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Energy of a Bloch Wall on the Band Picture. II. Perturbation Approach

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The "exchange stiffness" constant, which appears in the theory of the Bloch interdomain wall in ferromagnetics, can be calculated by computing the response of a saturated specimen to a small spatially varying perturbing field. This calculation is carried out here in the self-consistent field approximation, using running waves for the one-electron states, and the result is interpreted physically in terms of precession of the spins of moving electrons.

Combination of the present theory with the Stoner-Wohlfarth model of the ferromagnetic electrons in nickel does not give satisfactory results, probably because the latter model does not approximate the actual self-consistent field solution very well. However, application of the theory to the free electron gas is of interest as a confirmation of the validity of the perturbation approach.

It is shown that there exist, even in a ferromagnetic metal, quantum states orthogonal to all the low-lying states of the conventional band picture and having the properties of spin waves. The presumably universal relation between the exchange stiffness constant and the energies of spin waves of long wavelength is verified in the present approximation. It is shown that spin waves carry a current in a metal, though not in an insulator. For spin waves of long wavelength the present theory can be shown to include Slater's theory of spin waves in a ferromagnetic insulator, and *a fortiori* to include all previous theories based on the atomic model.

I. INTRODUCTION

THE energy, thickness, and other properties of the "Bloch wall" separating adjacent domains in a ferromagnetic medium depend upon the anisotropy constants of the medium and upon the extent to which the energy of the ferromagnetic electrons increases when the orientation of the magnetization vector is made spatially non-uniform.[1] This increase in energy per unit volume is commonly written, for cubic crystals,

$$W=A|\nabla\mathbf{M}|^2/M^2, \tag{1}$$

where $\mathbf{M}$ is the magnetization vector and A is a constant characteristic of the material. The form of Eq. (1) and the order of magnitude of A can be accounted for on the basis either of the atomic picture[1] or of the band picture[2] of the ferromagnetic electrons. Moreover, it has been shown[3] that A has a fundamental relation to the theory of spin waves and thus to the temperature variation of saturation magnetization at low temperatures, a relation which is probably valid regardless of the choice of any particular theoretical model for the ferromagnetic electrons. The theory of A given in I, though it provides a simple physical picture of the behavior of itinerant electrons in a Bloch wall, is not adapted to bringing out the way in which spin waves can arise out of the band picture. The present paper gives an alternative method of calculating A for the running-wave model, a method which is more complicated mathematically but which brings out the relation to spin waves and which is somewhat more promising for practical calculations.

The approach used in the present paper is based on the observation that if a specimen initially magnetized in the z-direction is acted on by a small sinusoidally varying torque tending to rotate the magnetization about the x-axis, the resulting variation in the direction of $\mathbf{M}$ will vary inversely as A, as will the change in the energy of the system. Thus, a calculation of this energy change by perturbation methods gives the value of A. Explicitly, we shall assume a model for the ferromagnetic electrons in which their electrostatic interactions are taken into account but magnetic and spin-orbit interactions are ignored, and shall consider the effect of adding a term

$$R\sum_i \sigma_y^{(i)} \sin\boldsymbol{\kappa}\cdot\mathbf{r}_i, \tag{2}$$

to the Hamiltonian, where $\sigma_y^{(i)}$ is a Pauli spin matrix for the ith electron, $\mathbf{r}_i$ is the position of this electron, $\boldsymbol{\kappa}$ is an infinitesimal vector, and R is an infinitesimal amplitude. An elementary phenomenological calculation, given in Sec. IIIB of reference 3, shows that the second-order energy perturbation ΔE due to (2) must, for a perturbation of sufficiently long wavelength, be interpretable in terms of A by

$$\Delta E=-\Omega R^2M^2/8\kappa^2A, \tag{3}$$

where Ω is the volume of the specimen and M is in Bohr magnetons per unit volume.

In this paper, as in I, the state of the ferromagnetic electrons will be approximated by the best possible determinant of one-electron wave functions, both in the unperturbed and in the perturbed state. As was explained in Sec. III of I, this approximation almost certainly gives too large a value for A. To calculate the effect of the perturbation (2) on the solution of the Fock-Dirac self-consistent field equations we may make use of the general perturbation formalism given by Peng[4] for these equations. A simplified version of this

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[1] F. Bloch, Z. Physik **74**, 295 (1932); L. Landau and E. Lifshitz, Physik. Z. Sowjetunion **8**, 153 (1935); E. Lifshitz, J. Phys. USSR **8**, 337 (1944); L. Néel, Cahiers phys. **25**, 1 (1944). For a summary see C. Kittel, Revs. Modern Phys. **21**, 541 (1949).

[2] C. Herring, Phys. Rev. **85**, 1003 (1952), hereafter cited as I.

[3] C. Herring and C. Kittel, Phys. Rev. **81**, 869 (1951).

[4] H. W. Peng, Proc. Roy. Soc. (London) **A178**, 499 (1941). Similar principles were employed earlier by J. Bardeen in his treatment of metallic conduction, Phys. Rev. **52**, 688 (1937).

formalism will be developed for the present problem in Sec. II while Appendix B will make use of Peng's formulas in full generality.

In Sec. III and Appendix B general expressions for the solution of the perturbation problem will be derived, expressions which can be used to establish a number of qualitative properties of the solution but which are too general for easy numerical evaluation. In this solution the perturbed one-electron wave functions will be obtained to the first order in the amplitude R of the perturbation and to the two lowest orders in its wave number κ. To the lowest order in κ, each perturbed wave function will turn out to be essentially the unperturbed running wave multiplied by a spatially variable spin function corresponding to orientation of the spin along the direction of the local macroscopic magnetization, a direction which varies from point to point of the crystal with an angular amplitude proportional to $1/\kappa^2$, as (3) shows. However, to get the energy to order $1/\kappa^2$, or equivalently to get the coefficient of $1/\kappa^2$ in the expression for the angular amplitude, it is necessary to know the terms of order $1/\kappa$ in the one-electron wave functions. When these terms are included it will be found that at any particular point of space the spins of different electrons differ in direction by an angle proportional to $1/\kappa$, i.e., to the gradient of the inclination of the macroscopic magnetization. These facts and their physical interpretation in terms of precessing spins will be discussed in Sec. IV.

Sections V and VI will be devoted to the obtaining of numerically explicit solutions, first for an actual metal using some rather crude approximations, and then for the idealized case of a free electron gas, which can be solved without approximations.

In Sec. VII it will be shown that a spin wave state of infinitesimal wave vector $\boldsymbol{\kappa}$ can be approximately represented by a linear combination of all the determinantal wave functions derivable from that of the ground-state by taking an electron out of one of the singly occupied levels and putting it back with reversed spin and with its wave vector increased by $\boldsymbol{\kappa}$. To the zeroth order in κ the coefficients of all these determinants are the same, but in the first order they differ. This representation of a spin wave is essentially the same as that given some time ago by Slater[5] for a ferromagnetic insulator; the same representation appears to be valid for a metal, although in the calculation of the energy for a metal certain terms not present in Slater's treatment must be included. An obvious consequence of the present picture, which will be discussed briefly in Sec. VII is, that spin waves in general carry a current in a metal, though not in an insulator. This result differs from that reported recently by Bogolyubov and Tyablikov[6] in that these authors consider only the case of an insulator, i.e., a crystal for which the ferromagnetic electrons completely fill a band, and predict a current for this case. It will be argued below that their conclusion is erroneous.

II. EQUATIONS OF THE PERTURBATION APPROACH

Let the one-electron wave equations of the self-consistent field problem be

$$[H+RK]\psi_i=\lambda_i\psi_i, \tag{4}$$

where K is an abbreviation for the $\sigma_y \sin\boldsymbol{\kappa}\cdot\mathbf{r}$ of (2), λ_i is the energy parameter, and H is the sum of the kinetic energy, the interaction with the ions of the lattice, the Coulomb potential, and the Fock exchange operator. The solutions $\psi_i^{(0)}$ of this system of equations when $R=0$ will be presumed known. To calculate the Bloch wall coefficient A by (3) we need the energy to the second order in R, and to compute this we must determine the ψ_i to the first order in R. The complicating feature of the latter problem is that the Coulomb and exchange operators in H depend on the ψ_i of all the occupied states. Although the problem can be solved formally without introducing any approximations regarding this dependence of H on the ψ_i (see Appendix B), the essential features of the exact solution can be derived much more simply by a treatment which assumes that the $\psi_i^{(0)}$ of both spins have the same orbitals, and that the small changes which the perturbation produces in the ψ_i merely produce an additional exchange field similar in effect to the original perturbing field (2), though of course of an entirely different magnitude. Since the more complete calculation shows that the error involved in using this simpler treatment is probably rather small, we shall use it here.

Both here and in Appendix B we shall calculate merely the difference between the unperturbed energy and the energy of the determinant of perturbed wave functions satisfying (4) and reducing to the unperturbed set as $R\to 0$. However, in a metal the total energy varies continuously not only with the form of the one-electron functions themselves, but also with the choice of which levels are filled and which are empty. It is, therefore, legitimate to ask whether the energy of the perturbed solution we shall obtain here might be lowered by a subsequent alteration of the occupation numbers of the various states. Fortunately, it can be shown that as far as the second order in R no such redistribution can lower the energy; the argument is given in Appendix A. We shall therefore worry no more about occupation numbers.

To the zeroth order in κ, the operator K connects each $\psi_i^{(0)}$ only with the two wave functions of the opposite spin which lie in the same band and have reduced wave vectors differing from that of $\psi_i^{(0)}$ by $\pm\boldsymbol{\kappa}$. Our assumption regarding the exchange field, stated roughly above, may now be described more precisely by saying that we shall assume the perturbed ψ_i to have the form

$$\psi_i=\psi_i^{(0)}+R[U_i^+\psi_{[i+\kappa]}^{(0)}+U_i^-\psi_{[i-\kappa]}^{(0)}], \tag{5}$$

where the square brackets in a subscript denote reversal of spin. Moreover, since changing the sign of $\boldsymbol{\kappa}$ in

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[5] J. C. Slater, Phys. Rev. **52**, 198 (1937).

[6] N. N. Bogolyubov and S. V. Tyablikov, J. Exptl. Theor. Phys. U.S.S.R. **19**, 256 (1949).

(2) is equivalent to changing the sign of R, we must have $U_i^-(\boldsymbol{\kappa}) = -U_i^+(-\boldsymbol{\kappa})$. Since a mixing of two states both of which are initially occupied does not affect the determinantal wave function, we shall adopt the convention that $U_i^\pm = 0$ when states $\mathbf{i}$ and $\mathbf{i}\pm\boldsymbol{\kappa}$ are both occupied.

When (5) is substituted into the expression for the exchange operator, first-order terms of the form $RU_i^\pm \partial H/\partial(RU_i^\pm)$ result. Noting that the one-electron energies λ_i are unchanged to the first order by the perturbation (see Appendix A), we have for the first-order part of the wave Eq. (4)

$$K\psi_i^{(0)} + \sum_\pm U_i^\pm \lambda_{[i\pm\kappa]} \psi_{[i\pm\kappa]}^{(0)} + \sum_{j,\pm} U_j^\pm [\partial H/\partial(RU_j^\pm)] \psi_i^{(0)} = \lambda_i \sum_\pm U_i^\pm \psi_{[i\pm\kappa]}^{(0)}, \quad (6)$$

the summation on j being of course confined to occupied states. Taking the scalar product of this with $\psi_{[i\pm\kappa]}^{(0)}$ we get

$$\begin{aligned} -K_{[i\pm\kappa],\,i} &= (\lambda_{[i\pm\kappa]} - \lambda_i) U_i^\pm + \sum_j [\partial H/\partial(RU_j^\pm)]_{[i\pm\kappa],\,i} U_j^\pm \\ &= \sum_j \Phi_{ij}(\pm\boldsymbol{\kappa}) U_j^\pm, \text{ say.} \end{aligned} \quad (7)$$

This system of simultaneous equations determines the $U_j^\pm$ for the occupied states j.

Several properties of the equation systems (6) and (7) are worth noting at this point. Since the function (5) has a spin direction which differs from that of $\psi_i^{(0)}$ by a small angle which varies sinusoidally with position, the operator $\partial H/\partial(RU_i^\pm)$ represents an exchange field at right angles to the z direction, roughly equivalent in its effect to an operator of the type (2), i.e., to a transverse magnetic field. We shall evaluate this exchange operator explicitly in Sec. V. Its matrix element which appears in (7) will approach a finite limit as $\kappa \rightarrow 0$, as will the λ term in Φ_{ij} and the term $K_{[i\pm\kappa],\,i}$. However, we cannot obtain the desired solution of (7) by considering only the limiting forms of its various coefficients as $\kappa \rightarrow 0$. If κ were zero, the energy of the crystal would not be changed by rotating the spins to a new orientation, and the response to the applied torque would be infinite. Mathematically this means that the determinant of the matrix Φ_{ij} approaches zero as $\kappa \rightarrow 0$. The U_j which satisfy

$$\sum_j \Phi_{ij}(0) U_j = 0,$$

can easily be constructed by comparing (5) with the expansion of the equation

$$\psi_j = \exp(i\boldsymbol{\varepsilon}\cdot\boldsymbol{\sigma}/2)\psi_j^{(0)}, \quad (8)$$

which corresponds to replacement of each $\psi_j^{(0)}$ by a state with the spin rotated by an infinitesimal amount ϵ about the direction $\boldsymbol{\varepsilon}$. The local state of the crystal in the presence of a perturbation with finite κ will be, in zeroth approximation, the state obtained by rotating the unperturbed spins to the local perturbed orientation, but to the next order in κ it will differ from this, and it is just this difference which is responsible for the stiffness which makes the response of the spin system to the perturbation finite.

We are therefore led to solve (7) by expanding all quantities in powers of κ. For a given direction of $\boldsymbol{\kappa}$ let

$$U_i^\pm = \pm U_i^0/\kappa^2 + U_i'/\kappa \pm U_i'' + \cdots \quad (9)$$

$$\Phi_{ij}(\pm\boldsymbol{\kappa}) = \Phi_{ij}^0 \pm \kappa\Phi_{ij}' + \kappa^2\Phi_{ij}'' + \cdots. \quad (10)$$

The range of values of $\mathbf{j}$ occurring in the summation on the right of (7) is that for which $\mathbf{j}$ is occupied, $[\mathbf{j}+\boldsymbol{\kappa}]$ empty. If this range is independent of $\boldsymbol{\kappa}$, as is the case when the doubly-filled orbitals comprise an integral number of bands, the equations resulting from insertion of (9) and (10) into (7) are quite simple, otherwise not. As the general case is considered in Appendix B, the present treatment will assume the former simpler alternative; because of the reciprocity between electrons and holes the results must be applicable to cases where the ferromagnetism is due to holes in a filled band, as well as to those involving electrons in an empty band. With the present assumption we get from (7),

$$\sum_j \Phi_{ij}^0 U_j^0 = 0, \quad (11)$$

$$\sum_j (\Phi_{ij}^0 U_j' + \Phi_{ij}' U_j^0) = 0, \quad (12)$$

$$\sum_j (\Phi_{ij}^0 U_j'' + \Phi_{ij}' U_j' + \Phi_{ij}'' U_j^0) = -K^0, \quad (13)$$

where

$$K^0 = \lim_{\kappa\rightarrow 0} K_{[i+\kappa],\,i} = \tfrac{1}{2}, \quad (14)$$

if we adopt the phase convention $\psi_{[i]}^{(0)} = \sigma_x \psi_i^{(0)}$.

III. SOLUTION OF THE EQUATIONS

The solution of (11) is most easily obtained from (8); it is

$$U_i^0 = U^0, \quad (15)$$

an as yet arbitrary constant independent of $\mathbf{i}$. The correctness of (15) can also be shown directly, by substituting it into (11) and using the explicit form of $\Phi_{ij}(0)$ from (7). Since $\lambda_{[i]}$ differs from λ_i precisely by virtue of the different exchange fields seen by electrons of the two states of spin, we have for $\kappa = 0$

$$\lambda_{[i]} - \lambda_i = -\sum_j [\partial H/\partial(RU_j)]_{[i]\,i}, \quad (16)$$

a result which is most easily derived from the explicit expression below for $\partial H/\partial(RU_j)$. Thus (11) is satisfied identically.

The value of U^0 can only be determined by solving (12) and (13). If we sum (13) on $\mathbf{i}$, the first term on the left goes out because of (11) and the Hermiticity of Φ_{ij}^0, while the second term can be transformed by (12) and the fact that Φ_{ji}' is also Hermitian. Solving for U^0 we get

$$U^0 = -NK^0/[\sum_{i,j} \Phi_{ij}'' - \sum_{i,j} b_i^* \Phi_{ij}^0 b_j], \quad (17)$$

where N is the number of uncompensated spins in the specimen and $b_i = U_i'/U^0$ satisfies

$$\sum_j \Phi_{ij}^0 b_j + \sum_j \Phi_{ij}' = 0. \quad (18)$$

This equation does not, of course, determine the b_j uniquely, since a constant independent of **j** can be added to any solution; however, such a constant has no effect on the value of the denominator of (17). The values of U_i' which actually occur physically could presumably be determined by analysis of higher equations of the form of (11), (12), and (13). We shall see in the next section that a simpler line of reasoning gives the requirement $\sum b_j=0$, and so removes the ambiguity without reference to the higher equations.

To the second order the mean value of the perturbation term (2) in the perturbed ground state of the assembly is, as in any problem involving displacement of equilibrium of a harmonic system by a small force, equal to $2\Delta E$, where ΔE is the change in total energy produced by the perturbation. Therefore, to the second order in R,

$$\Delta E=\tfrac{1}{2}\sum_i(\psi_i, RK\psi_i). \tag{19}$$

Using (5), (9), (14), and the reality of U^0, which follows from (17), this reduces to

$$\Delta E=2R^2NK^0U^0/\kappa^2, \tag{20}$$

to the lowest order in κ. (The next term is presumably O(1), since ΔE is even in κ.) Combining this with (17) and (3) gives the Bloch wall coefficient A. With $M=N/\Omega$, where Ω is the volume of the specimen, we have

$$A=(4\Omega)^{-1}\left[\sum_{i,j}\Phi_{ij}''-\sum_{i,j}b_i^*\Phi_{ij}^0 b_j\right]. \tag{21}$$

It is easily verified that the first term in brackets in (21) gives the value of A which would result if we were constrained to use only determinants of functions (5) with $U_i^{\pm}$ strictly independent of **i**. The possibility of using different coefficients for different electrons enables us to lower the energy further, and gives a negative contribution to A represented by the second term in brackets. For free electrons (see Sec. VI) the first term in (21) gives A for the model in which all perturbed states are required to have the same spatial variation of spin, as considered in I, Sec. VIII; however, this exact correspondence to the model considered there does not hold in general.

IV. INTERPRETATION IN TERMS OF PRECESSING SPINS

The physical significance of the analysis of the preceding section can be appreciated by considering the spin orientation for an electron in the **k**th state. If we split the unperturbed wave functions into orbital and spin parts according to

$$\psi_k^{(0)}=\chi_k\alpha \quad\text{or}\quad \chi_k\beta,$$

α and β being eigenfunctions ± 1 of σ_z, the perturbed wave function is, to the first two orders in κ,

$$\psi_k=\chi_k\alpha+RU^0[(1/\kappa^2)(1+\kappa b_k)\chi_{k+\kappa} \\ -(1/\kappa^2)(1-\kappa b_k)\chi_{k-\kappa}]\beta,$$

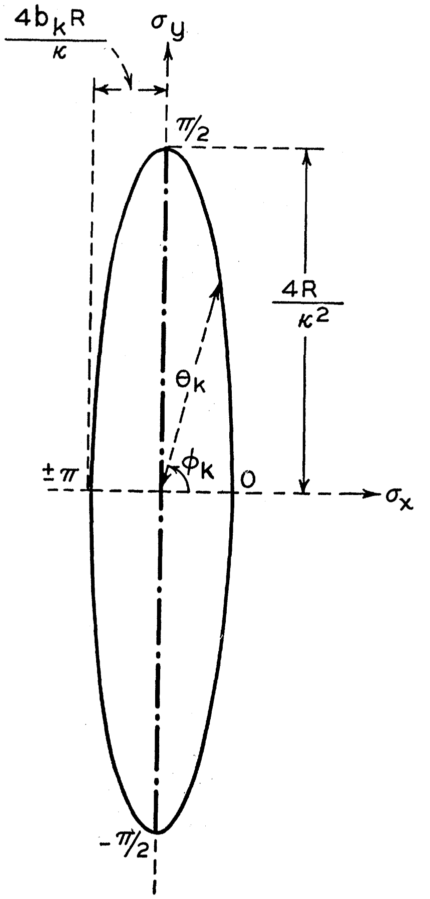

FIG. 1. Path of mean spin direction of **k**th electron on the unit sphere. Numbers are values of $\boldsymbol{\kappa}\cdot\mathbf{r}$. Dot-dash line is path of average spin direction of all electrons, as $\boldsymbol{\kappa}\cdot\mathbf{r}$ varies.

whence

$$\frac{\text{coeff.}\beta}{\text{coeff.}\alpha}=\exp(i\varphi_k)\tan\frac{\theta_k}{2} \\ =RU^0\left[\frac{1}{\kappa^2}\frac{(\chi_{k+\kappa}-\chi_{k-\kappa})}{\chi_k}+\frac{b_k}{\kappa}\frac{(\chi_{k+\kappa}+\chi_{k-\kappa})}{\chi_k}\right],$$

where, as in I, $\theta_k(\mathbf{r})$, $\varphi_k(\mathbf{r})$ are the polar angles of the direction along which the spin of the **k**th state has the eigenvalue $+\frac{1}{2}$. If we write

$$\chi_{k+\kappa}=\exp(i\boldsymbol{\kappa}\cdot\mathbf{r})[\chi_k+i\boldsymbol{\kappa}\cdot\mathbf{v}_k+\cdots], \tag{22}$$

and remember that θ_k is infinitesimal, this takes the simple form

$$\theta_k(\cos\varphi_k+i\sin\varphi_k) \\ =(4iR/\kappa^2)[\sin\boldsymbol{\kappa}\cdot\mathbf{r}+(\boldsymbol{\kappa}\cdot\mathbf{v}_k/\chi_k)\cos\boldsymbol{\kappa}\cdot\mathbf{r}] \\ +(4b_kR/\kappa)\cos\boldsymbol{\kappa}\cdot\mathbf{r}+O(1), \tag{23}$$

where $O(1)$ refers to the behavior as $\kappa\rightarrow 0$.

From (23) we see that in regions where $\boldsymbol{\kappa}\cdot\mathbf{r}$ is near an odd multiple of $\pi/2$, the spins of all the electrons will be practically parallel and oriented in a direction in the y–z plane (the plane $\varphi=\pm\pi/2$, in which the applied torque is trying to move it), this direction making an angle θ with the z-axis which is of order $1/\kappa^2$. At other points the orientation of the spin of any given state will in general not be in the y–z plane; the spin direction will show local fluctuations over each cell, but its mean direction in any cell will be that given by averaging (23) over the cell with weight $|\chi_k|^2$. The $\mathbf{v}_k$ term in (23) disappears from this average, since $\mathbf{v}_k$ and χ_k are orthogonal, and so it can be seen that as $\boldsymbol{\kappa}\cdot\mathbf{r}$ varies, the spin direction for the $\mathbf{k}$th state will describe an ellipse on the unit sphere as shown in Fig. 1. When $\boldsymbol{\kappa}\cdot\mathbf{r}$ is near a multiple of π, the spin of the $\mathbf{k}$th state will depart slightly from the mean spin direction of all the electrons, which is always in the y–z plane, the departure being in the x-direction and proportional to b_k times the rate at which the mean spin direction is changing with position. This can be interpreted in the same way as the free electron behavior discussed in I, the latter being in fact a special case of the present problem. A wave packet formed of states neighboring to $\mathbf{k}$ will, in moving through the crystal, be acted upon by a torque due to the exchange fields of the other electrons, this torque being in such direction as to tend to bring all spins into coincidence. This torque will cause the spin of the packet to precess, so that its projection on the unit sphere will move at right angles to the great circle joining it to the mean spin direction. If the mean spin direction moves back and forth in the y–z plane, as shown by the dot-dash line in Fig. 1, the spin direction of the wave packet will describe the ellipse shown.

The behavior of the average spin direction of all the electrons, which we have just mentioned, provides us with a simple way of showing how the arbitrary constant occurring in U_j', or b_j, must be chosen. We have seen that (18) does not determine b_j completely, but leaves us free to add to it any constant independent of $\mathbf{j}$. Now if the average of b_j over all electrons differs from zero, the average spin direction of all the electrons will describe an ellipse on the unit sphere as $\boldsymbol{\kappa}\cdot\mathbf{r}$ changes, while if the average of b_j is zero, the mean spin will always remain in the y–z plane. That the former is impossible is obvious from symmetry: As we move through the crystal in the x-direction, so that $\boldsymbol{\kappa}\cdot\mathbf{r}$ changes, there is no more reason for the average spin direction to describe a clockwise ellipse than a counterclockwise one. This argument can be formulated in mathematical terms by making use of the time-reversal symmetry[7] of the unperturbed Hamiltonian and the antisymmetry of the perturbation K, but we shall omit the details.

V. ROUGH EXPLICIT EVALUATION OF A

As we shall see in Secs. VII and VIII, the generality of the expression (21) (or (B.8) of Appendix B) for A is useful in that it enables certain relationships interpretable in terms of spin waves to be established rigorously for the self-consistent field model. However, it would be very difficult to evaluate (21) exactly for the rigorous self-consistent field solution for an actual ferromagnetic metal, since one would have to start with the wave functions of the unperturbed self-consistent field solution, evaluate various integrals over them to get $\Phi_{ij}{}^0$, Φ_{ij}', and Φ_{ij}'', and solve the integral Eq. (18). In this section we shall consider some approximations which, though crude, enable an explicit evaluation to be made while retaining the most important physical factors upon which the solution depends.

Consider the matrix element $[\partial H/\partial(RU_j{}^+)]_{[i+\kappa],\,i}$ which, according to (7), constitutes the most difficult term in $\Phi_{ij}(\boldsymbol{\kappa})$. Of the Coulomb and exchange operators in H, only the latter is changed in first order when (5) is substituted for $\psi_i{}^{(0)}$, and from the form of the exchange operator it is easy to show that the matrix element in question is simply the negative of the electrostatic interaction energy of the charge distributions

$$\chi_{i+\kappa}{}^*\chi_{j+\kappa} \quad\text{and}\quad \chi_j{}^*\chi_i, \tag{24}$$

where the χ's are the orbital parts of the $\psi^{(0)}$'s. Now the former of the distributions (24) is independent of $\boldsymbol{\kappa}$ for free electrons, and also in the limit of tight binding for a band arising from a nondegenerate atomic level. Although neither of these cases corresponds to the situation in actual ferromagnetics, one is tempted to explore the consequences of assuming that

$$-[\partial H/\partial(RU_j{}^+)]_{[i+\kappa],\,i}=J_{ji}=J_{ij}, \tag{25}$$

independently of $\boldsymbol{\kappa}$. With this assumption we have, taking the x axis in the direction of $\boldsymbol{\kappa}$,

$$\Phi_{ij}{}^0=\Delta\lambda_j\delta_{ji}-J_{ij}, \tag{26}$$

$$\Phi_{ij}'=(\partial\lambda_{[j]}/\partial j_x)\delta_{ji}, \tag{27}$$

$$\Phi_{ij}''=\tfrac{1}{2}(\partial^2\lambda_{[j]}/\partial j_x{}^2)\delta_{ji}, \tag{28}$$

where $\Delta\lambda_j=\lambda_{[j]}-\lambda_j=\sum_i J_{ij}$, the summation being over the singly-occupied orbitals only. Thus (18) reduces to

$$\textstyle\sum_i J_{ij}(b_j-b_i)+\partial\lambda_{[j]}{}^{(0)}/\partial j_x=0. \tag{29}$$

All the assumptions leading to (29) are valid for the free electron problem, and we shall use it without further approximation in the next section. In this section, however, we shall from now on make the further assumption that

$$J_{ij}=J/N, \tag{30}$$

independent of $\mathbf{i}$ and $\mathbf{j}$, where as before N is the number of singly occupied levels. This approximation, which of course is quite crude, amounts to assuming that the torque which the other electrons exert on the spin of an electron in the $\mathbf{j}$th state is in each region of space simply proportional to the departure of the spin orientation of the $\mathbf{j}$th state in that region from the local mean orienta-

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[7] E. Wigner, Nachr. Wiss. Gottingen, p. 546 (1932).

tion. Stoner[8] has elaborated the theory of ferromagnetism at some length on the basis of an analogous assumption.

With the assumption just mentioned, the solution of (29) which satisfies $\sum b_j = 0$ is

$$b_j = -J^{-1}\partial\lambda_{[j]}/\partial j_x. \tag{31}$$

Using this with (26), (28), and (30), the expression (21) for A becomes, if we assume cubic symmetry,

$$A = (24\Omega)^{-1}\sum_j[\nabla^2\lambda_{[j]} - 2|\nabla\lambda_{[j]}|^2/J], \tag{32}$$

the ∇ operators being, of course, differentiations in wave vector space. For the case where the holes in the d band can be treated as free particles with an effective mass m^*, a case which Stoner[8] has treated in detail and which Wohlfarth[9] has applied to nickel and its alloys, (32) becomes

$$\begin{aligned} A &= (N/4\Omega)(m/m^*)(1-4\bar{\lambda}/3J) \\ &= (N/4\Omega)(m/m^*)(1-2^{5/3}\epsilon_0/5k\theta'), \end{aligned} \tag{33}$$

where $\bar{\lambda} = \langle k^2 m/m^*\rangle_{\text{Av}}$ is the mean energy of the holes relative to the band edge, and where at the right we have translated $\bar{\lambda}$ and J into Stoner's notation by setting $J = 2k\theta'$ and $\epsilon_0 = \lambda_{\max}/2^{\frac{2}{3}}$, ϵ_0 being the maximum energy of a hole relative to the band edge for the case where the holes are distributed equally between the two states of spin. It is noteworthy that according to (33) a ferromagnetic spin arrangement should become unstable with respect to long wavelength fluctuations when $k\theta' < 2^{5/3}\epsilon_0/5 = 0.635\epsilon_0$,[10] while Stoner's criterion, based on a comparison of energies of states with different occupation numbers for the two spin directions, predicts ferromagnetism at 0°K whenever $k\theta' > 2\epsilon_0/3$. The criteria for the two kinds of stability are thus surprisingly close to each other.

One is tempted at this point to try to pick numerical values of m^*, ϵ_0, and $k\theta'$ for nickel and compare the prediction of (33) with the experimental value $A = 8 \times 10^{-7}$ sec/cm[11,3] although one could hardly expect quantitative agreement with so crude a model. Wohlfarth[9] suggests $\epsilon_0 = 0.17$ ev, $k\theta'/\epsilon_0 = 0.8$, values which when combined with $N = 0.6 \times$ number of atoms give 2.7×10^{-7} erg/cm for the product of the first two factors in (33), and 0.2 for the third factor. Alternatively, Slater[12] has attempted to evaluate the ferromagnetic properties of nickel *a priori;* his results, if interpreted in terms of the Stoner model, correspond to $\epsilon_0 = 0.24$ ev, $k\theta'/\epsilon_0 = 0.73$, values not far different from Wohlfarth's. However, the model used in Slater's calculation differs in one important respect from the Stoner model, in that the top of the d band is not a single state, but is highly degenerate, so that the holes occupy overlapping bands centered on different points of the Brillouin zone. It follows that the model used in deriving (33) is even cruder than one might at first suppose, since in addition to the error involved in assuming (25) and (30) there is undoubtedly a large error in assuming the relation of N, ϵ_0, and $\nabla^2\lambda_k$ to be the same as for free particles of some effective mass m^*. Correction of this error might well increase the computed A several times. While it is gratifying that a crude interpretation of Slater's calculations seems to lead to an A value of the right order of magnitude without use of any empirical parameters relating to the magnetic or electronic structure of nickel, it is obvious that such comparisons as we have been making cannot at present provide any quantitative evidence pro or con regarding the validity of the band picture.

VI. THE CASE OF FREE ELECTRONS

A gas of perfectly free electrons is known to be ferromagnetic in the self-consistent field approximation,[13] although an exact calculation of its ground state would probably show it to be nonferromagnetic.[14] As an essentially exact calculation of the Bloch wall coefficient A was given in I for free electrons in the self-consistent field approximation, it is of interest to show that the equations of the present paper coincide with those of I for this case, in spite of the different approach. This comparison provides an explicit illustration of the fact, physically obvious but mathematically less so, that one comes out with the same A regardless of whether one considers a complete reversal of the spin direction over the dimensions of a large specimen, as was done in I, or considers, as here, a truly infinitesimal perturbation of the spin orientations, i.e., one involving a change $\ll$ one unit in the total spin of the crystal.

The assumptions made in the previous sections as far as Eq. (29) are all valid for free electrons, within the limitations of the self-consistent field approximation. So to carry this approximation through rigorously for free electrons we only need to substitute into (29) the proper values of J_{ij} and $\lambda_{[j]}$, *viz.*, in atomic units,

$$J_{ij} = 8\pi/\Omega|\mathbf{i}-\mathbf{j}|^2. \tag{34}$$

$$\lambda_{[j]} = j^2. \tag{35}$$

With these substitutions (29) is identical with Eq. (20) of I if we interchange the x and z directions and identify

$$b_k \quad \text{with} \quad \xi_k/|\nabla\bar{\varphi}|, \tag{36}$$

where $\nabla\bar{\varphi}$ was defined in I to be the mean gradient of spin orientation, and ξ_k was the angle between the spin of the **k**th electron and the plane in which the macroscopic direction rotates. We can easily verify that the

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[8] E. C. Stoner, Proc. Roy. Soc. (London) **A165**, 372 (1938); **A169**, 339 (1939), Rep. Progr. Phys. **11**, 43 (1946).

[9] E. P. Wohlfarth, Proc. Roy. Soc. (London) **A195**, 434 (1949).

[10] I am grateful to Dr. E. P. Wohlfarth for correcting an arithmetical error in this coefficient, and for pointing out that the similarity of the two criteria for stability of the Stoner model is to be expected in view of the similarity of the two criteria for the free electron model, as found in I, Sec. VII.

[11] M. Fallot, Ann. phys. **6**, 305 (1936).

[12] J. C. Slater, Phys. Rev. **49**, 537, 931 (1936).

[13] F. Bloch, Z. Physik **57**, 545 (1929).

[14] E. Wigner, Trans. Faraday Soc. **34**, 678 (1938).

identification (36) is consistent with the expression (23) for the spin direction of the $\mathbf{k}$th electron. For in (23) the mean spin is in the direction $\varphi=\pi/2$ (see Fig. 1). At a point where $\boldsymbol{\kappa}\cdot\mathbf{r}$ is a multiple of 2π the deviation of the $\mathbf{k}$th spin from the plane $\varphi=\pi/2$ is the semi-minor axis of the ellipse of Fig. 1, equal to $4b_kR/\kappa$. Since at such a point the gradient of mean spin direction, $d\theta/dx$, is κ times the semi-major axis of the ellipse, we have

$$\text{semi-minor axis}=b_k d\theta/dx,$$

in agreement with (36). Finally, one can easily show, by using (18), (27), (28), (35), and (36), that (21) gives the same A as Eq. (25) of I.

It is interesting to consider the consequences of making the additional approximation $J_{ij}=J/N$ independent of $\mathbf{i}$ and $\mathbf{j}$, as was done in the preceding section, instead of using the correct expression (34). Two possible choices of J are the choice which gives the total exchange energy the correct value, and that which gives the correct difference in exchange energy between the magnetic and nonmagnetic states. Use of the former choice in (33) gives

$$A=(N/4\Omega)(1-0.267\pi k_{\max}), \tag{37}$$

while the latter choice gives

$$A=(N/4\Omega)(1-0.647\pi k_{\max}). \tag{38}$$

These may be compared with the correct value given by Eq. (26) or (27) of I, *viz.*,

$$A=(N/4\Omega)(1-0.7217\pi k_{\max}). \tag{39}$$

It will be seen that (38) is much superior to (37) and is in fact a surprisingly good approximation.

VII. RELATION TO SPIN WAVES

It was shown in reference 3 that, if Ψ_w designates the eigenfunction of the entire system of ferromagnetic electrons in the presence of the sinusoidal perturbation (2), the Ψ_w of a ferromagnetic insulator is asymptotically equal to the unperturbed ground-state eigenfunction Ψ_0 plus R/κ^2 times a linear combination of the two states $\Psi_{\pm\kappa}$ derivable from Ψ_0 by excitation of a single spin wave of wave vector $\pm\boldsymbol{\kappa}$. This means that for an insulator the wave function $\partial\Psi_w/\partial R$ is, in the limit $\kappa\rightarrow 0$, an excited eigenfunction of the unperturbed system, of the nature of a spin wave. It is, therefore, of interest to study the properties of $\partial\Psi_w/\partial R$ for a metal, where the other theories of spin waves are inapplicable, to see to what extent it is legitimate to regard this function as an eigenfunction of the system, of the spin wave type. Of course, the approach of the present paper is seriously limited, in that we have considered only determinantal approximations to Ψ_0 and Ψ_w; nevertheless, it is natural to hope that many qualitative properties of our approximate $\partial\Psi_w/\partial R$ may also be possessed by the true $\partial\Psi_w/\partial R$.

It is clear that if Ψ_w is normalized to unity independently of the perturbation amplitude R, the function $\partial\Psi_w/\partial R$ is orthogonal to Ψ_0, hence a linear combination of excited eigenfunctions. Its mean energy $\bar{E}$ is related to the energy change ΔE produced by the perturbation (2), since to the second order in R the mean of the unperturbed Hamiltonian H in the state $\Psi_w\sim\Psi_0+R\partial\Psi_w/\partial R$ is

$$\bar{E}_w=(E_0+R^2C\bar{E})/(1+R^2C), \tag{40}$$

where E_0 is the ground-state energy and C is the normalization integral of $\partial\Psi_w/\partial R$. Now to the second order in R the energy $\bar{E}_w$ lies above E_0 by the same amount that the energy of Ψ_w with the perturbed Hamiltonian lies below it. Equating (40) accordingly to $E_0-\Delta E$, where ΔE is given by (3), and solving for $\bar{E}$, we get

$$\bar{E}=E_0-\Delta E/R^2C. \tag{41}$$

This relation, though derived for the case where Ψ_0 and Ψ_w are true eigenfunctions of their respective Hamiltonians, is equally valid when E_w and E_0 represent the energies of the best determinantal approximations to the eigenfunctions, since the form of Peng's second-order energy expression (Eq. (B.4) of Appendix B) shows that even in the self-consistent field approximation the first-order wave function determines the second-order energy.

To evaluate (41) using the determinantal form for Ψ_w derived in Sec. III, we note first of all that as $\kappa\rightarrow 0$, (5), (9), and (15) give

$$C=\sum_i[|U_i^+|^2+|U_i^-|^2]\sim 2N|U^0|^2/\kappa^4.$$

Inserting this into (41) and using (17) for U^0 and (20) for ΔE we get

$$\bar{E}-E_0=\kappa^2\sum_{i,j}(\Phi_{ji}''-b_j^*\Phi_{ji}^0 b_i)/N=(4\Omega A/N)\kappa^2, \tag{42}$$

by (21). That the simplifying assumptions used in Secs. II and III are not responsible for this result can be shown by using in (41) the C and ΔE obtainable from the more general treatment of Appendix B, and noting that the same expression (42) results.

The field theory of spin waves developed in reference 3 gives an expression for the energy of a spin wave of wave number $\boldsymbol{\kappa}$ which is identical with (42). This coincidence of energies is more than merely suggestive of the validity of the field theory and the legitimacy of regarding $\partial\Psi_w/\partial R$ as an eigenfunction of the spin wave type. For if (42) is valid for the true eigenfunctions Ψ_w as well as for the determinantal approximations, the reasoning given in Sec. IIIC of reference 3 shows that an expansion of $\partial\Psi_w/\partial R$ in terms of eigenfunctions of the unperturbed Hamiltonian must consist almost entirely of states whose energies above the ground state differ from (42) by an amount which is $\ll$(42).

The characterization of $\partial\Psi_w/\partial R$ as a spin-wave state is supported by consideration of some of its other properties. In the present determinantal approximation the normalized state $\partial\Psi_w/\partial R$ is of the form

$$C^{-\frac{1}{2}}\partial\Psi_w/\partial R=2^{-\frac{1}{2}}(\Psi_\kappa-\Psi_{-\kappa}), \tag{43}$$

where Ψ_κ is a linear combination of all the wave functions $\Delta_\kappa(\mathbf{k})$ derivable from Ψ_0 by removing an electron from some singly-occupied state of wave vector $\mathbf{k}$ and putting it in a state of opposite spin with wave vector $\mathbf{k}+\boldsymbol{\kappa}$, the coefficients of all these wave functions being equal to within an error of order $\boldsymbol{\kappa}$. The functions $\Psi_{\pm\kappa}$ obviously correspond to spin waves of wave vectors $\pm\boldsymbol{\kappa}$, respectively. All the determinantal states $\Delta_\kappa(\mathbf{k})$ have mean energies above the ground state of the order of the exchange energy of an electron, a quantity which is $\gg$(42) when $\boldsymbol{\kappa}$ is small. Thus all the $\Delta_\kappa(\mathbf{k})$ are orthogonal to all the determinantal states derivable from the ground state by exciting one or a number of electrons with a total energy of excitation of the order of (42). The spin wave states are, therefore, orthogonal to all the states of comparable excitation energy which are considered in the conventional itinerant electron model. Moreover, it is easy to verify that when the state of the system is a linear combination of the ground state and one of these spin-wave states with a coefficient of the form $\exp(i\omega t)$, the mean spin direction in each region of the specimen precesses in time around a narrow cone, just as it would for the well-known spin-wave states of an insulator. Finally, as will be shown in detail in the next section, when the singly-occupied states completely fill a band the spin-wave states obtained from $\partial\Psi_w/\partial R$, using the approximations of this paper, reduce to those which are already familiar for insulators.

The preceding discussion suggests that approximate representations of states with several spin waves excited can be obtained by taking linear combinations of states derived from Ψ_0 by reversing the spins of several electrons, changing the wave vector of each by the wave vector of one of the spin waves. These states, like the singly-excited states just considered, will be independent of the low-lying excited states of the conventional itinerant electron model.

The present theory of spin waves in a metal predicts for them a property not possessed by the more familiar spin waves in an insulator, namely, that of carrying a current. From what has been said following Eq. (43), the spin wave eigenfunction is, in the approximation of Sec. III,

$$\Psi_\kappa=N^{-\frac{1}{2}}\textstyle\sum_j[1+\kappa b_j+O(\kappa^2)]\Delta_\kappa(\mathbf{j}), \tag{44}$$

where b_j is defined by (18). The total current operator I has no matrix elements connecting different ones of the determinants $\Delta_\kappa(\mathbf{j})$, and its mean value in the state $\Delta_\kappa(\mathbf{j})$ is $I_{j+\kappa}-I_j$, where I_j is the mean current of the one-electron state ψ_j. Therefore, the mean current of the spin-wave state is

$$\begin{aligned}(\Psi_\kappa,I\Psi_\kappa)&=N^{-1}\textstyle\sum_j[1+2\kappa\,\mathrm{Re}(b_j)](I_{j+\kappa}-I_j)+O(\kappa^3)\\&=N^{-1}\boldsymbol{\kappa}\cdot\textstyle\sum_j\nabla I_j+O(\kappa^3),\end{aligned} \tag{45}$$

since b_j is an odd function of $\mathbf{j}$ while ∇I_j is even. The differentiations in ∇ are, of course, with respect to the wave vector $\mathbf{j}$. For an insulator $\sum_j\nabla I_j$ vanishes, since the summation is over a full band, but for a metal it does not. Thus for a metal Eq. (45) will usually give a current of the same order as the current carried by an electron of the ferromagnetic band with wave vector $\boldsymbol{\kappa}$.

The present calculation seems to refute the claim made by Bogolyubov and Tyablikov[6] to the effect that the current is nonvanishing when the ground state has a full band of ferromagnetic electrons. For, if I understand their calculation correctly, they obtain this result for a spin-wave eigenfunction of the Bloch type, i.e., a linear combination of states derived from the ground state by reversing the spin of the electron in one of the atomic states. This eigenfunction is a special case of those considered in the present paper.

VIII. RELATION TO SLATER'S THEORY

The relation (42) enables us to calculate A if the spin wave energies are known, or to calculate the spin wave energies, to the first order in κ^2, if A is known. Since Slater[5] has given a method for the calculation of spin-wave energies for a ferromagnetic insulator, it is natural to ask how Slater's method is related to the methods of the present paper. Slater assumed the ground-state wave function Ψ_0 to be of determinantal form, and approximated the wave function Ψ_κ for a spin wave by a linear combination of the N^2 states obtainable from Ψ_0 by removing an electron from one of the N-occupied states, say the ith, and placing it, with reversed spin, in some state having the same orbital-wave function as some one of the initially occupied states, say the jth. In this section we shall begin by proving that the use of any such linear combination for Ψ_κ is equivalent to the use of a determinantal form for the wall functions Ψ_w related to the Ψ_κ by (43), at least to terms of the first order in the perturbation amplitude R.

The theorem which we shall prove first is actually a little more general than is required for application to Slater's work. It may be stated thus: Let Ψ_0 be a determinantal wave function, Φ_n any determinantal wave function constructed from Ψ_0 by removing an electron from some one-electron state and placing it in another, and let Φ be any linear combination of the Φ_n. Then the state $\Psi_0+\epsilon\Phi$ coincides with a certain determinantal wave function $\Psi_w(\epsilon)$ to within a difference of order ϵ^2 as $\epsilon\rightarrow 0$. The index n may have a discrete or continuous range, and the new one-electron state involved in Φ_n is not restricted to have any special relationship to those involved in Ψ_0.

The proof is very simple if we consider what at first sight seems to be a special case, namely, where each Φ_n is obtained by replacing the state ψ_n of the initially occupied set by a different state φ_n. The state $\Psi_0+\epsilon c_1\Phi_1$ is then a determinantal wave function differing from Ψ_0 in having the ψ_1 of the first column replaced by $\psi_1+\epsilon c_1\varphi_1$. The state $\Psi_0+\epsilon c_1\Phi_1+\epsilon c_2\Phi_2$, though not exactly of determinantal form, coincides to the first order in ϵ

with the determinantal wave function obtained from Ψ_0 by replacing ψ_1 by $\psi_1+\epsilon c_1\varphi_1$ and ψ_2 by $\psi_2+\epsilon c_2\varphi_2$. This can be continued to show that $\Psi_0+\epsilon\Phi$ is determinantal to the first order in ϵ.

To construct a general mathematical proof it is only necessary to show that no matter how many Φ_n's there are in the expression for Φ, this expression is always equivalent to one of the sort considered in the preceding paragraph. This can be done by using the creation and annihilation operators of quantized wave theory.[15] If $a(\psi)$ is the operator removing an electron from the one-electron state ψ, and $a^+(\varphi)$ is the operator introducing an electron into the state φ, the most general possible form for the wave function Φ mentioned in the theorem would be obtained by operating on Ψ_0 with an operator of the form

$$\sum\nolimits_{\varphi,\psi} B(\varphi,\psi)a^+(\varphi)a(\psi),$$

with φ and ψ completely unrestricted except for the requirement that ψ be initially occupied, φ initially empty. However, since any a or a^+ can be expressed as a linear combination of the corresponding operators going with any orthonormal set of wave functions, this operator can always be written in the form

$$\sum\nolimits_i c_i a^+(\varphi_i)a(\psi_i),$$

where the ψ_i are any orthonormal set spanning the initially occupied subspace, and the φ_i are a suitably chosen set of initially empty states, not necessarily orthogonal to each other. In the latter form the operator gives a wave function Φ of the form used in the preceding paragraph.

Note that no analogous theorem can be proved for the case where Φ contains terms involving two or more substitutions in Ψ_0, since linear combination of two determinants which differ in more than one column does not, in general, give a determinant.

It is now clear that, as far as spin waves of long wavelength are concerned, Slater's theory of spin waves must be a special case of that given here. Since Slater[5] has shown that the results obtained in earlier theories of spin waves, using the atomic approach, are included in those obtainable from his approach, these earlier theories are also special cases of the present treatment. However, the present approach is very different from Slater's and it is an interesting mathematical exercise to show that Slater's final energy expression is really identical with that obtainable from our Eq. (21) or Eqs. (B.8) and (B.9) of Appendix B. The details of this correspondence will not be given here; it will suffice merely to call attention to the formal similarity of the two terms in Slater's Eq. (31) to the two terms of our (B.9). To the accuracy of Slater's tight binding approximation this similarity can be shown to be an actual quantitative identity of each species of term, factor by factor.

Although the reasoning just mentioned illustrates in detail the equivalence of Slater's approach to that of this paper for a ferromagnetic insulator, it is worth noting that for the case of a metal, which Slater did not discuss, our expression (21) for A contains terms of quite a different physical nature from the two terms in Slater's Eq. (31). For in the verification of the correspondence of our results with Slater's it is necessary to use the fact that the second derivative of the energy parameter with respect to wave vector vanishes when summed over all states $\mathbf{i}$ and $\mathbf{j}$ in a filled band; if a partly filled band is present, as in a metal, this term will give a large contribution to our expression (21) for A, perhaps even larger than that given by Slater's whole expression.

This essential difference between filled and partly filled bands can be illustrated more concretely by considering the free electron problem. One might at first suppose that Slater's approach could be used for the free electron problem by replacing the actual ground state of this problem by a state in which almost-free electrons exactly fill a Brillouin zone, i.e., by starting as in the atomic-model calculations of Sec. VI of I and then improving the energy by Slater's method. But this would give completely wrong results: The correct solution of the wall problem for free electrons leads, as we have seen, to a determinantal wave function each of whose one-electron components is a linear combination of an originally occupied plane wave state of wave vector $\mathbf{k}$ and the states of opposite spin with wave vectors $\mathbf{k}\pm\boldsymbol{\kappa}$. Some of the latter would lie outside the hypothetical Brillouin zone just mentioned, and so one could not get anything resembling the correct wave function by Slater's method. The omission of terms containing plane waves outside the Brillouin zone is in fact the root of the fact that the approach used in Sec. VI of I gave such a poor approximation to A for free electrons.

APPENDIX A. EFFECT OF REDISTRIBUTION OF OCCUPATION NUMBERS

We wish to show that in the presence of the perturbation (2) the energy of the state with the same occupation numbers as the unperturbed ground state differs from the energy of the state with optimum choice of occupation numbers only by an amount of higher order than the second in the amplitude R of the perturbation. This will clearly be the case if it can be shown that the one-electron energies λ_i are unchanged to the first order by the perturbation, since the energy lowering which can be achieved by reshuffling is of the second order in the changes of the λ_i. The absence of first-order changes in the λ_i can easily be established. For it is clear that the self-consistent field solutions for R and $-R$ will be taken into each other by rotation of all spins through 180° about the z-axis, an operation represented by the Pauli matrix $i\sigma_z$ for each electron. We can, therefore, choose the one-electron functions ψ_j in such a way that they

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[15] P. Jordan and E. Wigner, Z. Physik **47**, 631 (1928).

depend continuously on R and satisfy

$$\psi_j(-R)=\omega_j\sigma_z\psi_j(R),$$

where $\omega_j=1$ for states which for the unperturbed system have the majority spin direction, and $=-1$ for the remaining states. The Coulomb and exchange operators in the one-electron Hamiltonian contain terms of the first order in R, and the diagonal matrix elements of these first-order operators, relative to the $\psi_i^{(0)}$, consist of terms of the same form as the first-order parts of the Coulomb and exchange integrals formed from a pair of states $\mathbf{i}$, $\mathbf{j}$. But each of the latter integrals has the same value for R and $-R$ since $|\omega_i|^2|\omega_j|^2=1$, and so the diagonal elements of the first-order operators must vanish. Since the diagonal elements of K also vanish, there can be no first-order term in any λ_i unless the perturbation connects two states of opposite spin with the same energy. This cannot occur for the model considered in the text, and for the more general cases considered in Appendix B it can occur at most for a number of states which is infinitesimal as $R\rightarrow 0$.

In applying the same sort of argument to problems other than the one considered in this paper, it should be borne in mind that the proof just given is valid only for cases where the diagonal elements of K vanish. Moreover, it may sometimes be possible to solve what is essentially one and the same physical problem in two different ways, one of which may involve a reshuffling of occupation numbers while the other does not. An example is the problem of computing the paramagnetic susceptibility χ of an assembly of free electrons which in the unperturbed state contains electrons of plus and minus spin in equal numbers. The familiar solution of this problem involves subjecting the assembly to a constant magnetic field H and computing the changes in occupation numbers of the states with plus and minus spin. It can be shown, however, that the same value of χ can be computed from the changes in the wave functions of the occupied states induced by a perturbing magnetic field of the form $H=H_0 \sin\boldsymbol{\kappa}\cdot\mathbf{r}$, without any change in occupation numbers. This is because the sinusoidally varying field corresponds to a K whose diagonal matrix elements all vanish, while the constant magnetic field does not.

APPENDIX B. CALCULATION OF A WITHOUT SIMPLIFYING ASSUMPTIONS

Results formally similar to (21) and (18) can be proved to hold for the rigorous solution of the Bloch wall problem in the self-consistent field approximation. In other words, it is not necessary to assume wave functions of opposite spin to have the same orbital parts, or to assume the perturbed wave functions to be of the form (5). The argument will be sketched very briefly here, primarily for the purpose of showing that (42) is always satisfied rigorously by a self-consistent field solution.

A convenient starting point is provided by the equations of Peng[4] for the alteration of a solution of Fock's equations by an external perturbation. Let the perturbed wave function of the ith state be written

$$\psi_i=\psi_i^{(0)}+R\sum\nolimits_\mu U_{\mu i}\psi_\mu^{(0)}, \tag{B.1}$$

where $\boldsymbol{\mu}$ runs over all empty states of spin opposite to $\mathbf{i}$. (Compare (5) of the text.) Peng's equations to determine the $U_{\mu i}$ are the generalization of (7) of the text, and are, in our notation,

$$\begin{aligned}-K_{\alpha j}=(\lambda_\alpha-\lambda_j)U_{\alpha j}+\sum\nolimits_{i,\mu}[(G_{\alpha\mu ij}-G_{\alpha\mu ji})U_{\mu i}^*\\+(G_{\alpha i\mu j}-G_{\alpha ij\mu})U_{\mu i}],\end{aligned} \tag{B.2}$$

where here and below it is to be understood that Greek suffixes run over empty states, Latin suffixes over filled states, and where the $G_{\alpha\mu ij}$ are Coulombic integrals of the form

$$\begin{aligned}G_{\alpha\mu ij}=\int\int\psi_\alpha^{(0)*}(\mathbf{r})\psi_\mu^{(0)*}(\mathbf{r}')\\\times\left(\frac{2}{|\mathbf{r}-\mathbf{r}'|}\right)\psi_j^{(0)}(\mathbf{r})\psi_i^{(0)}(\mathbf{r}')d\tau d\tau'.\end{aligned} \tag{B.3}$$

The second-order energy is given by

$$\lim_{R\rightarrow 0}\Delta E/R^2\equiv E^{(2)}=\mathrm{Re}\sum_{\mu,j}K_{j\mu}U_{\mu j}. \tag{B.4}$$

where Re means "real part of" [compare (19) of the text].

Our first step is to show that for the present problem (B.2) can be written symbolically in a form similar to the second Eq. (7) of the text, namely,

$$-K=\Phi U, \tag{B.5}$$

K and U being conceived as vectors, or one column matrices, whose components are labeled by indices $\mathbf{k}$, n, $\pm$, where $\mathbf{k}$ refers to the second suffix of a matrix element such as $U_{\mu k}$, n labels the band in which $\boldsymbol{\mu}$ lies, and $\mathbf{k}\pm\boldsymbol{\kappa}$ is the reduced wave vector of $\boldsymbol{\mu}$. The legitimacy of (B.5) is not at first obvious, since the first G term of (B.2) contains $U_{\mu i}^*$ instead of $U_{\mu i}$. However, we can show that (B.5) is justified for the particular case we are considering, where K is $\sigma_y \sin\kappa x$. Suppose for the moment that we have chosen a basis $\psi_i^{(0)}$ consisting entirely of real functions of the coordinates multiplied by the spin functions α or β. This can always be done, since the one-electron Hamiltonian is real. Then all the G's in (B.2) will be real, and all $K_{\alpha j}$ will be imaginary. Therefore, if we make the solution unique by requiring, as in Sec. 4, that the mean spin lie in the y–z plane, all the $U_{\mu j}$ must be imaginary, and relative to this basis we can replace $U_{\mu i}^*$ in (B.2) by $-U_{\mu i}$. A matrix equation of the form (B.5) will then hold relative to this basis, and by transformation an equation of the same form can be derived relative to any other basis. However, in using (B.5) we must remember that it is equivalent to (B.2) only when $U_{\mu i}$ represents an operator which takes real wave functions into imaginary ones. A simple analysis, which we omit, shows that the matrix describing Φ is Hermitian, i.e., that

$$\Phi_{kn\pm,\,k'n'\pm'}=\Phi_{k'n'\pm',\,kn\pm}{}^{*}.$$

The matrix, or operator, Φ and the "vector" U will of course depend on the wave vector $\boldsymbol{\kappa}$ of the perturbation, and can be expanded in power series analogous to (9) and (10). As $\kappa\rightarrow 0$, Φ approaches a limit Φ^0, and the invariance of the energy with respect to rigid rotations of the spin system requires that one of the eigenvalues of Φ^0 must be zero. It is not hard to show that, if the unperturbed system has no degeneracy other than that associated with spin rotations, the null eigenvalue has only the multiplicity two corresponding to two eigenvectors $u_1{}^0$, $u_2{}^0$ which may be specified to have the properties

$$(u_1{}^0)_{jn+}=-(u_1{}^0)_{jn-},\quad (u_2{}^0)_{jn-}=(u_2{}^0)_{jn+}. \tag{B.6}$$

If $\omega_p(\boldsymbol{\kappa})$ are the eigenvalues of $\Phi(\boldsymbol{\kappa})$ and $u_p(\boldsymbol{\kappa})$, the corresponding normalized eigenvectors, we can write the solution of (B.5) in the form

$$U=-\Phi^{-1}K=-\textstyle\sum_p(u_p,K)u_p/\omega_p. \tag{B.7}$$

Of the two eigenvectors u_1, u_2 whose eigenvalues ω_1, $\omega_2\rightarrow 0$ as $\kappa\rightarrow 0$, only the eigenvector u_1 will have in the limit a nonvanishing scalar product with K. As $\kappa\rightarrow 0$, all terms of the summation (B.7) except the one $p=1$ will be bounded; since we are interested only in the leading term in the energy as $\kappa\rightarrow 0$, which involves only the part of U which goes as $1/\kappa^2$, we can ignore the terms $p>1$. For the same reason we can replace $u_1(\boldsymbol{\kappa})$ by $u_1(0)=u_1{}^0$ in the numerator. By (B.4) the second-order energy is therefore, to order $1/\kappa^2$,

$$\Delta E/R^2=-|(K,u_1{}^0)|^2/\kappa^2\omega_1'', \tag{B.8}$$

where ω_1'' is the coefficient of κ^2 in the expansion of ω_1 in powers of κ. (The first-order coefficient ω_1' vanishes by symmetry.) Combination of (B.8) with (3) gives a value for the Bloch wall coefficient A which is proportional to ω_1''.

In the present case the null eigenvector $u_1{}^0$, though no longer having all its components equal as in the approximation of Sec. III, can be shown from (8) to be of the form $(u_1{}^0)_{jn\pm}=\pm a(\sigma_x)_{\mu j}$, where $\boldsymbol{\mu}$ is the state of the nth band with the same wave vector as $\mathbf{j}$ but opposite spin, and a is a normalizing constant. A straightforward calculation, which we omit, shows that as $\kappa\rightarrow 0$ the vector K becomes parallel to $u_1{}^0$, so that the numerator of (B.8) reduces to $|a|^2N^2$, where N is the number of uncompensated spins in the crystal.

The result (42) of Sec. VII can be derived from (B.7) and (B.8) without further knowledge of how ω_1'' is determined. However, we can get some insight into the range of validity of the calculations of Sec. III by sketching how ω_1'' can be calculated in principle. One of the most obvious ways of doing this is to expand the operator Φ in powers of κ and use perturbation theory. This can be done provided we take account of the fact that the range of values assumed by the set of suffixes $\mathbf{j}n\pm$ depends on $\boldsymbol{\kappa}$, since we allow only values for which the state of the nth band with wave vector $\mathbf{j}\pm\boldsymbol{\kappa}$ is empty. This fact gives rise to additional terms in the perturbation expression for ω_1'', in the form of integrals over a surface in wave vector space. In terms of operators Φ'' and Φ' defined analogously to (10),

$$\omega_1''=(u_1{}^0,\Phi''u_1{}^0)-\sum_{p>2}|(u_1{}^0,\Phi'u_p{}^0)|^2/\omega_p{}^0 \\ +\text{surface integrals}, \tag{B.9}$$

where $u_p{}^0$ and $\omega_p{}^0$ are respectively the pth eigenvector and eigenvalue of Φ^0. Note that the unknown factor a cancels out of (B.8).

It is obvious from (B.9) that electronic states which may be approximately described as "doubly occupied" have very little influence on the value of ω_1'', since the $\mathbf{j}n\pm$ component of $u_1{}^0$ is very small when j is such a state, while the surface integrals involve only regions of $\mathbf{j}$ space bordering the "singly-occupied" levels. The electron-hole reciprocity assumed in applying the results of Sec. III to a metal such as Ni can be justified by similar reasoning.