do in Eq. (C4). Thus the estimate of the δV term [of Eq. (C5)] used in Sec. 4 has the correct structure, but errs only in what is used for $V_0(p,p'|0)$. Since this V_0 is reduced to a constant in Eqs. (4.33) and (4.34), we conclude that the estimate of the new effects is not essentially the worse by use of the weaker iteration procedure.

However, the third remark above, the approximation for V_0 to be used in the first part of the square brackets of Eq. (C5), is a more difficult matter. If we had used a shielded expression as in Eq. (3.22), we would have obscured the Hermiticity that in Sec. 4 appears in $W^{(3)}$, and was referred to in the second paragraph below Eq. (C5). The weaker iteration procedure that led to Eq. (2.19), instead of to a shielding denominator as in Eq. (3.18), really affects only the V_0 term in Eq. (C5)

and does not affect the structure of the new type of term proportional to δV. Or, stated differently, the weaker iteration procedure affects primarily the spin-*inde*pendent details of the shielding in the potential function V in W, but does not affect the spin-dependent effects of the shielding that were the purpose of Sec. 4 to bring out. Moreover, even this spin-independent term's approximation cannot be too far off, since the major part of the spin-independent shielding comes from the $\delta(a-b)$ term in Eq. (2.2), the others acting as corrections which can then be treated by an iteration method with a fair degree of accuracy. It is hoped that a more accurate treatment can be made, but the difficulties become so great that the relatively simple treatment of Sec. 4 was considered to be the most useful way of presenting the problem.

High-Temperature Magnetic Susceptibility of Interacting Electrons in a Solid*

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In this paper we consider a pair of electrons in an energy band which interact through a short-range potential. The scattering amplitude is determined exactly, and the energies of states in which the two particles are bound together are found. The change in the density of two-particle states produced by the interaction is computed and used to calculate the second virial coefficient occurring in the expansion of the logarithm of the partition function in powers of the density. Inclusion of an external magnetic field allows determination of the magnetic susceptibility at high temperatures. The result has a form equivalent to that obtained in Stoner's theory of ferromagnetism, thereby justifying that theory in the high-temperature region and yielding an expression for the molecular-field parameter θ'.

I. INTRODUCTION

SOME years ago, Slater, Statz, and Koster[1] (SSK) considered the problem of two electrons in an empty band (or two holes in a full band) with a view to determining whether a triplet or singlet state of the pair has lower energy. They concluded that, if the band is nondegenerate, a singlet will always be the lower. Recent developments in scattering theory[2] led us to re-examine the model of SSK to investigate whether rigorous conclusions may be drawn from it concerning the statistical mechanics of a low-density electron (or hole) system.

In a two-body problem, the scattering amplitude is a useful quantity to calculate. Not only does it give information concerning actual scattering processes, but energies of bound states may be calculated, and, of

most importance for the present problem, the effect of the interaction on the two-particle density of states may be determined. Knowledge of the appropriate density of states makes possible calculations of important thermodynamic quantities.

One way of obtaining a relation between scattering, the density of states, and thermodynamics is through the virial expansion of quantum statistics.[3] It is well known that for a gas, the second virial coefficient can be exactly expressed in terms of integrals involving the scattering phase shifts. We show here how the virial expansion may be constructed in a solid-state problem, and give an exact expression for the second virial coefficient when only short-range interactions are included. This theory makes possible a general approach to the statistical mechanics of interacting excitations at low density.

Applications of the virial expansion in solid-state problems have not been developed extensively heretofore, presumably because the density of electrons in a

[1] J. C. Slater, H. Statz, and G. F. Koster, Phys. Rev. 91, 1323 (1953). (This paper is afterwards referred to as SSK.)

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

[3] K. Huang, *Statistical Mechanics* (John Wiley & Sons, Inc., New York, 1963), Chap. 14.

normal solid is so high that an expansion in powers of the density seems to be of little interest. There are, however, problems in which the behavior of a small number of carriers—electrons or holes—is of considerable interest. Ferromagnetism is actually one example of this, since in the case of nickel there is only about 0.6 hole per atom, and in nickel-copper alloys the density of holes can be reduced much further while the system remains ferromagnetic.

II. THE TWO-BODY PROBLEM

We begin by reviewing the equations derived by SSK for the two-electron system. One considers two electrons in a crystal, which is described by a set of one-particle Bloch wave functions $\Psi_s(\mathbf{k},\mathbf{r})$ and energy levels $\epsilon_s(\mathbf{k})$. (Here s is the band index and $\mathbf{k}$ is the wave vector.) Wannier functions $a_s(\mathbf{r}-\mathbf{R}_n)$ are defined by

$$a_s(\mathbf{r}-\mathbf{R}_n) = \frac{\Omega^{1/2}}{(2\pi)^{3/2}} \int e^{-i\mathbf{k}\cdot\mathbf{R}_n}\Psi_s(\mathbf{k},\mathbf{r})d^3k, \qquad (1)$$

in which Ω is the volume of the unit cell, $\mathbf{R}_n$ is a direct lattice vector, and the integration includes a single Brillouin zone. The two electrons have the Hamiltonian

$$H=H(1)+H(2)+\mathcal{V}(1,2), \qquad (2)$$

where the single-particle portions include the periodic potential of the crystal. Thus we have

$$H(1)\Psi_s(\mathbf{k},\mathbf{r}_1) = \epsilon_s(\mathbf{k})\Psi_s(\mathbf{k},\mathbf{r}_1). \qquad (3)$$

The wave function for the two-electron problem is expanded in Wannier functions

$$\Psi(1,2)=\sum_{s,t,mn} U_{st}(\mathbf{R}_m,\mathbf{R}_n)a_s(\mathbf{r}_1-\mathbf{R}_m)a_t(\mathbf{r}_2-\mathbf{R}_n). \qquad (4)$$

This expansion is substituted into the Schrödinger equation. After a straightforward calculation, one finds an equation satisfied by the coefficient U:

$$\sum_l [\mathcal{E}_s(\mathbf{R}_l)U_{st}(\mathbf{R}_m-\mathbf{R}_l, \mathbf{R}_n)+\mathcal{E}_t(\mathbf{R}_l)U_{st}(\mathbf{R}_m, \mathbf{R}_n-\mathbf{R}_l)]$$

$$+ \sum_{p,q,l,j} U_{pq}(\mathbf{R}_m-\mathbf{R}_j, \mathbf{R}_n-\mathbf{R}_l)$$

$$\times (s,t; m, n|\mathcal{V}|m-j, n-l; p,q)$$

$$=EU_{st}(\mathbf{R}_m,\mathbf{R}_n). \qquad (5)$$

In this equation, the matrix elements of the potential are given by

$$(s,t; m, n|\mathcal{V}|m-j, n-l; p,q)$$

$$= \int a_s{}^*(\mathbf{r}_1-\mathbf{R}_m)a_t{}^*(\mathbf{r}_2-\mathbf{R}_n)\mathcal{V}(1,2)a_p(\mathbf{r}_1-\mathbf{R}_m+\mathbf{R}_j)$$

$$\times a_q(\mathbf{r}_2-\mathbf{R}_n+\mathbf{R}_l)d^3r_1d^3r_2. \qquad (6)$$

The quantities $\mathcal{E}_s(\mathbf{R}_l)$ are Fourier coefficients of the

energy

$$\mathcal{E}_s(\mathbf{R}_l) = \frac{\Omega}{(2\pi)^3} \int e^{i\mathbf{k}\cdot\mathbf{R}_l}\epsilon_s(\mathbf{k})d^3k. \qquad (7)$$

It is possible to separate variables in (5) by taking out the motion of the center of mass of the pair. We define a function $F_{st}(\mathbf{R}_m-\mathbf{R}_n)$ by

$$U_{st}(\mathbf{R}_m,\mathbf{R}_n) = \exp[i\mathbf{K}\cdot(\mathbf{R}_m+\mathbf{R}_n)/2]F_{st}(\mathbf{R}_m-\mathbf{R}_n). \qquad (8)$$

The quantity $\mathbf{K}$ is essentially the momentum of the center of mass. The function F_{st} satisfies the equation

$$\sum_l [\mathcal{E}_s(\mathbf{R}_l)e^{-i\mathbf{K}\cdot\mathbf{R}_l/2}+\mathcal{E}_t(\mathbf{R}_l)e^{i\mathbf{K}\cdot\mathbf{R}_l/2}-E\delta_{l,0}]F_{st}(\mathbf{R}_n-\mathbf{R}_l)$$

$$+ \sum_{pq,jl} e^{i\mathbf{K}\cdot(\mathbf{R}_j+\mathbf{R}_l)/2}(s,t; n, 0|\mathcal{V}|n-l, -j; p,q)$$

$$\times F_{pq}(\mathbf{R}_n-\mathbf{R}_l+\mathbf{R}_j)=0. \qquad (9)$$

Since the Hamiltonian considered does not contain spin, the full two-body wave function is a product of a space function [which is given by Eq. (5)] and a spin function describing either a singlet or a triplet state. In a singlet state, the space wave function must be symmetric; for a triplet state it is antisymmetric. This leads to a requirement on F:

$$F_{st}(\mathbf{R}) = \pm F_{ts}(-\mathbf{R}), \qquad (10)$$

where the plus sign goes with the singlet and the minus sign with the triplet states.

We now make the rather drastic approximation of retaining only a single matrix element of the interaction. This is the one in which all the Wannier functions are centered on the same site: $R_n=R_j=R_l=0$. In addition, we consider only a single band. The single matrix element remaining is simply called V_0. (We also drop the band indices.) It is our intention to relax these restrictions to some extent in subsequent work, since the scattering technique we employ is applicable to any potential of finite range, but it should be observed that the matrix element we have retained is by far the largest. In considering only a single matrix element, we are dealing with a model which has been employed extensively in the past, and about which it is possible to make exact remarks.

With these assumptions, Eq. (9) reduces to

$$\sum_l [2\mathcal{E}(\mathbf{R}_n-\mathbf{R}_l)\cos\mathbf{K}\cdot(\mathbf{R}_n-\mathbf{R}_l)/2-E\delta_{nl}]F(\mathbf{R}_l)$$

$$+V_0F(0)=0. \qquad (11)$$

This is the equation we will solve. It is the same as that considered by SSK except that those authors neglected the center-of-mass momentum.

To solve the equation, we first need a set of normalized eigenfunctions of the Hamiltonian for free particles.

These functions $F^{(0)}(R_n)$ are given by

singlet state

$$F_{(s)}^{(0)}(\mathbf{R}_n) = \left[\frac{\Omega}{4\pi^3(1+\delta_{n,0})}\right]^{1/2} \cos\mathbf{k}\cdot\mathbf{R}_n; \quad (12)$$

triplet state

$$F_{(t)}^{(0)}(\mathbf{R}_n) = \left[\frac{\Omega}{4\pi^3}\right]^{1/2} \sin\mathbf{k}\cdot\mathbf{R}_n. \quad (13)$$

These functions are solutions for an energy E given by

$$E = E(\mathbf{K},\mathbf{k}) = \epsilon(\mathbf{K}/2+\mathbf{k}) + \epsilon(\mathbf{K}/2-\mathbf{k}). \quad (14)$$

Since the interaction contributes only when the relative coordinate is zero, it is evident that there is no scattering in triplet states. We do not consider the triplet states further in this section.

It is possible to solve Eq. (12) with the aid of a Green's function which, in the case of singlet states, is given by

$$\mathcal{G}_{\mathbf{K}}(\mathbf{R}_m,\mathbf{R}_n) = \frac{\Omega}{4\pi^3}[(1+\delta_{n,0})(1+\delta_{m,0})]^{-1/2}$$

$$\times \int \frac{\cos\mathbf{k}\cdot\mathbf{R}_m \cos\mathbf{k}\cdot\mathbf{R}_n d^3k}{E-E(\mathbf{K},\mathbf{k})+i\epsilon}. \quad (15)$$

We have chosen the Green's function which satisfies an outgoing wave boundary condition. It is easily verified that this function obeys the equation

$$\sum_l [2\mathcal{E}(\mathbf{R}_n-\mathbf{R}_l)\cos\tfrac{1}{2}\mathbf{K}\cdot(\mathbf{R}_n-\mathbf{R}_l) - E\delta_{n,l}]$$

$$\times \mathcal{G}_{\mathbf{K}}(\mathbf{R}_l,\mathbf{R}_m) = -\delta_{n,m}. \quad (16)$$

It is easily seen, with the aid of (16), that Eq. (11) becomes

$$F(\mathbf{R}_n) = F^{(0)}(\mathbf{R}_n) + V_0\mathcal{G}_{\mathbf{K}}(\mathbf{R}_n,0)F(0). \quad (17)$$

This equation can be solved immediately. The solution is

$$F(\mathbf{R}_n) = F^{(0)}(\mathbf{R}_n) + \frac{V_0\mathcal{G}_{\mathbf{K}}(\mathbf{R}_n,0)F^{(0)}(0)}{1-V_0\mathcal{G}_{\mathbf{K}}(0,0)}$$

$$= \left(\frac{\Omega}{4\pi^3}\right)^{1/2}\left[\frac{\cos\mathbf{k}\cdot\mathbf{R}_n}{(1+\delta_{n0})^{1/2}} + \frac{2^{-1/2}V_0\mathcal{G}_{\mathbf{K}}(\mathbf{R}_n,0)}{1-V_0\mathcal{G}_{\mathbf{K}}(0,0)}\right]. \quad (18)$$

To obtain the scattering amplitude, we require the asymptotic form of the Green's function $\mathcal{G}_{\mathbf{K}}(\mathbf{R}_n,0)$ for large $\mathbf{R}_n$. It follows from Eq. (15) with the use of the inversion symmetry of the energy that

$$\mathcal{G}_{\mathbf{K}}(\mathbf{R}_n,0) = \frac{\Omega}{4\pi^3}[2(1+\delta_{n,0})]^{-1/2}$$

$$\times \int \frac{e^{i\mathbf{k}\cdot\mathbf{R}_n}}{E-E(\mathbf{K},\mathbf{k})+i\epsilon}d^3k. \quad (19)$$

The evaluation of integrals of this type is discussed in Ref. 2. The asymptotic form of $\mathcal{G}_{\mathbf{K}}$ is

$$\mathcal{G}_{\mathbf{K}}(\mathbf{R}_n,0) = -\frac{\Omega}{4\pi\sqrt{2}|\mathbf{R}_n|}\sum_\gamma \frac{1}{\gamma}e^{i\mathbf{k}_0\cdot\mathbf{R}_n}, \quad (20)$$

in which $\mathbf{k}_0$ is a solution of

$$E = E(\mathbf{K},\mathbf{k}_0), \quad (21a)$$

whose direction is determined by

$$\left(\frac{\nabla_k E(\mathbf{K},\mathbf{k})}{|\nabla_k E(\mathbf{K},\mathbf{k})|}\right)_{\mathbf{k}_0} = \frac{\mathbf{R}_n}{|\mathbf{R}_n|}. \quad (21b)$$

The quantity γ is a function of the first and second derivatives of the energy evaluated at $\mathbf{k}_0$, whose detailed form does not concern us here. The summation runs over all the vectors $\mathbf{k}_0$ which may satisfy the conditions (21). We will note that in the case of a spherical band, γ is just the coefficient of k^2, e.g., $\epsilon(\mathbf{k}) = \gamma k^2$.

For the present calculation, we will consider only the case in which there is just one $\mathbf{k}_0$ which satisfies (21). Then the asymptotic form of $F(\mathbf{R}_n)$ is

$$F(\mathbf{R}_n) = \left(\frac{\Omega}{16\pi^3}\right)^{1/2}\left[e^{i\mathbf{k}\cdot\mathbf{R}_n} + e^{-i\mathbf{k}\cdot\mathbf{R}_n}\right.$$

$$\left. -\frac{V_0\Omega e^{i\mathbf{k}_0\cdot\mathbf{R}_n}}{4\pi\gamma|\mathbf{R}_n|(1-V_0\mathcal{G}_{\mathbf{K}}(0,0))}\right]. \quad (22)$$

We define the scattering amplitude f as the coefficient of $e^{i\mathbf{k}_0\cdot\mathbf{R}_n}/|\mathbf{R}_n|$ in (22)

$$f = -\frac{V_0\Omega}{4\pi\gamma(1-V_0\mathcal{G}_{\mathbf{K}}(0,0))}. \quad (23)$$

We require now an expression for $\mathcal{G}_{\mathbf{K}}(0,0)$. This is given by (15) for $n=m=0$. We define an effective density of states for fixed $\mathbf{K}$ by

$$G_{\mathbf{K}}(E) \equiv \frac{\Omega}{8\pi^3}\int \delta[E-E(\mathbf{K},\mathbf{k})]d^3k. \quad (24)$$

If $\mathbf{K} \to 0$

$$G_0(E) = \frac{1}{2}\frac{\Omega}{8\pi^3}\int \delta[\tfrac{1}{2}E-\epsilon(\mathbf{k})]d^3k = \tfrac{1}{2}\bar{G}\left(\frac{E}{2}\right), \quad (25)$$

where $\bar{G}$ is the ordinary single-particle density of states per atom. We have

$$\mathcal{G}_{\mathbf{K}}(0,0) = I_{\mathbf{K}}(E) - i\pi G_{\mathbf{K}}(E) \quad (26)$$

in which

$$I_{\mathbf{K}}(E) = P\int \frac{G_{\mathbf{K}}(E')}{E-E'}dE', \quad (27)$$

and P signifies that the principal value is required. For later use, we note that

$$I_0(0) = -\frac{1}{2} \int \frac{\bar{G}(E'/2)}{E'} dE'$$

$$= -\frac{1}{2} \int \frac{\bar{G}(E')}{E'} dE' \equiv -\tfrac{1}{2} I. \quad (28)$$

The last step serves as the definition of the symbol I, which we see is the average of E^{-1} over the band.

There are localized states of two electrons interacting with a repulsive short-range potential. These states were considered by SSK for $\mathbf{K}=0$. The situation here contrasts with that of ordinary quantum mechanics, where a bound state cannot be obtained for a repulsive potential. The energies of these states are determined by the poles of the scattering amplitude f. The condition is that

$$1 - V_0 \mathcal{G}_\mathbf{K}(0,0) = 0. \quad (29)$$

Since V_0 is real, solutions to (29) can occur only if the imaginary part of $\mathcal{G}$ vanishes. From (26) and (24), this means that, for a given $\mathbf{K}$, the energy E must be outside the continuum of states for that $\mathbf{K}$. Since V_0 is positive, a solution can occur only when $I_\mathbf{K}(E)$ is positive, that is, above the continuum. The localized two-particle states have higher energy than any state in the continuum for that $\mathbf{K}$. Let $E_B(\mathbf{K})$ be the energy of such a state. The condition (29) reduces to

$$1 = V_0 I_\mathbf{K}(E_B). \quad (30)$$

Since $I_\mathbf{K}(E)$ is monotonically decreasing above the band there can be only one bound state. Therefore, a single $E_B(\mathbf{K})$ curve is determined by (30). We will not analyze this function in detail here.

We require, however, the low-energy limit of the scattering amplitude. This is defined as

$$f_0 = \lim_{\substack{E \to 0 \\ K \to 0}} f = -\frac{V_0 \Omega}{4\pi\gamma} [1 + \tfrac{1}{2} V_0 I]^{-1}. \quad (31)$$

In order to make contact later on with theories of the imperfect Fermi gas, we also define a scattering length by

$$a = -\tfrac{1}{2} f_0 = (\Omega V_0 / 8\pi\gamma)[1 + \tfrac{1}{2} V_0 I]^{-1}. \quad (32)$$

The factor of $\tfrac{1}{2}$ in (32) arises because we have considered the scattering of two identical particles.

III. THE PARTITION FUNCTION

Our principal objective in this work is to investigate the thermodynamics of a system of particles, interacting through the short-range interaction V_0. A quantity of vital importance in this is the two-body partition functions, which we define to be

$$Z_2 = \mathrm{Tr} e^{-\beta H_2}, \quad (33)$$

in which H_2 is the Hamiltonian of Eq. (2), and $\beta = 1/kT$. The use of Z_2 in statistical problems will be discussed in the next section. At present we obtain a formal expression for the change in Z_2, ΔZ_2, produced by the two-particle short-range interaction $\mathcal{U}(1,2)$.

First, let us note that we can immediately eliminate the summation over spins implied by the trace operation, as far as ΔZ_2 is concerned. This occurs since we can classify all two-body states as either singlets or triplets. The interaction occurs only in the singlet states, so only these need be considered. Therefore, for the remainder of this section, we restrict the trace to the singlet state. With this understood we write

$$\mathrm{Tr} e^{-\beta H_2} = \mathrm{Tr} \int \delta(E - H_2) e^{-\beta E} dE$$

$$= -\frac{1}{\pi} \mathrm{Im}\, \mathrm{Tr} \int \frac{e^{-\beta E}}{E^+ - H_2} dE, \quad (34)$$

in which E^+ indicates that the energy is allowed to have a small positive imaginary part, which is set equal to zero after integration. We separate from the trace the contribution from the bound states, whose energies are $E_B(K)$. Hence

$$\mathrm{Tr} e^{-\beta H_2} = \sum_\mathbf{K} e^{-\beta E_B(\mathbf{K})}$$

$$- \frac{1}{\pi} \mathrm{Im}\, \mathrm{Tr}^{(c)} \int e^{-\beta E} \frac{1}{E^+ - H_2} dE. \quad (35)$$

The superscript (c) on the trace indicates that only continuum states are included. We now wish to exhibit explicitly the change due to interactions. We can write

$$\Delta Z_2 = \mathrm{Tr} e^{-\beta H_2} - \mathrm{Tr} e^{-\beta H_2^{(0)}}, \quad (36)$$

in which $H_2^{(0)}$ does not include any interaction. From the preceding argument, we evidently have

$$\mathrm{Tr} e^{-\beta H_2^{(0)}} = -\frac{1}{\pi} \mathrm{Im}\, \mathrm{Tr}^{(c)} \int e^{-\beta E} \frac{1}{E^+ - H_2^{(0)}} dE. \quad (37)$$

Following the procedures of Ref. 2, we write

$$\mathrm{Tr} \frac{1}{E^+ - H_2} = \frac{d}{dE} \log \det[E^+ - H_2]$$

$$= \frac{d}{dE} \log \det[E^+ - H_2^{(0)}]$$

$$+ \frac{d}{dE} \log \det\left(1 - \frac{1}{E^+ - H_2^{(0)}} \mathcal{U}\right).$$

Hence

$$\Delta Z_2 = \sum_{\mathbf{K}} \left\{ e^{-\beta E_B(\mathbf{K})} \frac{1}{\pi} \operatorname{Im} \int e^{-\beta E} \frac{d}{dE} \right.$$

$$\left. \times \log \det \left[1 - \frac{1}{E^+ - H_2{}^0} \mathcal{V} \right] dE \right\}$$

$$= \sum_{\mathbf{K}} \left\{ e^{-\beta E_B(\mathbf{K})} \frac{1}{\pi} \operatorname{Im} \int e^{-\beta E} \frac{d}{dE} \right.$$

$$\left. \times \log(1 - V_0 \mathcal{G}_{\mathbf{K}}(0,0)) dE \right\} \quad (38)$$

in which $\mathcal{G}_{\mathbf{K}}(0,0)$ is the quantity discussed in the previous section. Now using Eq. (26), we define a "phase shift" $\delta_{\mathbf{K}}$ by

$$\delta_{\mathbf{K}} = \tan^{-1} \frac{\pi V_0 G_{\mathbf{K}}(E)}{1 - V_0 I_{\mathbf{K}}(E)}. \quad (39)$$

We have that

$$\frac{d\delta_{\mathbf{K}}}{dE} = \operatorname{Im} \frac{d}{dE} \log[1 - V_0 \mathcal{G}_{\mathbf{K}}(0,0)]. \quad (40)$$

Since the term on the right side of (40) is seen from Ref. 2 to be proportional to the change in density of two-particle states, Eq. (40) expresses the change in density of states in terms of the phase shift in the conventional manner.[3,4] Since the interaction is short range, there is in this case only an s-wave phase shift.

For fixed $\mathbf{K}$, the two-particle states extend from E_0 to E_m (say) [with $E_0 = E(\mathbf{K},0)$]. It is evident that $G_{\mathbf{K}}(E) = 0$ for $E \leqslant E_0$ or $E \geqslant E_m$. Then it follows that

$$\delta_{\mathbf{K}}(E_0) = 0, \quad (41a)$$

$$\delta_{\mathbf{K}}(E_m) = 0 \quad \text{if} \quad 1 - V_0 I_{\mathbf{K}}(E_m) > 0, \quad (41b)$$

$$\delta_{\mathbf{K}}(E_m) = \pi \quad \text{if} \quad 1 - V_0 I_{\mathbf{K}}(E_m) < 0. \quad (41c)$$

Since $I_{\mathbf{K}}$ must go to zero as $1/E$ for large E, the condition $1 - V_0 I_{\mathbf{K}}(E_m) < 0$ implies that the equation $1 = V_0 I_{\mathbf{K}}(E)$ will be satisfied for some $E_B(\mathbf{K}) > E_m$, and hence that there is a localized state for that $\mathbf{K}$. Thus we see that in the case of a localized state, the phase shift goes to π at the top of the band—a reverse Levinson's theorem. Now we have

$$\Delta Z_2 = \sum_{\mathbf{K}} \left\{ e^{-\beta E_B(\mathbf{K})} \frac{1}{\pi} \int_{E_0}^{E_m} e^{-\beta E} \frac{\partial \delta_{\mathbf{K}}}{\partial E} dE \right\}. \quad (42)$$

We can integrate the second term by parts once, and make use of Eq. (41).

$$\Delta Z_2 = -\sum_{\mathbf{K}} \left[e^{-\beta E_m(\mathbf{K})} - e^{-\beta E_B(\mathbf{K})} \right]$$

$$- \frac{\beta}{\pi} \sum_{\mathbf{K}} \int_{E_0}^{E_m} \delta_{\mathbf{K}}(E) e^{-\beta E} dE. \quad (43)$$

This is our general expression for ΔZ_2. In the first term, the sum over $\mathbf{K}$ includes only those values of $\mathbf{K}$ for which a localized state exists. It will be observed that ΔZ_2 is inherently negative, which is to be expected since a repulsive interaction effectively raises the states in energy, or more precisely, shifts the density of states to higher energy.

IV. THE VIRIAL EXPANSION

In this section we consider the grand partition function Z for the system of interacting electrons or holes treated in Sec. III and develop a virial expansion by expanding $\log Z$ in powers of the density.[3,5] The existence of an applied magnetic field is considered implicitly and an application to the magnetic susceptibility of the system is given in the next section. The grand partition function is defined such that

$$\log Z = \log(1 + Z_1 e^\nu + Z_2 e^{2\nu} + \cdots), \quad (44)$$

with

$$Z_m = \operatorname{Tr}(e^{-\beta H_m}), \quad (45)$$

and $\nu = \beta \mu$, where μ is the chemical potential. Here, as in Eq. (33), the trace operation implies summation only over states which are antisymmetric in the space and spin coordinates together, and H_m is the Hamiltonian for m interacting particles. If the terms after the first in the expansion of Z are sufficiently small we may write

$$\log Z = (V/v_0)(e^\nu + b_2 e^{2\nu} + \cdots), \quad (46)$$

where

$$b_2 = (v_0/2V)(2Z_2 - Z_1{}^2). \quad (47)$$

V is the volume of the system, and v_0 is a quantity with the dimensions of volume independent of V, defined by

$$v_0 = V/Z_1. \quad (48)$$

The factor v_0/V is introduced so that b_2 will emerge as independent of V. The chemical potential $\mu = \nu/\beta$ is determined by the equation

$$n = (\partial/\partial \nu) \log Z, \quad (49)$$

where n is the number of particles in the volume V, and substituting from (46), we find

$$n v_0/V = e^\nu + 2b_2 e^{2\nu} + \cdots, \quad (50)$$

solving for e^ν we obtain

$$e^\nu = (n v_0/V) - 2b_2 (n v_0/V)^2 + \cdots, \quad (51)$$

and substitution into (46) yields

$$\log Z = n[1 - b_2(n v_0/V)]. \quad (52)$$

This is the virial expansion, the second virial coefficient being $-n v_0 b_2$, which is valid in the regime of sufficiently low densities, for a given temperature, or sufficiently high temperatures for a given density. Equation (47)

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[4] Similar use of a phase shift for impurity scattering problems may be found in A. Seeger, J. Phys. Radium **23**, 616 (1962).

[5] E. Beth and G. E. Uhlenbeck, Physica **4**, 915 (1937). C. Bloch and C. de Dominicis, Nucl. Phys. **10**, 509 (1959).

may be written

$$b_2 = (v_0/2V)(2\Delta Z_2 + 2Z_{20} - Z_1^2), \quad (53)$$

with ΔZ_2 defined by (36) and

$$Z_{20} = \mathrm{Tr}e^{-\beta H_2^{(0)}}, \quad (54)$$

where $H_2^{(0)}$ is the Hamiltonian for two noninteracting particles.

The calculation of Z_{20} is straightforward since the eigenvalues of $H_2^{(0)}$ are $\epsilon_i + \epsilon_j$, $i \neq j$, where ϵ_i is the energy of a one-particle state, the spin being included in the suffix i. Thus

$$Z_{20} = \sum_{i<j} \exp[-\beta(\epsilon_i + \epsilon_j)] \quad (55)$$

or

$$Z_{20} = \tfrac{1}{2}(Z_1^2 - \sum_i e^{-2\beta\epsilon_i}), \quad (56)$$

and substituting into (53) we obtain

$$b_2 = (v_0/2V)(2\Delta Z_2 - \sum_i e^{-2\beta\epsilon_i}). \quad (57)$$

The part of the second virial coefficient which is due to the interaction between particles may then be written

$$B_{\mathrm{int}} = -nv_0^2 \Delta Z_2/V = -nV\Delta Z_2/Z_1^2, \quad (58)$$

and ΔZ_2 is given by (43). This result for electrons or holes in a solid, when only short-range interactions are considered, is the analog of the well-known result for an imperfect gas (see, e.g., Ref. 3).

V. THE HIGH-TEMPERATURE MAGNETIC SUSCEPTIBILITY

The magnetization M of the system is given by

$$M = (kT/V)(\partial/\partial B)\log Z(\nu, V, T, B), \quad (59)$$

where B is the internal magnetic field. We consider here only the spin susceptibility. To find Z as a function of B we must determine the field dependence of b_2. Since only singlet states contribute to ΔZ_2 this quantity must be independent of B, so it is only necessary to evaluate v_0, which is related to Z_1 by (48), and the sum $\sum \exp(-2\beta\epsilon_i)$. It is convenient now to introduce spin explicitly by defining $\epsilon_{i\sigma}$ as the energy of a single-particle state of wave vector $\mathbf{k}_i$ and spin component σ, measured in units of $\hbar$, in the direction of the field. Thus

$$\epsilon_{i\sigma} = \epsilon(\mathbf{k}_i) - 2\mu_0\sigma B, \quad (60)$$

with $\mu_0 = g\mu_B$, where g is the spectroscopic splitting factor, approximately equal to 2, and μ_B is the Bohr magneton. Hence

$$Z_1 = \sum_{i,\sigma} \exp\{-\beta[\epsilon(\mathbf{k}_i) - 2\mu_0\sigma B]\}$$

$$= 2\cosh\beta\mu_0 B \sum_i \exp[-\beta\epsilon(\mathbf{k}_i)], \quad (61)$$

and similarly

$$\sum_{i,\sigma} \exp(-2\beta\epsilon_i) = 2\cosh2\beta\mu_0 B \sum_i \exp[-2\beta\epsilon(\mathbf{k}_i)]. \quad (62)$$

It is convenient to define

$$D = V^{-1}\Delta Z_2, \quad (63)$$

$$S_n = V^{-1}\sum \exp[-n\beta\epsilon(k_i)], \quad (64)$$

and then, from (48) and (61),

$$V/v_0 = 2VS_1 \cosh\beta\mu_0 B, \quad (65)$$

and from (57) and (62)

$$b_2 = v_0(D - S_2 \cosh2\beta\mu_0 B). \quad (66)$$

On substituting (65) and (66) into (46) we obtain

$$\log Z = 2VS_1 e^\nu \cosh\beta\mu_0 B + Ve^{2\nu}(D - S_2 \cosh2\beta\mu_0 B). \quad (67)$$

The magnetization M, given by (59) is now obtained by differentiating (67) with respect to B holding v fixed and then eliminating ν by means of (51). This leads to the expression

$$M = 2\mu_0(nv_0/V)\sinh\beta\mu_0 B$$
$$\times[S_1 - (D+S_2)(nv_0/V)\mathrm{sech}\beta\mu_0 B], \quad (68)$$

correct to terms in $(nv_0/V)^2$. The susceptibility of the system in small fields is easily obtained in the form

$$\chi = \left(\frac{\partial M}{\partial B}\right)_{B=0} = \frac{n\mu_0^2}{VkT}\left[1 - \frac{D+S_2}{S_1}\left(\frac{nv_0}{V}\right)\right]. \quad (69)$$

This expression exhibits the first two terms in a high-temperature expansion for χ and the conditions under which higher terms may be neglected are discussed later.[6] To the same order we may write

$$\frac{1}{\chi} = \frac{1}{\chi_0} - \frac{V}{n\mu_0^2}k\theta', \quad (70)$$

where χ_0 is the susceptibility for the system without interaction between particles and

$$\theta' = -\frac{DTn}{S_1}\left(\frac{v_0}{V}\right)_{B=0} = -\frac{DTn}{2VS_1^2}. \quad (71)$$

Comparison of (70) with the expression χ^{-1} in Stoner's collective electron theory[7] shows that the temperature θ' introduced here may be identified with the θ' of Stoner's theory. In that theory θ' is introduced empirically as a measure of the molecular field strength and is assumed to be temperature-independent. We shall show that, in a physically realistic high-tempera-

[6] The spin magnetic susceptibility of interacting electrons at low temperatures and high density has been considered by P. A. Wolff, Phys. Rev. 120, 814 (1960).

[7] See e.g., A. H. Wilson, Theory of Metals (Cambridge University Press, New York, 1953), Chap. 7.

ture regime, θ' defined by (71) is in fact, to a good approximation, temperature-independent, and furthermore is of the order of magnitude required by experiment. The present work therefore provides a justification of collective electron theory in the high-temperature regime, well above the Curie point for a ferromagnet.

We shall presently proceed to obtain an approximate expression for θ' in the regime of moderately high temperatures with $\epsilon_F \ll kT \ll \Delta\epsilon$, where ϵ_F is the Fermi energy and $\Delta\epsilon$ is the bandwidth. This regime exists, for example, in a Ni-Cu alloy. However, it is first of all instructive to consider the physically unrealistic case of extremely high temperatures where $kT \gg V_0$ and $kT \gg \Delta\epsilon$.

A. Extremely High Temperatures

In this limit ($\beta \to 0$) it is clear that $S_1 = N/V$, where N is the number of atoms in volume V. To evaluate D it is simplest to use an alternative expression for ΔZ_2 to that given in (38). ΔZ_2 is defined by (36) and clearly

$$\Delta Z_2 = \mathrm{Tr}\frac{1}{2\pi i}\oint e^{-\beta z}\left(\frac{1}{z-H_2}-\frac{1}{z-H_2{}^{(0)}}\right)dz, \quad (72)$$

where the integration is taken around a large contour enclosing all the poles of the integrand. By a procedure very similar to that used to obtain (38) we find

$$\Delta Z_2 = \frac{1}{2\pi i}\sum_{\mathbf{K}}\oint e^{-\beta z}\frac{d}{dz}\log[1-V_0\mathcal{G}_{\mathbf{K}}(0,0)], \quad (73)$$

where $\mathcal{G}_{\mathbf{K}}(0,0)$ is given by (19) with $R_n = 0$ and E^+ replaced by z. On the large contour the logarithms may be expanded in powers of z^{-1} and $e^{-\beta z}$ may be expanded in powers of βz. The result is an expansion of ΔZ_2 in powers of β and it is found that

$$\Delta Z_2 = -NV_0\beta \quad (74)$$

as $\beta \to 0$. Hence $D = -N\beta V_0/V$ and on substituting in (71) we obtain

$$2k\theta' = nV_0/N. \quad (75)$$

This result for the extreme high-temperature limit is just what is obtained if the Hamiltonian for the many-body system of particles with short-range interactions is treated in the Hartree-Fock approximation. In this case we have the approximate Hamiltonian

$$H' = \sum_{i,\sigma}\epsilon_{i\sigma}n_{i\sigma}+V_0(n_\uparrow n_\downarrow/N), \quad (76)$$

where $n_{i\sigma}$ is the occupation number of the one-particle state with wave vector $\mathbf{k}$ and spin σ and $n_\uparrow$, $n_\downarrow$ are the total numbers of particles with spin up and down, respectively. Stoner's collective electron theory is based on the Hamiltonian

$$H_s = \sum_{i,\sigma}\epsilon_{i\sigma}n_{i\sigma}-\tfrac{1}{2}nk\theta'\zeta^2, \quad (77)$$

where ζ is the relative magnetization defined by

$$\zeta = (n_\uparrow - n_\downarrow)/n. \quad (78)$$

Now H' and H_s are equivalent, differing only by a constant, and thus in the Hartree-Fock approximation the system behaves as a Stoner system with θ' given by (75). Since (75) has been derived exactly in the case of extremely high temperatures it is clear that in this limit the Hartree-Fock approximation is appropriate, as would be expected. It is well known[8] that the Hartree-Fock approximation fails completely at normal temperatures and the value of θ' given by (75) is much too large. For example, for the d band of a transition metal, V_0 may be of the order of 10 eV, while an appropriate value for $k\theta'$ is closer to 0.1 eV. In the next paragraph it is shown that at moderately high but physically accessible temperatures, the calculated value of θ' is much reduced and still remains essentially temperature-independent throughout the regime.

B. Moderately High Temperatures
($\varepsilon_F \ll kT \ll \Delta\varepsilon$, $\theta' < T$)

The conditions $kT \gg \epsilon_F$ and $T \gg \theta'$ are required in order that the virial expansion be valid, and are determined by demanding that the second term in square brackets in (69) should be much smaller than 1. The condition $kT \ll \Delta\epsilon$ is required in order that low-temperature approximations may be made in evaluating ΔZ_2. An example of a system for which this regime exists is provided by the holes in the d band in Ni-Cu alloys. In pure Ni, $\epsilon_F \sim 0.2$ eV, and as the percentage of Cu is increased to about 60%, $\epsilon_F \to 0$. For a single d band $\Delta\epsilon \approx 1$ eV, and θ' is of the same order as ϵ_F (see Ref. 8). To calculate θ' we must now evaluate D and S_1 in this regime.

To evaluate ΔZ_2 when $kT \ll \Delta\epsilon$, we need only retain the second term in (43), and by a change of variable this may be written

$$\Delta Z_2 \approx -\frac{\beta}{\pi}\sum_{\mathbf{K}}e^{-\beta E_0(\mathbf{K})}\int_0^\infty \delta_{\mathbf{K}}[E'+E_0(\mathbf{K})]e^{-\beta E'}dE'$$

$$\approx -\frac{\beta}{\pi}\sum_{\mathbf{K}}e^{-\beta E_0(\mathbf{K})}\int_0^\infty \delta_0(E')e^{-\beta E'}dE'. \quad (79)$$

Only small values of E' and $\mathbf{K}$ contribute significantly to ΔZ_2 and this justifies replacing the upper limit in the integral by ∞ and taking $\mathbf{K}=0$ in the integrand. We have taken $E_0(0)=0$ since

$$E_0(\mathbf{K}) = E(\mathbf{K},0) = 2\epsilon(\mathbf{K}/2), \quad (80)$$

and the zero of energy is chosen such that $\epsilon(0)=0$.

[8] See e.g., E. P. Wohlfarth, Rev. Mod. Phys. 25, 211 (1953).

Also from (39), (25), and (28)

$$\delta_0(E') = \tan^{-1}\frac{\pi V_0 \bar{G}(E'/2)}{2[1-V_0 I_0(E')]} \approx \frac{\pi V_0 \bar{G}(E'/2)}{2+V_0 I}, \quad (81)$$

where $\bar{G}(\epsilon)$ is the single-particle density of states per atom and $I = \langle E^{-1} \rangle$, the average of E^{-1} over the band where E is measured from the bottom of the band. The replacement of $I_0(E')$ by its value $-I/2$ at $E'=0$ is justified since $I_0(E')$ is a slowly varying function compared with $\bar{G}(E'/2)$ and the replacement of $\tan^{-1}$ by its argument is reasonable since $\bar{G}$ is small at the bottom of the band. These approximations are consistent with the assumption $\epsilon_F \ll kT$ which restricts us to low-particle densities. Thus from (79) and (81)

$$\Delta\chi_2 = -\frac{\beta V_0}{2+V_0 I}4N\left[\int_0^\infty \bar{G}(E/2)e^{-\beta E}dE\right]^2, \quad (82)$$

since the density of states per atom in a band with energies (80) is $4G(E/2)$. The integral in (82) may easily be expressed in terms of S_2, defined by (64) and we find, using (63)

$$D \approx -\frac{16S_2^2 V}{NkT}\frac{V_0}{2+V_0 I}. \quad (83)$$

Hence from (71)

$$k\theta' = \frac{n}{N}\frac{8S_2^2}{S_1^2}\frac{V_0}{2+V_0 I}. \quad (84)$$

It is readily shown that if the density of states $\bar{G}(\epsilon)$ follows any power law at the bottom of the band, $k\theta'$ is independent of temperature. In the case $G(\epsilon)\alpha\epsilon^{1/2}$ we find $8S_2^2/S_1^2 = 1$ and so

$$k\theta' = \frac{n}{N}\frac{V_0}{2+V_0 I}. \quad (85)$$

It is convenient to follow previous authors (see, e.g., Thompson et al.[9]) by introducing an effective exchange integral J defined by

$$2k\theta' = nJ/N, \quad (86)$$

and then[10]

$$J \approx 2V_0/(2+V_0 I). \quad (87)$$

Comparison of (86) and (75) shows that in the extreme high-temperature limit, corresponding to the Hartree-Fock approximation which includes no correlation effects, J is equal to V_0 which is the value of the straightforward exchange integral between any two Bloch functions. Thus the value of J given by (87) is an effective exchange integral between Bloch functions,

or alternatively an effective intra-atomic Coulomb integral. In the limit of zero bandwidth $I \to \infty$ and thus $J \to 0$, as is required, since in this limit correlation effects dominate and two particles are never on the same atom.

VI. DISCUSSION

The calculation of the magnetic susceptibility shows that in the regime of moderately high temperatures, well above the Curie point in a ferromagnet, a system of particles in a single band, with short-range interactions, behaves as a Stoner system with the molecular field parameter θ' given by (85). It may be concluded that in this temperature region the system behaves according to an effective Hamiltonian H_s, given by (77) with $\epsilon_{i\sigma}$ given by (60). Thus from the present view, and in the absence of a fundamental justification of Stoner's theory throughout the whole temperature range, collective electron theory may be regarded as an extrapolation to lower temperatures by means of the effective Hamiltonian H_s.

It is interesting to estimate the value of J for the Ni-Cu alloy system, although the present single band model is not strictly applicable. It is hoped to present a generalization of this work to the degenerate band case later. It is believed that the density of states of the d band in Ni exhibits a large peak in the neighborhood of the ferromagnetic Fermi energy, about 0.2 eV from the edge of the band.[11] If the holes in the d band are considered as occupying a single band, lying near the bottom (from the hole point of view) of the complete band, a reasonable estimate of $I = \langle E^{-1} \rangle$ should be the value of E^{-1} at the density of states peak, namely 5 eV^{-1}. Since $V_0 \approx 10$ eV, and then effectively cancels out, $J \approx 2/I \sim 0.4$ eV. This value is of the right order to give a good agreement with observed behavior of Ni and Ni-Cu alloys.[9] It should be noted that θ' is only temperature-independent in the first approximation and that small observed deviations from the predictions of collective electron theory may be attributed to a temperature-dependent correction term in θ'.

It is difficult to relate expression (87) to a result obtained by Hubbard[12] in which no average $\langle E^{-1} \rangle$ seems to appear. However, the present work may be related to the low-density theory of an imperfect Fermi gas (see Huang,[3] Chap. 13) by noticing that from (87)

$$J = 8\pi\gamma a/\Omega, \quad (88)$$

where a is the scattering length defined by (32). In the case of spherical energy surfaces $\gamma = \hbar^2/2m$ and the energy levels obtained by Huang are just those of the Hamiltonian H' in Eq. (76) with V_0 replaced by J, as given by (88). Thus Huang's treatment of magnetic properties is exactly equivalent to Stoner's theory with $\theta' \propto a$.

[9] E. D. Thompson, E. P. Wohlfarth, and A. C. Bryan, Proc. Phys. Soc. (London) **83**, 59 (1964).

[10] Our result for the effective exchange integral has also been obtained by J. Kanamori, Progr. Theoret. Phys. (Kyoto) **30**, 275 (1963), using multiple scattering theory.

[11] G. C. Fletcher, Proc. Phys. Soc. (London) **A65**, 192 (1952).

[12] J. Hubbard, Proc. Roy. Soc. (London) **A276**, 238 (1963).