

Spin-phonon interaction as possible necessity for superconductivity

E. Krüger

*Institut für Physik, Max-Planck-Institut für Metallforschung, Heisenbergstrasse 1, Postfach 800668,
D-7000 Stuttgart 80 (Büsnau), Germany*

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Within the framework of a generalized Heisenberg model, it is shown that under certain conditions the electron spins may couple to phonons by exchange interaction. This process, going beyond the Born-Oppenheimer approximation, is possibly necessary for superconductivity. From such a supposition, criteria for superconductivity are derived which prove to be true for 18 cubic-symmetry metals investigated recently.

I. INTRODUCTION

The generally accepted theory of superconductivity of metals is based upon an interaction between conduction electrons and phonons in the crystal.^{1,2} On the other hand, it has been argued by Matthias³ that superconductivity in transition metals is due to an electron-electron interaction. Schmidt *et al.*⁴ found that superexchange interactions possibly mediate pair formation in a great number of metals. In a more chemical approach to superconductivity by Krebs,⁵ and more recently by Johnson and Messmer,⁶ correlations were found between the occurrence of superconductivity and the existence of certain molecular orbitals at the Fermi energy, where Johnson and Messmer call superconductivity "delocalized conduction-electron antiferromagnetism." An experimental hint that there is a correlation between superconductivity and exchange interaction in *A15* superconductors was given by Ekbotte *et al.*⁷ These authors argue for the possibility that the electrons responsible for superconductivity are "bound through exchange interactions of antiferromagnetic type."

In discussions of this problem, exchange interactions and electron-phonon interaction are usually treated as alternative phenomena being responsible for superconductivity. In the present paper, it is argued that *both* types of interaction are necessary for a pairing of the electrons: On the one hand, the pairing is effected by an electron-electron exchange interaction \mathcal{W} which is strongly spin-dependent whereas, on the other hand, this interaction \mathcal{W} is mediated by spin-phonon exchange interaction. In the framework of our considerations, the superconducting state can therefore be described in terms of spin-dependent (or "magnetic") exchange interactions as well as by the Bardeen-Cooper-Schrieffer (BCS) theory² and its extensions. The spin dependence of \mathcal{W} is required to answer the question of which materials are superconductors and which are not.

The spin-phonon exchange interaction cannot be handled in the framework of the adiabatic or Born-Oppenheimer approximation. It will be described in terms of nonadiabatic localized functions depending on the electron coordinates as well as on coordinates characterizing the motion of the nucleus. The electrons of the

considered conduction band will be assumed to move in the potential of nuclei which are connected by springs realized by the core electrons and by the conduction electrons of the other partly filled bands. This, however, does not mean that the further influence of these remaining electrons is disregarded: The symmetry properties and the spin dependence of the localized functions belonging to the considered conduction band are largely determined by the fact that the localized states must be orthogonal to each other, to the core states, and to the states of the remaining conduction electrons. Thus the spin-phonon interaction which will be derived from these properties in the framework of a generalized Heisenberg model is due to direct exchange as well as to superexchange interaction.

In Sec. II a hypothetical narrow, partly filled isolated *s* band is considered. It is shown that under certain conditions the electron system may lower its Coulomb energy by coupling to the motion of the nuclei. This coupling has no further consequences within an isolated *s* band which, as is well known, never does exist in real metals.

In Sec. III the band structure of niobium is considered as an example for a metallic band structure. Niobium appears not to possess a conduction band which has the same symmetry as the considered *s* band. The situation, however, is drastically changed when the existence of the electron spin is taken into account and the localized functions are thus allowed to belong to a *double-valued* representation of the point group. In fact, niobium has a narrow, single (but degenerate) conduction band from which we may construct optimally localized functions belonging to a two-dimensional double-valued representation of the point group. This band, which will be called the " σ band," is (with respect to its symmetry type) a generalized *s* band. Also, in a narrow σ conduction band the electrons may lower their Coulomb energy (under the conditions given in Sec. II) by coupling to the motion of the nuclei. Within a σ band, however, the *spins* of the electrons also couple to the motion of the nuclei by exchange interaction.

From this we conclude in Sec. IV that the electron spins couple to phonons such that the angular momentum is conserved in the nonadiabatic electron-phonon system. The matrix elements of the resulting operator of spin-phonon interaction, $H_{s-ph}^{n\sigma}$, are given in terms of nonadia-

batic localized electron and phonon functions. Though we are not able to give $\underline{H}_{s,\text{ph}}^{\text{no}}$ explicitly (since these nonadiabatic functions are not available) we may derive one essential property of the electron-phonon system: In Sec. V we conclude from the conservation law of angular momentum that, at zero temperature, the electrons necessarily form Cooper pairs in a narrow σ band. From the comparison of the N -electron system with a classical system of N particles we give an argument indicating that spin-phonon coupling is necessary for superconductivity. On the basis of this assumption we present in Sec. VI criteria for superconductivity. A summary of our considerations has been published recently.⁸

II. COULOMB INTERACTION IN A NARROW s CONDUCTION BAND

We first consider a metal with an isolated narrow, partially filled s band. The Bloch functions $\phi_{\vec{k}}(\vec{r})$ belonging to this band can be transformed into Wannier functions,

$$w(\vec{r}-\vec{R}) = \frac{1}{\sqrt{M}} \sum_{\vec{k}}^{\text{band}} e^{-i\vec{k}\cdot\vec{R}} \phi_{\vec{k}}(\vec{r}), \quad (2.1)$$

having s symmetry,

$$\underline{P}(\alpha)w(\vec{r}-\vec{R}) = w(\vec{r}-\alpha\vec{R}) \quad \text{for } \alpha \in G_0. \quad (2.2)$$

$\underline{P}(\alpha)$ denotes an operator of the point group G_0 acting on a space function $f(\vec{r})$ according to

$$\underline{P}(\alpha)f(\vec{r}) = f(\alpha^{-1}\vec{r}), \quad (2.3)$$

and α is a point-group operation. For simplicity, only cubic-symmetry metals with symmorphic space group are considered. For these metals, the operators $\underline{P}(\alpha)$ are by themselves space-group operators.

Let

$$\underline{H} = \underline{H}_{\text{HF}} + \underline{H}_{\text{Cb}} - \underline{H}_d \quad (2.4)$$

be the Hamiltonian operator of the valence-electron system with

$$\underline{H}_{\text{HF}} = \sum_{\vec{R}, \vec{R}', s} \langle \vec{R} | \underline{H}_{\text{HF}} | \vec{R}' \rangle \underline{c}_{\vec{R}, s}^\dagger \underline{c}_{\vec{R}', s} \quad (2.5)$$

denoting the Hartree-Fock operator and

$$\underline{H}_{\text{Cb}} = \sum_{\vec{R}, s} \langle \vec{R}_1, \vec{R}_2 | \underline{H}_{\text{Cb}} | \vec{R}'_1, \vec{R}'_2 \rangle \underline{c}_{\vec{R}_1, s_1}^\dagger \underline{c}_{\vec{R}_2, s_2}^\dagger \underline{c}_{\vec{R}'_2, s_2} \underline{c}_{\vec{R}'_1, s_1} \quad (2.6)$$

as the operator of the Coulomb interaction. The operators $\underline{c}_{\vec{R}, s}^\dagger$ and $\underline{c}_{\vec{R}, s}$ create and annihilate, respectively, electrons in the localized states $|\vec{R}, s\rangle$ represented by the Wannier functions. \underline{H}_d subtracts that part of $\underline{H}_{\text{Cb}}$ which is already included in $\underline{H}_{\text{HF}}$; it does not matter in the following and will be suppressed for brevity.

$\underline{H}_{\text{Cb}}$ may be split into three parts,

$$\underline{H}_{\text{Cb}} = \underline{H}_c + \underline{H}_{\text{ex}} + \underline{H}_z, \quad (2.7)$$

with

$$\underline{H}_c = \sum_{\vec{R}, s} \langle \vec{R}_1, \vec{R}_2 | \underline{H}_{\text{Cb}} | \vec{R}_1, \vec{R}_2 \rangle \underline{c}_{\vec{R}_1, s_1}^\dagger \underline{c}_{\vec{R}_2, s_2}^\dagger \underline{c}_{\vec{R}_2, s_2} \underline{c}_{\vec{R}_1, s_1} \quad (2.8)$$

containing the matrix elements with $\vec{R}_1 = \vec{R}'_1$ and $\vec{R}_2 = \vec{R}'_2$,

$$\underline{H}_{\text{ex}} = \sum_{\vec{R}, s} \langle \vec{R}_1, \vec{R}_2 | \underline{H}_{\text{Cb}} | \vec{R}_2, \vec{R}_1 \rangle \underline{c}_{\vec{R}_1, s_1}^\dagger \underline{c}_{\vec{R}_2, s_2}^\dagger \underline{c}_{\vec{R}_1, s_2} \underline{c}_{\vec{R}_2, s_1} \quad (2.9)$$

containing the matrix elements with $\vec{R}_1 = \vec{R}'_2$ and $\vec{R}_2 = \vec{R}'_1$ and

$$\underline{H}_z = \sum_{\vec{R}, s} \langle \vec{R}_1, \vec{R}_2 | \underline{H}_{\text{Cb}} | \vec{R}'_1, \vec{R}'_2 \rangle \underline{c}_{\vec{R}_1, s_1}^\dagger \underline{c}_{\vec{R}_2, s_2}^\dagger \underline{c}_{\vec{R}'_2, s_2} \underline{c}_{\vec{R}'_1, s_1} \quad (2.10)$$

comprising the remaining matrix elements with $\{\vec{R}_1, \vec{R}_2\} \neq \{\vec{R}'_1, \vec{R}'_2\}$ where $\{\vec{R}_1, \vec{R}_2\} = \{\vec{R}'_1, \vec{R}'_2\}$ means $\vec{R}_1 = \vec{R}'_1$ and $\vec{R}_2 = \vec{R}'_2$ or $\vec{R}_1 = \vec{R}'_2$ and $\vec{R}_2 = \vec{R}'_1$.

\underline{H}_c is the operator of the Coulomb repulsion between the charge distribution of the localized states $|\vec{R}, s\rangle$. $\underline{H}_{\text{ex}}$ and \underline{H}_z originate from the motion of single electrons which "see" their instantaneous positions within their localized states. Both $\underline{H}_{\text{ex}}$ and \underline{H}_z are short-ranged interactions which would vanish if $\underline{H}_{\text{Cb}}$ were constant or if the Wannier functions would not overlap. $\underline{H}_{\text{ex}}$ is the familiar Heisenberg exchange operator acting on the electron spins. Since $\underline{H}_{\text{ex}}$ and \underline{H}_z are similar with respect to their physical origin, \underline{H}_z also may be expected to be the origin of an exchange interaction.

We show that under certain conditions \underline{H}_z may be the origin of an interaction coupling the electronic motion to the motion of the nuclei. In the following the operator $\underline{H}_{\text{ex}}$ is suppressed and the simplified operator

$$\underline{H} = \underline{H}_{\text{HF}} + \underline{H}_c + \underline{H}_z \quad (2.11)$$

is considered.

As a first step we make some general remarks on the (exact) ground state $|G'\rangle$ of the operator

$$\underline{H}' = \underline{H}_{\text{HF}} + \underline{H}_c \quad (2.12)$$

containing only the Hartree-Fock operator and the Coulomb repulsion. $|G'\rangle$ may be written in the form

$$|G'\rangle = \sum_i d_i |\phi_i\rangle, \quad (2.13)$$

where

$$|\phi_i\rangle = \underline{c}_{\vec{R}_1, s_1}^\dagger \underline{c}_{\vec{R}_2, s_2}^\dagger \cdots \underline{c}_{\vec{R}_N, s_N}^\dagger |0\rangle, \quad (2.14)$$

with N being the number of electrons belonging to the band and i labeling the $\binom{2M}{N}$ possible distributions of N electrons on $2M$ localized states.

If the Hartree-Fock energy is small compared to the Coulomb repulsion,

$$\langle G' | \underline{H}_c | G' \rangle \gg \langle G' | \underline{H}_{\text{HF}} | G' \rangle, \quad (2.15)$$

the electron system may be described in the framework of

the tight-binding approximation. The Coulomb repulsion of two electrons with different spin directions occupying localized states on the same lattice point \vec{R} is larger than the Coulomb repulsion of two electrons occupying adjacent localized states.⁹ Therefore, in (2.13) those numbers d'_i will dominate which belong to nearly homogeneous electron distributions $|\phi_i\rangle$ (2.14) as it is the case in the atomic or Heisenberg model.

If, on the other hand, the Hartree-Fock energy is much larger than the Coulomb repulsion,

$$\langle G' | \underline{H}_{\text{HF}} | G' \rangle \gg \langle G' | \underline{H}_c | G' \rangle, \quad (2.16)$$

the electrons exhibit a more random occupation often referred to as bandlike behavior.

For the real Hamiltonian neither (2.15) nor (2.16) is true. The system finds a compromise between atomiclike and bandlike behavior. As is well known, the conduction electrons tend to a more atomiclike behavior with decreasing bandwidth and to a more bandlike behavior with increasing bandwidth.

As a second step we consider the influence of \underline{H}_z on the electron system. From its definition (2.10) follows that \underline{H}_z generates virtual transitions between adjacent localized states. We assume therefore that (i) the ground state $|G\rangle$ of $\underline{H} = \underline{H}' + \underline{H}_z$ tends more toward random occupation than does $|G'\rangle$. Thus, due to \underline{H}_z , the balance bandlike and atomiclike behavior is shifted toward bandlike behavior and hence the Coulomb repulsion increases. This increase of the Coulomb repulsion will be small if $|G'\rangle$ already exhibits random occupation; it will be the larger increase as $|G'\rangle$ tends to have more homogeneous occupation. The (positive) energy difference

$$\Delta E = \langle G | \underline{H}' | G \rangle - \langle G' | \underline{H}' | G' \rangle \quad (2.17)$$

will hence increase with decreasing bandwidth.

The expectation value

$$\delta E = \langle G | \underline{H}_z | G \rangle \quad (2.18)$$

will also increase with decreasing bandwidth since, according to the above assumption (i), δE will decrease if the balance between random and homogeneous occupation in $|G\rangle$ is shifted toward random occupation. Thus the energy difference

$$\langle G | \underline{H} | G \rangle - \langle G' | \underline{H}' | G' \rangle = \Delta E + \delta E \quad (2.19)$$

will increase with decreasing bandwidth.

Further, we assume that (ii) \underline{H}_z is a small operator in the sense that $\delta E + \Delta E = 0$ for a certain bandwidth. We hence may expect that

$$\langle \vec{R}_1, \vec{R}_2 | \underline{H}_{cb}^n | \vec{R}'_1, \vec{R}'_2 \rangle = \frac{e^2}{2} \int \frac{\langle \vec{R}_1, n | \vec{q}, \vec{r} \rangle \langle \vec{R}_2, n | \vec{q}', \vec{r}' \rangle \langle \vec{r}', \vec{q}' | \vec{R}'_2, n \rangle \langle \vec{r}, \vec{q} | \vec{R}'_1, n \rangle}{|\vec{r} - \vec{r}'|} d\vec{r} d\vec{r}' d\vec{q} d\vec{q}', \quad (2.22)$$

becomes minimized for $\{\vec{R}_1, \vec{R}_2\} \neq \{\vec{R}'_1, \vec{R}'_2\}$. For simplicity we set

$$\langle \vec{R}_1, \vec{R}_2 | \underline{H}_{cb}^n | \vec{R}'_1, \vec{R}'_2 \rangle = 0 \text{ for } \{\vec{R}_1, \vec{R}_2\} \neq \{\vec{R}'_1, \vec{R}'_2\}, \quad (2.23)$$

and for nonadiabatic functions labeled by a distinct quan-

$$\delta E + \Delta E > 0 \quad (2.20)$$

in sufficiently narrow bands. Summarizing, we may state that the relationship

$$\langle G | \underline{H} | G \rangle > \langle G' | \underline{H}' | G' \rangle \quad (2.21)$$

probably holds in sufficiently narrow energy bands.

Relation (2.21) is essential for our considerations. Below (in the next section) (2.21) will be postulated for the narrowest bands which exist in the band structure of the metals. Here we continue to consider a hypothetical s band sufficiently narrow for (2.21) to apply.

Relation (2.21) means that the ground-state energy should increase when \underline{H}_z is activated. This, however, will not happen in reality. We remember that the short-ranged interaction \underline{H}_z emerged (besides the Coulomb repulsion \underline{H}_c) since an electron sees the momentary motion of the electrons which occupy adjacent localized states. The relation (2.21) was gained assuming that, within the localized states $|\vec{R}, s\rangle$, the electrons move on *rigid* orbitals given by the Wannier functions (2.1). By this assumption, *any* change of the electronic motion generated by \underline{H}_z can only be realized by virtual transitions to adjacent localized states. In reality, however, the electrons may also change their orbitals *within* their localized states. If (2.21) is true, the electrons will suppress (at least partly) their virtual transitions to adjacent states by changing their orbitals within their localized states.

A localized electron now moves in a potential depending on which of the adjacent localized states is occupied and on the momentary motion of the electrons within these states. Such an electronic motion, however, cannot be described within the framework of the adiabatic (or Born-Oppenheimer) approximation since such a motion yields, at a given moment, an electronic charge distribution within the localized states which is not symmetric with respect to the positions of the nuclei. Thus the nuclei become (for a time) accelerated in certain directions. The nonadiabatic localized states $|\vec{R}, n\rangle$ must therefore be represented by localized functions $\langle \vec{r}, \vec{q} | \vec{R}, n \rangle$ depending also on the acceleration \vec{q} of the nucleus on the lattice point \vec{R} . The number n labels different states of motion of the nucleus.

In terms of nonadiabatic localized functions the above statement reads as the following: If (2.21) holds, the conduction electrons lower their energy by coupling to the motion of the nuclei so that the modulus of the matrix elements,

number n .

The nonadiabatic operator of the Coulomb interaction is then given by

$$\underline{H}_{cb}^n = \sum_{\vec{R}, s} \langle \vec{R}_1, \vec{R}_2 | \underline{H}_{cb}^n | \vec{R}_1, \vec{R}_2 \rangle c_{\vec{R}_1, s_1}^{n\dagger} c_{\vec{R}_2, s_2}^{n\dagger} c_{\vec{R}_2, s_2}^n c_{\vec{R}_1, s_1}^n \quad (2.24)$$

(where the exchange term $\underline{H}_{\text{ex}}^n$ is still suppressed). The operators $\underline{c}_{\vec{R}s}^{n\dagger}$ and $\underline{c}_{\vec{R}s}^n$ create and annihilate, respectively, an electron with spin s in the localized state $|\vec{R}, n\rangle$. They obey (for fixed n) the well-known commutation rules of fermion operators,

$$\begin{aligned} [\underline{c}_{\vec{R}s}^n, \underline{c}_{\vec{R}'s'}^n]_+ &= 0, \quad [\underline{c}_{\vec{R}s}^{n\dagger}, \underline{c}_{\vec{R}'s'}^{n\dagger}]_+ = 0, \\ [\underline{c}_{\vec{R}s}^{n\dagger}, \underline{c}_{\vec{R}'s'}^n]_+ &= \delta_{\vec{R}\vec{R}'} \delta_{ss'}, \end{aligned} \quad (2.25)$$

since \underline{H}_{Cb}^n must be invariant with respect to the permutation of two localized states. The nonadiabatic localized functions are therefore orthogonal according to

$$\int \langle \vec{R}', n | \vec{r}, \vec{q} \rangle \langle \vec{r}, \vec{q} | \vec{R}, n \rangle d\vec{r} d\vec{q} = \delta_{\vec{R}\vec{R}'}. \quad (2.26)$$

\underline{H}_{Cb}^n commutes with the point-group operator product $\underline{P}(\alpha)\underline{Q}(\alpha)$,

$$[\underline{H}_{Cb}^n, \underline{P}(\alpha)\underline{Q}(\alpha)] = 0 \quad \text{for } \alpha \in G_0. \quad (2.27)$$

Thus the localized functions $\langle \vec{r}, \vec{q} | \vec{R}, n \rangle$ belong to a representation of the point group (since \underline{H}_{Cb}^n is diagonal) which is, in the case of the considered s band, the identical representation

$$\underline{P}(\alpha)\underline{Q}(\alpha)\langle \vec{r}, \vec{q} | \vec{R}, n \rangle = \langle \vec{r}, \vec{q} | \alpha\vec{R}, n \rangle \quad \text{for } \alpha \in G_0, \quad (2.28)$$

where $\underline{P}(\alpha)$ is still acting on \vec{r} and $\underline{Q}(\alpha)$ is acting on \vec{q} according to

$$\underline{Q}(\alpha)f(\vec{q}) = f(\alpha^{-1}\vec{q}). \quad (2.29)$$

As stated above, a nucleus becomes accelerated at a given moment when the electronic charge distribution within the localized state is unsymmetric (with respect to this nucleus) at this moment. It is essential, therefore, that Eq. (2.28) does *not* hold when $\underline{P}(\alpha)\underline{Q}(\alpha)$ is replaced by $\underline{P}(\alpha)$ alone. Under the action of $\underline{P}(\alpha)$ we obtain localized states in which the nucleus is (generally) not accelerated in the direction of the center of charge. Neither does Eq. (2.27) hold when $\underline{Q}(\alpha)$ is suppressed,

$$[\underline{H}_{Cb}^n, \underline{P}(\alpha)] \neq 0 \quad \text{for some } \alpha \in G_0 \quad (2.30)$$

[(2.27) is false if the commutator does not vanish for at least one $\alpha \in G_0$]. This again demonstrates that the electron system has gained new possibilities to move by coupling to the motion of the nuclei since the adiabatic Coulomb interaction (2.6) must commute with $\underline{P}(\alpha)$ (for $\alpha \in G_0$). In this context the ratio m_n/m_{el} of the mass of the nucleus and the electron is not relevant, since the amplitude of the acceleration \vec{q} is meaningless. From the largeness of this ratio we conclude as usual that the nuclei do not move far from the lattice points \vec{R} .

The nature of the interaction between the electronic motion and the motion of the nuclei characterized by (2.30) can be elaborated. The operator of the Coulomb interaction of the electrons,

$$\underline{H}_{Cb} = \frac{1}{2} \sum_{\substack{\mu, \nu \\ \mu \neq \nu}} \frac{e^2}{|\vec{r}_\mu - \vec{r}_\nu|}, \quad (2.31)$$

is independent of \vec{q} and hence we have

$$[\underline{H}_{Cb}, \underline{P}(\alpha)] = 0 \quad \text{for } \alpha \in G_0, \quad (2.32)$$

which appears to contradict the relation (2.30). The operator \underline{H}_{Cb}^n as given in (2.24), however, must be represented by

$$\underline{H}_{Cb}^n = \underline{P}^n \underline{H}_{Cb} \underline{P}^n, \quad (2.33)$$

where \underline{P}^n projects on the space A being spanned by wave functions of the form

$$|\phi_i^n\rangle = \underline{c}_{\vec{R}_1 s_1}^{n\dagger} \underline{c}_{\vec{R}_2 s_2}^{n\dagger} \cdots \underline{c}_{\vec{R}_N s_N}^{n\dagger} |0\rangle, \quad (2.34)$$

i.e., A is the space of wave functions being antisymmetric with respect to the permutation of two localized states labeled by \vec{R}, s and \vec{R}', s' .

\underline{P}^n commutes with any observable, therefore we have

$$[\underline{P}^n, \underline{P}(\alpha)\underline{Q}(\alpha)] = 0 \quad \text{for } \alpha \in G_0. \quad (2.35)$$

The operator

$$\underline{P}(\alpha)\underline{c}_{\vec{R}s}^{n\dagger}\underline{P}^\dagger(\alpha)$$

is, for some $\alpha \in G_0$, not a linear combination of operators $\underline{c}_{\vec{R}'s'}^{n\dagger}$ since, under the action of $\underline{P}(\alpha)$, we generally obtain nonadiabatic localized states in which the acceleration \vec{q} of the nucleus is not directed toward the center of charge. Thus

$$\underline{P}(\alpha)|\phi_i^n\rangle$$

does not belong to A for some $\alpha \in G_0$ and we have

$$[\underline{P}^n, \underline{P}(\alpha)] \neq 0 \quad \text{for some } \alpha \in G_0. \quad (2.36)$$

Relation (2.30) is then true in spite of the validity of Eq. (2.32). In other words, the assumption that the electron system lowers its own Coulomb energy by coupling to the motion of the nuclei does not violate physical principles since the Pauli principle is valid. In this sense the interaction coupling the electrons to the motion of the nuclei is due to the Pauli principle and may therefore be called an exchange interaction. However, it cannot be described in the familiar way in terms of an exchange integral.

The electronic charge distribution within the nonadiabatic localized states differs from that within the adiabatic states represented by the Wannier functions (2.1). To a first approximation we shall assume that the Coulomb repulsion is not crucially affected by this modification of the charge distribution, i.e., we replace \underline{H}_{Cb}^n by \underline{H}_c (2.8). The nonadiabatic Hamiltonian

$$\underline{H}^n = \underline{H}_{\text{HF}} + \underline{H}_{Cb}^n \quad (2.37)$$

is hence approximated by

$$\underline{H}' = \underline{H}_{\text{HF}} + \underline{H}_c, \quad (2.38)$$

as given in Eq. (2.12).

III. COULOMB INTERACTION IN A NARROW σ CONDUCTION BAND

The description of the nonadiabatic system as given in the preceding section is incomplete inasmuch as the nonadiabatic fermion operators $c_{\vec{R}s}^n$ (2.25) are still labeled by one purely electronic quantity, namely by the electron-spin quantum number s . For the conduction band, however, which will be considered in this section we must introduce fermion operators $c_{\vec{R}m}^n$ which no longer depend on s .

Consider, e.g., the band structure of Nb (Ref. 10) depicted in Fig. 1, in particular the band denoted by the heavy line. It is characterized by the representations

$$\Gamma_{25}^+, H_{25}^+, N_2, \text{ and } P_4$$

which belong to the band in the points Γ , H , N , and P (in the notation of Bouckaert, Smoluchowski, and Wigner¹¹). As shown in detail in Ref. 12 we cannot assign to this single band familiar Wannier functions which both are optimally localized and belong to a representation of the point group since Γ_{25}^+ , H_{25}^+ , and P_4 are three-dimensional.

The construction of optimally localized functions belonging to a representation of the point group, however, becomes possible in a natural way if we account for the existence of the electron spin. For the *double-valued* representations one has

$$D_{1/2} \times \Gamma_{25}^+ = \Gamma_7^+ + \Gamma_8^+, \quad D_{1/2} \times H_{25}^+ = H_7^+ + H_8^+, \quad (3.1)$$

$$D_{1/2} \times N_2 = N^+, \quad D_{1/2} \times P_4 = P_7 + P_8$$

with $D_{1/2}$ denoting the two-dimensional double-valued representation of the three-dimensional rotation group $O(3)$. It is easily seen that there exists a subset of double-valued representations, namely

$$\Gamma_7^+, H_7^+, N^+, \text{ and } P_7,$$

being compatible in the sense that H_7^+ , N^+ , and P_7 are subduced by Γ_7^+ .

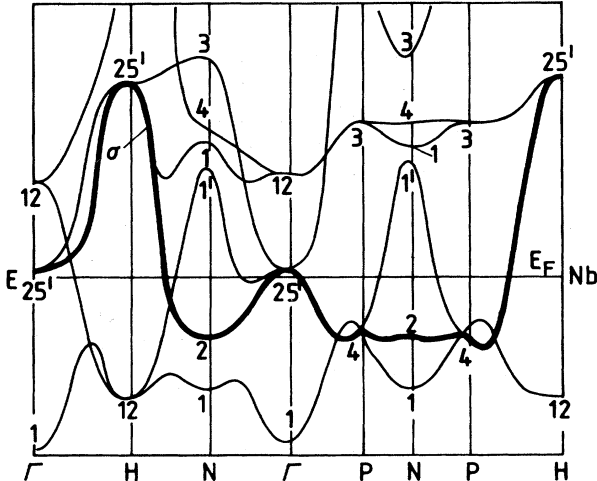


FIG. 1. Band structure of Nb after Mattheiss (Ref. 10). The heavy line denotes the σ band.

From this group-theoretical result it follows¹³ that we can assign to the considered single band "spin-dependent localized functions" (SLF) of the form

$$a_m(\vec{r}-\vec{R}, t) = \sum_{\vec{k}, s}^{\text{band}} f_{sm}(\vec{k}) u_s(t) \phi_{\vec{k}}(\vec{r}) e^{-i\vec{k} \cdot \vec{R}}, \quad (3.2)$$

transforming according to

$$\begin{aligned} \underline{P}(\alpha) \underline{S}(\alpha) a_m(\vec{r}-\vec{R}, t) \\ = \sum_{m'} d_{m'm}(\alpha) a_{m'}(\vec{r}-\alpha\vec{R}, t) \quad \text{for } \alpha \in G_0. \end{aligned} \quad (3.3)$$

Here $f_{sm}(\vec{k})$ is a \vec{k} -dependent unitary two-dimensional matrix and $u_s(t)$ are Pauli's spin functions. The matrices $d_{m'm}(\alpha)$ belong to Γ_7^+ . $S(\alpha)$ acts on the spin coordinate t according to

$$\underline{S}(\alpha) u_s(t) = \sum_{s'} D_{s's}(\alpha) u_{s'}(t) \quad \text{for } \alpha \in O(3), \quad (3.4)$$

with $D_{s's}(\alpha)$ belonging to the representation $D_{1/2}$. The index m labels the rows of the two-dimensional representation Γ_7^+ . It is convenient to set $m_1 = +\frac{1}{2}$ and $m_2 = -\frac{1}{2}$. In addition to (3.3) the SLF transform according to

$$\underline{K} a_m(\vec{r}-\vec{R}, t) = \pm a_{-m}(\vec{r}-\vec{R}, t), \quad (3.5)$$

by application of the time-inversion operator \underline{K} . We define the upper sign to belong to $m = +\frac{1}{2}$ and the lower sign to $m = -\frac{1}{2}$.

The matrix $f_{sm}(\vec{k})$ may be chosen such that (a) Eqs. (3.3) and (3.5) are true and (b)

$$\phi_{\vec{k}m}(\vec{r}, t) = \sum_s f_{sm}(\vec{k}) u_s(t) \phi_{\vec{k}}(\vec{r}) \quad (3.6)$$

varies smoothly (for fixed \vec{r} and t) in \vec{k} space¹³ though there exist several symmetry degeneracies. Such a choice of $f_{sm}(\vec{k})$ yields the optimally localized¹² SLF on the considered band. It is essential in the following that the matrix $f_{sm}(\vec{k})$ which belongs to the *optimally* localized SLF of the considered Nb band must necessarily depend on \vec{k} . This follows from the very fact that the considered band cannot be represented by Wannier functions belonging to a one-dimensional (single-valued) representation of the point group [the SLF (3.2) are identical with such Wannier functions if $f_{sm}(\vec{k})$ is independent of \vec{k}].

We define a σ band as a band to which we can assign SLF belonging to a (two-dimensional) double-valued representation of the point group and *cannot* assign Wannier functions belonging to a (one-dimensional) single-valued representation of the point group. Thus the matrix $f_{sm}(\vec{k})$ which belongs to the optimally localized SLF (3.2) of a σ band is not independent of \vec{k} .

If $f_{sm}(\vec{k})$ depends on \vec{k} the symmetry relation (3.3) does not hold when $\underline{P}(\alpha) \underline{S}(\alpha)$ is replaced by $\underline{S}(\alpha)$ alone. $\underline{S}(\alpha) a_m(\vec{r}-\vec{R}, t)$ is rather a linear combination of SLF,

$$\begin{aligned} \underline{S}(\alpha)a_m(\vec{r}-\vec{R},t) \\ = \sum_{R'm'} d(m,\vec{R};m',\vec{R}';\alpha)a_{m'}(\vec{r}-\vec{R}',t) \text{ for } \alpha \in G_0, \end{aligned} \quad (3.7)$$

which also belong to lattice points $\vec{R}' \neq \vec{R}$. In the following, the form of the coefficients $d(m,\vec{R};m',\vec{R}';\alpha)$ is meaningless except for the fact that, for some $\alpha \in G_0$,

there are nonvanishing coefficients with $\vec{R}' \neq \vec{R}$.

Since $f_{sm}(\vec{k})$ is unitary, the SLF are orthogonal to each other according to

$$\sum_t \int a_{m'}^*(\vec{r}-\vec{R}',t)a_m(\vec{r}-\vec{R},t)d\vec{r} = \delta_{\vec{R}\vec{R}'}\delta_{mm'}. \quad (3.8)$$

Neglecting the influence of the other bands, we may therefore write the operator of the Coulomb interaction of the electrons within the σ band in the form

$$\underline{H}_{Cb} = \sum_{\vec{R}m} \langle \vec{R}_1, m_1; \vec{R}_2, m_2 | \underline{H}_{Cb} | \vec{R}'_1, m'_1; \vec{R}'_2, m'_2 \rangle c_{\vec{R}_1, m_1}^\dagger c_{\vec{R}_2, m_2} c_{\vec{R}'_2, m'_2} c_{\vec{R}'_1, m'_1}, \quad (3.9)$$

where $c_{\vec{R}m}^\dagger$ and $c_{\vec{R}m}$ create and annihilate, respectively, an electron in the localized states represented by the SLF $a_m(\vec{r}-\vec{R},t)$ and

$$\begin{aligned} \langle \vec{R}_1, m_1; \vec{R}_2, m_2 | \underline{H}_{Cb} | \vec{R}'_1, m'_1; \vec{R}'_2, m'_2 \rangle \\ = \frac{e^2}{2} \sum_{t,t'} \int \frac{a_{m_1}^*(\vec{r}-\vec{R}_1, t) a_{m_2}^*(\vec{r}'-\vec{R}_2, t') a_{m'_1}(\vec{r}-\vec{R}'_1, t) a_{m'_2}(\vec{r}'-\vec{R}'_2, t')}{|\vec{r}-\vec{r}'|} d\vec{r} d\vec{r}'. \end{aligned} \quad (3.10)$$

Again we set

$$\underline{H}'^\sigma = \underline{H}_{HF} + \underline{H}_c^\sigma \quad (3.11)$$

and

$$\underline{H} = \underline{H}_{HF} + \underline{H}_c^\sigma + \underline{H}_z^\sigma$$

with

$$\underline{H}_c^\sigma = \sum_{R,m} \langle \vec{R}_1, m_1; \vec{R}_2, m_2 | \underline{H}_{Cb} | \vec{R}_1, m'_1; \vec{R}_2, m'_2 \rangle c_{\vec{R}_1, m_1}^\dagger c_{\vec{R}_2, m_2} c_{\vec{R}_2, m'_2} c_{\vec{R}_1, m'_1} \quad (3.12)$$

containing the matrix elements with $\vec{R}_1 = \vec{R}'_1$ and $\vec{R}_2 = \vec{R}'_2$ and \underline{H}_z^σ the matrix elements with $\{\vec{R}_1, \vec{R}_2\} \neq \{\vec{R}'_1, \vec{R}'_2\}$ (where the term \underline{H}_{ex} is still suppressed).

We now apply the arguments discussed in Sec. II for the hypothetical s band to the more realistic σ bands. Let $|G\rangle$ and $|G'^\sigma\rangle$ be the ground state of \underline{H} and \underline{H}'^σ (3.11), respectively. We postulate that

$$\langle G | \underline{H} | G \rangle > \langle G'^\sigma | \underline{H}'^\sigma | G'^\sigma \rangle \quad (3.13)$$

holds if the considered σ band is one of the narrowest bands within the band structure of the considered metal, and that the energy difference $\langle G | \underline{H} | G \rangle - \langle G'^\sigma | \underline{H}'^\sigma | G'^\sigma \rangle$ is at least of the order of the electron-thermal energy at temperatures well above the superconducting transition temperature T_c . We give three arguments corroborating this postulate.

(1) Experimentally, it is found that the d electrons of transition metals exhibit behavior characteristic of the atomic model.¹⁴ Since, as stated above, \underline{H}_z^σ restricts the validity of an atomic or Heisenberg model, it may be expected that there exists a mechanism making \underline{H}_z ineffective least for the narrowest bands. Such a mechanism will be derived from (3.13).

(2) Because of (3.7) the operator \underline{H}_c^σ (3.12) does not commute with $\underline{S}(\alpha)$,

$$[\underline{H}_c^\sigma, \underline{S}(\alpha)] \neq 0 \text{ for some } \alpha \in O(3), \quad (3.14)$$

since \underline{H}_c^σ is diagonal with respect to the SLF. The complete Coulomb interaction, on the other hand, commutes with $\underline{S}(\alpha)$,

$$[\underline{H}_{Cb}, \underline{S}(\alpha)] = 0 \text{ for } \alpha \in O(3), \quad (3.15)$$

since \underline{H}_{Cb} does not depend on the spin coordinates. Consequently, the interaction \underline{H}_z^σ restores the conservation of spin angular momentum. Such an interaction may be expected to be neither purely attractive nor purely repulsive, which raises the probability that the two basic assumptions labeled by (i) and (ii) in the preceding section are valid.

(3) \underline{H}_z^σ has the same order of magnitude as the exchange term \underline{H}_{ex} of \underline{H}_{Cb} since the matrix elements of both operators have the same form. Since the interaction \underline{H}_{ex} generates exchange effects as, e.g., ferromagnetism, even at room temperatures, it is conceivable that exchange effects can be derived also from a sufficiently large energy difference

$$\langle G | \underline{H} | G \rangle - \langle G'^\sigma | \underline{H}'^\sigma | G'^\sigma \rangle > 0.$$

From (3.13) we again conclude [cf. (2.37) and (2.38)] that \underline{H}_c^σ (3.12) is an approximation for the nonadiabatic Coulomb interaction

$$\underline{H}_{Cb}^{n\sigma} = \sum_{\vec{R}_m} \langle \vec{R}_1, m_1; \vec{R}_2, m_2 | \underline{H}_{Cb}^\sigma | \vec{R}_1, m'_1; \vec{R}_2, m'_2 \rangle \underline{c}_{\vec{R}_1, m_1}^{n\dagger} \underline{c}_{\vec{R}_2, m_2}^{n\dagger} \underline{c}_{\vec{R}_2, m'_2}^n \underline{c}_{\vec{R}_1, m'_1}^n \quad (3.16)$$

in a narrow σ band. The matrix elements of $\underline{H}_{Cb}^{n\sigma}$,

$$\begin{aligned} & \langle \vec{R}_1, m_1; \vec{R}_2, m_2 | \underline{H}_{Cb}^{n\sigma} | \vec{R}_1, m'_1; \vec{R}_2, m'_2 \rangle \\ &= \frac{e^2}{2} \sum_{t'} \int \frac{\langle \vec{R}_1, m_1, n | \vec{r}, t, \vec{q} \rangle \langle \vec{R}_2, m_2, n | \vec{r}', t', \vec{q}' \rangle \langle \vec{r}, t, \vec{q} | \vec{R}_1, m'_1, n \rangle \langle \vec{r}', t', \vec{q}' | \vec{R}_2, m'_2, n \rangle}{|\vec{r} - \vec{r}'|} d\vec{r} d\vec{r}' d\vec{q} d\vec{q}', \end{aligned} \quad (3.17)$$

are integrals over nonadiabatic localized functions of the form

$$\langle \vec{r}, t, \vec{q} | \vec{R}, m, n \rangle, \quad (3.18)$$

and $\underline{c}_{\vec{R}m}^{n\dagger}$ and $\underline{c}_{\vec{R}m}^n$ create and annihilate, respectively, electrons in localized states represented by the localized functions (3.18). The fermion operators $\underline{c}_{\vec{R}m}^{n\dagger}$ and $\underline{c}_{\vec{R}m}^n$ satisfy the commutation rules (2.25) and hence the localized functions are orthogonal according to

$$\begin{aligned} \sum_t \int \langle \vec{R}', m', n | \vec{r}, t, \vec{q} \rangle \langle \vec{r}, t, \vec{q} | \vec{R}, m, n \rangle d\vec{r} d\vec{q} \\ = \delta_{\vec{R}\vec{R}'} \delta_{mm'} \delta_{nn'}. \end{aligned} \quad (3.19)$$

The quantum number n labels again those functions for which

$$|\langle \vec{R}_1, m_1; \vec{R}_2, m_2 | \underline{H}_{Cb}^{n\sigma} | \vec{R}_1, m'_1; \vec{R}_2, m'_2 \rangle|$$

is a minimum for $\{\vec{R}_1, \vec{R}_2\} \neq \{\vec{R}'_1, \vec{R}'_2\}$. For simplicity we again set

$$\begin{aligned} \langle \vec{R}_1, m_1; \vec{R}_2, m_2 | \underline{H}_{Cb}^{n\sigma} | \vec{R}'_1, m'_1; \vec{R}'_2, m'_2 \rangle = 0 \\ \text{for } \{\vec{R}_1, \vec{R}_2\} \neq \{\vec{R}'_1, \vec{R}'_2\} \end{aligned} \quad (3.20)$$

and for nonadiabatic localized functions labeled by a distinct quantum number n . The existence of such functions is assumed in the following.

Since $\underline{H}_{Cb}^{n\sigma}$ (3.16) commutes with the point-group operators,

$$[\underline{H}_{Cb}^{n\sigma}, \underline{Q}(\alpha) \underline{P}(\alpha) \underline{S}(\alpha)] = 0 \quad \text{for } \alpha \in G_0, \quad (3.21)$$

the functions (3.18) belong to a representation of the point group which is Γ_7^+ in the case of the σ band of Nb and Γ_6^+ , Γ_6^- , Γ_7^+ , or Γ_7^- in the case of any given σ band. We then have

$$\begin{aligned} \underline{P}(\alpha) \underline{Q}(\alpha) \underline{S}(\alpha) \langle \vec{r}, t, \vec{q} | \vec{R}, m, n \rangle \\ = \sum_{m'} d_{m'm}(\alpha) \langle \vec{r}, t, \vec{q} | \alpha \vec{R}, m', n \rangle \quad \text{for } \alpha \in G_0, \end{aligned} \quad (3.22)$$

where still $\underline{P}(\alpha)$, $\underline{Q}(\alpha)$, and $\underline{S}(\alpha)$ act on \vec{r} , \vec{q} , and t , respectively.

It is essential that, according to (3.14), the interaction \underline{H}_c^σ (3.12) does not conserve the electron spin. Since \underline{H}_c^σ is the adiabatic approximation of the nonadiabatic Coulomb interaction $\underline{H}_{Cb}^{n\sigma}$ we cannot expect that $\underline{H}_{Cb}^{n\sigma}$ con-

serves the electron spin. Thus we have

$$[\underline{H}_{Cb}^{n\sigma}, \underline{S}(\alpha)] \neq 0 \quad \text{for some } \alpha \in O(3). \quad (3.23)$$

The Coulomb interaction \underline{H}_{Cb} (2.31) does not depend on the spin coordinates. The spins therefore couple to the motion of the nuclei by exchange interaction in the sense that

$$[\underline{P}^{n\sigma}, \underline{S}(\alpha)] \neq 0 \quad \text{for some } \alpha \in O(3), \quad (3.24)$$

where $\underline{P}^{n\sigma}$ projects on the space A^σ being spanned by wave functions of the form

$$|\phi_i^n\rangle = \underline{c}_{\vec{R}_1, m_1}^{n\dagger} \underline{c}_{\vec{R}_2, m_2}^{n\dagger} \cdots \underline{c}_{\vec{R}_N, m_N}^{n\dagger} |0\rangle. \quad (3.25)$$

Because of relation (3.24) the operators

$$\underline{S}(\alpha) \underline{c}_{\vec{R}m}^{n\dagger} \underline{S}^\dagger(\alpha)$$

cannot be expressed, for some $\alpha \in O(3)$, as a linear combination of the fermion operators $\underline{c}_{\vec{R}'m'}^{n\dagger}$. The momentarily unsymmetrical charge distribution within a nonadiabatic localized state, characterized by a distinct value of the acceleration \vec{q} of the nucleus, hence depends on the spin direction (that is, on the spin coordinate t). The localized functions satisfying Eq. (3.20) are not products of a space function and a spin function [and Eq. (3.22) does not hold if one of the operators $\underline{P}(\alpha)$, $\underline{Q}(\alpha)$, or $\underline{S}(\alpha)$ is suppressed].

The nonadiabatic Coulomb interaction $\underline{H}_{Cb}^{n\sigma}$ (3.16) does not conserve the electronic spin angular momentum. The conservation law of angular momentum, however, should hold also within the nonadiabatic system. Thus relation (3.15),

$$[\underline{H}_{Cb}, \underline{S}(\alpha)] = 0 \quad \text{for } \alpha \in O(3),$$

which holds in the adiabatic system, should be replaced by an analogous relation which holds in the nonadiabatic system.

Let

$$\underline{M}(\alpha) = \underline{T}_{\vec{R}} \underline{P}(\alpha) \underline{Q}(\alpha) \underline{S}(\alpha) \underline{T}_{\vec{R}}^{-1} \quad (3.26)$$

be those space-group operators which leave unchanged the position \vec{R} of the localized function on which they are acting,

$$\begin{aligned} \underline{M}(\alpha) \langle \vec{r}, t, \vec{q} | \vec{R}, m, n \rangle \\ = \sum_{m'} d_{m'm}(\alpha) \langle \vec{r}, t, \vec{q} | \vec{R}, m', n \rangle \quad \text{for } \alpha \in G_0. \end{aligned} \quad (3.27)$$

In Eq. (3.26) $\underline{T}_{\vec{R}}$ denotes an operator representing a

translation from the origin \vec{R}_0 (with $\alpha\vec{R}_0 = \vec{R}_0$) to \vec{R} . The operators $\underline{M}(\alpha)$ commute with the operators $\underline{c}_{\vec{R}m}^n$ in the same way as the $\underline{S}(\alpha)$ commute with the $\underline{c}_{\vec{R}s}$, where $\underline{c}_{\vec{R}s}$ still annihilates an electron with spin s in a state represented by the Wannier function $w(\vec{r} - \vec{R})$ (2.1):

$$\underline{S}(\alpha)\underline{c}_{\vec{R}s}\underline{S}^\dagger(\alpha) = \sum_{s'} D_{s's}(\alpha)\underline{c}_{\vec{R}s'}, \quad \text{for } \alpha \in O(3) \quad (3.28)$$

[cf. (3.4)] and

$$\underline{M}(\alpha)\underline{c}_{\vec{R}m}^n \underline{M}^\dagger(\alpha) = \sum_{m'} d_{m'm}(\alpha)\underline{c}_{\vec{R}m'}^n, \quad \text{for } \alpha \in G_0, \quad (3.29)$$

$$\underline{M}(\alpha)\langle \vec{r}, t, \vec{q} | \vec{R}, m, n \rangle \langle \vec{r}, t, \vec{q} | \vec{R}', m', n \rangle$$

$$= [\underline{T}_{\vec{R}} \underline{P}(\alpha) \underline{Q}(\alpha) \underline{S}(\alpha) \underline{T}_{\vec{R}}^{-1} \langle \vec{r}, t, \vec{q} | \vec{R}, m, n \rangle] [\underline{T}_{\vec{R}'} \underline{P}(\alpha) \underline{Q}(\alpha) \underline{S}(\alpha) \underline{T}_{\vec{R}'}^{-1} \langle \vec{r}, t, \vec{q} | \vec{R}', m', n \rangle] \quad (3.31)$$

when $\underline{M}(\alpha)$ acts on a product of two localized functions belonging to different lattice points \vec{R} and \vec{R}' . This relation (3.31) shows that, in this case, the operators $\underline{M}(\alpha)$ are not space-group operators since the $\underline{M}(\alpha)$ effect a rotation of the coordinates \vec{r}, t, \vec{q} around centers \vec{R} and \vec{R}' , respectively, which are different for the two localized states. Thus (3.30) does not follow from the symmetry behavior (3.21) of the Hamiltonian \underline{H}_{Cb}^{ng} ; it is rather an additional condition.

The nonadiabatic operator of the Coulomb interaction \underline{H}_{Cb}^{ng} (3.16) does not conserve the angular momentum,

$$[\underline{H}_{Cb}^{ng}, \underline{M}(\alpha)] \neq 0 \quad \text{for some } \alpha \in G_0. \quad (3.32)$$

This follows from the very fact that \underline{H}_{Cb}^{ng} has matrix elements with $\{m_1, m_2\} \neq \{m'_1, m'_2\}$. Firstly, such matrix elements vanish if the localized functions are products of a space function and a spin function as was the case for the narrow s band considered in the preceding section, or secondly if the operator \underline{H}_{Cb} (2.31) commutes with operators turning \vec{r}_μ and \vec{r}_ν around different centers \vec{R} and \vec{R}' , respectively. Since both conditions are not fulfilled, (3.32) is true. [The adiabatic approximation \underline{H}_c^g (3.12) of \underline{H}_{Cb}^{ng} also does not commute with any of the operators $\underline{M}(\alpha)$ since it has matrix elements (3.10) with $\{m_1, m_2\} \neq \{m'_1, m'_2\}$. This follows simply from the properties of the SLF as given in (3.2) if $f_{sm}(\vec{k})$ is not independent of \vec{k} .]

The conservation law of angular momentum is thus violated within the electron system when the electron spins couple to the motion of the nuclei. This we interpret in the following way: In the nonadiabatic system, the nuclei are permanently accelerated in various directions. This includes the possibility that $\underline{H}_{HF} + \underline{H}_{Cb}^{ng}$ may have a ground state in which even the average positions of the nuclei move. Such a motion actually occurs when, according to (3.32), the electron system must give off angular momentum to the periodic array of the nuclei. In the next section we will show that the average positions of the nuclei are moved in such a way that phonons are excited or absorbed.

[cf. (3.27)]. Thus $\underline{M}(\alpha)$ must be identified as an operator turning the total spin angular momentum of the nonadiabatic localized state, and

$$[\underline{H}^{ng}, \underline{M}(\alpha)] = 0 \quad \text{for } \alpha \in G_0 \quad (3.30)$$

as the conservation law of angular momentum in the nonadiabatic system. \underline{H}^{ng} denotes the complete Hamiltonian of the σ band electrons which will be given in (5.1). According to (3.26) it is

IV. SPIN-PHONON INTERACTION IN A NARROW σ BAND

In this section the operator of spin-phonon interaction $\underline{H}_{s-ph}^{ng}$ will be derived from (3.32). We will give its matrix elements in terms of the nonadiabatic localized functions and of phonon functions in order to show that $\underline{H}_{s-ph}^{ng}$ is uniquely given. In Secs. V and VI, however, we will not need the equations determining $\underline{H}_{s-ph}^{ng}$. The only property of this operator which is used in the following sections is the commutation rule (4.27) and the fact that it does not vanish in a narrow σ band.

Let

$$\underline{b}_{\vec{R}l} = \frac{1}{\sqrt{M}} \sum_{\vec{k}} \sum_{\rho=1}^3 g_{l\rho}(\vec{k}) e^{-i\vec{k} \cdot \vec{R}} \underline{b}_{\vec{k}\rho} \quad (4.1)$$

(where BZ is the Brillouin zone) be the boson operators annihilating phonons in the localized phonon states $|\vec{R}, l\rangle$ being represented by localized functions of the form $\langle \vec{q}_1, \vec{q}_2, \dots, \vec{q}_M | \vec{R}, l \rangle$, which may depend on the \vec{q} coordinate of each of the M nuclei (in the \vec{q} representation). The operators $\underline{b}_{\vec{R}l}$ are constructed from the acoustic phonons of Bloch form, $\underline{b}_{\vec{k}\rho}$ (\vec{k} is the reduced wave vector and ρ labels the three acoustic branches), in the same manner as generalized Wannier functions¹² are constructed from Bloch functions. Thus the \vec{k} -dependent unitary matrix $g_{l\rho}(\vec{k})$ may be chosen such that¹² the localized states are optimally localized and that they transform according to

$$\underline{Q}(\alpha)\underline{b}_{\vec{R}l}\underline{Q}^\dagger(\alpha) = \sum_{l'} D_{l'l}(\alpha)\underline{b}_{\vec{R}l'}, \quad \text{for } \alpha \in G_0, \quad (4.2)$$

where the matrices $D_{l'l}(\alpha)$ belong to Γ_{15} in every cubic crystal.¹⁵ The localized phonon states are assumed to be orthogonal to each other and to the electron states.

\underline{H}_{Cb}^{ng} as given by (3.16) may give rise to an electron-phonon coupling since matrix elements of the form

$$\begin{aligned}
& \langle \vec{R}'_1, l_1, \vec{R}'_2, l_2; \vec{R}_1, m_1; \vec{R}_2, m_2 | \underline{H}_{Cb}^{n\sigma} | \vec{R}_1, m'_1, \vec{R}_2, m'_2 \rangle \\
&= \frac{e^2}{2} \sum_{u'} \int (\langle \vec{R}'_1, l_1 | \vec{q}_1, \dots, \vec{q}_M \rangle \langle \vec{R}'_2, l_2 | \vec{q}'_1, \dots, \vec{q}'_M \rangle \langle \vec{R}_1, m_1, n | \vec{r}, t, \vec{q}_{\vec{R}_1} \rangle \langle \vec{R}_2, m_2, n | \vec{r}', t', \vec{q}'_{\vec{R}_2} \rangle \\
&\quad \times \langle \vec{r}', t', \vec{q}'_{\vec{R}_2} | \vec{R}_2, m'_2, n \rangle \langle \vec{r}, t, \vec{q}_{\vec{R}_1} | \vec{R}_1, m'_1, n \rangle / |\vec{r} - \vec{r}'| d\vec{r} d\vec{r}' d\vec{q}_1, \dots, d\vec{q}_M d\vec{q}'_1, \dots, d\vec{q}'_M
\end{aligned} \tag{4.3}$$

will generally not vanish if $\langle \vec{q}_1, \dots, \vec{q}_M | \vec{R}'_1, l_1 \rangle$ and $\langle \vec{q}_1, \dots, \vec{q}_M | \vec{R}'_2, l_2 \rangle$ depends on $\vec{q}_{\vec{R}_1}$ and $\vec{q}_{\vec{R}_2}$, respectively (where $\vec{q}_{\vec{R}}$ denotes the acceleration of the nucleus on the lattice point \vec{R}). The conservation law of angular momentum for such an electron-phonon interaction is still expressed by (3.30) in which $\underline{M}(\alpha)$ acts on the boson operators $b_{\vec{R}l}$ according to

$$\underline{M}(\alpha) b_{\vec{R}l} \underline{M}^\dagger(\alpha) = \sum_l D_{l'l}(\alpha) b_{\vec{R}l'} \quad \text{for } \alpha \in G_0, \tag{4.4}$$

with $D_{l'l}(\alpha)$ belonging to Γ_{15} . Though the nonadiabatic localized functions are not explicitly known, some properties of the matrix elements (4.3) may be derived from the conservation law of angular momentum.

Under the action of $\underline{M}(\alpha)$ the fermion operators $\underline{c}_{\vec{R}m}^n$ transform according to Eq. (3.29) in which the matrices $d_{m'm}(\alpha)$ belong to Γ_6^+ , Γ_6^- , Γ_7^+ , or Γ_7^- in any σ band (still since we only consider cubic metals). The fermion operator products in the nonadiabatic Coulomb interaction $\underline{H}_{Cb}^{n\sigma}$ (3.16),

$$\underline{c}_{\vec{R}_1 m_1}^{n\dagger} \underline{c}_{\vec{R}_2 m_2}^{n\dagger} \underline{c}_{\vec{R}_2 m'_2}^n \underline{c}_{\vec{R}_1 m'_1}^n,$$

$$F_{\kappa}^{j\lambda}(\vec{R}_1, \vec{R}_2) = \sum_{m_1, m_2, m'_1, m'_2} h_{\kappa}^{*j\lambda}(m_1, m_2; m'_1, m'_2) \langle \vec{R}_1, m_1; \vec{R}_2, m_2 | \underline{H}_{Cb}^{n\sigma} | \vec{R}_1, m'_1; \vec{R}_2, m'_2 \rangle. \tag{4.8}$$

The basis vectors $\underline{e}_{\kappa}^{j\lambda}(\vec{R}_1, \vec{R}_2)$ of the j th representation are transformed unitarily once more,

$$\underline{\bar{e}}_{\kappa}^{j\lambda}(\vec{R}_1, \vec{R}_2) = \sum_{\kappa'} d_{\kappa\kappa'}^{j\lambda}(\vec{R}_1, \vec{R}_2) \underline{e}_{\kappa'}^{j\lambda}(\vec{R}_1, \vec{R}_2) \tag{4.9}$$

in order to make $F_{\kappa}^{j\lambda}(\vec{R}_1, \vec{R}_2)$ independent of κ . Such a transformation is possible since the basis of an irreducible representation may be rotated such that the components of a given vector are equal. The coefficients $d_{\kappa\kappa'}^{j\lambda}(\vec{R}_1, \vec{R}_2)$, however, will depend on \vec{R}_1 and \vec{R}_2 . Now $\underline{H}_{Cb}^{n\sigma}$ has the form

$$\underline{H}_{Cb}^{n\sigma} = \sum_{\lambda, \kappa, j, \vec{R}_1, \vec{R}_2} F_{\kappa}^{j\lambda}(\vec{R}_1, \vec{R}_2) \underline{\bar{e}}_{\kappa}^{j\lambda}(\vec{R}_1, \vec{R}_2) \tag{4.10}$$

with

$$\begin{aligned}
& F_{\kappa}^{j\lambda}(\vec{R}_1, \vec{R}_2) \\
&= \sum_{m_1, \dots, m'_2} \bar{h}_{\kappa}^{*j\lambda}(\vec{R}_1, \vec{R}_2; m_1, m_2; m'_1, m'_2) \\
&\quad \times \langle \vec{R}_1, m_1; \vec{R}_2, m_2 | \underline{H}_{Cb}^{n\sigma} | \vec{R}_1, m'_1; \vec{R}_2, m'_2 \rangle
\end{aligned} \tag{4.11}$$

form, for fixed \vec{R}_1 and \vec{R}_2 , a basis of the representation $\Gamma_i^* \times \Gamma_i^* \times \Gamma_i \times \Gamma_i$ with $i=6+, 6-, 7+,$ or $7-$. In each of the four cases we have

$$\Gamma_i^* \times \Gamma_i^* \times \Gamma_i \times \Gamma_i = 2\Gamma_1 + \Gamma_{12} + \Gamma'_{25} + 3\Gamma'_{15}. \tag{4.5}$$

Let

$$\begin{aligned}
\underline{e}_{\kappa}^{j\lambda}(\vec{R}_1, \vec{R}_2) &= \sum_{m_1, \dots, m'_2} h_{\kappa}^{j\lambda}(m_1, m_2; m'_1, m'_2) \\
&\quad \times \underline{c}_{\vec{R}_1 m_1}^{n\dagger} \underline{c}_{\vec{R}_2 m_2}^{n\dagger} \underline{c}_{\vec{R}_2 m'_2}^n \underline{c}_{\vec{R}_1 m'_1}^n
\end{aligned} \tag{4.6}$$

represent the 16 unitarily transformed vectors belonging to the reduced representation where κ labels the row of the j th representation ($j=1, 12, 15', 25'$) and λ distinguishes the two and three different sets belonging to Γ_1 and Γ'_{15} , respectively.

$\underline{H}_{Cb}^{n\sigma}$ (3.16) can be written as the sum

$$\underline{H}_{Cb}^{n\sigma} = \sum_{\lambda, j, \kappa, \vec{R}_1, \vec{R}_2} F_{\kappa}^{j\lambda}(\vec{R}_1, \vec{R}_2) \underline{e}_{\kappa}^{j\lambda}(\vec{R}_1, \vec{R}_2), \tag{4.7}$$

where

and

$$\begin{aligned}
& \bar{h}_{\kappa}^{j\lambda}(\vec{R}_1, \vec{R}_2; m_1, m_2; m'_1, m'_2) \\
&= \sum_{\kappa'} d_{\kappa\kappa'}^{j\lambda}(\vec{R}_1, \vec{R}_2) h_{\kappa'}^{j\lambda}(m_1, m_2; m'_1, m'_2).
\end{aligned} \tag{4.12}$$

The two terms of $\underline{H}_{Cb}^{n\sigma}$ (4.10) with $j=1$,

$$\begin{aligned}
\underline{H}_1^{n\sigma} &= \sum_{\vec{R}_1, \vec{R}_2} [F^{11}(\vec{R}_1, \vec{R}_2) \underline{\bar{e}}_1^{11}(\vec{R}_1, \vec{R}_2) \\
&\quad + F^{12}(\vec{R}_1, \vec{R}_2) \underline{\bar{e}}_1^{12}(\vec{R}_1, \vec{R}_2)],
\end{aligned} \tag{4.13}$$

conserve the angular momentum according to

$$[\underline{H}_1^{n\sigma}, \underline{M}(\alpha)] = 0 \quad \text{for } \alpha \in G_0. \tag{4.14}$$

The other terms of $\underline{H}_{Cb}^{n\sigma}$ do not conserve the angular momentum since they do not belong to the identical representation. For $j \neq 1$ the operator $\underline{\bar{e}}_{\kappa}^{j\lambda}(\vec{R}_1, \vec{R}_2)$ creates a well-defined additional electronic angular momentum characterized by j and κ . Now phonon operators will be constructed annihilating just this angular momentum.

Consider phonon-pair operators of the form

$$b_{\vec{R}_1 l_1}^\dagger b_{\vec{R}_2 l_2}^\dagger,$$

where $b_{\vec{R} l}$ is given by (4.1). They transform according to

$$\begin{aligned} \underline{M}(\alpha) b_{\vec{R}_1 l_1}^\dagger b_{\vec{R}_2 l_2}^\dagger \underline{M}^\dagger(\alpha) \\ = \sum_{l_1', l_2'} D_{l_1' l_2' l_1 l_2}^*(\alpha) b_{\vec{R}_1 l_1'}^\dagger b_{\vec{R}_2 l_2'}^\dagger \quad \text{for } \alpha \in G_0, \end{aligned} \quad (4.15)$$

where the matrices $D_{l_1' l_2' l_1 l_2}^*(\alpha)$ belong to the representation $\Gamma_{15}^* \times \Gamma_{15}^*$. The reduction of this representation yields the direct sum

$$\Gamma_{15}^* \times \Gamma_{15}^* = \Gamma_1 + \Gamma_{12} + \Gamma_{25}' + \Gamma_{15}', \quad (4.16)$$

which contains each representation (4.5) exactly once.

Let

$$\underline{\beta}_{\vec{R}_1, \vec{R}_2}^j = \sum_{l_1, l_2} u_{\kappa}^j(l_1, l_2) b_{\vec{R}_1 l_1}^\dagger b_{\vec{R}_2 l_2}^\dagger \quad (4.17)$$

be the nine unitarily transformed basis vectors of the irreducible representations Γ_j (with $j=1, 12, 25', 15'$). $\Gamma_j \times \Gamma_j$ contains the identical representation Γ_1 exactly once, whereas $\Gamma_j \times \Gamma_{j'}$ does not contain Γ_1 if $j \neq j'$. Thus there exists a unitary matrix $g_{\kappa\kappa'}^{j\lambda}(\vec{R}_1, \vec{R}_2)$ so that, for a given \vec{R}_1 and \vec{R}_2 ,

$$\sum_{H, \kappa'} g_{\kappa\kappa'}^{j\lambda}(\vec{R}_1, \vec{R}_2) \underline{\epsilon}_{\kappa}^{j\lambda}(\vec{R}_1, \vec{R}_2) \underline{\beta}_{\kappa'}^j(\vec{R}_1, \vec{R}_2) \quad (4.18)$$

is a basis vector of Γ_1 . The most general basis vector of Γ_1 has the form

$$\sum_{\kappa} \underline{\epsilon}_{\kappa}^{j\lambda}(\vec{R}_1, \vec{R}_2) \underline{\beta}_{\kappa}^{j\lambda}(\vec{R}_1, \vec{R}_2) \quad (4.19)$$

with

$$\begin{aligned} \underline{\beta}_{\kappa}^{j\lambda}(\vec{R}_1, \vec{R}_2) = \sum_{\vec{R}_1', \vec{R}_2', \kappa'} c_{\kappa'}^{j\lambda}(\vec{R}_1, \vec{R}_2; \vec{R}_1', \vec{R}_2') \\ \times g_{\kappa\kappa'}^{j\lambda}(\vec{R}_1, \vec{R}_2) \underline{\beta}_{\kappa'}^j(\vec{R}_1', \vec{R}_2'), \end{aligned} \quad (4.20)$$

where the coefficients $c_{\kappa'}^{j\lambda}(\vec{R}_1, \vec{R}_2; \vec{R}_1', \vec{R}_2')$ are arbitrary except for

$$\sum_{\vec{R}_1', \vec{R}_2'} c_{\kappa}^{j\lambda}(\vec{R}_1, \vec{R}_2; \vec{R}_1', \vec{R}_2') c_{\kappa'}^{*j\lambda}(\vec{R}_1'', \vec{R}_2''; \vec{R}_1', \vec{R}_2') \\ = \delta_{\vec{R}_1' \vec{R}_1''} \delta_{\vec{R}_2' \vec{R}_2''} \quad (4.21)$$

$$\underline{H}_{s\text{-ph}}^{n\sigma} = \sum_{\vec{R}, m, l} \langle \vec{R}_1', l_1; \vec{R}_2', l_2; \vec{R}_1, m_1; \vec{R}_2, m_2 | \underline{H}_{Cb}^{n\sigma} | \vec{R}_1, m_1'; \vec{R}_2, m_2' \rangle b_{\vec{R}_1 l_1}^\dagger b_{\vec{R}_2 l_2}^\dagger \underline{\epsilon}_{\vec{R}_1 m_1}^{n\sigma} \underline{\epsilon}_{\vec{R}_2 m_2}^{n\sigma} \underline{\epsilon}_{\vec{R}_2 m_2'}^n \underline{\epsilon}_{\vec{R}_1 m_1'}^n + \text{H.c.}, \quad (4.28)$$

where the matrix elements of this operator are, in principle, given by (4.3). From (4.23) it follows [with (4.6), (4.17), (4.20), and (4.21)] that

$$\begin{aligned} \langle \vec{R}_1', l_1; \vec{R}_2', l_2; \vec{R}_1, m_1; \vec{R}_2, m_2 | \underline{H}_{Cb}^{n\sigma} | \vec{R}_1, m_1'; \vec{R}_2, m_2' \rangle \\ = \frac{1}{2} \sum_{\lambda, \kappa, \kappa', j \neq 1} \bar{h}_{\kappa}^{j\lambda}(\vec{R}_1, \vec{R}_2; m_1, m_2; m_1', m_2') g_{\kappa\kappa'}^{j\lambda}(\vec{R}_1, \vec{R}_2) c_{\kappa}^{j\lambda}(\vec{R}_1, \vec{R}_2; \vec{R}_1', \vec{R}_2') u_{\kappa}^j(l_1, l_2) F^{j\lambda}(\vec{R}_1, \vec{R}_2), \end{aligned} \quad (4.29)$$

in order for the transformation (4.20) to be unitary.

Thus if we replace in Eq. (4.10) the electronic operator

$$\underline{\epsilon}_{\kappa}^{j\lambda}(\vec{R}_1, \vec{R}_2)$$

by

$$\underline{\epsilon}_{\kappa}^{j\lambda}(\vec{R}_1, \vec{R}_2) \underline{\beta}_{\kappa}^{j\lambda}(\vec{R}_1, \vec{R}_2), \quad (4.22)$$

we obtain an interaction

$$\underline{H}_{s\text{-ph}} = \sum_{j, \lambda, \kappa, \vec{R}_1, \vec{R}_2} F^{j\lambda}(\vec{R}_1, \vec{R}_2) \underline{\epsilon}_{\kappa}^{j\lambda}(\vec{R}_1, \vec{R}_2) \underline{\beta}_{\kappa}^{j\lambda}(\vec{R}_1, \vec{R}_2), \quad (4.23)$$

conserving the angular momentum

$$[\underline{H}_{s\text{-ph}}, \underline{M}(\alpha)] = 0 \quad \text{for } \alpha \in G_0. \quad (4.24)$$

The summation over j in (4.23) is restricted to $j=12, 15'$, and $25'$. We may say that the phonon operator $\underline{\beta}_{\kappa}^{j\lambda}(\vec{R}_1, \vec{R}_2)$ annihilates the angular momentum created by $\underline{\epsilon}_{\kappa}^{j\lambda}(\vec{R}_1, \vec{R}_2)$. Thus from the conservation law of angular momentum we conclude that $\underline{\epsilon}_{\kappa}^{j\lambda}(\vec{R}_1, \vec{R}_2)$ creates a charge distribution which accelerates the nuclei in such a way that the phonon pair $\underline{\beta}_{\kappa}^{j\lambda}(\vec{R}_1, \vec{R}_2)$ arises. Therefore, we replace the operator $\underline{H}_{Cb}^{n\sigma}$ (3.16) by

$$\underline{\tilde{H}}_{Cb}^{n\sigma} = \underline{H}_1^{n\sigma} + \underline{H}_{s\text{-ph}}^{n\sigma} \quad (4.25)$$

with

$$\underline{H}_{s\text{-ph}}^{n\sigma} = \frac{1}{2} \underline{H}_{s\text{-ph}} + \frac{1}{2} \underline{H}_{s\text{-ph}}^\dagger, \quad (4.26)$$

where $\underline{H}_1^{n\sigma}$ and $\underline{H}_{s\text{-ph}}$ is given by (4.13) and (4.23), respectively.

Now the complete nonadiabatic Coulomb interaction $\underline{\tilde{H}}_{Cb}^{n\sigma}$ conserves the angular momentum since relation (4.14) holds for the Coulomb repulsion $\underline{H}_1^{n\sigma}$ and, according to (4.24), it is

$$[\underline{H}_{s\text{-ph}}^{n\sigma}, \underline{M}(\alpha)] = 0 \quad \text{for } \alpha \in G_0. \quad (4.27)$$

The interaction $\underline{H}_{s\text{-ph}}^{n\sigma}$ may be called a spin-phonon interaction since it is caused by coupling of the electron spins to the motion of the nuclei. It is an exchange interaction since the spins couple to the motion of nuclei by exchange interaction.

The operator $\underline{H}_{s\text{-ph}}^{n\sigma}$ can be written as

with $F^{j\lambda}(\vec{R}_1, \vec{R}_2)$ given by (4.11). All coefficients in this equation are determined by group theory except for the coefficients $c_k^{j\lambda}(\vec{R}_1, \vec{R}_2; \vec{R}'_1, \vec{R}'_2)$ depending on the form of the nonadiabatic localized electron and phonon functions. This uncertainty is meaningless since in the following we only need Eq. (4.27).

One problem cannot be solved by group theory: It is possible that a part of $\underline{H}_1^{n\sigma}$ also depends on phonon operators since both $\underline{\epsilon}_1^{1\lambda}(\vec{R}_1, \vec{R}_2)$ and $\underline{\epsilon}_1^{1\lambda}(\vec{R}_1, \vec{R}_2)\underline{\beta}_1^{1\lambda}(\vec{R}_1, \vec{R}_2)$ [cf. (4.22)] belong to Γ_1 . In this case this part of $\underline{H}_1^{n\sigma}$ would also belong to $\underline{H}_{s-ph}^{n\sigma}$. This question, however, is meaningless in the following.

V. SPIN-PHONON INTERACTION AT ZERO TEMPERATURE

Let

$$\underline{H}^{n\sigma} = \underline{H}_{HF} + \underline{H}_1^{n\sigma} + \underline{H}_{s-ph}^{n\sigma} + \underline{H}_{ph} \quad (5.1)$$

represent the Hamiltonian operator in a narrow σ band where $\underline{H}_1^{n\sigma}$ is the Coulomb repulsion (4.13), $\underline{H}_{s-ph}^{n\sigma}$ the spin-phonon interaction (4.28), and

$$\underline{H}_{ph} = \sum_{\vec{k}, \rho} E_{\vec{k}\rho} (b_{\vec{k}\rho}^\dagger b_{\vec{k}\rho} + \frac{1}{2}) \quad (5.2)$$

is the operator of phonon energy. The spin-independent electron-phonon interaction \underline{H}_{e-ph} (5.25) and the contribution of the electrons of the other conduction bands are disregarded. Assume that $\underline{H}_{s-ph}^{n\sigma} + \underline{H}_{ph}$ may be approximated by an electron-electron interaction \underline{W} by a canonical transformation in analogy to the well-known procedure first discussed by Fröhlich.¹ Now the Hamiltonian

$$\underline{H}_0^{n\sigma} = \underline{H}_{HF} + \underline{H}_1^{n\sigma} + \underline{W} \quad (5.3)$$

does not depend on boson operators and hence represents the electron-phonon system at zero temperature. Since $\underline{H}_{s-ph}^{n\sigma}$ conserves the angular momentum (4.27) we have

$$[\underline{W}, \underline{M}(\alpha)] = 0 \quad \text{for } \alpha \in G_0, \quad (5.4)$$

and thus (in the simplest case)

$$\underline{M}(\alpha) |G_0^{n\sigma}\rangle = |G_0^{n\sigma}\rangle \quad \text{for } \alpha \in G_0, \quad (5.5)$$

where $|G_0^{n\sigma}\rangle$ denotes the ground state of $\underline{H}_0^{n\sigma}$. Within $|G_0^{n\sigma}\rangle$, real phonons are not excited since $\underline{H}_0^{n\sigma}$ does not depend on phonon operators. The phonon system does not store angular momentum but only can mediate (via virtual phonons) a coupling between the electron spins. In the system represented by $\underline{H}_0^{n\sigma}$ the electron spin is hence a conserved quantity, yielding

$$[\underline{W}, \underline{S}(\alpha)] = 0 \quad \text{for } \alpha \in O(3) \quad (5.6)$$

and

$$\underline{S}(\alpha) |G_0^{n\sigma}\rangle = |G_0^{n\sigma}\rangle \quad \text{for } \alpha \in O(3). \quad (5.7)$$

Within this new system, the localized electron states are represented by adiabatic functions, i.e., by the spin-dependent localized functions (3.2) in the case of the considered σ band. This is because the nonadiabatic fermion operators $\underline{c}_{\vec{R}m}^{n\sigma}$ and $\underline{c}_{\vec{R}m}^n$ (as defined in Sec. III) are not

labeled by the spin quantum number s and hence any state in the space A^σ being spanned by wave functions of the form (3.25) does not satisfy (5.7). In fact, the electron system becomes adiabatic when $\underline{H}_{s-ph}^{n\sigma} + \underline{H}_{ph}$ is (approximately) replaced by \underline{W} though the electron spins still couple to the motion of nuclei at zero temperature. This coupling, however, mediates (via virtual phonons) an *electron-electron* interaction which now is represented by \underline{W} .

The interaction \underline{W} is just as an exchange interaction as is $\underline{H}_{s-ph}^{n\sigma}$. Though \underline{W} is not explicitly known at this state, we may derive from (5.5) and (5.7) that under the action of \underline{W} the electron spins are coupled in such a way that Cooper pairs arise.

At a first step we show that any given state generally does not satisfy both conditions (5.5) and (5.7). Consider the state

$$|\phi\rangle = \sum_m d(m_1, m_2, \dots, m_N) \underline{c}_{\vec{k}_1 m_1}^\dagger \underline{c}_{\vec{k}_2 m_2}^\dagger \cdots \underline{c}_{\vec{k}_N m_N}^\dagger |0\rangle, \quad (5.8)$$

with N being the number of electrons and

$$\underline{c}_{\vec{k}m}^\dagger = \frac{1}{\sqrt{M}} \sum_{\vec{R}} e^{-i\vec{k}\cdot\vec{R}} \underline{c}_{\vec{R}m}^\dagger, \quad (5.9)$$

where $\underline{c}_{\vec{R}m}^\dagger$ still creates an electron in the state $|\vec{R}, m\rangle$ represented by the SLF (3.2). The coefficients $d(m_1, m_2, \dots, m_N)$ are assumed to be chosen in such a way that

$$\underline{M}(\alpha) |\phi\rangle = |\phi\rangle. \quad (5.10)$$

Using

$$\underline{c}_{\vec{k}m}^\dagger = \sum_s f_{sm}^*(\vec{k}) \underline{c}_{\vec{k}s}^\dagger, \quad (5.11)$$

which follows from (3.2) [cf. (3.6)], we may transform $|\phi\rangle$ into the s representation,

$$|\phi\rangle = \sum_s d(\vec{k}_1, s_1, \vec{k}_2, s_2, \dots, \vec{k}_N, s_N) \times \underline{c}_{\vec{k}_1 s_1}^\dagger \underline{c}_{\vec{k}_2 s_2}^\dagger \cdots \underline{c}_{\vec{k}_N s_N}^\dagger |0\rangle, \quad (5.12)$$

with

$$d(\vec{k}_1, s_1; \vec{k}_2, s_2, \dots, \vec{k}_N, s_N) = \sum_m d(m_1, m_2, \dots, m_N) f_{s_1 m_1}^*(\vec{k}_1) \cdots f_{s_N m_N}^*(\vec{k}_N). \quad (5.13)$$

Assume that, for given values of $\vec{k}_1, \vec{k}_2, \dots, \vec{k}_N$, we have $\underline{S}(\alpha) |\phi\rangle = |\phi\rangle$ for $\alpha \in O(3)$. Assume further that one \vec{k} vector, e.g., \vec{k}_i , is slightly changed. That means that the coefficients $d(\vec{k}_1, s_1; \vec{k}_2, s_2, \dots, \vec{k}_N, s_N)$ are also modified since $f_{sm}^*(\vec{k})$ is not independent of \vec{k} in a σ band, and thus the relation $\underline{S}(\alpha) |\phi\rangle = |\phi\rangle$ for $\alpha \in O(3)$ in general will not hold when \vec{k}_i is changed.

As a second step we show that states of the form

$$|\phi_p\rangle = \underline{\beta}_{\vec{k}_1}^\dagger \underline{\beta}_{\vec{k}_2}^\dagger \cdots \underline{\beta}_{\vec{k}_N/2}^\dagger |0\rangle \quad (5.14)$$

fulfill both (5.5) and (5.7) where the new operators

$$\underline{\beta}_{\vec{k}}^{\dagger} = \underline{c}_{\vec{k}m}^{\dagger} \underline{c}_{-\vec{k},-m}^{\dagger} - \underline{c}_{\vec{k},-m}^{\dagger} \underline{c}_{-\vec{k},m}^{\dagger} \quad (5.15)$$

create symmetrized Cooper pairs. In this context we assume that the electron system is invariant under time inversion, i.e., we assume (3.5) to be true (the validity of this relationship has been proven in Ref. 13). Obviously, we have

$$[\underline{\beta}_{\vec{k}}^{\dagger}, \underline{M}(\alpha)] = 0 \quad \text{for } \alpha \in G_0. \quad (5.16)$$

With (5.11) we obtain

$$\begin{aligned} \underline{\beta}_{\vec{k}}^{\dagger} = \sum_{ss'} [f_{sm}^*(\vec{k}) f_{s',-m}^*(-\vec{k}) \underline{c}_{\vec{k},s}^{\dagger} \underline{c}_{-\vec{k},s'}^{\dagger} \\ - f_{s,-m}^*(\vec{k}) f_{s'm}^*(-\vec{k}) \underline{c}_{\vec{k},s}^{\dagger} \underline{c}_{-\vec{k},s'}^{\dagger}] \end{aligned} \quad (5.17)$$

leading to

$$\underline{\beta}_{\vec{k}}^{\dagger} = \underline{c}_{\vec{k}s}^{\dagger} \underline{c}_{-\vec{k},-s}^{\dagger} - \underline{c}_{\vec{k},-s}^{\dagger} \underline{c}_{-\vec{k},s}^{\dagger}, \quad (5.18)$$

since

$$f_{sm}(-\vec{k}) = \pm f_{-s,-m}^*(\vec{k}), \quad (5.19)$$

which follows from (3.5). The plus sign in Eq. (5.19) holds for $m=s$ and the minus sign for $m=-s$. In fact, (5.18) gives

$$[\underline{\beta}_{\vec{k}}^{\dagger}, \underline{S}(\alpha)] = 0 \quad \text{for } \alpha \in O(3). \quad (5.20)$$

Because of (5.16) and (5.20) the states $|\phi_P\rangle$ (5.14) fulfill both conditions (5.5) and (5.7).

In contrast to any given state, the paired state conserves the spin angular momentum and the exchange interaction \underline{W} , hence effects such as a paired state [or another *particular* state fulfilling both conditions (5.5) and (5.7)]. An essential property of \underline{W} can be derived from (5.4) and (5.6). Assume that \underline{W} may be represented by a two-electron interaction,

$$\begin{aligned} \underline{W} = \sum_{\vec{k},s} \langle \vec{k}_1, s_1; \vec{k}_2, s_2 | \underline{W} | \vec{k}'_1, s'_1; \vec{k}'_2, s'_2 \rangle \\ \times \underline{c}_{\vec{k},s_1}^{\dagger} \underline{c}_{\vec{k}_2, s_2}^{\dagger} \underline{c}_{\vec{k}'_2, s'_2} \underline{c}_{\vec{k}'_1, s'_1} \end{aligned} \quad (5.21)$$

As shown above, the only fermion operator combinations of the form

$$\sum_s d(s_1, s_2; s'_1, s'_2) \underline{c}_{\vec{k}_1, s_1}^{\dagger} \underline{c}_{\vec{k}_2, s_2}^{\dagger} \underline{c}_{\vec{k}'_2, s'_2} \underline{c}_{\vec{k}'_1, s'_1},$$

which commute with both $\underline{S}(\alpha)$ [for $\alpha \in O(3)$] and $\underline{M}(\alpha)$ (for $\alpha \in G_0$) are given by

$$\underline{\beta}_{\vec{k}}^{\dagger} \underline{\beta}_{\vec{k}},$$

[cf. (5.15)], and hence \underline{W} has the form

$$\underline{W} = \sum_{\vec{k}, \vec{k}'} \langle \vec{k} | \underline{W} | \vec{k}' \rangle \underline{\beta}_{\vec{k}}^{\dagger} \underline{\beta}_{\vec{k}'}, \quad (5.22)$$

Thus the interaction \underline{W} is strongly \vec{k} and spin dependent since

$$\begin{aligned} \langle \vec{k}_1, s_1; \vec{k}_2, s_2 | \underline{W} | \vec{k}'_1, s'_1; \vec{k}'_2, s'_2 \rangle = 0 \\ \text{for } \vec{k}_1 \neq -\vec{k}_2, \vec{k}'_1 \neq -\vec{k}'_2, s_1 \neq -s_2, \\ \text{or } s'_1 \neq -s'_2. \end{aligned} \quad (5.23)$$

The validity of Eq. (5.23) is the main feature which distinguishes \underline{W} from the electron-electron interaction

$$\underline{V} = \sum_{\vec{k},s} \langle \vec{k}_1, \vec{k}_2 | \underline{V} | \vec{k}'_1, \vec{k}'_2 \rangle \underline{c}_{\vec{k}_1, s_1}^{\dagger} \underline{c}_{\vec{k}_2, s_2}^{\dagger} \underline{c}_{\vec{k}'_2, s'_2} \underline{c}_{\vec{k}'_1, s'_1}, \quad (5.24)$$

which can be derived¹ from the spin-independent electron-phonon interaction

$$\underline{H}_{e-ph} = \sum_{\vec{k},s} \langle \vec{k}, \vec{k}_1 | \underline{H}_{e-ph} | \vec{k}'_1 \rangle \underline{b}_{\vec{k}}^{\dagger} \underline{c}_{\vec{k}_1, s}^{\dagger} \underline{c}_{\vec{k}'_1, s} + \text{H.c.} \quad (5.25)$$

by a canonical transformation of $\underline{H}_{e-ph} + \underline{H}_{ph}$. The non-vanishing matrix elements of \underline{W} , on the other hand, should be able to calculate to sufficient accuracy when $\underline{H}_{s-ph}^{n\sigma}$ is replaced by a spin-independent electron-phonon interaction of the form (5.25). It is true that $\underline{H}_{s-ph}^{n\sigma}$ (4.28) describes a two-electron two-phonon process. This, however, does not mean that the two phonons become excited (or absorbed) simultaneously since $\underline{H}_{s-ph}^{n\sigma}$ does not depend on time. The special form of $\underline{H}_{s-ph}^{n\sigma}$ should be interpreted by stating that, after a certain one-electron one-phonon process, the probability for another correlated one-electron one-phonon process rises. Thus for the calculation of the energy gap and other expectation values of the superconducting state it should be sufficient to replace $\underline{H}_{s-ph}^{n\sigma}$ by a one-electron, one-phonon interaction. Furthermore, since in an unpaired state the conservation of spin angular momentum is violated, \underline{W} is necessarily effecting a state in which the electrons form Cooper pairs, and hence \underline{W} will necessarily have a form required by theory for the onset of superconductivity. The accurate (two-electron, two-phonon) form of $\underline{H}_{s-ph}^{n\sigma}$ serves only to show the validity of (4.27) and hence to derive Eq. (5.23).

One may ask whether spin-phonon exchange interaction is necessary for superconductivity. A strong indication for such a necessity is the finding¹⁶ that those metals (such as Li, Na, K, Rb, Cs, Ca, Cu, Ag, and Au) which do not have a narrow, partly filled σ band do not become superconducting (at atmospheric pressure) down to the lowest temperatures investigated so far.

The assumption that spin-phonon exchange interaction is necessary for the Hamiltonian to have eigenstates in which the electrons form Cooper pairs would not contradict the theory of superconductivity which is based on the Eliashberg theory. As is well known, this theory is a perturbation theory in which the superconducting ground state is used as the zero approximation,¹⁷ i.e., this perturbation theory is applicable only to a Hamiltonian which has eigenstates in which the electrons form Cooper pairs. In the following we argue that as a matter of principle it is only \underline{W} that can have paired eigenstates.

Two electrons forming a Cooper pair (5.15) are described by *two* quantum numbers \vec{k} and s , whereas two unpaired electrons are characterized by *four* quantum numbers $\vec{k}_1, s_1, \vec{k}_2$, and s_2 . Accordingly, the number of degrees of freedom of the electronic motion (within a

small energy range Δ about the Fermi level) in a state of Cooper pairs is one-half that in an unpaired state. According to Eq. (5.22), the number of electronic coordinates on which \underline{W} depends also is one-half of those on which \underline{V} (5.24) depends. That is, only \underline{W} belongs to an N -electron system in which the electrons have one-half of the number of degrees of freedom of an unpaired state. In a classical system, the number of degrees of freedom of any state of motion of N particles is given by the number of independent coordinates on which the Hamiltonian function depends, i.e., it is prescribed. If this is also true in a quantum system, then \underline{V} has only unpaired eigenstates and it is the exchange interaction \underline{W} that has eigenstates in which the electrons form Cooper pairs.

Equation (5.23) is an equation of constraint. The effect of (5.23) may be described in terms of a quantity which in classical physics is called a constraining force that forces the electrons to form a state in which they have less degrees of freedom than in the normal state. If in a quantum system such constraining forces have a similar meaning as in a classical system, the Eliashberg theory would be applicable to the spin-phonon interaction only. As stated above, this would mean only a small extension of existing theories, though \underline{W} and \underline{V} have quite different physical interpretations. This new aspect might help to predict which materials become superconducting and which do not.

VI. CONDITION FOR SUPERCONDUCTIVITY

Assuming relationship (3.13) to hold in a narrow σ band, nonadiabatic localized functions satisfying (3.20) to exist, and (5.23) to be necessary for superconductivity, we formulate the following conditions for the occurrence of superconductivity.

(i) A metal is a superconductor only if one of its narrowest partly filled bands is a σ band.

The well-known BCS formula

$$T_c = 1.14\Theta e^{-1/N_0^{\sigma}V} \quad (6.1)$$

must then be replaced by

$$T_c = 1.14\Theta e^{-1/N_0^{\sigma}W}, \quad (6.2)$$

where N_0^{σ} is the density of states at the Fermi level of the electrons belonging to the σ band and W is a mean value of the matrix elements of \underline{W} .

The exchange interaction \underline{W} also depends on N_0^{σ} . We remember that the electron spins couple to the motion of the nuclei in order to suppress transitions represented by the matrix elements of \underline{H}_{Cb} (3.9) with $\{\vec{R}_1, \vec{R}_2\} \neq \{\vec{R}'_1, \vec{R}'_2\}$. Thus W will be large if there exists a great number of both occupied and unoccupied localized states in the σ band, i.e., if the σ band is nearly half-filled.

Therefore, the condition for high T_c in metals with comparable band structure (and comparable Debye temperature Θ) reads as follows.

(ii) T_c is higher the more closely the σ band is half-filled.

The first condition (i) proved indeed to be true for the 18 cubic-symmetry (superconducting and nonsupercon-

ducting) metals investigated recently.¹⁶ Comparing the four metals Nb, Ta, Mo, and W we found that, in accordance with Eq. (6.2) and the second condition (ii), the transition temperature T_c of these metals is higher as N_0^{σ} increases in size (cf. Fig. 1 of Ref. 16). Furthermore, band-structure calculations on a number of organic superconductors show that high T_c is connected with nearly half-filled narrow bands.¹⁸

To a first approximation, Eq. (6.2) does not depend on the spin-independent electron-phonon interaction or on the density of states at the Fermi level of the electrons which do not belong to the σ band. The influence of these quantities on the value of T_c will indeed be small since the interaction \underline{V} (5.24) does not follow Eq. (5.23), and hence superconductivity is, in the framework of our theory, a σ -band phenomenon. From (6.2), however, it cannot be concluded that only the σ -band electrons form Cooper pairs at zero temperature since σ -band electrons and non- σ -band electrons are coupled to each other by Coulomb interaction. The behavior of the non- σ -band electrons at zero temperature cannot yet be treated in this paper.

VII. SUMMARY

Since the conduction bands of metals are degenerate in several symmetry points of the Brillouin zone we generally cannot construct, from the conduction bands alone, Wannier functions which are both optimally localized and belong to a representation of the point group. Rather, we must combine several bands to a band group in order to construct "generalized" Wannier functions. Such a band group in general also contains completely filled and completely empty bands, and is energetically broader than the conduction bands alone.

The atomic or Heisenberg model is useful for metals with energetically narrow conduction bands. Therefore, if we want to apply this model to the conduction electrons of a given metal, we must assign the corresponding localized functions to (partly filled) bands or band groups which should be *as narrow as possible*. This can be achieved in a natural way if the existence of the electron spin is taken into account and the localized functions are then allowed to belong to a *double-valued* representation of the point group. The existence of such localized functions which are called spin-dependent localized functions is established by group theory. There are even metals which possess a *single* (but nonisolated) conduction band within their band structure which can be represented by optimally localized functions belonging to a two-dimensional, double-valued representation of the point group. Such single bands are called σ bands.

In this paper those cubic metals (such as Nb, V, Ta, Mo, W, and Al) have been considered which exhibit a narrow σ conduction band. By narrow we mean that the σ band is one of the *narrowest*, partly filled bands of these metals. We argue that, in the framework of the Heisenberg model, relationship (3.13) holds in sufficiently narrow conduction bands. This relationship is essential for our considerations. Since we cannot prove that the real metallic conduction bands are sufficiently narrow for (3.13) to apply, we postulate (3.13) to be true for the narrowest, partly filled bands which exist in the band struc-

ture of a given metal.

A second basic assumption is that there exist nonadiabatic localized functions satisfying Eq. (3.20), belonging to a representation of the point group [cf. (3.22)], and being orthogonal [cf. (3.19)]. From the properties of the localized functions and the conservation law of angular momentum we conclude that (a) the electron spins are coupled to phonons by exchange interaction in a narrow σ conduction band, and that (b) at zero temperature the electrons are coupled to each other via spin-phonon interaction in such a way that the electrons necessarily form Cooper pairs. The interaction \overline{W} effecting this electron-electron coupling at zero temperature is strongly momentum and spin dependent. Therefore, it resembles, with respect to this spin-dependence, the familiar Heisenberg interaction which couples the spins in a magnetic ordered state. The interaction \overline{W} , however, does not effect a state ordered in real space. The paired state may be called "ordered in \vec{k} space" in the sense that the momenta and spins of the electrons couple by exchange interaction in such a way that two electrons forming a Cooper pair have vanishing total momentum and total spin.

Since the interaction \overline{W} is mediated by virtual phonons, the transition from the unpaired state to the paired state is described in the familiar way by the BCS theory and its extensions. The question, however, of which materials are superconductors and which are not is treated in an unusual way in this paper.

The spin-phonon interaction does not act between single-electron spins and phonons. Rather, it couples the total electron system to the phonons in the sense that the electrons are coupled to each other and to phonons by ex-

change interaction. The phonons enter since the initial spin-spin exchange interaction does not conserve spin angular momentum within the electron system alone.

The spin-phonon interaction exists below and above the superconducting transition temperature T_c . We are not yet able to give the temperature T_s at which this interaction disappears. We believe that T_s is of the order of magnitude of Curie temperatures, and hence the spin-phonon interaction, or some effective spin-spin interaction, might be experimentally established in some superconductors even at room temperature. Such experiments might allow one to distinguish a superconductor from a nonsuperconductor at temperatures far above T_c .

In the framework of our considerations, the electronic behavior within the normal state below the superconducting transition temperature T_c (forced by a magnetic field) is still an open problem. At zero temperature, the electron spin must be a conserved quantity [cf. (5.6)] also in this "forced normal state." Since the electrons cannot pair, this state must have a different interesting feature distinguishing it from the normal state above T_c . One possible feature being compatible with the present theory would be the existence of a magnetic order within this forced normal state.¹⁹

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