

## Influence of Electron Interactions on Metallic Properties. II. Electron Spin Paramagnetism\*†

S. D. SILVERSTEIN

*Department of Physics, University of Illinois, Urbana, Illinois and Department of Physics,  
University of California, Berkeley, California*

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The static-electron-paramagnetic spin susceptibility has been calculated by a variational calculation about a polarized ground state, the polarization parameter being determined as the extremum condition on the ground-state energy. The basic techniques used are those of many-body perturbation theory in a fashion analogous to that used by Brueckner and Sawada, with the addition of a momentum transfer interpolation procedure designed to obtain relevant information in the region of metallic densities. General curves are given which should be appropriate to all free-electron-like metals in both the solid and liquid state. The effects of band structure in our application to the solid alkali metals are taken into account by the introduction of the Fermi level band masses in the kinetic energy term. The results obtained by this procedure are in agreement with experiment.

### I. INTRODUCTION

IN a previous paper (referred to as I),<sup>1</sup> we have applied a momentum transfer interpolation procedure to the calculation of the electronic specific heat of an interacting electron gas. Here we use the same principles to calculate the static-electron-paramagnetic susceptibility.

There are two approaches one can take to a perturbative calculation of the susceptibility: (1) The problem can be formulated in a time-dependent manner where a weak time-varying inhomogeneous field gradually flips the electron spins starting from an unpolarized state at  $t = -\infty$ ; or, alternatively, (2) one can concern himself with the dc response to a uniform field and formulate the problem as a variational calculation about a polarized ground state, the polarization parameter being determined as the appropriate extremum condition on the free energy of the system. The former method would, in principle, achieve the complete wave-vector-dependent dynamic susceptibility, a quantity of considerable interest for the magnetic properties of metals and metallic alloys.<sup>2</sup> However, an explicit calculation of the effects of electron correlations, within this framework, is quickly stifled due to the appearance of insoluble integrals. In Appendix C we discuss this point further. Wolff<sup>3</sup> used this former method in calculating the response to a static inhomogeneous magnetic field. In his treatment he linearized the equation of motion of the spin-density fluctuations (this corresponds to a  $T$ -matrix expansion of a single-electron hole polarization diagram) and obtained an integral equation which again, at least in principle, could be solved. We find the second method, although restricted to uniform static response, can easily handle the correlation effects and ultimately

produce numerical results for the susceptibility which conform quite favorably to the experimental measurements.

The variational method was first used by Sampson and Seitz.<sup>4</sup> There they assumed that the shift in the ground-state energy from the electron polarization could be obtained from an independent variation of the populations of the up and down spin states, the exchange and correlation corrections being evaluated with the aid of the Wigner expression for the correlation energy. Pines<sup>5</sup> carried out a calculation similar to that of Sampson and Seitz. His result differed markedly from theirs because of the use of the Bohm-Pines theory for the correlation energy. The results obtained by Pines were in relatively good agreement with experiment. However, this agreement was, in fact, somewhat fortuitous, because careful investigation shows that the Sampson-Seitz assumption of independent variations is not appropriate to the second-order perturbation calculation of the short-range correlation effects. A simple illustration of this is shown in Appendix B. Our approach is basically similar to Brueckner and Sawada's,<sup>6</sup> except, of course, we must treat the short-range interactions and retain the wave-vector dependence throughout.

The spin polarization of the electron gas is defined in the standard manner,

$$P = (n_{\downarrow} - n_{\uparrow}) / (n_{\uparrow} + n_{\downarrow}). \quad (1.1)$$

The spin density and Fermi momentum of a given spin state are represented by  $n_{\sigma} = \frac{1}{2}n(1 - \sigma P)$  and

$$p_{f\sigma} = (1 - \sigma P)^{1/3} p_f.$$

Here  $p_f$  is the Fermi momentum of either spin in an unpolarized medium, and  $\sigma$  takes on the values  $\pm 1$ . For small polarization, the ground-state energy of an electron gas in the presence of a weak uniform magnetic

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<sup>1</sup> S. D. Silverstein, Phys. Rev. **128**, 631 (1962).

<sup>2</sup> K. Yoshida, Phys. Rev. **106**, 893 (1957).

<sup>3</sup> P. A. Wolff, Phys. Rev. **120**, 814 (1960).

<sup>4</sup> J. B. Sampson and F. Seitz, Phys. Rev. **58**, 633 (1940).

<sup>5</sup> D. Pines, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1955), Vol. 1, p. 367.

<sup>6</sup> K. A. Brueckner and K. Sawada, Phys. Rev. **112**, 328 (1958).

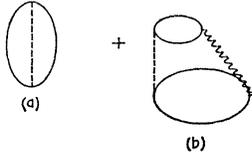


FIG. 1. RPA expansion of interaction energy.

field  $\mathcal{H}_0$  is given, through terms second order in the polarization, by<sup>7</sup>

$$E(e^2, P) = E(e^2, 0) - [\mu_B m \mathcal{H}_0 n P / p_f^2 (\alpha r_s)^2] + n P^2 A \text{ Ry.} \quad (1.2)$$

Here the term linear in  $P$  is the Zeeman energy;  $A = A_{\text{free}} = A_{\text{exch}} + A_{\text{corr}}$ , where

$$A_{\text{free}} = nm/3(\alpha r_s)^2 m^*; \quad A_{\text{exch}} = -1/3\pi\alpha r_s. \quad (1.3)$$

Also,  $\mu_B = eh/2mc$ , and  $\alpha$  is a constant equal to  $(4/9\pi)^{1/3}$ . We have added an effective mass into the kinetic energy term to account for the periodic ion potential in the specific application of our results to the alkali metals. From the extremum condition on the energy of (1.2), we obtain the ratio of the susceptibility to the corresponding free-electron value

$$\chi^*/\chi_{\text{free}} = [(m/m^*) - (\alpha r_s/\pi) + 3(\alpha r_s)^2 A_{\text{corr}}]^{-1}. \quad (1.4)$$

The unknown term which must be determined is the coefficient of the  $P^2$  term in the correlation energy of the polarized system. The contributions to  $A_{\text{corr}}$  from the long- and short-range interaction regions will be represented by  $a_{\text{LR}}(q)$  and  $a_{\text{SR}}(q)$ , respectively. The intermediate momentum-transfer region is represented by a smooth interpolation between the two regions, and the resultant value of  $A_{\text{corr}}$  is obtained from the

$$\Pi_{0\sigma}^P(\mathbf{q}, t) = -i\langle\Phi(P)|T\{\sum_{\mathbf{p}_1\mathbf{p}_2} c_{\mathbf{p}_1\sigma}(t)c_{\mathbf{p}_2+\mathbf{q},\sigma}c_{\mathbf{p}_1+\mathbf{q},\sigma^\dagger}(t)c_{\mathbf{p}_2\sigma^\dagger}\}|\Phi(P)\rangle. \quad (2.4)$$

Here the states  $|\Phi(P)\rangle$  correspond to the ground-state wave functions of a noninteracting polarized system. The average interaction energy is expressed in the interaction representation by

$$E_{\text{int}}(e^2 P) = \sum_{\mathbf{p}_1\sigma_1, \mathbf{q}, \mathbf{p}_2\sigma_2} \frac{\nu(\mathbf{q})}{2} \lim_{t \rightarrow 0^+} \frac{\langle\Phi(P)|T\{c_{\mathbf{p}_2+\mathbf{q},\sigma_2}c_{\mathbf{p}_1,\sigma_1}c_{\mathbf{p}_2,\sigma_2}^\dagger(t)c_{\mathbf{p}_1+\mathbf{q},\sigma_1}^\dagger(t^+)S\}|\Phi(P)\rangle}{\langle\Phi(P)|S|\Phi(P)\rangle}. \quad (2.5)$$

The contributions to the interaction energy of the long-wavelength interactions can be well described by the random phase approximation (RPA). The perturbation diagrams corresponding to this select group of terms in the  $S$ -matrix expansion are indicated in Fig. 1. There diagram (a) corresponds to the exchange energy, and diagram (b) represents the correlation energy. The long-range correlation energy is given by

$$E_{\text{corr}}(e^2 P) = \frac{-i}{2(2\pi)^4} \int_0^{e^2} \frac{de^2}{e^2} \int_{q < \beta_1 P} d^3q \int_{-\infty}^{+\infty} du \left\{ \frac{\nu(\mathbf{q}) \sum_{\sigma} \Pi_{0\sigma}^P(\mathbf{q}, u)}{[1 + \nu(\mathbf{q}) \sum_{\sigma} \Pi_{0\sigma}^P(\mathbf{q}, u)]} - \nu(\mathbf{q}) \sum_{\sigma} \Pi_{0\sigma}^P(\mathbf{q}, u) \right\}. \quad (2.6)$$

The integrand of (2.6) is analytic in the first and third quadrants of the complex  $u$  plane. It proves desirable to deform the contour to the imaginary axis. Also, transforming variable  $u \rightarrow qu$ , and performing the coupling-constant integration, we obtain upon conversion to  $r_s$  units,<sup>8</sup>

$$E_{\text{corr}}(e^2 P) = \frac{3n}{(4\pi\alpha r_s)^2} \int_{q < \beta_1} q d^3q \int_{-\infty}^{+\infty} du \{ \ln[1 + \nu(\mathbf{q}) \sum_{\sigma} \Pi_{0\sigma}^P(\mathbf{q}, iqu)] - \nu(\mathbf{q}) \sum_{\sigma} \Pi_{0\sigma}^P(\mathbf{q}, iqu) \} \text{ Ry.} \quad (2.7)$$

<sup>7</sup>  $\mathcal{H}_0 = 1$  unless explicitly indicated.

<sup>8</sup> Here momentum is in units of the Fermi momentum and energy is in units of twice the Fermi energy.  $r_s$  is defined as the radius of the spherical volume per electron in units of the Bohr radius, i.e.,  $r_s = (me^2/\hbar^2)(3V/4\pi N)^{1/3}$ .

numerical integration of  $a(q)$  over all momentum transfers.

## II. CONTRIBUTIONS TO THE CORRELATION ENERGY FROM DIFFERENT REGIONS OF MOMENTUM TRANSFER

In performing our calculations, we adopt the standard model of an electron gas in the presence of a uniform background of positive charge. The Hamiltonian for this system in the presence of a uniform magnetic field is given by

$$H = \sum_{\mathbf{p}\sigma} c_{\mathbf{p}\sigma}^\dagger \left( \frac{p^2}{2m} + \mu_B \sigma_x \mathcal{H}_0 \right) c_{\mathbf{p}\sigma} + \sum_{\mathbf{p}_1\sigma_1, \mathbf{q}, \mathbf{p}_2\sigma_2} \frac{\nu(\mathbf{q})}{2} c_{\mathbf{p}_1+\mathbf{q},\sigma_1}^\dagger c_{\mathbf{p}_2,\sigma_2}^\dagger c_{\mathbf{p}_2+\mathbf{q},\sigma_2} c_{\mathbf{p}_1,\sigma_1}. \quad (2.1)$$

Here we have neglected the uncoupled diamagnetic interactions. The ground-state energy of the polarized system can be most conveniently expressed in terms of the standard integral over the coupling constant:

$$E(e^2 P) = E(0, P) + \int_0^{e^2} \langle\langle H_{\text{int}} \rangle\rangle / e^2 d(e^2). \quad (2.2)$$

Here the average of the interaction Hamiltonian is evaluated with the use of polarized wave functions. In expanding the average of the interaction term, we make use of the propagators defined for the polarized system. These are: the free fermion propagator

$$G_{0\sigma}^P(\mathbf{p}, t) = -i\langle\Phi(P)|T\{c_{\mathbf{p}\sigma}(t)c_{\mathbf{p}\sigma}^\dagger(0)\}|\Phi(P)\rangle, \quad (2.3)$$

and the polarization propagator

The small  $q$  expansion of the bare polarization propagator is given by

$$\nu(\mathbf{q}) \sum_{\sigma} \Pi_{0\sigma}^P(\mathbf{q}, iqu) = (4\alpha r_s / \pi q^2) [\sum_{\sigma} R_{\sigma}^P(u) + O(q^2)], \quad (2.8)$$

where

$$\sum_{\sigma} R_{\sigma}^P(u) = 1 - u \tan^{-1}(1/u) - [P^2/9(1+u^2)^2] + O(P^4). \quad (2.9)$$

The long-range correlation energy can then be approximated by

$$E_{\text{corr}}(e^2 P) \cong \frac{3n}{(4\pi\alpha r_s)^2} \int_{q < \beta_1} q d^3q \left\{ I(P, q) - \frac{4\alpha r_s}{\pi q^2} \int_{-\infty}^{+\infty} \sum_{\sigma} R_{\sigma}^P(u) du \right\} \text{Ry}. \quad (2.10)$$

Here,  $I(P, q)$  is given by

$$I(P, q) = \int_{-\infty}^{+\infty} du \ln[1 + (4\alpha r_s / \pi q^2) \sum_{\sigma} R_{\sigma}^P(u)]. \quad (2.11)$$

We integrate  $I(P, q)$  by a procedure similar to that used by Nozières and Pines<sup>9</sup> in their calculation of the correlation energy of an unpolarized electron gas. This is accomplished by first partially integrating (2.11),

$$I(P, q) = - \int_{-\infty}^{+\infty} du \frac{\sum_{\sigma} u R_{\sigma}^P(u)}{(\pi q^2 / 4\alpha r_s) + \sum_{\sigma} R_{\sigma}^P(u)}. \quad (2.12)$$

The new form can be simply evaluated by contour-integral techniques. The mapping of the integrand of (2.12) in the complex  $u$  plane will exhibit branch points at  $u = \pm i$ , and poles at the zeros of the polarization-dependent dielectric constant. For small  $q$  and polarization  $P$ , the poles arise at

$$u_0(P, q) = u_0(0, q) + (P^2/4)(\pi q^2 / 3\alpha r_s)^{1/2}. \quad (2.13)$$

Here  $u_0(0, q)$  is the standard plasmon pole for the unpolarized system, and the  $P^2$  term corresponds to the displacement of the singularity due to the polarization.  $I(P, q)$  may then be calculated by integrating over the contour shown in Fig. 2. We obtain

$$I(P, q) = 2\pi u_0(P, q) + \int_c du \frac{u \sum_{\sigma} R_{\sigma}^P(u)}{(\pi q^2 / 4\alpha r_s) + \sum_{\sigma} R_{\sigma}^P(u)}, \quad (2.14)$$

where the contour  $c$  goes around the branch cut as indicated. The contribution from the integral along  $c$  can now be expanded as a power series in the momentum transfer:

$$\int_c du \frac{u \sum_{\sigma} R_{\sigma}^P(u)}{(\pi q^2 / 4\alpha r_s) + \sum_{\sigma} R_{\sigma}^P(u)} = \int_c du \frac{u \sum_{\sigma} R_{\sigma}^P(u)}{\sum_{\sigma} R_{\sigma}^P(u)} + O(q^2). \quad (2.15)$$

The integral on the right-hand side of (2.15) has been

<sup>9</sup> P. Nozières and D. Pines, Phys. Rev. **111**, 442 (1958).

shown to be equivalent to the logarithmic integral<sup>9</sup>

$$\int_c u \sum_{\sigma} R_{\sigma}^P(u) / \sum_{\sigma} R_{\sigma}^P(u) = \int_{-\infty}^{+\infty} \ln[3\mu^2 \sum_{\sigma} R_{\sigma}^P(u)] du. \quad (2.16)$$

On expanding (2.16) in powers of  $P$ , we obtain

$$\int_{-\infty}^{+\infty} du \ln[3\mu^2 \sum_{\sigma} R_{\sigma}^P(u)] = \int_{-\infty}^{+\infty} du \{ \ln[3\mu^2 R(u)] - [P^2/9(1+u^2)^2] + O(P^4) \}. \quad (2.17)$$

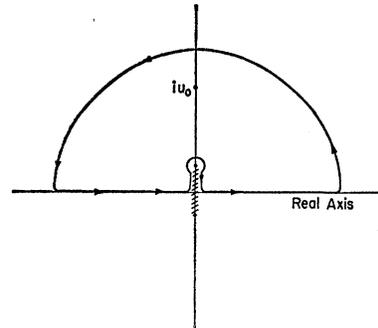
Hence, through terms of order  $P^2$ ,  $I(q)$  is given by

$$I(P, q) = I(0, q) + P^2 \left\{ \frac{q}{2} \left( \frac{\pi^3}{3\alpha r_s} \right)^{1/2} - \int_{-\infty}^{+\infty} \frac{du}{9(1+u^2)^2 R(u)} \right\}. \quad (2.18)$$

Here  $I(0, q)$  corresponds to the value in the absence of polarization. The second term on the right-hand side of (2.10) is expanded by making use of (2.9). The net results of all the expansions in both momentum transfer and polarization yield

$$E_{\text{corr}}^{\text{LR}}(e^2, P) = E_{\text{corr}}^{\text{LR}}(e^2, 0) + nP^2 \int_0^{\beta} dq \{ (0.102/r_s)q - (0.66/r_s^2)q^3 + (1.97/r_s^{5/2})q^4 \}. \quad (2.19)$$

FIG. 2. The mapping of the function  $\sum_{\sigma} u R_{\sigma}^P(u) / [(\pi q^2 / 4\alpha r_s) + \sum_{\sigma} R_{\sigma}^P(u)]$  into the complex  $u$  plane, and the contour used for the evaluation of  $I(P, q)$ .



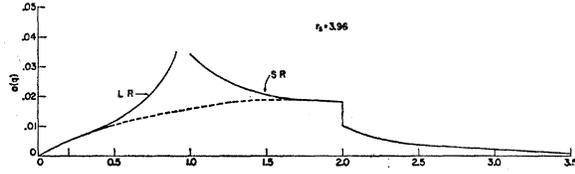


FIG. 3. Interpolation curve for density corresponding to Na:  $r_s = 3.96$ .

Therefore, through terms of order  $q^4$ ,  $a_{LR}(q)$  is given by

$$a_{LR}(q) = (0.102/r_s)q - (0.66/r_s^2)q^3 + (1.97/r_s^{5/2})q^4. \quad (2.20)$$

Here the  $q^4$  contribution arises from the shift in the

plasmon pole, whereas the other terms are contributed by the single-particle excitations. Thus, the collective behavior of the system serves to increase the correlation energy and decrease the susceptibility.

We now consider the short-range contribution to the correlation energy. In doing this, we follow a procedure analogous to that used in I. That is, we treat the short-range interactions by second-order perturbation theory where, for sufficiently large momentum transfer  $q \gtrsim 1.5p_F$ , the parallel spin-exchange contributions approximately cancel one-half of the direct interactions. Accordingly, the short-range correlation energy is approximated by

$$E_{\text{corr}}^{\text{SR}}(e^2, P) \cong \frac{i}{2(2\pi)^4} \sum_{\sigma_1 \sigma_2 (\sigma_1 \neq \sigma_2)} \int_{q > \beta_2 p_F} d^3 q d u \Pi_{0\sigma_1}^P(\mathbf{q}, u) \Pi_{0\sigma_2}^P(\mathbf{q}, u) v^2(\mathbf{q}). \quad (2.21)$$

The frequency integral of this term yields

$$E_{\text{corr}}^{\text{SR}}(e^2, P) = -\frac{3n}{32\pi^5} \int_{q > \beta_2} \frac{d^3 q}{q^4} \int d^3 p_1 d^3 p_2 \sum_{\sigma_1 \sigma_2 (\sigma_1 \neq \sigma_2)} \left\{ n_{p_1 - q/2}^{\sigma_1} (1 - n_{p_1 + q/2}^{\sigma_1}) \frac{n_{p_2 - q/2}^{\sigma_2} (1 - n_{p_2 + q/2}^{\sigma_2})}{\mathbf{q} \cdot (\mathbf{p}_1 + \mathbf{p}_2)} \right\} \text{Ry.} \quad (2.22)$$

Here  $n_p$  is the unit step function,

$$n_p^\sigma = \begin{cases} 1 & \text{for } p < (1 - \sigma P)^{1/3}, \\ 0 & \text{for } p > (1 - \sigma P)^{1/3}. \end{cases}$$

We now expand the short-range correlation energy in a power series in the polarization  $P$ . The expansion and subsequent integration is a straightforward but lengthy process, the details of which are further discussed in Appendix A. The result is expressed in the form

$$E_{\text{corr}}^{\text{SR}}(e^2, P) = E_{\text{corr}}^{\text{SR}}(e^2, 0) + nP^2 \int_{\beta_2}^{\infty} a_{\text{SR}}(q) dq + O(P^4), \quad (2.23)$$

where, for  $2(1-P)^{1/3} \geq q \geq \beta_2 \geq 1$

$$a_{\text{SR}}(q) = +\frac{1}{3\pi^2 q^2} \left\{ \frac{q^2}{6} + \left[ \frac{8}{3} - \frac{3}{2}q - \frac{1}{24}q^3 \right] \ln |1 + q/2| + \left[ \frac{3}{4}q^4 - \frac{89}{24}q^3 + 6q^2 - \frac{9}{2}q + \frac{8}{3} \right] \ln |1 - q/2| \right\}; \quad (2.24)$$

for  $q > 2(1+P)^{1/3}$ ,

$$a_{\text{SR}}(q) = \frac{1}{3\pi^2 q^2} \left\{ -\frac{2}{3}q + \left[ \frac{q^3}{3} - 4q \right] \ln q + \left[ -\frac{q^3}{6} + 2q - \frac{8}{3} \right] \ln |q - 2| + \left[ -\frac{q^3}{3} + 2q + \frac{8}{3} \right] \ln |q + 2| \right\};$$

and for  $2(1-P)^{1/3} \leq q \leq 2(1+P)^{1/3}$ ,

$$a_{\text{SR}}(2) = -(1/72\pi^2)(1 - 16 \ln 2).$$

We have now obtained both  $a_{LR}(q)$  (2.20) and  $a_{SR}(q)$  (2.24) in the forms desired for the momentum-transfer interpolation. These are plotted for the specific case of  $r_s = 3.96$  (Na) in Fig. 3. We note that the apparent discontinuity at  $q = 2$  is actually nonexistent. Here we have merely extended  $a_{SR}(q)$  for the regions  $1 \leq q \leq 2(1-P)^{1/3}$  and  $q \geq 2(1+P)^{1/3}$  to  $q = 2$ . The areas due to the extension will cancel. This can be seen from the fact that the values  $a_{SR}(q)$  in the momentum interval  $2(1-P)^{1/2} \leq q \leq 2(1+P)^{1/3}$  satisfies

$$a_{\text{SR}}(2) [\text{for } 2(1-P)^{1/3} \leq q \leq (1+P)^{1/3}] = \frac{1}{2} \{ a_{\text{SR}}(q=2) [\text{for } 1 \leq q \leq 2(1-P)^{1/3}] + a_{\text{SR}}(q=2) [\text{for } q \geq 2(1+P)^{1/3}] \}. \quad (2.25)$$

The form of the intermediate momentum-transfer region is now approximated by a smooth interpolation between the short- and long-range regions. The resulting values of  $A_{\text{corr}}$  are obtained from the numerical integration of  $a(q)$  over all momentum transfers.

TABLE I.  $\chi^*$  for alkali metals. Susceptibilities are given in cgs volume units  $\times 10^6$ .

	Li	Na	K	Rb	Cs
$r_s$	3.22	3.96	4.87	5.18	5.57
$(m_i^*/m)_{\text{sph}}^a$	1.32	1.00	1.02	0.99	1.06
$(m_i^*/m)_d^a$	1.66	1.00	1.09	1.21	1.76
$\chi_{\text{sph}}^*$	1.56	0.86	0.66	0.60	0.60
$\chi_d^*$	2.20	0.86	0.73	0.78	1.15
$\chi_{\text{exp}}$	$2.08 \pm 0.1^b$	$0.95 \pm 0.1^{b-d}$			

<sup>a</sup> F. S. Ham, Phys. Rev. **128**, 2524 (1962).

<sup>b</sup> See reference 12.

<sup>c</sup> See reference 13; value quoted there is  $0.89 \pm 0.04$ .

<sup>d</sup> See reference 14; value quoted there is  $1.13 \pm 0.05$ .

### III. RESULTS AND DISCUSSION

In Table I, we give the various values of  $A_{\text{corr}}$  together with the values of  $\chi^*$  obtained by the use of (1.4). As Pines has shown, the influence of band structure on the correlation corrections is small for the alkali metals, and the effects of the lattice can be taken into account by the introduction of the lattice effective mass into the kinetic energy term. Because we are dealing with the behavior of the electrons in the immediate vicinity of the Fermi surface, a proper account of the masses would correspond to the band theory masses evaluated at the Fermi level, suitably averaged to eliminate anisotropy effects. These new values, with consideration of Fermi surface distortion, have been recently calculated by Ham.<sup>10</sup> In the table we list Ham's values obtained in both the spherical band approximation,  $(m_i^*/m)_{\text{sph}}$ , and the values taking into account Fermi surface distortion,  $(m_i^*/m)_d$ . It is apparent, and more plausibly so, that the theoretical results obtained by using the averaged distorted masses are in better agreement with the experimental values.

The paramagnetic susceptibility has been directly measured for both Li and Na.<sup>11</sup> There have been later measurements reported in the literature for Na.<sup>12,13</sup> However, these seem to vary considerably. The error estimates on the first measurement by Schumacher and Slichter seem to almost cover the full spectrum, so we will use this value to compare our theoretical result with experiment. The experimental values were obtained by the use of the Kramers-Krönig relations to relate the susceptibility to the area under the spin-resonance absorption curve. The measured values were

$$\chi_{\text{Li}} = (2.08 \pm 0.1) \times 10^{-6} \text{ at } 300^\circ\text{K},$$

$$\chi_{\text{Na}} = (0.95 \pm 0.1) \times 10^{-6} \text{ at } 79^\circ\text{K},$$

in cgs volume units. The zero-temperature values are listed in the table. The theoretical value for Li, modified by a volume correction to yield the room-temperature

<sup>10</sup> F. S. Ham, Phys. Rev. **128**, 2524 (1962).

<sup>11</sup> R. T. Schumacher and C. P. Slichter, Phys. Rev. **101**, 58 (1956).

<sup>12</sup> R. T. Schumacher and W. E. Vehse, Bull. Am. Phys. Soc. **4**, 296 (1960).

<sup>13</sup> R. T. Schumacher and W. E. Vehse, J. Phys. Soc. Japan Suppl. **B-1**, 460, (1962).

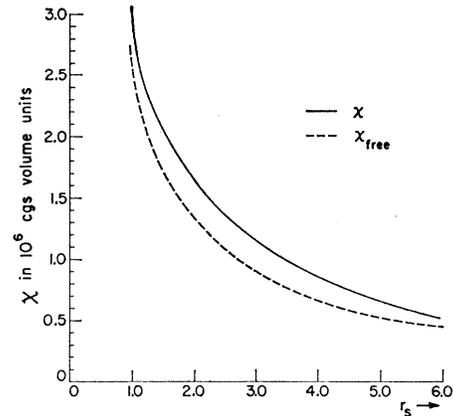


FIG. 4.  $\chi$  and  $\chi_{\text{free}}$  as a function of density for  $m^*/m=1$ .

result is

$$\chi_{\text{theo}}(\text{Li}) = 2.16 \times 10^{-6},$$

a result in agreement with experiment.

In Fig. 4 we have plotted the values of  $\chi$  and  $\chi_{\text{free}}$  as a function of density. These results are for  $m^*/m=1$ . The susceptibility for a given density and effective mass can be obtained from these curves by the use of the relation

$$\chi^* = \frac{\chi}{1 + [(m/m^*) - 1](\chi/\chi_{\text{free}})}. \quad (3.1)$$

The above relation enables one to obtain the values in the event of an alteration in the estimated band-theory masses.

We feel that  $A_{\text{corr}}$  should be accurate to the order of 20%. This estimate is obtained by considering radical deviations from the most obvious intermediate momentum-transfer interpolation. This degree of error would in turn reflect a 5 to 10% error in the static susceptibility  $\chi$ . Of course, these estimates do not incorporate the possible errors in the theoretical-band masses.

### ACKNOWLEDGMENTS

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### APPENDIX A

In this Appendix we outline the methods used to evaluate the integral (2.22). We desire the expansion in the polarization of

$$I(P, q) = \sum_{\mathbf{p}_1 \mathbf{p}_2} n_{\mathbf{p}_2 \downarrow} (1 - n_{\mathbf{p}_2 \uparrow}) n_{\mathbf{p}_1 \uparrow} (1 - n_{\mathbf{p}_1 \downarrow}) / \mathbf{q} \cdot (\mathbf{p}_1 + \mathbf{p}_2). \quad (A1)$$

Here  $n_{\mathbf{p}_2 \downarrow}$  and  $n_{\mathbf{p}_1 \uparrow}$  are unit step functions at the momenta  $(1+P)^{1/3}$  and  $(1-P)^{1/3}$ , respectively. Also, we have used the abbreviated notation  $\mathbf{p}^\pm = \mathbf{p} \pm \mathbf{q}/2$ .

To simplify this expression, we first multiply the numerator out

$$(n_{\mathbf{p}^- \downarrow} n_{\mathbf{p}_1^- \uparrow} - n_{\mathbf{p}_2^- \downarrow} n_{\mathbf{p}_1^- \uparrow} n_{\mathbf{p}_1^+ \uparrow} - n_{\mathbf{p}_2^- \downarrow} n_{\mathbf{p}_2^+ \downarrow} n_{\mathbf{p}_1^- \uparrow} + n_{\mathbf{p}_2^- \downarrow} n_{\mathbf{p}_2^+ \downarrow} n_{\mathbf{p}_1^- \uparrow} n_{\mathbf{p}_1^+ \uparrow}) / \mathbf{q} \cdot (\mathbf{p}_1 + \mathbf{p}_2). \quad (\text{A2})$$

$$I_1(P, q) = -\frac{1}{q(2\pi)^4} \int_0^{(1-P)^{1/3}} p_1^2 dp_1 \int_0^{(1+P)^{1/3}} p_2^2 dp_2 \int_{-1}^{+1} dx \int_{-1}^{+1} dy \frac{1}{(q + p_1 y + p_2 x)}, \quad (\text{A3})$$

and the terms arising from the volume within the intersection of displaced Fermi spheres,

$$I_2(P, q) = \frac{1}{q(2\pi)^4} \int_0^{(1-P)^{1/3}} p_2^2 dp_2 \int_{q-(1+P)^{1/3}}^{(1+P)^{1/3}} p_1^2 dp_1 \int_{-1}^{+1} dx \int_{[(1+P)^{1/3} - p_1^2 - q^2]^{1/2} p_1 q}^1 \frac{1}{(q + p_1 y + p_2 x)}; \quad (\text{A4})$$

$$I_3(P, q) = I_2(-P, q).$$

These expressions were now expanded as a power series in the polarization and then integrated to give the terms indicated in (2.24).

#### APPENDIX B

In this Appendix we discuss the approximation used by Pines to derive the short-range contributions to the susceptibility. Pines gave the susceptibility as

$$\chi = 2n\mu^2/\alpha, \quad (\text{B1})$$

$$\frac{E_{\text{corr}}^{\text{SR}}}{n} = \frac{3}{16\pi^5} \int_{q > \beta_2} \frac{d^3 q}{q^4} \int d^3 p_1 \int d^3 p_2 \frac{n_{\mathbf{p}_1 - \mathbf{q}/2} (1 - n_{\mathbf{p}_1 + \mathbf{q}/2}) n_{\mathbf{p}_2 - \mathbf{q}/2} (1 - n_{\mathbf{p}_2 + \mathbf{q}/2})}{\mathbf{q} \cdot (\mathbf{p}_1 + \mathbf{p}_2)} \text{Ry}. \quad (\text{B4})$$

This is to be compared with Eq. (2.22) of the text which corresponds to a polarized system. If the cutoff parameter  $\beta_2$  is assumed independent of  $r_s$ , the short-range correlation energy per particle will likewise be independent of  $r_s$  with a zero resulting value of  $\alpha_{\text{SR}}$ . The Bohm-Pines theory, however, prescribes a  $\xi r_s^{1/2}$  dependence of the cutoff parameter and consequently a nonzero value of  $\alpha_{\text{SR}}$ . If this, coupled with Sampson-Seitz, were a valid procedure, the values obtained would be equivalent to those obtained from the calculation with the retention of the explicit polarization dependence. However, this is not the case and can be verified by directly calculating both results in the long-wavelength limit; there the explicit evaluation of the polarization effects is considerably simplified.

#### APPENDIX C

In this Appendix we consider the dynamic paramagnetic response of an isotropic, translational invariant electron gas, with a center of symmetry to a weak magnetic test field  $\mathcal{H}(\mathbf{q}\omega)$ . For linear response

$$\langle M(\mathbf{q}\omega) \rangle = \chi_r(\mathbf{q}\omega) \mathcal{H}(\mathbf{q}\omega). \quad (\text{C1})$$

Here  $\chi_r(\mathbf{q}\omega)$  is the frequency and wave-vector-dependent retarded susceptibility. This is expressed in

We see that the last term will be antisymmetric under simultaneous reflection of both  $\mathbf{p}_1$  and  $\mathbf{p}_2$ . Hence, it will vanish upon integration.  $I(P, q)$  can now be expressed in terms of three simpler integrals of which we only have to evaluate two. These are

where

$$\alpha = (20/9)E_f + (8/9)E_{\text{ex}} + \alpha_{\text{LR}} + \alpha_{\text{SR}}. \quad (\text{B2})$$

Here  $\alpha_{\text{SR}}$  was given by

$$\alpha_{\text{SR}} = -\frac{4}{9} r_s \left( \frac{\partial}{\partial r_s} - \frac{\partial^2}{2 \partial r_s^2} \right) \frac{E_{\text{corr}}^{\text{SR}}}{n}. \quad (\text{B3})$$

The short-range correlation energy per particle for an unpolarized system is given by

terms of the magnetization density fluctuation operators by

$$\chi_r(\mathbf{q}\omega) = i \int_0^{\infty} dt e^{i\omega t} \langle [m_{\mathbf{q}}^z(t), m_{-\mathbf{q}}^z(0)] \rangle, \quad (\text{C2})$$

where

$$m_{\mathbf{q}}^z = -\mu_B \sum_l \sigma_l^z e^{-i\mathbf{q} \cdot \mathbf{r}_l} = -\mu_B \sum_{\mathbf{p}} c_{\mathbf{p}+\mathbf{q}, \sigma}^\dagger \sigma_z c_{\mathbf{p}, \sigma}. \quad (\text{C3})$$

For convenience we have quantized the system along the  $z$  axis. In (C2), the average is taken over the interacting electron system, generally characterized by a grand canonical ensemble. We find it convenient to define the following auxiliary functions:

$$\tilde{\chi}(\mathbf{q}\omega) = (i/2) \int_{-\infty}^{+\infty} dt e^{i\omega t} \langle [m_{\mathbf{q}}^z(t), m_{-\mathbf{q}}^z(0)] \rangle, \quad (\text{C4})$$

and

$$f(\mathbf{q}\omega) = \frac{1}{2} \int_{-\infty}^{+\infty} dt e^{+i\omega t} \langle m_{\mathbf{q}}^z(t) m_{-\mathbf{q}}^z(0) \rangle. \quad (\text{C5})$$

It is evident that

$$f^*(\mathbf{q}\omega) = f(\mathbf{q}\omega). \quad (\text{C6})$$

Also, the invariance properties of the trace under cyclic permutations give

$$f(\mathbf{q}\omega) = e^{\beta\omega} f(-\mathbf{q} - \omega). \quad (\text{C7})$$

Here  $\beta$  is  $1/kT$ . It is a simple matter to show that the real and imaginary parts of  $\chi_r(\mathbf{q}\omega)$  satisfy

$$\text{Im}\chi_r(\mathbf{q}\omega) = f(\mathbf{q}\omega)(1 - e^{-\beta\omega}) = -i\tilde{\chi}(\mathbf{q}\omega), \quad (\text{C8})$$

and

$$\text{Re}\chi_r(\mathbf{q}\omega) = P \int_{-\infty}^{+\infty} \frac{d\omega'}{2\pi} \frac{\text{Im}\chi_r(\mathbf{q}\omega')}{\omega' - \omega}. \quad (\text{C9})$$

The above dispersion relation is the well-known Kramers-Krönig relation for the retarded response functions. Before investigating the perturbation expansion, we will derive a simple sum rule on the retarded susceptibility. To do this we proceed as follows:

$$\frac{d\tilde{\chi}(\mathbf{q}, t=0)}{dt} = i \int_{-\infty}^{+\infty} \omega \tilde{\chi}(\mathbf{q}\omega) d\omega / 2\pi = \frac{1}{2} \langle [ [H, m_{\mathbf{q}}^z], m_{-\mathbf{q}}^z] \rangle. \quad (\text{C10})$$

The commutator of the spin-density fluctuations with the Hamiltonian of the interacting electron system can be simply evaluated. The results yield

$$\int_{-\infty}^{+\infty} \omega \tilde{\chi}(\mathbf{q}\omega) d\omega / 2\pi = i\mu_B^2 q^2 n / 2m. \quad (\text{C11})$$

Making use of (C8), we obtain our final sum rule

$$\int_{-\infty}^{+\infty} \omega \text{Im}\chi_r(\mathbf{q}\omega) d\omega / 2\pi = \mu_B^2 q^2 n / 2m. \quad (\text{C12})$$

We now define the time-ordered function,

$$\chi_T(\mathbf{q}t) = i \langle T \{ m_{\mathbf{q}}^z(t) m_{-\mathbf{q}}^z(0) \} \rangle. \quad (\text{C13})$$

The Fourier transform of this function is

$$\chi_T(\mathbf{q}\omega) = \int_{-\infty}^{+\infty} \frac{d\omega'}{2\pi} \left\{ \frac{1}{\omega' - \omega - i\epsilon} - \frac{e^{-\beta\omega'}}{\omega' - \omega + i\epsilon} \right\} f(\mathbf{q}\omega'). \quad (\text{C14})$$

Hence,

$$\begin{aligned} \text{Im}\chi_T(\mathbf{q}\omega) &= f(\mathbf{q}\omega)(1 + e^{-\beta\omega}); \\ \text{Re}\chi_T(\mathbf{q}\omega) &= P \int_{-\infty}^{+\infty} \frac{d\omega'}{2\pi} \frac{\tanh(\beta\omega'/2)}{\omega' - \omega} \text{Im}\chi_T(\mathbf{q}\omega'). \end{aligned} \quad (\text{C15})$$

By comparing (C15) and (C8), we can express the retarded susceptibility in terms of the time-ordered function

$$\chi_r(\mathbf{q}\omega) = \text{Re}\chi_T(\mathbf{q}\omega) + i \tanh(\beta\omega/2) \text{Im}\chi_T(\mathbf{q}\omega). \quad (\text{C16})$$

In the limit of zero temperature ( $\beta \rightarrow \infty$ ), where we further restrict consideration to positive frequencies, the retarded susceptibility and the time-ordered function are equivalent. To consider the zero-temperature perturbation calculation of  $\chi_T(\mathbf{q}\omega)$ , we convert

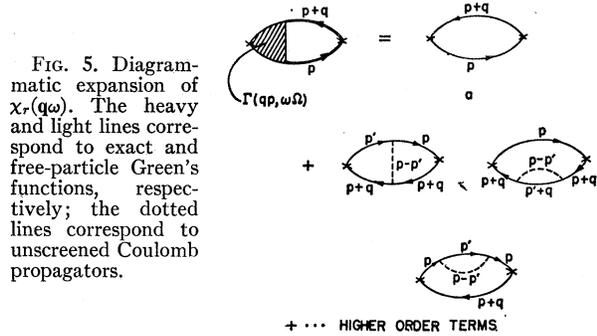


FIG. 5. Diagrammatic expansion of  $\chi_r(\mathbf{q}\omega)$ . The heavy and light lines correspond to exact and free-particle Green's functions, respectively; the dotted lines correspond to unscreened Coulomb propagators.

the expression to the interaction representation

$$\begin{aligned} \chi_T(\mathbf{q}\omega) &= i\mu_B^2 \int_{-\infty}^{+\infty} dt e^{i\omega t} \langle \Phi | T \{ \sum_{\mathbf{p}_1\sigma_1, \mathbf{p}_2\sigma_2} c_{\mathbf{p}_1+\mathbf{q}, \sigma_1}^\dagger(t) \sigma^z \\ &\quad \times c_{\mathbf{p}_1, \sigma_1}(t) c_{\mathbf{p}_2, \sigma_2}^\dagger \sigma^z c_{\mathbf{p}_2+\mathbf{q}, \sigma_2} S \} | \varphi \rangle \langle \varphi | S | \varphi \rangle. \end{aligned} \quad (\text{C17})$$

We note that the perturbation expansion of  $\chi_T(\mathbf{q}\omega)$  is similar to the renormalized polarization propagator  $\Pi(\mathbf{q}\omega)$  except for one rather important consideration. The appearance of the explicit spin dependence will cause the cancellation of terms corresponding to the summation of a chain of polarization diagrams. Therefore, one is left with the arduous task of evaluating the multiple exchange effects associated with a single polarization loop.  $\chi_T(\mathbf{q}\omega)$  can be represented by the diagrams in Fig. 5. There we have introduced the renormalized vertex function  $\Gamma(\mathbf{p}\mathbf{q}; \Omega)$ . The general expression for  $\chi_T(\mathbf{q}\omega)$  is

$$\begin{aligned} \chi_T(\mathbf{q}, \omega) &= \int \frac{d^3p d\Omega}{(2\pi)^4} \\ &\quad \times \Gamma(\mathbf{p}\mathbf{q}; \Omega) G(\mathbf{p}+\mathbf{q}; \Omega+\omega) G(\mathbf{p}; \Omega). \end{aligned} \quad (\text{C18})$$

As remarked in the introduction, Wolff has calculated the response to an inhomogeneous magnetic field by linearizing the equations of motion of the spin density fluctuations. In Fig. 6(a) we have indicated the  $T$ -matrix expansion of the vertex function. For the case of the response to a test charge, it has been shown that the linearization procedure (RPA) describes the correct high-density response of the system. However, this is not necessarily the case for magnetic response. The

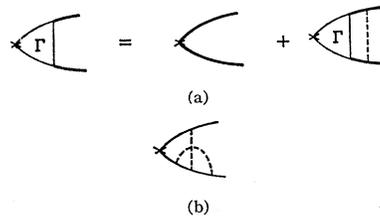


FIG. 6. (a)  $T$ -matrix expansion of the vertex function; (b) an example of a diagram omitted in the  $T$ -matrix expansion.

reason for this is that each term in the  $T$ -matrix expansion is an exchange interaction, and for each term selected by this procedure there are neglected terms of the same order in  $r_s$ . An example of a neglected term is indicated in Fig. 6(b). Nonetheless, the  $T$  matrix does sum a large subset of contributing diagrams, it will satisfy the sum rule (C12), and one could obtain useful information if only the integral equation were soluble.

At present this is not the case. Indeed, only the second-order perturbation integrals become manageable in the long-wavelength limit.

The evaluation of  $\chi_T(\mathbf{q}\omega)$  through second order is essentially equivalent to the polarizability calculation performed by DuBois.<sup>14</sup> We refer the reader to his work for the details; here we will just give the results. The lowest order contribution Fig. 5(a) is given by

$$\text{Re}\chi_T^{(1)}(\mathbf{q}\omega) = \frac{\mu_B^2 m}{2\alpha a_0 r_s \pi^2} \left\{ 1 + \frac{[1 - (q/2 - \omega/q)^2]}{2q} \ln \left| \frac{1 - q/2 + \omega/q}{1 + q/2 - \omega/q} \right| - \frac{[1 - (q/2 + \omega/q)^2]}{2q} \ln \left| \frac{1 + q/2 + \omega/q}{1 - q/2 - \omega/q} \right| \right\}, \quad (\text{C19})$$

and

$$\begin{aligned} \text{Im}\chi_r^{(1)}(\mathbf{q}\omega) &= (\mu_B^2 m / \alpha a_0 r_s \pi^2) \int_{p < 1 < 1+p+q} d^3 p \quad \text{for } 0 \leq \omega \leq (q^2/2 + q) \\ &= 0 \quad \text{for } \omega > (q^2/2 + q). \end{aligned} \quad (\text{C20})$$

Here  $a_0$  is the Bohr radius. The three second-order terms indicated by the diagrams in Fig. 5 diverge individually. However, their sum yields a convergent result. We have only been able to evaluate this sum in the static homogeneous limit; i.e.,

$$\lim_{q \rightarrow 0, \omega \rightarrow 0} \chi_r^{(2)}(\mathbf{q}\omega) \rightarrow e^2 m^2 \mu_B^2 / \pi^3. \quad (\text{C21})$$

Therefore, this procedure yields, even in the static

limit, only terms through second order. This result is

$$\chi_r(0,0) = \chi_p(1 + \alpha r_s / \pi), \quad (\text{C22})$$

where  $\chi_p$  is the free-electron Pauli susceptibility. We further note that (C22) and (1.4) are equivalent in the extreme high-density limit. There the Hartree-Fock term corresponds to the leading  $r_s$  correction.

<sup>14</sup> D. F. DuBois, Ann. Phys. (N. Y.) 7, 174 (1959); 8, 24 (1959).