Exchange Energy of an Electron Gas in a Periodic Potential

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We have derived general formulas for the exchange energy of an electron gas in a periodic potential, and for $E_{ex}(\mathbf{k})$, the "exchange energy of a single electron as a function of k." We evaluate these, with some approximations, for S-like bands; for $E_{ex}(\mathbf{k})$ we get

$$E_{ex}(\mathbf{k}) = [E_{ex}(\mathbf{k})]_{\text{free elect.}} - \frac{e^2 k_0}{\pi} \sum_{K_s \neq 0} n_s R^2(K_s) g\left(\frac{K_s}{k_0}, \frac{k}{k_0}\right),$$

where K_s is the magnitude of a reciprocal lattice vector, n_s is the number of vectors with that magnitude, $R(K_s)$ is a function which is derived from the wave functions of a single electron in the lattice, and $g(K_s/k_0, k/k_0)$ is calculated in the paper. The main conclusion of the paper is that even if $R(K_s)$ derives from a wave function which is far from a plane wave, the function $g(K_s/k_0, k/k_0)$ drops off so quickly as a function of K_s that for many practical cases, essentially the only contribution to the exchange energy comes from the plane wave component corresponding to $K_s = 0$. Thus, the plane wave expression for the exchange energy has a larger range of validity than might appear at first sight. A numerical evaluation of the total exchange energy is carried out for sodium.

I. INTRODUCTION

IN the theory of metals, it is well known[1] that if one neglects electron interactions, and uses free-electron wave functions to calculate metallic properties, one often gets good qualitative agreement with experiment. This agreement is frequently improved if one takes electron interactions into account using first-order perturbation theory and unsymmetrized (Hartree) wave functions. If one goes a step further, however, and calculates using antisymmetrized (Hartree-Fock) wave functions, then at least in one important respect, the agreement is impaired. That is, upon evaluating $E_{ex}(\mathbf{k})$, the "exchange energy as a function of k," one finds that the derivative of this function at the Fermi level is infinite. This implies that the level density goes to zero at the Fermi level, and this worsens the agreement with experiment for such properties as specific heat, paramagnetic susceptibility, etc.

Wigner[2,3] suggested that the above unhappy result might be improved by taking into account "correlation effects," i.e., by using wave functions which took into account the electron-electron repulsions more accurately than do the free-particle wave functions. The work of Bohm and Pines, Gell-Mann and Brueckner, and many others[4] on the free electron gas shows that this is correct; the inclusion of correlation effects does indeed improve the situation.

Nonetheless, one might well ask whether the same desirable result might be found in another direction. That is, the free electron model is unrealistic in at least one other respect besides that of neglecting the mutual

repulsion of the electrons: It neglects the periodic potential in which the electrons are assumed to move. Is it not possible then that we might improve agreement with experiment if we made the model more realistic by taking into account this periodic potential? This is one of the questions that this paper treats. The answer we find is: in principle, yes; in practice, no. That is, we find that taking the periodic potential into account, we do get an effect in the density of states which is such as to weaken the effect of the free particle singularity of dE_{ex}/dk in the neighborhood of the Fermi level. In practice, however, this seems to be too small numerically to restore agreement with experiment for the quantities mentioned above.

Aside from this question, it would clearly be useful to have general expressions for the total exchange energy in a periodic potential, and to investigate the possibility of evaluating these practically. There have been previous such evaluations,[5] but usually they have depended on special assumptions (e.g., tight binding) or on the assumption of special forms for the wave function. In this paper, we try to evaluate these expressions as generally as possible, and try to make clear the approximations that must be used in reducing the general expressions to practical ones that can be evaluated for specific substances.

II. INDEPENDENT ELECTRONS

In this section we shall write, for reference, some well-known formulas for a gas of n independent (i.e., not mutually interacting) electrons. These results, and the notation, are mainly taken from the book by Seitz.[6]

We assume that the electrons move in some common potential for which the one-electron Schrödinger equa-

[1] For a general review and an amplification of the remarks of this Introduction, as well as for extensive references, see D. Pines, in *Advances in Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1955), Vol. 1.

[2] E. P. Wigner, Phys. Rev. 46, 1002 (1934).

[3] E. P. Wigner, Trans. Faraday Soc. 34, 678 (1938).

[4] For references, see: *The Many Body Problem*, edited by D. Pines (W. A. Benjamin, Inc., New York, 1961).

[5] For a summary see: J. Reitz, in *Advances in Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1955), Vol. 1.

[6] F. Seitz, *Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940).

tion is soluble. Then for the assemblage, a general anti-symmetric wave function Ψ has the form

$$\Psi = \sum_P (-)^p P[\phi_1(1) \cdots \phi_n(n)], \qquad (1)$$

where $\phi_i(j)$ stands for a one-electron wave function consisting of a space function ψ_i (normalized to unity) times a spin function η_i:

$$\phi_i(j) = \psi_i(r_j)\eta_i(\zeta_j).$$

The probability $P(\mathbf{r}_1,\mathbf{r}_2)$ that one electron will be at $\mathbf{r}_1$ and the other at $\mathbf{r}_2$ is then

$$P(\mathbf{r}_1,\mathbf{r}_2) = \frac{1}{n(n-1)} \Big[\sum_{i,j}' |\psi_i(\mathbf{r}_1)|^2 |\psi_j(\mathbf{r}_2)|^2$$
$$- \tfrac{1}{2} \sum_{i,j}' \psi_i^*(\mathbf{r}_1)\psi_j^*(\mathbf{r}_2)\psi_i(\mathbf{r}_2)\psi_j(\mathbf{r}_1) \Big]. \quad (2)$$

A prime in a sum above means to omit the term $i=j$, but we can also choose to include it, providing we include it in both sums, since the terms for $i=j$ in the two sums are identical, and hence, cancel. In the special and well-known case of electrons in a box of volume $V=L^3$ with periodic boundary conditions (free electrons), the wave functions are

$$\psi_k = \frac{1}{\sqrt{V}} e^{i\mathbf{k}\cdot\mathbf{r}}, \quad \mathbf{k} = 2\pi\mathbf{m}/L,$$

where $\mathbf{m}$ is a vector with integral components. For this case, the formal index i in Eq. (2) is replaced by $\mathbf{k}$ and the sum is replaced by an integration,

$$\sum_i \rightarrow \frac{V}{(2\pi)^3} \int d\mathbf{k}.$$

Then

$$P(\mathbf{r}_1,\mathbf{r}_2) = \frac{4}{n(n-1)(2\pi)^6} \int \int (1 - \tfrac{1}{2}e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}}) d\mathbf{k}d\mathbf{k}', \quad (3)$$

where the integrals are over the interior of the Fermi sphere,[7] $|\mathbf{k}| < k_0 = (3\pi^2 n/V)^{1/3}$ and $\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$. The result of this last integration is well known; with $n \approx n-1$, it is

$$P(\mathbf{r}_1,\mathbf{r}_2) = \frac{1}{V^2} \Big[1 - \frac{9}{2} \frac{j_1^2(k_0 r)}{(k_0 r)^2} \Big]. \quad (4)$$

We see that the correlation function $P(\mathbf{r}_1,\mathbf{r}_2)$, for the system of electrons in a box, depends only on $\mathbf{r}$. For other systems, this will not necessarily be so. For future reference then, it is useful to imagine a center-of-mass coordinate $\mathbf{R} = (\mathbf{r}_1 + \mathbf{r}_2)/2$ introduced into (2) in addition to the coordinate $\mathbf{r}$ and to define the relative distribution function $p(\mathbf{r})$

$$p(\mathbf{r}) = \int P(\mathbf{r}_1,\mathbf{r}_2) d\mathbf{R} \equiv \int P(\mathbf{R}+\tfrac{1}{2}\mathbf{r}, \mathbf{R}-\tfrac{1}{2}\mathbf{r}) d\mathbf{R}. \quad (5)$$

For free electrons, we then have[8]

$$p(\mathbf{r}) = \frac{1}{V} \Big[1 - \frac{9}{2} \frac{j_1^2(k_0 r)}{(k_0 r)^2} \Big],$$

which differs trivially from (4), but in general the conceptual difference between $p(\mathbf{r})$ and $P(\mathbf{r}_1,\mathbf{r}_2)$ is important.

The second term in the pair distribution (2) is the "exchange" term. The total exchange energy E_{exchange} is then the expectation value of e^2/r_{12} for this exchange pair distribution times $n(n-1)/2 \approx n^2/2$, the number of pairs of electrons. That is,

$$E_{\text{exchange}} = -\left(\frac{n^2}{2}\right)\frac{9}{2V}\int_0^\infty \frac{j_1^2(k_0 r)}{(k_0 r)^2}\left(\frac{e^2}{r}\right)4\pi r^2 dr, \quad (6)$$

whence,

$$E_{\text{exchange}}/n = -(9\pi n e^2/4k_0^2).$$

The exchange energy can also be written as

$$E_{\text{exchange}} = \frac{n(n-1)}{2} \Big[\frac{V}{(2\pi)^3} \int E_{\text{ex}}(\mathbf{k}) d\mathbf{k} \Big], \quad (7)$$

where $E_{\text{ex}}(\mathbf{k})$ is the "exchange energy of a single electron as a function of $\mathbf{k}$", defined as

$$E_{\text{ex}}(\mathbf{k}) = -\frac{e^2}{2(2\pi)^3} \int \int \frac{e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}}}{r} d\mathbf{k}'d\mathbf{r}. \quad (8)$$

Integration yields the well-known result

$$E_{\text{ex}}(\mathbf{k}) = -\frac{e^2 k_0}{\pi} \Big\{ 2 + \frac{k_0^2 - k^2}{k_0 k} \ln\frac{|k_0+k|}{|k_0-k|} \Big\}. \quad (9)$$

If now we form dE_{ex}/dk we find that it has a logarithmic singularity at $k=k_0$; this implies that the density of states goes to zero at the Fermi level, with attendant difficulties which are discussed elsewhere.[1]

III. ELECTRONS IN A PERIODIC POTENTIAL; GENERAL FORMULAS

We take the one-electron wave functions $\psi_k(\mathbf{r})$ for the periodic potential as satisfying periodic boundary conditions on the walls of a box of large volume V. That is, we take

$$\psi_k(\mathbf{r}) = \frac{1}{\sqrt{V}} e^{i\mathbf{k}\cdot\mathbf{r}} u_k(\mathbf{r}), \quad (10)$$

where

$$u_k(\mathbf{r}) = \sum_i C_k(\mathbf{K}_i) e^{i\mathbf{K}_i\cdot\mathbf{r}}. \quad (11)$$

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[7] The factor of four on the right-hand side of (3), which factor maintains the normalization of $P(\mathbf{r}_1,\mathbf{r}_2)$, comes from the fact that there are two spin states for each space state, and that these states are included in defining the Fermi level.

[8] Formally, there is a slight difficulty here, in that $\int p(\mathbf{r})d\mathbf{r}$ should equal unity, but it is clear from the form of $p(\mathbf{r})$ that this integral is always slightly less than unity. The point is that over practically all the volume, which is, of course, considered to be much larger than the mean interparticle distance, the distribution function is $1/V$ so that $\int_V p(r)dr \approx 1$, to within terms of order (volume per particle/volume), that is, to within terms of order $1/n$.

It is useful to bear in mind the form this wave function takes in the free electron limit and in the tight-binding limit.[9] In the former case, the function $u_k(\mathbf{r})$ simply becomes unity, that is, the sum over reciprocal lattice vectors in (11) degenerates into one taken over only the first ($|\mathbf{K}_1|=0$) lattice vector. In the tight-binding limit, where the bands become infinitely narrow, we must set $\mathbf{k}=0$ and replace the sum over $\mathbf{K}_i$ by an integration over continuous vectors $\mathbf{K}$. In this case, $C_k(\mathbf{K}_i)$ goes into $C_a(\mathbf{K})$,[10] the Fourier transform of the atomic function which generated the band we are considering.

In accordance with the formulas of Sec. II, we assume the wave function ψ_k is normalized to unity over the volume V. If we have N unit cells (of Wigner-Seitz type) in this volume, this implies

$$\frac{N}{V}\int_{\substack{\text{unit}\\\text{cell}}} \sum_i \sum_j C_k^*(\mathbf{K}_i)C_k(\mathbf{K}_j)e^{i(\mathbf{K}_i-\mathbf{K}_j)\cdot\mathbf{r}}dv = 1.$$

Using the orthogonality relation

$$\int_{\substack{\text{unit}\\\text{cell}}} e^{i(\mathbf{K}_i-\mathbf{K}_j)\cdot\mathbf{r}}dv = \Omega\delta_{ij}, \tag{12}$$

where Ω is the volume of the unit cell, the normalization condition becomes

$$\sum_i |C_k(\mathbf{K}_i)|^2 = 1. \tag{13}$$

Now we discuss the distribution function $P(\mathbf{r}_1,\mathbf{r}_2)$. In the same way that (3) was derived, we get

$$P(\mathbf{r}_1,\mathbf{r}_2) = \frac{4}{n(n-1)(2\pi)^6}\int\int \{\,|u_k(\mathbf{r}_1)|^2|u_{k'}(\mathbf{r}_2)|^2$$

$$-\tfrac{1}{2}u_k^*(\mathbf{r}_1)u_{k'}^{\,*}(\mathbf{r}_2)u_k(\mathbf{r}_2)u_{k'}(\mathbf{r}_1)$$

$$\times\exp[i(\mathbf{k}\cdot\mathbf{r}_2+\mathbf{k}'\cdot\mathbf{r}_1-\mathbf{k}\cdot\mathbf{r}_1-\mathbf{k}'\cdot\mathbf{r}_2)]\}d\mathbf{k}d\mathbf{k}'. \tag{14}$$

From this we find the relative distribution $p(\mathbf{r})$, defined by (5). We get, using (12) and a change of variables,

$$p(\mathbf{r}) = \frac{1}{V}\int\int [1-\tfrac{1}{2}e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}}]$$

$$\times[\sum_j\sum_s\sum_l C_k(\mathbf{K}_j+\mathbf{K}_s)C_k(\mathbf{K}_j)$$

$$\times C_{k'}(\mathbf{K}_l+\mathbf{K}_s)C_{k'}(\mathbf{K}_l)e^{i\mathbf{K}_s\cdot\mathbf{r}}]d\mathbf{k}d\mathbf{k}'. \tag{15}$$

We can simplify the aspect of this by defining a new function $D(\mathbf{k},\mathbf{K}_s)$

$$D(\mathbf{k},\mathbf{K}_s) = \sum_j C_k(\mathbf{K}_j+\mathbf{K}_s)C_k(\mathbf{K}_j), \tag{16}$$

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[9] L. Eyges, Phys. Rev. 123 1673 (1961).
[10] Formally $C_k(\mathbf{K}_i) \to C_a(\mathbf{K}+\mathbf{k})$ in the tight-binding limit, but in fact k goes to zero in this limit (see reference 11).

and in terms of this, another characteristic function $F(\mathbf{k},\mathbf{k}',\mathbf{r})$ which recurs frequently:

$$F(\mathbf{k},\mathbf{k}',\mathbf{r}) = \sum_s D(\mathbf{k},\mathbf{K}_s)D(\mathbf{k}',\mathbf{K}_s)e^{i\mathbf{K}_s\cdot\mathbf{r}}. \tag{17}$$

We have then

$$p(\mathbf{r}) = \frac{1}{V}\int\int [1-\tfrac{1}{2}e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}}]F(\mathbf{k},\mathbf{k}',\mathbf{r})d\mathbf{k}d\mathbf{k}'. \tag{18}$$

Given $p(\mathbf{r})$ we can calculate $E_{\text{ex}}(\mathbf{k})$ and the total exchange energy in the same manner as for the free electron case. Thus,

$$E_{\text{ex}}(\mathbf{k}) = -\frac{e^2}{2(2\pi)^3}\int\int e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}}F(\mathbf{k},\mathbf{k}',\mathbf{r})d\mathbf{k}'d\mathbf{r}, \tag{19}$$

from which the total exchange energy can be derived using (7).

IV. EVALUATION OF THE GENERAL FORMULAS

Now we turn to the question of evaluating the general formulas of the last section for some specific cases. To do this, we must be able to compute the central function $F(\mathbf{k},\mathbf{k}',\mathbf{r})$. It is useful then to remark on some qualitative aspects of this function.

First, we make the obvious point that in the free-electron limit, when the potential vanishes, $F(\mathbf{k},\mathbf{k}',\mathbf{r})$ becomes unity.

$$F(\mathbf{k},\mathbf{k}',\mathbf{r}) \to 1, \quad \text{free electron limit.}$$

Let us then consider the opposite, tight-binding limit, when the lattice spacing goes to infinity. As we have noted, the function $C_k(\mathbf{K}_j)$ then goes over into $C_a(\mathbf{K})$, the atomic momentum space function from which the band was derived. Let $\phi_a(\mathbf{r})$ be the Fourier transform of this momentum space function.

$$\phi_a(\mathbf{r}) = \frac{1}{(2\pi)^{3/2}}\int C_a(\mathbf{K})e^{i\mathbf{K}\cdot\mathbf{r}}d\mathbf{K}. \tag{20}$$

Now, $\phi_a(\mathbf{r})$ represents the wave function of a single electron bound to some potential. If then we have two such electrons 1 and 2 (and neglect their mutual repulsion), the wave function for this system will be $\phi_a(\mathbf{r}_1)\phi_a(\mathbf{r}_2)$, and the corresponding probability distribution is just $|\phi_a(\mathbf{r}_1)|^2|\phi_a(\mathbf{r}_2)|^2$. From this, we get the probability distribution function for the *relative* coordinate r, which distribution we call $\chi(\mathbf{r})$.

$$\chi(\mathbf{r}) = \int |\phi_a(\mathbf{R}+\tfrac{1}{2}\mathbf{r})|^2|\phi_a(\mathbf{R}-\tfrac{1}{2}\mathbf{r})|^2d\mathbf{R}. \tag{21}$$

If now in Eq. (16) we replace $C_k(\mathbf{K}_i)$ by $C_a(\mathbf{K})$, insert the result in (17), replace sums by integrals, and use (20), then it is easy to prove that the right-hand side of (17) is just $\chi(\mathbf{r})$, and this is the result we sought.

$$F(\mathbf{k},\mathbf{k}',\mathbf{r}) \to \chi(\mathbf{r}) \text{ tight-binding limit.} \tag{22}$$

More generally, one would expect that for $\mathbf{r}$ small (with respect to the dimensions of the unit cell), $F(\mathbf{k},\mathbf{k'},\mathbf{r})$ resembles the atomic distribution $\chi(\mathbf{r})$, but that for larger r, it becomes a periodic function of $\mathbf{r}$.

So much for the tight-binding limit. Now we consider the general evaluation of $F(\mathbf{k},\mathbf{k'},\mathbf{r})$, with an eye to evaluating Eqs. (17), (18), and then $E_{\text{ex}}(\mathbf{k})$ and the total exchange energy. To calculate any of these, we must be able to do the integrals over $\mathbf{k}$ in Eqs. (7) and (8), and this means that the $\mathbf{k}$ dependence of $D(\mathbf{k},\mathbf{K}_s)$ must be somehow made explicit. One possibility, which enables at least partial progress, is to expand $D(\mathbf{k},\mathbf{K}_s)$ and $D(\mathbf{k'},\mathbf{K}_s)$ in Eq. (7) in spherical harmonics of the solid angles Ω_k and $\Omega_{k'}$ and then do the integrations over these solid angles. But this still leaves an integral over the *magnitudes* of $\mathbf{k}$ and $\mathbf{k'}$ and this cannot be done without knowing the complete k dependence of $D(\mathbf{k},\mathbf{K}_s)$. A more drastic approach, but one which leads to an analytic answer is to neglect the k dependence of $D(\mathbf{k},\mathbf{K}_s)$ completely, i.e. essentially expand it about $\mathbf{k}=0$. This is an approximation which is certainly good for narrow bands, for example, for the alkalies for which the effective mass is close to one, and it does lead to interesting qualitative results, so we shall discuss it in some detail. Also with an eye on the alkali metals, we shall calculate for S bands of cubic lattices, although a similar calculation is feasible for bands of other type and for other lattices.

We shall have to make various approximations in this calculation and to keep them clearly in evidence, we shall label them explicitly as we go along. We begin by recalling that we have found previously[11] that for S bands, an excellent approximation for the wave function $C_k(\mathbf{K}_i)$ often is

$$C_k(\mathbf{K}_i) \approx A(|\mathbf{K}_i|) + kB(|\mathbf{K}_i|)\cos\gamma + \cdots, \quad (23)$$

with γ the angle between $\mathbf{k}$ and $\mathbf{K}_i$. This already involves *Approximation I*: In it we have taken the angular dependence of the zeroth-order ($\mathbf{k}$-independent) part of the wave function, as that of a spherical harmonic with $l=0$, whereas, in principle (according to group theory), spherical harmonics of orders $l=4,6\cdots$ are permitted as well.

We have already mentioned *Approximation II*: In the expression (23), we neglect the $\mathbf{k}$ dependence of the wave function. We get then for the central function $D(\mathbf{k},\mathbf{K}_s)$

$$D(\mathbf{k},\mathbf{K}_s) \approx \sum_j A(|\mathbf{K}_j+\mathbf{K}_s|)A(|\mathbf{K}_j|). \quad (24)$$

Even with this approximation, the dependence of $D(\mathbf{k},\mathbf{K}_s)$ on $\mathbf{K}_s$ is too complicated for the integrations we shall have to do. Therefore, we expand $A(|\mathbf{K}_j+\mathbf{K}_s|)$ in the following way[11]:

$$A(|\mathbf{K}_j+\mathbf{K}_s|) = 4\pi \sum_{l=0}^{\infty} \sum_{m=-l}^{l} A_l(K_j,K_s)$$
$$\times Y_{lm}^*(\Omega_j) Y_{lm}(\Omega_s). \quad (25)$$

[11] L. Eyges, Phys. Rev. **126**, 93 (1962).

If we put this into (24), we find that the sum involves only[9] $A_0, A_4, A_6\cdots$ and we approximate it (*Approximation III*) by keeping only the term in A_0,

$$D(\mathbf{k},\mathbf{K}_s) \approx \sum_{K_j} n_j A_0(K_j,K_s)A(K_j) \equiv R(K_s). \quad (26)$$

Thus, $D(\mathbf{k},\mathbf{K}_s)$ is in this approximation, despite the notation, independent of k and a function only of the magnitude K_s, and it is then convenient to redefine it as $R(K_s)$, as we have done.

There is, incidentally, an interesting result we can derive immediately from this last equation. Consider $p(\mathbf{r})$, the relative distribution function defined by (5). With the above k-independent approximation, we can do the integrations over $\mathbf{k}$ and $\mathbf{k'}$, to get

$$p(r) = p(r)_{\text{free electron}} f(r),$$

where $p_{\text{free electron}}$ is the relative distribution function (5a) for free electrons, and where[12]

$$f(r) = \sum_s e^{i\mathbf{K}_s \cdot \mathbf{r}} R^2(K_s)$$

is a periodic function of r, which in the tight-binding limit simply becomes the $\chi(\mathbf{r})$ defined by (21).

With the simplified $D(\mathbf{k},\mathbf{K}_s)$ of Eq. (26), we now consider the calculation of $E_{\text{ex}}(\mathbf{k})$, the "exchange energy of an electron of wave number k." This is then

$$E_{\text{ex}}(\mathbf{k}) = -\frac{e^2}{2(2\pi)^3} \int\int e^{i(\mathbf{k}-\mathbf{k'})\cdot\mathbf{r}}$$
$$\times \sum_s R^2(K_s) e^{i\mathbf{K}_s\cdot\mathbf{r}} d\mathbf{k'} d\mathbf{r}. \quad (27)$$

Now we consider the sum over $\mathbf{K}_s$ in (27) to be broken up into one over the absolute magnitudes of K_s and one over the solid angles. We expand $e^{i\mathbf{K}_s\cdot\mathbf{r}}$ in Bessel functions of the magnitude $K_s r$; this expansion, when summed over the reciprocal lattice[9] solid angles, leaves only Kubic harmonics of type α, corresponding to $l=0,4,6\cdots$. As an approximation (*Approximation IV*) we keep only the $l=0$ term to get

$$E_{\text{ex}}(\mathbf{k}) = -\frac{e^2}{2(2\pi)^3} \int\int e^{i(\mathbf{k}-\mathbf{k'})\cdot\mathbf{r}}$$
$$\times \sum_{K_s} n_s R^2(K_s) j_0(K_s r) d\mathbf{k'} d\mathbf{r}.$$

[12] It is important in what follows to keep straight the difference in meanings of the subscript s in $\mathbf{K}_s$ and K_s. This is explained in reference 9, but we recapitulate here for convenience. In $\mathbf{K}_s$, the subscript stands for a triad of integers s_1,s_2,s_3 which defines the reciprocal lattice vector $\mathbf{K}_s$. If now we arrange these vectors in order of increasing magnitude, then K_s stands for the magnitude of the sth vector in this sequence. Correspondingly, n_s is the number of vectors of this magnitude. Also, we recall that Σ_s stands for a summation over all reciprocal lattice vectors, i.e., for a sum over all s_1,s_2,s_3, whereas Σ_{K_s} stands for a sum over the different magnitudes K_s. These points have to be kept in mind mainly in formulas like that preceding Eq. (27) in the text, in which both $\mathbf{K}_s$ and K_s appear simultaneously. In this case, it may be easiest to keep in mind that, e.g., $R^2(K_s)$ can be considered to stand for $R^2(|\mathbf{K}_s|)$.
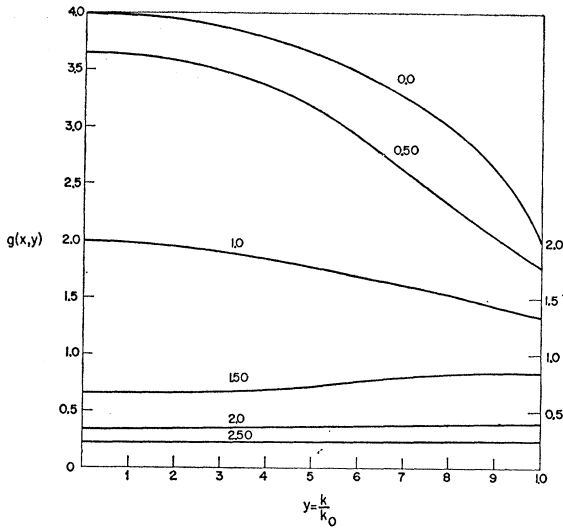
FIG. 1. The function $g(x,y)$, needed in the evaluation of $E_{ex}(\mathbf{k})$ according to Eq. (28). The numbers attached to the curves are values of $x=K_s/k_0$. The curve for $x=0$ is essentially the familiar one for the exchange energy as a function of k tor a free electron gas.

We can now carry out the integrations over the solid angles of $\mathbf{k}'$ and $\mathbf{r}$. For the $\mathbf{k}'$ integration, we assume spherical energy bands and an effective mass of unity, which is a sufficiently good approximation for our later application to Na. We find

$$E_{ex}(\mathbf{k}) = -\frac{e^2}{\pi}\sum_{K_s} n_s R^2(K_s)$$

$$\times \int_0^\infty \int_0^{k_0} j_0(kr)j_0(k'r)j_0(K_s r)k'^2 r\,dk'\,dr.$$

The integral is straightforward but tedious. One gets

$$E_{ex}(\mathbf{k}) = -\frac{e^2}{\pi}k_0 \sum_{K_s} n_s R^2(K_s) g\left(\frac{K_s}{k_0},\frac{k}{k_0}\right), \quad (28)$$

where, with $x=K_s/k_0$, $y=k/k_0$,

$$g(x,y) = \frac{1}{xy}\left\{ \frac{1}{3}\ln\frac{|1+x+y|\,|1-x-y|}{|1+x-y|\,|1-x+y|} + \frac{(x+y)}{2}\right.$$

$$\times\left(1-\frac{(x+y)^2}{3}\right)\ln\frac{|1+x+y|}{|1-x-y|} - \frac{(x-y)}{2}$$

$$\times\left.\left(1-\frac{(x-y)^2}{3}\right)\ln\frac{|1+x-y|}{|1-x+y|} + \frac{4}{3}xy\right\}. \quad (29)$$

We have, thus, represented $E_{ex}(\mathbf{k})$ as a sum of contributions, one from each different magnitude of a reciprocal lattice vector. The function $g(x,y)$ which determines the relative contribution of the different K_s is plotted in Fig. 1. The contribution for $K_s=0$ is de-

termined by $g(0,y)$. On evaluating the indeterminate form (29), this turns out to be, as it must, essentially the Eq. (9) for the exchange energy as a function of k for a free-electron gas,

$$g(0,y) = \left(\frac{1}{y}-y\right)\ln\frac{|1+y|}{|1-y|} + 2. \quad (30)$$

Moreover for $K_s=0$, it is easy to see from the normalization condition that $R(0)=1$, so we can write

$$E_{ex}(\mathbf{k}) = (E_{ex}(\mathbf{k}))_{\text{free electrons}}$$

$$-\frac{e^2 k_0}{\pi}\sum_{K_s\neq0} n_s R^2(K_s)g\left(\frac{K_s}{k_0},\frac{k}{k_0}\right). \quad (31)$$

This is the central formula of this paper.

V. NUMERICAL RESULTS AND DISCUSSION

To evaluate (31) for a specific substance, we must first calculate $R(K_s)$. We have done this numerically for Na, using the cellular wave function given by Wigner and Seitz.[13] Fourier transforming this, we find $A(K_i)$ and $A_0(K_i,K_j)$ defined by Eqs. (23) and (25), and thence, $R(K_s)$. We omit the details; the values of $R(K_s)$ for s running from one through eight are: 1.00, 0.015, -0.10, -0.020, $+0.040$, $+0.049$, $+0.029$, $+0.007$. Thus, $R(K_s)$ is a function which drops off very quickly with K_s. This simply reflects the fact that the wave function for Na is to a good approximation a single plane wave.

Now let us look at the effect of the periodic lattice on the level density near $k=k_0$. Qualitatively, we can read off this effect from Fig. 1. According to Eq. (28), the quantity of interest, $dE_{ex}/dk|_{k=k_0}$ is given, except for factors, by a sum over x of the slope $\partial g/\partial y|_{y=1}$. For x equal to zero, which is the free electron case, $\partial g/\partial y|_{y=1}$ has the (negative) logarithmic singularity which makes for the difficulties touched on in Sec. I. However, there is no such singularity for other values of x. In fact, this slope becomes positive for the larger values of x that actually pertain to[14] Na. Near $y=1$ then, the effect of this in the sum for $dE_{ex}/dk|_{k=k_0}$ is to partially counteract the large effect which arises from the point $x=0.0$. Unfortunately, although this partial cancellation exists in principle, in practice it is at least for Na, almost negligible. For as one can see from the curves of Fig. 1, $\partial g/\partial y|_{y=1}$ although indeed positive for x large enough

[13] Reference 6, p. 340.
[14] E. Wigner and F. Seitz, Phys. Rev. 46, 509 (1934).
[15] For Na, $x=K_s/k_0$ takes on the values $2.283(s-1)^{\frac{1}{2}}$, $s=1,2\cdots$.
[16] The n_j in this formula, as in reference 9, stands for the number of $(j-1)$st nearest neighbors in the reciprocal lattice. In reference 9, we gave a table, computed by hand, for n_j as a function of j. This calculation has been redone on a digital computer by Craig C. Work of this Laboratory, and he has found some errors in that table. The corrected version follows:

j	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
n_j	1	12	6	24	12	24	8	48	6	36	24	24	24	72	0	48	12	48

is also small numerically, and since it enters the expression of Eq. (28) along with the small weighting factor $R(K_s)$, the net effect on $dE_{ex}/dk|_{k=k_0}$ of the terms in (28) for $K_s \neq 0$ is negligible.

We have also calculated the total exchange energy, by numerical integration. The result for free electrons as given by Wigner and Seitz is -72.0 kg cal/mole. The effect of the periodic lattice has also been calculated by Wigner and Seitz, and they find that to three decimal places, there is no difference between the free electron and periodic value. Our result is essentially the same, although we get a slightly different numerical value for the difference between the free electron and periodic case, viz., about 0.005 kg cal/mole. The smallness of this correction is of course a consequence of the rapid decrease of $g(x,y)$ and $R(K_s)$ with K_s.

Spin-Wave Theory of Ferromagnetic Thin Films

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The spin-wave theory in the Holstein-Primakoff formulation is applied to thin ferromagnetic films. A magnetic anisotropy term is included in the Hamiltonian. A discussion is given of the dependence of the magnetic properties on the temperature and on the number n of monatomic layers of the thin film. The influence of possible parallel and perpendicular anisotropy is also discussed.

I. INTRODUCTION

THE first approach in the theory of ferromagnetic thin films is due to Kittel.[1] He showed that when the thickness of the thin film is smaller than approximately 10^{-5} cm, the film becomes a single domain, magnetized in a direction parallel to its surface.

By applying Bloch's theory of spin waves, Klein et al.[2,3] have studied such a single domain for various lattices. It should be mentioned that they have not taken into account the effect of magnetic anisotropy. This fact gives rise to a divergence in the final results for the magnetization if the state of the zero spin-wave vector is included in the sums which appear. With a view to avoiding this difficulty, Klein et al. have omitted this state in the corresponding sums, but they have not given a complete justification of this procedure.

Recently, Döring[4] tried to give a complete discussion of the questions which arise in Klein's calculation. He justified the omission of the zero spin-wave vector state, but showed that even in this case the correct calculations lead to a strange dependence of the magnetization on the dimensions of the surface of the thin film. Döring showed also that by introducing a magnetic anisotropy term in the Hamiltonian, this situation will no longer appear, i.e., the magnetization will no longer depend on the dimensions of the surface of the thin film. However, as is known,[5] when the anisotropy term is taken into account, it is no longer necessary to omit the zero spin-wave vector state and the divergences in the calculation of the magnetization will no longer appear. Döring has also discussed the cyclic condition for the perpendicular axis of the film, and has recalculated the magnetization, going further than Klein et al. to higher order terms.[6] It should be mentioned that Döring has not considered the case in which the magnetic anisotropy is perpendicular to the surface of the thin film.

In this paper, the spin-wave theory in the Holstein-Primakoff (H-P) formulation[7] will be developed for thin ferromagnetic films. We shall not take into account the spin-wave interactions, which, as Dyson[8] and Oguchi[9] have shown, do not influence the first approximation of the H-P method. Oguchi has concluded in his discussion,[10] which applies entirely to our case, that the first approximation in the H-P method gives the essential features of the problem, and that all the correction terms are quite small at low temperatures. In this manner, we restrict ourselves to the first approximation of the H-P method in this paper.

[1] C. Kittel, Phys. Rev. **70**, 965 (1946).
[2] M. J. Klein and R. S. Smith, Phys. Rev. **81**, 378 (1951).
[3] S. J. Glass and M. J. Klein, Phys. Rev. **109**, 288 (1958).
[4] W. Döring, Z. Naturforsch. **16a**, 1008, 1146 (1961).

[5] C. Herring and C. Kittel, Phys. Rev. **81**, 869 (1951). The authors showed that the magnetic anisotropy eliminates the divergences in the magnetization of a monatomic layer.
[6] In order to calculate these terms, Döring performed some approximations, some of which were not entirely justified.
[7] T. Holstein and H. Primakoff, Phys. Rev. **58**, 1098 (1940).
[8] F. J. Dyson, Phys. Rev. **102**, 1217, 1230 (1956).
[9] T. Oguchi, Phys. Rev. **117**, 117 (1960). See also, F. Keffer and T. Oguchi, ibid. **117**, 718 (1960).
[10] See reference 9, especially p. 122.