtain immediately

$$a_\alpha = -\langle\alpha|\varphi\rangle. \qquad (9)$$

Substituting this form in Eq. (8), the corresponding terms become the usual repulsive term in the pseudopotential,

$$\sum_\alpha (E-E_\alpha)|\alpha\rangle\langle\alpha|\varphi\rangle.$$

We may similarly seek the coefficient a_d by multiplying on the left side by a particular atomic d state $\langle d|$. We note from Eq. (7) that $\langle d|\Delta|d\rangle = 0$ and obtain

$$a_d = -\langle d|\varphi\rangle + \langle d|\Delta|\varphi\rangle/(E_d-E). \qquad (10)$$

We have obtained an additional term in the coefficient arising from the fact that the state $|d\rangle$ is not an eigenstate of the crystal Hamiltonian. Substituting Eqs. (9) and (10) back into Eq. (8), we obtain

$$T|\varphi\rangle+V|\varphi\rangle+\sum_\alpha(E-E_\alpha)|\alpha\rangle\langle\alpha|\varphi\rangle+\sum_d\left[(E-E_d)|d\rangle\right.$$

$$\left.\times\langle d|\varphi\rangle+|d\rangle\langle d|\Delta|\varphi\rangle+\Delta|d\rangle\langle d|\varphi\rangle\right]$$

$$-\sum_d\frac{\Delta|d\rangle\langle d|\Delta|\varphi\rangle}{E_d-E}=E|\varphi\rangle. \qquad (11)$$

We have of course noted that the atomic d states on the same atom are orthogonal to each other and have assumed, in addition, that atomic d states on neighboring atoms do not overlap each other appreciably. This will ordinarily be true to a good approximation; if it is not, we can of course modify δV in order to contract the "atomic" d states so that they in fact do not overlap. Deegan and Twose[3] explicitly truncated their d states. That could be done here, but a small overlap is clearly much less important in the perturbation calculation that we perform than in a band calculation. There, because of the exact solution of the equations, small nonorthogonalities can be greatly amplified in the results. It is convenient then to define a *transition-metal pseudopotential* by

$$W|\varphi\rangle=V|\varphi\rangle+\sum_\alpha(E-E_\alpha)|\alpha\rangle\langle\alpha|\varphi\rangle+\sum_d\left[(E-E_d)|d\rangle\right.$$

$$\left.\times\langle d|\varphi\rangle+|d\rangle\langle d|\Delta|\varphi\rangle+\Delta|d\rangle\langle d|\varphi\rangle\right]. \qquad (12)$$

Then Eq. (11) becomes

$$T|\varphi\rangle+W|\varphi\rangle-\sum_d\frac{\Delta|d\rangle\langle d|\Delta|\varphi\rangle}{E_d-E}=E|\varphi\rangle, \qquad (13)$$

which is the new pseudopotential equation. The final

terms on the left side are called the *hybridizing terms* for reasons that will become clear shortly.

Just as in the case of simple metals, this pseudopotential equation has been derived without approximation. (With suitably constructed δV, nonoverlapping d states can be constructed.) Equation (13) will have exactly the same eigenvalues (except for the deep core states) as the initial Schrödinger equation.

It is interesting to note that we may multiply on the left side by $\langle\varphi|$ and write the result in the form

$$(E_c-E)(E_d-E)-\sum_d\langle\varphi|\Delta|d\rangle\langle d|\Delta|\varphi\rangle=0, \qquad (14)$$

where $E_c=\langle\varphi|T+W|\varphi\rangle$. E_c will be free-electron-like if W is small. Thus, if matrix elements of Δ are slowly varying with φ, we obtain the familiar hybridization of a flat and a free-electron-like band as shown in Fig. 1. This is suggestive but very misleading. We may note that the treatment is applicable to a single transition-metal atom dissolved in a simple metal, in which case it would be natural to introduce only d states on that single atom. Nevertheless, an uncritical glance at Eq. (14) would suggest that there are two solutions for each wave number and the introduction of the single perturbing term has doubled the number of states. Clearly, we must be very careful in using this exact equation near resonance.

We should perhaps note in passing that pseudo-wavefunctions which satisfy Eq. (13) contained the same arbitrariness that is present in the pseudopotential equation for simple metals. We may, for example, add any linear combination of core states and d states to a pseudo-wave-function which satisfies Eq. (13). This will modify the coefficients a_α and a_d which enter Eq. (2) but the corresponding pseudo-wave-function will remain a solution to Eq. (13). As in the pseudopotential method for simple metals, this arbitrariness may be eliminated either by modifying the form of the pseudopotential or simply by the use of perturbation theory
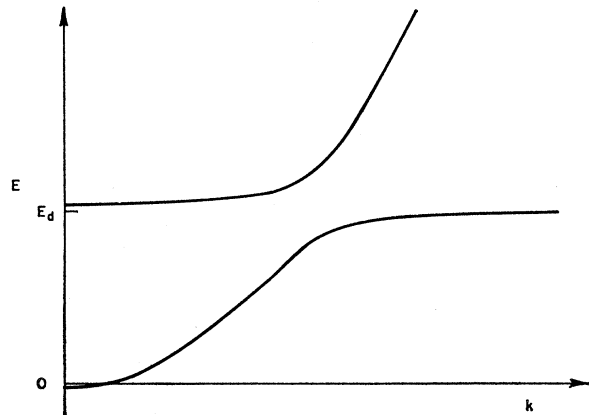

FIG. 1. Hybridization of a free electron and a flat band suggested by Eq. (14).

in the construction of the pseudo-wave-function. The latter approach will be used here. It is interesting that such an approach, used in simple metals, leads to a pseudopotential that is equal, to lowest order, to the optimized pseudopotential.

III. APPLICATION OF PERTURBATION THEORY

There is no ambiguity in the use of the pseudopotential equation (13) for states which are well removed from the resonance. In these states the admixture of the d state will be small; correspondingly, the third term as well as the second in Eq. (13) will be small. Mathematically, this follows from the large energy denominator $E_d - E$. To zero order in the pseudopotential and hybridizing terms the solutions of Eq. (13) are plane waves; to first order we obtain immediately a pseudo-wave-function given by

$$| \varphi \rangle = | \mathbf{k} \rangle + \sum_q{}' \frac{| \mathbf{k+q} \rangle \langle \mathbf{k+q} | W | \mathbf{k} \rangle}{E_k - E_{k+q}} - \sum_q; \frac{| \mathbf{k+q} \rangle}{E_k - E_{k+q}}$$
$$\times \sum_d \frac{\langle \mathbf{k+q} | \Delta | d \rangle \langle d | \Delta | \mathbf{k} \rangle}{E_d - E_k}. \quad (15)$$

The E_k in the energy denominators could be taken only to zero order; that is, $\hbar^2 k^2 / 2m$. However, it will be convenient at later stages to include some first-order terms with the zero-order energy, and write

$$E_k = \hbar^2 k^2 / 2m + \langle \mathbf{k} | W | \mathbf{k} \rangle. \quad (16)$$

We will similarly use this first-order energy to define a pseudopotential operator

$$W | \mathbf{k} \rangle = V | \mathbf{k} \rangle + \sum_\alpha (E_k - E_\alpha) | \alpha \rangle \langle \alpha | \mathbf{k} \rangle + \sum_d \left[(E_k - E_d) | d \rangle \right.$$
$$\times \langle d | \mathbf{k} \rangle + | d \rangle \langle d | \Delta | \mathbf{k} \rangle + \Delta | d \rangle \langle d | \mathbf{k} \rangle], \quad (17)$$

to be used in perturbation theory. This is the counterpart of the optimized pseudopotential for simple metals. Note that it is non-Hermitian in that the energy E_k is based upon the right-hand plane wave in any matrix element. We have exchanged the dependence upon the energy of the state under study for a dependence upon the right-hand state.

As for the pseudopotential in simple metals, the first-order pseudo-wave-function states of different energy are not orthogonal to each other. Mathematically, this arises here from the non-Hermiticity of the pseudopotential. [With a different definition than Eq. (17) it would arise from the energy dependence.] For any state the energy entering the pseudopotential in the first-order term depends upon the state in question, and $\langle \mathbf{k+q} | W | \mathbf{k} \rangle \neq \langle \mathbf{k} | W | \mathbf{k+q} \rangle^*$ when they enter first-order states of different energy. However, the corresponding true wave functions are orthogonal to first

order in W. In confirming this orthogonality we must, as in the simple-metal pseudopotential, regard $\langle d | \varphi \rangle$ as of the same order as $\langle d | \Delta | \varphi \rangle$, and as of half the order of W. The true wave function may be obtained by combining Eqs. (2), (9), and (10). To first order in the pseudopotential, and second order in Δ, the wave function may be written

$$\psi_k = | \mathbf{k} \rangle + \sum_q{}' \frac{| \mathbf{k+q} \rangle \langle \mathbf{k+q} | W | \mathbf{k} \rangle}{E_k - E_{k+q}}$$
$$- \sum_{q,d}{}' \frac{| \mathbf{k+q} \rangle \langle \mathbf{k+q} | \Delta | d \rangle \langle d | \Delta | \mathbf{k} \rangle}{(E_k - E_{k+q})(E_d - E_k)} - \sum_\alpha | \alpha \rangle \langle \alpha | \mathbf{k} \rangle$$
$$- \sum_d | d \rangle \langle d | \mathbf{k} \rangle + \sum_d \frac{| d \rangle \langle d | \Delta | \mathbf{k} \rangle}{E_d - E_k}. \quad (18)$$

This is the form to be used in the screening calculation. The orthogonality to first order of states of different wave number may be verified using such expressions and the form of W given in Eq. (17).

We also obtain the energy to second order in Δ:

$$E = E_k - \sum_d \frac{\langle \mathbf{k} | \Delta | d \rangle \langle d | \Delta | \mathbf{k} \rangle}{E_d - E}$$
$$+ \sum_q{}' \frac{| \langle \mathbf{k+q} | [W - \sum_d \Delta | d \rangle \langle d | \Delta / (E_d - E_k)] | \mathbf{k} \rangle |^2}{E_k - E_{k+q}}. \quad (19)$$

Note that the energy entering W is E_k in all matrix elements.

These expressions have been derived explicitly for states which differ in energy significantly from the resonant energy E_d. However, both in the calculation of screening and in the evaluation of the total energy we must sum all states and our expressions must be continued through the resonance. We will see that the vanishing energy denominators do not cause a problem but a direct summation over zero-order wave numbers may be seen to be incomplete.

We consider the simple problem of a single scattering resonance, which may also be solved exactly using phase-shift techniques. To be specific, we consider a spherically symmetric system with an $l = 2$ resonance and consider only states of a single component of angular momentum m. Thus, only a single resonant level need be considered. In this framework we may understand the meaning of our results by noting that the true wave function contains a term $a_d | d \rangle$ as well as the free-electron-like tail φ (and a linear combination of core states). We then note, from Eq. (10), that as we follow states, changing the energy through resonance, a_d changes sign. Alternatively, if we maintain the form of the state at the resonant center by retaining the same sign of the $| d \rangle$ term through resonance, we see that the free-electron-like tail φ changes sign. In terms of phase

shifts this corresponds of course to a π phase shift or the introduction of an additional state. It is now very clear what the perturbation theory has done. If we imagine slowly turning on the perturbation, then at energies below resonance the shift in each level is very small and is properly computed by our perturbation expansion. Above resonance each state is shifted in energy very nearly to the unperturbed position of the next lowest-lying unperturbed state. Our perturbation expression gives correctly the very small difference in energy between each perturbed level and the next lowest unperturbed level. A single perturbed state in the neighborhood of resonance has been left out if we simply sum over unperturbed states. This is illustrated in Fig. 2. This fact is indicated also by the first-order finding in Eq. (19) that states below resonance are lowered while states above appear to be raised. Clearly an attractive center, which can give rise to resonance, will lower the energy of each state.

Thus, in this problem, with the single scattering resonance, if we sum the energies of the states over unperturbed wave numbers, we may expect to include correctly the energies of all states but one. We might at first think that in a large system of N electrons the omission of a single state would not be important. However, this is not the case. The shift in each level calculated by perturbation theory is of order Δ^2/NE_F for a total change of order Δ^2/E_F. The introduction of an additional state at the energy E_d empties a state near the Fermi energy and therefore makes a contribution of the order of $E_d - E_F$ and is not of higher order in $1/N$. It is, in fact, of zero order and the corresponding energy must be computed carefully. If we introduce many resonant centers, we will introduce an equal number of additional states at resonance. In a pure transition metal, these will give rise to the d bands themselves. Thus Eq. (19), even if extended through resonance, is incomplete and we must seek the additional solutions.

It is appropriate to obtain these additional states by returning to the exact equations, taking a term $a_d|d\rangle$ as of zero order and the coefficients a_k of the admixed plane waves as of first order in Δ. We may then show that the resulting state is orthogonal to the conduction-band states given in Eq. (18) (we will call these k states to distinguish them) to first order in W (or second order in Δ), demonstrating that it is, in fact, an additional state and not simply a recalculation of states already included in the calculation.

We may readily see that if there exists more than one transition-metal atom in the system, we must take as our zero-order state an appropriate linear combination of d states on each of the atoms. Thus, until otherwise specified, the states $|d\rangle$ now refer to appropriate normalized orthogonal linear combinations of atomic d states on all of the atoms. Of course, for a perfect crystal these linear combinations would be Bloch sums. In a material with partially filled d bands we would find
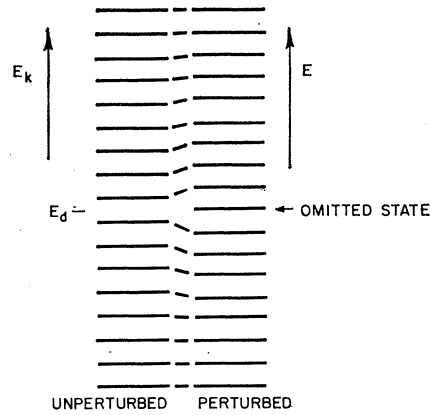

FIG. 2. Schematic diagram of the unperturbed and perturbed levels computed in perturbation theory when a resonance is introduced. The quantization of unperturbed levels arises from the crystal boundaries.

that some d-state energies would lie above resonance and some would lie below, and in the calculation of screening, for example, only those states occupied should be included. However, in cases in which the individual d bands are totally occupied or totally unoccupied we will eventually sum over states and the results may be written in terms of sums over single atomic d states.

We return to Eq. (8), taking a single coefficient equal to unity, and insert Eq. (9), which remains appropriate, for a_α:

$$T|\varphi\rangle + V|\varphi\rangle + \sum_\alpha (E - E_\alpha)|\alpha\rangle\langle\alpha|\varphi\rangle$$
$$+ (E_d - E - \Delta)|d\rangle = E|\varphi\rangle. \quad (20)$$

We immediately obtain an expression for the energy by multiplying on the left side by $\langle d|$. It may be written

$$E = E_d - \langle d|\Delta|\varphi\rangle + (E_d - E)\langle d|\varphi\rangle. \quad (21)$$

Since the admixed plane waves represented by $|\varphi\rangle$ are of first order in Δ, we see that the second term on the right side of Eq. (21) is of second order in Δ and the third is of fourth order. It will be useful in the perturbation calculation to note from this that $E - E_d$ is of second order in Δ. We may also note that to obtain the energy to fourth order in Δ we must obtain $|\varphi\rangle$ to third order in Δ.

We make explicit the expansion of $|\varphi\rangle$ in plane waves in Eq. (20) to obtain

$$\sum_{k'} a_{k'}\left(\frac{\hbar^2 k'^2}{2m} - E\right)|k'\rangle + \sum_{k'} a_{k'} V|k'\rangle + \sum_\alpha a_{k'}(E - E_\alpha)|\alpha\rangle$$
$$\times \langle\alpha|k'\rangle + (E_d - E - \Delta)|d\rangle = 0. \quad (22)$$

We mutliply on the left side by a particular plane wave

$\langle \mathbf{k} |$ and obtain

$$\left(E-\frac{\hbar^2 k^2}{2m}\right)a_{\mathbf{k}} = -\langle \mathbf{k}|\Delta|d\rangle + \sum_{\mathbf{k}'} a_{\mathbf{k}'}$$

$$\times[\langle \mathbf{k}|V|\mathbf{k}'\rangle + \sum_{\alpha}(E-E_{\alpha})\langle \mathbf{k}|\alpha\rangle\langle\alpha|\mathbf{k}'\rangle + (E_d - E)\langle \mathbf{k}|d\rangle]. \quad (23)$$

All but the first term on the right side are of third order in Δ, since $a_{\mathbf{k}'}$ is of order Δ. Furthermore, $E - \hbar^2 k^2 / 2m$ can be replaced by $E_d - E_{\mathbf{k}}$ to lowest order to obtain

$$a_{\mathbf{k}} = -\langle \mathbf{k}|\Delta|d\rangle/(E_d - E_{\mathbf{k}}) + O(\Delta^3). \quad (24)$$

Thus, to second order in Δ the eigenstate becomes

$$\psi_d = A_d\left(|d\rangle - \sum_{\mathbf{k}} \frac{|\mathbf{k}\rangle\langle \mathbf{k}|\Delta|d\rangle}{E_d - E_{\mathbf{k}}}\right), \quad (25)$$

where A_d is a normalization constant. This is the form which will be used in the screening calculation.

We may immediately obtain the normalization constant, and we will investigate the orthogonality of the ψ_d at the same time. Using Eq. (25), we obtain immediately

$$(\psi_{d'},\psi_d) = A_{d'}{}^*A_d\left[\delta_{d'd} + \sum_{\mathbf{k}}\left(-\frac{\langle d'|\mathbf{k}\rangle\langle \mathbf{k}|\Delta|d\rangle}{E_d - E_{\mathbf{k}}}\right.\right.$$
$$\left.\left.-\frac{\langle d'|\Delta|\mathbf{k}\rangle\langle \mathbf{k}|d\rangle}{E_{d'} - E_{\mathbf{k}}} + \frac{\langle d'|\Delta|\mathbf{k}\rangle\langle \mathbf{k}|\Delta|d\rangle}{(E_d - E_{\mathbf{k}})(E_{d'} - E_{\mathbf{k}})}\right)\right]. \quad (26)$$

We have used here the orthonormality of the $|d\rangle$. For the case $d' = d$ we obtain the normalization constant

$$A_d{}^*A_d = \left(1 - \sum_{\mathbf{k}}\frac{\langle \mathbf{k}|\Delta|d\rangle\langle d|\mathbf{k}\rangle}{E_d - E_{\mathbf{k}}} - \sum_{\mathbf{k}}\frac{\langle \mathbf{k}|d\rangle\langle d|\Delta|\mathbf{k}\rangle}{E_d - E_{\mathbf{k}}}\right.$$
$$\left. + \sum_{\mathbf{k}}\frac{\langle \mathbf{k}|\Delta|d\rangle\langle d|\Delta|\mathbf{k}\rangle}{(E_d - E_{\mathbf{k}})^2}\right)^{-1}. \quad (27)$$

For the orthogonality of the ψ_d we require

$$\sum_{\mathbf{k}}\left(-\frac{\langle d'|\mathbf{k}\rangle\langle \mathbf{k}|\Delta|d\rangle}{E_d - E_{\mathbf{k}}} - \frac{\langle d'|\Delta|\mathbf{k}\rangle\langle \mathbf{k}|d\rangle}{E_{d'} - E_{\mathbf{k}}}\right.$$
$$\left. + \frac{\langle d'|\Delta|\mathbf{k}\rangle\langle \mathbf{k}|\Delta|d\rangle}{(E_{d'} - E_{\mathbf{k}})(E_d - E_{\mathbf{k}})}\right) = 0 \quad (28)$$

for $d \neq d'$. The linear combinations $|d\rangle$ which satisfy this condition must be selected. This condition is satisfied by Bloch sums in a perfect crystal; then, for example, the $\langle \mathbf{k}|d\rangle$ are only nonzero for $\mathbf{k}$ having a reduced vector equal to that of $|d\rangle$, and all terms vanish if $|d\rangle$ and $|d'\rangle$ have different wave numbers. The orthogonality of states based upon different angular momentum

quantum numbers will guarantee the vanishing of all terms when the wave numbers of $|d\rangle$ and $|d'\rangle$ are the same. On the other hand, Eq. (28) would not be satisfied if we took the $|d\rangle$ to be single atomic d states. We proceed assuming that appropriate linear combinations have been taken. We will not need to know them in the end, but we will need to make use of the condition (28) in the evaluation of the energy.

It may also be readily verified that the state given in Eq. (25) is orthogonal to the conduction-band states $\psi_{\mathbf{k}}$ of Eq. (18) to order Δ^2.

We return to Eq. (23) and seek an evaluation of $a_{\mathbf{k}}$ to order Δ^3. To obtain a form which will be useful we must make transformations such that the factor multiplying $a_{\mathbf{k}}$ becomes $E_d - E_{\mathbf{k}}$ and such that the transition-metal pseudopotential appears on the right side. We note first from Eq. (21) that to second order in Δ

$$E_d - E \cong \langle d|\Delta|\varphi\rangle = \sum_{\mathbf{k}'} a_{\mathbf{k}'}\langle d|\Delta|\mathbf{k}'\rangle. \quad (29)$$

This equation is multiplied by $a_{\mathbf{k}}$, using Eq. (24) for the $a_{\mathbf{k}}$ on the right side and added to Eq. (23). Equation (28) is also used to rewrite the final term in Eq. (23). We obtain

$$\left(E_d - \frac{\hbar^2 k^2}{2m}\right)a_{\mathbf{k}} = -\langle \mathbf{k}|\Delta|d\rangle + \sum_{\mathbf{k}'} a_{\mathbf{k}'}$$

$$\left(\langle \mathbf{k}|V|\mathbf{k}'\rangle + \sum_{\alpha}(E - E_{\alpha})\langle \mathbf{k}|\alpha\rangle\langle\alpha|\mathbf{k}'\rangle\right.$$
$$\left. + \langle \mathbf{k}|d\rangle\langle d|\Delta|\mathbf{k}'\rangle - \frac{\langle \mathbf{k}|\Delta|d\rangle\langle d|\Delta|\mathbf{k}'\rangle}{E_d - E_{\mathbf{k}}}\right). \quad (30)$$

The term in α may be rewritten by replacing E by E_d, valid to the order to which we calculate. Finally, E_d may be replaced by $E_{\mathbf{k}'}$, since the difference is identically zero when $a_{\mathbf{k}'}$ is taken to lowest order; that difference may be written

$$\sum_{\mathbf{k}'} a_{\mathbf{k}'}(E_{\mathbf{k}'} - E_d)\langle \mathbf{k}|\alpha\rangle\langle\alpha|\mathbf{k}'\rangle$$

$$= -\sum_{\mathbf{k}'}\frac{\langle \mathbf{k}'|\Delta|d\rangle(E_{\mathbf{k}'} - E_d)\langle \mathbf{k}|\alpha\rangle\langle\alpha|\mathbf{k}'\rangle}{E_d - E_{\mathbf{k}'}}.$$

The energy differences may be cancelled, and since the plane waves $|\mathbf{k}'\rangle$ are a complete set, the two matrix elements in $\mathbf{k}'$ may be combined to give $\langle\alpha|\Delta|d\rangle$, which is equal to zero. By an almost identical argument we may show that

$$\sum_{\mathbf{k}'} a_{\mathbf{k}'}(E_{\mathbf{k}'} - E_d)\langle \mathbf{k}|d\rangle\langle d|\mathbf{k}'\rangle$$

is equal to zero and may be added to the right-hand side of Eq. (30). Finally, we must add and subtract a term

$$\sum_{\mathbf{k}'}' a_{\mathbf{k}'}\langle \mathbf{k}|\Delta|d\rangle\langle d|\mathbf{k}'\rangle$$

to the right side to complete in essence the matrix element of W. However, the terms in $|d\rangle\langle d|$ are not summed over d. We write the unsummed form $W(d)$. It is is important to notice that in this matrix element $\langle\mathbf{k}|W(d)|\mathbf{k}'\rangle$ the energy entering the pseudopotential is $E_{\mathbf{k}'}$; the pseudopotential is non-Hermitian and selects energies from the state appearing to the right side [see Eq. (17)]. We obtain

$$\left(E_d-\frac{\hbar^2k^2}{2m}\right)a_{\mathbf{k}}=-\langle\mathbf{k}|\Delta|d\rangle$$

$$+\sum_{\mathbf{k}'}a_{\mathbf{k}'}\left(\langle\mathbf{k}|W(d)|\mathbf{k}'\rangle-\frac{\langle\mathbf{k}|\Delta|d\rangle\langle d|\Delta|\mathbf{k}'\rangle}{E_d-E_{\mathbf{k}}}\right)$$

$$-\sum_{\mathbf{k}'}a_{\mathbf{k}'}\langle\mathbf{k}|\Delta|d\rangle\langle d|\mathbf{k}'\rangle. \quad (31)$$

We may now add and subtract the necessary sum over $d'\neq d$ so that $W(d)$ is replaced by W and the hybridization term is summed over d. The correction term to be added and subtracted is

$$C_d(\mathbf{k})=-\sum_{d'\neq d;\mathbf{k}'}\frac{\langle\mathbf{k}'|\Delta|d\rangle}{E_d-E_{\mathbf{k}'}}\Bigg(\langle\mathbf{k}|\Delta|d'\rangle\langle d'|\mathbf{k}'\rangle$$

$$+\langle\mathbf{k}|d'\rangle\langle d'|\Delta|\mathbf{k}'\rangle+(E_{\mathbf{k}'}-E_{d'})\langle\mathbf{k}|d'\rangle\langle d'|\mathbf{k}'\rangle$$

$$-\frac{\langle\mathbf{k}|\Delta|d'\rangle\langle d'|\Delta|\mathbf{k}'\rangle}{E_{d'}-E_{\mathbf{k}}}\Bigg), \quad (32)$$

where we have substituted for $a_{\mathbf{k}'}$ from Eq. (24).

It is now appropriate to take the diagonal terms, $\mathbf{k}'=\mathbf{k}$ in the first sum in Eq. (31), to the left-hand side; they may be combined with $\hbar^2k^2/2m$ to obtain $E_{\mathbf{k}}$. We solve for $a_{\mathbf{k}}$:

$$a_{\mathbf{k}}=[E_d-E_{\mathbf{k}}+\sum_{d'}\langle\mathbf{k}|\Delta|d'\rangle\langle d'|\Delta|\mathbf{k}\rangle/(E_{d'}-E_{\mathbf{k}})]^{-1}\Bigg[-\langle\mathbf{k}|\Delta|d\rangle+\sum_{\mathbf{k}'}'a_{\mathbf{k}'}\left(\langle\mathbf{k}|W|\mathbf{k}'\rangle-\sum_{d'}\frac{\langle\mathbf{k}|\Delta|d'\rangle\langle d'|\Delta|\mathbf{k}'\rangle}{E_{d'}-E_{\mathbf{k}}}\right)$$

$$-\sum_{\mathbf{k}'}a_{\mathbf{k}'}\langle\mathbf{k}|\Delta|d\rangle\langle d|\mathbf{k}'\rangle-C_d(\mathbf{k})\Bigg]. \quad (33)$$

For a third-order result the Δ^2 term in the energy denominator may be dropped in the final terms but not in the term $\langle\mathbf{k}|\Delta|d\rangle$. We may now evaluate Eq. (21) for the energy to fourth order in Δ. The final term in Eq. (21) may be written in a convenient form,

$$(E_d-E)\langle d|\varphi\rangle=\sum_{\mathbf{k}'}\langle d|\Delta|\varphi\rangle\langle d|\mathbf{k}'\rangle a_{\mathbf{k}'}$$

$$=-\sum_{\mathbf{k},\mathbf{k}'}\frac{\langle d|\Delta|\mathbf{k}\rangle\langle\mathbf{k}|\Delta|d\rangle\langle d|\mathbf{k}'\rangle a_{\mathbf{k}'}}{E_d-E_{\mathbf{k}}}. \quad (34)$$

The second term in Eq. (21),

$$-\langle d|\Delta|\varphi\rangle=\sum_{\mathbf{k}}-\langle d|\Delta|\mathbf{k}\rangle a_{\mathbf{k}},$$

can also be evaluated using Eq. (33). We see immediately that the contribution of the final sum in Eq. (33) will give a contribution just cancelled by that in Eq. (34).

We must also evaluate the term

$$\sum_{\mathbf{k}}\frac{\langle d|\Delta|\mathbf{k}\rangle C_d(\mathbf{k})}{E_d-E_{\mathbf{k}}}=-\sum_{\mathbf{k},\mathbf{k}'}\frac{\langle\mathbf{k}'|\Delta|d\rangle\langle d|\Delta|\mathbf{k}\rangle}{E_d-E_{\mathbf{k}}}$$

$$\times\sum_{d'\neq d}\left(\frac{E_{\mathbf{k}'}-E_{d'}}{E_d-E_{\mathbf{k}'}}\langle\mathbf{k}|d'\rangle\langle d'|\mathbf{k}'\rangle+\frac{\langle\mathbf{k}|d'\rangle\langle d'|\Delta|\mathbf{k}'\rangle}{E_d-E_{\mathbf{k}'}}\right.$$

$$\left.+\frac{\langle\mathbf{k}|\Delta|d'\rangle\langle d'|\mathbf{k}'\rangle}{E_d-E_{\mathbf{k}'}}-\frac{\langle\mathbf{k}|\Delta|d'\rangle\langle d'|\Delta|\mathbf{k}'\rangle}{(E_{d'}-E_{\mathbf{k}})(E_d-E_{\mathbf{k}'})}\right). \quad (35)$$

We may neglect the difference between E_d and $E_{d'}$; in most applications they will be taken equal, but differ only in first order in any case. Then, the first term is

seen to vanish just as did the corresponding term in Eq. (30). The contribution of the second and fourth terms may be combined as

$$-\sum_{d'\neq d;\mathbf{k}'}\frac{\langle\mathbf{k}'|\Delta|d\rangle\langle d'|\Delta|\mathbf{k}'\rangle}{E_d-E_{\mathbf{k}'}}$$

$$\times\sum_{\mathbf{k}}\left(\frac{\langle\mathbf{k}|d'\rangle\langle d|\Delta|\mathbf{k}\rangle}{E_d-E_{\mathbf{k}}}-\frac{\langle\mathbf{k}|\Delta|d'\rangle\langle d|\Delta|\mathbf{k}\rangle}{(E_d-E_{\mathbf{k}})(E_{d'}-E_{\mathbf{k}})}\right)$$

$$=\sum_{d'\neq d;\mathbf{k},\mathbf{k}'}\frac{\langle\mathbf{k}|\Delta|d'\rangle\langle d'|\Delta|\mathbf{k}'\rangle\langle\mathbf{k}'|\Delta|d\rangle\langle d|\mathbf{k}\rangle}{(E_d-E_{\mathbf{k}'})(E_{d'}-E_{\mathbf{k}})}, \quad (36)$$

where in the last step we have used the orthogonality relation (28). This term, with primed and unprimed indices interchanged (and the difference between E_d and $E_{d'}$ neglected), is equal and opposite to the remaining term in Eq. (35). Since we will eventually sum over d, this interchange will be allowed and we drop the contribution of Eq. (35) at this point. The remaining terms give the energy of the resonant state to fourth order in Δ:

$$E=E_d+\sum_{\mathbf{k}}\frac{\langle\mathbf{k}|\Delta|d\rangle\langle d|\Delta|\mathbf{k}\rangle}{E_d-E_{\mathbf{k}}+\sum_{d'}\langle\mathbf{k}|\Delta|d'\rangle\langle d'|\Delta|\mathbf{k}\rangle(E_{d'}-E_{\mathbf{k}})^{-1}}$$

$$+\sum_{\mathbf{k},\mathbf{k}'}'\frac{\langle\mathbf{k}'|\Delta|d\rangle\langle d|\Delta|\mathbf{k}\rangle}{(E_d-E_{\mathbf{k}'})(E_d-E_{\mathbf{k}})}$$

$$\times\left(\langle\mathbf{k}|W|\mathbf{k}'\rangle-\sum_{d'}\frac{\langle\mathbf{k}|\Delta|d'\rangle\langle d'|\Delta|\mathbf{k}'\rangle}{E_{d'}-E_{\mathbf{k}}}\right). \quad (37)$$

We finally see that when this energy is summed over d states, the result is unchanged by replacing the linear combinations $|d\rangle$ by single atomic d states. The use of proper linear combinations, and the orthogonality relation (28), was necessary to obtain this form, which depends upon the configuration of the atoms.

It may be apparent that when we sum over d states and over conduction-band states, there will be a considerable degree of cancellation. This will require some rewriting of the expressions, and we will return to that when we calculate the total energy.

IV. CALCULATION OF SCREENING

Up to this point we have taken the potential in the crystal as known. One contribution to that potential is, of course, the potentials due to the nuclei and the core electrons which can be superimposed directly. In addition, we require the potential due to the valence band and d states. In particular, we will need the oscillatory part of that potential, the screening potential. We have already found the corresponding wave functions to the appropriate order; we now need to obtain the corresponding electron density from which the potential is directly calculable. Although the result will be moderately simple, the algebra itself is quite complicated.

We begin with the conduction-band state given in Eq. (18) and evaluate

$$n_q(\mathbf{k}) = \int \psi_k^* e^{-i\mathbf{q}\cdot\mathbf{r}} \psi_k d\tau$$

to second order in Δ. The state has not been normalized, but it may readily be seen that the normalization factor is of second order in Δ and does not enter the first-order screening distribution. We make a small-core approximation in assuming that $\langle d|e^{i\mathbf{q}\cdot\mathbf{r}}|\alpha\rangle$ is equal to zero. This becomes true in the limit as $\mathbf{q}$ goes to zero by the orthogonality of the d and core states. This will always be a legitimate approximation for the wave numbers of interest. On the other hand, we retain terms of the form $\langle d|e^{-i\mathbf{q}\cdot\mathbf{r}}|d\rangle$ which approach 1 as $\mathbf{q}$ approaches zero and are, in fact, just equal to the Fourier transform of the charge density associated with the d state in question. Finally, we note that there are terms of the form $\langle \mathbf{k}-\mathbf{q}|W|\mathbf{k}\rangle^*/(E_k-E_{k-q})$. In computing charge densities we will add a contribution for a state $-\mathbf{k}$ for every state $\mathbf{k}$. Thus, we will obtain the correct density by replacing such contributions by the corresponding expression with $\mathbf{k}$ replaced by $-\mathbf{k}$, in which case the expression becomes $\langle \mathbf{k}+\mathbf{q}|W|\mathbf{k}\rangle/(E_k-E_{k+q})$. We obtain

$$n_q(\mathbf{k}) = 2\left(\frac{\langle \mathbf{k}+\mathbf{q}|W|\mathbf{k}\rangle}{E_k-E_{k+q}} - \frac{\langle \mathbf{k}+\mathbf{q}|\Delta|d\rangle\langle d|\Delta|\mathbf{k}\rangle}{(E_k-E_{k+q})(E_d-E_k)} - \sum_\alpha \langle \mathbf{k}+\mathbf{q}|\alpha\rangle\langle\alpha|\mathbf{k}\rangle - \sum_d \langle \mathbf{k}+\mathbf{q}|d\rangle\langle d|\mathbf{k}\rangle + \sum_d \frac{\langle \mathbf{k}+\mathbf{q}|d\rangle\langle d|\Delta|\mathbf{k}\rangle}{E_d-E_k} \right)$$
$$+ \sum_\alpha \langle \mathbf{k}|\alpha\rangle\langle\alpha|\mathbf{k}\rangle\langle\alpha|e^{-i\mathbf{q}\cdot\mathbf{r}}|\alpha\rangle + \sum_d \langle d|e^{-i\mathbf{q}\cdot\mathbf{r}}|d\rangle \left(\langle \mathbf{k}|d\rangle\langle d|\mathbf{k}\rangle - \frac{\langle \mathbf{k}|\Delta|d\rangle\langle d|\mathbf{k}\rangle}{E_d-E_k} - \frac{\langle \mathbf{k}|d\rangle\langle d|\Delta|\mathbf{k}\rangle}{E_d-E_k} + \frac{\langle \mathbf{k}|\Delta|d\rangle\langle d|\Delta|\mathbf{k}\rangle}{(E_d-E_k)^2} \right).$$

$$(38)$$

Four of these terms together form exactly what is called the "orthogonalization hole," based on the d states as well as the core states:

$$n_q{}^{\text{orth}}(\mathbf{k}) = -2\left(\sum_\alpha \langle \mathbf{k}+\mathbf{q}|\alpha\rangle\langle\alpha|\mathbf{k}\rangle + \sum_d \langle \mathbf{k}+\mathbf{q}|d\rangle\langle d|\mathbf{k}\rangle\right) + \sum_\alpha \langle \mathbf{k}|\alpha\rangle\langle\alpha|\mathbf{k}\rangle\langle\alpha|e^{-i\mathbf{q}\cdot\mathbf{r}}|\alpha\rangle + \sum_d \langle \mathbf{k}|d\rangle\langle d|\mathbf{k}\rangle\langle d|e^{-i\mathbf{q}\cdot\mathbf{r}}|d\rangle$$
$$\approx -\sum_\alpha \langle \mathbf{k}+\mathbf{q}|\alpha\rangle\langle\alpha|\mathbf{k}\rangle - \sum_d \langle \mathbf{k}+\mathbf{q}|d\rangle\langle d|\mathbf{k}\rangle. \quad (39)$$

This is just the difference in charge density between that associated with plane waves orthogonalized to the core and d states and the distribution from the plane waves themselves. The corresponding charge density is well localized at the cores and will have a magnitude of the order of $\frac{1}{10}$ of the valence charge at each ion. The approximate form given in Eq. (39) is valid when $\mathbf{q}$ times the d-states radius is small. It is called the "small-core approximation" and will be sufficient for most purposes. We may always use the exact form of the orthogonalization hole if we so choose.

We next turn to the charge density due to the d states as given in Eq. (25). Each state is multiplied by a normalization factor which, as in the case of conduction-band states, is of the order Δ^2. However, in this case we cannot ignore that factor, since the zero-order density, the density arising from atomic d states, is not uniform. The correction factor need be used only on the zero-order distribution, since the change in the first-order distribution is of second order. To second order in Δ the renormalized zero-order distribution becomes

$$n_q{}^0(d) = \langle d|e^{-i\mathbf{q}\cdot\mathbf{r}}|d\rangle\left[1 + \sum_k \left(\frac{\langle \mathbf{k}|\Delta|d\rangle\langle d|\mathbf{k}\rangle + \langle \mathbf{k}|d\rangle\langle d|\Delta|\mathbf{k}\rangle}{E_d-E_k} - \frac{\langle \mathbf{k}|\Delta|d\rangle\langle d|\Delta|\mathbf{k}\rangle}{(E_d-E_k)^2} \right)\right]. \quad (40)$$

It is interesting that the final three terms are of exactly the same form but of opposite sign to the final three terms in Eq. (38). However, in computing the d-state charge density we sum over all $\mathbf{k}$, whereas in Eq. (38)

we sum only up to the Fermi energy. Thus, these terms are cancelled by the corresponding terms in Eq. (38) only for k less than the Fermi wave number. We will find a similar cancellation in the other terms. The zero-order term in Eq. (40), $\langle d | e^{-i\mathbf{q}\cdot\mathbf{r}} | d \rangle$, is just the charge density due to an occupied atomic d state. We next find the remaining first-order terms in the integral

$$\int \psi_d{}^* e^{-i\mathbf{q}\cdot\mathbf{r}} \psi_d d$$

from Eq. (25), taking $A_d=1$

$$n_q{}^1(d) = -2 \sum_\mathbf{k} \frac{\langle \mathbf{k}+\mathbf{q} | d \rangle \langle d | \Delta | \mathbf{k} \rangle}{E_d - E_\mathbf{k}}$$
$$+ \sum_\mathbf{k} \frac{\langle \mathbf{k}+\mathbf{q} | \Delta | d \rangle \langle d | \Delta | \mathbf{k} \rangle}{(E_d - E_\mathbf{k})(E_d - E_{\mathbf{k}+\mathbf{q}})}. \quad (41)$$

We have again made a change of the dummy variable $\mathbf{k}$ to $-\mathbf{k}$ in order to combine two terms. In order to clarify the cancellation with corresponding terms in the conduction-electron density we must manipulate the final summation in Eq. (41).

We note that

$$[(E_d - E_\mathbf{k})(E_d - E_{\mathbf{k}+\mathbf{q}})]^{-1} \equiv [(E_d - E_\mathbf{k})^{-1} - (E_d - E_{\mathbf{k}+\mathbf{q}})^{-1}]$$
$$\times (E_\mathbf{k} - E_{\mathbf{k}+\mathbf{q}})^{-1}. \quad (42)$$

This is substituted into the final sum in Eq. (41), and in the second term $\mathbf{k}$ is changed to $-\mathbf{k}-\mathbf{q}$. Thus,

$$\sum_\mathbf{k} \frac{\langle \mathbf{k}+\mathbf{q} | \Delta | d \rangle \langle d | \Delta | \mathbf{k} \rangle}{(E_d - E_\mathbf{k})(E_d - E_{\mathbf{k}+\mathbf{q}})}$$
$$= 2 \sum_\mathbf{k} \frac{\langle \mathbf{k}+\mathbf{q} | \Delta | d \rangle \langle d | \Delta | \mathbf{k} \rangle}{(E_d - E_\mathbf{k})(E_\mathbf{k} - E_{\mathbf{k}+\mathbf{q}})}. \quad (43)$$

We have noted in obtaining this result that $E_{-\mathbf{k}} = E_\mathbf{k}$ and, for example, $\langle -\mathbf{k} | \Delta | d \rangle = \langle d | \Delta | \mathbf{k} \rangle$.

This completes the determination of the various terms in the charge density. We now sum Eq. (38) over all $\mathbf{k}$ less than the Fermi wave number k_F and sum $n_q{}^0(d) + n_q{}^1(d)$ over all d states. The resulting density contains four distinguishable contributions. First is the electron density n^d of occupied atomic d states. Second is the total orthogonalization hole n^{orth} which is of just the same form as in simple metal theory but with the d states counted as core states. Third is the usual screening contribution based upon the transition-metal pseudopotential W. The remaining terms all contain an explicit dependence upon Δ. They all cancel identically for $k < k_F$. We have, then, the total Fourier transform of the electron density due to conduction and d electrons

$$n_\mathbf{q} = n_\mathbf{q}{}^d + n_\mathbf{q}{}^{\mathrm{orth}} + n_\mathbf{q}{}^{\mathrm{scr}}, \quad (44)$$

with

$$n_q{}^{\mathrm{scr}} = 2 \sum_{k<k_F} \frac{\langle \mathbf{k}+\mathbf{q} | W | \mathbf{k} \rangle}{E_\mathbf{k} - E_{\mathbf{k}+\mathbf{q}}} + \sum_{k>k_F} \sum_d \left[\langle d | e^{-i\mathbf{q}\cdot\mathbf{r}} | d \rangle \left(\frac{\langle \mathbf{k} | \Delta | d \rangle \langle d | \mathbf{k} \rangle}{E_d - E_\mathbf{k}} + \frac{\langle \mathbf{k} | d \rangle \langle d | \Delta | \mathbf{k} \rangle}{E_d - E_\mathbf{k}} - \frac{\langle \mathbf{k} | \Delta | d \rangle \langle d | \Delta | \mathbf{k} \rangle}{(E_d - E_\mathbf{k})^2} \right) \right.$$
$$\left. + \frac{2\langle \mathbf{k}+\mathbf{q} | \Delta | d \rangle \langle d | \Delta | \mathbf{k} \rangle}{(E_d - E_\mathbf{k})(E_\mathbf{k} - E_{\mathbf{k}+\mathbf{q}})} - \frac{2\langle \mathbf{k}+\mathbf{q} | d \rangle \langle d | \Delta | \mathbf{k} \rangle}{E_d - E_\mathbf{k}} \right]. \quad (45)$$

At this stage we see, as we saw for the total energy, that the results are unchanged by replacing the linear combinations $|d\rangle$ by single atomic states.

The calculation is reduced to one equivalent to that in simple metals. The orthogonalization charge and Δ-dependent terms may be evaluated directly and the screening potential computed self-consistently.

We may note also that if we had used this method to describe the effects of a resonance which lies above the Fermi energy, the orthogonalization hole would remain the same, the screening would remain of the same form, the atomic d-state charge density would not be added, and all of the remaining terms, explicitly dependent on Δ, would be changed in sign and summed over $k < k_F$ rather than $k > k_F$. Also note that in the approximation that the d state is the same in the crystal as in the free atom, Δ goes to zero and the simple-metal pseudopotential result is obtained.

If we are willing to make a small-core approximation, as we suggested in the case of the orthogonalization

hole, we neglect the difference between, for example, $\langle \mathbf{k}+\mathbf{q} | d \rangle$ and $\langle \mathbf{k} | d \rangle$, and take $\langle d | e^{-i\mathbf{q}\cdot\mathbf{r}} | d \rangle$ equal to unity, to obtain

$$n_q{}^{\mathrm{scr}} \approx 2 \sum_{k<k_F} \frac{\langle \mathbf{k}+\mathbf{q} | W | \mathbf{k} \rangle}{E_\mathbf{k} - E_{\mathbf{k}+\mathbf{q}}}$$
$$+ \sum_{d; k>k_F} \left(\frac{2\langle \mathbf{k}+\mathbf{q} | \Delta | d \rangle \langle d | \Delta | \mathbf{k} \rangle}{(E_d - E_\mathbf{k})(E_\mathbf{k} - E_{\mathbf{k}+\mathbf{q}})} - \frac{\langle \mathbf{k} | \Delta | d \rangle \langle d | \Delta | \mathbf{k} \rangle}{(E_d - E_\mathbf{k})^2} \right).$$
$$(46)$$

Note that we cannot eliminate the final two terms using Eq. (43), since the derivation of that result required a sum over *all* $\mathbf{k}$. We will see, in the application to copper, that the screening field from the sum over $k > k_F$ will just cancel the hybridization term in the limit as $\mathbf{q} \to 0$. These terms are in essence the screening field for the hybridization term in the Hamiltonian.

We note that both Eqs. (45) and (46) conspire to avoid summations over the singular energy denominators $E_d - E_k$. If the d state lies below the Fermi energy we sum only over states above the Fermi energy. If the d states lie above, we sum only below.

We may take the Fourier transform of the $n_q{}^{scr}$ to obtain the screening density around a single center as a function of r. Clearly, the asymptotic form will show the familiar Friedel oscillations of the form $(\cos 2k_F r)/(k_F r)^3$, but with $\langle k+q|W|k\rangle - \langle k+q|\Delta|d\rangle\langle d|\Delta|k\rangle/(E_d - E_k)$ replacing the usual matrix element $\langle k+q|W|k\rangle$. (Note that the change in sign in the second term came from the sum over $k > k_F$ rather than $k < k_F$.)

V. TOTAL ENERGY

The calculation of the total energy is quite intricate, although the results are moderately simple. We have obtained the energies of individual states which must be modified, much as in the screening calculation, to obtain a convenient form.

We begin with the conduction-band energy given in Eq. (19). In that equation, the energy E appears in one energy denominator and must be inserted to order Δ^2 (to obtain the energy to order Δ^4); that is, we use the first two terms in Eq. (19) for E in that denominator. Equation (19) becomes

$$E = E_k - \sum_d \frac{\langle k|\Delta|d\rangle\langle d|\Delta|k\rangle}{E_d - E_k + \sum_{d'}\langle k|\Delta|d'\rangle\langle d'|\Delta|k\rangle/(E_{d'} - E_k)} + \sum_q{}' \frac{|\langle k+q|[W - \sum_d \Delta|d\rangle\langle d|\Delta/(E_d - E_k)]|k\rangle|^2}{E_k - E_{k+q}}. \tag{47}$$

We must also rewrite the d-state energy using essentially the same transformation as in Eq. (43). We rewrite the final term in Eq. (37) for the energy of a d state, using Eq. (42) and dropping the difference between $E_{d'}$ and E_d:

$$-\sum_{k,k'}{}' \sum_{d'} \frac{\langle k'|\Delta|d\rangle\langle d|\Delta|k\rangle\langle k|\Delta|d'\rangle\langle d'|\Delta|k'\rangle}{(E_d - E_{k'})(E_d - E_k)(E_d - E_k)}$$

$$= -\sum_{k,k'}{}' \sum_{d'} \frac{\langle k'|\Delta|d\rangle\langle d|\Delta|k\rangle\langle k|\Delta|d'\rangle\langle d'|\Delta|k'\rangle}{(E_k - E_{k'})(E_d - E_k)}$$

$$\times \left(\frac{1}{E_d - E_k} - \frac{1}{E_d - E_{k'}}\right). \tag{48}$$

But the term in $1/(E_d - E_{k'})$ vanishes because of cancellation of terms with k and k' interchanged. (The summand is odd under this interchange.)

The other term summed over k and k' in Eq. (37) is similarly transformed, and k and k' interchanged in the second term:

$$\sum_{k,k'}{}' \frac{\langle k|\Delta|d\rangle\langle d|\Delta|k\rangle\langle k|W|k'\rangle}{(E_d - E_{k'})(E_d - E_k)} = \sum_{k,k'}{}' \frac{\langle k'|\Delta|d\rangle\langle d|\Delta|k\rangle\langle k|W|k'\rangle + \langle k'|\Delta|d\rangle^*\langle d|\Delta|k\rangle^*\langle k'|W|k\rangle}{(E_d - E_k)(E_k - E_{k'})}. \tag{49}$$

The first sum on the right side of Eq. (49) may be rewritten, noting that [see Eq. (17)]

$$\langle k|W|k'\rangle = \langle k'|W|k\rangle^* + (E_{k'} - E_k)(\sum_\alpha \langle k|\alpha\rangle\langle\alpha|k'\rangle + \sum_d \langle k|d\rangle\langle d|k'\rangle). \tag{50}$$

We obtain for the energy, from Eq. (37),

$$E = E_d + \sum_k \frac{\langle k|\Delta|d\rangle\langle d|\Delta|k\rangle}{E_d - E_k + \sum_{d'}\langle k|\Delta|d'\rangle\langle d'|\Delta|k\rangle(E_{d'} - E_k)^{-1}} + \sum_{k,k'}{}' \frac{1}{E_k - E_{k'}}$$

$$\times \left[\frac{\langle k'|\Delta|d\rangle\langle d|\Delta|k\rangle\langle k'|W|k\rangle^* + \langle k'|W|k\rangle}{E_d - E_k}\left(\frac{\langle k'|\Delta|d\rangle\langle d|\Delta|k\rangle}{E_d - E_k}\right)^* - \frac{\langle k'|\Delta|d\rangle\langle d|\Delta|k\rangle}{E_d - E_k}\sum_{d'}\frac{\langle k|\Delta|d'\rangle\langle d'|\Delta|k'\rangle}{E_d - E_k}\right]$$

$$- \sum_{k,k'}{}' (\sum_\alpha \langle k|\alpha\rangle\langle\alpha|k'\rangle + \sum_{d'}\langle k|d'\rangle\langle d'|k'\rangle)\frac{\langle k'|\Delta|d\rangle\langle d|\Delta|k\rangle}{E_d - E_k}. \tag{51}$$

The final sum may be contracted using the completeness of the $|k'\rangle$:

$$\sum_{k',k}{}' |k'\rangle\langle k'| = \sum_k (1 - |k\rangle\langle k|). \tag{52}$$

Only the term $|k\rangle\langle k|$ in Eq. (52) contributes, since $\langle\alpha|\Delta|d\rangle = \langle d|\Delta|d\rangle = 0$. Thus, the final contribution in Eq. (51) may be written

$$\sum_k (\sum_\alpha \langle k|\alpha\rangle\langle\alpha|k\rangle + \sum_{d'}\langle k|d'\rangle\langle d'|k\rangle)\frac{\langle k|\Delta|d\rangle\langle d|\Delta|k\rangle}{E_d - E_k}. \tag{53}$$

It seems likely that this term arises from a nonorthogonality of ψ_k and ψ_d of third order in Δ and might be removed in a different formulation. Equation (53) is of fourth order in Δ and will be independent of the configuration of ions. It will be of little interest here; however, if it is correct, it should be included when the various electrostatic and electronic terms are collected to obtain the total cohesive energy. Because the term is suspect and has a negligible effect on our results, we drop it here.

We may now sum the remaining terms in Eq. (51) over all d states and sum the energy of the conduction-band states given in Eq. (47) over all $k < k_F$. We see immediately that all first- and second-order terms in the sum over Eq. (47), except the terms in W^2, are cancelled by corresponding terms in the sum over Eq. (51). This is reminiscent of the cancellation in the screening density. We divide the sum of eigenvalues in the usual way into a contribution to the free-electron energy

$$E_{fe} = \sum_{k < k_F} E_k + \sum_d E_d + \sum_{k > k_F} \frac{\langle k | \Delta | d \rangle \langle d | \Delta | k \rangle}{E_d - E_k + \sum_{d'} \langle k | \Delta | d' \rangle \langle d' | \Delta | k \rangle / (E_{d'} - E_k)^{-1}}. \tag{54}$$

To be consistent with the dropping of Eq. (53) we might drop the sum over d' in the denominator to obtain this structure-independent term valid to second order in Δ. We also obtain the contributions to the band-structure energy

$$E_{bs} = \sum_q {}' \left[\sum_{k < k_F} \frac{|\langle k+q | W | k \rangle|^2}{E_k - E_{k+q}} + \sum_{k > k_F} \left(\sum_d \frac{\langle k+q | \Delta | d \rangle \langle d | \Delta | k \rangle \langle k+q | W | k \rangle^*}{E_d - E_k} \right. \right.$$

$$\left. \left. + c.c. - \left| \sum_d \frac{\langle k+q | \Delta | d \rangle \langle d | \Delta | k \rangle}{E_d - E_k} \right|^2 \right) \frac{1}{E_k - E_{k+q}} \right]. \tag{55}$$

Just as in the simple metals, all matrix elements may be separated into a structure factor and a form factor, and an energy–wave-number characteristic may be defined. In these expressions, the states $| d \rangle$ may be taken to be single atomic d states.

As in the case of the screening calculation, it has been possible to eliminate divergent summations across the resonant energy. Again, the result becomes identical to that in the simple metals if Δ is taken equal to zero. Also, as in the treatment of screening, we may treat the case of an unoccupied d band by eliminating the sum over E_d, changing the sign of the summations with $k > k_F$, and letting those sums run over $k < k_F$.

This does not complete the calculation of the total energy. We must subtract an energy equal to the electron-electron interaction, which has been counted twice in this treatment, and we must add the Coulomb interaction between ions. This is a very intricate calculation, just as it was in the case of simple metals. However, the use of Eqs. (54) and (55), rather than their simple-metal counterparts, does not introduce any fundamental complication. It seems clear that it will be convenient (though not necessary) to again define an electrostatic energy based upon an effective valence. This will not include the nuclear charge corresponding to the atomic d states, since these are compensated by occupied d orbitals. Thus, it will be based upon a valence Z equal to the number of conduction-band electrons per atom but multiplied by a quantity like

$$1 - \sum_{\alpha, k} \langle k | \alpha \rangle \langle \alpha | k \rangle - \sum_{d, k} \langle k | d \rangle \langle d | k \rangle.$$

It will also be possible to construct an effective interaction between ions which will have an asymptotic form containing Friedel oscillations just as in the simple metals. In fact, it seems clear from Eq. (50) that the only modification in the form of the tail will be the re-replacement of the simple-metal matrix element $\langle k+q | W | k \rangle$ by

$$\left\langle k+q \left| W - \sum_d \frac{\Delta | d \rangle \langle d | \Delta}{E_d - E_k} \right| k \right\rangle,$$

the same replacement which arose in the screening calculation. Again, all of these results reduce to those for simple-metal pseudopotentials if Δ is taken equal to zero.

VI. EVALUATION OF THE HYBRIDIZATION TERM

The difference in crystal and atomic potential δV enters the analysis in two distinct ways. First, it enters the determination of E_d as $\langle d | \delta V | d \rangle$. Second, it enters the hybridizing potential Δ. For determining E_d we may well wish to include the anisotropy of δV which gives crystal-field splitting, particularly in the treatment of the perfect crystal. In the determination of Δ we will ordinarily be content with a spherical average; this will give results applicable to arbitrary arrangements of atoms.

It is possible to obtain δV systematically in the framework of the perturbation expansion, and that will be done here. However, in future applications it may well be desirable to obtain δV to higher order, since the

parameter E_d and $\langle \mathbf{k} | \Delta | d \rangle$ are so important and may be somewhat sensitive to the details of the potential. A similar refinement was found desirable in obtaining the shift in core energies in the simple metals due to the orthogonalization hole.[6] Therefore, before obtaining forms on the basis of perturbation expansion, we outline a more accurate approach.

We may write the electron density in the crystal as a superposition of single pseudoatom densities $\rho_a(\mathbf{r}-\mathbf{r}_i)$. It may even be sufficient to take these as free-atom densities. In that case, the change in potential comes only from the neighboring atoms and probably nearest neighbors are enough. We may then directly compute the shifts in E_d from the free-atom wave functions and obtain, for cubic crystals, a splitting into twofold- and threefold-degenerate states. In determining Δ, we may wish to take a spherical average $\rho(r)$ of the corresponding density. If each atom has N_n neighbors a distance r_0 away, this density becomes

$$\rho(r) = \tfrac{1}{2} N_n \int d\theta \, \sin\theta \, \rho_a((r^2 + r_0^2 - 2rr_0 \cos\theta)^{1/2}). \quad (56)$$

We may instead proceed more systematically, though possibly less accurately, in terms of our expansion. For this purpose it is convenient to begin with the *free-ion* d state (e.g., Cu^+) and free-ion energy in place of the *free-atom* state and energy $E_d{}^a$. Then the change in potential in going to the metal is simply the potential due to the other ions, to the conduction-electron density, and to the change in d-electron density. However, Δ is required only to lowest order (screening and orthogonalization terms are of order W or Δ^2). Thus, we need the potential due to the other ions and due to zero-order conduction electrons. If we seek a spherical average, the ion charge density becomes a set of concentric charged spheres giving a uniform, and therefore noncontributing, potential. The potential due to the zero-order electron density satisfies Poisson's equation for an electron density of Z/Ω_0, with Z the valence and Ω_0 the atomic volume:

$$-\nabla^2 \delta V(\mathbf{r}) = 4\pi Z e^2 / \Omega_0, \quad (57)$$

which may be immediately integrated for spherical symmetry to obtain

$$\delta V(r) = a_0 + Z e^2 r^2 / 2 r_c{}^3. \quad (58)$$

Here r_c is the Wigner-Seitz cell radius, $\Omega_0 = \tfrac{4}{3}\pi r_c{}^3$, and for copper we take $Z = 1$. Using this form, Δ may be readily evaluated.

We note further that this form would have been obtained had we simply made a Taylor expansion of $\delta V(r)$, kept terms to order r^2, and required that $\partial V / \partial r$

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[6] Reference 1, p. 275.

$= 0$ at the cell radius [note that in this region $V = -Ze^2/r + \delta V(r)$], also a plausible approach.

VII. APPLICATION TO COPPER

We here seek a determination only of the form factors; we have not attempted a calculation of the energy–wave-number characteristic. In doing this, we will make a number of approximations (in particular, a semilocal approximation) which are, of course, not necessary, but which considerably reduce the computations required.

All terms in the transition-metal psuedopotential and in the hybridization terms may be written explicitly as a sum over identical contributions from each of the copper atoms present. This is, of course, always true for the pseudopotential, and we note that the hybridization terms contain a sum over d which can be separated into a sum over individual atoms and a sum over d states on a particular atom. Thus each matrix element may be factored into a structure factor,

$$S(q) = N^{-1} \sum_j e^{-i\mathbf{q}\cdot\mathbf{r}_j}$$

and a form factor evaluated for a single atom. In that form factor the normalization volume entering the normalized plane waves becomes the atomic volume Ω_0 rather than the crystal volume $\Omega = N\Omega_0$.

Δ is taken to be spherically symmetric about each atom, and hybridization matrix elements, for example, may be written in terms of the radial d function in the usual way[7]:

$$\sum_d \langle \mathbf{k}+\mathbf{q} | \Delta | d \rangle \langle d | \Delta | \mathbf{k} \rangle = \frac{4\pi}{\Omega_0} 5 P_2(\cos\theta)$$

$$\times \left(\int dr \, r j_2(|\mathbf{k}+\mathbf{q}|r) \Delta P_{3d}(r) \right)\left(\int dr \, r j_2(kr) \Delta P_{3d}(r) \right).$$

$$(59)$$

The factor 5 is $2l+1$. The $P_2(\cos\theta)$ is the $l=2$ Legendre polynomial, and θ is the angle between $\mathbf{k}$ and $\mathbf{k}+\mathbf{q}$. The j_2 are spherical Bessel functions. Here we evaluate matrix elements for both initial and final states on the Fermi surface, so both $|\mathbf{k}+\mathbf{q}|$ and k will be taken to be the Fermi wave number k_F. Δ is a spherically symmetric potential which here will be determined by Eq. (58). The P_{3d} is the radial wave function for principal quantum number 3 and angular momentum quantum number 2. Other matrix elements with one or both Δ's omitted may be obtained directly by making the appropriate omissions in Eq. (59). Using Piper's[8] atomic d functions for Cu^+, using Eq. (58), and taking k_F

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[7] Reference 1, p. 276ff.
[8] W. W. Piper, Phys. Rev. 123, 1281 (1961).

$= 0.7198$ a.u., we find

$$\langle d \,|\, \delta V \,|\, d \rangle_s \equiv \int P_{3d}{}^2(r)\delta V dr = 0.0645 \text{ Ry},$$

$$\langle k \,|\, \delta V \,|\, d \rangle_s \equiv \left(\frac{4\pi}{\Omega_0}\right)^{1/2} \int dr\, r j_2(k_F r)\delta V P_{3d}(r) = 0.0640 \text{ Ry},$$

$$\langle k \,|\, d \rangle_s \equiv \left(\frac{4\pi}{\Omega_0}\right)^{1/2} \int dr\, r j_2(k_F r) P_{3d}(r) = 0.1117. \quad (60)$$

These were obtained by hand computation and are of limited accuracy. In addition, the use of Eq. (58) for $\delta V(r)$ could well lead to appreciable errors in the first two values. The subscript s signifies that angular factors are not included in these matrix elements but are correctly included through Eq. (59).

We first seek the matrix-element form factors for the transition-metal pseudopotential of Eq. (17). A semilocal approximation described in detail earlier[9] is to be made. In essence, this neglects k dependence of the pseudopotential by evaluating unscreened form factors for initial and final states lying on the Fermi surface, and then evaluating the screening as if these form factors applied to all electrons present; in doing this, we use the second-order correction[10] leading to proper behavior at long wavelengths. This calculation for copper is, in fact, almost identical to that performed earlier,[11] except for the addition of the two terms linear in Δ. In addition, we have taken a value of $E_k - E_d$ of 0.2 Ry, a value estimated from energy-band calculations,[2] rather than a value estimated from the term values which was appropriate when we treated the d states as core states.[11] In a more complete analysis we could estimate E_d within the framework of our theory as we have indicated earlier. Finally, we have used Kohn-Sham exchange for the interaction between conduction and core (including d) electrons rather than the Slater exchange used earlier. This would certainly seem appropriate, since we are specifically interested in the behavior of electrons at the Fermi energy and not electrons deep within the Fermi sea. It makes a sizeable difference, since the exchange potential with the d states is quite large. The contribution (unscreened) to the backscattering form factor is about -0.2 for Kohn-Sham exchange and -0.3 for Slater exchange. When important results are this sensitive to the particular treatment of exchange, the result from either method is suspect. Because of this uncertainty and because of the approximate treatment of Δ, the form factor that we compute must be viewed with some reservation.

The resulting pseudopotential form factor is similar to that obtained earlier and is shown in Fig. 3. Included in the potential is the electrostatic potential due to

[9] Reference 1, p. 282ff.
[10] Reference 1, p. 286.
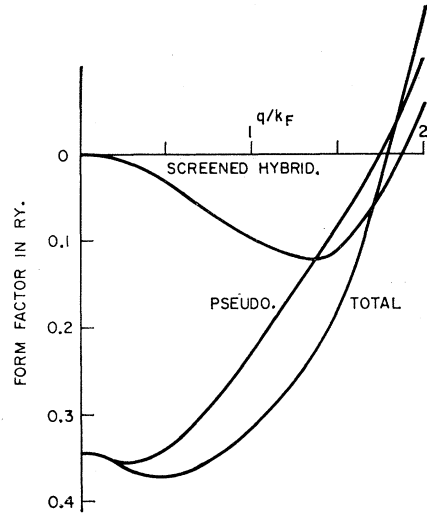[11] W. A. Harrison, Phys. Rev. **131**, 2433 (1963).

FIG. 3. Computed pseudopotential form factor for copper, screened hybridization form factor for copper, and the sum of the two. The total form factor enters the calculation of electronic properties in the same way as does the simple-metal form factors.

occupied d states, the orthogonalization hole including that due to orthogonalization to the d states, and the ordinary screening field which arises from the first summation in Eq. (46). It does not include the screening potential arising from the final terms in Eq. (46) since, as we indicated there, these represent screening of the hybridization term. Furthermore, it does not include an additional screening potential which will be discussed presently. Thus, the screening entering this pseudopotential, because of the semilocal approximation, consitutes a simple division of the unscreened form factor by the Hartree dielectric function for a free-electron gas with Fermi wave number equal to that of copper (except, again, for the above-mentioned second-order correction which leads to appropriate behavior at $q \to 0$).

We next evaluate the hybridization matrix element directly from Eqs. (59) and (60), using again $E_k - E_d = 0.2$ Ry. Finally, we seek to evaluate the potential arising from the final terms in Eq. (46). The evaluation of these terms is somewhat complicated, but is simplified considerably by the use again of semilocal approximation; that is, we take $\langle k+q \,|\, \Delta \,|\, d \rangle \langle d \,|\, \Delta \,|\, k \rangle$ as depending only on q and write for the next-to-last term in Eq. (46)

$$\sum_{k > k_F} \frac{2\langle k+q \,|\, \Delta \,|\, d \rangle \langle d \,|\, \Delta \,|\, k \rangle}{(E_d - E_k)(E_k - E_{k+q})} \approx \frac{4\Omega_0}{(2\pi)^3} \langle k+q \,|\, \Delta \,|\, d \rangle \langle d \,|\, \Delta \,|\, k \rangle$$

$$\times \int_{k_f}^{\infty} \frac{dk\, 2\pi k^2}{k_F{}^2 - 0.2 - k^2} \int_0^{\pi} \frac{d\theta \sin\theta}{-q^2 - 2kq \cos\theta}. \quad (61)$$

Here we have taken E_k to be the free-electron value, which is k^2 in rydbergs if the wave number is given in atomic units. The corresponding approximation is made for the *final* term in Eq. (46) and the resulting integrals

may be performed analytically. Angular integration in Eq. (61) may also be performed analytically, but we have not found an analytic form for the resulting integration over k. That integral was performed numerically for the values of q (0, $0.5k_F$, k_F, $1.5k_F$, and $2k_F$) for which the form factors had been computed. We obtain for the summation in Eq. (61) the result

$$\sum_{k>k_F} \frac{2\langle \mathbf{k+q}|\Delta|d\rangle\langle d|\Delta|\mathbf{k}\rangle}{(E_d-E_k)(E_k-E_{k+q})}$$

$$=\frac{\Omega_0}{4\pi^2 q}\langle \mathbf{k+q}|\Delta|d\rangle\langle d|\Delta|\mathbf{k}\rangle\alpha, \quad (62)$$

where the coefficients α is given by $2.69q/k_F$, 1.35, 2.78, 4.42, and 7.91 for the five values of q given above. To this we add the contribution of the final term in Eq. (46).

From this charge density we obtain a potential by directly using Poisson's equations. This potential enters as another contribution to the atomic potential and must be included in the self-consistent calculation of screening which enters the first term of Eq. (46). The net result is to divide this contribution by the Hartree dielectric function. This (contribution is in fact to be divided by the Hartree dielectric function even if it is computed accurately rather than in the semilocal approximation.) These terms, appropriately divided by the dielectric function are added to the matrix elements of the hybridization term to give the *screened hybridization form factors* shown in Fig. 3. We note that the effect of screening has been to cancel the hybridization term at long wavelengths.

If we now seek to treat electronic properties associated with the electrons at the Fermi surface, we begin with the pseudopotential equation (13). In zero order the pseudo-wave-functions are plane waves, and the transition-metal pseudopotential and hybridizing terms enter directly as the perturbation. Thus, properties are calculated exactly as in simple metals but with the pseudopotential matrix elements replaced by the sum of the transition-metal pseudopotential form factor and the form factor for the screened hybridization term. Thus, for the calculation of properties we use the total form factor shown in Fig. 3. That form factor, for example, gives directly the electron-phonon interaction in copper; the matrix element for normal scattering by a longitudinal phonon is simply the product of that form factor and the amplitude of the local dilatation. Such form factors enter directly the wide range of scattering problems which have been calculated in simple metals and determine the distortion of the Fermi surface.

The total form factor shown in Fig. 3 is quite reasonable. It approaches $-\frac{2}{3}E_F$ as $\mathbf{q} \to 0$. This is minus the reciprocal of the density of states at the Fermi energy (in the semilocal approximation) and is expected on very general grounds. The result at large q is also plaus-

ible. We note that the band gap at L (the center of the nearest zone face) obtained by Segall[2] is 0.4 Ry, corresponding to a form factor of 0.2 Ry. This is comparable to the back-scattering form factor of Fig. 3, which is 0.17 Ry; the signs are also positive in both cases. The two numbers are not quite measures of the same physical quantity, since the wave number difference between two opposite faces is 10% larger than $2k_F$. However, in the alkali metals the back-scattering form factors have generally agreed roughly with band gaps at the nearest zone face.

We have also estimated the resistivity of liquid copper using the form factors of Fig. 3 and the structure-factor data of Wagner, Ochen, and Joshi[12]; the calculation is quite simple.[13] We have ignored the difference in atomic volume of the liquid and the solid by using our form factors for solid densities with the structure factor at liquid densities. We obtain a value of 25 $\mu\Omega$ cm, to be compared with the observed 21 $\mu\Omega$ cm. The exact extent of this agreement is not significant both because of the failure to calculate form factors at the liquid densities and because of the well-known sensitivity of the calculation of liquid resistivities. However, the comparison does lend support to the methods proposed and to the form factors.

VIII. SUMMARY

Although the analysis has been rather complicated, the general drift of the argument and the principal results are rather clear. It may therefore be helpful to outline the argument made in the preceding pages.

We began with a self-consistent field approximation, assuming that there exists a potential $V(\mathbf{r})$ in terms of which the eigenstates are obtainable from the Schrödinger equation (1). The eigenstates of this equation include deep-lying core levels $|\alpha\rangle$, which are essentially the same as those of the free atom though the corresponding eigenvalues are shifted. We are not specifically interested in these states but in the higher-lying levels corresponding to conduction-band and d states. We seek a solution for these states by expanding the state $|\psi\rangle$ in an overcomplete set including atomic core states and atomic d states in addition to plane waves. We substitute such an expansion in Eq. (1); we eliminate the coefficients in the core states and d states and obtain an equation for the remaining plane-wave terms. These plane-wave terms are written collectively as the pseudo-wave-function $|\varphi\rangle$, and the equation which they satisfy is called the transition-metal pseudopotential equation (13). In this equation W is the transition-metal pseudopotential given in Eq. (17). The term quadratic in Δ is called the hybridizing term because of its close formal similarity to hybridization terms fre-

[12] C. N. J. Wagner, H. Ochen, and M. L. Joshi, Z. Naturforsch. **20A**, 325 (1965).
[13] Reference 1, pp. 134 (note that C in $\mu\Omega$ cm/Ry^2 at.% must be multiplied by 100 to give a value in $\mu\Omega$ cm/Ry^2) and p. 153ff.

quently introduced phenomenologically. This term can, of course, also be thought of in terms of a scattering resonance with width Δ at the energy E_d, and this terminology is convenient for describing it. Δ is defined in the neighborhood of any atom as the potential in the free atom minus the potential in the crystal (minus the expectation value of that difference taken with respect to the atomic d states). This potential enters because the atomic d states, in contrast to the core states, are not eigenstates of the crystal potential. The atomic d states are, however, assumed to be nonoverlapping. If this were not a good approximation, appropriately modified d states could be used. E_d is the expectation value of the Hamiltonian in the crystal taken with respect to atomic d states. E_α is, of course, the expectation value of the Hamiltonian in the crystal with respect to the core states $|\alpha\rangle$, and E_k is defined by $E_k = \hbar^2 k^2/2m + \langle k|W|k \rangle$.

Equation (13) is exact except for the approximation of nonoverlapping atomic d states; if it is solved exactly, the eigenvalues obtained are equal to those of the Schrödinger equation (1). [Strictly speaking, the E_k must be replaced by E in the third term in Eq. (17) for the pseudopotential to be exact.] The exact wave function is obtainable directly from the corresponding pseudo-wave-function. In that sense, Eq. (13), plays precisely the role of the pseudopotential equation in simple metals. In fact, if the parameter Δ is set equal to zero, implying that the atomic d states are solutions of the crystal Hamiltonian, then Eq. (13) becomes precisely the ordinary pseudopotential equation, and the pseudopotential given in Eq. (17) becomes the optimized pseudopotential for simple metals with core d states.

Of course, the main point of developing a pseudopotential equation is to allow the use of perturbation theory. Just as in the simple metals, it is appropriate to regard W as a perturbation and, for states well removed from resonance, the hybridizing term will also be small.

In zero-order solutions of Eq. (13) are plane waves, and perturbation theory proceeds in the usual pattern. W is regarded as a first-order quantity, as is Δ^2. We can see from Eq. (17) that we must then also regard quantities such as $\langle d|k \rangle$ as of the same order as Δ. We obtain the pseudo-wave-function and then the true wave function to first order in W [Eq. (18)] and the energy to second order [Eq. (19)].

In order to compute the screening potential, or the total energy, we must sum over all occupied states, and this requires the continuation of the results of perturbation theory through resonance. In this continuation, care must be taken because of the divergence of the hybridizing term. Examination shows that in summing over unperturbed states through this region, we omit a single true eigenstate for every d resonance which has been introduced. This is apparent both from the form of the first-order wave function and from the form

of the second-order energies. Thus, to complete a sum over states, we must evaluate these omitted wave functions and energies, again by perturbation theory.

To do this, we return to the Schrödinger equation (1), with ψ expanded in the same over-complete set, and again eliminate the coefficients of the core wave functions. We then, however, take as the unperturbed state the appropriate linear combinations of atomic d states and compute the admixture of plane waves by perturbation theory. This calculation is considerably more difficult than the calculation of states which in zero order are plane waves. In that case, perturbing terms were of order W or Δ^2 and ordinary second-order perturbation theory sufficed. In the calculation of d-like states, there are perturbing terms of order Δ, and to obtain an energy to second order in W, we must compute the wave function to third order in Δ. However, the analysis can be carried through and the resulting states [Eq. (25)] and energy [Eq. (37)] written in terms of matrix elements of Δ and of W. It is then verified that all of these states, the plane-wave-like states (which we call k states) and the d-like states, are orthogonal to each other to first order in W, confirming the assertion that these d-like states were omitted in the first summation through resonance and that the computed d-like states are not simply linear combinations of states already considered.

We then proceed with the screening calculation, computing the charge density in terms of the true wave functions obtainable from the first-order pseudo-wave-functions. Specifically, we compute the Fourier components n_q of the electron density. At this point the summation is only easily performed in the d-like states which have been constructed lie entirely above or entirely below the Fermi energy. This is the case, of course, in the noble metal, where they lie entirely below, and the alkaline earths, where they lie entirely above. In the latter case, even though the d-like states are unoccupied, we may expect significant improvement in the pseudopotential calculations by including atomic d states in the expansion and thereby making appropriate modifications of the pseudopotential. This may also be applicable in some transition metals where we may regard the d bands as sufficiently well separated that some may be said to be completely occupied and others completely empty. With this summation over all d states, the results are unchanged by replacing the appropriate linear combinations of atomic d states (for example, Bloch sums for perfect crystals) by sums over individual atomic d states. Then the sums over d state and k states [Eqs. (38)–(41)] both contain sums over wave vector k as well as over atomic d states. They are slightly different in form, however, and must be transformed before they can be conveniently combined. In addition, in the charge density due to k states the sums are of course restricted to $k < k_F$, while in the d states the sums are over all wave numbers.

When the proper combination has been made, the charge density may be divided into three distinct terms [Eq. (44)]. First is the charge density which would be calculated from occupied atomic d states. Second is exactly the orthogonalization hole which is computed in simple-metal theory but here including orthogonalization to d states as well as to core states. Third is a term which we call the screening term [Eq. (45)], which takes a more perspicuous form when written in a small-core approximation [Eq. (46)]. The leading term is linear in W and is of precisely the form obtained in simple-metal theory, though W is, of course, the transition-metal pseudopotential. There are two additional terms proportional to Δ^2 which we think of as the screening of the hybridization terms.

In obtaining the screening density self-consistently from Eq. (46), we note that the final terms lead to a charge density which enters W. However, they lead to a simple local potential; including them in W in this self-consistent calculation simply screens them with the Hartree dielectric function. It is convenient conceptually and mathematically to compute the screening of W as if there were no screening of the hybridization term and to define the screening of the hybridization terms as the final terms in Eq. (46) divided by the Hartree dielectric function. In the subsequent application to copper, we see that these terms just cancel the hybridization term at long wavelengths. This result, however, seems to depend on the semilocal approximation used there. (We may also note that the density of states, which is directly related to the $q=0$ form factor, is $\frac{3}{2}E_F$ only in the semilocal approximation.)

We note that the final summations determining the screening field avoid the divergence at resonance; the sum over the hybridizing terms is for $k>k_F$. In treating a case in which the d states lie above the Fermi energy, and are therefore unoccupied, the sign of this screening term is changed, and it is summed over $k<k_F$.

It is clear from Eq. (46) that the screening density will show the familiar Friedel oscillations in real space as it does in the simple metals, but with the matrix element $\langle \mathbf{k+q}|W|\mathbf{k}\rangle$ which enters the simple metals replaced by $\langle \mathbf{k+q}|W|\mathbf{k}\rangle - \langle \mathbf{k+q}|\Delta|d\rangle\langle d|\Delta|\mathbf{k}\rangle/(E_d - E_\mathbf{k})$.

We finally proceed to the calculation of the total energy. This calculation is formally quite similar to the calculation of the screening field. Transformations required to obtain a reasonably simple form are somewhat more complicated. We obtain, finally, a total energy which is immediately divided into three contributions. First is a contribution to the free-electron energy which is independent of the configuration of the atoms, and is given in Eq. (54). The result is quite plausible; it contains a sum of $E_\mathbf{k}$ and E_d over occupied states and a contribution from the hybridizing term. These contributions to the d states and the k states cancel for $k<k_F$, and therefore only appear for $k>k_F$.

We then obtain contributions to the band-structure energy, given in Eq. (55). We obtain a term in W^2 which is of the same form as in the simple metals plus additional terms in Δ. Altogether, this is just what would be obtained from the formula for simple metals by replacing $\langle \mathbf{k+q}|W|\mathbf{k}\rangle$ in the first term by $\langle \mathbf{k+q}|W|\mathbf{k}\rangle - \langle \mathbf{k+q}|\Delta|d\rangle\langle d|\Delta|\mathbf{k}\rangle/(E_d - E_\mathbf{k})$, but with all contributions from the hybridizing term being summed only over $k>k_F$.

Again by setting $\Delta=0$, the results reduce to those for simple metals. Again, if we treat a case in which the d states are unoccupied, the sign of the hybridization terms is changed and the sum is made over $k<k_F$. As in the case of screening, the regions of summation conspire to avoid the resonant energies.

It is clear from the form of the contribution of the band-structure energy that Friedel oscillations in the effective interaction between ions will arise and will differ from those in the simple metals by the same inclusion of hybridization terms with the pseudopotential which occurred in the screening calculation.

We then discuss the calculation of the hybridizing potential Δ. In perfect crystals, we may wish to use an anisotropic form to provide crystal-field splitting of the atomic d states and then to treat the different d bands separately. For more general applications to deformed or disordered structures it will be more appropriate to take a spherical average of Δ. We take the latter approach in the treatment of copper and propose a simple approximate form which is used in that analysis.

The treatment of copper itself is somewhat approximate; a semilocal approximation is made both for the treatment of the pseudopotential and for the treatment of the hybridization terms, and form factors are computed only for coupling between two states lying on the Fermi sphere.

The calculation follows closely an earlier attempt[11] to treat copper as a simple metal and the d states as core states. In fact, it was possible to use many of the parameters evaluated then. However, we replaced the Slater free-electron exchange by Kohn-Sham exchange, which now seems clearly preferable when we wish to focus our attention specifically on electrons at the Fermi surface. This made a sizeable shift in the form factors and for that reason casts some doubt on the values obtained. We also chose a value of 0.2 Ry for the energy $E_\mathbf{k} - E_d$, which was estimated from energy-band calculations. Otherwise, all numbers were calculated entirely from the equations derived here.

The resulting pseudopotential form factor, screened hybridization terms, and total form factor are shown in Fig. 3.

The total form factor is to be used directly in the calculation of electronic properties in exactly the same fashion that the pseudopotential form factor is in simple metals. It gives directly, for example, the electron-phonon interaction for normal scattering of longitudinal

phonons. We note further that the back-scattering form factor does not appear inconsistent with the large band gap at L found in energy-band calculations for copper. Finally, it is noted that its use in a calculation of the resistivity of liquid copper gives a reasonable result. It is recognized, however, that this calculation of form factors was rather crude.

A reformulation of this method in terms of a pseudo-Green's function is in progress and appears to allow for rather simpler derivations. In addition, more careful estimates of the pseudopotential form factor and hybridization term are in progress and will be extended to include the total energy.

ACKNOWLEDGMENT

Surface Roughness and the Absorption of Electromagnetic Waves in Simple Metals

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(Received 21 October 1968)

The reflection of electromagnetic waves impinging normally on the rough surface of a simple metal is theoretically investigated for frequencies small enough so that band effects are minimal. This is done by first examining the effects of the metallic surfaces on the single-particle states. The "effective roughness" for the single-particle states depends on their frequency, wave vector, and mean free path. It is found that the derivation of the reflectivity from the specular limit depends on an rms surface roughness depth when the characteristic roughness wavelength is smaller than the electron mean free path. If the surface is sufficiently rough on a longer-wavelength scale, it is found that the reflectivity can be smaller than that predicted by assuming that all electrons are diffusely reflected at the surface.

I. INTRODUCTION

IN discussing the electrical-transport properties of metals, the surface is usually described by a model in which it is assumed that a fraction p of the electrons are specularly reflected. The remaining fraction $1-p$ are diffusely scattered at the surface.[1-3] The quantity p is usually treated as an adjustable parameter, but theories for it do exist.[4] Experiments show that p is nearly zero under most circumstances but that it can be nearly 1 under favorable conditions.[5]

Although the above model appears to describe most reflectivity measurements adequately, we wish to describe the effects of the surface on the single-particle Green's function for a simple metal in terms of roughness parameters obtained from a microscopic theory. This Green's function is then used to calculate the normal incidence reflectivity of the metal at frequencies below which band effects are important. Besides being a more fundamental description, these parameters can also be used to calculate other effects such as the coupling of photons to the surface plasmon.[6]

The rest of this section will be devoted to an explanation of the method used. An equation for the single-particle Green's function will be obtained and solved in Sec. II. In Sec. III the normal incidence reflectivity of a simple metal will be calculated and discussed in the Drude limit. The Appendix contains some of the calculational details. The reader who is not acquainted with the Green's-function techniques should be able to partially follow the paper by thinking of G as a quantity that describes the propagation of electrons in the metal.

Consider a free Fermi gas confined to the slab $0 \leq z \leq d$ by infinitely high potential barriers and with periodic boundary conditions on a square of side L in the x-y plane.[7] This system, with perfectly reflecting surfaces, has single-particle wave functions and energies (as measured from the Fermi surface) given by

$$\phi(\mathbf{r}) = (2/\Omega)^{1/2} e^{i\mathbf{p}\cdot\boldsymbol{\rho}} \sin kz,$$
$$\epsilon_0(\mathbf{q}) = (\mathbf{q}^2/2m) - \mu = (\mathbf{p}^2 + k^2 - q_f^2)/2m, \quad (1)$$

where μ is the chemical potential or Fermi energy and q_f is the Fermi momentum. Cylindrical coordinates $\mathbf{r} = (\boldsymbol{\rho}, z)$ and units where $\hbar = 1$ are used throughout the paper. Wave numbers in the x-y plane, whose components take on integral multiples of $2\pi/L$, are denoted by $\mathbf{p}$, while those in the z direction are denoted by k, where k is restricted to integral multiples of π/d. Throughout the paper, $\mathbf{q}$ will denote the pair $(\mathbf{p}, k)$.

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