

structure due to this effect. Nevertheless, our calculations do give considerable improvement over those of the Hartree-Fock functions and show that the energy corrections calculated from a simple correlation factor are of the right magnitude to account for the difference between the experimental multiplet spacings with that predicted by the Hartree-Fock theory.

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Question of Size Corrections to the Steady Diamagnetic Susceptibility of Small Systems*

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The order of magnitude of the (orbital) diamagnetic susceptibility of a free-electron gas is investigated for the case of "small" systems. A small system is, by definition, one whose characteristic linear dimensions are very much less than the radii of the average classical electronic orbits in an applied dc magnetic field. For the case of plane-slab geometry, exactly the Landau susceptibility (i.e., no size effect) is obtained for Maxwell-Boltzmann statistics. Furthermore, on the basis of the latter calculation, it is explicitly demonstrated that the use of the WKB approximation leads to a spurious size effect, suggesting that this (or equivalent) approximations may be responsible for size corrections found by other authors. For the degenerate case, the Landau result is also obtained, to within a numerical factor. Finally, no size correction is obtained in the small size limit for an electron gas confined by a harmonic potential well; this further suggests that the Landau result is independent of the choice of boundary potential.

I. INTRODUCTION

THE purpose of this paper is to present the results of some investigations concerning the steady diamagnetic susceptibility of "small" systems of electrons. A "small" system is defined as one whose characteristic linear dimensions (L) are very much less than the average radii (R_c) of the classical electronic orbits¹ in an applied dc magnetic field. In treating this problem, it is customary to idealize² the real physical situation to that of a free-electron gas confined to a box. The surface of the box is then represented by a simple, and analytically tractable, potential barrier. The use of such a model seems justifiable in view of the fact that the very existence and order of magnitude of size corrections for small systems have not been definitely established. These are, indeed, the subjects of the present paper.

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¹ Specifically, if R_c is taken as the classical orbit radius corresponding to the mean-electron energy, $\langle E \rangle = \zeta$ or kT , according to whether the electron gas is taken to be degenerate or nondegenerate, respectively, then $L \ll R_c = (mc/eH)(2\langle E \rangle/m)^{1/2}$. As will be seen later, this is simultaneously the domain of validity for treating the magnetic-field proportional terms in the electronic Hamiltonian as a small perturbation.

² In so doing, one neglects the periodic potential, collision of the electrons with phonons and impurities, and the true scattering properties of the surface. Also, electron spin is neglected throughout.

The treatments to which the present work has reference, are those of Dingle,³ Part IV, and Ham.⁴ Dingle considers a cylindrical sample, for which he predicts an enhancement of the Landau diamagnetic susceptibility depending on the ratio of the radius of the cylinder to the electron wavelength at the Fermi energy. Ham does not specifically treat a "small" system. Rather, using a modification of the WKB approximation, he calculates surface corrections to "large" ($L \gg R_c$) systems, the sign and magnitude of which he finds extremely sensitive to the form of the surface potential.

The present paper began with an investigation of such effects by means of a detailed examination of a very simple geometrical model: namely, a plane-parallel slab, small (in the previously defined sense) in one dimension (at the boundaries of which the wave function is assumed to vanish), and satisfying periodic boundary conditions along the other two transverse dimensions. Such a geometry had been considered earlier by Papapetrou⁵ who obtained just the Landau result⁶ for a degenerate electron gas. In addition to confirming his calculation by an alternate procedure and obtaining

³ R. B. Dingle, Proc. Roy. Soc. (London) **A212**, 47 (1952).

⁴ F. S. Ham, Phys. Rev. **92**, 1113 (1953).

⁵ A. Papapetrou, Z. Physik **107**, 387 (1937). It should be pointed out that the present paper overlaps this reference to some extent. The addition contributions of the present work, however, are: (a) the calculation of the Landau susceptibility for Boltzmann statistics (not considered by Papapetrou); (b) the explicit demonstra-

a numerical correction to his result, we also obtain the Landau result for Boltzmann statistics. Moreover, by a careful examination of the latter calculation, it was found that the use of WKB energies in lieu of the correct energies found from perturbation theory, leads to a *spurious*, larger than normal, result. Thus, the WKB approximation is *not* valid for this case in spite of the fact that it applies to the "vast majority" of states. This result only emphasizes the well-known fact that, since diamagnetism is entirely a quantum effect and arises from a delicate cancellation of large terms, approximations valid for large quantum numbers may often yield spurious results.

To examine the sensitivity of the susceptibility to the choice of boundary potential, a calculation was made for a harmonic potential well, $V(y) = \frac{1}{2}m\Omega^2y^2$, which serves as a convenient prototype of a potential barrier which rises slowly, in contrast to the infinite potential well considered previously. While recognizing that this potential is perhaps somewhat special (as will be noted in the text, the form of the magnetic-field perturbation agrees with that of the well), we nevertheless consider this case instructive. Here, also, the Landau result was found in the limit of a small system (as defined in this case by $\hbar\omega_c = e\hbar H/mc \ll \hbar\Omega$). Hence, for the cases investigated, aside from the above-mentioned numerical correction to the Landau result for degenerate statistics, there is no indication of size and surface corrections of the types discussed in Refs. 3 and 4, which depend explicitly on the sample dimensions and/or the magnetic-field strength.

The program of the present paper is as follows. In Sec. II, the problem is formulated, and the magnetic-field-dependent corrections to the electronic energies are found by standard time-independent perturbation theory. In Appendix A, the series required for the evaluation of the second-order energy correction is summed by a contour integral technique. Using these

tion of the inadequacy of the WKB approximation based on calculation (a); (c) an alternate and independent calculation of the magnetic-field-dependent energies (specifically, the second-order energy corrections).

⁶ It should be pointed out that the use of periodic boundary conditions along the two long dimensions of the slab, has been cited by Dingle as being responsible for the Landau result obtained by Papapetrou. Such a criticism does not seem justified in view of the fact Papapetrou himself examined this question in a later paper [Z. Physik 112, 587 (1939)]. Using standing waves along all three directions, he found that for the vast majority of possible systems (i.e., of L_x, L_y, L_z), the standard result was reobtained. The only exceptions to this occurred for those cases where the ratio of the dimensions of the box in the plane normal to the applied magnetic field was a rational number. This geometrical feature implies a twofold degeneracy in the unperturbed standing wave states which, in turn, leads to a larger than normal susceptibility. However, in the opinion of the present author, such cases cannot be properly interpreted as implying a dependence of the diamagnetic susceptibility on the sample dimensions, since the smallest, ordinarily negligible, perturbations (impurities, the periodic potential, etc.) would be bound to lift such degeneracies, in view of the infinitesimal level spacing ($\sim 1/L$). Hence, the use of periodic boundary conditions along other than the thin dimension seems a justifiable model for small systems, and is used in the present paper.

results, the susceptibility calculations are given in Sec. III for both Maxwell-Boltzmann and Fermi-Dirac statistics. This is contrasted with the spurious size-dependent result found on the basis of the WKB energies. Finally, the case of the harmonic well potential is treated in Sec. IV, again with the Landau result.

II. ENERGY CALCULATIONS

We consider an infinite potential well defined by

$$\begin{aligned} V(y) &= 0, & |y| < L_y/2, \\ V(y) &= \infty, & |y| \geq L_y/2, \end{aligned} \quad (1.1)$$

with no dependence on x and z . Then, choosing a gauge $\mathbf{A} = (-Hy, 0, 0)$, where $H = H_z$ is the applied dc magnetic field, the electronic Hamiltonian is

$$\mathfrak{H} = \frac{1}{2m} \left(p_x + \frac{eHy}{c} \right)^2 + \frac{p_y^2}{2m} + \frac{p_z^2}{2m} + V(y).$$

The wave equation obeyed by the total wave function $\Psi(x, y, z)$ is

$$\mathfrak{H}\Psi(x, y, z) = E\Psi(x, y, z).$$

Following the standard procedure of setting $\Psi(x, y, z) = e^{i(k_x x + k_z z)}\chi(y)$, one obtains the wave equation obeyed by $\chi(y)$, namely,

$$\frac{d^2\chi(y)}{dy^2} + \frac{2m}{\hbar^2} \left\{ E_y - \frac{e^2 H^2 y^2}{2mc^2} - \frac{eH}{mc} \hbar k_{xy} \right\} \chi(y) = 0. \quad (1.2)$$

Following Papapetrou⁵ and Dingle,³ the magnetic-field terms in (1.2) are treated as small perturbations.⁷ The zeroth-order ($H=0$) eigenstates and energies are just standing wave solutions:

$$\begin{aligned} \chi(y) &= A \sin[2\pi n y / L_y]; & n &= 1, 2, 3, \dots \\ &= B \cos[2\pi(n' + \frac{1}{2})y / L_y]; & n' &= 0, 1, 2, \dots \end{aligned} \quad (1.3)$$

$$E_n^{(0)} = \frac{\hbar^2}{2m} \left(\frac{2\pi}{L_y} n \right)^2, \quad E_{n'}^{(0)} = \frac{\hbar^2}{2m} \left(\frac{2\pi}{L_y} (n' + \frac{1}{2}) \right)^2.$$

The first-order energy correction is simply the expectation value of the H^2 -proportional term in (1.2). For the odd solutions, for example, one gets

$$\begin{aligned} E_n^{(1)} &= \frac{e^2 H^2}{2mc^2} A \int_{-L_y/2}^{L_y/2} dy y^2 \sin^2 \left[\frac{2\pi n y}{L_y} \right] \\ &= \frac{e^2 H^2 L_y^2}{24mc^2} \left(1 - \frac{3}{2\pi^2 n^2} \right). \end{aligned}$$

⁷ As pointed out by Dingle, the condition given in footnote 1 is equivalent to $(e^2 H^2 L_y^2 / mc^2) \ll \langle E \rangle$, i.e., that the magnetic energy correction is small compared to the mean-electron energy. For perturbation theory to be applicable, however, it must further be assumed that $e^2 H^2 L_y^2 / mc^2$ be small compared to some mean-level spacing of the system (in the statistical sense). Since the magnetic field is taken as arbitrarily weak, this condition is assumed to be satisfied.

Doing the same for the even solutions, the first-order energy correction for both cases can be written in terms of a common quantum number, n_y :

$$E_{n_y}^{(1)} = \frac{e^2 H^2 L_y^2}{24mc^2} \left(1 - \frac{6}{\pi^2 n_y^2} \right); \quad n_y = 1, 2, 3, \dots \quad (1.4)$$

The calculation of the steady susceptibility requires all energy corrections to $O(H^2)$. Accordingly, the *second-order* energy correction due to the H -proportional term of (1.2) must be found. By symmetry, the only nonvanishing matrix elements of this term are those between the even and odd states:

$$V_{k_y, k_y'} = \frac{eH}{mc} \frac{2}{L_y} \int_{-L_y/2}^{L_y/2} dy y \sin(k_y y) \cos(k_y' y).$$

Integrating, we get

$$V_{k_y, k_y'} = \frac{eH}{mc} \frac{2}{L_y} \frac{\hbar k_x}{L_y} \times \left\{ \frac{\sin[(k_y + k_y')L_y/2]}{(k_y + k_y')^2} + \frac{\sin[(k_y - k_y')L_y/2]}{(k_y - k_y')^2} \right\}.$$

With

$$\begin{aligned} k_y &= (2\pi/L_y)n, \\ k_y' &= (2\pi/L_y)(n' + \frac{1}{2}), \\ (k_y \pm k_y')(L_y/2) &= \pi(n \pm n') \pm \pi/2, \end{aligned}$$

one finds, after some trigonometry, that

$$\sin[(k_y \pm k_y')L_y/2] = \pm (-1)^{n \pm n'},$$

$$V_{nn'} = \frac{eH}{mc} \frac{L_y}{2\pi^2} \frac{\hbar k_x}{2\pi^2} \times \left\{ \frac{(-1)^{n+n'}}{[n + (n' + \frac{1}{2})]^2} - \frac{(-1)^{n-n'}}{[n - (n' + \frac{1}{2})]^2} \right\}. \quad (1.5)$$

The second-order energy correction to the level n' is given by the standard formula⁸

$$E_{n'}^{(2)} = \sum_{n=1}^{\infty} \frac{|V_{nn'}|^2}{E_n^{(0)} - E_{n'}^{(0)}}. \quad (1.6)$$

Substituting (1.3) and (1.5) into (1.6), one gets

$$E_{n'}^{(2)} = \frac{e^2 H^2 L_y^4}{8mc \pi^6} k_x^2 S(n'),$$

where

$$S(n') = \sum_{n=1}^{\infty} \left\{ \frac{1}{[n + (n' + \frac{1}{2})]^4} + \frac{1}{[n - (n' + \frac{1}{2})]^4} - \frac{2}{[n + (n' + \frac{1}{2})]^2 [n - (n' + \frac{1}{2})]^2} \right\} \left\{ \frac{1}{(n' + \frac{1}{2})^2 - n^2} \right\}. \quad (1.7)$$

⁸ Due to the circumstance that the matrix elements connect only even and odd solutions, one need not be concerned about excluding the term $n=n'$ from the summation.

These series are evaluated in Appendix A by a summation of series method given by Morse and Feshbach.⁹ The essence of the method is to consider the contour integral of the summand, regarded as a function of a complex variable z , multiplied by a function $(\pi \cot \pi z)$ which has simple poles at the real integers with residues equal to one. The residues of the integrand at these latter points then give the required series, while the residues at the poles of the original summand can be evaluated by standard techniques. The sum of these contributions is equal to the integral over a large circle at infinity which can be shown to vanish, and hence, the required series can be evaluated. According to Appendix A, the result is

$$S(n') = \frac{\pi^4}{12} \frac{1}{(n' + \frac{1}{2})^2} \left\{ 1 - \frac{15}{4\pi^2} \frac{1}{(n' + \frac{1}{2})^2} \right\}. \quad (1.8)$$

The energy correction term $E_n^{(2)}$ is evaluated in an identical fashion. Writing this result and (1.8) in terms of the same index, n_y , which was introduced in (1.4), the total electronic energy to order H^2 is

$$\begin{aligned} E_{n_x n_y n_z} &= \frac{\hbar^2}{2m} \left[\left(\frac{2\pi}{L_x} \right)^2 n_x^2 + \left(\frac{\pi}{L_y} \right)^2 n_y^2 + \left(\frac{2\pi}{L_z} \right)^2 n_z^2 \right] \\ &+ \frac{e^2 H^2 L_y^2}{24mc^2} \left\{ \left[1 - \frac{6}{\pi^2 n_y^2} \right] \right. \\ &\left. + \frac{(\hbar^2/2m)(2\pi/L_x)^2 n_x^2}{(\hbar^2/2m)(\pi/L_y)^2 n_y^2} \left[1 - \frac{15}{\pi^2 n_y^2} \right] \right\}. \quad (1.9) \end{aligned}$$

III. SUSCEPTIBILITY CALCULATIONS

A. Boltzmann Statistics

With the definitions

$$a_x^2 = \beta \frac{\hbar^2 (2\pi)^2}{2m (L_x)^2}, \quad a_y^2 = \beta \frac{\hbar^2 (\pi)^2}{2m (L_y)^2}, \quad a_z^2 = \beta \frac{\hbar^2 (2\pi)^2}{2m (L_z)^2}, \quad (2.1)$$

$$b^2 = \beta \frac{e^2 H^2 L_y^2}{24mc^2}, \quad \beta = \frac{1}{kT},$$

the classical partition

$$Z = \sum_{n_x n_y n_z} \exp\{-\beta E_{n_x n_y n_z}\}$$

takes the form

$$\begin{aligned} Z &= Z_z^{(0)} \sum_{n_y=1}^{\infty} \exp\{-a_y^2 n_y^2 - b^2(1 - 6/\pi^2 n_y^2)\} \\ &\times \sum_{n_x=-\infty}^{\infty} \exp\left\{-a_x^2 n_x^2 \left[1 - \frac{b^2}{a_y^2} \left(\frac{1}{n_y^2} - \frac{15}{\pi^2 n_y^4} \right) \right]\right\}, \quad (2.2) \end{aligned}$$

⁹ P. M. Morse and H. Feshbach, *Methods of Theoretical Physics* (McGraw-Hill Book Company, Inc., New York, 1953), Vol. 1, p. 413.

where

$$Z_z^{(0)} = \sum_{n_z=-\infty}^{\infty} \exp\{-a_z^2 n_z^2\}. \quad (2.3)$$

The summation over n_x is carried out by replacing the sum by an integral. Expanding this result (which is a function of n_y^2) and the exponential appearing in the n_y sum to order b^2 , which is of sufficient accuracy for calculating the steady susceptibility, we get

$$Z = Z^{(0)} - Z_z^{(0)} Z_x^{(0)} b^2 \sum_{n_y=1}^{\infty} e^{-a_y^2 n_y^2} \times \left[\left(1 - \frac{6}{\pi^2 n_y^2}\right) + \frac{1}{2a_y^2} \left(\frac{1}{n_y^2} - \frac{15}{\pi^2 n_y^4}\right) \right], \quad (2.4)$$

where

$$Z^{(0)} = Z_x^{(0)} Z_y^{(0)} Z_z^{(0)}$$

is the field-free partition function, and $Z_x^{(0)}$ and $Z_y^{(0)}$ are defined in analogy with (2.3).

The series given in (2.4) can be readily summed by means of the Poisson sum formula¹⁰ relating the sum of a series to the sum of its Fourier transforms. Specifically, the Poisson formula reads

$$\sum_{k=-\infty}^{\infty} f(2\pi k) = \frac{1}{2\pi} \sum_{k=-\infty}^{\infty} \int_{-\infty}^{\infty} d\tau f(\tau) e^{-ik\tau}. \quad (2.5)$$

Applying (2.5) to the case $f(2\pi k) = e^{-a_y^2 k^2}$, one can derive the relation

$$\sum_{n_y=1}^{\infty} e^{-n_y^2 a_y^2} = \frac{\pi^{1/2}}{2a_y} - \frac{1}{2} + \frac{\pi^{1/2}}{a_y} \sum_{n_y=1}^{\infty} e^{-(\pi^2 n_y^2 / a_y^2)},$$

which applies for all $\text{Re}(a_y^2) > 0$. By successively multiplying the above result by a_y^4 and integrating from 0 to a_y , one can generate the necessary series for

$$\sum_{n_y=1}^{\infty} \left(\frac{e^{-n_y^2 a_y^2}}{n_y^2}\right) \quad \text{and} \quad \sum_{n_y=1}^{\infty} \left(\frac{e^{-n_y^2 a_y^2}}{n_y^4}\right).$$

By these means, the required series, to a sufficient number of terms for our purposes, are

$$\begin{aligned} \sum_{n_y=1}^{\infty} e^{-a_y^2 n_y^2} &= \frac{\pi^{1/2}}{2a_y} - \frac{1}{2} + \dots, \\ \sum_{n_y=1}^{\infty} (e^{-a_y^2 n_y^2} / n_y^2) &= -\frac{\pi^2}{6} - (\pi)^{1/2} a_y + \frac{1}{2} a_y^2 + \dots, \\ \sum_{n_y=1}^{\infty} (e^{-a_y^2 n_y^2} / n_y^4) &= \frac{\pi^4}{90} - \frac{\pi^2}{6} a_y^2 + \frac{2}{3} (\pi)^{1/2} a_y^3 + \dots. \end{aligned} \quad (2.6)$$

¹⁰ G. A. Korn, *Mathematical Handbook* (McGraw-Hill Book Company, Inc., New York, 1961).

The sum over n_y appearing in (2.4) then becomes, in expanded form,

$$a_y^{-2} \left(\frac{\pi^2}{12} - \frac{\pi^2}{12}\right) + a_y^{-1} \left(\frac{\pi^{1/2}}{2} - \frac{\pi^{1/2}}{2}\right) + a_y^0 \left(-\frac{1}{2} - 1^* + \frac{1}{4} + \frac{5^*}{4}\right) + a_y^1 \left(\frac{6}{\pi^{3/2}} - \frac{5}{\pi^{3/2}}\right), \quad (2.7)$$

the first nonvanishing contribution $\sim a_y^{-1}$. The asterisks (*) indicate that the respective contributions arise from the second and third sums in (2.6). These will be of importance when we later examine the consequences of using energies derived with use of the WKB approximation. Retaining the above contribution $\sim a_y^{-1}$, and using the standard thermodynamic expression for the susceptibility

$$\chi = \frac{1}{H} (kT) \frac{\partial}{\partial H} \ln Z \cong \frac{1}{H} (kT) \frac{1}{Z^{(0)}} \frac{\partial Z}{\partial H},$$

one finds, from (2.4) and (2.1) that

$$\chi = -\frac{\mu^2}{3kT} = \chi_{\text{Landau}}, \quad (2.8)$$

where $\mu = e\hbar/mc$ is the Bohr magneton. Thus, the diamagnetic susceptibility of a nondegenerate electron gas confined to a slab which is "small" in one dimension, is exactly the Landau value.

The Landau result is also obtained for the degenerate case. This result has been obtained previously,⁵ but will be summarized briefly for the sake of completeness. Before so doing, however it is of some interest, as mentioned earlier, to calculate the susceptibility using WKB energies. In particular, it will be shown that these energies, which are asymptotically correct only for large quantum numbers, lead to a *spurious* result, larger than χ_{Landau} , and depending on the sample dimension.

The WKB energies are readily obtained from (1.2) using the phase integral condition

$$(2m)^{1/2} \int_{-L_y/2}^{L_y/2} dy \left\{ E_y - \frac{e^2 H^2 y^2}{2mc^2} - \frac{eH}{mc} \hbar k_x y \right\}^{1/2} = n_y \hbar \pi. \quad (2.9)$$

Since, by definition, the second and third terms under the square-root sign are very much less than the first, the square root may be expanded to order H^2 . Carrying out the integrations, one obtains

$$E_y^{1/2} \frac{e^2 H^2 L_y^2}{48mc^2 E_y^{1/2}} - \frac{e^2 H^2 \hbar^2 k_x^2 L_y^2}{96m^2 c^2 E_y^{3/2}} = \frac{\hbar}{(2m)^{1/2}} \frac{\pi}{L_y} n_y.$$

Solving for E_y to order H^2 by iteration, one gets

$$E_y = \frac{\hbar^2}{2m} \frac{\pi^2}{L_y^2} n_y^2 + \frac{e^2 H^2 L_y^2}{24mc^2} \left\{ 1 + \frac{(\hbar^2/2m) k_x^2}{(\hbar^2/2m)(\pi^2/L_y^2) n_y^2} \right\}. \quad (2.10)$$

This result does not include the two “quantum” correction terms $(-6/\pi^2 n_y^2)$ and $(-15/\pi^2 n_y^4)$ contained in the square brackets of (1.9) which, it will be recalled, is the exact perturbation theory result to order H^2 . Going back to (2.7) one sees that the terms marked (*), which arise from the above-mentioned correction terms [these, in turn, arise from the second and third sums of (2.6)], would not appear if WKB energies were used. Hence, the first nonvanishing term would be a_y^0 , rather than a_y^1 , with the result that

$$\chi_{\text{WKB}} \sim \chi_{\text{Landau}} \times \left(\frac{L_y^2}{\hbar^2/2mkT} \right)^{1/2}.$$

Thus, the WKB approximation for this case gives a spurious size effect, depending on the ratio of the small dimension of the slab to the thermal deBroglie wavelength. It is of some interest that Dingle’s result (for cylindrical geometry) is larger than χ_{Landau} by such a factor [except for the appearance of a different exponent ($\frac{1}{6}$ instead of $\frac{1}{2}$), probably due to his different geometry, and the fact that $kT \rightarrow \zeta$, since he is dealing with a Fermi gas].

B. Degenerate Statistics

In this section, it is to be established that the solutions (1.9) lead to the Landau diamagnetism (to within a numerical factor) for the case of degenerate, Fermi-Dirac statistics. The procedure is the standard one of calculating the susceptibility from the free energy of a Fermi gas:

$$F = N\zeta - kT \sum_i \ln\{1 + \exp[(\zeta - E_i)/kT]\}, \quad (2.11)$$

by means of the relation¹¹

$$\chi = -(1/VH)(\partial F/\partial H)_\zeta. \quad (2.12)$$

Before getting into the calculation, it is useful to develop a kind of general thermodynamic perturbation expansion for F for the case of degenerate statistics. This development is analogous to the thermodynamic perturbation theory given by Landau and Lifshitz¹² for the case of the classical distribution function. We write E_i to terms up to second order in H :

$$E_i = E_i^{(0)} + E_i^{(1)} + E_i^{(2)},$$

the possibility of an $E_i^{(1)} \neq 0$ being included for the sake of generality. Then, performing a Taylor series expansion

¹¹ It should be pointed out that, for fixed N , ζ is a function of H and will contain a correction term $\sim H^2$ in the presence of the magnetic field. However, this does not affect M (or χ) due to the fact that $(\partial F/\partial \zeta) = 0$, which is the condition determining ζ . Hence, $dF/dH = (\partial F/\partial H)_\zeta + (\partial F/\partial \zeta)(\partial \zeta/\partial H) = (\partial F/\partial H)_\zeta$.

¹² L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Addison-Wesley Publishing Company, Inc., Reading, Massachusetts, 1958), p. 93.

of $\ln[1 + e^{(\zeta - E_i)/kT}]$ about $E_i^{(0)}$, one gets

$$\begin{aligned} & \ln[1 + e^{(\zeta - E_i)/kT}] \\ &= \ln[1 + e^{(\zeta - E_i^{(0)})/kT}] - \frac{1}{kT} \frac{1}{1 + e^{(E_i^{(0)} - \zeta)/kT}} E_i^{(2)} \\ & \quad - \frac{1}{2kT} \left[\frac{\partial}{\partial E} \left(\frac{1}{1 + e^{(E_i - \zeta)/kT}} \right) \right]_{E_i = E_i^{(0)}} \times [E_i^{(1)}]^2, \end{aligned}$$

including correction terms of order H^2 . Then,

$$\begin{aligned} F &= F^{(0)} + \sum_i E_i^{(2)} f(E_i^{(0)}) \\ & \quad + \frac{1}{2} \sum_i \left[\frac{\partial f(E_i)}{\partial E_i} \right]_{E_i = E_i^{(0)}} \times [E_i^{(1)}]^2, \quad (2.13) \end{aligned}$$

where $f(E_i) = (1 + e^{(E_i - \zeta)/kT})^{-1}$ is the Fermi distribution function.

Getting back to the case of slab geometry, from (2.13), (2.1), and (1.9), one must calculate the sum

$$\begin{aligned} F &= \frac{e^2 H^2 L_y^2}{24mc^2} \sum_{n_x n_y n_z} \left\{ \left(1 - \frac{6}{\pi^2 n_y^2} \right) + \frac{a_x^2 n_x^2}{a_y^2 n_y^2} \left(1 - \frac{15}{\pi^2 n_y^2} \right) \right\} \\ & \quad \times \frac{1}{1 + \exp[a_x^2 n_x^2 + a_y^2 n_y^2 + a_z^2 n_z^2 - \beta \zeta]}. \quad (2.14) \end{aligned}$$

We consider the evaluation of (2.14) in the limit $T \rightarrow 0$, where the Fermi function assumes a step function character. Then, since the quantity in curly brackets is independent of n_z , the sum over n_z gives just the range of n_z :

$$\sum_{n_z} (\dots) \rightarrow 2 \left(\frac{\beta \zeta - a_x^2 n_x^2 - a_y^2 n_y^2}{a_z^2} \right)^{1/2}. \quad (2.15)$$

Next, the sum over n_x is evaluated by replacing the summation by an integration. This gives the following two integrals whose evaluation is elementary:

$$\begin{aligned} & \int_{-[(\beta \zeta - a_y^2 n_y^2)/a_x^2]^{1/2}}^{[(\beta \zeta - a_y^2 n_y^2)/a_x^2]^{1/2}} dn_x [(\beta \zeta - a_y^2 n_y^2) - a_x^2 n_x^2]^{1/2} \\ & \quad = \frac{\pi (\beta \zeta - a_y^2 n_y^2)}{a_x 2}, \\ & \int_{-[(\beta \zeta - a_y^2 n_y^2)/a_x^2]^{1/2}}^{[(\beta \zeta - a_y^2 n_y^2)/a_x^2]^{1/2}} dn_x a_x^2 n_x^2 [(\beta \zeta - a_y^2 n_y^2) - a_x^2 n_x^2]^{1/2} \\ & \quad = \frac{\pi (\beta \zeta - a_y^2 n_y^2)^2}{a_x 8}. \end{aligned}$$

The evaluation of F then only requires carrying out the summation over n_y :

$$\begin{aligned} F &= \frac{e^2 H^2 L_y^2}{24mc^2} \frac{2\pi}{a_x a_z} \sum_{n_y=1}^{\alpha} \left\{ \left(1 - \frac{6}{\pi^2 n_y^2} \right) \left(\frac{\beta \zeta - a_y^2 n_y^2}{2} \right) \right. \\ & \quad \left. + \frac{1}{a_y^2} \left(\frac{1}{n_y^2} - \frac{15}{\pi^2 n_y^4} \right) \frac{(\beta \zeta - a_y^2 n_y^2)^2}{8} \right\}, \quad (2.16) \end{aligned}$$

where

$$\alpha = \left(\frac{\beta\zeta}{a_y^2}\right)^{1/2} \gg 1.$$

To evaluate these sums, we apply the Euler-MacLaurin expansion.¹⁰ This theorem states that if $f(x)$ and its derivatives exist and are continuous for $m \leq x \leq n$, then

$$\begin{aligned} \sum_{j=m}^n f(j) &= \int_m^n dx f(x) \\ &+ \frac{1}{2}[f(n) + f(m)] + \frac{1}{12}[f'(n) - f'(m)] \\ &- \frac{1}{720}[f'''(n) - f'''(m)] + \dots \end{aligned} \quad (2.17)$$

Applying (2.17) to (2.16), and using the identities

$$\begin{aligned} \sum_{n_y=1}^{\alpha} \frac{1}{n_y^2} &= \frac{\pi^2}{6} - \sum_{n_y=\alpha+1}^{\infty} \frac{1}{n_y^2}, \\ \sum_{n_y=1}^{\alpha} \frac{1}{n_y^4} &= \frac{\pi^4}{90} - \sum_{n_y=\alpha+1}^{\infty} \frac{1}{n_y^4}, \end{aligned}$$

one again finds that the summation over n_y develops as a series of terms of decreasing magnitude: $a_y^2\alpha^2$, $a_y^2\alpha^1$, $a_y^2\alpha^0$, \dots . Just as in the nondegenerate case, the final result depends crucially on a detailed cancellation of terms to a given order. The calculations are therefore given in Appendix B. Taking care to include all contributions to a given order in $a_y^2\alpha^n$, one obtains:

$$\begin{aligned} \sum_{n_y}(\dots) &= \left(\frac{1}{2} - \frac{1}{6} - \frac{1}{8} - \frac{1}{4} + \frac{1}{24}\right)a_y^2\alpha^3 \\ &+ \left(-\frac{1}{2} - \frac{1}{4} + \frac{1}{16} + \frac{15}{24} + \frac{1}{16}\right)a_y^2\alpha^2 \\ &+ \left(\frac{1}{\pi^2} - \frac{1}{12}\right)a_y^2\alpha = \left(\frac{1}{\pi^2} - \frac{1}{12}\right)a_y^2\alpha. \end{aligned}$$

Using (2.12), we find that

$$\begin{aligned} \chi &= -\frac{e^2\zeta^{1/2}}{12\pi\hbar c^2(2m)^{1/2}} \left(\frac{1}{\pi^2} - \frac{1}{12}\right) \\ &= \chi_{\text{Landau}} \times \frac{1}{2} \left(1 - \frac{\pi^2}{12}\right), \end{aligned} \quad (2.18)$$

which establishes our result. Although this expression exhibits no explicit size effects in as much as it is independent of R and H , it does differ from Papapetrou's result by the numerical factor indicated. It would therefore imply a magnetic-field dependence in going

from small to large systems. This is a direct consequence of a consistent application of the Euler-MacLaurin expansion as described in Appendix B, and has no simple physical interpretation, as far as can be seen by the present author.

IV. HARMONIC WELL CASE

In this section, we investigate the effect of the shape of the surface potential in the "small size" limit for a particularly simple case: namely, a harmonic well¹³ along the thin (y) dimension:

$$V(y) = \frac{1}{2}m\Omega^2 y^2. \quad (2.19)$$

Instead of (1.2), the wave equations for $\chi(y)$ becomes

$$\frac{\hbar^2}{2m} \frac{d^2\chi(y)}{dy^2} + \left[\frac{1}{2}m\Omega^2 y^2 + \frac{e^2 H^2 y^2}{2mc^2} + \frac{eH}{mc} \hbar k_x y \right] \chi = E\chi. \quad (2.20)$$

The "small size" approximation, which we shall use later, is just

$$(e^2 H^2 / mc^2) \ll m\Omega^2. \quad (2.21)$$

The zeroth-order ($H=0$) eigenstates and eigenvalues are simple harmonic oscillator solutions

$$\begin{aligned} \chi_N^{(0)} &= \Phi_N(\alpha y), \\ E_N^{(0)} &= \hbar\Omega(N + \frac{1}{2}), \end{aligned} \quad (2.22)$$

where $\Phi(\alpha y)$ is a normalized harmonic oscillator state, with excitation quantum number N , and

$$\alpha = (m\Omega/\hbar)^{1/2}$$

is a normalization constant.

The H -dependent energy corrections can be found by applying time-independent perturbation theory as before.¹⁴ It is simpler, however, to make use of the circumstance that the spatial dependence of the perturbation agrees with that of the well in order to obtain a frequency change and energy shift (to order H^2). The two procedures agree, as they must, with the result:

$$E_N = E_N^{(0)} - \frac{e^2 H^2}{2m^2 c^2} \frac{\hbar^2 k_x^2}{m\Omega^2} + \frac{e^2 H^2}{2mc^2} \frac{\hbar\Omega}{m\Omega^2} (N + \frac{1}{2}). \quad (2.23)$$

¹³ The harmonic well case perhaps earliest treated by C. G. Darwin, Proc. Cambridge Phil. Soc. **27**, 86 (1930). However, while Darwin obtains the Landau result in the limit $\Omega \rightarrow 0$ (in the notation of the present paper), we obtain the same result in the opposite limit $\hbar\omega_c \ll \hbar\Omega$ appropriate to a "small" system.

¹⁴ The calculation of the second-order energy correction is much simpler (than that for the case of the infinite barrier) due to the circumstance that, since $\langle N' | y | N \rangle \sim \delta_{N', N \pm 1}$, there are only a few number of terms to be summed.

The classical partition function is

$$Z = \sum_{n_x N n_z} e^{-\beta E_{n_x N n_z}}.$$

The n_x sum is carried out first. We have

$$Z_x^{(H)} = \sum_{n_x=-\infty}^{\infty} \exp \left\{ -\beta \frac{\hbar^2}{2m} \left(\frac{2\pi}{L_x} \right)^2 n_x^2 \left[1 - \frac{e^2 H^2}{mc^2} \frac{1}{m\Omega^2} \right] \right\} \\ \cong Z_x^{(0)} \left(1 + \frac{e^2 H^2}{2mc^2} \frac{1}{m\Omega^2} \right),$$

to order H^2 .

The sum over N can be written in the form

$$\sum_{N=0}^{\infty} \exp \left\{ -\beta \hbar \Omega \left(1 + \frac{e^2 H^2}{2mc^2} \frac{1}{m\Omega^2} \right) \left(N + \frac{1}{2} \right) \right\},$$

which, aside from the H^2 term, is just the geometric series required in the calculation of the ordinary Landau diamagnetism. The result is

$$\frac{1}{2} \operatorname{csch} \left[\frac{\beta \hbar \Omega}{2} \left(1 + \frac{e^2 H^2}{2mc^2} \frac{1}{m\Omega^2} \right) \right].$$

Expanding the csch and making explicit use of the small size condition (2.21), one obtains:

$$\frac{1}{2} \operatorname{csch} \frac{\beta \hbar \Omega}{2} \left[1 - \frac{\beta \hbar \Omega}{2} \frac{e^2 H^2}{2mc^2} \frac{1}{m\Omega^2} \coth \frac{\beta \hbar \Omega}{2} \right].$$

The partition function Z then becomes

$$Z^{(H)} = Z^{(0)} - Z_x^{(0)} Z_x^{(0)} \frac{e^2 H^2}{2mc^2} \frac{1}{m\Omega^2} \\ \times \frac{1}{2} \left[\coth \frac{\beta \hbar \Omega}{2} - \frac{1}{(\beta \hbar \Omega / 2)} \right], \quad (2.24)$$

the quantity in the square brackets being the Langevin function, $L(\beta \hbar \Omega / 2)$. Using the fact that the level spacing $\hbar \Omega$ is much less than kT , one has that $L(\beta \hbar \Omega / 2) \doteq \frac{1}{3}(\beta \hbar \Omega / 2)$. From the expression (2.17) for the susceptibility, one finally gets

$$\chi_{SHO} = -\frac{\beta}{3} \frac{e^2 \hbar^2}{4mc^2} = \chi_{\text{Landau}}. \quad (2.25)$$

This case can be thought of as a prototype of potentials which are slowly varying, in contrast to those whose variation with position is abrupt, the extreme case of which is the infinite square well considered in the first section. For both cases, one obtains the standard Landau result in the small size limit.

V. SUMMARY

In the present paper, the diamagnetic susceptibility has been calculated for a free-electron gas confined to a

system whose characteristic dimensions are small compared to the classical, mean, orbital radius of an electron in an applied magnetic field. The finite size of the system is taken into account only in that the wave function is required to vanish in some fashion beyond the boundaries of the system; no consideration has been given to the more difficult problem of the quantum mechanical scattering properties of the surface. Also, the effects of the periodic potential have been neglected.

The case of slab geometry has been emphasized due to the relative ease with which it can be treated. For this case, it has been shown that the Landau result obtains exactly in the small size limit for nondegenerate statistics, and to within a numerical factor in the degenerate case. In the case of Boltzmann statistics, it has demonstrated that the use of the WKB approximation disagrees with the result of perturbation theory (which is a bonafide approximation in the small size limit), and leads to an apparent enhancement of the diamagnetic susceptibility. As to the sensitivity of the susceptibility to the choice of boundary potential, no change in susceptibility was found for the case of a harmonic well using energies derived from perturbation theory. Although a general proof of the Landau result has not been provided for arbitrary geometries and surface potentials, it is thought that the results of the present paper do raise some question as to the reality of size effects in the steady diamagnetic susceptibility of small systems.

Added Note. Recent calculations by W. V. Houston and E. Lane [Bull. Am. Phys. Soc. **8**, 7, 528 (1963)] on the effect of a boundary on the diamagnetic susceptibility of free electrons, lead to the conclusion that the Landau treatment is quite accurate for this case. This is in agreement with the results of the present paper.

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APPENDIX A

In this Appendix, we present the calculation of the sum (1.7) which arises from the second-order energy correction term (1.6). The basic idea of the method⁹ was discussed in the text following (1.7).

Consider the sum

$$\sum_{n=1}^{\infty} \frac{1}{[n + (n' + \frac{1}{2})]^4} \frac{1}{n^2 - (n' + \frac{1}{2})^2}.$$

Let $n \rightarrow z$, $(n' + \frac{1}{2}) \rightarrow z_0$, where the z 's are complex

variables. Next, consider the contour integral

$$\frac{1}{2\pi i} \int_c dz \left[\frac{1}{(z+z_0)^4} \frac{1}{z^2-z_0^2} \right] \pi \cot(\pi z),$$

where the contour is over a complete, large circle at infinity. Let

$$f(z) = \left[\frac{1}{(z+z_0)^4} \frac{1}{z^2-z_0^2} \right] = \frac{1}{(z+z_0)^5} \frac{1}{z-z_0}.$$

Then, since, according to Morse and Feshbach

$$\lim_{z \rightarrow \infty} |zf(z)| = 0,$$

the integral at infinity vanishes. Since $\pi \cot \pi z$ has simple poles at real integer values, one has that

$$0 = \sum_{n=-\infty}^{\infty} \frac{1}{[n+(n'+\frac{1}{2})]^4} \frac{1}{n^2-(n'+\frac{1}{2})^2} + \sum [\text{residues of } f(z)\pi \cot \pi z \text{ at the poles of } f(z)],$$

or, breaking up the summation into the ranges

$$b_{-1} = \frac{1}{24} \left\{ -\frac{24 \cot \pi(-z_0)}{32 z_0^5} + \frac{24 \csc^2 \pi(-z_0)}{16 z_0^4} - \frac{24 \pi^3 \cot \pi(-z_0) \csc^3 \pi(-z_0)}{8 z_0^3} + 2\pi^4 \left[\frac{\csc^4 \pi(-z_0) + 2 \csc^2 \pi(-z_0) \cot^2 \pi(-z_0)}{z_0^2} \right] - \frac{1}{z_0} [6\pi^5 \csc^4 \pi(-z_0) \cot \pi(-z_0) + 4\pi^5 \csc^2 \pi(-z_0) \cot^3 \pi(-z_0)] \right\}.$$

Using the fact that $z_0 = n' + \frac{1}{2}$ is a half-integer, b_{-1} reduces to

$$b_{-1} = \frac{\pi^2}{16(n'+\frac{1}{2})^4} + \frac{\pi^4}{12(n'+\frac{1}{2})^2},$$

and the required sum is

$$\frac{\pi^2}{16(n'+\frac{1}{2})^4} + \frac{\pi^4}{12(n'+\frac{1}{2})^2} + \frac{1}{(n'+\frac{1}{2})^6}.$$

The sum of the third term of (1.7) can be treated in an analogous fashion. The result is

$$-\frac{3}{8} \frac{\pi^2}{(n'+\frac{1}{2})^4} + \frac{1}{(n'+\frac{1}{2})^6}.$$

Combining the two results, we finally obtain

$$S(n') = -\frac{5}{16} \frac{\pi^2}{(n'+\frac{1}{2})^4} + \frac{\pi^4}{12(n'+\frac{1}{2})^2} = \frac{\pi^4}{12} \frac{1}{(n'+\frac{1}{2})^2} \left\{ 1 - \frac{15}{4\pi^2} \frac{1}{(n'+\frac{1}{2})^2} \right\},$$

$n = (-\infty, -1), 0, (1, \infty)$, we write

$$-\sum_{n=1}^{\infty} \frac{1}{[n+(n'+\frac{1}{2})]^4} \frac{1}{n^2-(n'+\frac{1}{2})^2} - \sum_{n=1}^{\infty} \frac{1}{[n-(n'+\frac{1}{2})]^4} \frac{1}{n^2-(n'+\frac{1}{2})^2} = -\frac{1}{(n'+\frac{1}{2})^6} + \sum [\text{residues of } f(z)\pi \cot \pi z \text{ at the poles of } f(z)],$$

the left-hand side being the required summation of the first two terms of (1.7).

The residue at the simple pole $z = z_0$ is $\pi \cot \pi z_0 / (2z_0)^5 = 0$, since $\cot \pi z_0 = \cot \pi(n'+\frac{1}{2}) = 0$.

The residue at the fifth-order pole $z = -z_0$ may be evaluated by expanding $\pi \cot \pi z / (z - z_0)$ in a Taylor series about $z = -z_0$. Thus,

$$\frac{\pi \cot \pi z}{(z+z_0)^5(z-z_0)} = \frac{b_{-5}}{(z+z_0)^5} + \frac{b_{-4}}{(z+z_0)^4} + \dots + \frac{b_{-1}}{z+z_0} + \dots,$$

the residue b_{-1} being just

$$b_{-1} = \frac{1}{24} \frac{d^4}{dz^4} \left(\frac{\pi \cot \pi z}{z-z_0} \right)_{z=-z_0}.$$

Performing the indicated differentiation, one finds

which is the result quoted in (1.8).

The series associated with the second-order energy correction to an even level, i.e., $E_n^{(2)}$, can be calculated in an identical fashion. The net result is given by (1.9).

APPENDIX B

In this Appendix, we present the Euler-MacLaurin expansion of the series (2.16) required for the calculation of the susceptibility for the case of degenerate statistics.

The series (2.16) is rewritten in the form

$$\sum_{n_y=1}^{\infty} \left\{ \left(\frac{\beta \zeta}{2} + \frac{3}{\pi^2} a_y^2 \right) - \frac{\beta \zeta}{2} \frac{6}{\pi^2} \frac{1}{n_y^2} - \frac{a_y^2}{2} n_y^2 + \frac{1}{8 a_y^2} \left(\frac{1}{n_y^2} - \frac{15}{\pi^2 n_y^4} \right) \right\} \times [(\beta \zeta)^2 - 2(\beta \zeta) a_y^2 n_y^2 + a_y^4 n_y^4] = \sum_{i=1}^6 S_i, \quad (B1)$$

where

$$\alpha = (\beta \zeta / a_y^2)^{1/2} \gg 1.$$

One calculates

$$S_1 = \sum_{n_y=1}^{\alpha} \left(\frac{\beta\zeta}{2} + \frac{3}{\pi^2} a_y^2 \right) = \left(\frac{\beta\zeta}{2} + \frac{3}{\pi^2} a_y^2 \right) \alpha$$

$$= \frac{a_y^2}{2} \alpha^3 + \frac{3}{\pi^2} a_y^2 \alpha. \quad (B2)$$

Next,

$$S_2 = -\frac{\beta\zeta}{2} \frac{6}{\pi^2} \left[\sum_{n_y=1}^{\alpha} \frac{1}{n_y^2} - \sum_{n_y=\alpha+1}^{\infty} \frac{1}{n_y^2} \right]. \quad (B3)$$

Using the fact that

$$\sum_{n_y=1}^{\alpha} \frac{1}{n_y^2} = \frac{\pi^2}{6},$$

and evaluating the second sum of (B3) by means of (2.17), (B3) becomes

$$S_2 = -\frac{a_y^2 \alpha^2}{2} + \frac{3}{\pi^2} a_y^2 \alpha - \frac{3}{2\pi^2} a_y^2 \alpha^0 + \frac{1}{2\pi^2} a_y^2 \alpha^{-1} + \dots \quad (B4)$$

For S_3 , we get

$$S_3 = -\frac{a_y^2}{2} \sum_{n_y=1}^{\alpha} n_y^2 = -\frac{a_y^2 \alpha^3}{6} - \frac{a_y^2 \alpha^2}{4} - \frac{a_y^2 \alpha}{12} + \dots \quad (B5)$$

For S_4 , one has

$$S_4 = \frac{(\beta\zeta)^2}{8a_y^2} \sum_{n_y=1}^{\alpha} \left(\frac{1}{n_y^2} - \frac{15}{\pi^2 n_y^4} \right)$$

$$= -\frac{(\beta\zeta)^2}{8a_y^2} \sum_{n_y=\alpha+1}^{\infty} \left(\frac{1}{n_y^2} - \frac{15}{\pi^2 n_y^4} \right), \quad (B6)$$

where the vanishing of the difference of the sums from 1 to ∞ is a consequence of the equalities

$$\sum_{n_y=1}^{\infty} \frac{1}{n_y^2} = \frac{\pi^2}{6}, \quad \sum_{n_y=1}^{\infty} \frac{1}{n_y^4} = \frac{\pi^4}{90}.$$

Now, by (2.17), one again has

$$\sum_{n_y=\alpha+1}^{\infty} \frac{1}{n_y^2} = \alpha^{-1} - \frac{1}{2}\alpha^{-2} + \frac{1}{6}\alpha^{-3} + \dots,$$

$$\sum_{n_y=\alpha+1}^{\infty} \frac{1}{n_y^4} = \frac{1}{3}\alpha^{-3} + \dots.$$

Substituting these into (B6) gives

$$S_4 = -\frac{a_y^2 \alpha^3}{8} + \frac{a_y^2 \alpha^2}{16} - \frac{a_y^2 \alpha}{48} + \frac{5}{8\pi^2} a_y^2 \alpha + \dots \quad (B7)$$

In identical fashions, the remaining sums are found to be

$$S_5 = -\frac{\beta\zeta}{4} \sum_{n_y=1}^{\alpha} \left(1 - \frac{15}{\pi^2 n_y^2} \right)$$

$$= -\frac{a_y^2 \alpha^3}{4} + \frac{15}{24} a_y^2 \alpha^2 - \frac{15}{4\pi^2} a_y^2 \alpha + \dots, \quad (B8)$$

$$S_6 = \frac{a_y^2}{8} \sum_{n_y=1}^{\alpha} \left(n_y^2 - \frac{15}{\pi^2} \right)$$

$$= \frac{a_y^2 \alpha^3}{24} + \frac{a_y^2 \alpha^2}{16} + \frac{a_y^2 \alpha}{48} - \frac{15}{8\pi^2} a_y^2 \alpha. \quad (B9)$$

We now sum (B7) through (B9). The following numerical factors are found to multiply the terms of order $a_y^2 \alpha^3$, $a_y^2 \alpha^2$, $a_y^2 \alpha^1$:

$$a_y^2 \alpha^3: \quad \frac{1}{2} - \frac{1}{6} - \frac{1}{8} - \frac{1}{4} + \frac{1}{24} = 0,$$

$$a_y^2 \alpha^2: \quad -\frac{1}{2} + \frac{1}{4} - \frac{1}{16} + \frac{15}{24} - \frac{1}{16} = 0,$$

$$a_y^2 \alpha^1: \quad \frac{3}{\pi^2} + \frac{3}{\pi^2} - \frac{1}{12} - \frac{1}{48} + \frac{5}{8\pi^2}$$

$$= \frac{15}{4\pi^2} + \frac{1}{48} - \frac{15}{8\pi^2} = \left(\frac{1}{\pi^2} - \frac{1}{12} \right),$$

leading to the result given by (2.18).