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Superexchange and superconductivity: A possible correlation

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We analyze the possibility of pair formation between conduction electrons in a metal via exchange interactions with electrons of the atomic cores, in analogy with the phenomenon of "superexchange" between unpaired (d) electrons on two paramagnetic cations via electrons of a closed-shell anion in insulating solids. The matrix elements for the scattering of a pair state of conduction electrons with opposite momenta and z components of spin, into another pair state, are derived on the basis of a model, and evaluated by using simple orbital functions for the conduction and core electrons. An approximate solution for the energy gap at the Fermi level is obtained. The model is shown to incorporate the occurrence of itinerant-electron antiferromagnetic states in metals, recently discussed in the literature, under well-defined conditions. Applications are made to metals of the groups I*A* (Li to Cs), II*A* (Be to Ba), III*A* (Al to Tl), IV*A* (Sn and Pb), I*B* (Cu, Ag, and Au), and II*B* (Zn, Cd, and Hg). The results reproduce the observed trends regarding the occurrence, or absence, of superconductivity. The critical temperatures are of the correct order of magnitude. It is concluded that this mechanism, at least for the metals considered, can play a significant role in understanding Cooper-pair formation.

I. INTRODUCTION

The development of the theory of superconductivity culminated in 1957 with the publication of the Bardeen-Cooper-Schrieffer (BCS) theory,[1] based on the following "reduced" Hamiltonian H_{red} for the conduction electrons[2]:

$$H_{\text{red}} = \sum_{\vec{k},\sigma} \epsilon_{\vec{k}} c^{\dagger}_{\vec{k}\sigma} c_{\vec{k}\sigma} + \sum_{\vec{q},\vec{k}} V_{\vec{q}\vec{k}} c^{\dagger}_{\vec{q}\uparrow} c^{\dagger}_{-\vec{q}\downarrow} c_{-\vec{k}\downarrow} c_{\vec{k}\uparrow} \; . \qquad (1)$$

Here, $c^{\dagger}_{\vec{k}\sigma}$ and $c_{\vec{k}\sigma}$ are creation and annihilation operators for electrons with wave vector $\vec{k}$ and with z component σ of spin (up, ↑; and down, ↓). The one-electron (quasiparticle) part of (1) refers to the low-lying single-particle energies in the normal state of the metal according to the Landau theory of Fermi liquids. The matrix element $V_{\vec{q}\vec{k}}$ of a two-electron operator V in the second term of (1) describes the interaction between the pair states $(\vec{q}\uparrow, -\vec{q}\downarrow)$ and $(\vec{k}\uparrow, -\vec{k}\downarrow)$; thus, in each pair state the two electrons have opposite momenta and z components of spin. Such two-electron terms are not taken into account in Landau's treatment of Fermi liquids.

As has been emphasized by Cooper[3] in particular, the basic BCS equations are independent of the *origin* of $V_{\vec{q}\vec{k}}$. Consequently, *any* electron-electron interaction exhibiting the property that $V_{\vec{q}\vec{k}}$ is predominantly negative for $\vec{q},\vec{k}$ near the Fermi vector $\vec{k}_F$, can lead to superconductivity. On this basis alone the whole plethora of observed properties of superconductors can in principle be understood. BCS, in the further development of their theory, consider exclusively the case where $V_{\vec{q}\vec{k}}$ describes an indirect coupling between conduction electrons via electron-phonon interactions.

In this paper we shall analyze the additional possibility that $V_{\vec{q}\vec{k}}$ arises from exchange interactions between conduction electrons (near the Fermi level) via exchange effects with electrons of the atomic cores. The mechanism is to be viewed in analogy with the phenomenon of "superexchange," first considered by Kramers[4] in 1934. Here, unpaired electrons on two neighboring ($3d$) cations in an insulating solid are coupled via exchange interactions with electrons of a closed-shell anion. Such interactions lead to distinct spin patterns, antiferromagnetic, or ferrimagnetic if the cations have different spin moments, at low temperatures (order ~100 K or lower) in nonconducting solids, observable, e.g., through neutron-diffraction experiments. Evidence for the occurrence of this phenomenon is more than abundant. For a general review, we refer to Anderson.[5]

It must be asked at this point whether a similar phenomenon in *metals*, involving conduction electrons and closed-shell atomic cores, and leading to itinerant-electron antiferromagnetism, is at all feasible: *d*-electron wave functions in insulators are rather localized at the core lattice points, much more so than wave functions for nearly-free electrons. As a first step towards an answer we have, in earlier calculations[6] on cation-anion-cation superexchange, removed the cation nuclear charges. The singlet-spin pairing between the "cation" electrons was found to persist fully. This means that "Cooper pairs" can be formed without the aid of nuclear charges, and the question of whether this effect is still measurable for realistic conduction-electron wave functions must be answered on the basis of *quantitative* calculations.

In the standard terminology of the physics of many-electron systems, interactions between conduction-electron pair states can always be expressed in terms of an appropriately chosen dielectric tensor for the system considered. Since the range of exchange interactions via an atomic core does not extend beyond one lattice parameter, this interaction is described by that part of the dielectric tensor with wave vectors larger than the smallest reciprocal-lattice vector, i.e., by local-field effects.[7,8] The importance of such local-field effects for the possible occurrence of attractive-pair interactions (with respect to the Fermi level) has been emphasized.[9] In particular, these effects have been considered in connection with an exciton mechanism of superconductivity.[10,11] However, a theory of the dielectric tensor concerning conduction-electron exchange via core electrons is at present not available. In the following sections we will pursue the possibility of the assumed analogy between superexchange in insulators and a phonon-independent mechanism of superconductivity in terms of contributions supplementary to those obtained on the basis of the Fermi-liquid approximation for the many-electron system in metals.

II. THE MODEL

As a model system we consider a (nontransition) metal built up out of N atoms with a bcc, fcc, or hcp primitive cell, characterized ideally by one conduction band well separated from a fully occupied valence band. Each atom contributes a number of conduction electrons and, in the model, its core is described by two spin-paired electrons in a 1*s*-like shell. In the Fermi-liquid approximation the one-electron Hamiltonian $H_{[1]}(r)$ for each conduction electron has the form

$$H_{[1]}(\vec{r})=T(\vec{r})+V_n(\vec{r})+V_c(r) +e\int \rho(\vec{r}\,')g(|\vec{r}-\vec{r}\,'|)d^3r\,' \, . \qquad (2)$$

Here, T is the kinetic energy operator, e is the electronic charge, V_n is the interaction between the electron and the nuclear charges, and V_c is an averaged interaction with all the other conduction electrons. The last term in (2) describes the interaction energy due to the Coulomb potential $eg(|\vec{r}-\vec{r}\,'|)$ of a conduction electron and a given charge distribution $\rho(\vec{r}\,')$ associated with all the core electrons. [Exchange interactions between conduction and core electrons in terms of one-electron operators, i.e., statistical-exchange correlations in the self-consistent field, can also be included in (2).] In this equation we have described the conduction-electron system itself adopting the usual approximations. Explicitly, all Coulomb interactions such as $e\rho(\vec{r}\,')g(|\vec{r}-\vec{r}\,'|)$ are taken with respect to potentials which are screened by the sea of conduction electrons. The eigenvalue equation for the conduction-electron system in terms of the one-electron Hamiltonian $H_{[1]}(\vec{r})$, i.e.,

$$H_{[1]}(\vec{r})\psi_{\vec{k}}(\vec{r})=\epsilon_{\vec{k}}\psi_{\vec{k}}(\vec{r}) \, , \qquad (3)$$

yields orthogonal Bloch states $\psi_{\vec{k}}$, and corresponding one-electron energies $\epsilon_{\vec{k}}$. For the *formal derivation* of the off-diagonal matrix elements $V_{\vec{q}\,\vec{k}}$ in the reduced Hamiltonian (1), we suppose that Eq. (3) is solved exactly.

To investigate the possible occurrence of an indirect-exchange interaction between conduction electrons via electrons of the atomic cores (i.e., via fermions thus far not included in the description of the system), we start from two arbitrarily selected conduction electrons, labeled 1 and 2. We must now take the core-electron system explicitly into account, with electron labels $3,4,\ldots,2N+2$ (each core carries two electrons in the model). The two-conduction-electron Hamiltonian $H_{[2]}(\vec{r})$, with permutation group $\mathscr{S}_2$ is, in the Fermi-liquid approximation, given by

$$H_{[2]}(\vec{r}_1,\vec{r}_2)=H_{[1]}(\vec{r}_1)+H_{[1]}(\vec{r}_2) \, , \qquad (4)$$

i.e., by the sum of the two one-electron Hamiltonians (2). The physically allowed eigenstates belonging to (4) are the antisymmetrized products of solutions of the eigenvalue equation (3).

We now consider the system of $2N$ core electrons imbedded in the sea of conduction electrons. The Hamiltonian for this system reads

$$\begin{aligned} H_{[2N]}(3,4,\ldots,2N+2) &= \sum_{j=3}^{2N+2} [T(j)+V_n(j)+V_c(j)] \\ &\quad + \tfrac{1}{2}e^2 \sum_{i=3}^{2N+2} \sum_{\substack{j=3 \\ j\neq i}}^{2N+2} g(|\vec{r}_i-\vec{r}_j|) , \end{aligned} \qquad (5)$$

describing a system of $2N$ interacting electrons in the potential V_n of the nuclear charges and in the averaged potential V_c associated with the conduction electrons. Just as for the system (4) of two conduction electrons, we suppose that the eigenvalue equation associated with the Hamiltonian (5) is solved exactly. Together with the solutions of (4), this will enable us to derive *formal* expressions for the matrix elements $V_{\vec{q}\,\vec{k}}$ in (1). We do not consider excited states of the *core* system (see also below). Denoting the ground eigenstate and ground-state eigenvalue of the core system by ϕ_0 and E_0, respectively, we have

$$H_{[2N]}\phi_0 = E_0\phi_0 \; . \qquad (6)$$

The function ϕ_0 is antisymmetric with respect to permutations of the $2N$ electron labels (symmetry group $\mathscr{S}_{2N}$). Correlation terms are thus already included in ϕ_0 and E_0.

We form the (tensor) product of the eigenspaces of (4) and (5), i.e., the eigenspace of the sum $H_{[2]} + H_{[2N]}$, with permutation symmetry $\mathscr{S}_2 \times \mathscr{S}_{2N}$. Next, we compare the sum $H_{[2]} + H_{[2N]}$ with the *total* Hamiltonian H_{tot} of the system of two conduction and $2N$ core electrons, and we define a *difference operator* $\mathscr{V}$ by

$$\mathscr{V} \equiv H_{\text{tot}} - (H_{[2]} + H_{[2N]}) \; , \qquad (7)$$

which, upon examination, yields

$$\mathscr{V}(1,2,\ldots,2N+2) = e^2 g(|\vec{r}_1-\vec{r}_2|) + e^2 \sum_{p=1}^{2} \sum_{j=3}^{2N+2} g(|\vec{r}_p-\vec{r}_j|) - \sum_{p=1}^{2} e \int \rho(\vec{r}\,')g(|\vec{r}_p-\vec{r}\,'|)d^3r' \; . \qquad (8)$$

Strictly speaking, we should subtract in (8) also (twice) that part of the interaction between electrons 1 and 2 which is included in the averaged potential V_c. Equally, the interaction of the core electrons with that part of V_c stemming from electrons 1 and 2, should be subtracted. These terms, as well as the last term of (8), are one-electron potentials. In the application of the model to be discussed later on, these terms do not contribute to the indirect interaction. We shall, therefore, continue with the first two terms of (8) as the relevant difference operator.

It is essential to note that the introduction of the difference operator $\mathscr{V}$ implies an increase of permutation symmetry from $\mathscr{S}_2 \times \mathscr{S}_{2N}$, the permutation group of $H_{[2]} + H_{[2N]}$, to $\mathscr{S}_{2N+2}$, the permutation group of H_{tot}. We can, of course, extend the formalism in taking more than two conduction electrons into account, leading to still higher permutation symmetry of the total system. The corresponding contributions are higher-order terms in a cluster expansion and will be neglected here.

We now consider the matrix representation of the total Hamilton operator in the antisymmetrized (spin and orbital) product space of solutions of $H_{[2]}$ and $H_{[2N]}$. These functions are of the form (to simplify the notation, we denote the space and spin variables by the electron labels)

$$\mathscr{A}_{2N+2}\Phi_{\vec{k}}(1,2,\ldots,2N+2) \; , \qquad (9)$$

where $\mathscr{A}_{2N+2}$ is the antisymmetrizer with respect to $2N+2$ electron labels and where $\Phi_{\vec{k}}$ is the product function

$$\begin{aligned} \Phi_{\vec{k}}(1,2,\ldots,2N+2) \\ = \psi_{\vec{k}\uparrow}(1)\psi_{-\vec{k}\downarrow}(2)\phi_0(3,4,\ldots,2N+2) \; . \end{aligned} \qquad (10)$$

We will *first* derive the formal expression for the matrix elements of $\mathscr{V}$ in the basis (9), using the eigenvalue equations (3) and (6), and *then* evaluate this expression *by approximation.* This procedure is similar to the one adopted in standard perturbation theory, where formal expressions are derived assuming that a zeroth-order problem has been solved exactly.

Diagonalization of the matrix for H_{tot} leads to the secular equation

$$\left| \frac{\langle \Phi_{\vec{q}} \,|\, H_{\text{tot}} \,|\, \mathscr{A}_{2N+2}\Phi_{\vec{k}} \rangle - ES_{\vec{q}\,\vec{k}}}{S^{1/2}_{\vec{q}\,\vec{q}}S^{1/2}_{\vec{k}\,\vec{k}}} \right| = 0 \; , \qquad (11)$$

where E is an eigenvalue of the secular problem and $S_{\vec{q}\vec{k}}$ is an element of the overlap matrix, i.e.

$$S_{\vec{q}\vec{k}} = \langle \Phi_{\vec{q}} \,|\, \mathscr{A}_{2N+2} \Phi_{\vec{k}} \rangle \;.$$

With the use of the eigenvalue equations (3) and (6), together with the definition (7) of the difference operator $\mathscr{V}$, the secular equation can be written as

$$\left| \frac{\langle \Phi_{\vec{q}} \,|\, \mathscr{V} \,|\, \mathscr{A}_{2N+2}\Phi_{\vec{k}} \rangle + (2\epsilon_{\vec{q}} + E_0 - E) S_{\vec{q}\vec{k}}}{S^{1/2}_{\vec{q}\vec{q}} S^{1/2}_{\vec{k}\vec{k}}} \right| = 0 \;. \tag{12}$$

In the actual evaluation of the off-diagonal elements, to be discussed in the next section, the core eigenfunction Φ_0 is approximated by a single Slater determinantal wavefunction. The many-electron overlap-matrix elements $S_{\vec{q}\vec{k}}$ ($\vec{q} \neq \vec{k}$) then turn out to be identically zero. We will henceforth not consider the second term.

The off-diagonal elements of the secular determinant describe the scattering of a pair state into other pair states due to the difference operator. Consequently, the matrix elements $V_{\vec{q}\vec{k}}$, occurring in the reduced Hamiltonian of Eq. (1), are given by ($\vec{q} \neq \vec{k}$)

$$V_{\vec{q}\vec{k}} = \frac{\langle \Phi_{\vec{q}} \,|\, \mathscr{V} \,|\, \mathscr{A}_{2N+2}\Phi_{\vec{k}} \rangle}{S^{1/2}_{\vec{q}\vec{q}} S^{1/2}_{\vec{k}\vec{k}}} \;. \tag{13}$$

The diagonal elements of H_{tot} lead to a shift of the self-energy of a pair due to the refined description of the electron-electron interaction. Part of this interaction is included in $H_{[2]}$ and $H_{[2N]}$ as one-body potentials.

It is essential to note that conduction and core eigenfunctions are, in principle, *not* mutually orthogonal, as they are solutions of different eigenvalue equations [Eqs. (3) and (6), respectively].[12] As outlined above, the present approach entails analyzing two systems, which we will call I and II, separately: I is described by the Hamilton operator $H_{[2]}$, Eq. (4), the sum of two one-particle Hamiltonians for the conduction electrons (permutation group $\mathscr{S}_2$). System II is described by the Hamiltonian $H_{[2N]}$, Eq. (5), for the $2N$ core electrons (permutation symmetry $\mathscr{S}_{2N}$). This separation is adapted to the problem: Treating the whole system *directly* (permutation group $\mathscr{S}_{2N+2}$) would also give rise, in the configuration-interaction (i.e., scattering) matrix, to terms which refer to the core electrons *only*. Since we evaluate interactions between the two conduction electrons via the cores, such terms are irrelevant and are avoided in the present approach from the start. Our limitation to the core ground state stems from the fact that an increase of permutation symmetry from $\mathscr{S}_{2N}$ to $\mathscr{S}_{2N+2}$ must have negligible effects (mixing of excited states) for II, compared to the increase from $\mathscr{S}_2$ to $\mathscr{S}_{2N+2}$ for I.

III. APPROXIMATE EVALUATION OF $V_{\vec{q}\vec{k}}$

We can evaluate $V_{\vec{q}\vec{k}}$, Eq. (13), by approximation, replacing the exact total-core eigenfunction ϕ_0 by, e.g., its Hartree-Fock solution ϕ, i.e., the best single Slater determinantal function. The eigenfunctions of the Hartree-Fock operator are then orthogonal Bloch functions $\chi_{\vec{k}}(\vec{r})$. Thus ϕ is written as

$$\begin{aligned} &\phi(3,4,\ldots,2N+2) \\ &\quad = \mathscr{A}_{2N}[\chi_{\vec{k}_1\uparrow}(3)\chi_{k_1\downarrow}(4)\cdots \\ &\qquad \times \chi_{\vec{k}_N\uparrow}(2N+1)\chi_{\vec{k}_N\downarrow}(2N+2)] \;, \end{aligned} \tag{14}$$

describing a filled band.

In view of the short-range character of exchange interactions it is appropriate to transform the core Bloch functions $[\chi_{\vec{k}}(\vec{r})]$ to Wannier orbitals $[W_n(\vec{r})]$ localized at the sites with lattice vectors $(\vec{R}_n)$. The Hartree-Fock function ϕ is invariant under such a unitary transformation, so that we may write

$$\begin{aligned} \phi = \mathscr{A}_{2N}[&W_{1\uparrow}(3)W_{1\downarrow}(4)\cdots \\ &\times W_{N\uparrow}(2N+1)W_{N\downarrow}(2N+2)] \;. \end{aligned} \tag{15}$$

This function gives rise to the following core-electron charge distribution:

$$\rho(\vec{r}) = e \sum_{n=1}^{N} 2\,|\, W_n(\vec{r}) \,|^2 \;.$$

Furthermore, since $\mathscr{A}_{2N} \subset \mathscr{A}_{2N+2}$, the product function $\Phi_{\vec{k}}$ in (10) can be simply written as

$$\begin{aligned} &\Phi_{\vec{k}}(1,2,\ldots,2N+1,2N+2) \\ &\quad = \psi_{\vec{k}\uparrow}(1)\psi_{\vec{k}\downarrow}(2)W_{1\uparrow}(3)W_{1\downarrow}(4)\cdots \\ &\qquad \times W_{N\uparrow}(2N+1)W_{N\downarrow}(2N+2) \;. \end{aligned}$$

For the evaluation of the matrix elements (13) we integrate first over spin variables. The antisymmetrizer $\mathscr{A}_{2N+2}$ then leads to a projector $\mathscr{Q}_{2N+2}$ in orbital space. Since $\mathscr{V}$ does not contain pair interactions between core electrons, and since Wannier orbitals are orthogonal, only a very limited number of permutations contributes to $V_{\vec{q}\vec{k}}$. Specifically, one finds that the projector $\mathscr{Q}_{2N+2}$ reduces to

$$\mathcal{Q}_{2N+2}=\mathrm{I}+\sum_{n=1}^{N}\Bigg[-(p_{1,2n+1}+p_{2,2n+2})+\sum_{m=1}^{N}p_{1,2n+1}p_{2,2m+2}+\sum_{\substack{m=1\\ m\neq n}}^{N}(p_{1,2n+1,2m+1}+p_{2,2n+2,2m+2})$$

$$-\sum_{\substack{m,r\\ r\neq m}}(p_{1,2n+1}p_{2,2m+2,2r+2}+p_{2,2n+2}p_{1,2m+1,2r+1})\Bigg]\equiv\mathrm{I}+\sum_{n=1}^{N}P_n\;. \qquad (16)$$

Here, p denotes the (cyclic) permutation of the indexed electron labels, and I is the identity operator. P_n is the collection of permutations associated with the atomic site n (with lattice vector $\vec{\mathrm{R}}_n$) according to the wave function (15). With the abbreviation

$$s_{\vec{q}n}\equiv\langle\psi_{\vec{q}}\,|\,W_n\rangle$$

for the one-electron overlap integral, one readily arrives at the following expression for the many-electron overlap-matrix elements $S_{\vec{q}\vec{k}}$:

$$S_{\vec{q}\vec{k}}=(1-2N\,|s_{\vec{q}1}|^2)\delta_{\vec{q},\vec{k}}+N^2|s_{\vec{q}1}|^2|s_{\vec{k}1}|^2\delta_{\vec{q}-\vec{k},\vec{G}}\;, \qquad (17)$$

with $\vec{\mathrm{G}}$ an arbitrary vector of the reciprocal lattice, showing that the many-electron functions, for $\vec{q}-\vec{k}$ unequal to any vector of the reciprocal lattice, are orthogonal, verifying the validity of the statement made earlier in the discussion of Eq. (12). For the matrix element $\langle\Phi_{\vec{q}}\,|\,\mathcal{V}\mathcal{Q}_{2N+2}\,|\,\Phi_{\vec{k}}\rangle$ we then obtain

$$\langle\Phi_{\vec{q}}\,|\,\mathcal{V}\mathcal{Q}_{2N+2}\,|\,\Phi_{\vec{k}}\rangle=\langle\Phi_{\vec{q}}\,|\,\mathcal{V}\mathrm{I}\,|\,\Phi_{\vec{k}}\rangle+\sum_{n=1}^{N}\langle\Phi_{\vec{q}}\,|\,\mathcal{V}P_n\,|\,\Phi_{\vec{k}}\rangle$$

$$=e^2\langle\vec{q},-\vec{q}\,||\,\vec{k},-\vec{k}\rangle+N\langle\Phi_{\vec{q}}\,|\,\mathcal{V}P_1\,|\,\Phi_{\vec{k}}\rangle\;, \qquad (18)$$

where

$$\langle\vec{q},-\vec{q}\,||\,\vec{k},-\vec{k}\rangle\equiv\langle\psi_{\vec{q}}(1)\psi_{-\vec{q}}(2)\,|\,g(\,|\vec{r}_1-\vec{r}_2|\,)\,|\,\psi_{\vec{k}}(1)\psi_{-\vec{k}}(2)\rangle\;.$$

Expression (18) clearly identifies the interaction mechanisms incorporated in the model. The first matrix element involves conduction electrons only and represents their direct (screened) Coulomb repulsion. The second term is proportional to the number N of closed shells in the chosen volume of the metal; P_1 interchanges core- and conduction-electron labels. Thus this contribution is totally due to the presence of core electrons; it represents the *indirect*-exchange interaction between conduction electrons via the core electrons.

Most of the interactions and permutations involved in $\mathcal{V}P_1$ cancel out, or else they yield negligible contributions to (18). In order to collect the leading terms we neglect the differential overlap between Wannier functions centered on different sites, i.e., we set $W_1(\vec{r})W_m(\vec{r})=0$ if $m\neq 1$. Furthermore, we neglect matrix elements involving the Coulomb interaction between charge distributions referring to different sites, e.g., we set $\langle\vec{q},-\vec{q}\,||\,1,m\rangle=0$ if $m\neq 1$, since in normal metals the screened Coulomb interaction has a range of less than half the nearest-neighbor distance. With the use of these approximations the matrix element $V_{\vec{q}\vec{k}}$ can be written as

$$V_{\vec{q}\vec{k}}=e^2[\langle\vec{q},-\vec{q}\,||\,\vec{k},-\vec{k}\rangle+2N\,\mathrm{Re}(\langle\vec{q},1\,||\,1,-\vec{k}\rangle s_{-\vec{q}1}s_{1\vec{k}}-\langle\vec{q}1\,||\,11\rangle s_{-\vec{q}1}|s_{1\vec{k}}|^2+\tfrac{1}{2}\langle\vec{q},-\vec{q}\,||\,11\rangle\,|s_{1\vec{k}}|^2$$

$$+\langle\vec{q}1\,||\,\vec{k}1\rangle s_{-\vec{q}1}s_{1,-\vec{k}}-\langle\vec{q}1\,||\,\vec{k},-\vec{k}\rangle s_{-\vec{q}1}$$

$$-\langle\vec{q},-\vec{q}\,||\,1,-\vec{k}\rangle s_{1\vec{k}})](\,|1-N\,|s_{\vec{q}1}|^2|\,|1-N\,|s_{\vec{k}1}|^2|\,)^{-1}\;. \qquad (19)$$

In Eq. (19) Re represents the real part of the expression in the first set of parentheses. The first term in square brackets, i.e., the direct interaction between conduction electrons, is always positive. It depends on the sign and magnitude of the expression inside the parentheses, i.e., the indirect-exchange effect, whether or not $V_{\vec{q}\vec{k}}$ can become negative for $\vec{q}$ and $\vec{k}$ near the Fermi surface. We remark that $V_{\vec{q}\vec{k}}$ is not symmetric in $\vec{q}$ and $\vec{k}$. This "deficiency" is only a formal one; it can easily be remedied without changing the final results, by introducing in (11) the equality

$$H_{\text{tot}}\mathscr{A}_{2N+2}=\tfrac{1}{2}[H_{\text{tot}},\mathscr{A}_{2N+2}]_{+}\ .$$

We further note that the indirect contribution depends sensitively on the overlap; it obviously disappears if all one-electron orbitals should happen to be orthogonal. However, as was mentioned earlier, conduction- and core-electron orbitals are principally not orthogonal in the model, since they are solutions of different eigenvalue equations [Eq. (3) and, in this case, the Hartree-Fock approximation to Eq. (6), respectively].

IV. APPLICATION OF THE MODEL

Apart from the approximations inherent to the Fermi-liquid model, expression (19) for the matrix element $V_{\vec{q}\,\vec{k}}$ is not exact in our model system, since we have replaced the exact solution ϕ_0 for the core electrons by the Hartree-Fock function ϕ. Even then, drastic simplifications are necessary to arrive at numerical results. The first approximation concerns the Wannier function W_1, centered at the site of atom 1, with $\vec{R}_1=0$. Following the model outlined previously, the function W_1 has a nodeless behavior. For computational convenience we choose a Gaussian function (not normalized)

$$W_1(r)=e^{-\alpha r^2/2}\ . \tag{20}$$

The parameter α is a measure for the extension of the charge distribution of the core electrons; it depends on the "size" of the core and on the actual number of core electrons. The second approximation concerns the eigenfunction $\psi_{\vec{k}}(\vec{r})$ for the conduction electrons; this function is of the form $u_{\vec{k}}(\vec{r})e^{i\vec{k}\cdot\vec{r}}$ which we approximate by $u_0e^{i\vec{k}\cdot\vec{r}}$, i.e., neglecting the dependence of $u_{\vec{k}}(\vec{r})$ on the wave vector $\vec{k}$, and we choose a theta function[13] (not normalized),

$$\begin{aligned}\psi_{\vec{k}}(\vec{r})&=(\beta/2\pi)^{3/2}(\Omega/N)\\&\quad\times\sum_j e^{-(1/2)\beta(\vec{r}-\vec{R}_j)^2}e^{i\vec{k}\cdot\vec{r}}\\&=\sum_j e^{-G_j^2/2\beta}e^{i(\vec{G}_j+\vec{k})\cdot\vec{r}}\ ,\end{aligned} \tag{21}$$

where Ω is the volume of the metal containing N atoms, and $\vec{R}_j$ and $\vec{G}_j$ are vectors of the direct and of the reciprocal lattice, respectively.

This form for $\psi_{\vec{k}}(\vec{r})$ allows for the freedom of piling up electron charges on the atomic cores. For $\beta\to0$ we approach a free-wave representation, whereas for $\beta\to\infty$ the orbitals become sharply localized at the lattice vectors ($\vec{R}_j$). The parameter β must be chosen in some relation with the extension of the orbitals for those valence electrons of the atoms treated as conduction electrons in the model (see later).

With the Gaussian functions (20) and (21), well-known formulas can be employed for the evaluation of (19). In keeping within the realm of the approximations adopted we assume that the screened Coulomb potentials also have a Gaussian dependence on the distance r, i.e.,

$$g(r)=e^{-\kappa r^2}/|\vec{r}|\ . \tag{22}$$

The screening constant κ is chosen such that the function $e^{-\kappa r^2}$ and the screening function according to the Thomas-Fermi model have the same magnitude for a value equal to the Thomas-Fermi screening length. This equality leads to

$$\kappa=(4/\pi)(e^2m^*/\hbar^2)k_F\ , \tag{23}$$

where m^* is the effective mass of a conduction electron with wave-vector length k_F.

Using Eqs. (20)–(22), we obtain the following expressions for the overlap integrals and interelectronic matrix elements:

$$\langle\vec{k}\,|\,\vec{k}\rangle=\Omega\sum_j e^{-G_j^2/\beta}\ , \tag{24}$$

$$\langle W_1\,|\,W_1\rangle\equiv\langle1\,|\,1\rangle=\left[\frac{\pi}{\alpha}\right]^{3/2}, \tag{25}$$

$$\langle\vec{k}\,|\,1\rangle=\left[\frac{2\pi}{\alpha}\right]^{3/2}\sum_j\exp\left[-\frac{G_j^2}{2\beta}-\frac{(\vec{G}_j+\vec{k})^2}{2\alpha}\right], \tag{26}$$

$$\langle \vec{k}_1\vec{k}_2||\vec{k}_3\vec{k}_4\rangle = 16\pi^{3/2}\Omega \sum_{i,j,m,n} \exp\left[-\frac{G_i^2+G_j^2+G_m^2+G_n^2}{2\beta}\right]$$

$$\times F(16\kappa, |\vec{G}_i-\vec{G}_j-\vec{G}_m+\vec{G}_n+\vec{k}_1-\vec{k}_2-\vec{k}_3+\vec{k}_4|)$$

$$\times \delta_{\vec{G}_n+\vec{G}_m-\vec{G}_j-\vec{G}_i,\,\vec{k}_1+\vec{k}_2-\vec{k}_3-\vec{k}_4}\,, \qquad (27)$$

$$\langle \vec{k}_1 1||\vec{k}_2 1\rangle = 4\frac{\pi^3}{\alpha^{3/2}} \sum_{i,j} \exp\left[-\frac{G_i^2+G_j^2}{2\beta}-\frac{(\vec{G}_i-\vec{G}_j+\vec{k}_1-\vec{k}_2)^2}{4\alpha}\right]$$

$$\times F(4\kappa, |\vec{G}_i-\vec{G}_j+\vec{k}_1-\vec{k}_2|)\,, \qquad (28)$$

$$\langle \vec{k}_1 1||1\vec{k}_2\rangle = 16\frac{\pi^3}{\alpha^{3/2}} \sum_{i,j} \exp\left[-\frac{G_i^2+G_j^2}{2\beta}-\frac{(\vec{G}_i-\vec{G}_j+\vec{k}_1-\vec{k}_2)^2}{4\alpha}\right]$$

$$\times F(4(\alpha+4\kappa), |\vec{G}_i+\vec{G}_j+\vec{k}_1+\vec{k}_2|)\,, \qquad (29)$$

$$\langle \vec{k}_1 1||11\rangle = 2^{3/2}3^{1/2}\frac{\pi^3}{\alpha^{3/2}} \sum_{j} \exp\left[-\frac{G_j^2}{2\beta}-\frac{(\vec{G}_j+\vec{k})^2}{6\alpha}\right] F(3(\alpha+3\kappa), |\vec{G}_j+\vec{k}|)\,, \qquad (30)$$

$$\langle \vec{k}_1\vec{k}_2||\vec{k}_3 1\rangle = 2^{7/2}\frac{\pi^3}{\alpha^{3/2}} \sum_{i,j,m} \exp\left[-\frac{(G_i^2+G_j^2+G_m^2)}{2\beta}-\frac{(\vec{G}_i+\vec{G}_j-\vec{G}_m+\vec{k}_1+\vec{k}_2-\vec{k}_3)^2}{2\alpha}\right]$$

$$\times F(4\kappa, |\vec{G}_i-\vec{G}_m+\vec{k}_1-\vec{k}_3|)\,, \qquad (31)$$

where the function $F(x,G)$ is given by

$$F(x,G) = \frac{e^{-G^2/x}}{(xG^2)^{1/2}}\frac{2}{\sqrt{\pi}}\int_0^{(G^2/x)^{1/2}} e^{t^2}dt\,. \qquad (32)$$

All matrix elements occurring in expression (19) for $V_{\vec{q}\vec{k}}$ can be obtained from these relations.

V. SOLUTION OF THE GAP EQUATION

The gap function $\Delta_{\vec{q}}$ at zero temperature can be derived from the gap equation[2]

$$\Delta_{\vec{q}} = -\tfrac{1}{2}\sum_{\vec{k}} \frac{V_{\vec{q}\vec{k}}\Delta_{\vec{k}}}{(\epsilon_{\vec{k}}^2+\Delta_{\vec{k}}^2)^{1/2}}\,, \qquad (33)$$

where $\epsilon_{\vec{k}}$ is a one-electron energy with respect to the Fermi level. We remark that in this equation $V_{\vec{q}\vec{k}}$ should include the contributions from *all* relevant scattering processes. In the present approach we limit ourselves to taking into account the indirect exchange via closed shells only. For an isotropic gap function and an isotropic band structure according to

$$\epsilon_k = \frac{\hbar^2k^2}{2m^*} - \epsilon_F\,,$$

Eq. (33) can be cast into the form

$$\Delta_\epsilon = -\tfrac{1}{2}\int_{-\epsilon_c}^{+\epsilon_c} \frac{v_{\epsilon\epsilon'}\Delta_{\epsilon'}}{(\epsilon'^2+\Delta_{\epsilon'}^2)^{1/2}}d\epsilon'\,, \qquad (34)$$

where $\epsilon \equiv \epsilon_q$ and $\epsilon' \equiv \epsilon_k$; ϵ_c is a cutoff energy assumed by Morel and Anderson[14] to be of the order of ϵ_F, whereas $v_{\epsilon\epsilon'}$ is given by

$$v_{\epsilon\epsilon'} = \frac{(2m^*)^{3/2}}{8\pi^2\hbar^3}\Omega(\epsilon'+\epsilon_F)^{1/2}\int_0^\pi V_{\vec{q}\vec{k}}\sin v\, dv\,. \qquad (35)$$

The integration extends over the angle v enclosed by q and k at constant ϵ and ϵ'. The factor in front of the integral is due to (half) the density of states per unit energy and for one spin orientation.

A computer program has been written to calculate $V_{\vec{q}\,\vec{k}}$ for given values of $\vec{q}$, $\vec{k}$, α, β, k_F, and κ (we used thermal effective masses for m^* as listed in Kittel[15]) and for a given lattice type. Subsequently, $v_{\epsilon\epsilon'}$ was obtained by numerical integration according to Eq. (35).

In order to estimate the gap function Δ_ϵ, we illustrate in Fig. 1 a plot of $v_{0\epsilon'}$ vs ϵ', as typically obtained for those metals considered with $v_{00}<0$. The value of $v_{0\epsilon'}$ at $\epsilon'=0$ is denoted by W and corresponds to $-N(0)V$ in the BCS formalism. The tangent on $v_{0\epsilon'}$ at $\epsilon'=0$ intersects the ϵ' axis at δ. Depending on the material, W and δ may have positive or negative values; $|\delta|$ was roughly found at energies between $0.1\epsilon_F$ and ϵ_F.

The gap equation (34) cannot be solved in closed form for Δ_ϵ. Approximate solutions for the gap at the Fermi level Δ_0 are obtained on the basis of the following series expansion of $v_{0\epsilon'}$ around $\epsilon'=0$, truncated to linear terms in ϵ':

$$v_{0\epsilon'} \approx W(1-\epsilon'/\delta) \ . \tag{36}$$

Adopting the usual assumption that, near the Fermi energy, the gap function is independent of ϵ, i.e., $\Delta_\epsilon \approx \Delta_0$, one obtains

$$\Delta_0 \approx -\frac{1}{2}\int_{-\epsilon_c}^{+\epsilon_c} \frac{v_{0\epsilon'}\Delta_0}{(\epsilon'^2+\Delta_0^2)^{1/2}}\,d\epsilon' \ . \tag{37}$$

The integration extends over the energy range where $v_{0\epsilon'}$ is well approximated by Eq. (36), and thus for $\epsilon_c \approx |\delta|$. Regarding the denominator in the integrand, larger values of ϵ' are assumed to give contributions to Δ_0 of minor importance. If $W>0$, Eq. (37) only leads to the trivial solution $\Delta_0=0$, i.e., a superconducting ground state does not exist in this case. For $W<0$, however, one is led to the additional nontrivial solution

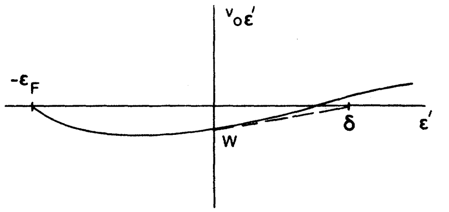

FIG. 1. Typical plot of $v_{0\epsilon'}$ [Eq. (35) with $\epsilon=0$] vs ϵ' as obtained from the numerical calculations with v_{00} $(\equiv W)<0$.

$$\Delta_0 \approx 2\epsilon_c \exp(1/W) \ . \tag{38}$$

With the substitution $\epsilon_c \approx |\delta|$ (see above), the order-of-magnitude estimate for the gap at the Fermi level becomes

$$\Delta_0 \approx 2|\delta|\exp(1/W), \quad W<0 \tag{39}$$

i.e., of the same form as the BCS expression. The critical temperature T_c can then be obtained from the well-known relation $\Delta_0=1.76k_BT_c$.

VI. MODEL CALCULATIONS

We present the following:

(1) We will first analyze the *general* behavior of the parameter W with respect to the orbital parameters α and β in the electron functions used. *If* the mechanism proposed in this paper for an indirect coupling between two conduction electrons is at all feasible, positive *and* negative values for the quantity W should arise. Furthermore, critical temperatures for superconductivity, predicted from the (negative) values of W, should be of the order of magnitude observed for superconducting metals.

Concerning the *sign* of W, we concentrate on $W(\alpha,\beta)=0$. As numerical input data for a specific calculation we choose first the bcc lattice and the *atomic density* of cesium together with two different values for the screening constant κ. The first value, $\kappa_1=0.62$ a.u.$^{-2}$ ($=2.18$ Å^{-2}), is obtained from Eq. (23) for cesium, whereas a second value $\kappa_2=0.40$ a.u.$^{-2}$ ($=1.43$ Å^{-2}) is chosen in order to investigate the dependence of the results on κ. In Fig. 2 plots *a* and *b*, corresponding with $W(\alpha,\beta)=0$, are given for a one- and two-conduction-electron system, respectively. Inside the curves the parameter W is negative; the dashed curves represent the influence of changing κ from 0.62 to 0.40 a.u.$^{-2}$.

Figure 2 shows that, at least for a definite area (α,β), negative values for W are obtained. Subsequent calculations, but now keeping the atomic density constant in the fcc and hcp lattice structures (with $c/a=1.7$ an average value for Mg and Zn), lead to very similar $W(\alpha,\beta)=0$ plots (Figs. 3 and 4). A variation in the value of κ slightly changes the negative regions. On the other hand, the increase of the length k_F of the Fermi vector in going from one- to two-conduction-electron systems results in a considerable decrease of these areas. In order to illustrate these plots with some numerical data we list in Tables I and II the results of the calculations in the bcc, fcc, and hcp structures with $\kappa=0.62$ a.u.$^{-2}$ and with $m^*=m$, for the one- and

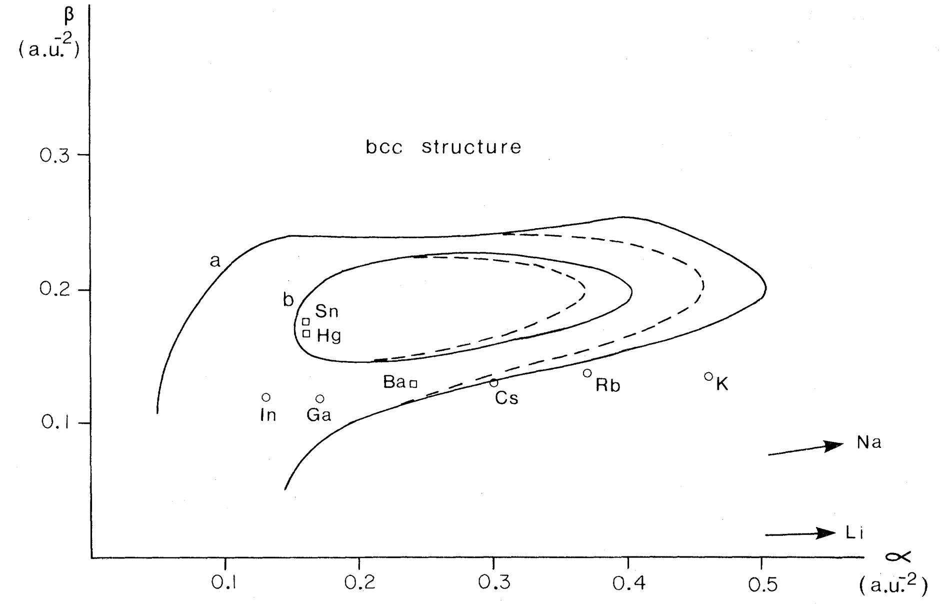

FIG. 2. Plots for $W(\alpha,\beta)=0$ for a one-conduction-electron system (outer curves a, $k_F=0.341$) and a two-conduction-electron system (inner curves b, $k_F=0.429$) in the bcc structure. The solid curves apply for a screening constant $\kappa=0.62$ a.u.$^{-2}$, the dashed curves apply for $\kappa=0.40$ a.u.$^{-2}$ W values inside the curves are negative; outside the curves they are positive. The sign ○ refers to one-conduction-electron systems, the sign □ refers to two-conduction-electron systems. The metals Hg, Ga, In, and Sn are also included, although they do not possess the bcc structure.

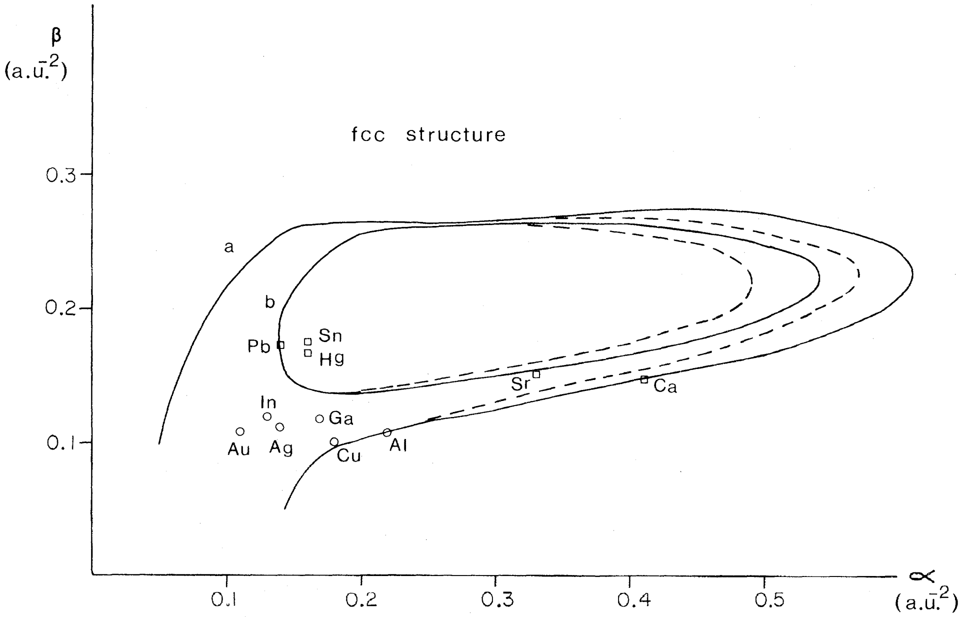

FIG. 3. Same as Fig. 2, but now for a fcc lattice. The metals Hg, Ga, In, and Sn are also included, although they do not possess the fcc structure.

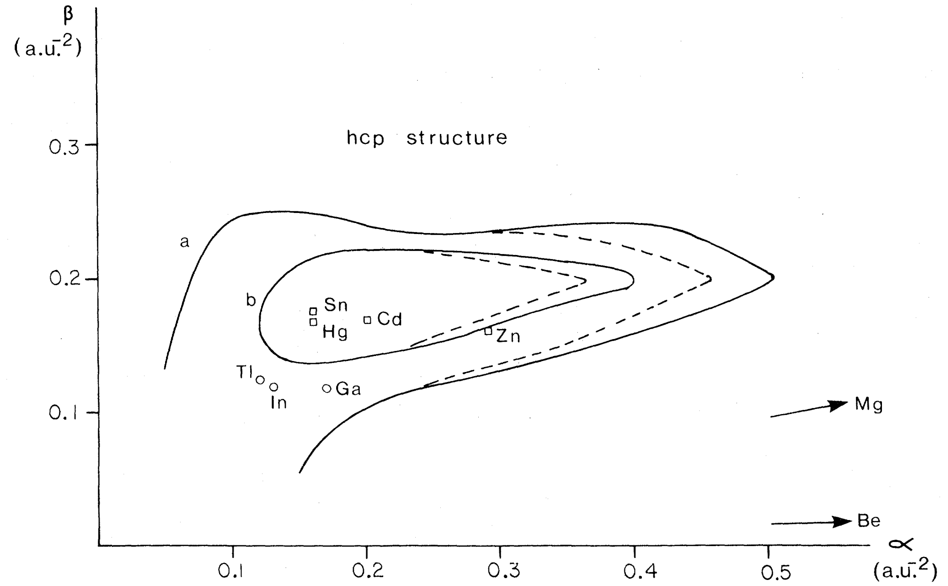

FIG. 4. Same as Fig. 2, but now for a hcp lattice ($c/a=1.7$). The metals Hg, Ga, In, and Sn are also included, although they do not possess the hcp structure.

two-conduction-electron systems, respectively. The order of magnitude of the resulting critical temperatures will be discussed later.

(2) In the next step of our model calculations, i.e., application of the model to various metal groups in the Periodic Table, one is faced, for each metal, with the task of consistently determining the parameters α and β, associated with the core (Gaussian) and theta functions, respectively. We shall consider the IA metals (alkalis), the IIA metals (earth-alkalis), the (monovalent) IB metals Cu, Ag, and Au, and the (divalent) IIB metals Zn, Cd, and Hg. To also incorporate into the present approach the IIIA metals (Al,Ga,In,Tl) and the IVA metals (Sn,Pb), we assume these metals to behave effectively as monovalent and divalent, respectively; i.e., only the outer p electrons are treated as conduction electrons. In all cases, the cores form closed-shell systems. As a consequence only s-type conduction bands can occur in the model.

Furthermore, in analogy with standard analyses of the superexchange mechanism, only electrons in the *outer part* of the ion core are supposed to contribute to the indirect interaction. As a specific choice the electrons in the outermost sp (IA,IIA) and d (IB,IIB) shells are taken into account for the evaluation of the core parameter α in the model. In the IIIA and IVA metals the outer ns electrons are contracted with the d core. For the *qualitative* aspects of the results the precise definition of the core system is not of primary importance.

Consider now a pair of conduction electrons and one core. Using Herman-Skillman calculations[16] for the expectation values of r^2, in neutral atoms, we relate the parameters α and β as follows (i and j denote different metals):

$$\alpha_i/\alpha_j=\sum_{\text{core } j}\langle r^2\rangle \Big/ \sum_{\text{core } i}\langle r^2\rangle ,$$

and, for each metal,

$$\gamma\equiv\beta/\alpha=\left[\sum_{\text{core}}\langle r^2\rangle/2\right]\Big/\left[\sum_{\text{cond}}\langle r^2\rangle/z\right], \tag{40'}$$

noting that α and β are inversely proportional to $\langle r^2\rangle$. The quantities $\sum_{\text{core}}\langle r^2\rangle$ and $\sum_{\text{cond}}\langle r^2\rangle$ represent the contributions of the core electrons and of the outer valence electron(s) to the total $\langle r^2\rangle$ value of the atom, respectively. The factors 2 and z in (40′) reflect the occupation number of the core functions and the number of conduction electrons per atom, respectively. This procedure of relating the parameters α and β for all metals leaves us with *only one* parameter to be determined.

As a last step in the determination of α and β we correlate these parameters with earlier work on indirect-exchange interactions. In an analysis of 180° superexchange in a number of ionic solids, on the basis of a three-center four-electron model and

TABLE I. (a) Values for the parameter W, times 10^3, for a one-conduction-electron system in the body-centered cubic (bcc) structure, as a function of the Gaussian core parameter α and the parameter β in the theta function for the conduction electron. The atomic density is taken equal to that of metallic Cesium (at 5 K and atmospheric pressure). a_{bcc} is the lattice parameter, k_F is the length of the Fermi wave vector, and κ is the screening constant; bcc structure, $\rho_{AT}=0.001\,34$ a.u.$^{-3}$ (Cs), $a_{\mathrm{bcc}}=11.427$ a.u. (Cs), $k_F=0.341$ a.u.$^{-1}$, $\kappa=0.62$ a.u.$^{-2}$ (Cs). (b) Same as (a), but now for a one-conduction-electron system in the face-centered cubic (fcc) structure and $a_{\mathrm{fcc}}=14.397$ a.u. (c) Same as (a) but now for a one-conduction-electron system in the hexagonal close-packed (hcp) structure ($c/a=1.7$) and $a_{\mathrm{hcp}}=10.046$ a.u. and $c_{\mathrm{hcp}}=17.078$ a.u.

α (a.u.$^{-2}$) \ β (a.u.$^{-2}$)	0.05	0.10	0.15	0.20	0.25	0.30
			(a)			
0.05	-80	-26	186	405	546	639
0.10	-231	-377	-419	-90	220	426
0.15	12	-106	-361	-301	80	433
0.20	98	16	-209	-277	110	627
0.25	130	68	-118	-227	110	721
0.30	145	94	-60	-183	62	630
0.35	153	110	-19	-137	26	480
0.40	157	121	13	-90	-18	365
0.45	160	129	40	-44	33	299
0.50	162	135	62	-2	61	271
0.55	163	140	82	35	92	266
0.60	164	144	96	70	125	273
			(b)			
0.05	-54	-1	204	433	589	692
0.10	-207	-339	-401	-125	176	389
0.15	17	-97	-372	-418	-94	261
0.20	99	20	-226	-424	-148	359
0.25	131	70	-136	-370	-160	459
0.30	146	96	-79	-312	-189	403
0.35	153	111	-37	-251	-201	277
0.40	158	122	-4	-190	-182	168
0.45	160	126	25	-132	-141	117
0.50	162	135	48	-79	-90	107
0.55	163	140	69	-32	-37	121
0.60	164	144	87	11	14	148
			(c)			
0.05	-60	-88	36	272	450	570
0.10	-213	-448	-669	-331	62	321
0.15	16	-121	-418	-385	8	376
0.20	99	13	-214	-285	92	594
0.25	132	68	-114	-217	112	705
0.30	146	95	-56	-172	71	631
0.35	153	111	-15	-130	32	489
0.40	158	122	17	-86	21	372
0.45	160	130	43	-44	33	303
0.50	162	136	65	-4	58	271
0.55	163	141	84	34	88	264
0.60	164	145	100	67	120	270

TABLE II. (a) Values for the parameter W, times 10^3, for a two-conduction-electron system in the body-centered cubic (bcc) structure, as a function of the Gaussian core parameter α and the parameter β in the theta function for the conduction electrons. The atomic density is taken equal to that of metallic cesium. a_{bcc} is the lattice parameter, k_F is the length of the Fermi wave vector, and κ is the screening constant. bcc structure; $\rho_{AT}=0.00134$ a.u.$^{-3}$ (Cs), $a_{\mathrm{bcc}}=11.427$ a.u. (Cs), $k_F=0.429$ a.u.$^{-1}$, $\kappa=0.62$ a.u.$^{-2}$ (Cs). (b) Same as (a), but now for a two-conduction-electron system in the face-centered cubic (fcc) structure and $a_{\mathrm{fcc}}=14.397$ a.u. (c) Same as (a) but now for a two-conduction-electron system in the hexagonal close-packed (hcp) structure ($c/a=1.7$) and $a_{\mathrm{hcp}}=10.046$ a.u. and $c_{\mathrm{hcp}}=17.078$ a.u.

α (a.u.$^{-2}$) \ β (a.u.$^{-2}$)	0.05	0.10	0.15	0.20	0.25	0.30
			(a)			
0.05	192	207	339	545	710	826
0.10	158	129	142	275	444	593
0.15	158	105	12	38	214	431
0.20	170	115	−11	−49	129	418
0.25	180	129	1	−64	107	441
0.30	187	140	21	−54	95	431
0.35	191	150	43	−31	90	394
0.40	194	158	65	−3	96	358
0.45	196	164	86	29	112	337
0.50	198	169	105	62	137	330
0.55	199	174	122	94	165	335
0.60	199	178	138	125	195	348
			(b)			
0.05	193	208	340	564	752	886
0.10	160	133	128	242	411	570
0.15	159	108	−8	−38	104	319
0.20	171	117	−31	−147	−35	241
0.25	181	130	−18	−167	−79	240
0.30	187	142	4	−154	−92	232
0.35	192	151	26	−126	−89	205
0.40	194	158	48	−90	−70	180
0.45	196	165	70	−51	−39	171
0.50	198	170	90	−11	1	178
0.55	199	174	108	29	44	198
0.60	200	178	125	66	88	226
			(c)			
0.05	191	177	254	433	601	729
0.10	158	97	36	124	298	469
0.15	158	91	−35	−37	139	368
0.20	170	110	−25	−72	105	395
0.25	180	128	−1	−67	104	436
0.30	187	141	23	−51	100	435
0.35	191	151	46	−28	95	402
0.40	194	159	68	0	99	365
0.45	196	165	88	31	113	342
0.50	198	171	106	62	136	332
0.55	199	175	124	93	163	335
0.60	200	179	139	123	192	347

using 1s-type *Slater* functions $\lambda^{3/2}\pi^{-1/2}\exp(-\lambda r)$, De Jongh and Block[17] found excellent agreement with experiments for $\lambda(F^-)=1.11$ a.u.$^{-1}$ (=2.10 Å^{-1}), the orbital parameter of the doubly occupied function representing the core of the fluorine ion. Although in these calculations perturbation theory was employed we adopt this numerical result in the present paper in order to estimate *all* parameters α and β simultaneously.

Imposing the simple condition[18]

$$\langle r\rangle_{(1s\ \text{Gaussian})}\equiv\langle r\rangle_{(1s\ \text{Slater})} \tag{41}$$

we find as the corresponding core parameter for F$^-$ on the basis of a 1s Gauss function

$$\alpha=\left[\frac{4}{3\sqrt{\pi}}\right]^2(1.11)^2\approx 0.70\ \text{a.u.}^{-2}\ .$$

Then, comparing the diamagnetic suceptibilities χ of F$^-$ and of the cesium core, all parameters α and β are determined through the additional relation

$$\alpha(\text{F}^-)/\alpha(\text{Cs})=\chi_{\text{core}}(\text{Cs})/\chi(\text{F}^-)\ . \tag{42}$$

This relation arises because susceptibilities are proportional to expectation values of r^2, and thus inversely proportional to the core parameters. From earlier work[19] we take the value $\chi(\text{F}^-)\approx-12\times10^{-6}$ emu/g atom. The value for cesium is calculated as the ratio of the contribution of the core (34.4 a.u.^{2}) to the total expectation value of r^2 (88.4 a.u.^{2}), times the value of the (total) susceptibility of cesium (-77.5×10^{-6} emu/g atom) listed in Ref. 20. From relation (42) we then obtain $\alpha(\text{Cs})\approx0.30$ a.u.$^{-2}$.

(3) With the values of the Gaussian orbital parameters determined above we can now carry out the calculations for the various metals considered. In order to present the computational results in a general picture, independent of the actual lattice parameters, all lattice structures have been expanded (isotropically) such that the *atomic densities* are equal to that of cesium. This type of scaling on the cesium density leads, for each metal, to a (one-dimensional) scale factor $s=[\rho/\rho(\text{Cs})]^{1/3}$. In scaling terms (keeping the products αr^2, βr^2, κr^2, and $i\vec{k}\cdot\vec{r}$ invariant) the parameters α, β, and κ are changed proportionally with s^{-2}, whereas the scaled Fermi lengths of common-valent metals coincide with $k_F(\text{Cs})$ and $(2)^{1/3}k_F(\text{Cs})$, in the one- and two-conduction-electron systems, respectively. Using these scaled parameters, i.e., $\tilde{\alpha}=\alpha s^{-2}$, $\tilde{\beta}=\beta s^{-2}$, $\tilde{\kappa}=\kappa s^{-2}$, $\tilde{k}_F=k_F(\text{Cs})$, or $2^{1/3}k_F(\text{Cs})$, one readily verifies that the corresponding value of the scaled parameter $\tilde{W}$ is related to the original value W as $\tilde{W}=sW$. Neglecting the relatively small influence of κ on the general $W=0$ plots (Figs. 2–4, dashed curves), we thus conclude that the *scaled* calculations already reflect the sign of the *nonscaled* calculations of W.

In Table III we list the various quantities mentioned in the text which have been utilized in the determination of the parameters α and γ [with $\alpha(F^-)=0.70$ a.u.$^{-2}$]. Furthermore, the atomic densities, scale factors s and the scaled values $\tilde{\alpha}$ and $\tilde{\kappa}$ are reported. In Figs. 2–4, the points with coordinates $(\tilde{\alpha},\tilde{\beta})$ of each metal are plotted in the corresponding lattice structure.

(4) In considering Figs. 2, 3, and 4 (bcc, fcc, and hcp lattices, respectively) we make the following observations:

(a) The fcc lattice has the most extensive negative-W domain, both for one- and two-conduction-electron systems. The plots for the bcc and hcp lattices are very similar.

(b) Two-conduction-electron systems have the smaller α,β domain of negative W. This fact is directly related to the larger k_F: The overlap integral between the conduction-electron wave function with $k\approx k_F$ and the core function decreases with increasing k_F [see Eq. (26)].

(c) Decreasing the screening (lowering κ), i.e., going from the solid to the dashed curves in the figures, reduces the negative-$W(\alpha,\beta)$ region. At the same time, the W values are found to become more extreme, i.e., negative values are more negative, positive values more positive, than for $\kappa=0.62$ a.u.$^{-2}$.

(d) Increasing β at constant α, i.e., increasing the localized component of the conduction-electron wave function, favors negative values of W, which is to be expected.

(e) Increasing α at constant β, i.e., reducing the core, disfavors negative values of W for similar reasons.

(f) The fact that different plots are obtained for different lattices, at the *same* atomic density and in a *one*-core approximation [see text preceding Eq. (19)], arises from the fact that in the expression (19) for $V_{\vec{q}\,\vec{k}}$ summations occur over vectors of the reciprocal lattices, these being different for the three structures.

We will now make a number of comments regarding the metals considered in their respective crystal structures. It is to be noted that the lattice parameters (and thus the atomic densities) mostly refer to room-temperature values. In addition, Hg (rhombohedral), Ga (complex), In (tetragonal), and Sn (diamond structure) fall outside the scope of

TABLE III. Values for the various quantities occurring in the text. γ is the ratio β/α [Eq. (40′)], $\alpha/\alpha(\mathrm{Cs})$ is the ratio according to Eq. (40), ρ is the atomic density, s is the scale factor equal to $[\rho/\rho(\mathrm{Cs})]^{1/3}$, κ is the screening constant [Eq. (23), including effective masses]. The last two columns list the scaled screening constants and core parameters [with $\alpha(\mathrm{Cs})=0.3$], respectively. Atomic units are used throughout.

	Lattice	$\sum_{\text{core}}\langle r^2\rangle$	$\sum_{\text{cond}}\langle r^2\rangle$	γ	$\alpha/\alpha(\mathrm{Cs})$	$\rho\times 10^5$	s	κ	$\tilde{\kappa}$	$\tilde{\alpha}$ $\alpha(\mathrm{Cs})=0.3$
Li	bcc	0.85	16.7	0.03	40.5	696	1.73	1.64	0.55	4.05
Na	bcc	5.9	19.2	0.15	5.83	393	1.43	0.78	0.38	0.85
K	bcc	16.8	28.6	0.29	2.05	208	1.16	0.63	0.47	0.46
Rb	bcc	23.6	32.2	0.37	1.46	170	1.08	0.59	0.51	0.37
Cs	bcc	34.4	39.6	0.43	1.00	134	1.00	0.62	0.62	0.30
Be	hcp	0.45	16.6	0.03	76.4	1791	2.37	0.44	0.08	4.07
Mg	hcp	4.4	23.3	0.19	7.82	638	1.68	1.20	0.42	0.83
Ca	fcc	13.5	37.0	0.36	2.55	341	1.37	1.42	0.76	0.41
Sr	fcc	19.8	43.5	0.46	1.74	264	1.25	1.37	0.87	0.33
Ba	bcc	29.6	54.7	0.54	1.16	234	1.20	0.93	0.63	0.24
Cu	fcc	12.6	11.3	0.56	2.73	1259	2.11	1.26	0.28	0.18
Ag	fcc	21.2	13.3	0.80	1.62	866	1.86	0.81	0.23	0.14
Au	fcc	26.4	13.4	0.99	1.30	872	1.87	0.93	0.27	0.11
Zn	hcp	9.4	17.1	0.55	3.66	975	1.94	0.90	0.24	0.29
Cd	hcp	17.5	20.8	0.84	1.97	685	1.72	0.69	0.23	0.20
Hg	Rhomb.	22.6	21.6	1.05	1.52	631	1.68	1.72	0.61	0.16
Al	fcc	14.1	14.5	0.49	2.44	890	1.88	1.21	0.34	0.22
Ga	Complex	19.8	14.2	0.70	1.74	755	1.78	0.45	0.14	0.17
In	Tetrag.	30.6	16.6	0.92	1.12	566	1.62	0.96	0.37	0.13
Tl	hcp	36.5	17.6	1.04	0.94	518	1.57	0.78	0.32	0.12
Sn	Diam.	25.9	23.7	1.09	1.33	536	1.59	1.09	0.43	0.16
Pb	fcc	31.8	25.9	1.23	1.08	488	1.54	1.66	0.70	0.14

structures considered. We have included these metals in the figures for all three configurations.

A. Metals with the bcc structure: The alkali metals and Ba

The scaled screening parameters $\tilde{\kappa}$ are 0.55 for Li; 0.38 for Na; 0.47 for K; 0.51 for Rb; 0.62 for Cs; 0.63 for Ba. Metallic lithium, sodium, and potassium are definitely outside the $W(\alpha,\beta)=0$ curves and thus are not superconducting according to the model, and according to experiment. Metallic rubidium lies outside the curve for $\kappa_1=0.62$ a.u.$^{-2}$, thus definitely in the positive-W region for its own $\tilde{k}$ value of 0.51. Metallic cesium falls almost precisely on the $W=0$ curve. It is found experimentally[21] to become superconducting under high pressures. Although the phenomena involved are apparently quite complex (phase transitions), a simple explanation in terms of the present model would be that increased pressure increases β, and thus moves the point for Cs vertically into the negative-W region. It has indeed been shown in the literature that at high pressures the 6s valence electron of Cs goes over into the more inner atomic 5d state,[22] which produces in the model the increase of β desired. The same phenomenon has been suggested to occur with Ba under high pressures,[23] which is consistent with the results obtained on the basis of the model (see Fig. 2). The high-pressure phase for barium (Ba II) has been identified[24] as hcp; Figure 4 indicates that on this basis *alone* Ba could not become a superconductor.

B. Metals with the fcc structure: Ca,Sr,Cu,Ag,Au,Al,Pb

The scaled screening parameters $\tilde{\kappa}$ are 0.76 for Ca; 0.87 for Sr; 0.28 for Cu I; 0.23 for Ag; 0.27 for Au; 0.34 for Al; and 0.70 for Pb. Calcium lies definitely outside the $W<0$ region, whereas strontium lies practically on the $W=0$ lines for $\kappa_1=0.62$ a.u.$^{-2}$ and $\kappa_2=0.40$ a.u.$^{-2}$, and even slightly inside for its own $\tilde{\kappa}$ value of 0.87. Aluminum, treated as a one-conduction-electron system, is found to lie just on the edge of the negative-W domain. In fact, extensive pseudopotential calculations by Carbotte and Dynes[25] show good agreement with the experimental critical temperature (1.2 K) on the basis of the BCS phonon-mediated coupling mechanism. The same applies to Pb, for which metal Carbotte and Dynes[25] again found good agreement with experimental values. It is to be noted that, both for Al and Pb, a change in κ has a negligible effect on W (Fig. 3).

C. Metals with the hcp structure: Be,Mg,Zn,Cd,Tl

The scaled screening parameters $\tilde{\kappa}$ are 0.08 for Be; 0.42 for Mg; 0.24 for Zn; 0.23 for Cd; and 0.32 for Tl. Of these metals Be is found to lie far outside the $W=0$ curves, although experimentally[26] it is (very weakly) superconducting. Also, the point for Mg lies outside the $W<0$ domain, whereas Zn (barely), Cd, and Tl are inside. These metals are thus superconducting according to the model, in agreement with experiment.

The points for Hg (rhombohedral), Ga (complex), In (tetragonal), and Sn (diamond structure) lie well inside the $W<0$ domain in all three structures (Figs. 2–4). We thus expect these metals to be superconducting also in their own structure.

The sensitivity of the results with respect to the α value for Cs can, in the figures, be easily investigated at constant γ by changing the distances from the origin for the metals considered by the percentage increase or decrease of that of Cs (all ratios γ remaining constant). It should also be emphasized that the distance from a point to the $W=0$ curve(s) is not a measure of the *magnitude* of $|W|$; Figures 2–4 just give information on the *sign* of W (see also Tables I and II). The only statement we can make is that points close to the $W=0$ curves have $W\approx 0$.

In spite of the fact that it is difficult to attempt drawing quantitative conclusions from Tables I and II, due to the extreme sensitivity of T_c with respect to W, the following observations are significant [note that, in calculating W occurring in the equation for the *critical temperature,* the tabulated W values must, for each metal, be divided by the scaling parameter s and multiplied by m^*/m; see Eq. (35)]:

(i) Metallic cesium: $\alpha=0.30$ a.u.$^{-2}$, $\beta=0.13$ a.u.$^{-2}$, $m^*/m=1.43$, $s=1$. From linear extrapolation of the data given in Table I(a) we obtain $\tilde{W}=W\approx 1.5\times 10^{-3}$, i.e., $(m^*/m)W\approx 2\times 10^{-3}$, thus positive. For $|\delta|=1$ eV and a transition temperature $T_c=5$ K we obtain $W\approx -0.09$, which implies $\beta\approx 0.16$ a.u.$^{-2}$. Thus a 25% increase of β due to a high-pressure transition $6s\rightarrow 5d$ is sufficient to render cesium superconducting.

(ii) From the tables we infer that $1<|\Delta W/\Delta\beta|<10$ at $W\approx 0$ covers both one- and two-conduction-electron systems. Then, with $T_c=(\text{const})e^{1/W}$ we have

$$|\Delta T_c/T_c| = |(1/W^2)\Delta W/\Delta\beta| \ |\Delta\beta| ,$$

the constant amounting to 13 200 K for $|\delta|=1$ eV. For example, if $W\approx -0.1$, then $T_c\approx 0.5$ K and $50<|\Delta T_c/\Delta\beta|<500$, in the units considered, implying that, with $\Delta\beta=0.01$ a.u.$^{-2}$, $0.5<\Delta T_c<5$ K, illustrating the very steep dependence of T_c on β.

(iii) Except for the fcc lattice, the calculated values for $|W|$ of two-conduction-electron systems inside the $W<0$ region are, in comparison, low, as can be seen, e.g., from Table II(c) (hcp). A minimum, $W\approx -0.1$, is found for $\alpha\approx 0.20$ and $\beta\approx 0.18$.

For cadmium, with $\tilde{\alpha}=0.20$, $\tilde{\beta}=0.17$, $\tilde{\kappa}=0.23$, $s=1.72$, $m^*/m=0.73$, and $T_c(\text{expt})\approx 0.6$ K, a value of $\tilde{W}=-0.23$ ($|\delta|=1$ eV) should be obtained. In this context, it should be noted that the screening parameter $\tilde{\kappa}$ for Cd is very low. We know that negative values of W become more negative inside the $W<0$ domain upon decreasing the screening. For $\kappa=0.4$, the minimum value of W is likely to amount to -0.12; a calculation with a screening parameter of 0.23 would lead to a still more negative value of W.

(iv) Metallic mercury: $\tilde{\alpha}=0.16$, $\tilde{\beta}=0.17$, $m^*/m=1.88$, $s=1.68$, and $\tilde{\kappa}=0.61$. By linear extrapolation from Table II(b) we find $\tilde{W}\approx -33\times 10^{-3}$. A critical temperature of 1 K is obtained for $\tilde{W}=-94\times 10^{-3}$ ($|\delta|=1$ eV), whereas $T_c=$ 4K for $\tilde{W}=-110\times 10^{-3}$. The values $\tilde{\alpha}=0.20$ and $\tilde{\beta}=0.20$ already yield $\tilde{W}=-147\times 10^{-3}$ [$T_c=29$ K; $T_c(\text{expt})=4.2$ K].

VII. CONCLUDING REMARKS

In conclusion we note the following:

(1) In spite of the phenomenal success of the BCS

theory in explaining a broad spectrum of properties of superconductors, doubts have arisen over the years, particularly since about 1975, as to whether the phonon-mediated coupling mechanism between conduction electrons can be the only or, in a number of cases, even the principal source of superconductivity. Observed properties of a number of metals and alloys (anomalous conduction-electron spin resonance, nuclear magnetic resonance, magnetization, and other phenomena) have led to the suggestion that itinerant-electron antiferromagnetism might in those metals be the source of Cooper-pair formation.[27–29] The same mechanism has also been suggested on a theoretical basis.[30]

We emphasize once more that the indirect-exchange coupling proposed in the present paper, leading to itinerant-electron antiferromagnetism, is postulated as one mechanism through which superconductivity can arise. As mentioned earlier extensive calculations by Carbotte and Dynes[25] on Pb and Al, using pseudopotential methods, have shown that in these metals the indirect (nonexchange) interaction between conduction electrons via lattice vibrations is most likely the dominant mechanism for superconductivity. Looking back at the results of Fig. 2, where it is seen that Pb and Al are *just on the edge* of the area where $W<0$, we conclude that the phonon-mediated coupling may indeed play the dominant role in these metals.

(2) A necessary condition for the occurrence of superconductivity is that the interaction between conduction electrons be attractive with respect to a (supposedly any) one-electron description; this in turn requires, in the superexchange formalism considered in the present paper, that the wave functions for these electrons be of a sufficiently atomic type near the cores. A measure for this degree of localization is, in the model, given by the parameter $\gamma=\beta/\alpha$, where β is the theta-function parameter for the conduction electrons and where α is the Gaussian parameter characterizing the core electrons. For $\beta\rightarrow 0$ the conduction-electron wave functions become plane waves, and $\gamma\rightarrow 0$. As a result the net interaction between the conduction electrons is repulsive, i.e., pair formation cannot occur (see also Figs. 2–4). As γ increases the conduction-electron wave functions become more and more atomic near the cores; this is the case going from top to bottom in the Periodic Table for all the metals considered (see Table III). Experiments show that only the heaviest metals in the columns I*A* and II*A* (with the exception of Be) become superconducting under high pressure (Cs and Ba). Previous attempts[31–33] to explain such regularities have not been strikingly successful.

(3) Similar "atomic" characteristics of superconductivity have, on an empirical basis, been proposed by Gambino and Seiden.[34] They consider a quantity E_1, the difference in energy between the ground state of an atom and its first excited state, as the dominant parameter. They then connect E_1 (linearly) with "the repulsion a conduction-electron experiences when it enters the core region." A large value of E_1 implies that the electron is kept away from the core. It then can interact only weakly with the core; from such a relationship these authors deduce an empirical electron-core pseudopotential. There is clearly a relation between our model parameter γ and E_1: If γ is small, then E_1 must be large, and the converse is also true. Thus although the mechanisms leading to pairing are very different in the two cases (γ: superexchange; E_1: electron-phonon interactions), qualitative conclusions regarding correlations with other physical quantities considered by Gambino and Seiden (cohesive energy, melting temperature, Debye temperature, thermal expansion) are the same.

(4) A more complete theory involving the present indirect-exchange mechanism as well as lattice vibrations will be attempted in a planned future publication. It is to be noted that in such an analysis the indirect interaction via phonons is not just a component to be added to the indirect-exchange mechanism since the total wave function must always be antisymmetrized including the core electrons.

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[12] It is always possible to expand any core eigenfunction $\tilde{\phi}$ of the Hamiltonian (5) in terms of a linear combination of antisymmetrized products from the complete (orthonormal) set $\{\psi_{\vec{k}}\}$ obtained by solving the eigenvalue equation (3) for $H_{[1]}$. Then, in the spin and orbital product space of solutions of $H_{[1]}$ and $H_{[2N]}$, we have, in principle, e.g.,

$$\int \psi^*_{\vec{k}}(3)\tilde{\phi}(3,\ldots,2N+2)\,d\tau_3 \neq 0\ ,$$

i.e., $\psi_{\vec{k}}$ will generally occur, in the expansion of $\tilde{\phi}$, with a nonzero coefficient.

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