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Multiple-Scattering Methods in the Theory of Solids*

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The formalism of solid-state scattering theory is applied to the construction of the t matrix for a pair of electrons interacting through a repulsive potential of finite range. Expressions for t are obtained in suitable limits for three cases: (1) a potential acting only at a single site and in a single band, (2) a potential acting at a single site but connecting a pair of bands, and (3) a potential acting in a single band but extending to first neighbors. The results are applied to the determination of an optical potential which can be used in a study of the range of excited electrons in metals, and to the determination of the ground-state energy of a low-density system. The ground-state energy is examined as a function of spin alignment, leading to the development of criteria for the occurrence of ferromagnetism in the low-density limit. It is shown that for repulsive, finite-range interactions, ferromagnetism does not occur for very low densities, whatever the band structure is.

I. INTRODUCTION

In this paper we will consider the calculation of the ground-state energy of a low-density system of fermions interacting by repulsive forces of finite range in the presence of a periodic potential. Our work is intended as an approximate method of studying the energies of electrons in crystals which should be applicable in the case in which a small number of electrons or holes are present in a narrow energy band. Therefore, it should be possible to use these techniques in the energy-band theory of ferromagnetism, particularly with reference to situations in which the magnetic properties are determined by a small number of carriers.

It has been known for several years that the energy of a low-density system of interacting fermions at zero temperature can be determined from the t matrix.[1] The fundamental result is that if E is the energy of the interacting system, and E_0 is the energy of the system if the particles do not interact, then

$$E=E_0+\sum_{m,n}\langle mn|t|mn\rangle. \tag{1.1}$$

The elements of the t operator are expressed on the basis of free (but properly symmetrized) two-particle states described generally by the quantum numbers m,n. We will discuss this basis more completely below. The sum in (1.1) includes only those states which are occupied in the ground configuration.

The t matrix obeys an integral equation which is quite similar to that satisfied by the ordinary scattering matrix for two particles. This equation can be represented formally by

$$t=V+V\mathcal{G}t \tag{1.2}$$

in which V is the two-body interaction and $\mathcal{G}$ is a two-body Green's function. This Green's function can be represented at low densities by

$$\mathcal{G}=(E-H_0)^{-1}Q \tag{1.3}$$

in which H_0 is the Hamiltonian for two noninteracting particles. The operator Q destroys states which are occupied in the ground configuration. This has the consequence that the t matrix is real for occupied states. We do not include in $\mathcal{G}$ any modification of the single-particle energies by the interaction since this is unimportant for sufficiently low density.

Our first objective in this paper is to develop a method for the computation of the t matrix defined by (1.2) in solid-state problems. Our approach is based on the formalism of solid-state scattering theory,[2] and is applicable in the case of finite range forces. (The precise definition of finite range will be given below.) In particular, an expression for t will be derived whose evaluation can be accomplished by operations on matrices of finite dimensionality. Sections 2, 3, and 4 are devoted to this calculation. Section 2 contains the definitions and properties of the two-body states which are employed; Sec. 3 presents expressions for matrix elements of the potential and the Green's function; and Sec. 4 contains the explicit construction of t.

Applications of the method are studied in Secs. 5, 6, and 7. In Sec. 5, an effective one-body potential is obtained which contains an imaginary part for states above the Fermi surface; this potential is calculated explicitly in a limiting case for electrons in a single band interacting on a single site. Interactions connecting bands and interactions extending to first neighbors are studied in Sec. 6, which contains a calculation of the relevant t-matrix elements in these cases. Finally, in Sec. 7, the preceding results are applied to the theory of ferromagnetism. Criteria are obtained for the occurrence of ferromagnetism when electrons are present in a single band and in degenerate bands. These criteria are studied for somea pproximate band models.

II. TWO-PARTICLE STATES

We consider a system of electrons in a crystal lattice, composed of monatomic unit cells of volume Ω. If the electrons did not interact with each other, the system

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[1] C. Bloch and C. de Dominicis, Nucl. Phys. **10**, 509 (1959). N. M. Hugenholtz, in *The Many Body Problem*, edited by C. de Witt (John Wiley & Sons, Inc., New York, 1959), p. 1.

[2] J. Callaway, J. Math. Phys. **5**, 783 (1964).

could be exactly described in terms of one-electron wave functions (Bloch functions) $\psi_\alpha(\mathbf{k},\mathbf{r})$. Here, α is the band index and $\mathbf{k}$ the wave vector. These functions are eigenfunctions of the single-particle Hamiltonian $H^{(0)}(i)$ with energies $E_\alpha(\mathbf{k})$

$$H^{(0)}(i)\psi_\alpha(\mathbf{k},\mathbf{r}_i)=E_\alpha(\mathbf{k})\psi_\alpha(\mathbf{k},\mathbf{r}_i)\,. \tag{2.1}$$

$H^{(0)}(i)$ includes the periodic potential. The Bloch functions are normalized so that

$$\int\psi_\alpha{}^*(\mathbf{k},\mathbf{r})\psi_\beta(\mathbf{k}',\mathbf{r})d^3r=\delta_{\alpha\beta}\delta(\mathbf{k}-\mathbf{k}')\,. \tag{2.2}$$

Localized functions (Wannier functions) are found from the Bloch functions by

$$a_\alpha(\mathbf{r}-\mathbf{R}_n)=\frac{\Omega^{1/2}}{(2\pi)^{3/2}}\int\exp(-i\mathbf{k}\cdot\mathbf{R}_n)\psi_\alpha(\mathbf{k},\mathbf{r})d^3k \tag{2.3}$$

in which $\mathbf{R}_n$ is a lattice vector and the integration includes a single Brillouin zone.[3]

For the purpose of evaluating the elements of t, we need two different sets of basis states. Since the sum in (1.1) includes only occupied states, we need for this purpose a set of two-particle functions characterized by wave vectors and band indices. First, however, we must distinguish between triplet and singlet states of the electron pair. In a triplet state the space part of the wave function must be antisymmetric; in the singlet case it must be symmetric. We define the functions

$$\begin{aligned}\Phi_{\alpha\beta}{}^{(s,t)}(\mathbf{p},\mathbf{q};\mathbf{r}_1,\mathbf{r}_2)=(2)^{-1/2}[&\psi_\alpha(\mathbf{p},\mathbf{r}_1)\psi_\beta(\mathbf{q},\mathbf{r}_2)\\&\pm\psi_\alpha(\mathbf{p},\mathbf{r}_2)\psi_\beta(\mathbf{q},\mathbf{r}_1)]\,.\end{aligned} \tag{2.4}$$

The + sign goes with the singlet state $\Phi^{(s)}$; the minus sign goes with the triplet state. We will frequently omit the superscripts s and t.

It will be observed that these functions have the symmetry

$$\Phi_{\alpha\beta}(\mathbf{p},\mathbf{q};\mathbf{r}_1,\mathbf{r}_2)=\pm\Phi_{\beta\alpha}(\mathbf{q},\mathbf{p};\mathbf{r}_1,\mathbf{r}_2)\,. \tag{2.5}$$

It follows from (2.5) that the set of functions Φ is redundant if one considers all possible values of α, β, $\mathbf{q}$, $\mathbf{p}$. This redundancy can be removed by restricting one of the momentum variables to a half-space.

It is convenient to introduce total and relative wave vectors through

$$\begin{aligned}\mathbf{K}&=\mathbf{p}+\mathbf{q}\,,\\2\mathbf{k}&=\mathbf{p}-\mathbf{q}\,.\end{aligned} \tag{2.6}$$

In order to avoid the introduction of another symbol to represent a wave function, we write the result of this substitution as

$$\begin{aligned}\Phi_{\alpha\beta}(\mathbf{K},\mathbf{k};\mathbf{r}_1,\mathbf{r}_2)=2^{-1/2}\bigg[&\psi_\alpha\Big(\frac{\mathbf{K}}{2}+\mathbf{k},\mathbf{r}_1\Big)\psi_\beta\Big(\frac{\mathbf{K}}{2}-\mathbf{k},\mathbf{r}_2\Big)\\&\pm\psi_\alpha\Big(\frac{\mathbf{K}}{2}+\mathbf{k},\mathbf{r}_2\Big)\psi_\beta\Big(\frac{\mathbf{K}}{2}-\mathbf{k},\mathbf{r}_1\Big)\bigg]\,.\end{aligned} \tag{2.7}$$

The symmetry relation (2.5) now implies that only half of $\mathbf{k}$ space need be considered in the expansion of an arbitrary two-particle wave function provided that all pairs of bands are included.

The wave function (2.7) is normalized except for $k=0$, in which case an additional factor of $2^{-1/2}$ is required. Since we will be concerned with integrations over $\mathbf{p}$ and $\mathbf{q}$, and a finite change in the value of a function at a single point does not affect the value of an integral, we will not include this factor explicitly.

The two-particle Bloch functions are convenient for the evaluation of sums such as (1.1). However, in order to determine the elements of t, it is much more convenient to work in a different basis. We want a set of functions characterized by a definite value of the total wave vector $\mathbf{K}$, but depending on a relative lattice coordinate $\mathbf{R}_i$ instead of a relative wave vector. We will denote such functions as $\psi_{\alpha\beta,i}{}^{(s,t)}(\mathbf{K},\mathbf{r}_1,\mathbf{r}_2)$. They are given by

$$\begin{aligned}\psi_{\alpha\beta' i}{}^{(s,t)}&(\mathbf{K},\mathbf{r}_1,\mathbf{r}_2)\\&=\Omega^{1/2}[16\pi^3(1+\delta_{i,0})]^{-1/2}\exp(i\mathbf{K}\cdot\mathbf{R}_i/2)\\&\quad\times\sum_n\exp(i\mathbf{K}\cdot\mathbf{R}_n)[a_\alpha(\mathbf{r}_1-\mathbf{R}_n-\mathbf{R}_i)a_\beta(\mathbf{r}_2-\mathbf{R}_n)\\&\qquad\pm a_\alpha(\mathbf{r}_2-\mathbf{R}_n-\mathbf{R}_i)a_\beta(\mathbf{r}_1-\mathbf{R}_n)]\,.\end{aligned} \tag{2.8}$$

As before, the + sign is associated with a singlet state, and the − sign with a triplet state.

These functions satisfy Bloch's theorem for total wave vector $\mathbf{K}$:

$$\begin{aligned}\psi_{\alpha\beta,i}(\mathbf{K},\,&\mathbf{r}_1+\mathbf{R}_l,\,\mathbf{r}_2+\mathbf{R}_l)\\&=\exp(i\mathbf{K}\cdot\mathbf{R}_l)\psi_{\alpha\beta,i}(\mathbf{K},\mathbf{r}_1,\mathbf{r}_2)\,.\end{aligned} \tag{2.9}$$

They have the symmetry

$$\psi_{\alpha\beta,i}(\mathbf{K},\mathbf{r}_1,\mathbf{r}_2)=\pm\psi_{\beta\alpha,-i}(\mathbf{K},\mathbf{r}_1,\mathbf{r}_2)\,. \tag{2.10}$$

In (2.10), the subscript $-i$ indicates that $-\mathbf{R}_i$ replaces $\mathbf{R}_i$ in (2.8).

It follows from (2.10) that the set $\psi_{\alpha\beta,i}$ is redundant as the $\Phi_{\alpha\beta}$ were. Therefore we may restrict sums over coordinate i to half the crystal or alternatively we include a factor $\frac{1}{2}(1+\delta_{i,0})$ and sum over all values of i.

The orthonormality properties of the $\psi_{\alpha\beta,i}$ are summarized by

$$\begin{aligned}\int\psi_{\gamma\delta,j}{}^*&(\mathbf{K}',\mathbf{r}_1,\mathbf{r}_2)\psi_{\alpha\beta,i}(\mathbf{K},\mathbf{r}_1,\mathbf{r}_2)d^3r_1d^3r_2\\&=\delta(\mathbf{K}-\mathbf{K}')[(1+\delta_{i,0})(1+\delta_{j,0})]^{-1/2}\\&\quad\times[\delta_{\alpha,\gamma}\delta_{\beta,\delta}\delta_{i,j}\pm\delta_{\alpha,\delta}\delta_{\beta,\gamma}\delta_{i,-j}]\,.\end{aligned} \tag{2.11}$$

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[3] The utility of Wannier functions in calculations similar to this is sometimes questioned on the basis that they are not invariant under a change of phase of the basic Bloch functions. It can be seen, however, that the expression for the ground-state energy is unaffected by such a transformation. We will therefore assume that the phase of the Bloch functions is chosen so as to make the Wannier functions as localized as possible.

If the basic Bloch functions are complete, so that they satisfy the relation

$$\sum_{\alpha} \int \psi_\alpha^*(\mathbf{k},\mathbf{r})\psi_\alpha(\mathbf{k},\mathbf{r}')d^3k=\delta(\mathbf{r}-\mathbf{r}'), \qquad (2.12)$$

then it can be shown that the two-electron functions satisfy

$$\sum_{\alpha\beta}\sum_{i} \tfrac{1}{2}(1+\delta_{i,0})\int \psi_{\alpha\beta,i}^*(\mathbf{K},\mathbf{r}_1,\mathbf{r}_2)\psi_{\alpha\beta,i}(\mathbf{K},\mathbf{r}_1',\mathbf{r}_2')d^3K$$
$$=\tfrac{1}{2}[\delta(\mathbf{r}_1-\mathbf{r}_1')\delta(\mathbf{r}_2-\mathbf{r}_2')\pm\delta(\mathbf{r}_1-\mathbf{r}_2')\delta(\mathbf{r}_2-\mathbf{r}_1')]. \qquad (2.13)$$

This relation guarantees that any properly symmetric or antisymmetric two-electron function may be expanded in the $\psi_{\alpha\beta,i}$.

Next, we require the transformation equations connecting the two sets of functions we have introduced. In general, we have to write

$$\Phi_{\alpha\beta}{}^{(s,t)}(\mathbf{K},\mathbf{k},\mathbf{r}_1,\mathbf{r}_2)=\sum_i \tfrac{1}{2}(1+\delta_{i,0})\int d^3K'$$
$$\times F_{\alpha\beta}{}^{(s,t)}(\mathbf{K},\mathbf{K}',\mathbf{k},\mathbf{R}_i)\psi_{\alpha\beta,i}{}^{(s,t)}(\mathbf{K}',\mathbf{r}_1,\mathbf{r}_2). \qquad (2.14\text{a})$$

This expression is, however, more cumbersome than is necessary. It turns out that $F_{\alpha\beta}$ depends on $\mathbf{K}$ and $\mathbf{K}'$ only through a multiplicative factor $\delta(\mathbf{K}-\mathbf{K}')$. We find it convenient to suppress such factors, and work within specific subspaces characterized by definite $\mathbf{K}$. Hence, instead of (2.14a), we have

$$\Phi_{\alpha\beta}(\mathbf{K},\mathbf{k},\mathbf{r}_1,\mathbf{r}_2)=\sum_i \tfrac{1}{2}(1+\delta_{i,0})F_{\alpha\beta}(\mathbf{k},\mathbf{R}_i)$$
$$\times\psi_{\alpha\beta,i}(\mathbf{K},\mathbf{r}_1,\mathbf{r}_2). \qquad (2.14\text{b})$$

It can be verified that

$$F_{\alpha\beta}{}^{(s,t)}(\mathbf{k},\mathbf{R}_i)=\left(\frac{\Omega}{2\pi^3}\right)^{1/2}\frac{\exp(i\mathbf{k}\cdot\mathbf{R}_i)}{(1+\delta_{i,0})^{1/2}} \quad (\alpha\neq\beta). \qquad (2.15)$$

If $\alpha=\beta$, Eq. (2.5) enables us to choose symmetrized functions

$$F_{\alpha\beta}{}^{(s)}(\mathbf{k},\mathbf{R}_i)=\left(\frac{\Omega}{2\pi^3}\right)^{1/2}\frac{\cos\mathbf{k}\cdot\mathbf{R}_i}{(1+\delta_{i,0})^{1/2}} \qquad (2.16\text{a})$$

$$F_{\alpha\beta}{}^{(t)}(\mathbf{k},\mathbf{R}_i)=\left(\frac{\Omega}{2\pi^3}\right)^{1/2}\sin\mathbf{k}\cdot\mathbf{R}_i. \qquad (2.16\text{b})$$

Attention is called to the normalizing factors which differ by a factor of 2 from what one might expect.

III. MATRIX ELEMENTS

In this section, we compute matrix elements of the Green's function and the potential on the basis of the functions $\psi_{\alpha\beta,i}$ defined in the previous section.

Let us first consider the Green's function. The quantities we require are denoted by

$$\langle\gamma\delta,Kj'|\mathcal{G}|\alpha\beta,Ki\rangle$$
$$=\int \psi_{\gamma\delta,j}^*(\mathbf{K}',\mathbf{r}_1,\mathbf{r}_2)[E-H^{(0)}(1,2)]^{-1}$$
$$\times Q\psi_{\alpha\beta,i}(\mathbf{K},\mathbf{r}_1,\mathbf{r}_2)d^3r_1d^3r_2. \qquad (3.1)$$

This may be evaluated with the use of (2.8) and (2.3). One point deserves comment: When the Wannier functions appearing in ψ are expanded in terms of Bloch functions, the operator Q eliminates those which pertain to states which are occupied in the ground configuration. We finally obtain

$$\langle\gamma\delta,\mathbf{K}'j|\mathcal{G}|\alpha\beta,\mathbf{K}i\rangle$$
$$=\delta(\mathbf{K}-\mathbf{K}')\Omega(8\pi^3)^{-1}[(1+\delta_{i,0})(1+\delta_{j,0})]^{-1/2}$$
$$\times\left[\delta_{\alpha,\gamma}\delta_{\beta,\delta}\int\frac{\exp(i\mathbf{k}\cdot(\mathbf{R}_j-\mathbf{R}_i))}{E-E_{\alpha\beta}(\mathbf{K},\mathbf{k})}\eta_\alpha{}^+\eta_\beta{}^-d^3k\right.$$
$$\left.\pm\delta_{\alpha,\delta}\delta_{\beta,\gamma}\int\frac{\exp(i\mathbf{k}\cdot(\mathbf{R}_j+\mathbf{R}_i))}{E-E_{\alpha\beta}(\mathbf{K},\mathbf{k})}\eta_\alpha{}^+\eta_\beta{}^-d^3k\right]. \qquad (3.2)$$

As usual, the + sign in (3.2) occurs for singlet states, the − sign for triplet states. The quantity $E_{\alpha\beta}(\mathbf{K},\mathbf{k})$ appearing in the denominator is defined by

$$E_{\alpha\beta}(\mathbf{K},\mathbf{k})=E_\alpha\!\left(\frac{\mathbf{K}}{2}+\mathbf{k}\right)+E_\beta\!\left(\frac{\mathbf{K}}{2}-\mathbf{k}\right). \qquad (3.3)$$

Finally, the symbols $\eta_\alpha{}^+$, $\eta_\beta{}^-$ represent unit step functions:

$$\eta_\alpha{}^+=\eta\left[E_\alpha\!\left(\frac{\mathbf{K}}{2}+\mathbf{k}\right)-E_F\right],$$
$$\eta_\beta{}^-=\eta\left[E_\beta\!\left(\frac{\mathbf{K}}{2}-\mathbf{k}\right)-E_F\right], \qquad (3.4)$$

where $\eta(x)=0$ if $x\leqslant 0$; $\eta(x)=1$ if $x>0$, and E_F is the Fermi energy of the ground configuration.

The presence of step functions in (3.2) has the consequence that the denominators in the integrals do not vanish for $E\leqslant E_F$. The integrals are therefore well defined as they stand. If, however, we are interested in the case $E>E_F$, then it would be necessary to specify the manner in which the singularity is to be treated. Conventionally, this is done by the addition of an infinitesimal imaginary part to the energy which is allowed to vanish after the integral has been performed. The Green's function then acquires an imaginary part through the identity

$$\lim_{\epsilon\to 0}\frac{1}{x+i\epsilon}=P\!\left(\frac{1}{x}\right)-i\pi\delta(x).$$

Next, we consider matrix elements of the potential. These are

$$\begin{aligned}&\langle\gamma\delta,\mathbf{K}'j|V|\alpha\beta,\mathbf{K}i\rangle\\&=\int\psi_{\gamma\delta,j}{}^*(\mathbf{K}',\mathbf{r}_1,\mathbf{r}_2)V(\mathbf{r}_1-\mathbf{r}_2)\psi_{\alpha\beta,i}(\mathbf{K},\mathbf{r}_1,\mathbf{r}_2)d^3r_1d^3r_2\\&=\delta(\mathbf{K}-\mathbf{K}')\exp(i\mathbf{K}\cdot(\mathbf{R}_i-\mathbf{R}_j)/2)\\&\quad\times[(1+\delta_{i,0})(1+\delta_{j,0})]^{-1/2}\sum_m\exp(i\mathbf{K}\cdot\mathbf{R}_m)\\&\quad\times[V_{\gamma\delta,\alpha\beta}(j,0,i+m,m)\\&\qquad\pm V_{\gamma\delta,\beta\alpha}(j,0;m,i+m)].\qquad(3.5)\end{aligned}$$

The ± sign has its usual significance. The multiplicative factor $\delta(\mathbf{K}-\mathbf{K}')$ occurs for any potential depending on the relative position only, and indicates that such interactions conserve the total wave vector. The quantities in square brackets are given by

$$\begin{aligned}V_{\gamma\delta,\alpha\beta}(j,0;i+m,m)=&\int a_\gamma{}^*(\mathbf{r}_1-\mathbf{R}_j)a_j{}^*(\mathbf{r}_2)V(\mathbf{r}_1-\mathbf{r}_2)\\&\times a_\alpha(\mathbf{r}_1-\mathbf{R}_i-\mathbf{R}_m)a_\beta(\mathbf{r}_2-\mathbf{R}_m)d^3r_1d^3r_2.\qquad(3.6)\end{aligned}$$

Throughout this paper we will be concerned with forces of finite range only. By this we mean that there exists some lattice vector R_0 such that

$$\langle\gamma\delta,\mathbf{K}'j|V|\alpha\beta,\mathbf{K}i\rangle=0\quad\text{if}\quad R_i>R_0\quad\text{or}\quad R_j>R_0.\qquad(3.7)$$

We will also restrict ourselves to a finite set of bands.

As a consequence of the presence of the **K**-conserving delta functions in both $\mathcal{G}$ and V, we are permitted to consider subspaces of the two-particle Hilbert space characterized by functions of fixed **K**. We can calculate t in such a subspace, dropping the multiplicative delta functions. We shall denote by $\langle\gamma\delta,j|\mathcal{O}|\alpha\beta,i\rangle_{\mathbf{K}}$ the matrix element of a wave-vector-conserving operator $\mathcal{O}$ with the delta function removed.

IV. CONSTRUCTION OF THE t MATRIX

Let

$$\begin{aligned}&(\gamma\delta,\mathbf{K}'\mathbf{k}'|t|\alpha\beta,\mathbf{K}\mathbf{k})\\&=\delta(\mathbf{K}-\mathbf{K}')(\gamma\delta,\mathbf{k}'|t|\alpha\beta,\mathbf{k})_{\mathbf{K}}\\&=\int\Phi_{\gamma\delta}{}^*(\mathbf{K}',\mathbf{k}';\mathbf{r}_1,\mathbf{r}_2)t(1,2)\Phi_{\alpha\beta}(\mathbf{K},\mathbf{k};\mathbf{r}_1,\mathbf{r}_2)d^3r_1d^3r_2.\end{aligned}\qquad(4.1)$$

Then from (2.14b) we have that

$$\begin{aligned}&(\gamma\delta,\mathbf{k}'|t|\alpha\beta,\mathbf{k})_{\mathbf{K}}\\&\quad=\sum_{i,j}\tfrac{1}{4}(1+\delta_{i,0})(1+\delta_{j,0})F_{\gamma\delta}{}^*(\mathbf{k}',\mathbf{R}_j)\\&\qquad\times\langle\gamma\delta,j|t|\alpha\beta,i\rangle_{\mathbf{K}}F_{\alpha\beta}(\mathbf{k},\mathbf{R}_i).\qquad(4.2)\end{aligned}$$

We will investigate the matrix elements of t as calculated on the basis of the $\psi_{\alpha\beta,j}$.

A formal solution of Eq. (1.2) is

$$t=V(1-\mathcal{G}V)^{-1}.\qquad(4.3)$$

Therefore, we have

$$\begin{aligned}\langle\gamma\delta,j|t|\alpha\beta,i\rangle_{\mathbf{K}}=&\sum_{\mu\nu}\sum_{l}\tfrac{1}{2}(1+\delta_{l,0})\langle\gamma\delta,j|V|\mu\nu,l\rangle_{\mathbf{K}}\\&\times\langle\mu\nu,l|[1-\mathcal{G}V]^{-1}|\alpha\beta,i\rangle_{\mathbf{K}}.\qquad(4.4)\end{aligned}$$

We will examine this equation in detail. Let us adopt the following convention for arranging the matrix elements. Each row and column is characterized by a site index and a band index. We agree to group all the band pairs for a given site. For example, if we consider the ninth site and have two bands to consider, we get rows and columns labeled 1, 1, 9; 1, 2, 9; 2, 1, 9; 2, 2, 9. The assumption that the potential is of finite range, both in the sites and in the bands, which was discussed at the end of the last section, implies that the nonzero portion of the V matrix is of finite dimension.

On the basis of the $\psi_{\alpha\beta,i}$, the matrix representing V in a subspace of fixed K has the block form

$$V=\begin{pmatrix}U_{aa}&0\\0&0\end{pmatrix},\qquad(4.5)$$

where the submatrix U_{aa} contains all the nonzero elements of the potential. Let us divide the matrix of $\mathcal{G}$ in the same way

$$\mathcal{G}=\begin{pmatrix}g_{aa}&g_{ab}\\g_{ba}&g_{bb}\end{pmatrix}.\qquad(4.6)$$

Then the matrix $I-\mathcal{G}V$ has the (subdivided form)

$$I-\mathcal{G}V=\begin{pmatrix}I_{aa}-g_{aa}U_{aa}&0\\-g_{ba}U_{aa}&I_{bb}\end{pmatrix}.\qquad(4.7)$$

Consider the submatrix in the upper-left portion. This is a finite matrix and can be inverted.

$$[I_{aa}-g_{aa}U_{aa}]^{-1}=P_{aa}/D,\qquad(4.8)$$

where

$$D=\det[I_{aa}-g_{aa}U_{aa}],\qquad(4.9)$$

$$[I-\mathcal{G}V]^{-1}=\begin{pmatrix}P_{aa}/D&0\\g_{ba}U_{aa}P_{aa}/D&I_{bb}\end{pmatrix}.\qquad(4.10)$$

Then, on multiplying by V on the left, we get

$$V[I-\mathcal{G}V]^{-1}=\begin{pmatrix}U_{aa}P_{aa}/D&0\\0&0\end{pmatrix}.\qquad(4.11)$$

Thus we see that, on the basis considered, the nonzero portion of t has the same dimensionality as the nonzero portion of V. We can now write Eq. (4.2) in the form

$$\langle\gamma\delta,\mathbf{k}'|t|\alpha\beta,\mathbf{k}\rangle_{\mathbf{K}}=D^{-1}\sum_{ij}\tfrac{1}{4}(1+\delta_{i,0})(1+\delta_{j,0})F_{\gamma\delta}{}^{*}(\mathbf{k}',\mathbf{R}_j)\times\langle\gamma\delta,j|VP|\alpha\beta,i\rangle_{\mathbf{K}}F_{\alpha\beta}(\mathbf{k},\mathbf{R}_i)\quad(4.12)$$

in which the formal definition of the matrix P is given by

$$\langle\gamma\delta,j|[1-\mathcal{G}V]^{-1}|\alpha\beta,i\rangle_{\mathbf{K}}=D^{-1}\langle\gamma\delta,j|P|\alpha\beta,i\rangle_{\mathbf{K}}\quad(4.13)$$

and with D defined in (4.9). All the sums in Eqs. (4.12) are finite as a consequence of the basic assumption that the potential is of finite range. The quantity $\langle\gamma\delta,j|VP|\alpha\beta,i\rangle_{\mathbf{K}}$ in Eq. (4.12) refers to the matrix product of V and P. It is apparent from Eq. (4.10) that Eq. (4.13) refers only to those basis states corresponding to the nonzero portion of V.

An important special case of (4.12) is that in which the potential acts only when $R_j=R_l=0$, and there is only one band α to consider. Potentials of this type have been estensively used in the theory of ferromagnetism[4–7]

$$V_0=\langle\alpha\alpha,0|V|\alpha\alpha,0\rangle_{\mathbf{K}}\quad(4.14)$$

and

$$\mathcal{G}_0=\langle\alpha\alpha,0|[E-H_0]^{-1}|\alpha\alpha,0\rangle_{\mathbf{K}}.\quad(4.15)$$

Then $D=1-\mathcal{G}_0V_0$. With the use of Eq. (2.16) we have

$$(\alpha\alpha,\mathbf{k}'|t^{(s)}|\alpha\alpha,\mathbf{k})_{\mathbf{K}}=\frac{\Omega}{4\pi^3}\frac{V_0}{1-\mathcal{G}_0V_0}\text{(singlet state)}\quad(4.16)$$

and this is independent of $\mathbf{k}$ and $\mathbf{k}'$. The elements of t are zero in the triplet state in this case.

In cases where the range of the potential is not zero, it is still sometimes possible to simplify the computation of t still further. Recall that the computation of t involves the inversion of a matrix whose dimensionality is determined by the range of the potential. It is therefore desirable to reduce this matrix as nearly as possible to diagonal form. Some progress in this direction is made possible by group-theoretical considerations. We suppose that $\mathbf{K}$ is in the interior of the Brillouin zone.

The discussion here parallels that of Ref. 2. The potential in this case has the symmetry of the point group of the total wave vector $\mathbf{K}$. Except in special cases, where $\mathbf{K}$ designates a symmetry point or axis of the Brillouin zone, this group contains only the unit element, and no reduction beyond that afforded by the separation of singlet and triplet states is possible. However, the special cases where the group of $\mathbf{K}$ is not trivial are important enough to deserve a detailed discussion. Let us designate functions transforming according to the irreducible representations of the group of $\mathbf{K}$ by subscripts r, s. If the representation is degenerate, these subscripts are to be generalized appropriately to designate particular rows as well. We construct symmetrized functions by means of a unitary transformation

$$C_{s,\alpha\beta}(\mathbf{k},\mathbf{R}_m)=\sum_m{}'U(s,\mathbf{R}_m)F_{\alpha\beta}(\mathbf{k},\mathbf{R}_m).\quad(4.17)$$

The summation over m includes all the different vectors which can be found from any one of them by applying the operators of the group. All these vectors have the same length. A prime on the summation sign indicates such a restricted sum.

We define transformed matrices through the equations

$$\begin{aligned}\delta_{s,t}V_{s,\alpha\beta,\mu\nu}(\mathbf{K},i,l)&=\sum_{i,l}{}'\,U(s,\mathbf{R}_i)\langle\alpha\beta,i|V|\mu\nu,l\rangle_{\mathbf{K}}\times U^{\dagger}(\mathbf{R}_l,t)\\ \delta_{s,t}P_{s,\alpha\beta,\mu\nu}(\mathbf{K},i,l)&=\sum_{i,l}U(s,\mathbf{R}_i)\langle\alpha\beta,i|P|\mu\nu,l\rangle_{\mathbf{K}}\times U^{\dagger}(\mathbf{R}_l,t).\end{aligned}\quad(4.18)$$

In constructing the matrix P in the new representation, it doesn't matter in principle whether we first transform V and then find P or invert the full $1-\mathcal{G}V$ and then transform. Of course, the former procedure is more convenient. The determinant D can be expressed as a product of factors each arising from a particular irreducible representation, and each factor appears a number of times equal to the degeneracy of the representation.

$$D=\prod_s D_s.\quad(4.19)$$

In (4.19), D_s is constructed by considering only those portions of $1-\mathcal{G}V$ which, after transformation, involve representation s.

The submatrices P_s defined in (4.18) also contain a product of factors D_r for all $r\neq s$. Let us use this fact to define a reduced submatrix $\bar{P}_s$ through

$$P_{s,\alpha\beta,\mu\nu}(\mathbf{K},i,l)=\Big(\prod_{r\neq s}D_r\Big)\bar{P}_{s,\alpha\beta,\mu\nu}(\mathbf{K},i,l).\quad(4.20)$$

This has the consequence that a portion of the matrix $[1-\mathcal{G}V]^{-1}$ corresponding to representation s contains only a single factor from the determinant:

$$\sum_{i,l}U(s,\mathbf{R}_i)\langle\alpha\beta,i|[1-\mathcal{G}V]^{-1}|\mu\nu,l\rangle_{\mathbf{K}}U^{\dagger}(\mathbf{R}_l,t)=\delta_{s,t}D_s{}^{-1}\bar{P}_{s,\alpha\beta,\mu\nu}(\mathbf{K},i,l).\quad(4.21)$$

Since the transformation whose elements are $U(s,R_j)$ is unitary, we have

$$\sum_s U^{\dagger}(\mathbf{R}_i,s)U(s,\mathbf{R}_l)=\delta_{i,l},\quad(4.22)$$

where the summation over s includes each row of a degenerate representation. We now have with the use

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of Eqs. (4.17)–(4.22),

$$(\gamma\delta,\mathbf{k}'|t|\alpha\beta,\mathbf{k})_{\mathbf{K}}=\sum_s D_s^{-1}\bar{\sum_{i,j}}\tfrac{1}{4}(1+\delta_{i,0})(1+\delta_{j,0})$$
$$\times C_{s,\gamma\delta}^*(\mathbf{k}',\mathbf{R}_i)(V\bar{P})_{s,\gamma\delta,\alpha\beta}(\mathbf{K},i,j)C_{s,\alpha\beta}(\mathbf{k},\mathbf{R}_j).\quad(4.23)$$

In (4.23), the t-matrix element is separated into portions coming from each of the irreducible representations of the group of $\mathbf{K}$. This separation is particularly useful when the symmetrized functions C_s have different dependences on the wave vector in lowest order, since to a given order of approximation, certain representations may be discarded. The bar on the summation indicates that we get contributions to the sum over sites only from different lattice-vector types. There is one contribution from each symmetrized linear combination $C_{s,\alpha\beta}$.

In considering the construction of the symmetrized functions $C_{s,\alpha\beta}$, we note that if the band indices are equal, the basis functions $F_{\alpha\beta}$ which are combined to form the C_s are even or odd with respect to inversion according as we consider singlet or triplet states. This restricts, to some extent, the choice of representations s which, for a given $\mathbf{K}$, can contribute to (4.23). Only those representations can contribute which have the property that functions transforming according to that representation can be constructed from even (or odd) basis functions. For example, if $\mathbf{K}=0$, and $\alpha=\beta$, the singlet state contains contributions from Γ_1, Γ_{12}, etc; the triplet state has contributions from Γ_{15}. Of course, in any case, only those representations which have basis functions of the form $\exp(i\mathbf{k}\cdot\mathbf{R}_i)$ with $R_i<R_0$ can contribute. Thus for a simple cubic lattice, assuming nearest-neighbor interactions, at $K=0$ only the three representations named above can contribute.

One rather important conclusion can be immediately inferred from these considerations. If we are studying a one-band model of a low-density system so that we require the t matrix only for small k, k', then the contribution from singlet states will remain finite as these wave vectors approach zero (unless as is the case for spin waves, accidental cancellations occur); while the contribution from triplet states is proportional to kk'. Hence, insofar as contributions from terms in the t matrix of order k^2 can be neglected, only interaction in singlet states need be considered. However, in a two-band or multiband system, triplet interactions will contribute in the low-density limit.

V. OPTICAL POTENTIAL AND GROUND-STATE ENERGY

For use in applications to the theory of ferromagnetism, we require an expression for the energy of the ground state. This is, of course, given formally by Eq. (1.1), but it is desirable at this point to present something which is more explicit. As a byproduct, we also obtain the "optical potential" which is of considerable interest in itself.

The states $|mn\rangle$ which appear in Eq. (1.1) are symmetrized combinations of one-particle states, each of which is described by a wave vector, a band index, and a spin index. For instance, we replace m by the triple $\mathbf{p}\alpha\boldsymbol{\sigma}$. We can now define an "optical potential" for an electron with wave vector $\mathbf{p}$ and spin $\boldsymbol{\sigma}$ in band α.

$$V(\mathbf{p}\alpha\boldsymbol{\sigma})=\sum_{q\beta\sigma'}(\mathbf{p}\alpha\boldsymbol{\sigma},\mathbf{q}\beta\boldsymbol{\sigma}'|t|\mathbf{p}\alpha\boldsymbol{\sigma},\mathbf{q}\beta\boldsymbol{\sigma}').\quad(5.1)$$

As long as there is no spin ordering, which we will neglect at this point, the optical potential will not depend on $\boldsymbol{\sigma}$. It is convenient now to separate the sum into contributions from triplet and singlet states, introducing thereby the symmetrized two-particle states described in Sec. II.

$$V(\mathbf{p}\alpha)=\sum_{\mathbf{q}\beta}[\tfrac{3}{2}(\mathbf{p}\alpha,\mathbf{q}\beta|t^t|\mathbf{p}\alpha,\mathbf{q}\beta)$$
$$+\tfrac{1}{2}(\mathbf{p}\alpha,\mathbf{q}\beta|t^s|\mathbf{p}\alpha,\mathbf{q}\beta)].\quad(5.2)$$

The interaction energy is to be computed from Eq. (1.1), which can be expressed in terms of the optical potential (5.1). It is important to recall that the two-particle states are redundant. A factor of $\frac{1}{2}$ must be inserted if we are to sum over all values of $\mathbf{p}\alpha\boldsymbol{\sigma}$ corresponding to occupied one-particle states. This factor therefore prevents pair interactions from being counted twice. Thus we have

$$E=E_0+\tfrac{1}{2}\sum_{\mathbf{p}\alpha\sigma}V(\mathbf{p}\alpha\boldsymbol{\sigma}).\quad(5.3a)$$

From the derivation in Ref. 1, which leads to our basic Eq. (1.1), it follows that Eq. (5.3a) will be correct in the low-density limit for a system of fermions interacting by repulsive forces of finite range.

The transition from a summation to integration in the application of Eq. (5.3) is made with the usual replacement of $\sum$ by $\mathcal{V}/8\pi^3\int d^3p$, where $\mathcal{V}$ is the volume of the system. Thus

$$E=E_0+\frac{\mathcal{V}}{16\pi^3}\sum_{\beta\sigma}\int d^3p\,V(\mathbf{p}\alpha\boldsymbol{\sigma}).\quad(5.3b)$$

As an example, let us consider the very simple potential described in Eq. (4.14). Other examples will be considered in subsequent sections. In applying Eq. (5.2), we note that the necessary factors of 2π are already contained in (4.16) so that

$$V(\mathbf{p}\alpha)=\frac{\Omega}{8\pi^3}\int d^3q\frac{V_0}{1-\mathcal{G}_0V_0}.\quad(5.4)$$

Equation (5.4) may be used for states above as well as below the Fermi surface. Let us consider first the latter case, in the low-density limit in which $\mathcal{G}_0$ may be replaced by its constant value for states at the bottom of the band. For this case, we have from Ref. 6

$$\lim_{\substack{E\to 0\\ K\to 0}} \mathcal{G}_0 = -\tfrac{1}{2}I\,, \tag{5.5a}$$

where

$$I = \frac{\Omega}{8\pi^3}\int \frac{d^3q}{E(\mathbf{q})} = \left\langle \frac{1}{E} \right\rangle. \tag{5.5b}$$

I is therefore the average value of $1/E$ over the entire band. Since the integration over q includes only occupied states, we get

$$V = \frac{\Omega k_F^3}{6\pi^2}\,\frac{V_0}{1+\frac{1}{2}V_0 I}. \tag{5.6}$$

The average interaction energy per particle is

$$E_{\mathrm{int}} = \frac{\Omega k_F^6\, \mathcal{V}}{36\pi^4 N}\,\frac{V_0}{1+\frac{1}{2}V_0 I} = \tfrac{1}{4}\rho\Omega\frac{V_0}{1+\frac{1}{2}V_0 I} \tag{5.7}$$

in which we have used the relation $k_F^3 = 3\pi^2\rho$, where $\rho = N/\mathcal{V}$ is the density of particles. This relation can be transformed into a more familiar form by observing that the scattering length a resulting from the interaction V_0 is, according to Ref. 6, for a spherical band with $E(\mathbf{k}) = \gamma\mathbf{k}^2$

$$a = \frac{\Omega}{8\pi\gamma}\,\frac{V_0}{1+\frac{1}{2}V_0 I}. \tag{5.8}$$

Thus

$$E_{\mathrm{int}} = 2\pi\gamma\rho a$$

and

$$V(p,\alpha) = \frac{4}{3\pi}(k_F a)E_F = 4\pi\gamma\rho a. \tag{5.9}$$

This result is seen to be equivalent to the low-density interaction energy for a hard-sphere Fermi gas if we put $\gamma = \hbar^2/2m$.[8] In fact, the simple potential (4.14) gives a theory quite analogous to that of the hard-sphere Fermi gas if the proper identifications are made.

Another application of the optical potential concerns the question of the mean free path of hot electrons in metals. This problem has been studied both experimentally and theoretically.[8–12] Experimental results for the mean free path contain contributions from both electron-electron and electron-phonon scatterings; here we shall consider only the former. As a consequence of dielectric screening, it is probably reasonable to assume as a first approximation that two electrons interact only when they are on the same site. If we confine our attention to a single band, the interaction is characterized by the matrix element given in Eq. (4.14).

In this case, we are concerned with states above the Fermi surface. For such states, the potential $V(\mathbf{p}\alpha)$ is complex:

$$V(\mathbf{p},\alpha) = U + iW. \tag{5.10}$$

The electron mean free path is determined from the imaginary part W. The problem is quite analogous to the optical model of the nucleus,[13] and in fact, it is this analogy to which we call attention in referring to $V(\mathbf{p}\alpha)$ as the optical-model potential. A formal expression for W is determined easily. We put

$$\mathcal{G}_0 = g_R + i g_i.$$

Since V_0 is real, we have at once

$$W = \frac{\Omega}{8\pi^3}\int \frac{V_0^2 g_i}{(1-g_R V_0)^2 + V_0^2 g_i^2}\,d^3q. \tag{5.11}$$

Calculations of electron mean free paths based on Eq. (5.11) are in progress and will be reported subsequently. A preliminary account has already been published elsewhere,[14] so we will give here only the result in the low-density limit for states of wave vector p close to the Fermi surface in a spherical band.

$$W = -\frac{2}{\pi}(k_F a)^2 E_F\big((p/k_F) - 1\big)^2. \tag{5.12}$$

VI. EXTENDED POTENTIALS

We now consider the determination of the t matrix for two more complicated cases of interest in the theory of ferromagnetism. These include (1) an interaction restricted to a single site but coupling two bands, and (2) the case of an interaction extending to first neighbors.

Slater, Statz, and Koster considered the case in which two electrons (or holes) in an otherwise empty band interact through a short-range potential.[7] They concluded that if only a single band was considered, the spins would not be parallel, but that if two bands were included, it was possible for the triplet state of the pair to lie below the singlet. The techniques described in this paper enable a more rigorous discussion of this question, and lead to a rather different conclusion: that ferromagnetism will not occur in the limit of vanishing density.

Let the bands considered be designated by indices 0, 1. We denote the matrix elements of the interaction potential by

$$\langle \gamma\delta,0|V|\alpha\beta,0\rangle_{\mathbf{K}} = V_{\gamma\delta,\alpha\beta}. \tag{6.1}$$

It is easy to show that the elements $V_{\alpha\alpha,\alpha\alpha}$, $V_{\alpha\beta,\alpha\beta}$, and $V_{\alpha\beta,\beta\alpha}$ are real (without any assumptions concerning the Wannier functions). For simiplicity and to reduce the number of independent parameters somewhat, we

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follow Slater, Statz, and Koster[7] by assuming that the elements $V_{\alpha\alpha,\alpha\beta}(\beta\neq\alpha)$ are zero.

In the triplet state, the construction of the t matrix is particularly simple. It is seen from Eq. (1.1) that we require only the diagonal elements of t. Let us introduce the abbreviations

$$\alpha=V_{01,01}-V_{01,10}\,, \tag{6.2a}$$

$$g_{01}=\frac{\Omega}{8\pi^3}\int[E-E_{01}(\mathbf{K},\mathbf{k})]^{-1}\eta_0{}^{+}\eta_1{}^{-}d^3k\,. \tag{6.2b}$$

Then the triplet potential-energy submatrix has the form

$$V=\tfrac{1}{2}\alpha\begin{pmatrix}1 & -1\\ -1 & 1\end{pmatrix}, \tag{6.3}$$

where the rows and columns are numbered by the band index pairs 01, 10. Likewise, the relevant portion of the matrix $\mathcal{G}$ is, on this basis,

$$\mathcal{G}=\tfrac{1}{2}g_{01}\begin{bmatrix}1 & -1\\ -1 & 1\end{bmatrix}. \tag{6.4}$$

These results follow from Eqs. (3.2) and (3.5). Then, following the procedures of Sec. 4, we have, on the basis of functions defined in Eq. (2.8),

$$\mathbf{t}^{t}=\frac{1}{2}\frac{\alpha}{1-g_{01}\alpha}\begin{pmatrix}1 & -1\\ -1 & 1\end{pmatrix}. \tag{6.5}$$

The singlet state is more complicated. Let us introduce the additional abbreviations

$$g_{00}=\langle 00,0|\mathcal{G}|00,0\rangle_{\mathbf{K}}\,,\qquad V_0=V_{00,00}\,, \tag{6.6a}$$

$$g_{11}=\langle 11,0|\mathcal{G}|11,0\rangle_{\mathbf{K}}\,,\qquad V_1=V_{11,11}\,, \tag{6.6b}$$

$$\beta=V_{01,01}+V_{01,10}\,,\qquad V_{01}=V_{00,11}\,. \tag{6.6c}$$

Then the singlet potential-energy submatrix is

$$V^{s}=\begin{bmatrix}V_0 & 0 & 0 & V_{01}\\ 0 & \frac{1}{2}\beta & \frac{1}{2}\beta & 0\\ 0 & \frac{1}{2}\beta & \frac{1}{2}\beta & 0\\ V_{10} & 0 & 0 & V_1\end{bmatrix}. \tag{6.7}$$

The rows and columns are numbered by the index pairs 00, 01, 10, 11. The appropriate Green's function submatrix is

$$\mathcal{G}^{s}=\begin{bmatrix}g_{00} & 0 & 0 & 0\\ 0 & \frac{1}{2}g_{01} & \frac{1}{2}g_{01} & 0\\ 0 & \frac{1}{2}g_{01} & \frac{1}{2}g_{01} & 0\\ 0 & 0 & 0 & g_{11}\end{bmatrix}. \tag{6.8}$$

After a simple calculation, we find the following nonzero diagonal elements of t for singlet states

$$t_0=t_{00,00}=\frac{V_0(1-g_{11}V_1)+g_{11}|V_{01}|^2}{(1-g_{00}V_0)(1-g_{11}V_1)-g_{00}g_{11}|V_{01}|^2}\,, \tag{6.9}$$

$$t_{10}=t_{10,10}=t_{01,01}=\frac{1}{2}\frac{\beta}{1-g_{01}\beta}\,, \tag{6.10}$$

$$t_1=t_{11,11}=\frac{V_1(1-g_{00}V_0)+g_{00}|V_{01}|^2}{(1-g_{00}V_0)(1-g_{11}V_1)-g_{00}g_{11}|V_{01}|^2}\,. \tag{6.11}$$

Equations (6.9) and (6.11) may be written in a more convenient form if we define the combinations

$$V_0'=V_0+g_{11}|V_{01}|^2/(1-g_{11}V_1)\,, \tag{6.12}$$

$$V_1'=V_1+g_{00}|V_{01}|^2/(1-g_{00}V_0)\,. \tag{6.13}$$

Since a_0 and a_1 are orthogonal, we expect that $|V_{01}|<V_0$ or V_1. At energies below the Fermi energy in the respective bands, g_{00} and g_{11} are negative. Thus, for occupied states, $V_0'<V_0$ and $V_1'<V_1$. With these substitutions, we have

$$t_0=V_0'/(1-g_{00}V_0')\,, \tag{6.14}$$

$$t_1=V_1'/(1-g_{11}V_1')\,. \tag{6.15}$$

Equations (6.14) and (6.15) and their obvious generalizations can be shown to hold when any number of bands are considered if V_0', V_1', etc., are suitably defined.

In order to obtain matrix elements on the basis of symmetrized Bloch functions, it is necessary to multiply (6.5), (6.14), and (6.15) by $\Omega/4\pi^3$ to take account of the functions F in Eq. (4.12). When this is done, the similarity to the one-band result, Eq. (4.16), is obvious. A two-band model introduces more elements of and causes a redefinition of the effective potential, but does not alter the general structure. In particular, in the limit of a large effective potential

$$t_{ij,ij}\propto-\tfrac{1}{2}(1+\delta_{ij})g_{ij}{}^{-1}\,. \tag{6.16}$$

These results have one interesting consequence for the optical-model calculations discussed in Sec. 5. If the occupied states are confined to band 0, say, and the excited electron is also in band 0, then Eq. (5.4) which defines the optical-model potential remains valid when a second band is considered, provided that V_0 is replaced by V_0' as defined in (6.12). Also, if the energy of the excited state in band 0 does not equal that of any state in band 1, then V_0' is real so that Eq. (5.4) remains valid.

Let us next determine the form of the t matrix when the interaction extends to nearest neighbors. Only one band is considered. This situation is in a certain sense complementary to that just discussed, and we shall find that here also, the general structure of the t matrix remains similar to that of Eq. (4.16).

We determine the matrix elements of the potential from Eq. (3.5). Since there is only one band in this instance, we drop all band indices. We assume that we have a lattice structure such that two sites which are nearest neighbors of the origin are not nearest neighbors of each other. Simple-cubic and body-centered-cubic lattices are examples of this situation. With references to Eq. (3.5) and (3.6), we have in the singlet state

$$\langle 0|V|0\rangle_{\mathbf{K}}=\sum_m \exp(i\mathbf{K}\cdot\mathbf{R}_m)V(0,0;m,m). \quad (6.17)$$

In the sum over m, we retain only the terms in which $m=0$ or is a nearest neighbor of the origin. We denote the result by a. If, as is the case for integrals determined from s-like atomic functions, $V(0,0;m,m)$ is independent of the direction of R_m, we have

$$\langle 0|V|0\rangle_{\mathbf{K}}=a=V_0+V(0,0,d,d)S(\mathbf{K},d), \quad (6.18)$$

where

$$S(\mathbf{K},d)=\sum_m \exp(i\mathbf{K}\cdot\mathbf{R}_m); \quad (R_m=d)$$

and d is the nearest-neighbor distance. Next, consider

$$\langle 0|V|i\rangle_{\mathbf{K}}=\sqrt{2}\exp(i\mathbf{K}\cdot\mathbf{R}_i/2)\sum_m \exp(i\mathbf{K}\cdot\mathbf{R}_m)\times V(0,0;m+i,m). \quad (6.19)$$

The leading terms in this sum come from $m=0$ and $m=-i$; other terms are three-center integrals. We suppose again that the integrals are independent of direction, and write

$$\langle 0|V|i\rangle_{\mathbf{K}}=2\sqrt{2}\cos\tfrac{1}{2}\mathbf{K}\cdot\mathbf{R}_i V(0,0;d,0)=b\cos\frac{\mathbf{K}\cdot\mathbf{R}_i}{2}, \quad (6.20)$$

where $b=2\sqrt{2}V(0,0,d,0)$.

Similarly, we have the diagonal matrix element $\langle i|V|i\rangle_{\mathbf{K}}$, where $\mathbf{R}_i$ is a nearest neighbor of the origin. In this case, if three-center integrals are dropped, the result is

$$\langle i|V|i\rangle_{\mathbf{K}}=c=V(d,0;d,0)+V(d,0;0,d). \quad (6.21)$$

If we agree to discard all three- and four-center integrals, there is no contribution from the general element $\langle j|V|i\rangle_{\mathbf{K}}$ for $i\neq j\neq 0$.

The preceding results pertain to the singlet state. In the triplet state, it is readily verified that the elements $\langle 0|V|0\rangle_{\mathbf{K}}$ and $\langle 0|V|i\rangle_{\mathbf{K}}$ are zero. A nonzero contribution is furnished by the elements.

$$\langle i|V|i\rangle_{\mathbf{K}}=f=V(d,0;d,0)-V(d,0;0,d). \quad (6.22)$$

We next consider the Green's functions. We need the elements involving nearest-neighbor sites. In order to simplify the calculations we will assume that a situation of tight binding holds in which the one-particle energies are given by

$$E(\mathbf{k})=E_0+E_1\sum_i \cos\mathbf{k}\cdot\mathbf{R}_i \quad (6.23)$$

in which the sum includes only those sites $\mathbf{R}_i$ which are nearest neighbors of the origin. The parameter E_1 will be left unspecified. It has, however, a simple physical significance as the first-neighbor interaction integral.

The assumption expressed in Eq. (6.23) is valuable because it provides us with a set of identities which substantially reduce the number of independent quantities which have to be calculated. Consider the first-neighbor singlet Green's function. From Eq. (3.2) we have

$$\langle 0|\mathcal{G}|i\rangle_{\mathbf{K}}=\frac{\Omega}{4\pi^3\sqrt{2}}\int d^3k\frac{\cos\mathbf{k}\cdot\mathbf{R}_i}{E-E(\mathbf{K},\mathbf{k})}\eta^+\eta^- \quad (6.24)$$

in which $\mathbf{R}_i$ is a nearest-neighbor-site vector. The quantity $E(\mathbf{K},\mathbf{k})$ can be written as

$$E(\mathbf{K},\mathbf{k})=E\left(\frac{\mathbf{K}}{2}+\mathbf{k}\right)+E\left(\frac{\mathbf{K}}{2}-\mathbf{k}\right)$$
$$=2\left[E_0+E_1\sum_i \cos\frac{\mathbf{K}\cdot\mathbf{R}_i}{2}\cos\mathbf{k}\cdot\mathbf{R}_i\right]. \quad (6.25)$$

Hence, we have, after a little algebra

$$\sum_i \cos\frac{\mathbf{K}}{2}\cdot\mathbf{R}_i\langle 0|\mathcal{G}|i\rangle_{\mathbf{K}}=(E_1\sqrt{2})^{-1}\left[(E-2E_0)\times\langle 0|\mathcal{G}|0\rangle_{\mathbf{K}}-\frac{\Omega}{8\pi^3}\int d^3k\eta^+\eta^-\right]. \quad (6.26)$$

The second term in (6.26) is the fraction of the volume of the Brillouin zone in which the twin conditions $E(\mathbf{K}/2+\mathbf{k})>E_F$ and $E(\mathbf{K}/2-\mathbf{k})>E_F$ are satisfied. In the low-density limit in which $E_F\rightarrow 0$ and only states with $K\rightarrow 0$ are occupied, this quantity approaches unity. We define $U(\mathbf{K})$ by

$$\frac{\Omega}{8\pi^3}\int d^3k\eta^+\eta^-=1-U(\mathbf{K}) \quad (6.27)$$

so that U vanishes in this limit. Thus

$$\sum_i \cos\frac{\mathbf{K}}{2}\cdot\mathbf{R}_i\langle 0|\mathcal{G}|i\rangle_{\mathbf{K}}=(E_1\sqrt{2})^{-1}[(E-2E_0)\times\langle 0|\mathcal{G}|0\rangle_{\mathbf{K}}-1+U(\mathbf{K})]. \quad (6.28)$$

For special values of $\mathbf{K}$, this result may be simplified through the use of symmetry properties of the Green's function. Let $\mathbf{R}_i$ and $\mathbf{R}_l$ be nearest-neighbor site vectors, so that $\mathbf{R}_i=\boldsymbol{\alpha}\mathbf{R}_l$, where $\boldsymbol{\alpha}$ is an orthogonal transformation in the point group of the crystal. Then

$$\langle 0|\mathcal{G}|i\rangle_{\mathbf{K}}=\frac{\Omega}{4\pi^3\sqrt{2}}\int\frac{\cos\boldsymbol{\alpha}^{-1}\mathbf{k}\cdot\mathbf{R}_l}{E-E(\mathbf{K},\mathbf{k})}\eta^+\eta^- d^3k.$$

Now let $\mathbf{k}'=\boldsymbol{\alpha}^{-1}\mathbf{k}$. The Jacobian of this transformation is unity. Also, since the energy is invariant under such a transformation, we have

$$E\left(\frac{\mathbf{K}}{2}\pm\mathbf{k}\right)=E\left(\boldsymbol{\alpha}^{-1}\frac{\mathbf{K}}{2}\pm\mathbf{k}'\right).$$

Thus,

$$\langle 0|\mathcal{G}|i\rangle_{\mathbf{K}}=\langle 0|\mathcal{G}|l\rangle_{\alpha^{-1}\mathbf{K}}. \tag{6.29}$$

Also, we have $E(-\mathbf{K},\mathbf{k})=E(\mathbf{K},\mathbf{k})$. Thus, if $\boldsymbol{\alpha}$ is such that $\boldsymbol{\alpha}\mathbf{K}=\mathbf{K}$, then

$$\langle 0|\mathcal{G}|i\rangle_{\mathbf{K}}=\langle 0|\mathcal{G}|l\rangle_{\mathbf{K}}=\langle 0|\mathcal{G}|-i\rangle_{\mathbf{K}}=\langle 0|\mathcal{G}|-l\rangle_{\mathbf{K}}. \tag{6.30}$$

This result reduces the number of independent first-neighbor Green's functions. In particular, for $K=0$, there is only one such function, so that Eq. (6.28) becomes

$$\langle 0|\mathcal{G}|i\rangle_0=(zE_1\sqrt{2})^{-1}[(E-2E_0)\times\langle 0|\mathcal{G}|0\rangle_0-1+U(0)] \tag{6.31}$$

in which the number of nearest neighbors is denoted by z. We also infer that $\langle 0|\mathcal{G}|0\rangle_{\mathbf{K}}$ has full cubic symmetry under rotation of $\mathbf{K}$, and that $\langle 0|\mathcal{G}|i\rangle_{\mathbf{K}}$ is even in $\mathbf{K}$.

A similar argument can be applied to the Green's function $\langle i|\mathcal{G}|j\rangle_{\mathbf{K}}$ where both $\mathbf{R}_j$ and $\mathbf{R}_i$ are nearest neighbors of the origin. Suppose as before that $\mathbf{R}_i=\boldsymbol{\alpha}\mathbf{R}_l$ and also that $\mathbf{R}_j=\boldsymbol{\alpha}\mathbf{R}_n$. Then we have

$$\langle i|\mathcal{G}|j\rangle_{\mathbf{K}}=\langle l|\mathcal{G}|n\rangle_{\alpha^{-1}\mathbf{K}}. \tag{6.32}$$

In addition we have also

$$\begin{aligned}\langle i|\mathcal{G}|j\rangle_{\mathbf{K}}&=\langle -i|\mathcal{G}|j\rangle_{\mathbf{K}}=\langle i|\mathcal{G}|-j\rangle_{\mathbf{K}}\\&=\langle -i|\mathcal{G}|-j\rangle_{\mathbf{K}}=\langle i|\mathcal{G}|j\rangle_{-\mathbf{K}}=\langle j|\mathcal{G}|i\rangle_{\mathbf{K}},\end{aligned} \tag{6.33}$$

etc. As a consequence we see that for a simple cubic crystal for $\mathbf{K}=0$, there are only two independent Green's functions of this type: $\langle i|\mathcal{G}|i\rangle_0$ and $\langle i|\mathcal{G}|j\rangle_0$, $j\neq i$, $-i$. There are also two and three independent Green's functions in body-centered and face-centered cubic lattices, respectively. Since $\langle i|\mathcal{G}|j\rangle_{\mathbf{K}}$ is even in $\mathbf{K}$, the foregoing statement must hold up to second order in $\mathbf{K}$.

An identity involving $\langle j|\mathcal{G}|i\rangle_{\mathbf{K}}$ can also be derived. We consider only the singlet Green's function. From Eq. (3.2), this can be written as

$$\langle j|\mathcal{G}|i\rangle_{\mathbf{K}}=\frac{\Omega}{4\pi^3}\int\frac{\exp(i\mathbf{k}\cdot\mathbf{R}_j)\cos\mathbf{k}\cdot\mathbf{R}_i}{E-E(\mathbf{K},\mathbf{k})}\eta^+\eta^-d^3k. \tag{6.34}$$

Now we form the sum, involving all nearest neighbors, then use (6.24) and (6.25). After some algebra we have

$$\sum\cos\frac{\mathbf{K}}{2}\cdot\mathbf{R}_i\langle j|\mathcal{G}|i\rangle_{\mathbf{K}}=(\sqrt{2}E_1)^{-1}(E-2E_0)\langle 0|\mathcal{G}|j\rangle_{\mathbf{K}}-\frac{\Omega}{8\pi^3E_1}\int\exp(i\mathbf{k}\cdot\mathbf{R}_j)\eta^+\eta^-d^3k. \tag{6.35}$$

In the low-density limit, the excluded volume is small. Since

$$\int\exp(i\mathbf{k}\cdot\mathbf{R}_j)d^3k=0 \tag{6.36}$$

when the integral includes an entire Brillouin zone, we see that in the low-density limit the second term on the right side of (6.35) vanishes. Let us define

$$U(\mathbf{K},\mathbf{R}_j)=\frac{\Omega}{8\pi^3}\int(1-\eta^+\eta^-)\exp(i\mathbf{k}\cdot\mathbf{R}_j)d^3k \tag{6.37}$$

so that $U(\mathbf{K})=U(\mathbf{K},0)$, where $U(\mathbf{K})$ was defined in Eq. (6.27). Thus we get

$$E_1\sum_i\cos\frac{\mathbf{K}}{2}\cdot\mathbf{R}_i\langle j|\mathcal{G}|i\rangle_{\mathbf{K}}=2^{-1/2}(E-2E_0)\langle 0|\mathcal{G}|j\rangle_{\mathbf{K}}+U(\mathbf{K},\mathbf{R}_j). \tag{6.38}$$

We will now proceed to construct the t matrix for nearest-neighbor interactions. From the beginning we will stay in the low-density limit which means that, as long as we consider only occupied states, only small values of $\mathbf{K}$ are important. We therefore put $K=0$.

At this point, we follow the procedures of Sec. 4. It is possible to find a unitary transformation U which will reduce the potential and Green's-function matrices for $K=0$. (In general, this will not be possible for arbitrary $\mathbf{K}$, so that in such a case one must invert the matrix of dimension $z/2+1$.) The irreducible representations of interest in constructing t are found as follows:

For singlet states we have contributions from the representations of the cubic point group of even parity and such that functions transforming appropriately can be constructed from components $\cos\mathbf{k}\cdot\mathbf{R}_i$, where $\mathbf{R}_i$ is a nearest neighbor. For triplet states, odd-parity representations are required, and the components are $\sin\mathbf{k}\cdot\mathbf{R}_i$. However, since we are concerned with low densities, we need only Γ_1, for the singlet states. Since the functions $C(\mathbf{k},\mathbf{R}_i)$ for triplet states are formed from $\sin\mathbf{k}\cdot\mathbf{R}_i$ the triplet contribution to the diagonal elements of t is of order k^2, and is neglected here. If we were to include it, the lowest representation to contribute would be Γ_{15}.

For the nearest neighbors, the contribution to U from Γ_1 is $U(\Gamma_1,R_i)=(2/z)^{1/2}$. After applying this transformation, we are concerned only with the 2×2 submatrices coming from Γ_1. These are as follows [with reference to Eqs. (6.18)–(6.21)]:

$$V_1=\begin{pmatrix}a & \frac{1}{2}bz^{1/2}\\ \frac{1}{2}bz^{1/2} & c\end{pmatrix} \tag{6.39}$$

$$\mathcal{G}_1=\begin{pmatrix}\mathcal{G}_0 & \frac{1}{2}z^{1/2}\mathcal{G}_1\\ \frac{1}{2}z^{1/2}\mathcal{G}_1 & \mathcal{G}_s\end{pmatrix} \tag{6.40}$$

in which $\mathcal{G}_0=\langle 0|\mathcal{G}|0\rangle_0$, $\mathcal{G}_1=\langle 0|\mathcal{G}|i\rangle_0$, i is any first neighbor, and

$$\begin{aligned}\mathcal{G}_s=\tfrac{1}{2}\sum_i\langle i|\mathcal{G}|j\rangle_0&=(2\sqrt{2}E_1)^{-1}(E-2E_0)\mathcal{G}_1\\&=2^{1/2}z\mathcal{G}_1.\end{aligned} \tag{6.41}$$

In the second step in Eq. (6.41), we have used the low-density forms of Eq. (6.35).

It is now a straightforward matter to go through the algebra involved in Eq. (4.23). The result is greatly simplified with the use of (6.31). First, let us calculate the determinant D_1. This is, with the use of (6.31),

$$D_1 = 1 + (2zE_1)^{-1}(V_0'' - a) - V_0''\mathcal{G}_0 , \qquad (6.42)$$

where

$$V_0'' = a + 2^{1/2}zb + zc + (2E_1)^{-1}(\tfrac{1}{2}b^2z - ac) . \qquad (6.43)$$

The form of D_1 is similar to that of the denominator appearing in Eqs. (4.16) and (6.14) with the exception that the term $(V_0'' - a)/2zE_1$ appears. After some algebra involving use of the Green's-function identities, we have, with some restoration of indices

$$(\alpha\alpha,\mathbf{k}|t^s|\alpha\alpha,k)_0 = \frac{\Omega V_0''}{4\pi^3 D_1} = \frac{\Omega}{4\pi^3} \frac{V_0''}{1 + (2zE_1)^{-1}(V_0'' - a) - V_0''\mathcal{G}_0} . \qquad (6.44)$$

The resemblance between Eqs. (6.44), (6.14), and (4.16) should be noted carefully. The t-matrix element has the same general form in each example. In particular, in the limit of large effective potential, we obtain $t^s \propto 2/I$ [where I is defined in Eq. (5.5b)] for each case. Moreover, the addition of other sites to the one-band, one-site problem seems to have the effect of increasing the effective potential. This remark cannot be rigorously proved, but is quite plausible since E_1 will be negative for a band with a minimum at $k=0$, and we expect $c > b$, while b should be of the general order of magnitude of $|E_1|$. Since we do not wish to consider a detailed model of a crystal with specific wave functions, we will not consider this point further. In the next section, most of our arguments will be based on the large-interaction limit of t.

VII. APPLICATION TO FERROMAGNETISM

We will now apply these results to an investigation of the conditions under which particles interacting as described in the preceding sections might become ferromagnetic. Specificially, we will show rigorously that at sufficiently low densities ferromagnetism will not occur. At higher densities, a transition to a ferromagnetic state is possible, but we are unable to make a completely definitive statement as to whether it does occur since high-order terms in a certain series must be examined.

Our approach here resembles quite closely that of Kanamori.[5] In addition, a very closely related problem concerning the possible ferromagnetism of a gas of hard-sphere fermions has been examined by Ehrman[15] and Huang.[16] Our conclusions are in many respects similar to theirs, differences being primarily due to our inclusion of band structure effects.

We desire to obtain a condition for ferromagnetism. It should first be mentioned that in discussing the ferromagnetic state, we will consider only unsaturated ferromagnetism. In the unsaturated ferromagnetic state, there is a slight excess of spin parallel to some direction, whereas in the completely ferromagnetic state, all spins are aligned. We consider here the unsaturated case, since it is possible to express a condition for its occurrence in terms of quantities evaluated at the Fermi energy in the nonferromagnetic material. This is not possible for the state of complete alignment.

In the following discussion we will refer in the common manner to spin up and spin down, or to states of + spin and those of − spin. It should be realized, however, that the discussion, perhaps in spite of appearances, is reasonably free of ambiguity concerning spin directions. We may define ferromagnetism as any state in which more than $\frac{3}{4}$ of the pairs of particles are in triplet states, and less than $\frac{1}{4}$ are in singlet states. It is this definition which is actually implied.

Moreover, we will examine this problem only in the low-density limit in which the elements of t are constant. The results of the previous section indicate that in this case it is not particularly important to distinguish between the situations in which interactions occur on a single site and that in which they extend to first neighbors. The latter case is slightly more favorable to ferromagnetism, since the t-matrix elements are larger on account of the term $(V_0'' - a)/2zE_1$ in (6.44)

Let us consider a set of N-degenerate bands, by which we mean that, even in the low-density limit, there is some occupation of states in each band. The bands are represented by $E_\alpha(\mathbf{p})$ ($\alpha = 1, 2\cdots, \mathrm{N}$), the functions E_α being computed with the electron interaction neglected. Also, going with each $E_\alpha(\mathbf{p})$, there is a density of states $G_\alpha(E)$, which we take to refer to a single spin direction. Let us also define a total density of states

$$G(E) = \sum_{\alpha=1}^{N} G_\alpha(E) \qquad (7.1)$$

and adopt the convention that the energy of the lowest occupied state is $E=0$. Then states of the noninteracting system are occupied up to a Fermi energy μ, which is determined by

$$2\int_0^\mu G(E)dE = \rho , \qquad (7.2)$$

where ρ is the density of particles.

Now consider the possibility of ferromagnetism. If it occurs, the density of electrons of the majority spin (up) will be greater than that of electrons of spin down by an amount we denote by $\rho\zeta$. We wish to compute the total energy of the system as a function of ζ. It is convenient in doing this to regard the electrons of up

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[15] J. B. Ehrman, Phil. Mag. 43, 404 (1957).

[16] K. Huang, *Statistical Mechanics* (John Wiley & Sons, Inc., New York, 1963), Chap. 13.

and down spins as having different Fermi energies, which we denote by $\mu_\pm$, and we also put $\mu_\pm=\mu+\delta\mu_\pm$.

It is first necessary to relate $\delta\mu_\pm$ to ζ. This is easily done by examining the condition

$$\int_0^{\mu\pm} G(E)dE=\tfrac{1}{2}\rho(1\pm\zeta)\,. \qquad (7.3)$$

If the integral on the left side of (7.3) is expanded to second order in $\delta\mu$, we find, correct to second order in ζ,

$$\delta\mu_\pm=\pm\rho\zeta/2G(\mu)-\rho^2\zeta^2G'(\mu)/8G^3(\mu)\,. \qquad (7.4)$$

In Eq. (7.4), $G'(\mu)$ denotes the derivative of the density of states at the Fermi energy. We can now calculate the average energy E_0 [the first term in (1.1) and (5.3a)]. If

$$2\mathcal{V}\int EG(E)dE=E_a\,, \qquad (7.5)$$

where $\mathcal{V}$ is the volume of the entire system, we get

$$E_0=E_a+\mathcal{V}\frac{\rho^2\zeta^2}{4G(\mu)}\,. \qquad (7.6)$$

This result is correct to second order in ζ and is independent of the detailed band shape except through the assumption that $G(\mu)$ exists.

We must now calculate the change in potential energy. This calculation becomes more complex if more than one band must be considered, so we consider the one-band case first. If the nonzero element of t is constant, acting only in the singlet state, we have, with the use of Eqs. (4.16) and (5.5), a potential energy

$$\text{P.E.}=\mathcal{V}\Omega t_0\int_0^{\mu+\delta\mu_+} G(E)dE\int_0^{\mu+\delta\mu_-} G(E)dE\,, \qquad (7.7\text{a})$$

where

$$t_0=V_0/(1-\mathcal{G}_0V_0)=V_0/(1+\tfrac{1}{2}V_0I)\,, \qquad (7.7\text{b})$$

We obtain after a simple calculation

$$\text{P.E.}=\tfrac{1}{4}\mathcal{V}\Omega\rho^2t_0(1-\zeta^2)\,. \qquad (7.8)$$

The total energy per particle is found by adding (7.6) and (7.8), and then dividing by the number of particles $\rho\mathcal{V}$. We get

$$\frac{E_0}{N}=\frac{E_a}{N}+\frac{\rho\Omega}{4}\left[t_0+\zeta^2\left(\frac{1}{\Omega G(\mu)}-t_0\right)\right]. \qquad (7.9)$$

The condition for ferromagnetism in the one-band model is evidently

$$\Omega G(\mu)t_0\geqslant 1\,. \qquad (7.10)$$

This condition was first obtained by Kanamori.[5] In the special case of a parabolic band [$E(k)=\gamma k^2$], we have

$$G(\mu)=k_F/4\pi^2\gamma\,.$$

Then, with the use of the scattering length given in (5.8), the condition becomes

$$k_Fa\geqslant\frac{\pi}{2}\,, \qquad (7.11)$$

which was obtained by Huang[16] for a hard-sphere Fermi gas. A more elaborate calculation for the hard-sphere Fermi gas was attempted by Ehrman,[15] who suggests that if the calculation is made properly at higher densities, the number $\pi/2$ on the right of (7.11) should be raised to 1.674, an increase of less than 10%.

It should be emphasized that the relation (7.10) is, in the low-density approximation, valid regardless of the range of the interaction either with respect to the site index or the band index, provided that states in only one band are occupied. It is necessary to inquire under what circumstances the condition can be satisfied, and in particular, if it can be satisfied at densities low enough so that the assumption of constant t_0 remains valid. We have not proved rigorously that if it is satisfied ferromagnetism will necessarily result, because we have not shown that the ferromagnetic state would have a lower energy than that of some other order and state—for instance, a spin-density wave. Such a possibility seems, however, somewhat remote in view of the work of Kohn and Nettel.[17]

The condition for the occurrence of ferromagnetism, Eq. (7.10), becomes independent of V_0 when V_0 is large. Then we must have

$$2\Omega G(\mu)/I\geqslant 1\,. \qquad (7.12)$$

In this form, the condition actually depends on the band shape rather than the bandwidth. This may be seen if we multiply the energy band function $E(\mathbf{k})$ by a constant λ. It can then be determined that (7.12) is independent of λ. A similar argument shows that the magnitude of the energy difference between ferromagnetic and nonferromagnetic states is proportional to λ, and thus vanishes if the bandwidth tends to zero.

Next, we will show that (7.11) cannot be satisfied at all. To do this, we require an expression for k_Fa. For the parabolic band, the quantity I appearing in (5.8) and (7.7b) is given by

$$I=\frac{\Omega}{8\pi^3}\int\frac{d^3k}{\gamma k^2}\,.$$

We underestimate this quantity (thereby favoring ferromagnetism) if we replace the actual Brillouin zone by the sphere of equal volume (whose radius is k_m). Then we find immediately

$$I=\frac{\Omega k_m}{2\pi^2\gamma} \qquad (7.13\text{a})$$

and

$$k_Fa=[c+2k_m/\pi k_F]^{-1}\,, \qquad (7.13\text{b})$$

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[17] W. Kohn and S. J. Nettel, Phys. Rev. Letters 5, 8 (1960).

where c is a positive constant: $c=(\Omega V_0 k_F/8\pi\gamma)^{-1}$. We then observe that the condition (7.11) cannot be satisfied for $k_m/k_F \geqslant 1$. But k_m must be greater than k_F since the Fermi surface must lie within the Brillouin zone, from which our conclusion follows.

In the general case, we observe that since $G(E)$ approaches zero continuously as E approaches zero, for any finite t_0 it is always possible to find a density low enough so that (7.10) is not satisfied. In other words, ferromagnetism cannot occur for vanishingly small densities if only one band is occupied. This result is essentially the same as that of Slater, Statz, and Koster.

Next, let us try to find an example in which ferromagnetism will occur, that is, we will invent a simple density of states which, for some value of the Fermi energy μ (and therefore of the density ρ), satisfies Eq. (7.10). Moreover, the density should be low. It is apparent from the structure of Eqs. (7.10) and (7.7b) that in order to accomplish this we need $G(\mu)$ large, but we must not make I unduly large at the same time. In order to do this, we want to have a high sharp peak in $G(E)$ near the bottom of the band, since if μ falls in the peak, $G(\mu)$ will be large, but by keeping the peak narrow, we will not affect I so strongly. In this short calculation, we will assume that V_0 is large enough so that t_0 can be replaced by its limiting value of $2/I$.

Let us assume the following simple form for $G(E)$

$$G(E)=aE^{1/2}(E_m-E)^{1/2} + bE^{n/2}(E_0-E)^{n/2}\eta(E_0-E) \qquad (7.14)$$

in which η is a unit step function:

$$\eta(x)=1 \quad \text{for} \quad x>0\,,$$
$$\eta(x)=0 \quad \text{for} \quad x<0\,.$$

The integer n appearing in the second term is arbitrary. The quantities a and b are assumed to be positive. This function gives a simple representation of an energy band whose width is E_m ($E_m>E_0$ by hypothesis) on which is superimposed a peak which occurs close to $E_0/2$. The height and width of the peak are controlled by adjusting the parameters b, E_0, n as required. We suppose that this band can contain at most one electron of each spin, so that

$$\int_0^{E_m} \Omega G(E)dE=1\,. \qquad (7.15)$$

This gives one relation between the parameters

$$\frac{\pi E_m{}^2}{8}a+bE_0{}^{n+1}B\left(\frac{n}{2}+1,\frac{n}{2}+1\right)=1 \qquad (7.16)$$

in which B is a beta function. We must therefore have (defining a combination parameter z)

$$z=bE_0{}^{n+1}B\left(\frac{n}{2}+1,\frac{n}{2}+1\right)\leqslant 1\,. \qquad (7.17)$$

A simple calculation shows that

$$I=\frac{\pi}{2}E_m a+bE_0{}^n B\left(\frac{n}{2},\frac{n}{2}+1\right). \qquad (7.18)$$

To obtain very nearly the maximum advantage from the peak we have inserted, we will put $\mu=E_0/2$. Also, we will define a quantity $l=E_m/E_0$ ($l>1$). After a straightforward calculation, it is possible to express the condition for ferromagnetism in the form

$$\frac{2(2l-1)^{1/2}}{\pi l}\left[1-z\left[1-\frac{\pi l^2}{4B\left(\frac{n}{2}+1,\frac{n}{2}+1\right)2^n(2l-1)^{1/2}}\right]\right] \times\left[1-z\left(1-\frac{l}{2}\frac{n+1}{n}\right)\right]^{-1}\geqslant 1\,. \qquad (7.19)$$

When values of the beta function are inserted in (7.19), it is seen to be possible to satisfy the condition for some values of $z\leqslant 1$, for any value of $n\geqslant 3$, and any value of l. In particular, for large values of l and n, we can in this simple model, achieve ferromagnetism for small values of z, thus remaining in a low-density region.

One other example to which the criterion (7.10) may be applied is the simple cubic lattice with an energy band

$$E=E_0+2E_1(\cos k_x a+\cos k_y a+\cos k_z a) \qquad (7.20)$$

in which a is the lattice parameter and E_1 is negative. This band was also considered in Sec. VI. In this case, the quantity I is known as is the density of states.[18] Equation (7.10) (with $t_0=2/I$) yields the result that ferromagnetism will occur provided the Fermi energy is such that

$$[\Omega G(\mu)]\geqslant 0.123/|E_1|\,. \qquad (7.21)$$

Since the maximum value of the density of states is about

$$[\Omega G(E)]_{\max}\approx 0.145/|E_1| \qquad (7.22)$$

ferromagnetism would appear to be possible in this case. Consideration of the actual form of the density of states shows, however, that this value of the density of states is not attained until the band is nearly $\frac{1}{3}$ full, and we do not know whether the approximations involved in the derivation of (7.10) are still valid.

Our general discussion would be more rigorous if it could be shown that the approximation of a constant t matrix is not too bad for reasonable densities. This question is quite difficult to answer for bandshapes which are favorable to ferromagnetism. A numerical calculation for the case of the parabolic band, which will not be described in detail here, suggests that the optical potential, which is given by Eq. (5.4), varies

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[18] T. Wolfram and J. Callaway, Phys. Rev. **130**, 2207 (1963).

remarkably little from its value for $p=0$ all the way up to the Fermi energy for a wide range of densities. In this case, at least, the approximation is excellent.

We may summarize this study of the condition for ferromagnetism in the low-density limit with only one band occupied as follows:

(1) For sufficiently low particle density, regardless of the nature of the density of states, ferromagnetism is impossible. This conclusion is rigorously true.

(2) For some band shapes, such as the parabolic band, ferromagnetism appears to be impossible for all particle densities.

(3) If the density of states contains a sharp peak at low energy, ferromagnetism is predicted if the Fermi energy falls in the peak. This conclusion is, however, not quite rigorous for two reasons: (1) higher terms (in the density) in the t-matrix expansion have not been examined for bandshapes for which ferromagnetism is predicted, and (2) the possibility of a spin ordering more complicated than ferromagnetism has not been considered.

Now we will discuss the condition for ferromagnetism when more than one band is occupied. The basic objective is to determine whether the existence of exchange coupling between electrons in different bands but "on the same atom" materially increases the tendency toward ferromagnetism with respect to the one-band situation discussed earlier. This clearly relates to the old question as to whether the exchange coupling, which tends to align the spins of electrons in partially filled shells of free atoms, is of major importance in the theory of ferromagnetism of metals. Of course, our use of the t matrix implies that we can discuss this question only in the low-density limit.

Let us assume that N bands are degenerate at $E=0$. In this case, Eq. (7.6) remains valid (recall that G is the combined density of states). The calculation of the potential energy must, however, be repeated.

In place of Eq. (7.7a) we have instead

$$\text{P.E.}=\mathcal{V}\Omega\sum_{\alpha\beta}\sum_{\sigma,\sigma'}t_{\alpha\beta}(\sigma,\sigma')\int_0^{\mu+\delta\mu_\sigma}G_\alpha(E)dE \times\int_0^{\mu+\delta\mu_{\sigma'}}G_\beta(E)dE. \tag{7.23}$$

In this equation $t_{\alpha\beta}(\sigma,\sigma')$ refers to a matrix element of t involving two electrons whose spins are σ and σ'. The sum over spins can readily be expressed in terms of triplet and singlet states. To simplify the rather lengthy expression which is obtained, we define the notation

$$\int_0^{\mu+\delta\mu_\sigma}G_\alpha(E)dE=\rho_{\alpha\sigma}. \tag{7.24}$$

Then we have

$$\text{P.E.}=\mathcal{V}\Omega\sum_{\alpha\beta}\{t_{\alpha\beta}{}^t[\rho_{\alpha+}\rho_{\beta+}+\rho_{\alpha-}\rho_{\beta-}+\rho_{\alpha+}\rho_{\beta-}] +t_{\alpha\beta}{}^s\rho_{\alpha+}\rho_{\beta-}\}. \tag{7.25}$$

The calculation is facilitated by the expansion

$$\rho_{\alpha\pm}=\rho_\alpha(\mu)+\delta\mu_\pm G_\alpha(\mu)+\tfrac{1}{2}(\delta\mu_\pm)^2G_\alpha'(\mu) \tag{7.26}$$

valid for small differences in the numbers of electrons of "up" and "down" spin. The quantities $\delta\mu_\pm$ can be related to the spin excess through Eq. (7.4), which still holds. We will not give the details of the rather tedious calculation. To order ζ^2, we have

$$E_0/N=E_a/N+\rho\Omega\sum_{\alpha\beta}(3t_{\alpha\beta}{}^t+t_{\alpha\beta}{}^s)\rho_\alpha\rho_\beta/\rho^2 +\zeta^2[\rho/4G(\mu)-\tfrac{1}{2}k\theta'] \tag{7.27}$$

in which $\rho_1=\rho_1(\mu)$ etc., and

$$k\theta'=[\rho\Omega/2G(\mu)^2]\sum_{\alpha\beta}\{(t_{\alpha\beta}{}^s-t_{\alpha\beta}{}^t)G_\alpha(\mu)G_\beta(\mu) +(3t_{\alpha\beta}{}^t+t_{\alpha\beta}{}^s)\rho_\alpha[G'(\mu)G_\beta(\mu)/G(\mu)-G_\beta'(\mu)]\}. \tag{7.28}$$

The quantity $k\theta'$ has been defined so that the expression for the spin dependence of the total energy would, for small σ, have the same form as that occurring in the collective electron theory. The condition for the occurrence of ferromagnetism is now

$$2G(\mu)k\theta'/\rho=[\Omega/G(\mu)]\sum_{\alpha\beta}[(t_{\alpha\beta}{}^s-t_{\alpha\beta}{}^t)G_\alpha(\mu)G_\beta(\mu) +(3t_{\alpha\beta}{}^t+t_{\alpha\beta}{}^s)\rho_\alpha s_\beta G_\beta(\mu)]\geqslant 1, \tag{7.29}$$

where

$$s_\beta=G_\beta(\mu)^{-1}[G'(\mu)G_\beta(\mu)/G(\mu)-G_\beta'(\mu)] =\left(\frac{d}{dE}\ln\frac{G}{G_\beta}\right)_\mu. \tag{7.30}$$

One conclusion can be obtained immediately. We may assume that $G_\alpha(E)$ approaches zero as $E^{1/2}$ when E goes to zero (regardless of α). It follows that the left-hand side of (7.29) goes to zero as $\mu^{1/2}$ as $\mu\rightarrow 0$; thus for sufficiently low densities, the inequality (7.29) cannot be satisfied. Thus, just as we saw to be the case in the one-band problem, ferromagnetism will not occur at vanishingly low densities, regardless of how strong the interaction is. At this point our conclusions differ from those of Slater and Koster, who suggested as a result of their study of the two-particle problem, that ferromagnetism might be possible in the case of degenerate bands at arbitrarily low densities.

The general condition may perhaps be interpreted more easily if we examine a two-band case explicitly: Let us introduce the ratio of the density of states of bands 0, 1 at energy E:

$$r(E)=G_1(E)/G_0(E).$$

We can choose to number the bands in such a way that $r(\mu)<1$, that is, $G_0(\mu)>G_1(\mu)$. Also we note that $s_0(E)=-s_1(E)$. Then, on introducing r and performing the sum, we put (7.29) in the form:

$$\Omega G_0(\mu)[1+r(\mu)]^{-1}\{t_{00}{}^s+r^2(\mu)t_{11}{}^s+2r(\mu)(t_{01}{}^s-t_{01}{}^t) +[s_0(\mu)/G_0(\mu)][\rho_0 t_{00}{}^s-\rho_1 t_{11}{}^s +(\rho_1-\rho_0)(3t_{01}{}^t+t_{01}{}^s)]\}\geqslant 1. \quad (7.31)$$

Let us begin to examine (7.31) by first introducing the assumption that the two bands have the same shape near the Fermi energy so that $r(E)$ is nearly constant near $E=\mu$. This condition would be satisfied for two spherical bands with different effective masses, for instance. Then $s_0(\mu)$ may be neglected and only the first term survives. Since $r\leqslant 1$, the contribution from the first two terms of (7.31) (including the term $1+r$ in the denominator) will be less than or equal to ΩG_0 times the larger of $t_{00}{}^s$ and $t_{11}{}^s$. There is no reason to expect this contribution to the inequality to be appreciably more favorable to ferromagnetism than in the one-band case; in fact, the contrary seems more probable. However, there remains the additional term proportional to

$$2(t_{01}{}^s-t_{01}{}^t)=\frac{2V_{01,10}}{[1-g_{01}V_{01,01}]^2-g_{01}{}^2V_{01,10}}. \quad (7.32)$$

This is the "true" exchange term. It is probably always much smaller than the leading term involving $t_{00}{}^s$ or $t_{11}{}^s$. First, we always expect $V_{01,10}\ll V_{01,01}$; and second, the screening, which is dominated by the large element with $V_{01,01}$, is quite strong. The term $1-g_{01}V_{01,01}$ is squared.

Thus, the "true" exchange term does make some small contribution to the dominant $t_{00}{}^s$ and $t_{11}{}^s$ terms. It is certainly unlikely that it would ever make the dominant contribution to $k\theta'$ although it might be possible that this contribution would make the difference between paramagnetism and ferromagnetism in some material. In the case in which the two bands are spherical, the term (7.32) does make it possible, in principle, to satisfy the criterion (7.31). This only occurs, however, for extreme values of the parameters.

We will look briefly at the remaining term in (7.31). The quantity s_0 can be large in magnitude if the Fermi energy is in the vicinity of a critical point. Either sign is possible in this case, and it is conceivable that an important contribution could be obtained. Also, a positive contribution, proportional to $\mu^{3/2}$ to lowest order, results in the case in which band 0 is narrow and band 1 is wide. Thus, this term may be of some significance in the $s-d$ exchange interaction. Further investigation would require a more detailed band model than is appropriate here.

VIII. SUMMARY

A useful set of properly symmetrized two-electron wave functions has been introduced which facilitates calculation of the t matrix.

Explicit formulas have been obtained for elements of the t matrix in the low-density limit for (1) interactions in a single band on a single site, (2) interactions on a single site connecting a pair of bands, and (3) interactions in a single band extending to first neighbors.

An expression has been obtained for an effective one-body "optical potential," which has been evaluated in a simple example.

The occurrence of unsaturated ferromagnetism in a low-density system has been studied. The ferromagnetic state is predicted to be the ground state of the system, subject to certain possible reservations concerning other kinds of spin ordering not discussed here, in the case of the interactions mentioned above, if certain inequalities are satisfied. It can be concluded rigorously that ferromagnetism cannot occur for sufficiently low particle density, whatever the band structure. Somewhat less rigorously, ferromagnetism is predicted to be possible for certain band structures, particularly favorable conditions existing when the Fermi energy is close to the maximum of a narrow peak in the density of states.