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Many-Body Effects on Diamagnetism of Free and Bloch Electrons^{*†}

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The effect of the electron-electron interactions on diamagnetic susceptibility is investigated using the Green's-function formalism. General expressions for the Green's function and eigenvalues of the effective one-particle Hamiltonian of the Coulomb gas are developed through second order in the magnetic field strength. Specializing to the Hartree-Fock approximation, the Sampson-Seitz prescription is proven: The susceptibility is given by the Landau-Peierls formula applied to the quasiparticle energy. Energy-band electrons are treated in the Hartree-Fock approximation, yielding a quasiparticle term plus an explicit many-body correction to the orbital paramagnetism. The quasiparticle term corresponds to treating the self-energy operator as a nonlocal pseudopotential. The explicit many-body correction is shown to be small for sodium and bismuth.

I. INTRODUCTION

The first calculation of the effect of Coulomb interactions upon diamagnetism was carried out by Sampson and Seitz,¹ who assumed without proof that the diamagnetic susceptibility for a gas of interacting electrons is given by applying the Landau-Peierls³ formula to the Hartree-Fock eigenvalue. For the case of spherical symmetry, this yields

$$\chi = \frac{1}{12} \left(\frac{e}{\pi \hbar c} \right)^2 \int dE \left(\frac{1}{3} \frac{dE}{dk} + \frac{2}{3} k \frac{d^2E}{dk^2} \right) \frac{\partial f(E)}{\partial E}, \quad (1.1)$$

where E is the Hartree-Fock eigenvalue, f is the Fermi-Dirac distribution function, and k is the magnitude of the wave vector. This conjecture is very plausible but needs proof, as the magnetic field affects the energies and wave functions of all electrons, not just those at the Fermi surface. The present paper contains the first published proof of the Sampson-Seitz prescription. More recently, March and Donovan,⁴ Pines,⁵ and Fletcher and Larson⁶ all have applied the Landau-Peierls formula to the equilibrium quasiparticle energy calculated in the Bohm-Pines^{5,7} theory of electron correlation. We shall refer to these calculations

as applications of the Sampson-Seitz prescription.

Fundamental calculations of the many-body effects on the diamagnetism of the Coulomb gas have been carried out by a number of workers. Kanazawa⁸ applied the Bohm-Pines transformation to the current operator in the presence of the magnetic field, and Wentzel⁹ used the pair model, but both authors neglected the effect of exchange. Kanazawa and Matsudaira¹⁰ carried out a complete Green's-function treatment in the high-density limit. Fujita and Usui¹¹ extended Wentzel's method to include the screened exchange. Stephen¹² used the free-particle Green's function in a magnetic field and calculated the first-order exchange effects by summing the ring diagrams. Ashkin¹³ used the linear response theory of Martin and Schwinger¹⁴ and devised an approximation for the two-particle Green's function which included the long-range correlations. Tsai, Wadati, and Isihara¹⁵ carried out a calculation similar to Stephen's, but carried it to one higher power of r_s , the average interparticle spacing. Rajagopal and Jain¹⁶ expressed the susceptibility in terms of a vertex function in the case of a statically screened interaction. They then solved the integral equation for the vertex function, using a

variational method. The more recent calculations^{10-13,15,16} all agree in the high-density, low-temperature limit if the trivial error in the screening constant is corrected in two of the papers.^{10,11}

The application of the Sampson-Seitz prescription to the Bohm-Pines quasiparticle energy agrees with the fundamental calculations at high density if both results are expressed in terms of the screening constant. However, there is considerable disagreement at metallic densities. The fundamental result,^{12,15} which really is not valid at metallic densities, predicts a 30-60% increase in diamagnetism for the alkali metals. On the other hand, the best calculation⁶ using the Sampson-Seitz prescription predicts corrections ranging from +8 to -4%.

We would like to prove the Sampson-Seitz prescription under the most general conditions possible for several reasons: (i) The prescription has the form of many of the results of Fermi liquid theory,¹⁷ and would be aesthetically very pleasing; (ii) calculations using the prescription are much easier to perform than direct calculations, and one could easily take advantage of improvements in the theory of the quasiparticle spectrum; (iii) the prescription probably offers the best chance of obtaining reliable results at metallic densities. In Sec. II, we treat the Coulomb gas at low temperature using the Green's-function formulation of Kadanoff and Baym.¹⁸ We construct in k space the effective one-particle Hamiltonian and the equation of motion of the Green's function in the presence of the magnetic field. We find general expressions for the eigenvalues of the effective Hamiltonian and for the Green's function correct through second order in the magnetic field strength. We then specialize to the Hartree-Fock approximation, which allows us to find an expression for the change in total energy of the system which is analogous to Fermi liquid theory. This expression leads to a proof of the Sampson-Seitz prescription. A discussion is given of the possibility of extending the proof beyond the Hartree-Fock approximation.

Until recently, the only calculations of the many-body effects on the diamagnetism of band electrons was in the effective-mass model.^{5,6} Some work has now appeared on the diamagnetism of excitonic insulators¹⁹ and on the diamagnetism^{20,21} in the Hubbard²² model. Fukuyama²⁰ has recently calculated the many-body effects on the diamagnetism of the one-dimensional weak-potential model. In Sec. III we treat general energy bands using the Hartree-Fock approximation. The result for the diamagnetism can be divided into two terms. The first term, which we call the quasiparticle term, is the diamagnetism calcu-

lated treating the self-energy as a one-particle nonlocal pseudopotential. The recent theory of Misra and Roth²³ should be well adapted to evaluating the first term. The second term is an explicit many-body correction to the orbital paramagnetism which is similar to the correction to spin paramagnetism, but may be difficult to evaluate in general. In two extreme cases, an isolated s band and two strongly interacting bands, the second term is found to be unimportant.

The present work treats only the low-temperature limit. The three works^{12,13,24} which treat the high-temperature limit all get different results. We also do not treat the many-body effects on the de Haas-van Alphen effect, which has already been treated by Luttinger²⁵ and by Bychkov and Gorkov.²⁶ We take into account only the Coulomb interactions. Tani²⁷ has concluded that the phonon-mediated interaction has a very small effect upon the diamagnetism. Finally, for the most part, we neglect the effect of interaction upon the spin paramagnetism, which is well known.¹⁷

II. COULOMB GAS

A. Exact Results

We first concentrate on obtaining an expression for the total energy in the presence of the magnetic field, as at low temperatures the magnetic susceptibility can be calculated from the appropriate derivative of the total energy with respect to the magnetic field strength. The total energy can be expressed in terms of the one-particle Green's function.^{18,28} In the presence of the magnetic field the equation of motion may be written²⁶

$$(z - \mathcal{H})G(\vec{r}, \vec{r}', z) = \delta(\vec{r} - \vec{r}'), \quad (2.1)$$

where G is the one-particle Green's function, z is the complex energy, and \mathcal{H} is the effective one-particle Hamiltonian given by

$$\begin{aligned} \mathcal{H}\varphi(\vec{r}) = & (1/2m)(-i\vec{\nabla} - \frac{1}{2}\vec{s} \times \vec{r})^2 \varphi(\vec{r}) \\ & + \int d^3r'' \Sigma(\vec{r}, \vec{r}'', z) \varphi(\vec{r}''). \end{aligned} \quad (2.2)$$

In the above, Σ is the self-energy, \hbar and c have been set equal to unity, and the vector potential is in the symmetric gauge $\vec{A} = \frac{1}{2}\vec{B} \times \vec{r}$, so that the vector \vec{s} is given by $\vec{s} = e\vec{B}$ (in restored units, $\vec{s} = e\vec{B}/\hbar c$). The self-energy contains the effects of the Coulomb interactions and depends upon the magnetic field strength. The total energy per unit volume is given by¹⁸

$$\begin{aligned} E_{\text{tot}} = & 2 \int \frac{d\omega}{2\pi} \frac{1}{2} \left[\omega + \frac{1}{2m} \left(-i\vec{\nabla} - \frac{1}{2}\vec{s} \times \vec{r} \right)^2 \right] \\ & \times G\langle \vec{r}, \vec{r}', \omega \rangle |_{\vec{r}=\vec{r}'}, \end{aligned} \quad (2.3)$$

where the factor 2 is the spin degeneracy, the in-

tegral is along the real energy axis, and $G^<$ is given by an analytic continuation of G across the real energy axis.¹⁸

In the absence of the magnetic field, G , $G^<$, and Σ all depend upon the coordinate differences so that the equation of motion is easily solved by transforming to k space. The vector potential term in the effective Hamiltonian destroys the translational invariance, but G , $G^<$, and Σ can be written as products of a "Peierls phase factor" and a part which depends upon the coordinate difference alone,²⁹

$$G(\vec{r}, \vec{r}', z) = e^{i\vec{s} \cdot \vec{r}\vec{r}'/2} \bar{G}(\vec{r} - \vec{r}', z). \quad (2.4)$$

The phase factor has the effect of translating the origin of the vector potential.

$$\begin{aligned} & (-i\vec{\nabla} - \frac{1}{2}\vec{s} \times \vec{r}) G(\vec{r}, \vec{r}', z) \\ &= e^{i\vec{s} \cdot \vec{r}\vec{r}'/2} [-i\vec{\nabla} - \frac{1}{2}\vec{s} \times (\vec{r} - \vec{r}')] \bar{G}(\vec{r} - \vec{r}', z). \end{aligned} \quad (2.5)$$

Substituting the expressions for G and Σ into Eq. (2.1), commuting the differential operator through the Peierls factor, and multiplying on the left by $\exp(\frac{1}{2}i\vec{s} \cdot \vec{r} \times \vec{r}')$, we find

$$\begin{aligned} & \{z - [-i\vec{\nabla} - \frac{1}{2}\vec{s} \times (\vec{r} - \vec{r}')]^2/2m\} \bar{G}(\vec{r} - \vec{r}', z) \\ &= \int d^3r'' e^{i\vec{s} \cdot [(\vec{r} - \vec{r}'') \times (\vec{r}'' - \vec{r}')] / 2} \\ & \times \bar{\Sigma}(\vec{r} - \vec{r}'', z) \bar{G}(\vec{r}'' - \vec{r}', z) = \delta(\vec{r} - \vec{r}'). \end{aligned} \quad (2.6)$$

Thus the Peierls transformation has produced an equation which depends only upon the coordinate differences. We now introduce the Fourier transforms of \bar{G} and $\bar{\Sigma}$:

$$\bar{G}(\vec{r}, z) = (2\pi)^{-3} \int d^3k e^{i\vec{k} \cdot \vec{r}} \bar{G}(\vec{k}, z), \quad (2.7a)$$

$$\bar{G}(\vec{k}, z) = \int d^3r e^{-i\vec{k} \cdot \vec{r}} \bar{G}(\vec{r}, z). \quad (2.7b)$$

Note that we follow Kadanoff and Baym in using the same symbol for \bar{G} and its Fourier transform, letting the argument denote which quantity is meant.

The expression for the total energy (2.3) is easily transformed by using the result (2.5) twice, and by noting that both the vector potential term and the Peierls phase vanish when $\vec{r} = \vec{r}'$. When Fourier transformed, the energy expression becomes

$$E_{\text{tot}} = \text{Tr} \left[\frac{1}{2}(\omega + k^2/2m) \bar{G}^<(\vec{k}, \omega, \vec{s}) \right], \quad (2.8)$$

where Tr stands for $2(2\pi)^{-4} \int d^3k \int d\omega$. Equation (2.8) is the same as in the absence of the magnetic field except that $\bar{G}^<$, which is a function of \vec{s} , replaces the Green's function in the absence of the field, $G_0^<(\vec{k}, \omega) = G^<(\vec{k}, \omega, 0)$. Thus the total energy depends upon the magnetic field only through $\bar{G}^<$. To find the low-field susceptibility, we need to obtain $\bar{G}^<$

correct through order s^2 .

In the Fourier transformation of the transformed equation of motion (2.6), the kinetic energy operator goes over to $(\vec{k} - \frac{1}{2}i\vec{s} \times \vec{\nabla}_k)^2/2m$, following well-known replacement rules.^{3,30} The self-energy term gives a new result:

$$\begin{aligned} & \int d^3r \int d^3r'' e^{-i\vec{k} \cdot (\vec{r} - \vec{r}'')} e^{-i\vec{s} \cdot [(\vec{r} - \vec{r}'') \times (\vec{r}'' - \vec{r}')] / 2} \\ & \times \bar{\Sigma}(\vec{r} - \vec{r}'') \bar{G}(\vec{r}'' - \vec{r}') \\ &= \int d^3r_1 \int d^3r_2 e^{-i\vec{k} \cdot (\vec{r}_1 + \vec{r}_2)} e^{i\vec{s} \times \vec{r}_2 \cdot \vec{r}_1 / 2} \bar{\Sigma}(\vec{r}_1) \bar{G}(\vec{r}_2) \\ &= \int d^3r_2 \bar{\Sigma}(\vec{k} - \frac{1}{2}\vec{s} \times \vec{r}_2) e^{-i\vec{k} \cdot \vec{r}_2} \bar{G}(\vec{r}_2) \\ &= \bar{\Sigma}(\vec{q} - \frac{1}{2}\vec{s} \times \vec{\nabla}_k) \bar{G}(\vec{k}) \Big|_{\vec{q}=\vec{k}}. \end{aligned} \quad (2.9)$$

In the first step above we have put $\vec{r}_1 = \vec{r} - \vec{r}''$ and $\vec{r}_2 = \vec{r}'' - \vec{r}'$, and used the fact that integrating over all \vec{r}_1 and \vec{r}_2 is the same as integrating over all \vec{r} and \vec{r}'' . In the second step the coefficient of \vec{r}_1 in the total phase becomes the argument of the Fourier transform of $\bar{\Sigma}$. In the last step we use the result that $i\vec{\nabla}_k$ operation on $e^{-i\vec{k} \cdot \vec{r}_2}$ yields \vec{r}_2 times the exponential; however, the gradient must not operate on the \vec{k} in the argument of $\bar{\Sigma}$. The result is similar to the standard replacement rule,³⁰ but does not suffer from any ambiguity as all the components of $\vec{q} - \frac{1}{2}i\vec{s} \times \vec{\nabla}_k$ commute with each other. Finally the transformed equation of motion may be written

$$(z - \mathcal{H}_{\text{op}}) \bar{G}(\vec{k}, z, \vec{s}) = 1, \quad (2.10a)$$

$$\begin{aligned} \mathcal{H}_{\text{op}} \varphi(\vec{k}) &= [(\vec{k} - \frac{1}{2}\vec{s} \times \vec{\nabla}_k)^2/2m] \varphi(\vec{k}) \\ &+ \bar{\Sigma}(\vec{q} - \frac{1}{2}\vec{s} \times \vec{\nabla}_k, z, \vec{s}) \varphi(\vec{k}) \Big|_{\vec{q}=\vec{k}}. \end{aligned} \quad (2.10b)$$

This is the first time that the complete equation of motion in the presence of the magnetic field has been written in k space.

A formal solution of Eq. (2.10) can be written in terms of the normalized eigenfunctions of the effective Hamiltonian $\mathcal{H}_{\text{op}} \varphi_\alpha(\vec{k}) = E_\alpha \varphi_\alpha(\vec{k})$,

$$\bar{G}(\vec{k}, z, \vec{s}) = \int d^3k' \sum_\alpha \frac{\varphi_\alpha(\vec{k}) \varphi_\alpha^*(\vec{k}')}{z - E_\alpha}. \quad (2.11)$$

Though Eq. (2.11) is not valid for a general non-Hermitian Hamiltonian, it holds in this case as the φ_α will be shown to form a complete set.

We now need to find the eigenfunctions and eigenvalues at least through order s^2 . We start by noting that the magnetic field has its effect on the motion perpendicular to the magnetic field, and that the self-energy has cylindrical symmetry about the magnetic field, i. e., we may write $\bar{\Sigma}(\vec{k}) = \bar{\Sigma}(\rho^2, k_z)$, where the z direction is chosen parallel to the magnetic field and $\vec{\rho} \equiv (k_x, k_y, 0)$. We also define the operators acting perpendicular to the magnetic

field

$$\vec{K}_{op} \equiv \left(k_x + \frac{1}{2} is \frac{\partial}{\partial k_y}, k_y - \frac{1}{2} is \frac{\partial}{\partial k_x}, 0 \right), \quad (2.12a)$$

$$\vec{Q}_{op} \varphi(\vec{k}) \equiv \left(q_x + \frac{1}{2} is \frac{\partial}{\partial k_y}, q_y - \frac{1}{2} is \frac{\partial}{\partial k_x}, 0 \right) \varphi(\vec{k})|_{\vec{a}=\vec{0}}, \quad (2.12b)$$

with the convention that in calculating products of components of \vec{Q}_{op} , all derivatives are taken before \vec{q} is set equal to $\vec{\rho}$. Thus the eigenvalue equation may be written

$$[(k_z^2 + \vec{K}_{op}^2)/2m + \tilde{\Sigma}(Q_{op}^2, k_z, z, s)] \varphi_\alpha(\vec{k}) = E_\alpha \varphi_\alpha(\vec{k}). \quad (2.13)$$

Note that K_{op}^2 could just as well be written Q_{op}^2 in the eigenvalue equation. In Appendix A, we show that the eigenfunctions of K_{op}^2 are also eigenfunctions of $(Q_{op}^2)^n$, and that if $\tilde{\Sigma}$ can be expanded in a power series in ρ^2 , then it can be shown that

$$\tilde{\Sigma}(Q_{op}^2, k_z, \vec{s}) = \tilde{\Sigma}(K_{op}^2, k_z, z, s) + s^2 D \tilde{\Sigma}(K_{op}^2) + O(s^4). \quad (2.14)$$

In the second term above ρ^2 is replaced by K_{op}^2 in the quantity $s^2 D(\rho^2) \tilde{\Sigma}(\rho^2)$, where the operator D is defined by

$$D(x) \tilde{\Sigma}(x) \equiv \frac{1}{3} x \frac{d^3 \tilde{\Sigma}}{dx^3} + \frac{1}{2} \frac{d^2 \tilde{\Sigma}}{dx^2}. \quad (2.15)$$

Thus we have shown that the eigenfunctions of K_{op}^2 are also the exact eigenfunctions of \mathcal{K}_{op}^2 , a result which has been stated without proof by Bychkov and Gorkov.²⁶ The eigenfunctions of K_{op}^2 are well known to form a complete set. In polar coordinates

$$\varphi_{\lambda\mu}(\rho, \theta) = \mathcal{N} e^{-\rho^2/s} \rho^{|\mu|} L_\lambda^{|\mu|}(2\rho^2/s) e^{i\mu\theta}, \quad (2.16a)$$

where

$$\mathcal{N} = [\pi(\frac{1}{2}s)^{|\mu|+1} (\lambda + |\mu|)! / \lambda!]^{-1/2} \quad (2.16b)$$

and

$$L_\lambda^\mu(t) = \sum_{\nu=0}^{\lambda} \binom{\lambda+\mu}{\lambda-\nu} \frac{(-t)^\nu}{\nu!} \quad (2.16c)$$

is a Laguerre polynomial.³¹ The corresponding eigenvalue of K_{op}^2 is $(2\lambda + |\mu| - \mu + 1)s$. The eigenvalues of \mathcal{K}_{op}^2 are given by replacing K_{op}^2 by its eigenvalues. For the case $\mu = 0$,

$$E_\lambda(k_z) = [(2\lambda + 1)s + k_z^2]/2m + \tilde{\Sigma}((2\lambda + 1)s, k_z) + s^2 D \tilde{\Sigma}((2\lambda + 1)s, k_z). \quad (2.17)$$

The Onsager replacement rule $\rho^2 - (2\lambda + 1)s$ is well known,²⁵ but the second-order correction terms are new. The result (2.17) is in agreement with the result derived by Roth³² in the case of noninteracting Bloch electrons.

We now substitute the eigenfunctions and eigenvalues into the formal solution (2.11) for \vec{G} . The

integration over k' causes all terms for $\mu \neq 0$ to vanish, yielding

$$\vec{G}(\rho^2, k_z, z, s) = 2 \sum_\lambda \frac{(-1)^\lambda e^{-\rho^2/s} L_\lambda(2\rho^2/s)}{z - E_\lambda(k_z)}, \quad (2.18)$$

where $L_\lambda \equiv L_\lambda^0$. As the eigenfunctions are exact and E_λ is good to order s^2 , Eq. (2.18) for \vec{G} is also good to order s^2 . For noninteracting electrons, Eq. (2.18) is the result derived by Rajagopal.³³ In Appendix B we use the properties of Laguerre polynomials to evaluate the summation through order s^2 ,

$$\vec{G}(\rho^2, k_z, z, s) = \frac{1}{z - \epsilon(\rho^2, k_z)} - s^2 D(\rho^2) \frac{1}{z - \epsilon(\rho^2, k_z)}, \quad (2.19)$$

where

$$\epsilon(\rho^2, k_z) = k^2/2m + \tilde{\Sigma}(\rho^2, k_z) + s^2 D(\rho^2) \tilde{\Sigma}, \quad (2.20)$$

$k^2 = \rho^2 + k_z^2$, and D is the operator defined in Eq. (2.15). The leading term in \vec{G} resembles the Green's function in the absence of the magnetic field except that ϵ depends upon the magnetic field strength. The eigenvalue has two correction terms of order s^2 , the explicit $s^2 D \tilde{\Sigma}$ term in Eq. (2.20) and the change in $\tilde{\Sigma}(\rho^2, k_z)$ with magnetic field. We shall deal approximately with the change in $\tilde{\Sigma}$ in Sec. II B, but our expression (2.19) for \vec{G} and the analogous one for $\vec{G}^<$ are general (through order s^2). In the absence of interactions our expression for $G^<$ is equivalent to the expansion to order s^2 of the Green's function found by Sondheimer and Wilson.³⁴

B. Self-Consistent-Field Approximation

We now make two simplifying approximations which make further progress easy. At the end of this subsection we discuss the possibility of improving the derivation. First we neglect the dependence of the self-energy upon the complex energy z . In this case the function $\vec{G}^<$ is easily calculated¹⁸

$$\vec{G}^<(\vec{k}, \omega, s) = 2\pi [1 - s^2 D(\rho^2)] f(\epsilon) \delta(\omega - \epsilon), \quad (2.21)$$

where f is the Fermi-Dirac distribution function and ϵ is given by Eq. (2.20) with z suppressed. As D operates on the ϵ in the argument of the Dirac δ function, it is best in evaluating the total energy (2.8) to place the ω to the right of D before performing the integration on ω , yielding

$$E_{\text{tot}} = 2 \int \frac{d^3k}{(2\pi)^3} \frac{1}{2} \left(\frac{k^2}{2m} (1 - s^2 D) f + (1 - s^2 D) \epsilon f \right). \quad (2.22)$$

In Appendix C we show that for functions with cylindrical symmetry $D(\epsilon f) = \epsilon Df + f D\epsilon$ under the integral sign. Furthermore, $s^2 D\epsilon = s^2 D\tilde{\Sigma} = s^2 D\tilde{\Sigma}_0$ to order s^2 , so that the $-s^2 f D\epsilon$ term cancels the

$(s^2 D \bar{\Sigma})f$ part of the $(1) \times \epsilon f$ term, so that we have

$$E_{\text{tot}} = 2 \int \frac{d^3 k}{(2\pi)^3} \left(\frac{k^2}{2m} + \frac{1}{2} \bar{\Sigma} \right) (1 - s^2 D) f(\epsilon). \quad (2.23)$$

We now introduce the following quantities:

$$\bar{\Sigma} = \Sigma_0 + \delta\Sigma, \quad (2.24a)$$

$$\epsilon_0 = (k^2/2m) + \Sigma_0, \quad (2.24b)$$

$$(1 - s^2 D) f(\epsilon) = f(\epsilon_0) + \delta f + \Delta f, \quad (2.24c)$$

$$\Delta f = -s^2 D f(\epsilon_0) + s^2 (D \Sigma_0) \frac{\partial f(\epsilon_0)}{\partial \epsilon_0}, \quad (2.24d)$$

$$\delta f = \delta\Sigma \frac{\partial f(\epsilon_0)}{\partial \epsilon_0}. \quad (2.24e)$$

The relations above are correct to order s^2 . Note that δf is the change in the distribution function due to the change in form of the self-energy operator in the magnetic field, and Δf is the change coming from the action of the operator Q_{op}^2 . This separation of changes will be very useful in Sec. III. Note that all changes in f are confined to the region of the Fermi surface. Using the above notation, we rewrite the total energy

$$E_{\text{tot}} = 2(2\pi)^{-3} \int d^3 k \left(k^2/2m + \frac{1}{2} \Sigma_0 + \frac{1}{2} \delta\Sigma \right) \times [f(\epsilon_0) + \delta f + \Delta f]. \quad (2.25)$$

We now introduce the Hartree-Fock approximation in order to get an expression for the change in the self-energy. The Hartree-Fock approximation for the self-energy in configuration space is¹⁸

$$\Sigma(\vec{r}, \vec{r}') = - (2\pi)^{-1} \int d\omega G^<(\vec{r}, \vec{r}', \omega) v(\vec{r} - \vec{r}'), \quad (2.26a)$$

which leads to

$$\begin{aligned} \bar{\Sigma}(\vec{k}) &= - (2\pi)^{-4} \int d\omega \int d^3 k' \bar{G}^<(\vec{k}') V(\vec{k}' - \vec{k}) \\ &= - (2\pi)^{-3} \int d^3 k' [f(\epsilon_0') + \delta f + \Delta f] V(\vec{k}' - \vec{k}), \end{aligned} \quad (2.26b)$$

using Eqs. (2.21) and (2.24c). In the above, $v(\vec{r} - \vec{r}')$ is the interparticle interaction and $V(\vec{k} - \vec{k}')$ is its Fourier transform. We have neglected the Hartree term which cancels the potential of the positive background charge. Because Eq. (2.26b) is linear in f , Σ_0 and $\delta\Sigma$ are given separately by the integrals involving $f(\epsilon_0)$ and $\delta f + \Delta f$, respectively. Thus the change in the self-energy is proportional to the change in the distribution function, and so is proportional to s^2 . As δf depends upon $\delta\Sigma$, Eq. (2.26b) is an integral equation for $\delta\Sigma$. The integral equation can be solved,³⁵ but it is not necessary for our purpose. We require only the integral of $f_0 \delta\Sigma$, which can be evaluated by the following theorem:

$$\int d^3 k \delta\Sigma f(\epsilon_0) = - (2\pi)^{-3} \int d^3 k \int d^3 k' [\delta f(\vec{k}') + \Delta f(\vec{k}')] \times V(\vec{k} - \vec{k}') f[\epsilon_0(\vec{k})]$$

$$= \int d^3 k' [\delta f(\vec{k}') + \Delta f(\vec{k}')] \Sigma_0(\vec{k}'), \quad (2.27)$$

where we have used the symmetry of the potential $V(\vec{k} - \vec{k}') = V(\vec{k}' - \vec{k})$. It is this theorem which allows the change in energy of all the particles to be expressed in terms of quantities near the Fermi surface. Applying the theorem to the $\frac{1}{2} \delta\Sigma f(\epsilon_0)$ term in the total energy expression (2.25) and neglecting $\delta\Sigma(\Delta f + \delta f)$ terms which are of order s^4 , we have

$$E_{\text{tot}} = 2(2\pi)^{-3} \int d^3 k \left[(k^2/2m + \frac{1}{2} \Sigma_0) f(\epsilon_0) + \epsilon_0 (\delta f + \Delta f) \right]. \quad (2.28)$$

The first term is the total energy in the absence of the magnetic field and the second term gives the change in energy to order s^2 . The second term has the same form as results in Fermi liquid theory,^{17,18,28} i. e., the integral of the equilibrium quasiparticle energy times the change in the distribution function.

We calculate the magnetic susceptibility by taking the derivative of the thermodynamic potential Ω ,³⁶

$$\chi = -B^{-1} \left. \frac{\partial \Omega}{\partial B} \right|_{B=0}, \quad (2.29a)$$

$$\Omega = E_{\text{tot}} - \mu N - TS, \quad (2.29b)$$

where μ is the energy of the Fermi level, N is the density of particles, and S is the entropy. In taking the derivative μ is held constant. As we are interested in the susceptibility at very low temperature T , we neglect the term TS . The part of the thermodynamic potential proportional to s^2 is then given by

$$\delta\Omega = 2(2\pi)^{-3} \int d^3 k (\epsilon_0 - \mu) (\delta f + \Delta f). \quad (2.30)$$

The terms in $\delta f + \Delta f$ proportional to $\partial f / \partial \epsilon$ are finite only near the Fermi surface, where $\epsilon - \mu$ is small. Integrals of the type $\int d^3 k (\epsilon_0 - \mu) \partial f / \partial \epsilon$ are proportional to T^2 and can be neglected at low temperatures. Thus the only part of $\delta f + \Delta f$ that remains is $-s^2 D f(\epsilon_0)$. Taking the derivative indicated in (2.29a), we find

$$\chi = 4e^2 (2\pi)^{-3} \int d^3 k (\epsilon_0 - \mu) D f(\epsilon_0). \quad (2.31)$$

In Appendix C we show by partial integrations and ignoring terms of the order of T^2 that Eq. (2.31) reduces to the Sampson-Seitz result, Eq. (1.1). At the low temperatures where our derivation holds, we have (in restored units)

$$\chi = - \frac{1}{12} \left(\frac{e}{\pi \hbar c} \right)^2 \left(\frac{1}{3} \frac{dE}{dk} + \frac{2}{3} k_F \frac{d^2 E}{dk^2} \right)_{k=k_F}, \quad (2.32)$$

where k_F is the radius of the Fermi surface.

If $V(\vec{r} - \vec{r}')$ is taken as the bare Coulomb inter-

action, we have the original Sampson-Seitz relation.¹ However, the divergence associated with the long range of the Coulomb potential makes the result unphysical. It has been shown³⁷ that the use of the Hartree-Fock approximation with a screened potential gives many of the same results as the random-phase approximation. In order to get a comparison formula, we choose the static Thomas-Fermi potential whose Fourier transform is

$$V(\vec{k}) = 4\pi e^2 / (k^2 + \eta^2 k_F^2). \quad (2.33)$$

The self-energy and its derivatives are easily evaluated with this potential, yielding³⁵

$$\chi/\chi_0 = 1 + (\alpha r_s / 6\pi) [4 - (\frac{3}{2}\eta^2 + 1) \ln(1 + 4/\eta^2) + 2\eta^2 / (4 + \eta^2)], \quad (2.34)$$

where $\alpha = (4/9\pi)^{1/3} = 1/k_F r_s$ and r_s is the dimensionless average interparticle spacing, $N = 3m^3 e^6 / 4\pi r_s^3 \hbar^6$. Equation (2.34) agrees exactly with the result (3.3b) of Rajagopal and Jain.¹⁶ When the screening constant is small, Eq. (2.34) becomes

$$\chi/\chi_0 = 1 + (\alpha r_s / 6\pi)(4 + 2 \ln \frac{1}{2}\eta). \quad (2.35)$$

All the most recent fundamental calculations^{10-13,15,16} agree with Eq. (2.35) with suitable choices of η . Four of the works^{12,13,15,16} agree with taking the Thomas-Fermi value $\eta^2 = 4\alpha r_s / \pi$. The other two works have an η^2 only half as large, apparently due to leaving out the spin degeneracy factor in the density of states. The leading terms in r_s of the results found using the Sampson-Seitz prescription and the Bohm-Pines quasiparticle energy⁴⁻⁶ also agree with Eq. (2.35), with η^2 being the cutoff parameter β^2 , which is taken variously between 0.53 and 0.71 of the Thomas-Fermi η^2 . Equation (2.35) with the Thomas-Fermi η gives small corrections for small r_s (1.06 for $r_s = 1$) but large corrections for metallic densities (1.53 for $r_s = 5$). The result of Tsai, Wadati, and Isihara,¹⁵ which is good to r_s^2 , gives 1.65 at $r_s = 5$. These formulas are not expected to be accurate at metallic densities as the expansion parameter $\alpha r_s / \pi$ is equal to 0.83 at $r_s = 5$. However, Eq. (2.34) gives only 1.02 for $r_s = 5$. The most accurate calculation⁶ using the Sampson-Seitz and Bohm-Pines schemes gives 0.997 - 1.009 at $r_s = 5$.

It seems likely that the Sampson-Seitz prescription can give a reasonable estimate of the susceptibility at metallic densities. When used with the Thomas-Fermi potential model, it gives the exact high-density results. It gives comparable results at metallic densities for both the Thomas-Fermi potential model and the Bohm-Pines method, and it is known that the Bohm-Pines method gives reasonable results for the correlation energy at metallic densities. However, it would be very de-

sirable to carry through the derivation in higher approximation. Especially pleasing would be a derivation of the type in Fermi liquid theory. As was noted before, the total energy (2.8) is the same functional of $\tilde{G}^<$ as in the absence of the magnetic field. Also, the equation of motion (2.10) has the same form as in the absence of the magnetic field except for the operator replacement. The self-energy depends upon the magnetic field, but in the Hartree-Fock approximation $\tilde{\Sigma}$ is the same functional of $\tilde{G}^<$ that Σ_0 is of $G_0^<$ in the same approximation. This is also true in the random-phase approximation, as the Peierls phases all cancel so that the Fourier transform of a random-phase approximation diagram contribution to $\tilde{\Sigma}$ is expressed as the integrals of simple products. The result is not generally true outside the random-phase approximation, the simplest example being the Born exchange diagram.³⁸ Within the random-phase approximation a generalized version of the theorem (2.27) is possible, so that one can find an expression for the diamagnetism in terms of integrals involving the self-energy. One would like to use the same methods as in Fermi liquid theory^{17,18,28,39} to evaluate the integrals on ω and find a result for the change in total energy which depends only upon the quasiparticle properties near the Fermi surface. However, these methods work easily when the change in $G^<$ involves first-order derivatives with respect to k , while our operator D involves higher derivatives. Actually, to calculate the magnetic susceptibility, one must calculate to second order in the perturbation $\vec{p} \cdot \vec{A}$, whereas our transformation to k space has changed the problem to one of calculating to first order in a perturbation proportional to s^2 .

III. BAND ELECTRONS

A. General Energy-Band Structure

We now treat the case of interacting electrons in a fixed, periodic potential. The equation of motion is still given by Eq. (2.1), but with the effective one-particle Hamiltonian modified to include the period lattice potential U_L :

$$\mathcal{H}(-i\vec{\nabla} - \frac{1}{2}\vec{s} \times \vec{r}) \varphi(\vec{r}) = \mathcal{H}_0(-i\vec{\nabla} - \frac{1}{2}\vec{s} \times \vec{r}) \varphi(\vec{r}) + \int d^3r' \Sigma(\vec{r}, \vec{r}') \varphi(\vec{r}'), \quad (3.1a)$$

where

$$\mathcal{H}_0(-i\vec{\nabla} - \frac{1}{2}\vec{s} \times \vec{r}) = (-i\vec{\nabla} - \frac{1}{2}\vec{s} \times \vec{r})^2 / 2m + U_L(\vec{r}), \quad (3.1b)$$

and $U_L(\vec{r} + \vec{R}) = U_L(\vec{r})$, where \vec{R} is any crystal translation vector. We retain the constant part of the Hartree potential in U_L to avoid a divergence, but include the varying part in the self-energy. As before, some of the translational symmetry can be regained by introducing the Peierls factor²⁹

$$G(\vec{r}, \vec{r}', z, s) = e^{-i\vec{s} \cdot \vec{r}\vec{r}'/2} \bar{G}(\vec{r}, \vec{r}', z, s), \quad (3.2a)$$

where \bar{G} no longer depends upon the coordinate difference but follows

$$\bar{G}(\vec{r} + \vec{R}, \vec{r}' + \vec{R}, z, s) = \bar{G}(\vec{r}, \vec{r}', z, s). \quad (3.2b)$$

The equation of motion can be transformed to a form the same as (2.6), except for the inclusion of the periodic potential U_L . The total energy per unit volume is modified by the periodicity,

$$\begin{aligned} E_{\text{tot}} &= 2(2\pi v_0)^{-1} \int d\omega \int d^3r \frac{1}{2} [\omega + \mathcal{H}_0(-i\vec{\nabla} - \frac{1}{2}\vec{s} \times \vec{r})] \\ &\quad \times G^<(\vec{r}, \vec{r}', \omega, s) \Big|_{\vec{r}=\vec{r}'} \\ &= \frac{1}{2} \text{Tr} \{ [\omega + \mathcal{H}_0(-i\vec{\nabla} - \frac{1}{2}\vec{s} \times \vec{r})] G^<(\vec{r}, \vec{r}', \omega, s) \}, \end{aligned} \quad (3.3)$$

where v_0 is the total volume of the crystal. Expressing $G^<$ in terms of $\bar{G}^<$, commuting the Peierls factor through the differential operator using Eq. (2.5), and setting $\vec{r} = \vec{r}'$ in factors other than $\bar{G}^<$ produces an equation similar to (3.3) with $G^<$ replaced by $\bar{G}^<$ and without the vector potential term.

We now introduce the same approximations as in Sec. II, in order to reduce the energy expression to a more convenient form. First, we neglect the frequency dependence of the self-energy, so that the frequency dependence of $G^<$ is given by a Dirac δ function. We also express $G^<$ in terms of the eigenfunctions of the effective one-particle Hamiltonian in configuration space,

$$G^<(\vec{r}, \vec{r}', \omega, z) = \sum_{\alpha} \varphi_{\alpha}(\vec{r}) f(E_{\alpha}) \varphi_{\alpha}^*(\vec{r}') 2\pi\delta(\omega - E_{\alpha}), \quad (3.4)$$

where

$$\mathcal{H}(-i\vec{\nabla} - \frac{1}{2}\vec{s} \times \vec{r}) \varphi_{\alpha}(\vec{r}) = E_{\alpha} \varphi_{\alpha}(\vec{r}). \quad (3.5)$$

Using this form, the term proportional to the integral of $\omega G^<$ in Eq. (3.3) can be written

$$\frac{1}{2} \text{Tr} [\sum_{\alpha} E_{\alpha} \varphi(\vec{\nabla}) f(E_{\alpha}) \varphi_{\alpha}^*(\vec{r}') 2\pi\delta(\omega - E_{\alpha})]$$

$$\begin{aligned} \text{Tr} [\delta\Sigma(\vec{r}, \vec{r}') G_0^<(\vec{r}, \vec{r}')] &= (2\pi)^{-2} v_0^{-1} \int d^3r \int d^3r' \int d\omega \int d\omega' \{ 2\delta(\vec{r} - \vec{r}') \int d^3r'' v(\vec{r} - \vec{r}'') [\delta G^<(\vec{r}'', \vec{r}'') + \Delta G^<(\vec{r}'', \vec{r}'')] \\ &\quad - v(\vec{r} - \vec{r}') [\delta G^<(\vec{r}, \vec{r}') + \Delta G^<(\vec{r}, \vec{r}')] \} G_0^<(\vec{r}, \vec{r}') = \text{Tr} \{ [\delta G^<(\vec{r}, \vec{r}') + \Delta G^<(\vec{r}, \vec{r}')] \Sigma_0(\vec{r}', \vec{r}') \}, \end{aligned} \quad (3.10)$$

where we have used $v(\vec{r} - \vec{r}') = v(\vec{r}' - \vec{r})$. We now substitute for $\bar{G}^<$ and $\bar{\Sigma}$ Eqs. (3.9) and (2.24a), respectively, into the total energy expression (3.7), multiply out the terms, apply theorem (3.10), and obtain for the thermodynamic potential

$$\begin{aligned} \Omega &= \text{Tr} [(\mathcal{H}_0 + \frac{1}{2}\Sigma_0 + \frac{1}{2}\delta\Sigma - \mu)(G_0^< + \delta G^< + \Delta G^<)] \\ &= \text{Tr} [(\mathcal{H}_0 + \frac{1}{2}\Sigma_0 - \mu) G_0^<] + \text{Tr} [(\mathcal{H}_0 + \Sigma_0 - \mu) \\ &\quad \times (\delta G^< + \Delta G^<)] + \frac{1}{2} \text{Tr} [\delta\Sigma(\delta G^< + \Delta G^<)]. \end{aligned} \quad (3.11)$$

$$\begin{aligned} &= \frac{1}{2} \text{Tr} [\mathcal{H}(-i\vec{\nabla} - \frac{1}{2}\vec{s} \times \vec{r}) G^<(\vec{r}, \vec{r}')] \\ &= \frac{1}{2} \text{Tr} \{ [\mathcal{H}_0(-i\vec{\nabla}) + \bar{\Sigma}] \bar{G}^<(\vec{r}, \vec{r}') \}. \end{aligned} \quad (3.6)$$

The last step is obtained by noting that $\mathcal{H}(-i\vec{\nabla} - \frac{1}{2}\vec{s} \times \vec{r}) G^<(\vec{r}, \vec{r}')$ is given by an expression similar to Eq. (2.6) and when $\vec{r} = \vec{r}'$ the vector potential term and the Peierls phases vanish. Thus the total energy may be written

$$E_{\text{tot}} = \text{Tr} \{ [\mathcal{H}_0(-i\vec{\nabla}) + \frac{1}{2}\bar{\Sigma}] \bar{G}^< \}, \quad (3.7)$$

which is the analog of Eq. (2.23).

We now introduce the Hartree-Fock approximation¹⁶

$$\begin{aligned} \Sigma(\vec{r}, \vec{r}') &= (2\pi)^{-1} \int d\omega [2\delta(\vec{r} - \vec{r}') \int d^3r'' \\ &\quad \times G^<(\vec{r}'', \vec{r}'') v(\vec{r} - \vec{r}'') - v(\vec{r} - \vec{r}') G^<(\vec{r}, \vec{r}')]. \end{aligned} \quad (3.8)$$

The factor 2 on the Hartree term is the spin degeneracy. As Σ and $G^<$ carry the same Peierls phase factor and the phase vanishes for $\vec{r} = \vec{r}'$ Eq. (3.8) also holds for $\bar{\Sigma}$ and $\bar{G}^<$. We also define, in analogy to Eqs. (2.24),

$$\bar{G}^<(\vec{r}, \vec{r}') = G_0^<(\vec{r}, \vec{r}') + \delta G^<(\vec{r}, \vec{r}') + \Delta G^<(\vec{r}, \vec{r}'), \quad (3.9)$$

where $\delta G^<$ is the change in $G_0^<$ when Σ_0 is replaced by $\Sigma_0 + \delta\Sigma$ but no other change is made in the equation of motion, and $\Delta G^<$ is the change in $G_0^< + \delta G^<$ when the vector potential and Peierls phases are introduced into the transformed equation of motion. The order in which the changes are made is now important, in contrast to the case of the Coulomb gas, as there can be changes of the order of s , and the total change of the order s^2 can involve a cross term. Because Eq. (3.8) is linear in $G^<$, $\delta\Sigma$ is given in terms of $\delta G^< + \Delta G^<$. We may now prove the same type of theorem as Eq. (2.27),

As before, the first term gives the thermodynamic potential in the absence of the magnetic field. The second term is analogous to Eq. (2.30). The third term cannot be discarded as each change, $\delta\Sigma$ and $\delta G^< + \Delta G^<$, could have a part proportional to s , giving a term proportional to s^2 .

In Appendix D we prove that at low temperatures,

$$\text{Tr} [(\mathcal{H}_0 + \Sigma_0 + \frac{1}{2}\delta\Sigma - \mu) \delta G^<] = 0. \quad (3.12)$$

This result is the same as that of Luttinger and

Ward⁴⁰ that the thermodynamic potential is stationary with respect to the self-energy, except that our result is good to second order in $\delta\Sigma$ and their result is not limited to the Hartree-Fock approximation at low temperatures. Using this result we may rewrite the change in the thermodynamic potential (3.11)

$$\delta\Omega = \text{Tr}[(\mathcal{H}_0 + \Sigma_0 + \delta\Sigma - \mu) \Delta G^<] - \frac{1}{2} \text{Tr}(\delta\Sigma \Delta G^<) \quad (3.13)$$

We redistributed the $\delta\Sigma \Delta G^<$ term so that the first term has the form of the change in thermodynamic potential for an independent particle system whose one-particle Hamiltonian is given by $\mathcal{H}_0 + \Sigma_0 + \delta\Sigma$. (Remember that $\Delta G^<$ is the change in $G^<$ when the vector potential is introduced into the same one-particle Hamiltonian.) The evaluation of the first term will give a result proportional to B^2 with a coefficient which depends upon the effective Hamiltonian $\mathcal{H}_0 + \Sigma_0 + \delta\Sigma$. Taking the zero-field limit in operation (2.29a) gives a result depending upon the field-independent effective Hamiltonian. Thus this term represents the susceptibility calculated treating the effective Hamiltonian as an independent-particle Hamiltonian, and we call it the quasiparticle term. In this term we may drop the $\delta\Sigma$ and replace $\Delta G^<$ by $\Delta_0 G^<$, the change in $G^<$ when the vector potential is introduced into $\mathcal{H}_0 + \Sigma_0$. The third term represents explicit many-body corrections. In this term $\delta\Sigma$ and $\Delta G^<$ need be correct to first order in s only, so that $\Delta G^<$ may be replaced by $\Delta_0 G^<$. The magnetic susceptibility can then be written

$$\chi = - (2e^2/s^2) \{ \text{Tr}[(\mathcal{H}_0 + \Sigma_0 - \mu) \Delta_0 G^<] - \frac{1}{2} \text{Tr}[\delta\Sigma \Delta_0 G^<] \} \quad (3.14)$$

The standard theory of diamagnetism of non-interacting band electrons⁴¹ does not apply directly to the evaluation of the quasiparticle term because of the self-energy operator. However, we shall now show that the translational properties of the self-energy operator are the same as those of a nonlocal pseudopotential. In the simplest case, the pseudopotential is given by⁴²

$$V_P \varphi(\vec{r}) = \int d^3r' P(\vec{r}, \vec{r}') \varphi(\vec{r}'), \quad (3.15a)$$

$$P(\vec{r}, \vec{r}') = \sum_{\alpha} \chi_{\alpha}(\vec{r})(E_{\alpha} - \omega) \chi_{\alpha}^*(\vec{r}'), \quad (3.15b)$$

where the χ_{α} are the eigenfunctions of the core electrons, which can be taken as the Peierls³ wave functions

$$\chi_{n\vec{k}}(\vec{r}) = \sum_{\vec{R}} e^{i\vec{s} \cdot \vec{R} \times \vec{r}/2} e^{i\vec{k} \cdot \vec{R}} a_n(\vec{r} - \vec{R}), \quad (3.16)$$

where $a_n(\vec{r} - \vec{R})$ is an orbital localized on the atom at \vec{R} . If the overlap between the core functions a_n on different atoms can be neglected, the kernel P has the translation property $P(\vec{r} + \vec{R}, \vec{r}' + \vec{R})$

$= \exp[-\frac{1}{2}i\vec{s} \times (\vec{r} - \vec{r}') \cdot \vec{R}] P(\vec{r}, \vec{r}')$. This is equivalent to the translation properties of G and Σ , Eq. (3.2a). Therefore the quasiparticle term can be calculated by the theory of Misra and Roth,²³ which gives the diamagnetism of independent band electrons in the pseudopotential formulation.

The explicit many-body correction has the same form as, but opposite sign from, the many-body correction to the Pauli spin paramagnetism. Thus it is plausible to regard the final term in (3.14) as a correction to the orbital paramagnetism, which is composed of the crystalline paramagnetism analogous to the Pauli paramagnetism plus an interband term analogous to the Van Vleck paramagnetism. It is not hard to show that if one includes the electron spin, which adds a term $\sigma_z \mu_B B$ to the effective Hamiltonian, the change in the thermodynamic potential becomes

$$\delta\Omega = \text{Tr}[(\mathcal{H}_0 + \Sigma_0 + \sigma_z \mu_B B - \mu) \Delta_0 G^<] + \text{Tr}(\sigma_z \mu_B B \delta G^<) - \frac{1}{2} \text{Tr}(\delta\Sigma \Delta_0 G^<), \quad (3.17)$$

where μ_B is the Bohr magneton, σ_z is the Pauli spin operator, $\delta G^<$ is the change in $G_0^<$ due to the change in the form of the self-energy, and $\Delta_0 G^<$ is the change in $G_0^<$ due to the action of the vector potential and the $\sigma_z \mu_B B$ term. In the Coulomb gas case the equality $\text{Tr}(\sigma_z \mu_B B \delta G^<) = \text{Tr}(\delta\Sigma \Delta_0 G^<)$ holds, and the correction has the same form as, but opposite sign from, the orbital paramagnetism correction. With further calculation, the correction to the spin paramagnetism can be brought to the standard result.^{17,43} When the spin is neglected in the Coulomb gas case, $\Delta_0 G^<$ is of the order s^2 so that the explicit correction can be ignored. The quasiparticle term then reduces to the Sampson-Seitz result obtained in Sec. II. In the band case, $\delta\Sigma$ must be found by solving an integral equation, which is simplified by needing $\delta\Sigma$ only to first order in s .

B. Luttinger-Kohn Representation

The two band models considered in this paper are treated in the Luttinger-Kohn (LK) representation,⁴⁴ which is an extension of the $\vec{k} \cdot \vec{p}$ method to include perturbations. As it is an expansion in powers of \vec{k} , the method is particularly useful when only a small part of the Brillouin zone needs to be treated. We first write the equation of motion in the LK representation, i.e., in terms of the basis function $e^{i\vec{k} \cdot \vec{r}} u_{n0}(\vec{r})$,

$$\left\{ \left[z - \frac{1}{2m} (\vec{k} - \frac{1}{2}i\vec{s} \times \vec{\nabla}_k)^2 \right] I - \frac{1}{m} \vec{P} \cdot (\vec{k} - \frac{1}{2}i\vec{s} \times \vec{\nabla}_k) - \vec{\Sigma}(\vec{q} - \frac{1}{2}i\vec{s} \times \vec{\nabla}_k) \right\} \vec{G} |_{\vec{q}=\vec{k}} = I. \quad (3.18)$$

In the above \vec{P} is the momentum at the symmetry point, $G(k)$ and \vec{P} are matrices with respect to the band indices, and I is the unit matrix. The self-energy matrix is given by

$$\begin{aligned} \tilde{\Sigma}_{nn'}(\vec{k}) &= \int d^2r \int d^3r' e^{i\vec{k}\cdot(\vec{r}'-\vec{r})} u_{n0}^*(\vec{r}) \tilde{\Sigma}(\vec{r}, \vec{r}') u_{n'0}(\vec{r}') \\ &= \tilde{\Sigma}_{nn'}(0) + \langle n0 | e^{-i\vec{k}\cdot\vec{r}} [\tilde{\Sigma}, e^{i\vec{k}\cdot\vec{r}}] | n'0 \rangle. \end{aligned} \quad (3.19)$$

A similar Hamiltonian has been developed in the Bloch representation by Kane.⁴⁵ Expanding to second order in s , we may rewrite (3.18) as

$$[(zI - \mathcal{H}_0 - \tilde{\Sigma}) - B_1 - B_2] \tilde{G} = I, \quad (3.20)$$

where $\mathcal{H}_0 + \tilde{\Sigma}$ is the effective Hamiltonian without the vector potential (but $\tilde{\Sigma} = \Sigma_0 + \delta\Sigma$ still depends upon s), B_1 is the first-order term

$$\begin{aligned} B_1 &= -\frac{1}{2} i [\vec{\nabla}_k (\mathcal{H}_0 + \tilde{\Sigma})] \cdot \vec{s} \times \vec{\nabla}_k \\ &= -\frac{1}{2} i [(\vec{P}/m) + (\vec{k}I/m) + \vec{\nabla}_k \tilde{\Sigma}] \cdot \vec{s} \times \vec{\nabla}_k \\ &= -(i/2m)(\vec{\pi} + \vec{k}I) \cdot \vec{s} \times \vec{\nabla}_k, \end{aligned} \quad (3.21)$$

and B_2 is the second-order term

$$\begin{aligned} B_2 &= -\frac{1}{8} (\vec{\nabla}_q \cdot \vec{s} \times \vec{\nabla}_k)^2 [\mathcal{H}_0 + \tilde{\Sigma}(\vec{q})] \Big|_{\vec{q}=\vec{k}} \\ &= -\frac{1}{8} s^2 \left[\frac{1}{m} \left(\frac{\partial^2}{\partial k_x^2} + \frac{\partial^2}{\partial k_y^2} \right) + \left(\frac{\partial^2 \tilde{\Sigma}}{\partial k_x^2} \right) \frac{\partial^2}{\partial k_x^2} \right. \\ &\quad \left. - 2 \left(\frac{\partial^2 \tilde{\Sigma}}{\partial k_x \partial k_y} \right) \frac{\partial^2}{\partial k_x \partial k_y} + \left(\frac{\partial^2 \tilde{\Sigma}}{\partial k_y^2} \right) \frac{\partial^2}{\partial k_y^2} \right]. \end{aligned} \quad (3.22)$$

The quantity $\vec{\pi}$ defined in (3.21) is m times the velocity operator. Letting \tilde{G}_0 be the solution without the vector potential, $(z - \mathcal{H}_0 - \tilde{\Sigma})^{-1}$, the Green's function through second order in s can be written

$$\tilde{G} = \tilde{G}_0 + \tilde{G}_0 B_1 \tilde{G}_0 + \tilde{G}_0 B_1 \tilde{G}_0 B_1 \tilde{G}_0 + \tilde{G}_0 B_2 \tilde{G}_0. \quad (3.23)$$

We may also express \tilde{G}_0 in terms of the zero-field Green's function G_0 ,

$$\tilde{G}_0 = G_0 + G_0 \delta\Sigma G_0 + G_0 \delta\Sigma G_0 \delta\Sigma G_0, \quad (3.24)$$

to second order. For calculating the quasiparticle term, \tilde{G}_0 may be replaced by G_0 in (3.23). In calculating the explicit correction we need only the first-order terms, which are additive,

$$\tilde{G} = G_0 + G_0 \delta\Sigma G_0 + G_0 B_1 G_0. \quad (3.25)$$

The Green's function for the Coulomb gas may be calculated from (3.23) and (3.24), and after some manipulation agrees with the result found in Sec. II A.

The zero-field $\vec{k} \cdot \vec{p}$ Hamiltonian may be expanded in \vec{k} , for application when \vec{k} is small. Expanding the off-diagonal matrix elements of the self-energy to second order in \vec{k} yields

$$\{[z - \mathcal{E}^0(\vec{k})]I - (\vec{\pi} \cdot \vec{k}/m) - (\vec{k} \cdot \vec{\alpha} \cdot \vec{k})/2m\} G_0 \cong I, \quad (3.26)$$

where the tensor $\vec{\alpha}$ is defined as

$$\alpha_{ij} = \delta_{ij} + m \frac{\partial^2 \Sigma_0}{\partial k_i \partial k_j}, \quad i, j = x, y \quad (3.27)$$

and

$$\mathcal{E}_n^0(k) = \mathcal{H}_{nn}(0) + \Sigma_{nn}^0(k) + k^2/2m.$$

If we let g_0 be the solution of (3.26) for $k=0$, $[(z - \mathcal{E}^0)I]^{-1}$, then the solution for G_0 is very similar in form to Eq. (3.23).

C. Isolated s Band

We now take up the case in which the Fermi level lies in a band which has s -like symmetry at the center of the Brillouin zone and which is far in energy from all other bands. Kjeldaas and Kohn⁴⁶ used this model and the LK representation in their calculation of the independent-particle diamagnetism of the alkali metals. They calculated the conduction electron susceptibility as a power series in k_0 , the average radius of the Fermi surface. The lowest-order term is proportional to k_0 , and is equal to the Landau-Peierls diamagnetism to that order. The second term is proportional to k_0^3 , and includes interband terms. The next term is proportional to k_0^5 , and was not calculated by Kjeldaas and Kohn, though they concluded that it could be important for lithium.

We shall first estimate the explicit correction to lowest order in k_0 , for which we need expressions for the first order in s changes, $\Delta_0 G^\zeta$ and δG^ζ , to lowest order in k . Making use of the s -, p -, and d -like symmetry at the center of the zone, one can show that first terms involving the s band are off-diagonal and proportional to k . This result is closely related to the fact that the effective angular momentum operators, such as $i\vec{\pi} \times g_0 \vec{\pi}/m$, are diagonal in this symmetry and have zero eigenvalue on s -like states. Thus there is no orbital paramagnetism contribution at the zone center. As the factor $B_1 G_0$ already is proportional to k , we may write

$$\Delta_0 G \cong g_0 B_1 G_0.$$

In carrying out the analytic continuation to find $\Delta_0 G^\zeta$, terms containing f and df/dE are encountered. On integration the latter produces a factor proportional to the density of states at the Fermi level, $N(\mu)$, which is proportional to k_0 ; while the former produces a factor proportional to the carrier density, which is proportional to k_0^3 . Keeping only the df/dE term, we find

$$\begin{aligned} \Delta G_{n'n}^\zeta &\cong i (\vec{\pi} \cdot \vec{s} \times \vec{\nabla}_k G_0^\zeta)_{n'n} / 2m (\mathcal{E}_n - \mathcal{E}_{n'}) \\ &= 2\pi \delta(\omega - \mathcal{E}_n) i \vec{\pi}_{n'n} \cdot \vec{s} \times \vec{\nabla}_k f(\mathcal{E}_n) / 2m (\mathcal{E}_n - \mathcal{E}_{n'}) \end{aligned}$$

$$= 2\pi\delta(\omega - \mathcal{E}_n)\Delta\rho_{n'n}, \quad (3.28)$$

where n is the band index for the conduction band and $\rho_{n'n}$ is the Dirac density matrix.

As there are no diagonal matrix elements of $\Delta G^<$ to lowest order, $\delta\Sigma$ is off-diagonal, and we have for the corresponding change in $G^<$

$$\begin{aligned} \delta\rho_{n'n} &= (2\pi)^{-1} \int d\omega (g_0 \delta\Sigma g_0)_{n'n}^< \\ &= \delta\Sigma_{n'n} [f(\mathcal{E}_n) - f(\mathcal{E}_{n'})] / (\mathcal{E}_n - \mathcal{E}_{n'}). \end{aligned} \quad (3.29)$$

The factor $f_n - f_{n'}$ will produce a factor k_0^3 , so that we shall neglect $\delta G^<$, though it is not difficult to include it and solve the integral equation for $\delta\Sigma$ to lowest order.

The relation between the self-energy and the Green's function is very simple in the $\vec{k} \cdot \vec{p}$ approximation,

$$\bar{\Sigma}_{n'n}(\vec{k}) = - (2\pi)^{-4} \int d\omega \int d^3k' V(\vec{k} - \vec{k}') G_{n'n}^<(\vec{k}') . \quad (3.30)$$

In the above, umklapp terms such as $V(\vec{k} - \vec{k}' + \vec{K})$ have been neglected, where \vec{K} is a reciprocal lat-

tice vector. We find approximately

$$\begin{aligned} \delta\Sigma_{n'n}(\vec{k}) &= - \frac{i\vec{\pi}_{n'n} \times \vec{s}}{2m(\mathcal{E}_n - \mathcal{E}_{n'})} \int \frac{d^3k'}{(2\pi)^3} V(\vec{k} - \vec{k}') \\ &\quad \times \vec{\nabla}_{k'} \mathcal{E}_n(\vec{k}') \frac{\partial f(\mathcal{E}_n(\vec{k}'))}{\partial \mathcal{E}_n} . \end{aligned} \quad (3.31)$$

We need $\delta\Sigma$ evaluated at the Fermi surface only, and

$$\delta\Sigma_{n'n}(k_F) = i\vec{\pi}_{n'n} \times \vec{s} \cdot \vec{\nabla}_k \mathcal{E}_n(k) N(\mu) F_1 / 2m(\mathcal{E}_n - \mathcal{E}_{n'}) , \quad (3.32)$$

where

$$F_1 = \int d\varphi' \int d\theta' \sin\theta' v(\vec{k} - \vec{k}') \cos\theta_{kk'} , \quad (3.33)$$

is a familiar integral from Fermi liquid theory (giving the correction to the quasiparticle mass). As $\vec{\nabla}_k \mathcal{E}$ is proportional to k and $N(\mu)$ is proportional to k_0 , $\delta\Sigma$ is proportional to k_0^2 . Finally, the correction to the thermodynamic potential is

$$\begin{aligned} -\frac{1}{2} \text{Tr}(\delta\Sigma \Delta G^<) &= -\frac{1}{2} \sum_n \sum_{n' \neq n} (2\pi)^{-4} \int d\omega \int d^3k \delta\Sigma_{nn'}(\vec{k}) \Delta G_{n'n}^<(\vec{k}) \\ &= \frac{1}{2} \sum_n \sum_{n' \neq n'} \left(\frac{\vec{\pi}_{n'n} \times \vec{s} \cdot \vec{\nabla}_k \mathcal{E}_n}{2m(\mathcal{E}_n - \mathcal{E}_{n'})} N(\mu) \right)^2 F_1 = \frac{1}{16} \left(\sum_n \sum_{n' \neq n'} \frac{|\pi_{n'n}^x|^2 + |\pi_{n'n}^y|^2}{m^2(\mathcal{E}_n - \mathcal{E}_{n'})^2} \pi^2 N_0 \frac{\partial \mathcal{E}}{\partial k_F} \right) \frac{s^2 N_0}{\pi^2} \frac{\partial \mathcal{E}}{\partial k_F} F_1 . \end{aligned} \quad (3.34)$$

Note that the correction is positive, so the correction to the susceptibility is diamagnetic (reduced orbital paramagnetism). The product $N(\mu) \partial \mathcal{E} / \partial k_F$ is equal to k_0^2 / π^2 , so that the whole term is proportional to k_0^4 , one order higher than the highest term retained by Kjeldaa and Kohn. The factor in the parentheses is the total admixture of other states into the s band at the Fermi level, and is roughly equal to $[(m^*/m_0) - 1]^2$, which is about 0.001 for sodium but about 0.1 for lithium. Now F_1 is of the order of $4\pi e^2 / \eta^2 k_0^2$. Using the Thomas-Fermi value for η and putting in the expression for s in terms of B , we find a correction to the susceptibility of the order of

$$\delta\chi = \frac{3}{2} [(m^*/m_0) - 1]^2 \chi_{LP} , \quad (3.35)$$

where LP denotes the Landau-Peierls value. Thus we see that the correction is small for sodium, $\sim 0.2\%$, but is important for lithium $\sim 15\%$.

The quasiparticle term may be different from the calculation of Kjeldaa and Kohn because of the terms coming from the self-energy. One sees that the terms linear in k can be handled by replacing \vec{P} by $\vec{\pi}$; one of us has shown³⁵ that to order k_0 the susceptibility is again given by the Landau-

Peierls term operating on the quasiparticle energy. Any change in the k_0^3 term should be unimportant for sodium (where the k_0^3 term is 2% of the k_0 term), but may be appreciable for lithium. Because the explicit correction is small, the method of Misra and Roth²³ should give the complete answer provided the correct pseudopotential is used.

D. Two Strongly Interacting Bands

Finally, we treat another extreme case, that of two bands close together in energy and interacting so strongly that all other bands may be neglected. This case applies to the Lax model⁴⁷ of the conduction electrons in bismuth, and to a special point in the Brillouin zone of graphite.⁴⁸ The $\vec{k} \cdot \vec{p}$ Hamiltonian is expanded about a symmetry point (L , H , respectively) which is not at the zone center. The matrix elements of the momentum between the two states at the symmetry point are non-zero, so for small values of k the linear terms dominate and we neglect the quadratic terms. The effective one-particle Hamiltonian in the absence of the magnetic field is

$$\mathcal{H}_0 + \Sigma_0 = \begin{pmatrix} -\mathcal{E} & \pi_1 k_x + i\pi_2 k_y \\ \pi_1 k_x - i\pi_2 k_y & \mathcal{E} \end{pmatrix}, \quad (3.36)$$

where, for bismuth

$$\mathcal{E} = [(\frac{1}{2}E_G)^2 + \pi_3^2 k_x^2]^{1/2}, \quad (3.37)$$

and E_G is the energy gap, which is due to the spin-orbit coupling in bismuth. Note that when the linear approximation is valid the many-body effects merely alter the value of the π_i . Thus for certain properties, model calculations which use the experimental values of π_i implicitly include the many-body effects. In particular, the quasiparticle susceptibility will be given by the independent-particle calculations of Fukuyama and Kubo,⁴⁹ and of Buot.⁵⁰ In our notation the quasiparticle contribution to the change in the thermodynamic potential at absolute zero is given by

$$\delta\Omega_{QP} = (s^2 \pi_1 \pi_2 / 3\pi \pi_3) [\sinh^{-1}(2E_c/E_G) - \sinh^{-1}(2\eta/E_G)], \quad (3.38)$$

where $\eta = [\mu^2 - (\frac{1}{2}E_G)^2]^{1/2}$ and E_c is a cutoff energy of the order of the bandwidth. Buot⁵¹ has shown that this expression gives excellent agreement with experiment when the proper values of the parameters are chosen.

We shall now estimate the explicit correction to the orbital paramagnetism. The zero-field Green's function is easily found by inverting the 2 by 2 matrix $zI - \mathcal{H}_0 - \Sigma_0$,

$$G_0 = \frac{1}{[z - E_1(\vec{k})][z - E_2(\vec{k})]} \times \begin{pmatrix} z - \mathcal{E} & \pi_1 k_x + i\pi_2 k_y \\ \pi_1 k_x - i\pi_2 k_y & z + \mathcal{E} \end{pmatrix}, \quad (3.39)$$

where

$$E_{1,2}(\vec{k}) = \mp [(\frac{1}{2}E_G)^2 + \pi_1^2 k_x^2 + \pi_2^2 k_y^2 + \pi_3^2 k_z^2]^{1/2}. \quad (3.40)$$

Straightforward calculation yields the first-order change

$$\Delta_0 G = G_0 B_1 G_0 = \frac{s\pi_1 \pi_2}{(z - E_1)^2 (z - E_2)^2} \begin{pmatrix} z - \mathcal{E} & 0 \\ 0 & -z - \mathcal{E} \end{pmatrix}. \quad (3.41)$$

After manipulation which uses the facts that

$$E_1 = -E_2, \quad z - \mathcal{E} = z - E_1 + E_1 - \mathcal{E},$$

$$(z - E_1)^{-2} = \partial(z - E_1)^{-1} / \partial E_1,$$

and

$$(2\pi)^{-1} \int d\omega [(z - E_1)^{-1} (z - E_2)^{-1}] = (f_1 - f_2) / (E_1 - E_2),$$

we find

$$\Delta_0 \rho_{11,22} = \frac{s\pi_1 \pi_2}{4E_2} \left[\pm \left(\frac{\partial f_1}{\partial E_1} - \frac{\partial f_2}{\partial E_2} \right) + \frac{\mathcal{E}}{E_2} \left(\frac{\partial f_1}{\partial E_1} + \frac{\partial f_2}{\partial E_2} - \frac{f_1 - f_2}{E_2} \right) \right]. \quad (3.42)$$

The reason the trace of $\Delta_0 G^<$ is not zero for these expressions is that there are two points in the Brillouin zone connected by time reversal. The sum of the trace of $\Delta_0 G^<$ for both points is zero. As the eigenfunctions and eigenvalues of the Hamiltonian (3.36) are easily found, we have also derived the same $\Delta_0 G^<$ by using the same techniques as we used for free electrons.

Including the change in $G^<$ due to the change in Σ , we again arrive at an integral equation for $\delta\Sigma$ which can be easily solved. However, the solution for $\delta\Sigma$ is equal to the $\delta\Sigma$ calculated ignoring $\delta G^<$, divided by a factor roughly equal to $1 - N_L(\mu)/N_T(\mu)$, where $N_L(\mu)$ is the density of states for one spin of the conduction electrons at one L point and $N_T(\mu)$ is the total density of states. Because of the contribution of the free holes N_T is more than an order of magnitude greater than N_L in bismuth, so that we ignore $\delta G^<$.

The explicit correction due to the $\Delta_0 G^<$ in Eqs. (3.42) is diamagnetic, and is a symmetric function of the Fermi level μ . However, we now show that it is negligible for bismuth. First we consider that the Fermi level is in band 2, $\mu > \frac{1}{2}E_G$, and estimate the effect due to the first $\partial f_2 / \partial E_2$ term. We find

$$\delta\Sigma'_{22} = \frac{s\pi_1 \pi_2 \pi e^2}{\epsilon_0} \int \frac{d^3 k'}{(2\pi)^3} \frac{1}{[q^2 + (\vec{k} - \vec{k}')^2] E_2(\vec{k}')} \frac{\partial f_2}{\partial E_2} = -\delta\Sigma'_{11} \cong -s\pi_1 \pi_2 \pi e^2 N_L(\mu) / \epsilon_0 q^2 \mu. \quad (3.43)$$

In the above q is the Thomas-Fermi screening constant, $q^2 = 4\pi e^2 N_T(\mu) / \epsilon_0$, where ϵ_0 is the background dielectric constant. For bismuth⁵² $\epsilon_0 = 99$, $q = 0.003 \text{ \AA}^{-1}$, and the maximum extent of the Fermi surface⁵¹ is $k = 0.03 \text{ \AA}^{-1}$, so we have overestimated the integral by neglecting $\vec{k}' - \vec{k}$ compared to \vec{q} . The contribution to the explicit correction becomes

$$-\frac{1}{2} \text{Tr}(\delta\Sigma \Delta_0 G^<) \cong e^2 (\pi_1 \pi_2)^2 \pi s^2 [N_L(\mu)]^2 / 4\epsilon_0 q^2 \mu^2 = (s^2 \pi_1 \pi_2 / 3\pi \pi_3) [3\pi^2 e^2 \pi_1 \pi_2 \pi_3 N_L^2(\mu) / 4\epsilon_0 q^2 \mu^2]. \quad (3.44)$$

The factor in the square brackets on the right-hand side of the second line of (3.44) is roughly equal to the fractional correction to the quasiparticle susceptibility. The density of states for this model is

$$N_L(\mu) = \mu \eta / 2\pi^2 \pi_1 \pi_2 \pi_3, \quad (3.45)$$

so that the correction factor becomes

$$\delta\chi / \chi_{QP} \cong 3e^2 [\mu^2 - (\frac{1}{2}E_G)^2] / 16\pi^2 \epsilon_0 q^2 \pi_1 \pi_2 \pi_3. \quad (3.46)$$

Using the experimental values of the π_i , the cor-

rection factor is about 3×10^{-4} for $\mu = E_G$, and thus is negligible.

Next we consider that the Fermi level lies in

$$\begin{aligned} -\frac{1}{2} \text{Tr}(\delta \Sigma \Delta_0 G') &\cong \left(\frac{s \pi_1 \pi_2}{4} \right)^2 \frac{4 \pi e^2}{\epsilon_0} \int \frac{d^3 k}{(2\pi)^3} \int \frac{d^3 k'}{(2\pi)^3} \frac{\mathcal{E}(\vec{k})}{E_2^3(\vec{k})} \frac{1}{q^2 + (\vec{k} - \vec{k}')^2} \frac{\mathcal{E}(\vec{k}')}{E_2^3(\vec{k}')} \\ &\cong \frac{s^2 \pi_1 \pi_2}{3 \pi \pi_3} \left[\frac{3 e^2}{4 \pi \epsilon_0} \int \frac{d^3 k}{(2\pi)^3} \int \frac{d^3 k'}{(2\pi)^3} \frac{\mathcal{E}(\vec{k}) \pi_1 \pi_2 \bar{\pi} \mathcal{E}(\vec{k}')}{E_2^3(\vec{k}) [q^2 + (\vec{k} + \vec{k}')^2] E_2^3(\vec{k}')} \right], \end{aligned} \quad (3.47)$$

where $\bar{\pi} = (\pi_1 \pi_2 \pi_3)^{1/3}$. Again the factor in square brackets is roughly the fractional correction to the quasiparticle susceptibility. The double integral in the final line is dimensionless. The integrals are limited to a finite volume, which we overestimate by using the volume of the Brillouin zone. A rough estimate of the integral is $\ln[E_c / (E_G + \bar{\pi} q)] / 16 \pi$, where E_c is the cutoff energy. The value of $3 e^2 / 4 \pi \epsilon_0$ is about 0.015, so we find this correction is also negligible. The change in this term when the Fermi level is in one of the bands is a fraction of the value just calculated, and thus is negligible.

Thus we find that the orbital magnetism is given by the quasiparticle term, which is the same as the independent particle calculation with experimental values of the π_i . This is just the calculation of Buot, which gives excellent agreement with experiment.

IV. CONCLUSIONS

In Sec. II we proved that the Sampson-Seitz prescription gives the orbital diamagnetism of a Coulomb gas if two conditions are met: (i) The transformed self-energy is the same functional of the transformed Green's function to second order in the magnetic field strength as when the magnetic field is zero, and (ii) the self-energy in the absence of the magnetic field is independent of the frequency. A model meeting these conditions is a gas interacting through a statically screened potential and treated in the Hartree-Fock approximation. Even though this model gives many of the results of the random phase approximation, it would be very gratifying to extend the proof to a more rigorous approximation. The Sampson-Seitz prescription offers a simple way to think of diamagnetism and provides an easy way to calculate a more accurate diamagnetism whenever an advance is made in the theory of the self energy in the absence of the magnetic field. In Sec. II we did find general expressions for the frequency-dependent Green's function and effective one-particle energy eigenvalue in the magnetic field. These expressions may be of use in generalizing the proof of the Sampson-Seitz prescription.

the forbidden gap, so that $f_1 = 1$ and $f_2 = 0$, and only the $f_1 - f_2$ term contributes. We find for the total correction

In Sec. III we treated the case of interacting electrons in a periodic potential in the same two approximations as used in Sec. II. We derived a quasiparticle prescription: The diamagnetism is to be calculated treating the self-energy as a nonlocal pseudopotential and ignoring the change with magnetic field in the transformed self-energy. It was pointed out that the theory of Misra and Roth does just that, and if the correct pseudopotential is used their theory includes both the band structure and many-body effects. We also found an explicit many-body correction to the orbital paramagnetism which has the same form as, but opposite sign from, the many-body correction to the spin paramagnetism. The correction tends to be diamagnetic in simple cases. We showed that the correction is negligible for sodium, but may increase the diamagnetism of lithium by about 15%. The correction was also found to be negligible for the two-band model of bismuth. We cannot as yet compare our results to those of Fukuyama,²⁰ who calculated for the different two-band model generated by a weak cosine potential. However his corrections are both diamagnetic and paramagnetic, and are not symmetric about the middle of the energy gap.

We have not explicitly considered the question of the change in screening with magnetic field. This effect would be included in a complete many-body calculation, but in our models we have kept the screening of the electron-electron interaction independent of magnetic field. Hebborn and March⁵³ have shown that the correction to the screening parameter η^2 is proportional to $s^2 r_s^5$. This could cause a fractional change in the susceptibility proportional to r_s^2 , which should be included. However, in the Bohm-Pines theory⁵ the value of η is chosen so that the derivative of the total energy with respect to η is zero, which would give no correction to the susceptibility. Glasser and Kaplan⁵⁴ have pointed out that the change in the screening of the lattice potential should cause corrections to the susceptibility. This effect is partially included in our calculation of the change in self-energy $\delta \Sigma$. Glasser and Kaplan⁵⁴ find that the effect vanishes for zero absolute temperature. Brown, Hebborn,

TABLE I. Magnetic properties of lithium and sodium. All experimental quantities are for $T=80^\circ\text{K}$. The units of susceptibility are dimensionless, often written emu/cm^3 .

Property	Li	Na	Comments
$10^6 \chi_{\text{tot}}$	1.86 ± 0.06	0.585 ± 0.015	Experimental, Collings ^a
$10^6 \chi_p$	1.98 ± 0.10	1.05 ± 0.10	Experimental ^b average
$10^6 \chi_i$	-0.06 ± 0.002^c	-0.22 ± 0.02^d	Theoretical
$10^6 \chi_d$	-0.02 ± 0.16	-0.25 ± 0.14	Deduced from above
$10^6 \chi_d$	-0.267	-0.219	Free-electron theory, $m = m_0$
$10^6 \chi_d$	-0.202	-0.228	Free-electron, $m^*/m_0=1.32, 0.96$
$10^6 \chi_d$	-0.31 ± 0.005	-0.221 ± 0.002	Coulomb gas, $m^*/m_0=1.45, 0.98$, Fletcher and Larson ^e
$10^6 \chi_d$	-0.150	-0.235	Coulomb gas, $m^*/m_0=2.17, 1.21$, Isihara and Tsai ^f
$10^6 \chi_d$	-0.19	-0.27	Coulomb gas, $m^*/m_0=1.66, 1.00$, corrected Isihara and Tsai
$10^6 \chi_d$	-0.074	-0.23	Band effects only, Kjeldaas and Kohn ^g
$10^6 \chi_d$	-0.252	-0.214	Band effects only, Papadopoulos and Jones ^h
$10^6 \chi_d$	-0.233	-0.208	Pseudopotential method, Misra and Roth ⁱ

^aE. W. Collings, *J. Phys. Chem. Solids* **26**, 949 (1965).

^bR. Hecht, *Phys. Rev.* **132**, 966 (1963), and references therein.

^cW. A. Goddard, *J. Chem. Phys.* **48**, 1008 (1968).

^dReference 57.

^eReference 6.

^fReference 59.

^gReference 46, with corrected value for Na.

^hG. J. Papadopoulos and A. V. Jones, *J. Phys. F* **1**, 593 (1971).

ⁱReference 23.

and Scanes⁵⁵ disagree, finding a fractional correction which is proportional to r_s^{-5} and whose largest value is 2% for lithium.

In comparing with experiment, one usually writes for the alkali metals $\chi_{\text{tot}} = \chi_i + \chi_p + \chi_d$, where χ_{tot} is the total magnetic susceptibility, χ_i is the ionic diamagnetism, χ_p is the spin paramagnetism, and χ_d is the orbital diamagnetism of the conduction electrons. This separation is valid when the ion core is much smaller than the atomic volume and the spin-orbit coupling is small, conditions met by lithium and sodium. In Table I we list the best values of these quantities. The χ_{tot} values are modern experimental values at liquid-nitrogen temperatures. The χ_p values are the averages of four and three measurements all with stated uncertainty of $\pm 0.1 \times 10^{-6}$, and all within the uncertainty adopted for the table. The χ_i values are calculated from accurate wave functions, Hartree-Fock for Na^+ and correlated for Li^+ . The value of χ_i for sodium is about equal to χ_d , so it is important to have an accurate value. It has been concluded⁵⁶ that the experimental values of χ_i for Na^+ are unreliable, though the value -0.2×10^{-6} was adopted. The Hartree-Fock value for Ne is only 3% greater than the experimental value,⁵⁷ and the

Hartree-Fock approximation should be even better for Na^+ because of the greater nuclear attraction. For comparison, Van Vleck's⁵⁸ value gives -0.18×10^{-6} and Isihara and Tsai⁵⁹ use a value of -0.29×10^{-6} , which is based on experiments with compounds. Our diamagnetism deduced from the above mentioned quantities differs significantly from earlier values, as all three quantities have changed.

We also list various theoretical values in Table I, including the free-electron (noninteracting) values using both the free-electron mass and the "bare" band mass (effective mass including the lattice and Hartree potentials only). Fletcher and Larson⁶ and Isihara and Tsai⁵⁹ modified their Coulomb gas calculations by using a band effective mass. Fletcher and Larson correctly used the "bare" band masses but Isihara and Tsai used effective masses derived from the low-temperature heat capacity, which already contain large many-body corrections.⁶⁰ Therefore we also list the results of Isihara and Tsai calculated with the correct effective masses. For comparison, we also give the results of two calculations which include the band structure but ignore the many-body effects. For sodium, most calculations agree that

neither band nor many-body effects are very important. The new "experimental" value agrees with all theoretical values, including the value of Misra and Roth, which we consider the most accurate. For lithium, the deviations are larger. Our results indicate that the correct value should be a little larger than Misra and Roth's, perhaps $\chi_d = -0.26 \times 10^{-6}$, which seems to be outside the experimental uncertainty. Unfortunately, χ_d is so small that high accuracy is needed in χ_{tot} and χ_p in order to resolve the uncertainty.

Finally, the correction to the orbital paramagnetism could conceivably be a new mechanism for superconductivity. In simple cases the solution for $\delta\Sigma$ involves a denominator approximately equal to $1 - vN(\mu)$, where v is an integral involving the interaction and $N(\mu)$ is the density of states. If the factor $vN(\mu)$ were equal to unity, there could be a spontaneous diamagnetism, if the explicit correction remains diamagnetic. A spontaneous diamagnetism would be a Meissner effect and thus would imply superconductivity. This argument is analogous to the theory of free-electron ferromagnetism, which does not exist because of the screening effects.⁶¹ The values of $vN(\mu)$ estimated in Sec. III are small, and it is likely that they are always less than unity.

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APPENDIX A: EIGENFUNCTIONS AND EIGENVALUES OF THE ONE-PARTICLE OPERATORS

We start by expressing functions of the operator Q_{op}^2 in terms of K_{op}^2 . The quantity $(Q_{op}^2)^n$ may be written as $K_{op}^2(Q_{op}^2)^{n-1}$, as the k_x and k_y in K_{op}^2 on the left are not affected by the derivatives in Q_{op}^2 . We can bring the K_{op}^2 through to the right by using the commutation relation which is easily proved,

$$[K_{op}^2, Q_{op}^2] = s^2 + s^2(\vec{k} - \vec{q}) \cdot \vec{\nabla}_k + 2i\vec{q} \cdot \vec{s} \times \vec{k}. \quad (A1)$$

If there are no derivative operators to the left of the commutator we may put $\vec{q} = \vec{k}$, obtaining s^2 . If there is one Q_{op}^2 to the left, its action on the right-hand side of (A1) produces

$$Q_{op}^2 [K_{op}^2, Q_{op}^2] = 3s^2 Q_{op}^2. \quad (A2)$$

If there are several powers of Q_{op}^2 to the left, each one acts individually on the right-hand side of (A1), which is linear in k :

$$(Q_{op}^2)^\lambda [K_{op}^2, Q_{op}^2] = (2\lambda + 1)s^2 (Q_{op}^2)^\lambda. \quad (A3)$$

Finally we can use (A3) repeatedly to obtain

$$\begin{aligned} (Q_{op}^2)^n &= K_{op}^2 (Q_{op}^2)^{n-1} \\ &= (Q_{op}^2)^{n-1} K_{op}^2 + (n-1)s^2 (Q_{op}^2)^{n-2}. \end{aligned} \quad (A4)$$

The result (A4) also can be used repeatedly until all Q_{op}^2 have been replaced by combinations of K_{op}^2 . As the eigenfunctions of K_{op}^2 are eigenfunctions of $(K_{op}^2)^n$, they are also eigenfunctions of $(Q_{op}^2)^n$.

We need the eigenvalues to second order in s , for which iteration of (A4) gives

$$(Q_{op}^2)^n = (K_{op}^2)^n + \frac{1}{8} s^2 n(n-1)(2n-1)(K_{op}^2)^{n-2} + O(s^4). \quad (A5)$$

If the self-energy can be expanded in powers of ρ^2 , we have after operator replacement

$$\begin{aligned} \bar{\Sigma}(Q_{op}^2) &= \sum_n A_n (Q_{op}^2)^n \\ &= \bar{\Sigma}(K_{op}^2) + s^2 \left[\frac{1}{8} K_{op}^2 \bar{\Sigma}'''(K_{op}^2) + \frac{1}{2} \bar{\Sigma}''(K_{op}^2) \right] + O(s^4), \end{aligned} \quad (A6)$$

where the primes stand for derivatives with respect to ρ^2 (or K_{op}^2). This completes the proof of Eq. (2.14).

APPENDIX B: EVALUATION OF SUMMATIONS

We wish to evaluate sums of the type

$$S = 2 \sum_\lambda (-1)^\lambda e^{-\rho^2/s} L_\lambda(2\rho^2/s) F[(2\lambda+1)s], \quad (B1)$$

where F is a function which can be Taylor expanded. The most important contribution to the sum comes from the region where the relations $L_{\lambda+1} = -L_\lambda = L_{\lambda-1}$ are approximately satisfied. Combining this with the recursion relation³¹

$$(\lambda+1)L_{\lambda+1} - (2\lambda+1-2\rho^2/s)L_\lambda + \lambda L_{\lambda-1} = 0, \quad (B2)$$

we find the standard replacement rule $(2\lambda+1)s = \rho^2$. We thus expand $F[(2\lambda+1)s]$ about this value, and, to evaluate the sums, make use of the generating function³¹

$$J(t, z) = e^{-tz/(1-z)} / (1-z) = \sum_\lambda z^\lambda L_\lambda(t). \quad (B3)$$

The zero-order term is given by setting $z = -1$, while the higher-order terms are found by taking derivatives with respect to z and then setting $z = -1$. Calling

$$S_n = 2 \sum_\lambda (-1)^\lambda e^{-\rho^2/s} [(2\lambda+1)s - \rho^2]^n L_\lambda(2\rho^2/s), \quad (B4)$$

we find $S_0 = 1$, $S_1 = 0$, $S_2 = -s^2$, $S_3 = -2s^2\rho^2$, and $S_4 = 20s^4$. Higher-order terms are proportional to higher powers of s . Combining these results with the Taylor expansion of F , we have

$$S = F(\rho^2) - \frac{1}{3}s^2\rho^2 F'''(\rho^2) - \frac{1}{2}s^2 F''(\rho^2) + O(s^4), \quad (B5)$$

where the primes stand for the derivatives with respect to ρ^2 . This result then involves the same operator D that appears in the eigenvalue equation. When F is taken to be $[z - E_\lambda(k_x)]^{-1}$, Eq. (2.19) is obtained.

APPENDIX C: PROPERTIES OF THE OPERATOR D

The integral over k space can be separated into the integral over k_z and the integral over k_x and k_y . For cylindrically symmetric functions the two-dimensional integration $(2\pi)^{-2} \int dk_x dk_y$ can be replaced by $(4\pi)^{-1} \int d\rho^2$. Using the notation $\rho^2 = x$, we consider integrals of the type

$$I = \int_0^\infty dx F(x) Dg(x), \quad (C1)$$

where $F(x)$ and $g(x)$ are differentiable functions which are everywhere finite, and at least one of which vanishes rapidly as x approaches infinity. A series of partial integrations yields

$$I = -\frac{1}{6} F(x) \frac{\partial g}{\partial x} \Big|_{x=0} + \int_0^\infty dx \left(\frac{1}{3} x \frac{\partial^2}{\partial x^2} F + \frac{1}{6} \frac{\partial F}{\partial x} \right) \frac{\partial g}{\partial x}. \quad (C2)$$

In the above, we have discarded all terms evaluated at infinity, and those terms proportional to x at $x=0$. Further partial integration yields

$$I = -\frac{1}{6} \left(F \frac{\partial g}{\partial x} + g \frac{\partial F}{\partial x} \right)_{x=0} - \int_0^\infty dx g(x) DF(x). \quad (C3)$$

The first term in Eq. (C3) is equal to $\int_0^\infty dx D(Fg)$, so that (C3) proves the result that under the integral $D(Fg) = FDg + gDF$.

We now apply (C2) to evaluate Eq. (2.31), so that $g = f(\epsilon_0)$, the Fermi distribution function, and $F = \epsilon_0 - \mu$. At low temperatures $\partial f / \partial x = 0$ unless $\epsilon_0(x) = \mu$. Thus the term evaluated at $x=0$ vanishes, as at least one of the factors is always zero.

Furthermore $D\mu = 0$, so the integrand is equal to $fD\epsilon_0$. Returning to the k notation, we note that ϵ_0 is a spherically symmetric function, depending upon $k_x^2 + k_y^2 + k_z^2 = x + k_z^2$. Thus

$$\frac{\partial \epsilon_0}{\partial x} = \frac{1}{2k} \frac{\partial \epsilon_0}{\partial k} \quad (C4)$$

and

$$\frac{\partial^2 \epsilon_0}{\partial x^2} = \frac{1}{2k} \frac{\partial}{\partial k} \left(\frac{1}{2k} \frac{\partial \epsilon_0}{\partial k} \right) = \frac{1}{4k^2} \left(\frac{\partial^2 \epsilon_0}{\partial k^2} - \frac{1}{k} \frac{\partial \epsilon_0}{\partial k} \right). \quad (C5)$$

The integral I now becomes

$$I = \frac{1}{4\pi} \int d^2k \left[\frac{\rho^2}{3k^2} \left(\frac{\partial^2 \epsilon_0}{\partial k^2} - \frac{1}{k} \frac{\partial \epsilon_0}{\partial k} \right) + \frac{1}{3k} \frac{\partial \epsilon_0}{\partial k} \right] \frac{1}{2k} \frac{\partial \epsilon_0}{\partial k} \frac{\partial f}{\partial \epsilon_0}. \quad (C6)$$

Including the integral on k_z and the multiplying factors, Eq. (2.31) becomes

$$\chi = \frac{e^2}{36\pi^2} \int_0^\infty dk \left(2k \frac{\partial^2 \epsilon_0}{\partial k^2} + \frac{\partial \epsilon_0}{\partial k} \right) \frac{\partial \epsilon_0}{\partial k} \frac{\partial f}{\partial \epsilon_0}, \quad (C7)$$

where we have evaluated the angular integrals by making use of the fact that the average of $(\rho/k)^2$ is equal to $\frac{2}{3}$. We change to an integration on ϵ_0 and use the fact that at low temperatures $\partial f / \partial \epsilon = -\delta(\epsilon_0 - \mu)$ to find

$$\chi = -\frac{e^2}{36\pi^2} \left(2k \frac{\partial^2 \epsilon_0}{\partial k^2} + \frac{\partial \epsilon_0}{\partial k} \right)_{k=k_F}. \quad (C8)$$

This result gives Eq. (2.32) on restoration of the units.

APPENDIX D: PROOF THAT THE THERMODYNAMIC POTENTIAL IS STATIONARY TO SECOND ORDER IN THE SELF-ENERGY

We wish to prove that the quantity given in Eq. (3.12) is zero at low temperatures. The same formula gives the total change in the thermodynamic potential due to a change in the self-energy when Eq. (3.10) is valid. In both cases δG is the change in G due to the change in self-energy alone, and is given in Eq. (3.24). As in our approximation $\delta \Sigma$ is independent of frequency, we may perform the integration on frequency before substituting into Eq. (3.12). We shall use the Bloch representation, in which $\mathcal{H}_0 + \Sigma_0$ and G_0 are diagonal. We find

$$\delta \rho_{mn} = (2\pi)^{-1} \int d\omega \delta G_{mn}^{0<} = \delta \Sigma_{nn} \frac{\partial f_n}{\partial \mathcal{E}_n} + \frac{1}{2} (\delta \Sigma_{mm})^2 \frac{\partial^2 f_n}{\partial \mathcal{E}_n^2} + \sum_{n' \neq n} \frac{\delta \Sigma_{nn'} \delta \Sigma_{n'n}}{\mathcal{E}_n - \mathcal{E}_{n'}} \left(\frac{f_n - f_{n'}}{\mathcal{E}_n - \mathcal{E}_{n'}} + \frac{\partial f_n}{\partial \mathcal{E}_n} \right), \quad (D1)$$

$$\delta \rho_{n'n} = [(f_n - f_{n'}) / (\mathcal{E}_n - \mathcal{E}_{n'})] \delta \Sigma_{n'n}, \quad n' \neq n, \quad (D2)$$

where $f_n = f(\mathcal{E}_n)$ and $\mathcal{E}_n(k)$ is the eigenvalue of $\mathcal{H}_0 + \Sigma_0$. We need the off-diagonal $\delta \rho$ only to first order to calculate the quantity (3.12) to second order. When these expressions are substituted into Eq. (3.12), two terms are produced of the form $\int d^3k (\mathcal{E}_n - \mu) \partial f_n / \partial \mathcal{E}_n$. These terms are proportional to the square of the absolute temperature and will be neglected. Two other terms involve $\int d^3k (\Sigma_{nn})^2 [(\mathcal{E}_n - \mu)(\partial^2 f / \partial \mathcal{E}_n^2) + \partial f_n / \partial \mathcal{E}_n]$, which after partial integration takes the same form as the first two terms discussed above. Finally, we are left with the terms

$$\int \frac{d^3k}{(2\pi)^3} \sum_n \sum_{n' \neq n} \frac{\delta \Sigma_{nn'} \delta \Sigma_{n'n}}{(\mathcal{E}_n - \mathcal{E}_{n'})^2} [(\mathcal{E}_n - \mu)(f_{n'} - f_n) + \frac{1}{2} (\mathcal{E}_n - \mathcal{E}_{n'}) (f_n - f_{n'})]. \quad (D3)$$

The factor outside the square brackets is even with respect to interchange of n and n' , while the factor inside the brackets is odd. Thus the double summation is zero, completing the proof.

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PHYSICAL REVIEW B

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Metal-Insulator Transition in Solid Hydrogen*

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The transition between compressed molecular hydrogen and metallic hydrogen is investigated from the point of view of a metal-insulator transition. By studying how the electronic states in metallic hydrogen change when nearest-neighbor protons are moved closer together it is found that the transition should occur at a pressure in the neighborhood of 3 Mbar. The metastability of metallic hydrogen at low pressures is investigated and it is found that at zero pressure and temperature metallic hydrogen would last only a fraction of a second.

I. INTRODUCTION

There is at present great interest in the possibility of producing metallic hydrogen in the laboratory. In this connection it is important to have some estimate of what pressure is needed to produce metallic hydrogen and whether metallic hydrogen would be metastable at low pressures. Estimates of the pressure needed to make metallic hydrogen vary all the way from 0.25 to 20 Mbar.^{1,2} In this paper we will discuss the transition between compressed molecular hydrogen and metallic hydrogen from the point of view of a metal-insulator transition. This point of view allows us to estimate the transition pressure in a simple way and also to investigate whether metallic hydrogen is metastable at low pressures.

Our method is based on calculating the distortion of the electronic wave functions in metallic hydrogen as nearest-neighbor protons are moved closer together. That is, metallic hydrogen with protons regularly spaced in a bcc or hcp array will be perturbed by decreasing the separation of nearest neighbors while keeping the over-all density constant (see Fig. 1). If the protons are moved only a little or if the density is high enough, moving the protons will produce only a small change in the electronic wave functions. However, if the protons are moved substantially closer together and if the density is low enough the change in the electronic wave functions can be large. We might ask if the change in the electronic wave functions can be so large that the wave functions become localized around pairs of protons. The localized electrons would of course not be free to move and hence in this case the perturbed metal would be an insulator. If we approximate the electronic wave

functions in the metal by plane waves, then the criterion for electrons becoming localized can be approximated by the condition that an electron of average energy forms a bound state in the potential near two protons that have been moved closer together.

In the normal metal, where a cell contains only one proton, it is energetically favorable for an electron to be unbound. However, in the perturbed metal where there are two protons in a cell it may be energetically favorable for an electron to become localized. In other words, the decrease in potential energy due to the attraction of an extra proton may more than compensate for the increase in kinetic energy of the localized electron. The

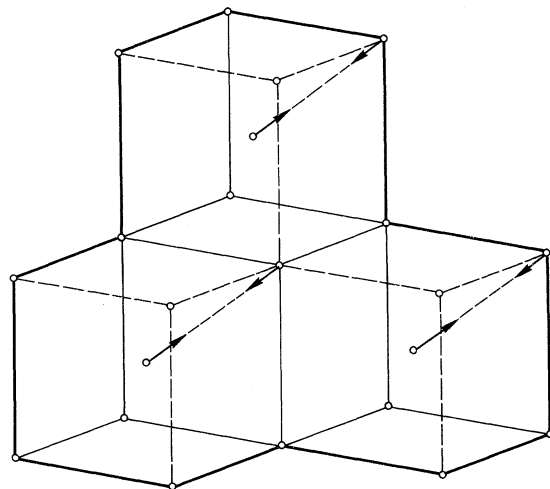


FIG. 1. Displacement of nearest-neighbor protons in a body-centered-cubic structure.