Spin-Dependent Potential Functions in a Generalized Hartree-Fock Equation*

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The exchange term in the generalized Hartree-Fock equation found by the Green's-function method is investigated with an electron gas in a metal in mind. This term contains a generalized exchange charge density and a generalized exchange potential function. The latter not only is shielded, but contains effects depending on the spin of the particle being described by the Hartree-Fock equation. This spin dependence is calculated for spin deviations periodic in the lattice, and also for the case of static spin density waves. The original Overhauser spin-density-wave integral equation, arising from a perturbation in the exchange charge density, now must incorporate the corresponding perturbation in the exchange potential function. It is shown that the two perturbations are of the same order of magnitude, and that the constant solution of the integral equation is no longer valid under the same type of approximation.

1. INTRODUCTION

IT has been shown by Hubbard[1] in 1957 that the potential function that appears in the exchange potential of the Hartree-Fock equation for a system of electrons (in a metal, say) should be shielded. Shielding of one sort or another has been used in solid-state problems long before that, however, one of the earliest examples perhaps being the screening in electron-phonon scattering.[2] The screening in the Hartree-Fock exchange potential and the screening in scattering problems are intimately related, since both can be formulated in terms of the response of the system to a disturbance. Therefore, we can sometimes usefully allow the results of scattering theory to serve as a guide to the shielding in the exchange term of the Hartree-Fock equation, when the former has been studied more completely than the latter. Now in the case of electron-phonon scattering, it is well known that an exchange correction should be taken into account in the shielding.[3,4] This correction can be treated[3] by adding a bare potential disturbance to the Hartree-Fock equation (in the exchange term of which the potential must be shielded, but that is not the problem yet), and then calculating by perturbation theory the response of the "direct" and "exchange" terms to this disturbance. The latter response is the exchange correction. Another procedure[4] is to include "diagonal" exchange terms in the canonical transformation method for screening. Both give the same results. We therefore in this paper shall search for a *corresponding* exchange correction in the potential function that appears in the exchange term of the Hartree-Fock equation. One important reason for doing this is that this exchange correction is spin dependent, so that in problems concerning magnetic impurities in a metal, or in fact in any magnetic problem, the spin dependency of the shielding must be taken into account. We shall see in fact that it must be playing an important role in the problem of static spin density waves.[5]

The starting point for the paper is the formulation of the "generalized Hartree-Fock equation" that comes from Green's function theory. If we define the usual Green's function as $G_\sigma(1,1')$, depending on the spin σ of particles at points 1, $(x_1 y_1 z_1 t_1)$, and 2, and if we use the variational derivative form of the Green's function equation[6a] (we shall use Ref. 6 for our constant source of Green's function lore), we have for a system of electrons interacting by means of a (bare) Coulomb potential

$$\left(i\frac{\partial}{\partial t_1}+\frac{\nabla_1^2}{2m}-U(1\sigma)\right)G_\sigma(1,1')+\int d2[i\sum_{\sigma 2} G_{\sigma 2}(2,2^+)]$$

$$\times v(1-2)G_\sigma(1,1')-\int d3d4[iG_\sigma(1,3)]$$

$$\times\sum_{\sigma'} V_{\sigma\sigma'}(3,4|1)G_\sigma(4,1')=\delta(1-1'), \quad (1.1)$$

the notation being identical to that in Ref. 6, except for

$$V_{\sigma\sigma'}(3,4|1)=\int d2v(1-2)\left[-\frac{\delta}{\delta U(2\sigma')}G_\sigma(3,4)^{-1}\right], \quad (1.2)$$

$$v(1-2)=\delta(t_{12})e^2/r_{12}. \quad (1.3)$$

$U(1,\sigma)$ is a spin-dependent perturbing potential. Equation (1.1) is our generalized Hartree-Fock equation. It is rigorous. It is of Hartree-Fock form in that the interactions are divided into two parts, one of which can be identified as the "direct" term, the other as the "exchange" term. The direct term contains an obvious density function

$$i\sum_{\sigma 2} G_{\sigma 2}(2,2^+) \quad (1.4)$$

[1] J. Hubbard, Proc. Roy. Soc. (London) A243, 336 (1957).
[2] J. Bardeen, Phys. Rev. 52, 688 (1937).
[3] M. Bailyn, Phys. Rev. 117, 974 (1960).
[4] D. Hone, Phys. Rev. 120, 1600 (1960).
[5] A. W. Overhauser, Phys. Chem. Solids 13, 71 (1960); Phys. Rev. 128, 1537 (1962).
[6] L. P. Kadanoff and G. Baym, *Quantum Statistical Mechanics* (W. A. Benjamin, Inc., New York, 1962). Various references in the present paper are to the following pages: (6a) Eq. (5–12); (6b) see p. 156 for not unrelated chain-breaking approximations; (6c) see, for example, Eq. (3.3), and below Eq. (3.22); (6d) see p. 19; (6e) Eq. (1.10).

times the *bare* Coulomb potential, whereas the exchange term contains an exchange density

$$iG_\sigma(1,3) \tag{1.5}$$

times a quite complicated shielded three-point potential function $V_{\sigma\sigma'}(3,4|1)$, which has yet to be evaluated. The screening referred to in the first paragraph refers to the screening contained in this V. It will contain an exchange correction, as we shall see. From our point of view, the solution of the many-body problem consists in finding $V_{\sigma\sigma'}(3,4|1)$ as a function of the G's.

In order to make a one-electron equation out of this (i.e., to find the elementary excitations), we set the left-hand side equal to zero, replacing the time derivative by an energy eigenvalue. If we replace the G function by a wave function

$$\varphi_{p\sigma}(\mathbf{r}) \exp(-iE_{p\sigma}t) \tag{1.6}$$

and divide out the exponential factor (or alternatively integrate over t) we get

$$[E_{p\sigma}+\nabla_1{}^2/2m - U(1\sigma)]\varphi_{p\sigma}(\mathbf{r}_1)+W_{\text{direct}}(\varphi_{p\sigma})$$
$$+W_{\text{ex},\sigma}(\varphi_{p\sigma}(\mathbf{r}_1))=0, \tag{1.7}$$
where

$$W_{\text{direct}}(\varphi_{p\sigma})=\int d2[i\sum_{\sigma_2}G_{\sigma_2}(2,2^+)]$$
$$\times v(1-2)\varphi_{p\sigma}(\mathbf{r}_1), \tag{1.8}$$
$$W_{\text{ex},\sigma}(\varphi_{p\sigma'}(\mathbf{r}_1))=\int d3d4[iG_\sigma(1,3)]$$
$$\times\sum_{\sigma_2}V_{\sigma\sigma_2}(3,4|1)\varphi_{p\sigma'}(\mathbf{r}_4). \tag{1.9}$$

This "effective wave equation" has a number of peculiar properties as a one-particle equation (see Ref. 7, pp. 61–62). Foremost among these is that W is in general not Hermitean, which implies that the eigenvalues are not necessarily real, in which case the particles would decay and we have an unstable situation. In this paper, we shall be interested in situations, where Eq. (1.7) has the same character as an ordinary one-electron equation, and we shall assume Hermiticity in what follows. A second peculiarity is that W_{ex} depends on time in general [or alternatively on E if we had integrated over time: see below Eq. (1.6)]. This problem disappears if we make approximations which reduce $V(3,4|1)$ to a "local" interaction ($t_1=t_3=t_4$). In Sec. 4, and in Appendix A we make such approximations. Thirdly, the equation is nonlinear. This is nothing really novel, however, as the ungeneralized Hartree-Fock equation is also nonlinear.

The problem we set for ourselves is the evaluation of V in some special cases, mainly, to see how the spin dependency enters in and how it would modify previously made calculations[3-5] which treated it as spin independent.

In Sec. 2, we obtain the equation for V, and reduce it to a form accessible to solution by an iteration procedure. The zeroth iteration consists in neglecting all exchange effects. The V calculated on that basis is then substituted back into Eq. (1.1) for the first iterated equation. We then find that accompanying the response of the exchange charge density, there is a response from the (shielding in the) exchange potential function, the latter being quite a bit more complicated than the former.

In Sec. 3, the spin deviations are assumed to have the periodicity of the lattice. We find general expressions on the basis of the first iterated equations of Sec. 2. The result contains both the responses of the exchange charge density and of the exchange potential function, the presence of the latter providing a different answer from that in Refs. 3 and 4 even for the case of no spin deviations. Polarization effects of a modified Wolff[8] type enhance all the spin effects.

In Sec. 4, we apply the formalism to Overhauser's spin-density waves, and it is found that the spin dependency of the exchange potential function is a not negligible effect. The resulting integral equation was not solved, however, and it is not clear under what conditions it has solutions (other than the trivial one).

In Appendix A we reduce the spin-independent shielding of Sec. 3 to more familiar form, and include there a calculation of the Wolff polarization that indicates it to be rather large under certain conditions. In Appendix B, an estimate of one of the new terms in Sec. 4 is made. And in Appendix C, a comparison of two iteration procedures is made.

It may help to avoid confusion to point out that we are using the term "Hartree-Fock" in a very loose way. Our generalized Hartree-Fock equation, (1.1), is rigorous, and is not at all the Hartree Fock *approximation* of Ref. 6. To get the latter from the former, we would replace $V_\sigma(4,3|1)$ by $\delta(3-4)v(4-1)$.

2. THE EQUATION FOR V

From Eq. (1.2), it is clear[6] that an equation for V can be obtained if we invert Eq. (1.1), obtaining thereby an equation for G^{-1}, and then take its variational derivative

$$\left(i\frac{\partial}{\partial t_1}+\frac{\nabla_1{}^2}{2m}-U(1\sigma)\right)\delta(1-1')+\int d2[i\sum_{\sigma_2}G_{\sigma_2}(2,2^+)]v(1-2)\delta(1-1')$$

$$-\int d3[iG_\sigma(1,3)]\sum_{\sigma'}V_{\sigma\sigma'}(31'|1)=G_\sigma(1,1')^{-1}, \tag{2.1}$$

[7] V. L. Bonch-Bruevich and S. V. Tyablikov, *The Green's Function Method in Statistical Mechanics* (North-Holland Publishing Company, Amsterdam, 1962).

[8] P. Wolff, Phys. Rev. **120**, 814 (1960). This result was also obtained by the method of Ref. 3; see M. Bailyn, Scientific Paper 029-B000-P2, Westinghouse Research Laboratories, 1961 (unpublished).

$$V_\sigma(ab|c) = \delta(a-b)\left\{v(a-c) - \int d3d4d5v(a-3)\sum_{\sigma'} L_{\sigma'}(3,4,5,3)V_{\sigma'}(4,5|c)\right\} + \int d3d4d5V_\sigma(4,5|c)$$

$$\times [L_\sigma(a,4,5,3)V_\sigma(3,b|a)] + i\int d2d3v(c-2)G_\sigma(a,3)\sum_{\sigma_2} \delta V_\sigma(3,b|a)/\delta U(2\sigma_2), \quad (2.2)$$

where

$$L_\sigma(1,2,3,4) = iG_\sigma(1,2)G_\sigma(3,4). \tag{2.3}$$

In Eq. (2.2) we have used the notation

$$V_\sigma(ab|c) = \sum_{\sigma'} V_{\sigma\sigma'}(ab|c), \tag{2.4}$$

as that is the quantity that appears everywhere. It should be noted however that if the disturbance U is a magnetic field or such like

$$U(2,\pm) = \pm H\mu_0, \tag{2.5}$$

then the response to the magnetic field is not the sum as in Eq. (2.4), but

$$\mu_0^{-1}M_\sigma(1,2|3) \equiv -\frac{\delta}{\delta U(3+)}G_\sigma^{-1}(1,2) + \frac{\delta}{\delta U(3-)}G_\sigma^{-1}(1,2), \tag{2.6}$$

whose equation is

$$M_\sigma(a,b|c) \mp \mu_0\delta(a-b)\delta(a-c)$$

$$= -\int d3d4d5v(a-3)\sum_{\sigma'} L_{\sigma'}(3453)M_{\sigma'}(4,5|c)\delta(a-b) + \int d3d4d5M_\sigma(4,5|c)$$

$$\times [L_\sigma(a,4,5,3)V_\sigma(3,b|a)] - i\int d3G_\sigma(a,3)\left[\frac{c}{\delta U(c,+)} - \frac{\delta}{\delta U(c,-)}\right]V_\sigma(3,b|a), \quad \sigma=\pm. \quad (2.7)$$

Equations (2.2) and (2.7) are the basic equations to solve. Once a solution is obtained, we then can substitute back into Eqs. (1.1) or (2.1).

In comparing with Ref. 6, notice that our self-energy in Eq. (2.1) is divided into a Hartree part plus an exchange part, whereas in Ref. 6 [see Eqs. (4)–(8)] the separation is most frequently into a Hartree-Fock part (which is our Hartree term plus the exchange term with V replaced by v) and a collision part. Thus our exchange term contains the collision effects of Ref. 6.

To solve Eq. (2.2) we must make some approximations. The major one concerns the second variational derivative term, and constitutes the "chain-breaking" approximation. The simplest plan is just to neglect the second variational term altogether. This leads to an equation that corresponds to the simplest treatment of responses including exchange, as in Refs. 3 and 4. This result can be used without great error, but a more systematic approach is the following.

Consider as a zeroth iteration the equations resulting from neglect of all exchange terms. This means neglect of the last term on the left in Eq. (2.1) and the last two on the right in Eq. (2.2), these two having come from

the former one. In this zeroth iteration we get the standard Green's function equation for the shielding from Eq. (2.2)

$$V_\sigma^{(0)}(a,b|c) = \delta(a-b)v_s(a,c), \tag{2.8}$$

where v_s is independent of spin and satisfies

$$v_s(a,c) = v(a-c) - \int v(a-3)\sum_\sigma L_\sigma(3443)v_s(4,c). \tag{2.9}$$

Then for a first iteration, use this in Eq. (2.1) and compute Eq. (2.2). The resulting equation has the same form as Eq. (2.2) itself, except that $V_\sigma(3,b|a)$ is replaced (in the last two terms) by $\delta(3-b)v_s(b,a)$. In particular the last term is

$$iG_\sigma(a,b)Q(b,a|c), \tag{2.10}$$

where

$$Q(b,a|c) = \int d2v(c-2)\sum_\sigma \frac{\delta v_s(b,a)}{\delta U(2\sigma)}. \tag{2.11}$$

The equation for Q is obtained from Eq. (2.9) by taking a variational derivative

$$Q(b,a|c) = -i\sum_\sigma \int v(b-3)[L_\sigma(64,43,35)+L_\sigma(63,34,45)]V_\sigma(5,6|c)v_s(4,a) - \int v(b-3)\sum_\sigma L_\sigma(3443)Q(4,a|c), \quad (2.12)$$

where

$$L_\sigma(123456) = G_\sigma(12)G_\sigma(34)G_\sigma(56). \tag{2.13}$$

The last term in Eq. (2.12) provides a shielding of the exact same type as in Eq. (2.9): It changes the $v(b-3)$ of the first term in Eq. (2.12) to $v_s(b,3)$. It is convenient to define

$$\Lambda_\sigma(a45b)=\int d2d3[v_s(b,3)v_s(2,a)+v_s(b,2)v_s(3,a)]L_\sigma(522334).\qquad(2.14)$$

Then Eqs. (2.2) and (2.7) in this first iteration read[8a]

$$V_\sigma(a,b|c)=\delta(a-b)\left\{v(a-c)-\int d3d4d5v(a-3)\sum_{\sigma'}L_{\sigma'}(3453)V_{\sigma'}(4,5|c)\right\}+v_s(b,a)\int d4d5V_\sigma(4,5|c)L_\sigma(a45b)$$

$$+G_\sigma(a,b)\int d4d5\sum_{\sigma'}V_{\sigma'}(4,5|c)\Lambda_{\sigma'}(a45b);\qquad(2.15)$$

$$M_\sigma(a,b|c)\mp\mu_0\delta(a-b)\delta(a-c)$$

$$=-\int d3d4d5\delta(a-b)v(a-3)\sum_{\sigma'}L_{\sigma'}(3453)M_{\sigma'}(45|c)+v_s(b,a)\int d4d5M_\sigma(4,5|c)L_\sigma(a45b)$$

$$+G_\sigma(a,b)\int d4d5\sum_{\sigma'}M_{\sigma'}(45|c)\Lambda_{\sigma'}(a45b),\quad\sigma=\pm.\qquad(2.16)$$

The last terms represent the response of the potential function in the exchange term of Eq. (2.1). They depend on spin. The next to last terms are the response of the exchange charge density (and correspond to what was calculated in Refs. 3 and 4). They also depend on spin. The second part of the curly bracket in Eq. (2.15) is the response of the Coulomb charge density, and constitutes the standard shielding term. It is independent of spin. For this reason, the corresponding term in Eq. (2.16) is of little significance.

It is interesting to note that if we allow deviations of up-spin wave functions from down-spin wave functions, and if these are small, then V^+ and M^- are of zeroth order and V^- and M^+ are of first order, where

$$V^\pm\equiv\tfrac{1}{2}(V_+\pm V_-),\quad M^\pm\equiv\tfrac{1}{2}(M_+\pm M_-).\qquad(2.17)$$

The zeroth-order response to a magnetic field is then from Eq. (2.20)

$$M^-(a,b|c)=\mu_0\delta(a-b)\delta(a-c)+v_s(b,a)$$

$$\times\int d4d5M^-(4,5|c)L_0(a45b),\qquad(2.18)$$

where L_0 is the zeroth-order part of L_σ. Taking components of this equation provides exactly the spin polarization of Wolff.[8] Thus the response in the ex-

change charge density provides a spin polarization as calculated by Wolff, and the response of the exchange potential function provides nothing new to zeroth order. Of course, once we use the full expression Eq. (2.15) for V in Eq. (2.7), we should get new terms.

Equation (2.15) will be used below in Sec. 3. However, it is still too complicated for many purposes, and we shall write down now a weaker iteration procedure on the basis of which we shall be able to make calculations in Sec. 4. The relationship between the two methods is discussed in Appendix C. In the previous scheme we took the solution neglecting exchange, Eqs. (2.8), (2.9), and substituted back into Eq. (2.1), and proceeded from there. Here we shall take the solution neglecting exchange and substitute back into Eq. (2.2) *itself*. This then is the first step of an iteration procedure dealing with just the equation for V. The result is

$$V_\sigma(a,b|c)\cong\delta(a-b)v_s(a,c)$$

$$+v_s(b,a)\int d4v_s(4,c)L_\sigma(a44b)$$

$$+G_\sigma(a,b)\int d4v_s(4,c)\sum_{\sigma'}\Lambda_{\sigma'}(a44b).\qquad(2.19)$$

A detailed discussion of the error involved relative to that of Eq. (2.15) is given in Appendix C.

3. SYSTEMS WITH SPIN DEVIATIONS PERIODIC IN THE LATTICE

If the spin deviations have the periodicity of the lattice, then the well-known expansion[6c] of the Green's

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[8a] *Note added in proof.* It has been pointed out that Eq. (2.15) is a generalization of Eq. (68) of G. Baym and L. P. Kadanoff, Phys. Rev. **124**, 287 (1961). A systematic expansion procedure has been derived by L. Hedin (to be published): See his Notes "On the $N+1$ Electron Problem," from the Solid State Science Division of the Argonne National Laboratory, Argonne, Illinois (unpublished).

function in the imaginary time domain

$$G_\sigma(1,2) = \sum_k (-i\beta)^{-1} \varphi_{k\sigma}(\mathbf{r}_1) \varphi_{k\sigma}(\mathbf{r}_2)^* \sum_{z_k} \exp(-iz_k t_{12})/(z_k - E_k),$$

(3.1)

$$z_k = \pi\nu(-i\beta)^{-1} + \mu, \quad \nu = \pm 1, \pm 3, \cdots,$$

contains functions of Bloch form

$$\varphi_{k\sigma}(\mathbf{r}) = \sum_K u_{k,K,\sigma} \exp[i(\mathbf{k}+\mathbf{K})\cdot\mathbf{r}],$$

(3.2)

where the $\mathbf{K}$'s are reciprocal lattice vectors, and the $\mathbf{k}$'s are restricted to one zone. Thus

$$G_\sigma(1,2) = (-i\beta)^{-1} \sum_k \sum_{K_1 K_2} \exp\{-iz_k t_{12} + i(\mathbf{k}+\mathbf{K}_1)\cdot\mathbf{r}_1 - i(\mathbf{k}+\mathbf{K}_2)\cdot\mathbf{r}_2\} G_\sigma(k|\mathbf{K}_1\mathbf{K}_2),$$

(3.3)

where

$$G_\sigma(k|\mathbf{K}_1\mathbf{K}_2) = u_{k,K_1,\sigma} u_{k,K_2,\sigma}^* (z_k - E_k)^{-1}.$$

(3.4)

Similarly, letting $\mathbf{p}$ be unrestricted,

$$L_\sigma(1,2,3,4) = (-i\beta)^{-2} \sum_{kk'} \sum_{K_1\cdots K_4} \exp\{i(k, 1-2) + i(k', 3-4) + i\mathbf{K}_1\cdot\mathbf{r}_1 + \cdots + i\mathbf{K}_4\cdot\mathbf{r}_4\} iG_\sigma(k|\mathbf{K}_1\mathbf{K}_2) G_\sigma(k'|\mathbf{K}_3\mathbf{K}_4),$$

(3.5)

$$v_s(1,2) \cong (-i\beta)^{-1} \sum_p v_s(p) \exp[i(p, 1-2)].$$

We shall also need a component

$$\Lambda_\sigma(p_1|p,p'|p_2) = (-i\beta)^{-3} \int da\,db\,d4\,d5\, \Lambda_\sigma(a45b) \exp\{-i(a,p_1) + i(4,p) - i(5,p') + i(b,p_2)\}.$$

(3.6)

In this, we have used k to mean a four-vector $(\mathbf{k}, z_k)$, and (k,a) to mean a scalar product in four dimensions. Further, in what follows we shall mean by $k+\mathbf{K}$ a four vector $(\mathbf{k}+\mathbf{K}, z_k)$.

With these expressions and expansions in mind, we seek now to solve Eq. (2.15). To do this, we take the Fourier component in the imaginary time domain[6d] $(0, -i\beta)$

$$V_\sigma(pp'|p'') \equiv \int_0^{-i\beta} da\,db\,dc \exp\{-i(p, a-c)$$
$$+ i(p', b-c) + i(p'', c)\} V_\sigma(a,b|c). \quad (3.7)$$

Using the boundary condition[6e]

$$G_\sigma(1,2)|_{t_1=0} = -\exp(\beta\mu) G(1,2)|_{t_1=-i\beta}, \quad (3.8)$$

in Eq. (2.15), we conclude that the frequencies appropriate to the various fourth components of the p's

are

$$z_p = \pi\nu/(-i\beta) + \mu, \quad \nu = \pm 1, \pm 3, \cdots,$$
$$z_{p'} = \pi\nu'/(-i\beta) + \mu, \quad \nu' = \pm 1, \pm 3, \cdots, \quad (3.9)$$
$$\Omega_{p''} = \pi\nu''/(-i\beta), \quad \nu'' = 0, \pm 2, \cdots.$$

We shall use Ω to mean even integers (as above) and z to mean odd integers, in what follows.

Now by forming the component of the type in Eq. (3.7) of the Eq. (2.15), we obtain "component equations," containing the inhomogeneous term $v(p-p')\delta_{p'',0}$. We shall then suppose that only those component V's are not zero that have this inhomogeneous term nonzero, in its equation. That is, we shall seek a self-consistent set of solutions of the form

$$V_\sigma\backslash pp'|p'') = \delta_{p'',0} V_\sigma(p,p'). \quad (3.10)$$

Using this form, and the above expansion coefficients, we then find for the component equations corresponding to Eq. (2.15)

$$V_\sigma(p,q) = v(p-q) - v(p-q) \sum_{\sigma' k} L_{\sigma'}(k+p, k+q) V_{\sigma'}(k+p, k+q)$$

$$+ \sum_k N_\sigma^k(k+p, k+q) V_\sigma(k+p, k+q) + \sum_{k,\sigma'} Q_{\sigma,\sigma'}^k(k+p, k+q) V_{\sigma'}(k+p, k+q), \quad (3.11)$$

where

$$L_\sigma(k+p, k+q) = \sum_{K_1\cdots K_4} \delta_{K_1-K_2+K_3-K_4,0} iG_\sigma(k+p-\mathbf{K}_2|\mathbf{K}_1\mathbf{K}_2) G_\sigma(k+q-\mathbf{K}_3|\mathbf{K}_3\mathbf{K}_4), \quad (3.12)$$

$$N_\sigma^k(k+p, k+q) = \sum_{K_1\cdots K_4} \delta_{K_1-K_2+K_3-K_4,0} v_s(k+K_1-K_2) iG_\sigma(k+p-\mathbf{K}_2|\mathbf{K}_1\mathbf{K}_2) G_\sigma(k+q-\mathbf{K}_3|\mathbf{K}_3\mathbf{K}_4), \quad (3.13)$$

$$Q_{\sigma\sigma'}^k(k+p, k+q) = \sum_{k'K_1K_2} G_\sigma(k'|\mathbf{K}_1\mathbf{K}_2) \Lambda_{\sigma'}(p-k'-\mathbf{K}_1|k+p, k+q|q-k'-\mathbf{K}_2). \quad (3.14)$$

The summation index $\mathbf{k}$ in Eq. (3.11) is not restricted to one zone. However, the first argument of $G(p\,|\,\mathbf{K},\mathbf{K}')$, namely $\mathbf{p}$, must be so restricted. The entire dependence on the details of the lattice potential is contained in the complicated L's, N's, and Q's, leaving the equation for V relatively simple.

To solve Eq. (3.11) we shall suppose that the dependence on p and q other than through the combination $p-q$ is small. This is of course exact for the first two terms on the right, but not for the other two because of the dependence of N^k and Q^k on the superscript. An averaging has been used in the corresponding scattering problem,[3,4] and we shall perform a similar type of approximation here. We introduce the sums

$$L_\sigma(p-q)=\sum_k L_\sigma(k+p,\,k+q)\,,\qquad(3.15)$$

$$N_\sigma(p,q)=\sum_k N_\sigma{}^k(k+p,\,k+q)\,,\qquad(3.16)$$

$$Q_{\sigma\sigma'}(p,q)=\sum_k Q_{\sigma\sigma'}{}^k(k+p,\,k+q)\,,\qquad(3.17)$$

and rewrite Eq. (3.11) as

$$V_\sigma(p,q)+\sum_{\sigma'} V_{\sigma'}(p,q)L_{\sigma'}(p-q)v(p-q)-V_\sigma(p,q)N_\sigma(p,q)$$

$$-\sum_{\sigma'} V_{\sigma'}(p,q)Q_{\sigma\sigma'}(p,q)=v(p-q)+\cdots\,,\quad(3.18)$$

where the dots indicate terms that depend only on the difference between $V_\sigma(p,q)$ and $V_\sigma(p+k,\,q+k)$, such terms dropping out completely if $V_\sigma(p,q)$ depended only on $p-q$. Thus we propose another iteration procedure in which these terms are neglected in the zeroth iteration, and we shall in fact stop at this stage, although it is not too difficult to compute (formally) corrections to it.[3] Notice that the $V(p,q)$ in Eq. (3.18) depends on p and q explicitly, because of the presence of $N(p,q)$ and $Q(p,q)$.

Using the abbreviations

$$V_\pm=V_\pm(p,q)\qquad \mathfrak{N}_\pm=N_\pm+Q_{\pm\pm}+Q_{\mp\pm}$$

$$L_\pm=L_\pm(p-q)\qquad\qquad\qquad\qquad(3.19)$$

$$v=v(p-q)\qquad \mathfrak{N}_\pm{}'=N_\pm+Q_{\pm\pm}-Q_{\mp\pm}$$

we solve Eq. (3.18)

$$V_+=v\Bigg\{\Big[1+(L_++L_-)v-\tfrac12(\mathfrak{N}_++\mathfrak{N}_-)\Big]$$

$$-\frac{\mathfrak{N}_+{}'-\mathfrak{N}_-{}'}{1-\mathfrak{N}_-{}'}\frac12[1+2L_-v-\mathfrak{N}_-]\Bigg\}^{-1}.\quad(3.20)$$

The equation for V_- is obtained from this by interchanging $+$ and $-$ everywhere. This is the basic result of this section.

This result can be made a bit more transparent by noting that to first order (in spin deviations) the second square bracket is equivalent to the first. Since it is al-

ready multiplied by a factor of first order, we can write to first order in the denominator

$$V_\pm(p,q)=\bar v_s(p,q)S_\pm(p,q)\,,\qquad(3.21)$$

where $\bar v_s$ is a modified version of the shielding found previously by the author[3] apropos of electron-phonon scattering,

$$\bar v_s(p,q)=v(p-q)\{1+v(L_++L_-)-\tfrac12(\mathfrak{N}_++\mathfrak{N}_-)\}^{-1},\,(3.22)$$

the $\mathfrak{N}$'s containing the response from both the exchange charge density and the exchange potential function, and where $S_\pm$ is a new spin-dependent factor

$$S_\pm(p,q)=\left[1\mp\frac12\frac{\mathfrak{N}_+{}'-\mathfrak{N}_-{}'}{1-\tfrac12(\mathfrak{N}_+{}'+\mathfrak{N}_-{}')}\right]^{-1}$$

$$\cong 1\pm\frac12\frac{\mathfrak{N}_+{}'-\mathfrak{N}_-{}'}{1-\tfrac12(\mathfrak{N}_+{}'+\mathfrak{N}_-{}')};\qquad(3.23)$$

the last form here is not as accurate as the first if the effects are large. The last form writes the spin effect as a separate term. Notice the denominator $1-\tfrac12(\mathfrak{N}_+{}'+\mathfrak{N}_-{}')$ in all the spin effects. This is a modified version of the Wolff spin polarization[8] modified through the presence of the Q's in $\mathfrak{N}'$, i.e., through the response of the exchange potential function. The Q's cancel in zeroth order of spin deviations, however, so that $\mathfrak{N}' \to N$ in that case, and the modification disappears.

In the case of long waves ($p \to q$), we can solve Eq. (3.11) exactly, for only the terms proportional to $v(p-q)$ need be considered. The result is then

$$\operatorname*{Lim}_{p\to q}V_\pm(p,q)$$

$$=[L_++L_--L_\mp(\mathfrak{N}_\pm{}'-\mathfrak{N}_\mp{}')(1-\mathfrak{N}_\mp{}')^{-1}]^{-1}.\quad(3.24)$$

This shows a spin effect even in the limit. Had we used Eq. (3.21), we would have found that the spin-dependent factor S would not have been altered in structure at all in going to the limit.

4. SPONTANEOUS SPIN-DENSITY WAVES

In this section we apply the formulation of Secs. 1 and 2 to the problem of static spin density waves. We follow the procedure of Overhauser without change, the only difference arising from our more complicated potential function, the effect of which can be anticipated before doing any calculations. Overhauser's method is to compute the matrix elements of the exchange term in the Hartree-Fock equation. These matrix elements depend on the exchange charge density explicitly, and if this charge density is regarded as spin dependent to first order, then an expansion in "spin-density waves" is possible. But the coefficients in the expansion depend on the same type of matrix elements that one was calculating in the first place. Thus the expansion constitutes a homogeneous integral equation for these matrix ele-

ments. Nontrivial solutions to it would imply spontaneous static spin-density waves. We are not interested here in any refinements of this procedure, or on the minimizing of the energy that is required for the stability of these waves, or such matters. We are interested only in the setting up of the equation itself. Our argument is then very simple: Whereas Overhauser considered only the perturbation arising from a spin-dependent *exchange-charge density*, it follows from Eq. (1.7) of Sec. 1 that the shielding in the generalized *exchange-potential function* is also spin dependent, and should also be expanded in spin waves. The purpose of this section is to outline how this takes place, and to show that the effect is not negligible. Unfortunately, the resulting integral equation is so complicated that we cannot get any explicit solutions, but we nevertheless can conclude that in problems of this sort, the spin dependence of the shielding must be taken into account.

We first shall repeat the theory of Overhauser in our notation. In general, we need from Eq. (1.9)

$$W_\sigma(\mathbf{1}',\mathbf{1}) = \int dr_1 d2 d3 \psi_{1'}(r_1)^* \psi_1(r_2)$$
$$\times iG_\sigma(1,3)V_\sigma(32|1), \quad (4.1)$$

(where we shall leave off the subscript "ex" on W for the rest of this section), of which the spin dependency is our primary interest. Overhauser considered only the spin dependency of G_σ. For V_σ, he eventually uses a delta function potential. Thus, in our notation, he uses for $V_\sigma(3,2|1)$ in Eq. (2.19) just the first term

$$V_\sigma(3,2|1) \cong \delta(3-2)v_s(2,1), \quad (4.2)$$

to which first "locality" is applied

$$v_s(2,1) = \delta(t_2-t_1)v_s(r_{21}), \quad (4.3)$$

and then the delta function approximation is applied

$$v_s(r_{21}) = A\delta(r_{21}). \quad (4.4)$$

Then he proceeds to calculate W. [His derivation is stated more generally than is implied by Eq. (4.4), but the results upon which he hypothesizes about spin density waves are obtained on its basis. We content ourselves with comparing with the simplest of his arguments. We shall in fact not need Eq. (4.4) until the very end.]

Our procedure is to use the full expression, Eq. (2.19), apply locality to it, and finally to use the delta function

approximation. We get three terms

$$W_\sigma(\mathbf{1}',\mathbf{1}) = \sum_{i=1}^{3} W_\sigma^{(i)}(\mathbf{1}',\mathbf{1}) = \sum_i \int dr_1 d2 d3 \psi_{1'}(r_1)^* \psi_1(r_2)$$
$$\times iG_\sigma(1,3)V_\sigma^{(i)}(3,2|1), \quad (4.5)$$

where

$$V_\sigma^{(1)}(3,2|1) = \delta(3-2)v_s(2,1), \quad (4.6)$$

$$V_\sigma^{(2)}(3,2|1) = v_s(2,3)\int d4 v_s(4,1)L_\sigma(3,4,4,2), \quad (4.7)$$

$$V_\sigma^{(3)}(3,2|1) = G_\sigma(3,2)\int d4 v_s(4,1)\sum_{\sigma'} \Lambda_{\sigma'}(3,4,4,2). \quad (4.8)$$

$W^{(1)}$ is the Overhauser term. $W^{(2)}$ is the spin effect from the exchange charge density in the shielding, and $W^{(3)}$ is the spin effect from the exchange potential function in the shielding.

We now wish to obtain the locality of the $V^{(i)}$'s. To get the locality simply of $v_s(2,1)$, as already appears in the Overhauser term, we go back to Eq. (2.9), and notice that in the standard[6] expansion of L

$$L_\sigma(3,4,4,3) = iG_\sigma(3,4)G_\sigma(4,3) = -(-i\beta)^{-1}$$
$$\times \sum_{\nu=0,\pm2\cdots} \sum_{p_1 p_2} \Phi_{p_1 p_2}^\sigma(r_3 r_4 r_4 r_3)$$
$$\times F(p_1 p_2|\Omega_\nu) \exp(-i\Omega_\nu t_{34}), \quad (4.9)$$

where

$$F(p_1 p_2|\Omega) = (f_{p_1}-f_{p_2})[E_{p_2}-E_{p_1}+\Omega]^{-1}, \quad (4.10)$$

and where generally we write

$$\Phi_{p_1 p_2 \cdots}^\sigma(r_a r_b r_c r_d \cdots)$$
$$= [\varphi_{p_1\sigma}(r_a)\varphi_{p_1\sigma}(r_b)^*][\varphi_{p_2\sigma}(r_c)\varphi_{p_2\sigma}(r_d)^*]\cdots, \quad (4.11)$$

we get the desired locality $(t_3=t_4)$ by ignoring the frequency dependence in F. This is the style of approximation by which we shall obtain locality in the other terms.

In Eq. (4.7), we want again $t_1=t_2=t_3$. We have on the basis of the locality of the v_s's that $t_1=t_4$ and $t_2=t_3$. But the factor $L_\sigma(3,4,4,2)$ by the approximation above gives $t_3=t_4$, which gives us what we wish.

In Eq. (4.8), we have Λ_σ, which is given by Eq. (2.14). In Λ_σ appears a product of three Green's functions, for which the expansion is

$$G(1,2)G(3,4)G(5,6)\Big|_{\substack{t_1=t_6 \\ t_2=t_3 \\ t_4=t_5}} = i(-i\beta)^{-2} \sum_{\nu,\nu'} \Phi_{p_1 p_2 p_3}^\sigma(r_1\cdots r_6)F(p_1 p_2 p_3|\Omega_\nu \Omega_{\nu'}) \exp(-i\Omega_\nu t_{12}-i\Omega_{\nu'}t_{13}). \quad (4.12)$$

Again the procedure is to ignore the frequency dependence in F:

$$F(p_1 p_2 p_3|\Omega\Omega') \cong F(p_1 p_2 p_3|0,0) \equiv F(p_1 p_2 p_3),$$

$$F(p_1 p_2 p_3) = F(p_2 p_3 p_1) = F(p_2 p_1 p_3) = \frac{[E_1(f_2-f_3)(1-2f_1)]+[\ ]+[\ ]}{(E_1-E_2)(E_2-E_3)(E_3-E_1)}. \quad (4.13)$$

This gives locality to $V^{(3)}$. The empty brackets are obtained by cyclical rotation of the indices in the first one. The three potentials are now

$$V_\sigma^{(1)}(3,2|1)=\delta(t_{12})\delta(3-2)v_s(r_{21}),\tag{4.14}$$

$$V_\sigma^{(2)}(3,2|1)=-\delta(t_{12})\delta(t_{23})\int dr_4 v_s(r_{41})v_s(r_{23})\tfrac{1}{2}\sum_{p_1p_2}F(\mathbf{p_1p_2})\Phi_{p_1p_2}^{\sigma}(\mathbf{r_3r_4r_4r_2}),\tag{4.15}$$

$$V_\sigma^{(3)}(3,2|1)=\delta(t_{12})\delta(t_{23})\int dr_4 v_s(r_{41})G_\sigma(3,2)\tfrac{1}{2}\sum_{p_1p_2p_3}F(\mathbf{p_1p_2p_3})$$

$$\times\int dr_5 dr_6[v_s(r_{26})v_s(r_{53})+v_s(r_{25})v_s(r_{63})]\sum_{\sigma'}\Phi_{p_1p_2p_3}^{\sigma'}(\mathbf{r_4r_5r_5r_6r_6r_4}).\tag{4.16}$$

We proceed to calculate the W's of Eq. (4.5).

Following Overhauser, we introduce the spin-dependent wave function

$$\varphi_{p\sigma}(r)=\psi_\mathbf{p}(r)+b_{\mathbf{p+Q},\mathbf{p}}^{(\sigma)}\psi_{\mathbf{p+Q}}(r)+b_{\mathbf{p-Q},\mathbf{p}}^{(\sigma)}\psi_{\mathbf{p-Q}}(r),\tag{4.17}$$

where $\mathbf{Q}$ is a wave vector to be determined, where by first-order perturbation theory

$$b_{\mathbf{p'},\mathbf{p}}^{(\sigma)}=-b_{\mathbf{p},\mathbf{p'}}^{(\sigma)*}=W_\sigma(\mathbf{p'},\mathbf{p})(E_{\mathbf{p'}}-E_\mathbf{p})^{-1},\tag{4.18}$$

and where the ψ's mean plane-wave functions. In computing Eqs. (4.5), we find two possibilities $\mathbf{l'}=\mathbf{l}+\mathbf{Q}$, and $\mathbf{l'}=\mathbf{l}-\mathbf{Q}$, of interest. We consider from now on only the former.

For $W^{(1)}$, we get from Eqs. (4.5), (4.14), and (4.17)

$$W_\sigma^{(1)}(\mathbf{l'},\mathbf{l})=\int d\mathbf{r_1}d\mathbf{r_2}\sum_\mathbf{p}f_\mathbf{p}\varphi_{p\sigma}(r_1)\varphi_{p\sigma}(r_2)^*v_s(r_{21})\psi_{\mathbf{l'}}(\mathbf{r_1})^*\psi_\mathbf{l}(\mathbf{r_2})$$

$$=\sum_p W_\sigma(\mathbf{p+Q},\mathbf{p})B_{\mathbf{l'l}}^{(1)}(\mathbf{p+Q},\mathbf{p}),\tag{4.19}$$

where

$$B_{\mathbf{l'l}}^{(1)}(\mathbf{p+Q},\mathbf{p})=(f_\mathbf{p}-f_{\mathbf{p+Q}})[E_{\mathbf{p+Q}}-E_\mathbf{p}]^{-1}v_s(\mathbf{p-l}).\tag{4.20}$$

This is Overhauser's result.

For $W^{(2)}$, we get from Eqs. (4.5), (4.15), and (4.17)

$$W_\sigma^{(2)}(\mathbf{l'},\mathbf{l})=-\tfrac{1}{2}\sum_{p_1p_2p_3}\Psi_{\mathbf{l'l}}^{\sigma}(\mathbf{p_1}|\mathbf{p_2p_3})f_{p_1}F(\mathbf{p_2p_3}),\tag{4.21}$$

where

$$\Psi_{\mathbf{l'l}}^{\sigma}(\mathbf{p_1}|\mathbf{p_2p_3})=\int d\mathbf{r_1}\cdots d\mathbf{r_4}v_s(r_{23})v_s(r_{41})\psi_{\mathbf{l'}}(\mathbf{r_1})^*\psi_\mathbf{l}(\mathbf{r_2})\Phi_{p_1p_2p_3}(\mathbf{r_1r_3r_3r_4r_4r_2}).\tag{4.22}$$

We find after a tedious calculation, manipulation of signs of dummy indices, and use of the identity in Eq. (4.18) that Eqs. (4.21) and (4.22), for $\mathbf{l'}=\mathbf{l}+\mathbf{Q}$ give

$$W_\sigma^{(2)}(\mathbf{l'},\mathbf{l})=\sum_p W_\sigma(\mathbf{p+Q},\mathbf{p})B_{\mathbf{l'l}}^{(2)}(\mathbf{p+Q},\mathbf{p}),\tag{4.23}$$

where

$$B_{\mathbf{l'l}}^{(2)}(\mathbf{p+Q},\mathbf{p})=\tfrac{1}{2}\sum_{p_1p_2}f_{p_1}[F(\mathbf{p_2},\mathbf{p})-F(\mathbf{p_2},\mathbf{p+Q})][E_{\mathbf{p+Q}}-E_\mathbf{p}]^{-1}$$

$$\times[\delta_{\mathbf{l},\mathbf{p_1+p_2+p}}v_s(\mathbf{p-l})v_s(\mathbf{p_1-l'})+\delta_{-\mathbf{l'},\mathbf{p_1+p_2+p}}v_s(\mathbf{p_2+l})v_s(\mathbf{p_1+l'})]$$

$$+\tfrac{1}{2}F(\mathbf{p},\mathbf{p+Q})\sum_{p_1p_2}\delta_{\mathbf{l},\mathbf{p_2-p_1+p}}F(\mathbf{p_1p_2})v_s(\mathbf{l-p_2})v_s(\mathit{p_{21}}).\tag{4.24}$$

This represents the spin effect stemming from the exchange charge density in the exchange term of the shielding. The second p_1p_2 sum here came from the first-order part of $G_\sigma(1,3)$ in Eq. (4.5), $i=2$, paralleling the origin of $B_{\mathbf{l'l}}^{(1)}$.

For $W^{(3)}$ we get from Eqs. (4.5), (4.16), and (4.17)

$$W_\sigma^{(3)}(\mathbf{l}',\mathbf{l}) = -\sum_{\mathbf{p}\mathbf{p}'}\sum_{\mathbf{p}_1\mathbf{p}_2\mathbf{p}_3} f_\mathbf{p} f_{\mathbf{p}'} F(\mathbf{p}_1\mathbf{p}_2\mathbf{p}_3) v_s(p_{12}) v_s(p_{23}) v_s(p_{31}) X_{\mathbf{l}'\mathbf{l}}^\sigma, \tag{4.25}$$

where

$$X_{\mathbf{l}'\mathbf{l}}^\sigma = V^{-1}\int d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 \psi_{\mathbf{l}'}(\mathbf{r}_1)^* \psi_\mathbf{l}(\mathbf{r}_2)\,\varphi_{\mathbf{p}\sigma}(\mathbf{r}_1)\,\varphi_{\mathbf{p}\sigma}(\mathbf{r}_3)^*\,\varphi_{\mathbf{p}'\sigma}(\mathbf{r}_3)\,\varphi_{\mathbf{p}'\sigma}(\mathbf{r}_2)^*$$

$$\times[\exp(-i\mathbf{r}_1\cdot\mathbf{p}_{31}-i\mathbf{r}_2\cdot\mathbf{p}_{23}-i\mathbf{r}_3\cdot\mathbf{p}_{12})+\exp(-i\mathbf{r}_1\cdot\mathbf{p}_{31}-i\mathbf{r}_2\cdot\mathbf{p}_{12}-i\mathbf{r}_3\cdot\mathbf{p}_{23})]. \tag{4.26}$$

The square bracket in χ comes from use of plane waves in the Φ of Eq. (4.16), valid since the sum over σ' contains no first-order terms. After another tedious calculation we find

$$W_\sigma^{(3)}(\mathbf{l}',\mathbf{l}) = \sum_\mathbf{p} W_\sigma(\mathbf{p}+\mathbf{Q},\,\mathbf{p}) B_{\mathbf{l}'\mathbf{l}}^{(3)}(\mathbf{p}+\mathbf{Q},\,\mathbf{p}), \tag{4.27}$$

where

$$B_{\mathbf{l}'\mathbf{l}}^{(3)}(\mathbf{p}+\mathbf{Q},\,\mathbf{p}) = -\sum_{\mathbf{p}_1\mathbf{p}_2\mathbf{p}_3}\sum_{\mathbf{p}'} F(\mathbf{p},\,\mathbf{p}+\mathbf{Q}) f_{\mathbf{p}'} v_s(p_{12}) v_s(p_{23}) v_s(p_{31}) F(\mathbf{p}_1\mathbf{p}_2\mathbf{p}_3)$$

$$\times\delta_{\mathbf{p},1+\mathbf{p}_{31}}[\delta_{\mathbf{p}',1-\mathbf{p}_{23}}+\delta_{\mathbf{p}',1-\mathbf{p}_{12}}+\delta_{\mathbf{p}',1'-\mathbf{p}_{12}}+\delta_{\mathbf{p}',1'-\mathbf{p}_{23}}]. \tag{4.28}$$

This represents the spin effect stemming from the exchange potential function in the exchange term of the shielding.

We are thus in a position to write the integral equation by adding Eqs. (4.19), (4.23), and (4.27), and substituting into Eq. (4.5). Defining

$$W^\pm(\mathbf{l}',\mathbf{l}) = W_+(\mathbf{l}',\mathbf{l})\pm W_-(\mathbf{l}',\mathbf{l}), \tag{4.29}$$

we get

$$W^\pm(\mathbf{l}',\mathbf{l}) = \sum_\mathbf{p} W^\pm(\mathbf{p}+\mathbf{Q},\,\mathbf{p})\sum_{i=1}^3 B_{\mathbf{l}'\mathbf{l}}^{(i)}(\mathbf{p}+\mathbf{Q},\,\mathbf{p}), \tag{4.30}$$

where the B's are given by Eqs. (4.20), (4.24), and (4.28).

To solve, we set

$$W^+(\mathbf{l}',\mathbf{l}) = 0. \tag{4.31}$$

For W^-, we have the possibility of a static spin-density wave of wave vector $\mathbf{Q}$ of the Overhauser type provided there exist nontrivial solutions to Eq. (4.30). As stated at the outset of this section, we find extra terms, $B^{(2)}$ and $B^{(3)}$, beyond what Overhauser found, but we find it impossible as yet to solve the equations.

It is of interest to write the B's for the case where the v_s function is approximated by a delta function, as in Eq. (4.4):

$$B_{\mathbf{l}'\mathbf{l}}^{(1)}(\mathbf{p}+\mathbf{Q},\,\mathbf{p}) = AF(\mathbf{p},\,\mathbf{p}+\mathbf{Q}), \tag{4.32}$$

$$B_{\mathbf{l}'\mathbf{l}}^{(2)}(\mathbf{p}+\mathbf{Q},\,\mathbf{p}) = A^2\{\sum_{\mathbf{p}_1\mathbf{p}_2}[F(\mathbf{p}_2,\mathbf{p})-F(\mathbf{p}_2,\,\mathbf{p}+\mathbf{Q})][E_{\mathbf{p}+\mathbf{Q}}-E_\mathbf{p}]^{-1} f_{\mathbf{p}_1}\delta_{1,\mathbf{p}_1+\mathbf{p}_2+\mathbf{p}}$$

$$+\tfrac{1}{2}F(\mathbf{p},\,\mathbf{p}+\mathbf{Q})\sum_{\mathbf{p}_1\mathbf{p}_2}\delta_{1,\mathbf{p}_2-\mathbf{p}_1+\mathbf{p}}F(\mathbf{p}_1\mathbf{p}_2)\}, \tag{4.33}$$

$$B_{\mathbf{l}'\mathbf{l}}^{(3)}(\mathbf{p}+\mathbf{Q},\,\mathbf{p}) = A^3 F(\mathbf{p},\,\mathbf{p}+\mathbf{Q})\sum_{\mathbf{p}_1\mathbf{p}_2\mathbf{p}_3}\sum_{\mathbf{p}'} F(\mathbf{p}_1\mathbf{p}_2\mathbf{p}_3) f_{\mathbf{p}'}\delta_{\mathbf{p},1+\mathbf{p}_{31}}[\delta_{\mathbf{p}',1-\mathbf{p}_{23}}+\delta_{\mathbf{p}',1-\mathbf{p}_{12}}+\delta_{\mathbf{p}',1'-\mathbf{p}_{12}}+\delta_{\mathbf{p}',1'-\mathbf{p}_{23}}]. \tag{4.34}$$

It is immediately evident that the solution appropriate to Eq. (4.32) alone, namely,

$$W^{(-)}(\mathbf{l}',\mathbf{l}) = \text{const}, \tag{4.35}$$

is no longer a solution when $B^{(2)}$ and $B^{(3)}$ are taken into account, even on the delta function approximation. The new terms are of the order (A/E_F) and $(A/E_F)^2$ times the original term. The value of A, according to Overhauser, is of the order of E_F (the Fermi level), so that there is no assurance that the new terms are small. We have calculated the first part of Eq. (4.33) in Appendix B to verify this. The equation is so complicated that it is not clear under what conditions a nontrivial solution may exist. In any case, if there is a nontrivial solution, there is no guarantee that the Q value for it would necessarily lie near the Q Overhauser found. Unfortunately, we can do little more here than point to this new source of effects, and to claim that it is not, apparently, a negligible one.

5. CONCLUSIONS

In the preceding sections we have investigated the nature of the potential function in the exchange term of the generalized Hartree-Fock equation, subject to a

basic chain-breaking approximation which amounts to an iteration procedure using for zeroth iteration the solution neglecting exchange. This procedure also linearizes the equation for the potential. In Sec. 3, for spin deviations periodic with the period of the lattice, the spin-*in*dependent part of the potential turned out to be a Coulomb potential shielded in a way slightly different from that found previously for the electron-phonon scattering problem. In the same section, the spin-*de*pendent part of the shielding was found, and it could take most rigorously the form of an alteration in the spin-independent shielding denominator as shown in Eq. (3.20), or, to within a first-order approximation, it could be regarded as a multiplicative factor in the potential as in Eq. (3.21), or, finally, it could be regarded as a separate term in the potential as shown in Eq. (3.23). The spin effects are always enhanced by a Wolff-type polarization, and this enhancement may be rather large (Appendix A), especially for metals with distorted Fermi surfaces. Perhaps this is the reason why substances like copper are the most important for exhibiting anomalies when magnetic impurities are present.

In Sec. 4, we showed how these considerations affect the spin density wave calculation of Overhauser. The integral equation determining the spin-density wave matrix elements contain now terms arising from the spin effect in the shielding of the potential in the exchange term of the Hartree-Fock equation (generalized). The new terms are apparently of the same order of magnitude as the original ones that arose from the spin effect in the exchange charge density in the Hartree-Fock equation. The new integral equation is sufficiently complicated to imply that solutions beyond the trivial one would be hard to find.

The general conclusion is that in a one-electron equation, the spin dependence of the shielding in the potential may play an important role in magnetic problems.

ACKNOWLEDGMENTS

APPENDIX A: EVALUATION OF THE EXCHANGE SHIELDING AND THE POLARIZATION

We reduce in this Appendix the terms N_0 and Q_{00}

$$N_0(p,q) = i \sum_k G_0(p+k)G_0(q+k)v_s(k), \qquad (A1)$$

$$Q_{00}(p,q) = \sum_{kk'} G_0(k')\Lambda_0(p-k'|k+p, k+q|q-k'), \quad (A2)$$

in the denominator of Eq. (3.22) [see Eq. (3.19)] for the exchange shielding, and in the solution of Eq. (2.18) for the spin polarization. We do this on a free-electron

model for the space integrals, and using a "local" approximation (see Sec. 4) for the time integrals.

First consider N. In space-time integrals it is

$$N_0(p,q) = \int\int_0^{-i\beta} da\,db\,v_s(a,b)[iG_0(a-c)G_0(c-b)]$$

$$\times \exp[-i(\mathbf{p}\cdot\mathbf{r}_{ac}+\mathbf{q}\cdot\mathbf{r}_{cb})$$

$$+i(z_p t_{ac}+z_q t_{cb})]. \quad (A3)$$

The local approximation allows us to use

$$v_s(a,b) \cong \delta(t_{ab})v_s(r_{ab}); \quad v_s(k) \cong v_s(\mathbf{k}), \qquad (A4)$$

and to neglect the subsequent Ω dependence in the expansion of $iG(a-c)G(c-b)$, (where $t_b=t_a$) given by Eq. (4.9). The ν sum in Eq. (4.9) yields $\delta(t_{ac})$ so that there is no dependence in Eq. (A3) on z_p or z_q. The result is

$$N_0(p,q) = \sum_{\mathbf{p}'} F(\mathbf{p}', \mathbf{p}'-\mathbf{p}+\mathbf{q})v_s(\mathbf{p}'-\mathbf{p}), \qquad (A5)$$

which is the same as found in Refs. 3 and 4.

In the limit of small $\mathbf{s}=\mathbf{q}-\mathbf{p}$, we have

$$N_0(p,p) = V(8\pi^3)^{-1}\int d\mathbf{p}'\left(-\frac{\delta f_{p'}}{\partial E'}\right)v_s(\mathbf{p}'-\mathbf{p})$$

$$= V(8\pi^3)^{-1}\int dS'|\nabla E'|^{-1}v_s(\mathbf{p}'\cdot\mathbf{p})\cdots$$

integral over Fermi surface. (A6)

Using a Bohm-Pines cutoff expression (cutoff frequency $k_c=0.353k_0r_s^{1/2}$, where r_s is the Wigner Seitz radius in atomic units, and k_0 the radius of the Fermi sphere)

$$v_s(\mathbf{p}) = 4\pi e^2 p^{-2} \quad p > k_c$$

$$= 0 \qquad\qquad p < k_c, \qquad (A7)$$

and using free-electron energies, we obtain from Eq. (A6)

$$N_0(p,p) = (\pi a_h p)^{-1}\ln[(k_0+p)k_c^{-1}] \quad p > k_0-k_c$$

$$= (\pi a_h p)^{-1}\ln[(k_0+p)|k_0-p|^{-1}]$$

$$p < k_0-k_c, \quad (A8)$$

where $a_h = \hbar^2/me^2$. Thus, some limiting cases are

$$N_0(k_0,k_0) = (\pi a_h k_0)^{-1}\ln(2k_0/k_c),$$

$$N_0(0,0) = (\pi a_h k_0)^{-1} = 0.558 \text{ (Cu)}. \qquad (A9)$$

If we wish to do better than a free-electron calculation, we must have an analytic expression for $|\nabla E|^{-1}$. Short of this we may multiply the result in Eq. (A8) by some average correction such as

$$\epsilon = \left[\int dS|\nabla E|^{-1}\right]\bigg/\left[\int dS|\nabla E|^{-1}\right]_{\text{free electron}}. \quad (A10)$$

Values for ϵ can be obtained from specific-heat data

TABLE I. The shielding factor in the long-wave limit for monovalent metals. a is the lattice constant, related to the k_0 of Appendix A by $k_0 a = (12\pi^2)^{1/3}$ for fcc lattices and by $k_0 a = (6\pi^2)^{1/3}$ for bcc lattices, in angstrom units. ϵ is given by Eq. (A11), and the N is the long-wave limit of the function defined in Eq. (A1). The quantity $(1-N)^{-1}$ is the polarization effect on the matrix element. And $(1-N)^{-2}$ is the polarization effect on the transition probability.

Factor	Li	Na	K	Rb	Cs	Cu	Ag	Au
a	3.43	4.22	5.20	5.56	5.92	3.61	4.08	4.07
ϵ	1.22	0.885	0.862	0.841	0.794	1.44	1.02	1.16
$(1-N)^{-1}$	3.94	2.53	2.88	2.91	2.76	4.72	2.50	3.17
$(1-N)^{-2}$	15.5	6.40	8.30	8.48	7.61	22.3	6.25	10.2

(Ziman,[9]) or effective mass data. In Table I, we tabulate the values for some materials. We notice that when the Fermi surface gets distorted, the polarization gets quite large.[10]

Next we turn to Q. Notice that Q does not enter the polarization $1-\mathfrak{R}'$ (to zeroth order). It provides a correction to the spin-independent shielding however.

In space-time integrals, Eq. (A2) becomes

$$Q(p,q) = [V(-i\beta)]^{-1} \int da\,db\,4G_0(a-b)\Lambda_0(a44b)$$

$$\times \exp[-i(a,p)+i(4, p-q)+i(b,q)]. \quad (A11)$$

Expanding Λ_0 according to Eq. (2.14), using the local approximation of Eqs. (4.12), (4.13), we find

$$\Lambda_0(a44b) = iV^{-1}(-i\beta)^{-2} \sum_{kk'} v_s(k)v_s(k')$$

$$\times \exp[i(k,b)-i(k',a)] \sum_{p_1p_2p_3} F(p_1p_2p_3)$$

$$\times \exp[i(z_k - z_{k'})t_4 + i\mathbf{r}_4 \cdot (\mathbf{p}_1 - \mathbf{p}_3)]$$

$$\times [\delta(\mathbf{k}' - \mathbf{p}_1 + \mathbf{p}_2, 0)\delta(\mathbf{k} + \mathbf{p}_2 - \mathbf{p}_3, 0)$$

$$+ \delta(\mathbf{k} + \mathbf{p}_1 - \mathbf{p}_2, 0)\delta(\mathbf{k}' - \mathbf{p}_2 + \mathbf{p}_3, 0)], \quad (A12)$$

where the sum on k contains four components. We neglect the z_k dependence of $v_s(k)$ (the local approximation again), and find after a calculation

$$Q(p,q) = \sum_{k,k'} F(q+k, k', p+k)v_s(q+k-k')$$

$$\times v_s(p+k-k')f_{p+q+k-k'}. \quad (A13)$$

This is as far as we go in reducing Q.

APPENDIX B: ORDER OF MAGNITUDE OF $B^{(2)}$

We here calculate the first part of $B^{(2)}$ in Eq. (4.33) in order to demonstrate that it appears to be of the same

[9] J. Ziman, *Electrons and Phonons* (Oxford University Press, New York 1960), pp. 109, 114.
[10] The calculations that led to Table I were first written up in the report mentioned in footnote 8.

order of magnitude as the original term $B^{(1)}$ in Eq. (4.32). The first part of $B^{(2)}$, B', can be written

$$B' = A^2[C_{1,p}f_p - C_{1+Q,p+Q}f_{p+Q} - D_{1,p} + D_{1+Q,p+Q}]$$

$$\times [E_p - E_{p+Q}]^{-1}, \quad (B1)$$

where

$$C_{1,p} = \sum_k f_k[E_{1-p-k} - E_p]^{-1}, \quad (B2)$$

$$D_{1,p} = \sum_k f_k f_{1-p-k}[E_{1-p-k} - E_p]^{-1}. \quad (B3)$$

We content ourselves with calculating C on a free-electron model for the energy. Integrating over $\cos(\mathbf{l}-\mathbf{p}, \mathbf{k})$, we find

$$C_{1,p} = \frac{2m}{\hbar^2 k_0^2}\frac{Vk_0^3}{8\pi^2}I(\kappa',\kappa) = cE_F^{-1}I(\kappa',\kappa), \quad (B4)$$

where k_0 is the radius of the Fermi sphere, V is the volume, c is a constant of order of magnitude 1 ($= \frac{3}{4}$ for a bcc lattice, and $= \frac{3}{2}$ for an fcc one), and where E_F is the Fermi energy. Here

$$J(\kappa',\kappa) = -\frac{1}{\kappa'}\int_0^1 dx \times \ln\left|\frac{(x-\kappa')^2 - \kappa^2}{(x+\kappa')^2 - \kappa^2}\right|, \quad (B5)$$

with the abbreviations

$$x = k/k_0, \quad \kappa' = |\mathbf{l} - \mathbf{p}|/k_0, \quad \kappa = p/k_0. \quad (B6)$$

The integral in Eq. (B5) can be carried out, and we find

$$I(\kappa',\kappa) = (\kappa')^{-1}\{x_1 - \frac{1}{2}(x_1^2 - 1)\ln[(x_1+1)|x_1-1|^{-1}]$$

$$+ x_2 - \frac{1}{2}(x_2^2 - 1)\ln[(x_2+1)|x_2-1|^{-1}]\}, \quad (B7)$$

where

$$x_1 = \kappa' + \kappa, \quad x_2 = \kappa' - \kappa. \quad (B8)$$

The function I is of order of magnitude 1. A few limiting cases are

$$\lim_{\kappa' \to 0} I(\kappa',\kappa) = 2,$$

$$\lim_{\kappa \to 0} I(\kappa',\kappa) = 2\{1 - ((\kappa'^2 - 1)/2\kappa)$$

$$\times \ln[(2\kappa+1)|2\kappa-1|^{-1}]\}, \quad (B9)$$

$$\lim_{\kappa \to \kappa'} I(\kappa',\kappa) = 2\{1 - ((4\kappa^2 - 1)/4\kappa)$$

$$\times \ln[(2\kappa+1)|2\kappa-1|^{-1}]\}.$$

Thus from Eq. (B4), C is of the order of magnitude $1/E_F$. But A, according to Overhauser,[3] is also of the same order. Hence we conclude that the calculated term in $B^{(2)}$ is of the same order of magnitude as the original term $B^{(1)}$.

APPENDIX C: COMPARISON OF THE TWO ITERATION PROCEDURES

In this Appendix, we apply the formalism of Sec. 3 to the problem of Sec. 4, and thereby assess the approximation that went into the latter.

Using the spin-density wave expansion of Eq. (4.17) in the form

$$\varphi_{p\sigma}(r) = \sum_Q b_{p+Q,p}{}^{(\sigma)}\psi_{p+Q}(\mathbf{r}), \qquad (C1)$$

where $\mathbf{Q}$ can take on values $+\mathbf{Q}$, $-\mathbf{Q}$, and 0, the $\pm\mathbf{Q}$

values of b given by Eq. (4.18), and the $\mathbf{Q}=0$ value given by

$$b_{\mathbf{p},\mathbf{p}}{}^{(\sigma)} = 1, \qquad (C2)$$

we see that the formalism of Sec. 3 is immediately applicable once we identify the $\mathbf{K}$ index with $\mathbf{Q}$, and set in Eq. (3.3):

$$G(p\,|\,\mathbf{Q}_1\mathbf{Q}_2) = b_{p+Q,p}{}^{(\sigma)}b_{p+Q,p}{}^{(\sigma)*}[z_p - E_p]^{-1}. \qquad (C3)$$

Then the components of the type in Eq. (3.7) of Eq. (2.15) yield

$$V_\sigma(p,p'\,|\,p'') = v(p-p')\delta_{p'',0} - (-i\beta)^{-1}\sum_{\sigma'}\sum_{kk'Q} G_{\sigma'}(k\,|\,\mathbf{Q}_1\mathbf{Q}_2)G_{\sigma'}(k'\,|\,\mathbf{Q}_3\mathbf{Q}_4)v(p-p')$$

$$\times V_{\sigma'}(k+\mathbf{Q}_2, k'+\mathbf{Q}_3\,|\,p''+p-p'-k+k'-\mathbf{Q}_2+\mathbf{Q}_3)\delta(p-p'-k+k'-\mathbf{Q}_1+\mathbf{Q}_4, 0)$$

$$+ (-i\beta)^{-1}\sum_{k,k',Q} G_\sigma(k\,|\,\mathbf{Q}_1\mathbf{Q}_2)G_\sigma(k'\,|\,\mathbf{Q}_3\mathbf{Q}_4)v_s(p-k-\mathbf{Q}_1)\delta(p-p'-k+k'-\mathbf{Q}_1+\mathbf{Q}_4, 0)$$

$$\times V_\sigma(k+\mathbf{Q}_2, k'+\mathbf{Q}_3\,|\,p''+p-p'-k+k'-\mathbf{Q}_2+\mathbf{Q}_3) + \sum_{Q\,k,\kappa,\kappa'} G_\sigma(k\,|\,\mathbf{Q}_1\mathbf{Q}_2)$$

$$\times\sum_{\sigma'} V_{\sigma'}(\kappa, \kappa'\,|\,-\kappa+\kappa'+p-p'+p'')\Lambda_{\sigma'}(p-k-\mathbf{Q}_1\,|\,\kappa, \kappa'\,|\,p'-k-\mathbf{Q}_2). \qquad (C4)$$

We get Eq. (3.11) from this rather general expression by seeking only the $V(p,p'\,|\,0)$ components. But here we regard each $G(\cdots\,|\,\mathbf{Q}_1\mathbf{Q}_2)$ to be of nth order if n of the Q's are nonzero. It can readily be seen from the equation that $V(p,p'\,|\,0)$ is of zeroth order, and $V_\sigma(p,p'\,|\,\pm\mathbf{Q})$ is of first order. Thus the equation for $V(p,p'\,|\,0)$ is the same as in Sec. 3, except that to zeroth order, all the L's, N's, and $Q_{\sigma\sigma'}$'s of Sec. 3 are spin independent. The solution for $V(p,p'\,|\,0)$ is then given by Eq. (3.22) on the assumption that $V(p,p') = V(p+k, p'+k)$ [see Eq. (3.18)].

The equation for $V_\sigma(p,p'\,|\,\mathbf{Q})$, $Q\neq0$, has two types of terms on the right in Eq. (C4), one containing only $V(\cdots\,|\,0)$, the other containing $V_\sigma(\cdots\,|\,Q)$, the latter from the third $\pm$ term on the right. One can lump this latter $V_\sigma(\cdots\,|\,\mathbf{Q})$ dependent term with the left-hand side and solve for $V_\sigma(p,p'\,|\,\mathbf{Q})$ in terms of $V(\cdots\,|\,0)$. This gives a polarization effect of the same type as in Eq. (2.18), and as appears in Eq. (3.20) in the $1-\mathfrak{R}'$ factor in the denominator.

By this procedure, we can find from Eq. (4.1) the first-order contributions to W (first order being denoted by δ's) in the form

$$\delta W_\sigma(l',l) = \int dr_1 d2 d3 \psi_{l'}(r_1)^*\psi_l(r_2)[i\delta G_\sigma(1,3)V_0(32\,|\,1)$$

$$+ iG_0(1,3)\delta V_\sigma(32\,|\,1)], \qquad (C5)$$

where the subscript "0" means zeroth-order part. The V_0 here to be used has the components $V(p,p'\,|\,0)$ described above, and the $\delta V_\sigma(3,2\,|\,1)$ has the components $V_\sigma(p,p'\,|\,\pm\mathbf{Q})$ described above. In this general manner, one can proceed to compute δW, from which the integral equation should follow.

To the first part of the square bracket in Eq. (C5) there corresponds the $W^{(1)}$ of Eq. (4.19), the last term in $W^{(2)}$ [i.e., in $B^{(2)}$ of Eq. (4.24)], and an unseparated-out contribution to $W^{(3)}$ of Eqs. (4.27), (4.28). To the second part of the bracket corresponds the first term of $W^{(2)}$ and the other part of $W^{(3)}$. It was thought desirable to lump the contributions as in $W^{(1)}$, $W^{(2)}$, and $W^{(3)}$ in Sec. 4, primarily because the two parts of $W^{(3)}$ separately are not Hermitean, but together they are. [The one part comes from the first-order part of $G(1,3)$, the other from the first-order part of $G(3,2)$. See Eqs. (4.5) and (4.8).]

To obtain from Eq. (C4) the approximation actually used in Sec. 4, we (1) neglect the polarization effect, (2) in the equation for $V(p,p'\,|\,\mathbf{Q})$, use $V_0(p,p'\,|\,0) = v_s(p,p')$ on the right, and (3) for the V_0 in the first term of the square bracket of Eq. (C5), use the right-hand side of Eq. (3.18), with $V_0 = v_s$ there. We shall amplify this relation below.

First of all, the neglect of spin polarization is not a crucial matter. It will modify the details of the results, but not the order of magnitude or significance. Furthermore, its inclusion would enhance the importance of the δV term in Eq. (C5). Since our purpose is to demonstrate the importance of this term, the neglect of the polarization effect gives us an underestimate. To have included it would have amounted to altering the value to be ascribed to some of the A's in Eqs. (4.33) and (4.34).

Secondly, the equation for $V(\cdots\,|\,\mathbf{Q})$ described above reduces to the same expression [in terms of $V(p,p')$] that is implied by Eq. (2.19) (in terms of v_s), for in the latter, the only contributions stem from the L_σ and G_σ factors in the last two terms on the right, just as they

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.