PHYSICAL REVIEW VOLUME 134, NUMBER 4A 18 MAY 1964

Effect of Correlation on the Ferromagnetism of Transition Metals

MARTIN C. GUTZWILLER
*IBM Zurich Research Laboratory, Ruschlikon, Zurich, Switzerland**

(Received 17 October 1963; revised manuscript received 13 December 1963)

The wave function for the electrons is investigated when a set of narrow bands (valence states) has its energies within a wide band (conduction states). The valence states are linear combinations of localized states which are attached to each lattice site. The intra-atomic Coulomb and exchange integrals for the localized states are much larger than the bandwidths of the valence states. Some of the narrow bands are neither completely empty nor completely filled. The wave function is therefore expected to be correlated, because it is disadvantageous for the electrons to crowd into the same lattice site, or take up some configuration contrary to Hund's rule. This correlation is important in transition metals, where it is considered to be the cause of ferromagnetism. The correlated wave function is obtained by applying to the uncorrelated antisymmetrized product of Bloch functions an operator which provides each configuration of localized valence states with an appropriate amplitude and phase factor. The procedure is worked out in detail for the case of few particles (electrons or holes) in the narrow bands with the help of a diagram analysis. The localized orbits of different lattice sites do not have to be orthogonal to one another, and the computational rules are actually simplified thereby. The example of a twofold degenerate band such as the upper part of the 3*d* band in Ni is treated, and the conditions for the occurrence of ferromagnetism are stated in the case of few 3*d* holes per lattice site.

INTRODUCTION

THE present work studies the correlation of electrons in a situation which is considered as typical for the 3*d* electrons in a transition metal. The characteristic features of the valence and the conduction electrons in the transition metals are not obtained from first principles, but they are assumed according to a number of experimental facts and their intuitive interpretation in order to yield a model Hamiltonian. The aim is therefore to find an approximate ground-state wave function for the model Hamiltonian, and to investigate the mechanisms which tend to favor a ferromagnetic ground state.

In accord with other theories for the transition metals[1] it is assumed that there is a fairly clear cut distinction between three types of electronic states: the core states representing the atomic 1*s*, 2*s*, 2*p*, 3*s*, and 3*p* orbits, the valence states corresponding to the atomic 3*d* orbits, and the conduction states corresponding to the atomic 4*s* orbits. Each set of states is orthogonal to the two others, and there will be no correlation between two orbits belonging to different sets.

This is the most obvious assumption about the electrons in a transition metal, and it is certainly not definitive. But it is felt that this complete separation between the 3*d* and the 4*s* electrons can be lifted in a later, refined model without basically changing the present results.

There is some striking experimental evidence in favor of the independence and completely different orbital character of the valence electrons on one hand and of the conduction electrons on the other. Neutron diffraction in iron[2] has shown that the magnetization density in the lattice is mostly concentrated very tightly around the lattice sites, whereas a small fraction of the total magnetization is distributed uniformly throughout the lattice. The simple linear dependence of magnetization on the alloy composition, e.g. in the Ni-Cu system,[3] seems to indicate that the Bloch states which carry most of the magnetization are being filled quite independently from the presence of conduction electrons.

The conduction electrons are formally included in the present investigation. Unlike the valence states which are defined in terms of tightly localized orbits, the conduction states may best be thought of as plane waves which were orthogonalized to the core and valence states. The lowest conduction state is assumed to lie well below all the valence states, and the highest conduction state well above. The noncrossing rule makes it inevitable to introduce bands which are conduction like in part of their Brillouin zone and valence like in the remaining part. In the transition region the Bloch states are a mixture of the two kinds, but all these transition regions together will be assumed to occupy a volume in reciprocal space which is small compared to the volume of one Brillouin zone. With this hypothesis all the actual computations will bear out the kinematic and dynamic independence of the conduction states from the valence states. The presence of the conduction electrons in the crystal manifests itself then mainly through the seemingly arbitrary number of valence electrons even in a "simple" metal, such as pure Fe, Co, and Ni. Other effects of the conduction electrons are harder to evaluate and will be either implicitly contained or completely neglected. The screening of the

---

* Present address: IBM Watson Laboratory, Columbia University, New York, New York.

[1] Cf. in particular the review article of J. H. van Vleck, Rev. Mod. Phys. **25**, 220 (1953) which gives a qualitative description of the problems discussed in the present work.

[2] C. G. Shull and Y. Yamada, *Proceedings of the International Conference on Magnetism and Crystallography*, Vol. III, 1 (1961); J. Phys. Soc. Japan **17**, Suppl. B (1962).

[3] H. C. van Elst, B. Lubach, and G. J. van den Berg, Physica **28**, 1297 (1962).

nuclear charge by the conduction electrons is implicitly taken into account through the effective crystal potential, but the coupling of the spins of *3d* electrons through the conduction electrons is not mentioned at all since its treatment belongs to a more refined model.

The *3d* electrons are characterized by the localized (at each lattice site) states which they occupy. No precise description of these atomic states is needed besides their transformation properties under the symmetry operations of the lattice, and the crucial assumption that two such localized orbits at different lattice sites have a small overlap integral. The smallness of this overlap is not a consequence of a clever choice, such as in a Wannier function, but a genuine expression for the tightness of the *3d* orbits around their lattice site. Therefore, the matrix elements for a transition of a localized *3d* electron to a neighboring lattice site due to kinetic energy and the crystal potential, are always smaller (by a factor of the order of the overlap integral) than the matrix elements for a transition within the same lattice site. The transitions between lattice sites due to the Coulomb repulsion or exchange between electrons are smaller by the square of the overlap integral than the transition within one lattice site. The only transitions between lattice sites which are admitted by the model Hamiltonian are therefore the ones due to the kinetic energy and the crystal potential. Those terms determine the band structure of the *3d* electrons. The bandwidth is then smaller than the intra-atomic Coulomb and exchange integrals.

There are three terms in the model Hamiltonian: (i) kinetic energy and crystal potential terms, (ii) Coulomb repulsion terms at the same lattice site, (iii) exchange terms at the same lattice site. Terms involving the integral over four orbits at the same lattice site, but not of the ordinary Coulomb repulsion or the ordinary exchange type, are neglected. They are not necessarily small, but it is believed that the important ordering of atomic levels at one particular lattice site can already be understood on the basis of the Coulomb repulsion and exchange integrals. In particular Hund's rule for an atomic system follows already from such a reduced Hamiltonian.

Since the two particle terms (ii) and (iii) are larger than the one particle terms (i), the resulting problem is one of strong interaction. It is, however, complicated by the nonvanishing overlap between orbits on different lattice sites. The usual formulation in terms of creation and annihilation operators for the localized states has to be modified. The destruction operator for a given state is not exactly the Hermitian conjugate of its creation operator. Although this complication does not arise in the usual formulation, it does not really make the computations more awkward. It turns out that the various expectation values for the correlated wave function can be evaluated only in the limit of few particles (electrons or holes) compared to the number of lattice sites. The nonvanishing overlap integrals help to simplify the general rules in the diagrammatic analysis, although the number of diagrams is increased.

The present investigation amplifies considerably a short account published earlier.[4] The main idea is still the same. The uncorrelated antisymmetrized product of Bloch states is modified by applying operators which essentially project the uncorrelated wave function into a subspace of configurations with the appropriate correlations. The resulting correlated wave function is believed to be a good approximation to the ground state for all densities of electrons or holes. Practical results, however, i.e., the calculation of various expectation values, have been possible only in the limit of low-particle densities (with the exception of one statement concerning the occupation probability for valence states inside the Fermi surface in the case of a nondegenerate band, cf. Ref. 4). In the earlier account there was neither the possibility of nonvanishing overlap, nor of degenerate bands, nor of conduction states, nor of combining configurations according to Hund's rule. All these new features are brought out in the example of a twofold degenerate band, where ferromagnetism is favored by both terms, (ii) and (iii).

For the nonferromagnetic state the intra-atomic Coulomb-repulsion terms (ii) are more effective in scattering the particles into Bloch states of high energy, because two uncorrelated particles crowd more often into the same lattice site if their spins are antiparallel. Although this effect is probably not serious enough to induce ferromagnetism, it may come close to canceling the loss in band energy which particles of the same spin experience due to the exclusion principle. The dependence of this mechanism on the density of states was shown in the earlier account, and is again found in the example at the end of this report. But now, there is also the effect of the intra-atomic exchange which had been pointed out by Slater[5] and which is due to the terms (iii). Whereas one may hope to show some day that the terms (ii) can never induce ferromagnetism at all by themselves, it would still seem highly arbitrary to neglect them altogether in the discussion of ferromagnetism and consider only the terms (iii).

A brief account of the following sections will now be given. The first- and second-order density functions are defined in Sec. 1 together with the relevant overlap integrals. The creation and destruction operators are introduced in Sec. 2 and the important projection operators for the localized valence states are studied. The basic idea for the definition of a correlated wave function is explained in Sec. 3 by studying the correlation energy due to intra-atomic Coulomb repulsion in the simplest possible case of all Coulomb integrals being equal. The correlated wave function is defined in Sec. 4 quite generally by applying a suitable set of operators (projections operators for the various states of the whole

---

[4] Martin C. Gutzwiller, Phys. Rev. Letters **10**, 159 (1963).

[5] J. C. Slater, H. Statz, and G. F. Koster, Phys. Rev. **91**, 1323 (1953).

ion of each lattice site) to the uncorrelated antisymmetrized product of Bloch states. The same idea is realized in Sec. 5 in a slightly different manner, which will then help to expand all expectation values in powers of the particle density.

The computation of expectation values for the correlated wave function is outlined in Sec. 6; it leads to evaluating the expectation value of a product of creation and destruction operators for the uncorrelated wave function. The latter expectation values are represented in Sec. 7 by diagrams which contain vertices, solid lines for particle propagators, and dotted lines for overlap integrals. The usual breaking up of a diagram into closed linked diagrams is performed in Sec. 8; also it is shown how to obtain diagrams with external points from closed linked diagrams.

The first-order density function is studied in Sec. 9 in order, first to eliminate a number of simple diagrams which lead to a renormalization of the initial uncorrelated wave function, and second, to obtain all the terms up to second order in the particle density. The second-order density function is similarly treated in Sec. 10. The main correlation parameters occur at most quadratically and can therefore easily be determined by minimizing the expectation value for the total energy. This procedure is applied in Sec. 11 to the twofold-degenerate band characteristic of the upper end of the 3*d* band. The conditions for ferromagnetism are then stated. The density of states per unit interval of energy at the upper end of the valence band has to be larger than the average density in the limit of very strong localized Coulomb repulsion. The degeneracy of the valence band is important in the more realistic case where the Coulomb repulsion is not infinitely larger than the bandwidth so that two holes can occasionally crowd into the same lattice site.

The results of the last section are derived for a small density of valence holes and are based on the assumed correlated wave function. This wave function constitutes a guess which may not be particularly good for low densities, because the correlation may spread over many neighbors for low-particle densities as opposed to densities of about 1 per atom. Since the low-density case can be treated directly with the help of the ladder approximation, the present investigation may be viewed as an attempt to propose a wave function for all densities and to treat it in the limit where exact results can be obtained.

1. THE SINGLE-ELECTRON WAVE FUNCTIONS

The lattice is made up of L identical atoms in some elementary arrangement, say face-centered cubic. The lattice sites are labeled by the letters f, g, or h. To each site belongs a set of single-electron wave functions, which we shall divide into three categories: core states (corresponding to 1*s*, 2*s*, 2*p*, 3*s*, 3*p* levels); valence states (corresponding to 3*d* levels); and conduction states (corresponding to 4*s* levels).

The core states are assumed orthogonal to the valence and conduction states of all atomic sites. Also, the core states are uncorrelated, so that they contribute only through the first-order density function $\rho_1(x,y)$, namely

$$\begin{aligned}\rho_1(x,y)=N\int dx_2\cdots\int dx_N\\ \times\Psi(x,x_2,\cdots,x_N)\Psi^*(y,x_2,\cdots,x_N)\\ =\sum\chi(x)\chi^*(y)+\text{contribution from}\\ \text{valence states and conduction states,}\quad(1)\end{aligned}$$

where the first term on the right is from the core states.

In this formula the core states χ may be either localized or Bloch-like. The contribution of the valence and conduction states to ρ_1 is complicated because of correlation. The contribution of the core states to the second-order density function $\rho_2(\xi,x;\eta,y)$ is then already contained in

$$\begin{aligned}\rho_2(\xi,x;\eta,y)=\tfrac{1}{2}N(N-1)\int dx_3\cdots dx_N\\ \times\Psi(\xi,x,x_3,\cdots,x_N)\Psi^*(\eta,y,x_3,\cdots,x_N)\\ =\tfrac{1}{2}[\rho_1(\xi,\eta)\rho_1(x,y)-\rho_1(\xi,y)\rho_1(x,\eta)]\\ +\text{properly correlated part arising}\\ \text{from valence and conduction states.}\quad(2)\end{aligned}$$

Since the effects of the core states are completely described by (1) and (2) together with their orthogonality to the valence and conduction states, it is quite feasible not to mention the core states any more in working out a correlated wave function for the valence and conduction states. Therefore, the first term in (1) will be mentioned again only when it comes to computing the total energy of the crystal. In keeping with this procedure we shall now call N the number of electrons in valence and conduction states only, and the total wave function Ψ will have only as many variables x as there are electrons in valence and conduction states. Formulas (1) and (2) are interpreted henceforth without the first term on the right-hand side of (1). The eventual inclusion of core states is easily performed.

The localized valence and conduction states are $\varphi_{\beta g}(x)$, where g is the label of the atomic site, β is the band index (including spin index), and x is the combination of spatial and spin variable. The band index is sometimes labeled α or γ. Bloch states are constructed by

$$\psi_{\kappa k}(x)=(1/L^{1/2})\sum_{\beta g}V_{\kappa k,\beta g}\varphi_{\beta g}(x).\qquad(3)$$

k is a wave vector of the first Brillouin zone and κ is the index of the band. The coefficient $V_{\kappa k,\beta g}$ depends on the lattice site g through a factor $\exp(ikg)$, but the dependence on the indices κ and β may be quite complicated. In particular, $\psi_{\kappa k}$ may contain, for certain combinations of κ and k, contributions from both valence and conduction states. The exact values of $V_{\kappa k,\beta g}$ will result from some secular problem, exactly as the band structure is obtained in the tight-binding approximation. The variety of Bloch states $\psi_{\kappa k}$ depends directly on the initial choice of localized valence and conduction states $\varphi_{\beta g}$.

Formula (3) can be inverted by writing

$$\varphi_{\beta g}(x)=(1/L^{1/2})\sum_{\kappa k} U_{\beta g,\kappa k}\psi_{\kappa k}(x)\,, \tag{4}$$

where one has the relations

$$\begin{aligned}(1/L)\sum_{\kappa k} U_{\alpha f,\kappa k}V_{\kappa k,\gamma h}&=\delta_{\alpha\gamma}\delta_{fh}\,,\\ (1/L)\sum_{\beta g} V_{\lambda l,\beta g}U_{\beta g,\kappa k}&=\delta_{\lambda\kappa}\delta_{lk}\,.\end{aligned} \tag{5}$$

The coefficients $U_{\beta g,\kappa k}$ depend on g through the factor $\exp(-ikg)$.

The Bloch functions $\psi_{\kappa k}(x)$ will be assumed orthonormal to one another, i.e.,

$$\int \psi_{\lambda l}{}^{*}(x)\psi_{\kappa k}(x)dx=\delta_{\lambda\kappa}\delta_{lk}\,. \tag{6}$$

But the localized orbitals $\varphi_{\beta g}(x)$ will not be assumed orthonormalized, and this makes it necessary to introduce their overlap integrals

$$\begin{aligned}R(\alpha f,\gamma h)=\int \varphi^{*}{}_{\alpha f}(x)\,\varphi_{\gamma h}(x)dx\\ =(1/L)\sum_{\kappa k} U^{*}{}_{\alpha f,\kappa k}U_{\gamma h,\kappa k}\,.\end{aligned} \tag{7}$$

The only restriction which may be imposed for convenience is

$$R(\alpha f,\gamma f)=\delta_{\alpha\gamma}\,, \tag{8}$$

so that the localized orbits belonging to the same lattice site are orthonormalized. Also, the values of $R(\alpha f,\gamma h)$ differ from zero only when the sites of f and h are close to each other, and then they are small compared to 1 in all cases except when the indices α and γ refer both to conduction states.

Two remarks are in order at this point. First, it is convenient to introduce the nonorthogonality integrals R, even if they should be ultimately assumed to vanish. Indeed, the results of the diagrammatic analysis of Sec. 7 are more easily expressed if the values of $R(\alpha f,\gamma h)$ are not immediately simplified to $\delta_{\alpha\gamma}\delta_{fh}$. Second, it may be that certain simple types of correlations, special cases of the ones to be introduced in Sec. 4, do not necessitate the assumption of $R(\alpha f,\gamma h)$ being different from $\delta_{\alpha\gamma}\delta_{fh}$. Indeed the nonorthogonality of the valence states may be taken fully into account by a proper choice of the correlation parameters. An example is the Heitler-London theory of the hydrogen molecule. But no such equivalence between correlation parameters and nonorthogonality integrals has been found in the more general case to be discussed in the following sections for the Ni-Cu alloys.

2. SECOND QUANTIZED FORMALISM

The many-electron wave functions may be treated most conveniently in the formalism of second quantization. Therefore, we introduce creation operators $c^{\dagger}{}_{\kappa k}$ and annihilation operators $c_{\kappa k}$ corresponding to the Bloch functions $\psi_{\kappa k}(x)$ of (3). These operators satisfy the anticommutation relations

$$\begin{aligned}c^{\dagger}{}_{\kappa k}c_{\lambda l}+c_{\lambda l}c^{\dagger}{}_{\kappa k}&=\delta_{\kappa\lambda}\delta_{kl}\,,\\ c_{\kappa k}c_{\lambda l}+c_{\lambda l}c_{\kappa k}&=0\,,\\ c^{\dagger}{}_{\kappa k}c^{\dagger}{}_{\kappa k}+c^{\dagger}{}_{\kappa k}c^{\dagger}{}_{k}&=0\,.\end{aligned} \tag{9}$$

The localized states $\varphi_{\beta g}(x)$ are created by

$$a^{\dagger}{}_{\beta g}=\frac{1}{L^{1/2}}\sum_{\kappa k} U_{\beta g,\kappa k}c^{\dagger}{}_{\kappa k}\,, \tag{10}$$

and they are destroyed by the operators

$$b_{\beta g}=\frac{1}{L^{1/2}}\sum_{\kappa k} V_{\kappa k,\beta g}c_{\kappa k}\,. \tag{11}$$

It is important to notice that $b^{\dagger}{}_{\beta g}\neq a^{\dagger}{}_{\beta g}$ because the localized orbits are not orthonormalized. However, one has

$$\begin{aligned}a^{\dagger}{}_{\alpha f}b_{\gamma h}+b_{\gamma h}a^{\dagger}{}_{\alpha f}&=\delta_{\alpha\gamma}\delta_{fh}\,,\\ a^{\dagger}{}_{\alpha f}a^{\dagger}{}_{\gamma h}+a^{\dagger}{}_{\gamma h}a^{\dagger}{}_{\alpha f}&=0\,,\\ b_{\alpha f}b_{\gamma h}+b_{\gamma h}b_{\alpha f}&=0\,.\end{aligned} \tag{12}$$

These relations follow from (9) and (5). Other anticommutators between a's and b's can be expressed in terms of the overlap integral R of (7).

A one-particle operator $Q_1(x,y)$ with matrix elements

$$\langle\kappa k|Q_1|\lambda l\rangle=\int \psi^{*}{}_{\kappa k}(x)dx\int \psi_{\lambda l}(y)dyQ_1(x,y)\,, \tag{13}$$

is given in second quantized formalism by

$$Q_1=\sum_{\kappa k,\lambda l} c^{\dagger}{}_{\kappa k}\langle\kappa k|Q_1|\lambda l\rangle c_{\lambda l}\,. \tag{14}$$

In terms of the matrix elements

$$\langle\alpha f|Q_1|\gamma h\rangle=\int \varphi^{*}{}_{\alpha f}(x)dx\int \varphi_{\gamma h}(y)dyQ_1(x,y)\,, \tag{15}$$

the operator Q_1 becomes in the second quantized formalism

$$Q_1=\sum_{\alpha f,\gamma h} b^{\dagger}{}_{\alpha f}\langle\alpha f|Q_1|\gamma h\rangle b_{\gamma h}\,, \tag{16}$$

which is obtained directly from (13) and (14) by inserting (3) and (11).

In the same manner, a two-particle operator

$Q_2(\xi,x;\eta,y)$ with matrix elements

$$\langle\alpha_1f_1\alpha_2f_2|Q_2|\gamma_1h_1\gamma_2h_2\rangle=\tfrac{1}{2}\int d\xi\int dx\int d\eta\int dy$$
$$\times\begin{vmatrix}\varphi^*{}_{\alpha_1f_1}(\xi) & \varphi^*{}_{\alpha_2f_2}(\xi)\\ \varphi^*{}_{\alpha_1f_1}(x) & \varphi^*{}_{\alpha_2f_2}(x)\end{vmatrix}Q_2(\xi,x;\eta,y)$$
$$\times\begin{vmatrix}\varphi_{\gamma_1h_1}(\eta) & \varphi_{\gamma_2h_2}(\eta)\\ \varphi_{\gamma_1h_1}(y) & \varphi_{\gamma_2h_2}(y)\end{vmatrix}\qquad(17)$$

is given in second quantized form by the formula

$$Q_2=\sum_{(\alpha_1f_1,\alpha_2f_2)}\ \sum_{(\gamma_1h_1,\gamma_2h_2)}b^\dagger{}_{\alpha_2f_2}b^\dagger{}_{\alpha_1f_1}$$
$$\times\langle\alpha_1f_1\alpha_2f_2|Q_2|\gamma_1h_1\gamma_2h_2\rangle b_{\gamma_1h_1}b_{\gamma_2h_2}.\qquad(18)$$

The summation goes only over different pairs $(\alpha_1f_1,\alpha_2f_2)$ and $(\gamma_1h_1,\gamma_2h_2)$. The formulas (16) and (18) have been derived because in this work the assumption of orthonormality is not made for the localized states, so that there remains the question whether the a or the b operators are to be used in representing Q_1 and Q_2.

The operator $a^\dagger{}_{\beta g}b_{\beta g}=P_{\beta g}$ destroys the electron in the localized state $\varphi_{\beta g}(x)$ and then creates right back again. This operator acting on an arbitrary many electron state isolates that part which has an electron in the localized state $\varphi_{\beta g}(x)$. In view of

$$P^2{}_{\beta g}=a^\dagger{}_{\beta g}b_{\beta g}a^\dagger{}_{\beta g}b_{\beta g}=a^\dagger{}_{\beta g}b_{\beta g}=P_{\beta g}\,,\qquad(19)$$

the operator $P_{\beta g}$ is indeed a projection operator. However, it is not a Hermitian operator, and has to be handled with some care. One way of examining it in more detail is to express $a^\dagger{}_{\beta g}$ in terms of $b^\dagger{}_{\beta g}$. With the help of (5), (10), and (11) one finds

$$a^\dagger{}_{\beta g}=\sum_{\alpha f}b^\dagger{}_{\alpha f}R(\alpha f,\beta g)\,,\ =b^\dagger{}_{\beta g}+\sum_{\alpha f\neq g}b^\dagger{}_{\alpha f}R(\alpha f,\beta g)\,.\qquad(20)$$

The last step is a consequence of the orthonormalization (8) for the localized states belonging to the same lattice site. If the index β refers to a valence state, the second term on the right hand side of (20) is small to the extent that the overlaps between a localized valence state and all localized states on neighbors are small. The overlap between a valence and a conduction state is small because of the different angular symmetry, and the overlap between two valence states is small because of their tight localization. In this sense the operator $P_{\beta g}$ is approximately Hermitian for the localized valence states.

Since the projection operator $P_{\beta g}$ is not Hermitian we cannot associate a measurable quantity with it. As long as $P_{\beta g}$ is only used to construct some correlated wave function for the whole crystal, the lack of Hermiticity is not a drawback. But $P_{\beta g}$ cannot be used to answer the question as to the probability of finding the localized valence state $\varphi_{\beta g}$ occupied. Such detailed knowledge may be of no interest. However, one may find it useful to answer the more general question as to the average number of electrons in localized valence states. A Hermitian operator whose expectation value answers the last question can be constructed under certain additional assumptions which do not seem unduly restrictive. For instance, the conduction states may be defined as plane waves which were orthogonalized not only to the core states but also to the valence states. An operator can then be constructed whose expectation value gives the average number of electrons in conduction states, and therefore the difference between the total number of electrons and the number of electrons in conduction states gives the number of electrons in valence states. We shall use such a number in the future whenever this seems convenient.

3. ABOUT THE CORRELATION IN THE VALENCE STATES

With the help of the projection operator $P_{\beta g}$ the contribution of the localized valence state $\varphi_{\beta g}$ to the wave function Ψ of the whole crystal can be investigated. More generally, one can speak about the configurations Φ which contribute to Ψ. A configuration is a set of localized valence states, and it can be described by enumerating the index pairs βg which make up the configuration. To each configuration Φ belongs a projection operator which is just the product of $P_{\beta g}$ for the indices belonging to the configurations Φ, and of $(1-P_{\beta g})$ for the indices of valence states not belonging to the configuration Φ.

The total wave function Ψ can now be written as a sum over all possible configurations Φ of localized valence states in the crystal. The terms in this sum are not mutually orthogonal, but for the discussion of that part of the Hamiltonian which refers to the valence states of one particular atom only, the lack of orthogonality may be temporarily forgotten.

The largest contributions to these intra-atomic energy terms, besides the kinetic energy and the potential energy in the field of the nucleus and the core electrons, come from the mutual Coulomb repulsion of the valence states (since the core states are always occupied, their repulsion provides merely a constant shift). Indeed all the Coulomb repulsion integrals between valence states contain one term which is the largest and identical in all of them.[6] It is the Coulomb repulsion between two spherically symmetric charge distributions, each with total charge equal to one electronic charge, and a radial dependence equal to that of the valence states. If ν of the valence states at a particular atom are occupied, this term in the Coulomb repulsion becomes simply $C\nu(\nu-1)/2$.

For some arbitrary wave function Ψ, the number ν of occupied valence states at some particular atom is, in general, not fixed. Ψ may contain configurations Φ

---

[6] John C. Slater, *Quantum Theory of Atomic Structure* (McGraw-Hill Book Company, Inc., New York, 1960), Vol. I, pp. 311, 490.

which have different numbers of occupied valence states at the particular atom under examination. To the approximation where the configurations Φ are considered mutually orthogonal, a probability p_ν can be defined for Ψ, to have exactly ν occupied valence states at the particular atom. p_ν is simply the sum of the squares of all those configurations Φ which occur in the expansion of Ψ and have exactly ν occupied valence states at the particular atom.

Since the Coulomb repulsion $C\nu(\nu-1)/2$ is the largest among the many two-particle terms, it is important for the wave function Ψ to minimize the quantity

$$\tfrac{1}{2}\sum \nu(\nu-1)p_\nu = q\,, \tag{21}$$

with the summation going over the possible occupation numbers of the valence states, e.g., ν goes from 0 to 10 for the entire set of $3d$ states. There are two obvious conditions to be satisfied for the set of probabilities p_ν. The normalization condition is

$$\sum p_\nu = 1\,, \tag{22}$$

and the total number of valence electrons is given by, say, $\bar{n}$ per atom on the average, so that

$$\sum \nu p_\nu = \bar{n}\,. \tag{23}$$

The solution to this simple minimization problem is found most easily in the following way. $\bar{n}$ is assumed to lie between two integers μ and $\mu+1$, i.e.,

$$\mu < \bar{n} < \mu+1\,. \tag{24}$$

q can then be expressed with the help of (22) and (23) as

$$q = (\mu/2)(2\bar{n}-\mu-1) + \tfrac{1}{2}\sum (\mu-\nu)(\mu+1-\nu)p_\nu\,. \tag{25}$$

The coefficients of p_μ and $p_{\mu+1}$ vanish, whereas the coefficients of all the other p's are positive. Therefore, q reaches its minimum for the values

$$\begin{gathered} p_\mu = \mu+1-\bar{n}\,, \quad p_{\mu+1} = \bar{n}-\mu\,, \\ p_\nu = 0 \quad \text{for} \quad \nu \neq \mu \quad \text{and} \quad \nu \neq \mu+1\,. \end{gathered} \tag{26}$$

The values of p_μ and $p_{\mu+1}$ are obtained from (22) and (23) after all the other p_ν's have been set equal to zero.

The statement expressed in (26) has some striking consequences. For example, in the case of iron we have $\mu = 7$, and it follows that any reasonable wave function Ψ for the whole iron crystal should contain only configurations which have either 7 or 8 occupied valence states on each atom. Similarly, in Ni we have $\mu = 9$ and there ought not to be any configuration with less than 9 valence ($3d$) electrons at any lattice site.

The requirement (26) is generally violated by the itinerant electron model. Let us consider for example the Ni-Cu alloy with $100p$ atomic percent Cu substituted for Ni. We shall assume that $0.6-p$ holes per atom have to be distributed equally over two degenerate valence bands in the ferromagnetic ground state, and over four degenerate valence bands in the nonferromagnetic ground state. In terms of the numbers ν of holes we then have

$$p_\nu = \binom{2}{\nu}\left(1-\frac{0.6-p}{2}\right)^{\nu}\left(1+\frac{0.6-p}{2}\right)^{2-\nu} \quad \text{ferromagnetic,}$$

$$p_\nu = \binom{4}{\nu}\left(1-\frac{0.6-p}{4}\right)^{\nu}\left(1+\frac{0.6-p}{4}\right)^{4-\nu} \quad \text{nonferromagnetic.}$$

The second term in (25) becomes equal to $(0.6-p)^2/4$ for the ferromagnetic and $3(0.6-p)^2/8$ for the nonferromagnetic case.

The Coulomb repulsion C can be estimated as follows. The outermost $3d$ electrons see at least 1.6 unscreened nuclear charges. But since there are at least two of these outermost $3d$ orbits, the average unscreened nuclear charge in these orbits must be at least 2 so that such an outermost $3d$ orbit can be thought of as a hydrogenic $3d$ orbit in the field of an He nucleus. If we think of one of the two mutually repelling electronic charge distributions as completely concentrated at the nucleus (this tends to overestimate the value of C, but the hydrogenic $3d$ orbit has been chosen rather conservatively), C becomes equal to 4/9 Ry. The Coulomb repulsion energy is, therefore, $(0.6-p)/9$ Ry per hole for the ferromagnetic and $(0.6-p)/6$ Ry per hole for the nonferromagnetic case.

The surplus of Coulomb-repulsion energy for pure Ni, i.e., $p=0$, corresponds, according to our rough estimate, to about 10 000°K in the ferromagnetic and to about 15 000°K in the nonferromagnetic itinerant model, whereas the Curie temperature in Ni is found to be 650°K. It seems futile to discuss the itinerant model further without a serious attempt to find a modified wave function which is not beset by the large surplus of Coulomb repulsion in either the ferromagnetic or the nonferromagnetic state.

Since there are many configurations Φ with not more than $\mu+1$ and not less than μ occupied valence states on any lattice site, a good wave function Ψ for the whole crystal is expected to be a linear combination of all such configurations. Indeed any configuration Φ by itself does not give a particularly low expectation value for the kinetic energy and crystal potential terms in the Hamiltonian which correspond to a single electron moving in an effective potential of the lattice symmetry. Exactly these last terms were minimized by the itinerant model. They constitute the first order if the terms in the Hamiltonian are arranged in ascending powers of the overlap R between valence orbits on neighboring sites. The Coulomb repulsion C belongs to the zero order in such an expansion.

The basic idea is then to enforce the result (26) upon the itinerant model wave function by eliminating those configurations which violate the requirement (26) at some particular lattice site. Such a correlation corresponds exactly to the correlation in the Heitler-London wave function for the hydrogen molecule. But since we have now to do with $3d$ orbits the requirement (26) still leaves many configurations at each lattice site, so that some additional correlation beyond the Heitler-London type (26) seems indicated. In particular Hund's rule should now be enforced at each lattice site.

4. A CORRELATED WAVE FUNCTION FOR THE VALENCE ELECTRONS

The ground state Ψ_0 in the itinerant electron model is obtained from the vacuum state Φ_0 by creating N electrons in Bloch states $\psi_{\kappa k}(x)$. Therefore, we have

$$\Psi_0 = \prod_{(\kappa k)} c^\dagger{}_{\kappa k} \Phi_0 , \tag{27}$$

where the set (κk) of occupied Bloch states is chosen in some manner, e.g., such as to minimize the expectation value of the total energy. The particular choice of the Bloch functions $\psi_{\kappa k}$ and the set (κk) is not under discussion right now, and we shall assume that both the functions $\psi_{\kappa k}(x)$ and the set (κk) have been determined once for all.

Ψ_0 is now expanded into configurations Φ of localized valence states by the method described at the beginning of the last section. The new (correlated) wave function Ψ is then obtained by transforming each configuration $\Phi(\alpha_1 f_1, \cdots, \alpha_M f_M)$ in the expansion of Ψ_0 into a linear combination of related configurations $\Phi(\gamma_1 h_1, \cdots, \gamma_M f_M)$. Most generally this transformation is described by an operator whose matrix elements give the coefficient of the configuration $\Phi(\gamma_1 h_1, \cdots, \gamma_M h_M)$ in the transformation of the configuration $\Phi(\alpha_1 f_1, \cdots, \alpha_M f_M)$.

A more specific assumption has to be made. As the most stringent assumption we will assume that the above operator O does not transfer electrons from one lattice site to another. Then it is helpful to simplify matters by assuming O to effect transfers of electrons within one atom independently of the transfers of electrons in neighboring atoms. We have, therefore, a set of operators $O^{(0)}$, $O^{(1)}$, $O^{(2)}$, $\cdots$ applicable to lattice sites which are occupied by 0, 1, 2, $\cdots$ electrons in the valence shell. The determination of these operators O is essentially equivalent to bringing about the necessary correlation of the valence states. In terms of the creation and annihilation operators we can write

$$O^{(\nu)} = \sum_{(\gamma_1 \cdots \gamma_\nu)} \sum_{(\alpha_1 \cdots \alpha_\nu)} \langle \gamma_1 \cdots \gamma_\nu | O^{(\nu)} | \alpha_1 \cdots \alpha_\nu \rangle \times a^\dagger{}_{\gamma_\nu} \cdots a^\dagger{}_{\gamma_1} b_{\alpha_1} \cdots b_{\alpha_\nu} (1 - P_{\alpha_{\nu+1}}) \cdots (1 - P_{\alpha_{10}}) , \tag{28}$$

to be summed over all different groups of ν indices $(\alpha_1 \cdots \alpha_\nu)$ and $(\gamma_1 \cdots \gamma_\nu)$. In the case of $3d$ bands there is a maximum of 10 different indices.

For example the requirement (26) is enforced by setting all $O^{(\nu)} = 0$, except $O^{(\mu)} = O^{(\mu+1)} = 1$. This constitutes the generalization of the Heitler-London model for the hydrogen molecule. A somewhat weaker correlation is brought about by allowing the $O^{(\nu)}$ to deviate from the above value, but keeping each $O^{(\nu)}$ a multiple of the unit matrix.

It is now evident how Hund's rule can be favored. The configuration at each lattice site can be expanded into the states corresponding to the various spectral levels. The operators O can now be chosen so as to eliminate certain unfavorable spectral levels, or at least to reduce their contributions, whereas the levels which are lowest according to Hund's rule can be left unreduced. Therefore, the operators O may have off-diagonal elements. The values of the matrix elements of O can be determined variationally.

5. ALTERNATIVE FORMULATION FOR THE CORRELATED WAVE FUNCTION

If one is interested in a metal with only few electrons in the valence band, it is natural to expand all the results in powers of the density of valence electrons in the lattice. The operator O of the previous section is then best replaced by a slightly different expression which will be defined in this section.

The operator O will be expressed in terms of matrix elements $\vartheta_0 = 1$, $\vartheta_1(\gamma,\alpha)$, $\vartheta_2(\gamma_1\gamma_2,\alpha_1\alpha_2)$, etc. These matrix elements are numbers out of which $\langle \gamma_1 \cdots \gamma_\nu | O^{(\nu)} | \alpha_1 \cdots \alpha_\nu \rangle$ can be computed by taking all kinds of combination of ϑ_0, ϑ_1, ϑ_2, $\cdots$ and summing them.

First there is a summation over ν from 0 to 10 and for each ν a summation over all different ν-tuples $(\alpha_1 \cdots \alpha_\nu)$. Second, for each ν there is a summation over all partitions $P^{(\nu)}$ of the integer ν. Third, for each partition there is a summation over all possible groupings of the ν-tuple $(\alpha_1 \cdots \alpha_\nu)$ according to P, and over all permutations of $(\gamma_1 \cdots \gamma_\nu)$. A particular grouping of $(\alpha_1 \cdots \alpha_\nu)$ is written as $(\alpha^1 \cdots \alpha^\nu)$ where $\alpha^1 \cdots \alpha^\mu$ are associated with the 1's of the partition P, $(\alpha^{\mu_1+1}\alpha^{\mu_1+2})$, $(\alpha^{\mu_1+3}\alpha^{\mu_1+4})$, $\cdots$ with the 2's, etc. The permutation of $(\gamma_1 \cdots \gamma_\nu)$ is written $(\gamma^1 \cdots \gamma^\nu)$. With these preliminaries one can now write

$$O = \frac{1}{\omega} \sum_{\nu=0}^{10} \sum_{(\alpha_1 \cdots \alpha_\nu)} \sum_{(\gamma_1 \cdots \gamma_\nu)} \sum_{P^{(\nu)}} \sum_{\substack{\text{groupings} \\ \text{of } (\alpha_\alpha \cdots \alpha_\nu)}} \sum_{\substack{\text{permutations} \\ \text{of } (\gamma_1 \cdots \gamma_2)}} \times \vartheta_1(\gamma^1\alpha^1)\vartheta_1(\gamma^2\alpha^2) \cdots \vartheta_2(\gamma^{\mu_1+1}\gamma^{\mu_2+1}\alpha^{\mu_1+1}\alpha^{\mu_1+2}) \cdots \times a^\dagger{}_{\gamma\nu} \cdots a^\dagger{}_{\gamma 1} b_{\alpha 1} \cdots b_{\alpha\nu} . \tag{29}$$

The term $\nu = 0$ is put equal to 1.

The factor $1/\omega$ expresses the fact that the same wave function Ψ results, if the left-hand and the right-hand sides of (29) are just multiples of each other with the same factor for all operators.

Since the operators $O^{(\nu)}$ have an intuitive interpretation according to the preceding section, the problem arises of finding the matrix elements ϑ from known operators O by solving Eq. (29). The special case of the O's being chosen according to the requirement (26) is treated in the Appendix A. We shall assume that $\omega = 1$ from now on. This implies that $O^{(0)} = 1$, or in other words, that a configuration will not be discriminated against for having no electrons at all at some particular lattice site. Such an assumption is only reasonable if

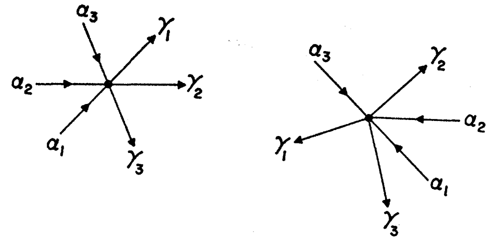

FIG. 1. Two equivalent vertices corresponding to ϑ_3.

there are fewer valence electrons on the average in the lattice than lattice sites.

The theory has been phrased in terms of electrons, but in the case of almost-filled bands it is more appropriate to consider the holes in the valence bands. This is done simply by switching the positions of $a^\dagger$ with respect to b in (28) and (29). The projection operator $1-P=1-a^\dagger b=ba^\dagger$ appearing in (28) then goes into $a^\dagger b=P$, which tests the absence of a hole exactly as $1-P$ tested the absence of an electron. Again, an equivalence between (28) and (29) can be established only in the cases where there is no physical reason to discriminate against a configuration for having no holes at all at some particular lattice site. Since the present investigation is directed mostly toward the understanding of the Ni-Cu alloys, all the following calculations will be done for the case of an almost-full valence band.

A picture can be associated with any particular term in (29), if each factor ϑ_ν is represented by a heavy dot, called a vertex, with ν directed lines across. The endpoints of the lines are labeled on the incoming end by α, and on the outgoing end by γ. A combination of such representations of ϑ's is called a picture. Two pictures are called equivalent if they can be brought to congruence including the labeling of lines, by shifting their parts. Figure 1 shows two equivalent vertices.

Conversely, given a picture, i.e., a combination of vertices with labeled ingoing and outgoing lines, one associates a product of ϑ's and operators $a^\dagger$, b with it. To each vertex corresponds a factor $\nu!\vartheta_\nu$ with the arguments occurring in the picture. Formula (29) can then be expressed as a sum over all pictures to be made with two sets of labels $(\alpha_1\cdots\alpha_{10})$ and $(\gamma_1\cdots\gamma_{10})$.

6. CALCULATION OF EXPECTATION VALUES

The correlated wave function Ψ is now given by

$$\Psi=\prod_g O_g\Psi_0\,, \tag{30}$$

where O_g is the operator (29) belonging to the lattice site g. Since Ψ_0 represents almost filled valence bands, $a^\dagger$ is replaced formally by b everywhere, and vice versa, everything else in (29) remaining at its place. The first thing to be done is the computation of the absolute value $(\Psi|\Psi)$ of the correlated wave function Ψ.

Formula (29) is inserted in (30) by attaching an additional index g to the ϑ_μ, b_γ, and $a^\dagger{}_\alpha$. The product over the lattice sites is worked out for both Ψ and Ψ^*, the scalar product is taken term by term, and the results are added up. Each term in this last sum can be represented by a picture in the following way:

To each $\vartheta_{\mu g}$ or $\vartheta^*{}_{\mu g}$ associate a heavy dot called a vertex, to be labeled by the lattice site g. Each operator $a^\dagger{}_{\alpha g}$ associated with $\vartheta_{\mu g}$ is represented by a solid line with an arrow going into the vertex of $\vartheta_{\mu g}$, and each operator $a_{\alpha g}$ associated with $\vartheta^*{}_{\mu g}$ is represented by a solid line with an arrow coming out of the vertex of $\vartheta^*{}_{\mu g}$. Each operator $b_{\gamma g}$ associated with $\vartheta_{\mu g}$ is represented by a dotted line leaving the vertex of $\vartheta_{\mu g}$, and the operator $b^\dagger{}_{\gamma g}$ associated with $\vartheta^*{}_{\mu g}$ is represented by a dotted line going into the vertex of $\vartheta^*{}_{\mu g}$. The lines are labeled exactly as the operators they represent. Figure 2 is an example of such a picture representing a term in $(\Psi|\Psi)$. Two pictures like Fig. 2 are called identical if they can be brought to congruence including labels and directions by merely shifting the parts of the picture without ever detaching a line from its vertex. If one permutes the arguments $\gamma_1\cdots\gamma_\mu$ in $\vartheta_{\mu g}$ the same picture arises according to this definition.

Conversely, given a picture like Fig. 2, it is immediately possible to write down the corresponding term in the evaluation of $(\Psi|\Psi)$. For each vertex with μ incoming solid lines one writes an operator

$$\mu!\vartheta_{\mu g}(\gamma_1\cdots\gamma_\mu\alpha_1\cdots\alpha_\mu)b_{\gamma_\mu g}\cdots b_{\gamma_1 g}a^\dagger{}_{\alpha_1 g}\cdots a^\dagger{}_{\alpha_\mu g}$$

with the corresponding labels, and analogously for each vertex with μ outgoing solid lines. All operators belonging to a ϑ^* are written to the left of all operators belonging to a ϑ. The order of operators belonging to different lattice sites is immaterial. Operators belonging to the same lattice site have to be pulled together in the order suggested by (29). A particular label βg on $a^\dagger$ can then not occur more than once, and similarly any particular label on b, $b^\dagger$, or a cannot occur more than once. The freedom left in ordering the operators belonging to different lattice sites cannot change the expectation value of the whole operator product because of the simple anticommutators (12) for $a^\dagger$ and b.

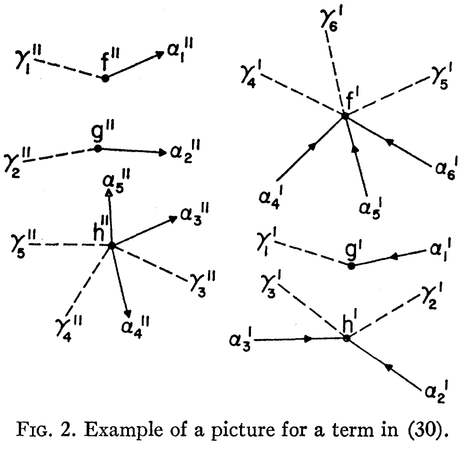

FIG. 2. Example of a picture for a term in (30).

The absolute value $(\Psi|\Psi)$ becomes now a sum over all different pictures like Fig. 2, where one associates an operator with each picture according to the rules of the previous paragraph, and then computes the expectation values of that operator with the wave function Ψ_0.

The computation of an expectation value like $(\Psi|b^\dagger_{\alpha f}b_{\gamma h}|\Psi)$ which arises from the one particle operator (16) is done in almost the same way. $b^\dagger_{\alpha f}$ is represented by a small cross labeled αf with an ingoing dotted line, and $b_{\gamma h}$ is represented by a small cross labeled γh with an outgoing dotted line, in addition to all the features in the pictures for $(\Psi|\Psi)$. Everything stays the same as with $(\Psi|\Psi)$ except the operators associated with ϑ^* have to be written to the left of $b^\dagger_{\alpha f}b_{\gamma h}$, and the operators associated with ϑ stand to the right. The small crosses associated with $b^\dagger_{\alpha f}$ and $b_{\gamma h}$ are called external points to distinguish them from the vertices (heavy dots).

7. EVALUATION IN TERMS OF DIAGRAMS

The expectation value of the operator associated with a picture like Fig. 2 can be evaluated for the uncorrelated wave function Ψ_0 with the help of Wick's theorem. According to this theorem one has to run through all complete systems of contractions, that is through all ways of grouping the annihilation and creation operators into pairs. The contribution of such a complete system of contractions is given by the product of the expectation values of each pair in the contraction for the wave function Ψ_0. The order of the operators in each pair has to be the same as in the original operator, and there is a sign to be determined from the number of permutations necessary in order to bring the partners of each pair together.

In the case of the uncorrelated wave function Ψ_0 only the pairs consisting of one annihilation and one creation operator give a nonvanishing result. There are four types of such pairs and their expectation values are easily computed with the help of the definitions (10) and (11), as well as the relations (5). They are

$$\begin{aligned}
&(\Psi_0|a_{\alpha f}a^\dagger_{\gamma h}|\Psi_0)=W(\alpha f,\gamma h),\\
&(\Psi_0|b_{\alpha f}a^\dagger_{\gamma h}|\Psi_0)=\sum_{\beta g}S(\alpha f,\beta g)W(\beta g,\gamma h),\\
&(\Psi_0|a_{\alpha f}b^\dagger_{\gamma h}|\Psi_0)=\sum_{\beta g}W(\alpha f,\beta g)S(\beta g,\gamma h),\\
&(\Psi_0|b^\dagger_{\alpha f}b_{\gamma h}|\Psi_0)=S(\gamma h,\alpha f)\\
&\qquad-\sum_{\beta' g'\beta'' g''}S(\gamma h,\beta'' g'')W(\beta'' g'',\beta' g')S(\beta' g',\alpha f),
\end{aligned}\tag{31}$$

where W and S are defined by

$$W(\alpha f,\gamma h)=\frac{1}{L}\sum_{(\kappa k)}U^*_{\alpha f,\kappa k}U_{\gamma h,\kappa k},$$

$$S(\alpha f,\gamma h)=\frac{1}{L}\sum_{\kappa k}V_{\kappa k,\alpha f}V_{\kappa k,\gamma h}.\tag{32}$$

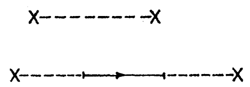

FIG. 3. Simplest diagrams for ρ_1.

The summation over (κk) means that only those indices κk are included in the summation which correspond to empty Bloch states of Ψ_0. It is easily checked that the matrix $S(\alpha f,\gamma h)$ is just the inverse of the overlap matrix $R(\alpha f,\gamma h)$ defined in (7).

It is immediately evident from writing down the operator corresponding to a picture like Fig. 2 that a and $a^\dagger$, as well as $b^\dagger$ and b, have always to be paired in the sequence in which they appear in the first and last formula of (31). However, the pairs made up of b and $a^\dagger$, or of a and $b^\dagger$, may occur in either sequence, except if the two partners of such a pair belong to the same lattice site. In that case b always precedes $a^\dagger$, and a precedes $b^\dagger$, exactly as in the second and third formula of (31). If b and $a^\dagger$, or a and $b^\dagger$ do not belong to the same lattice site, the commutation relations (12) tell us that only the sign of the expectation value changes when the order of the partners in the pair is changed. But this sign change is accounted for when the over-all sign to be attached to the product of the quantities (31) is determined.

A complete system of contractions can be represented with the help of pictures like Fig. 2 in the following way. A pair of the type $aa^\dagger$ is represented by simply connecting the two solid lines representing a and $a^\dagger$, the arrow points from a to $a^\dagger$. Similarly a pair of type $ba^\dagger$ is represented by tying the dotted line of b to the solid line of $a^\dagger$, inserting a short cross line such as in Fig. 3 at the point where the dotted and the solid lines meet. This short cross line marks the end of the dotted and the beginning of the solid line, and corresponds to the summation over βg which appears in the formula (31) for $(\Psi_0|b_{\alpha f}a^\dagger_{\gamma h}|\Psi_0)$. A similar treatment is given to a pair $ab^\dagger$. Finally, since a pair $b^\dagger b$ gives rise to two terms as shown in (31), it will be represented in two ways as shown in Fig. 3, first by simply connecting the two dotted lines of $b^\dagger$ and b, and second by joining the dotted line of $b^\dagger$ with the dotted line of b through the intermediary of a directed solid line. The arrows go from b to $b^\dagger$ which is reflected in the inverted arguments of the last formula in (31) as compared to the preceding formulas in (31). The minus sign appearing in the last part of $(\Psi_0|b^\dagger_{\alpha f}b_{\gamma h}|\Psi_0)$ will be absorbed in the general rules determining the overall sign. This pictorial representation of a particular complete system of contractions by connecting the appropriate lines in a picture like Fig. 2 is called the diagram associated with that system of contractions. Two diagrams are identical if they can be brought into complete congruence (including labels and arrows) by shifting the lines in the drawing without ever breaking any of them.

In the present formulation the particle lines (solid or dotted) run from one vertex to another, but they do not run through a vertex. None of the solid lines at some vertex is in a particular relationship with any given dotted line belonging to the same vertex, and vice versa. However, if one starts from a given diagram in order to write its contribution to $(\Psi|\Psi)$, the result depends on the order in which the arguments α and γ are listed in the ϑ corresponding to some particular vertex. In establishing the over-all sign to be attached to the contribution, it is convenient to adopt the following rule: The particle line ending in α_i at some vertex ϑ_μ continues on the other side with the particle line labeled γ_i, and the particle line ending in γ_j in ϑ_ν^* continues with α_j. In this manner all particle lines are joined two by two to form so-called loops. A closed loop closes itself in the diagram, an open loop ends at external points, which are the ones represented by small crosses. The over-all sign to be associated with a particular diagram is obtained in the following manner. The solid and dotted lines are organized into loops according to the rules of the previous paragraphs. A factor (-1) is now inserted for each segment of solid line in the diagram and for each closed loop.

In the original picture, e.g., in Fig. 2, the labels associated with outgoing solid lines were all different from one another; similarly, the labels of the incoming solid lines were all different; and similarly for the dotted lines, excepting the labels of dotted lines attached to external points. The expectation value associated with a picture like Fig. 2 is the sum over the contributions from all different diagrams to be drawn from the picture. The sum of these contributions is easily found to be an antisymmetric function of the labels associated with solid outgoing lines, of the labels associated with solid incoming lines, etc. As long as the over-all sign and the individual factors associated with a diagram are determined by the above rules, using in particular only the pair expectation values (31), it is formally possible to let labels of outgoing solid lines coincide, or to let labels of incoming solid lines coincide, etc. The sum over all diagrams associated with a picture containing identical labels on outgoing solid lines, or on incoming solid lines, etc., will give a vanishing result.

Therefore, it is now possible to let all the labels in a diagram run through all admissible values, independently of one another. The restriction to admissible values refers to the fact that only localized valence states are involved, but no conduction states. The overcounting resulting from this mutual independence makes it necessary to divide by

$$\mu_1!\mu_2!\cdots\nu_1!\nu_2!\cdots(1!)^{\nu_1+\mu_1}(2!)^{\nu_2+\mu_2}\cdots$$

where $\mu_1,\mu_2,\cdots$ is the number of $\vartheta_1,\vartheta_2,\cdots$, and $\nu_1,\nu_2,\cdots$ is the number of $\vartheta^*{}_1,\vartheta^*{}_2,\cdots$ in the diagram.

In summary, the expectation values of Ψ can be written as a sum over all different diagrams. A diagram consists of vertices, solid lines, dotted lines, and possibly external points. There are two kinds of vertices, with outgoing solid (incoming dotted) lines and with incoming solid (outgoing dotted) lines. There are two kinds of external points, with one incoming dotted line, and with one outgoing dotted line. Each line going out of one vertex (or external point) has to be tied to a line going into some vertex (or external point). A solid line is tied directly to another solid line; a solid line is tied to a dotted line, and vice versa, by inserting a short cross bar at the joining point; a dotted line can be tied either directly to another dotted line, or indirectly through the intermediary of a solid line segment, as shown in Fig. 3. Each vertex is labeled as a lattice site, and the lines going into and coming out of a vertex carry labels of band indices for localized valence states. Each external point carries the label of a lattice site with band index. The lattice site labels on the vertices and the external points are all different from one another. Similarly the band index labels on any particular vertex are different from one another. Two diagrams are different, if they cannot be brought to coincidence including the direction of lines and the labels on them by simply shifting the vertices on the paper without breaking any lines.

The contribution of a diagram is obtained as follows:

(1) To each vertex associate a factor ϑ_μ or $\vartheta^*{}_\mu$ where μ is the number of incoming or outgoing solid lines;

(2) Attach a different lable βg to each short cross bar in the diagram;

(3) With each solid line from αf to γh associate a factor $W(\alpha f,\gamma h)$;

(4) With each dotted line from αf to γh associate a factor $S(\alpha f,\gamma h)$;

(5) Insert a factor (-1) for each solid line and each closed loop in the diagram;

(6) Insert a factor

$$1/\mu_1!\mu_2!\cdots\nu_1!\nu_2!\cdots(1!)^{\nu_1+\mu_2}(2!)^{\nu_2+\mu_2}\cdots,$$

where μ_1 is the number of ϑ_1,μ_2 the number of ϑ_2, etc., ν_1 the number of $\vartheta^*{}_1$, etc. in the diagram;

(7) Sum independently over all labels excepting naturally the labels of external points, the labels associated with vertices run only over the band indices of localized valence states, whereas the labels associated with short cross bars run over all band indices (valence and conduction).

A special rule applies to the diagrams with more than one pair of external points, such as occur in the computation of Q_2 in (18) which involves the operators $b^\dagger{}_{\alpha_2f_2}b^\dagger{}_{\alpha_1f_1}b_{\gamma_1h_1}b_{\gamma_2h_2}$. If the open loops go from γ_1h_1 to α_2f_2 (rather than α_1f_1) and from γ_2h_2 to α_1f_1 (rather than α_2f_2) an extra factor (-1) has to be inserted.

In the following discussion of particular diagrams it is convenient to distinguish various types of labels which appear in the diagrams by the following rules: The double label consisting of a small Greek letter for the band index and a small Latin letter for the lattice site is replaced by one capital letter. An external point with outgoing dotted line is labeled Γ', and one with incoming dotted line is labeled Γ''. An outgoing dotted line on a vertex is labeled H', and an incoming dotted line on a vertex is labeled H''. A short cross bar is labeled G' when it joins an incoming solid line to an outgoing dotted line, and it is labeled G'' when it joins an outgoing solid line to an incoming dotted line. Finally, an incoming solid line on a vertex is labeled F' and an outgoing solid line on a vertex is labeled F''. Clearly, the labels Γ' and Γ'' are fixed, the labels F', F'', H', and H'' run through all localized valence states in the lattice, whereas the labels G' and G'' run through all localized states (valence and conduction) in the lattice. Also the labels Γ' and Γ'' may stand for valence as well as for conduction states.

8. LINKED DIAGRAMS

Any part of a diagram which can be completely separated from the remaining diagram without breaking any line, is called an unlinked part. Once a diagram is divided up completely into unlinked parts, its total contribution can easily be obtained from calculating the separate contributions for each unlinked part, the total being equal to the product of its parts.

Unlinked parts without external points are called closed linked diagrams, if they cannot be broken up further into unlinked parts. The contributions of all closed linked diagrams appear simply as a factor

$$\exp\Big[\sum_{\text{closed linked}} \Lambda\Big] \tag{33}$$

to the diagrams with external lines. Λ stands for the number calculated, according to the rules of the previous section, for a particular closed linked diagram.

Since (33) is just the normalization integral (Ψ,Ψ), this factor divides out if ρ_1 and ρ_2 are computed with a normalized correlated wave function Ψ. Therefore, we can write with the help of (16) and (18)

$$\rho_1(x,y)=\sum_{\Gamma'\Gamma''}\varphi_{\Gamma'}(x)\varphi^*{}_{\Gamma''}(y)\times\sum_{\substack{\text{open linked with}\\ \text{2 external points}}}\Lambda(\Gamma'\Gamma''), \tag{34}$$

$$\begin{aligned}\rho_2(\xi,x;\eta,y)={}&\tfrac{1}{2}\rho_1(\xi,\eta)\rho_1(x,y)-\rho_1(\xi,y)\rho_1(x,\eta)\\ &+\tfrac{1}{2}\sum_{(\Gamma'_1\Gamma'_2)(\Gamma''_1\Gamma''_2)}\begin{vmatrix}\varphi_{\Gamma'_1}(\xi) & \varphi_{\Gamma'_1}(x)\\ \varphi_{\Gamma'_2}(\xi) & \varphi_{\Gamma'_2}(x)\end{vmatrix}\\ &\times\begin{vmatrix}\varphi^*{}_{\Gamma''_1}(\eta) & \varphi^*{}_{\Gamma_2''}(y)\\ \varphi^*{}_{\Gamma''_1}(\eta) & \varphi^*{}_{\Gamma_2''}(y)\end{vmatrix}\\ &\times\sum_{\substack{\text{open linked with}\\ \text{4 external points}}}\Lambda(\Gamma'_1\Gamma'_2,\Gamma''_1\Gamma''_2).\end{aligned} \tag{35}$$

The interest of the last formula lies in the net separation of the "properly correlated" part of ρ_2 by the diagram analysis, i.e., the part of ρ_2 which cannot be simply understood as the effect of many-particle statistics and the exclusion principle.

According to the last two formulas it is only necessary to obtain the contributions of all open linked diagrams with two or four external points. These diagrams can be obtained in a systematic fashion from the closed linked diagrams, of which there are fewer, of course.

A closed linked diagram can be associated to each open linked diagram by simply joining the end points of each open loop, i.e., joining Γ' and Γ'', Γ'_1 and Γ''_1, Γ'_2 and Γ''_2. In doing this, a diagram may arise which is not allowed under previously established rules. Indeed, the external points are always reached by a dotted line, but these dotted lines may not be attached at their other ends to a point H' of H''. Instead, they may both be attached to a point G' or G''. The closing of such an open loop would then lead to a sequence solid-dotted-solid line where neither end of the dotted line is attached to a point H' or H'', contrary to our rules. However, in view of (5) and (32), such an illegal sequence may be contracted into one solid line, and in this way a legitimate closed linked diagram is obtained.

Conversely, it is evident that we obtain all open linked diagrams if we open in turn every solid or dotted line, or every couple of solid and/or dotted lines in all closed linked diagrams, provided the diagram does not decay into two unlinked parts. The rule for opening solid or dotted lines is simple. First write the expression for the closed linked diagram. Second, in order to obtain the contribution to ρ_1 make in turn the following replacements.

$$\begin{aligned}W(HF)&\rightarrow\sum_{G'_0G''_0}W(HG'_0)S(G'_0\Gamma'')S(\Gamma'G''_0)W(G''_0F),\\ S(HF)&\rightarrow -S(H\Gamma'')S(\Gamma'F),\end{aligned} \tag{36}$$

for every factor W and S. Third, in order to obtain the contribution to the properly correlated part of ρ_2 make the replacements (36) in turn on every couple of factors with the pairs of external points (Γ''_1,Γ'_1) and (Γ''_2,Γ'_2). The over-all sign remains the same as in the closed linked diagram.

9. THE FIRST-ORDER DENSITY FUNCTION

The original expression for ρ_1 contains two terms which cannot be associated with a closed linked diagram. Their diagrams are given in Fig. 3, and their contributions to ρ_1 follow directly from the last formula (31) together with (3) and (11)

$$\sum_{[\kappa k]}\psi_{\kappa k}(x)\psi^*{}_{\kappa k}(y), \tag{37}$$

where $[\kappa k]$ is the set of Bloch states which are occupied by electrons. The complementary set, occupied by holes, is designated by (κk). This is just the ρ_1 from the uncorrelated wave function Ψ_0 which forms the base for the itinerant electron model.

It is of interest to notice that the total number of electrons in the lattice

$$N=\int dx\rho_1(x,x) \tag{38}$$

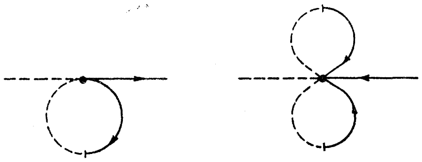

FIG. 4. Examples of bubbles.

is correctly given by (37). The correction terms which come from more complicated diagrams have to cancel one another in the integral (38). This fact is easily seen from (36) if we note that the integral (38) for any open linked diagram with two external points is equal to (± 1) times the contribution of the corresponding closed linked diagram; $+1$, if the open diagram resulted from opening a solid line; -1, if the open diagram resulted from opening a dotted line. A contribution to N from opening a solid line in a closed linked diagram is exactly canceled by the contribution to N from opening a dotted line in the same closed linked diagram.

This last property of the diagrams enables us to order the contributions to ρ_1 according to powers in the density m of holes in the valence band. m is defined as the ratio M/L where M is the average number of holes in localized valence states for the whole lattice. The order of some diagram is simply the power of m which occurs in the contribution of the associated closed linked diagram.

There are more terms of order one than (37). They arise from the closed linked diagrams which contain only ϑ_1, but no ϑ_2, ϑ_3, etc. Due to the simple structure of these diagrams they can all be evaluated. Their contribution together with (37) leads to substituting each occupied state $\psi_{\kappa k}(x)$ by a state $\bar{\psi}_{\kappa k}(x)$.

It is shown in Appendix B, how taking account of ϑ_1 throughout all possible diagrams is tantamount to redefining W in terms of $\bar{\psi}_{\kappa k}$ rather than $\psi_{\kappa k}$ and to a proper modification of the operators $\vartheta_2, \vartheta_3, \cdots$.

Another class of simple diagrams for ρ_1 is provided by the opening of the dotted and the solid lines in one of the two partial diagrams in Fig. 4. The vertices to which these "bubbles" are attached have other ingoing and outgoing lines, but the additions implied in all those other lines can be performed even before opening the bubbles. The result appears to the bubbles exactly as ϑ_1 would have appeared to them. Quite generally, any part of a diagram which can be reduced to ϑ_1 by taking loops off a vertex, appears to that diagram like a ϑ_1 insertion. Therefore, the effect of all such "dangling" parts in a diagram can be treated exactly as the effect of ϑ_1 contributions was treated in Appendix B.

The following result emerges: The treatment of ϑ_1 insertions is extended to include the "dangling" parts of a diagram. All that appears in the redefinition of Appendix B is the sum of ϑ_1 and all possible dangling parts. Since $\vartheta_1, \vartheta_2, \vartheta_3, \cdots$ are essentially determined by the assumptions concerning $O^{(1)}, O^{(2)}, O^{(3)} \cdots$ it seems that one is not free to choose ϑ_1 so as to cancel all the dangling parts. But the freedom to choose Ψ_0 still remains, and one might determine $\vartheta_1, \vartheta_2, \vartheta_3, \cdots$ variationally in order to determine $O^{(1)}, O^{(2)}, O^{(3)}, \cdots$ afterwards. In that case it is just as well to take $\vartheta_1=0$ and neglect all diagrams with dangling parts. We shall adopt this last viewpoint in the future development.

Up to the second order in the density of holes there is only one closed linked diagram out of which contributions to ρ_1 arise. This diagram is given in Fig. 5. It is of second order in ϑ_2. With assumed values for the constants determining the band structure, and for the overlap integrals, the band-structure term in the expectation value of the energy becomes, therefore, quadratic in ϑ_2. The Coulomb-repulsion term related to these second-order terms in ρ_1 is not only quartic in ϑ_2, but also in the density of holes, so that it can be neglected with respect to the band-structure term arising from ρ_1.

The explicit calculation of ρ_1 is done most easily and most usefully in terms of the Fourier transforms with respect to the lattice sites. Since ϑ_2 differs from zero only when all of its arguments are at the same lattice site, the Fourier transform does not affect ϑ_2 which simply becomes independent of the momenta exchanged between its in- and outgoing dotted and solid lines. Since the band indices are all carried along explicitly, the wave vectors k are always to be reduced to the first Brillouin zone. This implies conservation of wave vectors at each vertex up to a vector of the reciprocal lattice.

The terms in ρ_1 corresponding to the diagrams of Fig. 5 can easily be written down if the overlap $R(\alpha f,\gamma h)$ is simplified to $\delta_{\alpha\gamma}\delta_{fh}$. The localized orbits are then effectively Wannier states, and the two vertices of the diagrams in Fig. 5 have to be at the same lattice site. The particle propagator $W(F''F')$ has to be evaluated at the same lattice site $f'=f''$. It is shown in Appendix C that these assumptions have the following consequences. W differs from zero only if the orbits with band indices α' and α'' belong to the same irreducible representation of the crystal symmetry operations around the fixed lattice site $f'=f''$. For subsets $\{\alpha'\}$ and $\{\alpha''\}$ of the same irreducible representation, W is a multiple of the unit matrix.

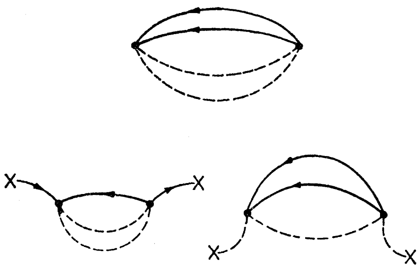

FIG. 5. Only closed linked diagram contributing to ρ_1 in the second order of density, and the two ρ_1 diagrams arising from it.

As long as the spin variable is specifically excluded from transformation under the crystal symmetry operations, W may have nonvanishing elements between orbits of the same irreducible representation, but different spin directions. Such a situation is typical of an uncorrelated wave function Ψ_0 which describes an antiferromagnetic metal or one with some kind of spiral structure. Although such cases are not hard to handle, we shall simplify matters by writing down our formulas in their absence. It follows then that

$$W(\alpha''f,\alpha'f)=m_\alpha\delta_{\alpha'\alpha''}\,, \tag{39}$$

where m_α is the probability of finding the orbit $\alpha=\alpha'=\alpha''$ at f occupied by a hole.

The Fourier transforms are written in terms of

$$u_{\beta\kappa}(k)=e^{ikg}U_{\beta g,\kappa k}\,. \tag{40}$$

According to (4) this quantity indicates the contribution of $\psi_{\kappa k}(x)$ to the localized states of index β. There is no simple relationship between κ and β. In the most general case the index κ simply numbers the consecutive Bloch functions belonging to the wave vector k. However, if the picture of a conduction band as somehow distinguishable from the valence bands is at all significant, the following assumptions about $u_{\beta\kappa}(k)$ can be made. For given β and κ the quantity $u_{\beta\kappa}(k)$ varies with the wave vector k fairly abruptly in such a manner that in most regions of the Brillouin zone $\psi_{\kappa k}(x)$ can be called either valence-like or conduction-like. Since $u_{\beta\kappa}(k)$ is assumed to be a continuous function of k, the transition regions have a nonvanishing but small volume in the reciprocal space.

The propagation function $W(\alpha f,\gamma h)$ of (32) is now written as

$$W(\alpha f,\gamma h)=\frac{1}{L}\sum_{(\kappa k)} u^*{}_{\gamma\kappa}(k)u_{\alpha\kappa}(k)e^{ik(f-h)}\,. \tag{41}$$

According to the above assumptions concerning $u_{\beta\kappa}(k)$ the propagation of a hole from αf to γh is done mainly by those terms κk in the sum which have the same character as α and γ. In particular, if α and γ have different character $W(\alpha f,\gamma h)$ is small, and if α and γ refer both to valence states $W(\alpha,f,\gamma h)$ does not exceed the density m of holes in valence states. It is this last statement which allows us to classify diagrams according to the number of solid lines in them.

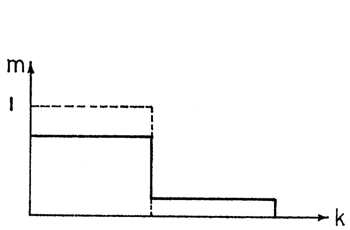

FIG. 6. Schematic distribution of holes in reciprocal space with (drawn out) and without (dotted) correlation.

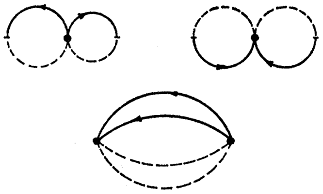

FIG. 7. Diagrams contributing to the properly correlated part of ρ_2 in the second order of density.

The contribution of the diagrams in Fig. 5 to ρ_1 becomes

$$\frac{4}{L}\sum_{k(\kappa)(\lambda)}\;\sum_{\alpha\beta(\beta'\beta'')\gamma}\psi_{\kappa k}(x)u_{\alpha\kappa}(k)$$
$$\times\vartheta_2\begin{pmatrix}\alpha & \beta\\ \beta' & \beta''\end{pmatrix}m_\beta\vartheta_2{}^*\begin{pmatrix}\gamma & \beta\\ \beta' & \beta''\end{pmatrix}u_{\gamma\lambda}{}^*(k)\psi_{\lambda k}{}^*(y)$$
$$-\frac{4}{L}\sum_{k\kappa\lambda}\;\sum_{\alpha\beta(\beta'\beta'')\gamma}\psi_{\kappa k}(x)u_{\alpha\kappa}(k)$$
$$\times\vartheta_2{}^*\begin{pmatrix}\beta' & \beta''\\ \alpha & \beta\end{pmatrix}m_{\beta'}m_{\beta''}\vartheta_2\begin{pmatrix}\beta' & \beta''\\ \gamma & \beta\end{pmatrix}u_{\gamma\lambda}{}^*(k)\psi_{\lambda k}{}^*(y)\,. \tag{42}$$

The summations (κ) and (λ) are restricted to the labels which are occupied by holes in Ψ_0, and the summation over $(\beta'\beta'')$ goes over all pairs of valence state indices. Since all indices α, β, β', β'', γ refer to valence states, only those indices κ and λ contribute to (42) which correspond to valence like states. The interpretation of (42) is therefore meant to apply only to valence states.

The first term in (42) describes a decrease in the occupation probability for those states which were originally fully occupied by valence holes. The second term spreads the holes which were freed by the first term over the whole available reciprocal space of valence character. The situation is schematically shown in Fig. 6. The kinetic energy and crystal-potential terms in the total energy can be obtained immediately.

10. THE SECOND-ORDER DENSITY FUNCTION

The closed linked diagrams which give contributions to the properly correlated part of ρ_2 have to have at least two solid and two dotted lines. On the other hand, as long as we are interested only in terms up to the second order in the density of holes, the only diagrams to be considered have not more than two solid lines. This shows that the only contributions of interest come from the diagrams in Fig. 7. Again these diagrams are at most of the second order in ϑ_2, so that the determination of ϑ_2 by minimizing the expectation value of the total energy for the correlated wave function Ψ is straightforward up to the second order in the density of holes.

The case of small overlap between valence states is of particular interest. The largest terms in the Hamiltonian are the Coulomb integrals with all orbits belonging to the same lattice site. The contribution of the diagrams above can then be evaluated quite easily,

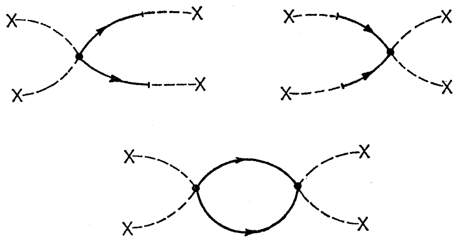

FIG. 8. The diagrams which contribute to the formula (43).

because in the lowest order of density and overlap only the diagrams in Fig. 8 with all external points at the same lattice site as that of ϑ_2 make a contribution.

The computation is straightforward for the same assumptions as were used in the derivation of (42). Together with the contribution of the valence hole term in (37) to the first term in (35) one finds for the terms in ρ_2 which are quadratic in the density

$$\bar{\rho}_2=\frac{1}{2}\sum_{(\alpha_1\alpha_2)(\gamma_1\gamma_2)}\begin{vmatrix}\varphi_{\alpha_1}(x) & \varphi_{\alpha_1}(\xi)\\ \varphi_{\alpha_2}(x) & \varphi_{\alpha_2}(\xi)\end{vmatrix}\begin{vmatrix}\varphi^*{}_{\gamma_1}(y) & \varphi^*{}_{\gamma_1}(\eta)\\ \varphi^*{}_{\gamma_2}(y) & \varphi^*{}_{\gamma_2}(\eta)\end{vmatrix}$$
$$\times\sum_{(\beta_1\beta_2)}\left[\delta\begin{pmatrix}\alpha_1 & \alpha_2\\ \beta_1 & \beta_2\end{pmatrix}+2\vartheta_2\begin{pmatrix}\alpha_1 & \alpha_2\\ \beta_1 & \beta_2\end{pmatrix}\right]m_{\beta_1}m_{\beta_2}$$
$$\times\left[\delta\begin{pmatrix}\gamma_1 & \gamma_2\\ \beta_1 & \beta_2\end{pmatrix}+2\vartheta^*{}_2\begin{pmatrix}\gamma_1 & \gamma_2\\ \beta_1 & \beta_2\end{pmatrix}\right] \quad (43)$$

at each lattice. The summations go over all different couples of valence states $(\alpha_1\alpha_2)$, $(\beta_1\beta_2)$, and $(\gamma_1\gamma_2)$. The function $\delta=1$ if the couples $(\alpha_1\alpha_2)$ and $(\beta_1\beta_2)$ are equal, otherwise $\delta=0$.

The function (41) is positive definite for $x=y$ and $\xi=\eta$. For given values of the densities m_β the ϑ_2 can be chosen such as to make $\bar{\rho}_2$ vanish. Such a requirement is reasonable if the one-center Coulomb and exchange integrals are much larger than the nearest neighbor overlaps divided by the atomic distance. This is just the assumption of narrow bands, and it leads immediately to a formula for ϑ_2, namely

$$2\vartheta_2\begin{pmatrix}\alpha_1 & \alpha_2\\ \gamma_1 & \gamma_2\end{pmatrix}=-\delta\begin{pmatrix}\alpha_1 & \alpha_2\\ \gamma_1 & \gamma_2\end{pmatrix}. \quad (44)$$

With this value for ϑ_2 one can compute the corrections to ρ_1 up to the second order in the densities m_β according to the preceding section. The redistribution of electrons in reciprocal space because of the strong correlation (44) is different according to the distribution of electrons in Ψ_0. Therefore, (44) already leads to a difference between ferromagnetic and nonferromagnetic arrangement of electrons in Ψ.

The advantage which correlation (44) gives to the ferromagnetic state, arises from having to overcome less accidental crowding of holes on the same site in Ψ_0. Correlation (44) forces fewer holes to be scattered outside of the Fermi surface if the holes all have the same spin direction. Correlation (44), however, prevents the electrons from taking advantage of the energy gain they experience when two of them crowd into the same lattice site with their spins parallel.

Quite generally some energy gain can be expected if the ϑ_2 as given in (44) is reduced by some small quantity ϵ,

$$2\vartheta_2\begin{pmatrix}\alpha_1 & \alpha_2\\ \gamma_1 & \gamma_2\end{pmatrix}=-\delta\begin{pmatrix}\alpha_1 & \alpha_2\\ \gamma_1 & \gamma_2\end{pmatrix}+\epsilon\begin{pmatrix}\alpha_1 & \alpha_2\\ \gamma_1 & \gamma_2\end{pmatrix}, \quad (45)$$

since the correlation energy connected with (43) increases with ϵ^2, whereas the single-particle energy due to the redistribution of electrons in reciprocal space decreases with ϵ. The coefficient of the former increase is of the order of the one-center Coulomb integral C, whereas the coefficient in the latter decrease is of the order of the valence bandwidth $\bar{E}$. Stabilization occurs at $\epsilon=\bar{E}/C$; the energy gain per lattice site is $\bar{E}^2/C$ times the density of holes squared.

The constant C to be inserted again depends on the spin arrangement in Ψ. The expression (44) has to be integrated over $x=y$ and $\xi=\eta$ with the kernel $e^2/|x-\xi|$. The resulting integral over the products of the 2 by 2 determinants is just equal to the Coulomb integral minus the exchange integral in the important case $(\alpha_1\alpha_2)=(\gamma_1\gamma_2)$. The exchange integral differs from zero only when α_1 and α_2 have the same spin, so that C is smaller in the ferromagnetic case, i.e., the energy gain from relaxing the correlation (42) is greater.

Among the off-diagonal elements $(\alpha_1\alpha_2)\neq(\gamma_1\gamma_2)$ some lead to exchange integrals (spin-flip transition). In the nonferromagnetic case, these off-diagonal elements may be expected to enforce Hund's rule locally to some extent.

11. TWOFOLD DEGENERATE VALENCE BAND

As the simplest possible application of the formulas (42) and (43), the case of a twofold degenerate band will be treated. This corresponds to the conditions in the Ni-Cu alloys, where the d states are in a cubic environment and there are some holes in the Bloch states made up of the x^2-y^2 and $2z^2-x^2-y^2$ states.

With the single particle Hamiltonian H_0 for the kinetic energy and the crystal potential one has $H_0\psi_{\kappa k}(x)=E_{\kappa k}\psi_{\kappa k}(x)$. In computing the expectation value of H_0 for the correlated wave function Ψ a quantity similar to the left-hand side of (39) arises. By the same group theoretical arguments as in Appendix C, it can be shown for valence states α and γ that

$$\frac{1}{L}\sum_{(k\kappa)}u^*{}_{\gamma\kappa}(k)E_{\kappa k}u_{\alpha\kappa}(k)=m_\alpha E_\alpha\delta_{\alpha\gamma}, \quad (46)$$

which defines the energy E_α, the average energy of the valence holes in the state α. The expectation value of H_0 becomes with the help of (42) for the correlated wave function, omitting the contribution of the conduction-like states as being unaffected by the correlation,

$$\sum_{\alpha}(\bar{E}_\alpha-m_\alpha E_\alpha)+4\sum_{\alpha\beta(\beta'\beta'')}\vartheta_2\begin{pmatrix}\alpha & \beta\\ \beta' & \beta''\end{pmatrix}\times[m_\alpha m_\beta E_\alpha-m_{\beta'}m_{\beta''}\bar{E}_\alpha]\vartheta_2^*\begin{pmatrix}\alpha & \beta\\ \beta' & \beta''\end{pmatrix},\quad(47)$$

where $\bar{E}_\alpha$ is the average energy of all the states in the band α. $\bar{E}_\alpha$ arises formally if in (46) the index κk is summed over all values, and the factor m_α on the right hand side is dropped. The Hermitian character of ϑ_2, i.e.,

$$\vartheta_2^*(\beta'\beta'',\alpha\beta)=\vartheta_2(\alpha\beta,\beta'\beta''),\quad(48)$$

has been assumed in writing (47). The correlation term in (47) is positive, because $E_\alpha>\bar{E}_\alpha$, i.e., the holes in Ψ_0 have chosen to occupy the highest states available.

In treating the twofold degenerate band, the total density of valence holes is denoted by m, the two orbits by a and b, the spin directions by attaching an arrow to the orbital label. In the ferromagnetic case each band is occupied by $m/2$ holes per lattice site, which gives an average energy E_f according to (46). In the nonferromagnetic case the corresponding quantities are $m/4$ and E_n. In computing the Coulomb-interaction terms according to (43) we shall assume that only the ordinary Coulomb repulsion and exchange integrals are different from zero. Therefore, only the terms containing

$$\begin{aligned}A&=e^2\int\int\frac{dxdy}{|x-y|}|\varphi_a(x)|^2|\varphi_a(y)|^2,\\ B&=e^2\int\int\frac{dxdy}{|x-y|}|\varphi_b(x)|^2|\varphi_b(y)|^2,\\ C&=e^2\int\int\frac{dxdy}{|x-y|}|\varphi_a(x)|^2|\varphi_b(y)|^2,\\ J&=e^2\int\int\frac{dxdy}{|x-y|}\varphi_a(x)\varphi^*{}_b(x)\cdot\varphi_b(y)\varphi^*{}_a(y),\end{aligned}\quad(49)$$

are taken into account for the evaluation of (43). Correspondingly, among the ϑ_2 only those will be assumed to be different from zero which immediately relate to the above integrals. Therefore, the following abbreviations are introduced for the nonferromagnetic case

$$\begin{aligned}&2\vartheta_2\begin{pmatrix}a\uparrow & a\downarrow\\ a\uparrow & a\downarrow\end{pmatrix}=1-\epsilon_A,\\ &2\vartheta_2\begin{pmatrix}b\uparrow & b\downarrow\\ b\uparrow & b\downarrow\end{pmatrix}=1-\epsilon_B,\\ &2\vartheta_2\begin{pmatrix}a\uparrow & b\downarrow\\ a\uparrow & b\downarrow\end{pmatrix}=2\vartheta_2\begin{pmatrix}a\downarrow & b\uparrow\\ a\downarrow & b\uparrow\end{pmatrix}=1-\epsilon_C,\\ &2\vartheta_2\begin{pmatrix}a\uparrow & b\uparrow\\ a\uparrow & b\uparrow\end{pmatrix}=2\vartheta_2\begin{pmatrix}a\downarrow & b\downarrow\\ a\downarrow & b\downarrow\end{pmatrix}=1-\epsilon_D,\\ &2\vartheta_2\begin{pmatrix}a\uparrow & b\downarrow\\ a\downarrow & b\uparrow\end{pmatrix}=2\vartheta_2\begin{pmatrix}a\downarrow & b\uparrow\\ a\uparrow & b\downarrow\end{pmatrix}=\epsilon_J.\end{aligned}\quad(50)$$

In the ferromagnetic case only

$$2\vartheta_2\begin{pmatrix}a\uparrow & b\uparrow\\ a\uparrow & b\uparrow\end{pmatrix}=1-\epsilon\text{ occurs.}$$

In this terminology the expectation value for the energy per lattice site is given in the ferromagnetic case by

$$4\bar{E}-mE_f+(m^2/2)(1-\epsilon)^2(E_f-\bar{E})+(m^2/4)\epsilon^2(C-J),\quad(51)$$

and in the nonferromagnetic case by

$$\begin{aligned}4\bar{E}-mE_n&+(m^2/8)(E_n-\bar{E})\{(1-\epsilon_A)^2+(1-\epsilon_B)^2\\ &+2(1-\epsilon_C)^2+2(1-\epsilon_D)^2+2\epsilon_J^2\}\\ &+(m^2/16)\{A\epsilon_A^2+B\epsilon_B^2+2(C-J)\epsilon_D^2\\ &+2C(\epsilon_C^2+\epsilon_J^2)-4J\epsilon_C\epsilon_J\}.\end{aligned}\quad(52)$$

The remaining terms in the Coulomb repulsion are the same in the ferromagnetic and in the nonferromagnetic situations.

The minima are reached for

$$\epsilon=\frac{2(E_f-\bar{E})}{C-J+2(E_f-\bar{E})},\quad(53)$$

with the energy (51) becoming

$$4\bar{E}-mE_f+\frac{m^2}{4}\frac{2(E_f-\bar{E})(C-J)}{C-J+2(E_f-\bar{E})}.\quad(54)$$

Since E_f is very near the top of the band structure if m is small, the quantity $2(E_f-\bar{E})$ can be interpreted as the width of the band. For the nonferromagnetic case one finds

$$\begin{aligned}\epsilon_A&=\frac{2(E_n-\bar{E})}{A+2(E_n-\bar{E})},\\ \epsilon_B&=\frac{2(E_n-\bar{E})}{B+2(E_n-\bar{E})},\\ \epsilon_C&=\frac{2(E_n-\bar{E})(C+2E_n-2\bar{E})}{(C+2E_n-2\bar{E})^2-J^2},\\ \epsilon_D&=\frac{2(E_n-\bar{E})}{C-J+2(E_n-\bar{E})},\\ \epsilon_J&=\frac{2(E_n-\bar{E})J}{(C+2E_n-\bar{E})^2-J^2}\end{aligned}\quad(55)$$

with the energy (52) equal to

$$\begin{aligned}4\bar{E}-mE_n+\frac{m^2}{16}\biggl\{&\frac{2(E_n-\bar{E})A}{A+2(E_n-\bar{E})}\\ &+\frac{2(E_n-\bar{E})B}{B+2(E_n-\bar{E})}+2\frac{2(E_n-\bar{E})(C-J)}{C-J+2(E_n-\bar{E})}\\ &+2\frac{C(C+2E_n-2\bar{E})-J^2}{(C+2E_n-2\bar{E})^2-J^2}2(E_n-\bar{E})\biggr\}.\end{aligned}\quad(56)$$

The quantities ϵ are related by the equation $\epsilon_D-\epsilon_C=\epsilon_J$. By virtue of this relation the sum of all ϑ_2 operators commutes with every component of the total spin of the atom. A group of atomic states, e.g., the triplets made with the orbitals a and b which differ only in the direction of the total spin, occur with the same weight in Ψ, provided they had the same weight in Ψ_0. The expectation value for any component of the total spin vanishes at each lattice site, in Ψ as well as in Ψ_0. But the expectation value for the square of the total spin at any given lattice site may have changed.

The occurrence of ϵ_J can be viewed in the following way. $\bar{\rho}_2$ as given by (43) becomes diagonal in the two-particles wave functions $(a\uparrow a\downarrow)$, $(b\uparrow b\downarrow)$, $(a\uparrow b\uparrow)$, $(a\downarrow b\downarrow)$, $(a\uparrow b\downarrow)+(a\downarrow b\uparrow)$, $(a\uparrow b\downarrow)-(a\downarrow b\uparrow)$. The coefficients of the last two are $m^2(1-\epsilon_C+\epsilon_J)^2/16$ and $m^2(1-\epsilon_C-\epsilon_J)^2/16$. The correlated wave function Ψ prefers therefore the triplet over the singlet, even if there is no ferromagnetism present. Ψ is an example of how Hund's rule can be enforced even in unfilled bands.

In comparing (54) and (56) one notices that the last term in (54) is still smaller than the last two terms in (56) provided $(E_n-\bar{E})<(E_f-\bar{E})(1+J/C)$. This condition should be satisfied since one expects the d band to have a reasonable energy density at its top, so that $E_n-E_f\ll E_f-\bar{E}$ for small density of holes. If one assumes for simplicity's sake that the last term in (54) is equal to the last two terms in (56), and also that $A=B$, then the question is whether or not $m(E_n-E_f)$ is smaller than $m^2(E_n-\bar{E})A/4(A+2E_n-2\bar{E})$. If so, the ferromagnetic correlated state Ψ_f has a lower expectation value for the total energy than the nonferromagnetic Ψ_n.

If the band is parabolic at its top, $E_n-E_f\sim m^{2/3}$, and ferromagnetism is not possible in the present theory. If the density of states as a function of energy reaches a nonvanishing value ν_0 at the top of the band, $m(E_n-E_f)$, is quadratic in m, and ferromagnetism occurs, provided

$$2\nu_0(E_n-\bar{E})>[1+2(E_n-\bar{E})/A]. \tag{57}$$

The density ν_0 is meant to refer to only one of the four bands, arising from the spin and the orbital degeneracy.

One may consider $2(E_n-\bar{E})$ as the width of the d band; $2\nu_0(E_n-\bar{E})$ is then the density of states at the top measured against the density of states resulting from a uniform distribution of the states throughout the band. The inequality (57) requires ν_0 to be larger than the average of ν throughout the band by a factor $2[1+2(E_n-\bar{E})/A]$. In particular, this condition is satisfied if there is a peak in the density of states at its top, such as one may find in the fcc cubic structure.

It may be interesting to note the following: In a nondegenerate band with the Coulomb repulsion integral between localized states given by A, the condition for ferromagnetism is again (57). However, the ferromagnetic state in the nondegenerate band does not have the additional advantage which is due to the last term in (54) being smaller than the last two terms in (56). This advantage of the degenerate band over the nondegenerate band vanishes only in the case of very strong Coulomb repulsion between the two degenerate orbits. Therefore, the results of this section bring out the importance of degeneracy for achieving ferromagnetism.

ACKNOWLEDGMENTS

The author wishes to express his indebtedness to Professor R. Brout, Dr. S. Nettel, and Dr. H. Thomas for many very helpful discussions and suggestions.

APPENDIX A

Equation (29) has to be solved in the special case where $O^{(\nu)}$ differs from zero only if the set of band indices $(\gamma_1\cdots\gamma_\nu)$ coincides with the set $(\alpha_1\cdots\alpha_\nu)$, the factor associated with $O^{(\nu)}$ being independent of the set $(\gamma_1\cdots\gamma_\nu)=(\alpha_1\cdots\alpha_\nu)$. The ϑ_μ will be assumed to have these same properties. It is then not necessary to write down two sets of indices for every operator $O^{(\nu)}$ or ϑ_μ, and even the common set of band indices no longer has to be mentioned since the factors associated with $O^{(\nu)}$ depend only on the number ν for $O^{(\nu)}$ or μ for ϑ_μ. We shall, therefore, only discuss these factors. Since the indices $(\gamma_1\cdots\gamma_\mu)$ in ϑ_μ can still be permuted with respect to the indices $(\alpha_1\cdots\alpha_\mu)$ which are always supposed to be in some standard order; the quantity $\mu!\,\vartheta_\mu$ will always occur in the forthcoming argument.

The formulas (28) and (29) have now to be matched. We take a set of m indices $\beta_1,\cdots,\beta_m$ and collect the coefficients of $a^\dagger{}_{\beta_m}\cdots a^\dagger{}_{\beta_1}b_{\beta_1}\cdots b_{\beta_m}$ in (29) and in the sum over ν of (28), where we have to insert the definition (19) of the projection operator P_β. In this manner we find that

$$\frac{1}{\omega}\sum_{\substack{\mu_1+2\mu_2+\cdots=m,\\ \mu_1\geq 0,\mu_2\geq 0,\cdots}}\frac{m!}{\mu_1!\mu_2!\cdots}\vartheta_1{}^{\mu_1}\vartheta_2{}^{\mu_2}\cdots =\sum_{\nu=0}^{m}(-1)^{m-\nu}\binom{m}{\nu}O^{(\nu)}. \tag{A1}$$

In order to solve this system of equations we multiply each side with $z^m/m!$ where z is an arbitrary real number, and add over all values of m. This gives

$$\frac{1}{\omega}\exp(\vartheta_1 z+\vartheta_2 z^2+\cdots)=e^{-z}\sum_{\nu=0}^{\infty}\frac{z^\nu}{\nu!}O^{(\nu)}, \tag{A2}$$

after some elementary algebra. The terms with $m=0$ were put equal to one; ω can be fixed by the condition $O^{(0)}=1/\omega$.

The case $O^{(0)}=0$ presents difficulties in this formulation. Although they could have been avoided, it seems important to bring out quite clearly that equation (29) is useless as $O^{(0)}$ tends to zero. $O^{(0)}=0$ means that any configuration with at least one lattice site completely empty is excluded in the correlated wave function. A requirement like $O^{(0)}=0$ is absolutely reasonable when there are at least as many particles as lattice sites. The present theory can, therefore, be expected to break down if it is physically necessary to discriminate against configurations with completely empty lattice sites. However, as long as such a condition does not have to be imposed, we can set $\omega=1$, since only the relative weights between the $O^{(\nu)}$ and between the ϑ_μ are physically significant.

The case of greatest interest is

$$O^{(0)}=O^{(1)}=1\,,\quad O^{(2)}=\epsilon\,, \tag{A3}$$

from which we obtain

$$\vartheta_1 z+\vartheta_2 z^2+\cdots=\ln\left(1+z+\epsilon\frac{z^2}{2}\right)-z$$

$$=\sum_{n=1}^{\infty}(-1)^{n-1}z^n\sum_{\nu=0}^{\nu=n-1}\frac{1}{n-\nu}\binom{n-\nu}{\nu}\left(\frac{\epsilon}{2}\right)^{\nu}-z\,. \tag{A4}$$

This gives for ϑ_1, ϑ_2, $\cdots$ the values

$$\vartheta_1=0\,,\qquad \vartheta_2=-\tfrac{1}{2}(1-\epsilon)\,,$$
$$\vartheta_3=\tfrac{1}{3}-(\epsilon/2)\,,\quad \vartheta_4=-\tfrac{1}{4}(1-6\epsilon+\epsilon^2)\,,\quad \text{etc.} \tag{A5}$$

The chain of equations can be broken off at any point.

If ω is left explicitly in the relation between ϑ_μ and $O^{(\nu)}$ the conditions

$$O^{(0)}=\frac{1}{\omega}\,,\quad O^{(1)}=1\,,\quad O^{(2)}=\epsilon\,, \tag{A6}$$

lead to the equations

$$\ln\left(1+\omega z+\epsilon\omega\frac{z^2}{2}\right)-z=\vartheta_1 z+\vartheta_2 z^2+\cdots \tag{A7}$$

$$\vartheta_1=\omega-1\,,\qquad \vartheta_2=-\frac{\omega}{2}(\omega-\epsilon)\,,$$

$$\vartheta_3=\omega^2\left(\frac{\omega}{3}-\frac{\epsilon}{2}\right)\,,\quad \vartheta_4=-\frac{\omega^2}{4}(\omega^2-6\omega\epsilon+\epsilon^2)\,,\quad \text{etc.} \tag{A8}$$

The case $\epsilon=1$, $\omega\to\infty$ is physically sound, but mathematically useless in terms of ϑ_1, ϑ_2, etc.

APPENDIX B

The two diagrams of Fig. 3 which contribute to (37) can be interpreted as follows. The first diagram gives ρ_1 for the wave function where all Bloch states κk are filled. The second diagram subtracts from the first the contribution

$$\sum_{(\kappa k)}\psi_{\kappa k}(x)\psi^*{}_{\kappa k}(y) \tag{B1}$$

which comes from the empty Bloch states of Ψ_0.

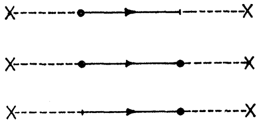

FIG. 9. Simple ρ_1 diagrams containing ϑ_1.

If we combine this last contribution to ρ_1 with the three contributions of Fig. 9, we can write the result as

$$\sum_{(\kappa k)}\bar{\psi}_{\kappa k}(x)\bar{\psi}^*{}_{\kappa k}(y)\,, \tag{B2}$$

with the new Bloch state

$$\bar{\psi}_{\kappa k}(x)=\psi_{\kappa k}(x)+\sum_{\alpha\beta\gamma\lambda}\psi_{\lambda k}(x)u_{\alpha\lambda}(k)S_{\alpha\beta k}\vartheta_1(\beta\gamma)u_{\gamma\kappa}(k)\,. \tag{B3}$$

We have used the Fourier transform

$$S_{\alpha\beta k}=\sum_{g}S(\alpha o,\beta g)e^{ikg}\,. \tag{B4}$$

The result of all the other diagrams with only ϑ_1 can be stated with the help of a matrix $T_{\kappa\lambda}(k)$ which has for every k as many rows and columns as there are holes with wave vector k in Ψ_0. We have

$$T_{\kappa\lambda}=\delta_{\kappa\lambda}+\sum_{\alpha\beta\gamma}\{u_{\alpha\kappa}S_{\alpha\beta}\vartheta_1(\beta\gamma)u^*{}_{\gamma\lambda}+u_{\alpha\kappa}\vartheta^*{}_1(\beta\alpha)S_{\beta\gamma}u^*{}_{\gamma\lambda}$$
$$+u_{\alpha\kappa}\vartheta^*{}_1(\beta'\alpha)S_{\beta'\beta''}\vartheta_1(\beta''\gamma)u^*{}_{\gamma\lambda}\}\,, \tag{B5}$$

where all the sums over band indices are taken at fixed wave vector k. Instead of subtracting (B1) or (B2) from the ρ_1 of a wave function with all Bloch states κk filled, one has now to subtract

$$\sum_{\kappa\lambda k}\bar{\psi}_{\kappa k}(x)T^{-1}{}_{\kappa\lambda}\bar{\psi}^*{}_{\lambda k}(y)\,. \tag{B6}$$

The inverse of T which is inserted in (B6) as compared to (B2), simply normalizes the functions $\bar{\psi}_{\kappa k}(x)$. The term coming from the second diagram of Fig. 3 has, therefore, been replaced by a very similar term, namely one that arises from replacing the Bloch states $\psi_{\kappa k}(x)$ by the properly orthonormalized modification of $\bar{\psi}_{\kappa k}(x)$. Indeed, the states $\bar{\psi}_{\kappa k}(x)$ are not orthonormal, but one can find linear combinations which are orthonormal, say $\tilde{\psi}_{\kappa k}(x)$, and (B6) transforms then to

$$\sum_{(\kappa k)}\tilde{\psi}_{\kappa k}(x)\tilde{\psi}^*{}_{\kappa k}(y)\,. \tag{B7}$$

Let us now examine an arbitrary diagram without any ϑ_1 in it. The particle lines connecting two vertices

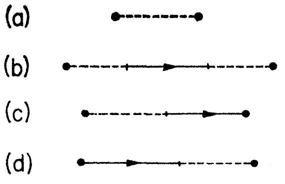

FIG. 10. The four possible particle lines between vertices if $\vartheta_1=0$.

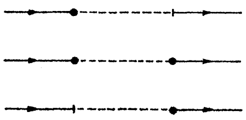

FIG. 11. The three possible insertions of ϑ_1 into a solid line.

or connecting a vertex to an external point are of the four different types shown in Fig. 10. (An external point is equivalent to a connection with a vertex.) The occurrences of ϑ_1 can arise in the following two ways.

First, the solid lines in Figs. 10(b), 10(c), and 10(d) are broken up an arbitrary number of times by inserting one of the three pieces shown in Fig. 11. The effect of these insertions is equivalent to the substitution

$$W(\alpha f,\gamma h)=\frac{1}{L}\sum_{(\kappa k)} U^*{}_{\alpha f,\kappa k}U_{\gamma h,\kappa k}\rightarrow \frac{1}{L}\sum_{(\kappa\lambda k)} U^*{}_{\alpha f,\kappa k}T^{-1}{}_{\kappa\lambda}U_{\gamma h,\lambda k}. \tag{B8}$$

Second, a ϑ_1 can be inserted at the ends of the solid lines in Figs. 10(b), 10(c), and 10(d) without breaking them. This gives the five diagrams listed in Fig. 12.

Combining Fig. 10(b) with Figs. 12(a), 12(b), and 12(c) is tantamount to substituting

$$W(G''G')\rightarrow \sum_{F''F'}[\delta_{F''G'}+\vartheta^*{}_1(F''G'')] \times W(F''F')[\delta_{F'G'}+\vartheta_1(F'G')] \tag{B9}$$

in the diagram 10(b). The substitution (B9) in Fig. 10(c) or Fig. 10(d) can be justified only if the interpretation of the vertex to the right of Figs. 10(c), 10(d), 12(d), and 12(e) is changed by introducing a fictitious label G'' into Figs. 10(c) and 10(d), and G' into Figs. 12(d) and 12(e). This is done by the substitutions

$$\vartheta_2(H'_1H'_2,F'_1F'_2)\rightarrow \sum_{G'_1G'_2}\tilde{\vartheta}_2(H'_1H'_2,G'_1G'_2) \times[\delta_{G'_1F'_1}+\vartheta_1(G'_1F'_1)][\delta_{G'_2F'_2}+\vartheta_1(G'_2F'_2)],$$

$$\vartheta^*{}_2(H''_1H''_2,F''_1F''_2)\rightarrow \sum_{G''_1G''_2}[\delta_{F''_1G''_1}+\vartheta_1(F''_1G''_1)] \times[\delta_{F''_2G''_2}+\vartheta_1(F''_2G''_2)]\tilde{\vartheta}^*{}_2(H''_1H''_2,G''_1G''_2), \tag{B10}$$

and similar formulas for ϑ_3, etc. If the vertices in Figs. 10(c) and 10(d) are interpreted as $\tilde{\vartheta}_2$, $\tilde{\vartheta}_3$, etc., then the combined effect of Figs. 10(c) and 10(d) as well as 12(d) and 12(e) is again described by the substitution (B9). In all three diagrams 10(b), 10(c), and 10(d), the effect of ϑ_1 insertions is now described by the combined substitutions (B8) and (B9).

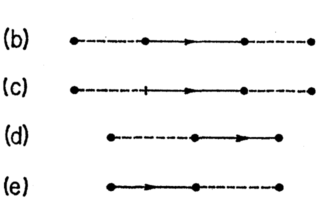

FIG. 12. The five possible ϑ_1 insertions without breaking a solid line.

Now, it follows immediately from (4) that

$$\sqrt{L}\int\psi^*{}_K(x)\psi_G(x)dx=U_{GK}, \tag{B11}$$

which shows with (32) that

$$W(F''F')=\int\psi^*{}_{F''}(x)dx \times\int\psi_{F'}(y)dy\sum_{(K)}\psi_K(x)\psi^*{}_K(y). \tag{B12}$$

K is used as abbreviation for the index pair κk. On the other hand, if we insert into this formula the sum over all K, rather than only the K of the holes, then we can write

$$\begin{aligned}\frac{1}{L}\sum_K U^*{}_{F''K}U_{F'K}&=\int\psi^*{}_{F''}(x)dx\int\psi_{F'}(y)dy \times\sum_{G'G''}\psi_{G'}(x)S(G'G'')\psi^*{}_{G''}(y)\\&=\sum_{G'G''}R(F''G')S(G'G'')R(G''G')\\&=R(F''F').\end{aligned} \tag{B13}$$

If we take the Fourier transform as in (B4) and insert (40), it follows that

$$\sum_\kappa u^*{}_{\alpha\kappa}(k)u_{\gamma\kappa}(k)=R_{\alpha\gamma k}=\sum_g R(\alpha o,\gamma g)e^{ikg}. \tag{B14}$$

From this last relation, we find that

$$\sqrt{L}\int\bar{\psi}^*{}_K(x)\psi_G(x)dx=U_{GK}+\sum_F\vartheta_1(GF)U_{FK}. \tag{B15}$$

Therefore, the combination of (B8) and (B9), i.e., the elimination of all ϑ_1 from the diagrams, is effected by substituting

$$W(F''F')\rightarrow\int\psi^*{}_{F''}(x)dx\int\psi_{F'}(y)dy \times\sum_{(\kappa\lambda k)}\bar{\psi}_{\kappa k}(x)T^{-1}{}_{\kappa\lambda}\bar{\psi}^*{}_{\lambda k}(y) \tag{B16}$$

and replacing all ϑ_2, ϑ_3, $\cdots$ by $\tilde{\vartheta}_2$, $\tilde{\vartheta}_3$, $\cdots$.

APPENDIX C

The Bloch waves $\psi_{\kappa k}(x)$ are assumed to arise from some secular problem as a linear combination of the functions $\psi_{\beta g}(x)$. Under a coordinate transformation $x=Tx'+t$ compatible with the lattice, one has

$$\psi_{\kappa k}(x)=e^{ikt}\psi_{\kappa k'}(x') \quad \text{with} \quad k=Tk'. \tag{C1}$$

Also one has for the localized orbits

$$\psi_{\beta g}(x)=\sum_{\alpha} T_{\beta\alpha}\psi_{\alpha f} \quad \text{with} \quad g=Tf+t, \tag{C2}$$

where the matrix $T_{\beta\alpha}$ gives the transformation of the orbits corresponding to the coordinate transformation T.

In view of the orthonormality of the functions $\psi_{\kappa k}(x)$ one finds for the coefficients U_{GK} of (4) the formula

$$\frac{1}{\sqrt{L}}U_{GK}=\int \psi^{*}{}_{K}(x)\psi_{G}(x)dx. \tag{C3}$$

If one inserts (C1) and (C2) it follows that

$$U_{GK}=e^{-ikt}\sum_{\alpha} T_{\beta\alpha}U_{FK'}, \tag{C4}$$

with $F=(\alpha f)$, $G=(\beta g)$, $K=(\kappa k)$, $K'=(\kappa k')$. Any expression depending on U_{GK}, ψ_{K}, ψ_{G}, K, G, etc., can be written in terms of $U_{FK'}$, $\psi_{K'}$, ψ_{F}, K', F, etc., with the help of (C1), (C2) and (C4). In the new expression in which only the latter quantities and the coefficients $T_{\beta\alpha}$ occur, it is possible to replace again $F \rightarrow G$, $K' \rightarrow K$, etc. If the resulting expression coincides with the original one, it is called invariant with respect to the transformation T.

Now one has for W as defined in (32) the transformation

$$W(G''G')=\sum_{\alpha'\alpha''} T^{*}{}_{\beta''\alpha''}T_{\beta'\alpha'}W(F)'F'' \tag{C5}$$

according to (C4). In order to obtain (39) we now put $t=0$, $g''=g'=f''=f'$. The arguments in W are then simply $\beta''\beta'$ and $\alpha''\alpha'$.

The formula (C5) is now averaged over all symmetry operations of the lattice which leave the lattice site $g=f$ fixed. This gives

$$W(\beta''\beta')=\sum_{\alpha'\alpha''}\left(\frac{1}{l}\sum_{T} T^{*}{}_{\beta''\alpha''}T_{\beta'\alpha'}\right)W(\alpha''\alpha'). \tag{C6}$$

If the orbits have been grouped according to the irreducible representation to which they belong, it is possible to apply one of the important results of group representation theory.[7]

$$\frac{1}{l}\sum_{T} D^{(j'')}{}_{\beta''\alpha''}(T)D^{(j')}{}_{\beta'\alpha'}(T)=\frac{1}{j}\delta_{j'j''}\delta_{\beta'\beta''}\delta_{\alpha'\alpha''}, \tag{C7}$$

where $D^{(j)}{}_{\beta\alpha}(T)$ is the matrix representing T in the representation j, the indices α', β', α'', β'' being restricted to the values relevant to j' and j''. j is the dimension of the representation j. l is the number of operations in the group. If (C7) is inserted into (C6) the formula (39) and the explanation preceding it follow immediately.

---

[7] Cf. Eugene P. Wigner, *Group Theory and its Application to the Quantum Mechanics of Atomic Spectra*, translated by T. T. Griffin (Academic Press, Inc., New York, 1959), p. 83.