number theory correction terms for Eq. (48) are

$$\delta V(E_a)_{lmn}=R(a_{lmn})$$
$$=R\Big(\int_{E(n_1,\,n_2,\,n_3)\leqslant E_a}\exp[2\pi i(ln_1+mn_2+nn_3)]\times dn_1dn_2dn_3\Big), \quad (49)$$

where the number of states less than E_a is $G(E_a)=V(E_a)+\Sigma_{l,m,n}a_{lmn}$. It would appear that to compute Eq. (49) by analogy to Eq. (47) one might proceed as follows. In Eq. (49) dn_i is replaced by dp_idq_i/h and n_i is replaced by

$$n_i=\int_{H(p,\,q)\leqslant E_a}dp_idq_i/h=n_i(E_a,\,[p,\,q]_i'), \quad (50)$$

i.e., by the area of the p_iq_i cross section of the surface $H(pq)=E_a$ in phase space. ($[p,\,q]_i'$ means the set of p's and q's except p_i, q_i.) Since this is subsequently to be integrated over all phase space by Eq. (49), in Eq. (50) when substituted into Eq. (49), E_a is again replaced by $H(pq)$. Thus Eq. (49) becomes, computed in analogy to Eq. (47),

$$a_{lmn}=\int_{H(p,\,q)<E_a}\exp\{2\pi i(ln_1(H(p,\,q)[p,\,q]_1')+mn_2(H(p,\,q)[p,\,q]_2')+nn_3(H(p,\,q)[p,\,q]_3'))\}\cdot dp_1\cdots dq_3/h^3, \quad (51)$$

where the n_i in the exponent are the cross sections as given by Eq. (50).

This scheme has been applied to give exact results for the simple problem of the particle in a box and the harmonic oscillator. Its success, or some modification of it, when applied to problems where the variables are not separable or there are several particles with interaction remains to be determined. One may expect that the critical point method, and the methods of combinatorial analysis will find application in such problems.

It is a pleasure to acknowledge the benefit of numerous discussions in the course of this work with M. C. Steele.

PHYSICAL REVIEW VOLUME 88, NUMBER 3 NOVEMBER 1, 1952

Application of the Theory of Numbers to the Magnetic Properties of a Free Electron Gas*

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(Received June 5, 1952)

The methods of number theory are used to find the magnetic properties of a free electron gas. The mathematical procedure which connects number theory to quantum mechanics is given in detail since the same or a similar method may be useful in other problems of solid state and nuclear physics.

The magnetic moment calculation is given in three parts. For the case in which surface states are not considered the results obtained are in agreement with those of previous workers. But when the use of a finite container (rectangular box) to hold the electrons is considered, it is no longer possible to neglect surface states. Through the use of the WKB approximation it is found that the surface states give rise to new size-dependent terms in both the oscillatory and nonoscillatory parts of the magnetic moment. The oscillatory corrections are generally negligible compared to the usual de Haas-van Alphen effect. However, the nonoscillatory correction, which is diamagnetic in character, can be larger than the Landau diamagnetism for properly chosen magnetic field strengths and containter sizes.

The calculation is concluded with a consideration of the effect of the electron spin. It is found, in agreement with other workers, that the only effect of spin on the oscillatory part of the magnetic moment is to introduce a phase change of $\pm\pi$ in alternate terms. The "surface" diamagnetic correction due to a finite container is found to be independent of electron spin.

Details on the use of the method of critical points for evaluating integrals asymptotically are given in the appendix.

I. INTRODUCTION

THE extension of Landau's[1] original work on the diamagnetism of free electrons has already been undertaken by several different methods. Landau[2] himself showed that in addition to the nonperiodic diamagnetic susceptibility the electron gas should exhibit the de Haas-van Alphen[3] effect. Sondheimer and Wilson[4] have recently confirmed this result by an elegant use of the density matrix. However, neither of the above-mentioned papers attempted to find the effect brought about by using a finite container to hold the electrons. It is well known[5] that the absence of diamagnetism of free electrons in classical theory is dependent upon the behavior of the electrons on the surface of the container. The preceding paper in this

* Based on a thesis presented for the degree of Doctor of Philosophy at the University of Maryland, June, 1952.

[1] L. Landau, Z. Physik. **64**, 629 (1930).

[2] D. Shoenberg, Proc. Roy. Soc. (London) **A170**, 341 (1939), (quoting L. Landau).

[3] W. J. de Haas and P. H. van Alphen, Proc. Acad. Sci. Amsterdam **33**, 1106 (1930).

[4] E. H. Sondheimer and A. H. Wilson, Proc. Roy. Soc. (London) **A208**, 173 (1951).

[5] See, for example, J. H. Van Vleck, *Theory of Electric and Magnetic Susceptibilities* (Oxford University Press, London, 1932), p. 100.

issue by M. F. M. Osborne deals at great length with the relation between the classical and quantum theoretical results for a cylindrical container. In the present paper, we shall deal with a rectangular box as the container. Although this choice of geometry has the drawback of not allowing the boundary conditions to be satisfied on all the surfaces, it has the advantage of permitting an analytical solution for the surface effects. On the other hand, Osborne's geometry only allowed an order of magnitude calculation. At first we shall neglect the surface effects and show how number theoretical methods can be used to obtain a result which is in complete agreement with other workers.[2,4] Following this we shall extend the problem to take into account the finite size of the box. This calculation will use both the WKB approximation and number theory. Finally we shall indicate how the electron spin affects the result.

II. PRELIMINARY FORMULAS AND THEIR RELATION TO NUMBER THEORY

A. Free Energy

The free energy of a system of N noninteracting electrons is

$$F=NE_0-kT\sum_i \log(1+e^{(E_0-E_i)/kT}), \tag{1}$$

where E_0 is the Fermi energy, k is Boltzmann's constant, T is the absolute temperature, and E_i are the energy levels for any one of the electrons. E_0 and N are related through the normalizing condition

$$N=\sum_i 1/(1+e^{(E_i-E_0)/kT}). \tag{2}$$

Both Eqs. (1) and (2) are derived on the assumption that there are only electrons of one value of spin present in the system. When both values of spin are allowed, all sums are multiplied by two if N still refers to the total number of electrons.[6] We now assume the existence of an energy distribution function $\rho(E)$, where

$$G(E)=\int_0^E \rho(E)dE \tag{3}$$

represents the number of states having energies equal to or less than E. Then the sums in Eqs. (1) and (2) can be replaced by integrals. The free energy can then be written

$$F=NE_0-kT\int_{E_L}^{\infty} \rho(E)\log(1+e^{(E_0-E)/kT})dE, \tag{4}$$

where E_L is the lowest energy level of the electron. Integrating by parts gives

$$F=NE_0-\left[-kTG(E_L)\log(1+e^{(E_0-E_L)/kT}) + \int_{E_L}^{\infty} G(E)f(E)dE\right], \tag{5}$$

where $f(E)$ is the Fermi function

$$f(E)=1/(1+e^{(E-E_0)/kT}). \tag{6}$$

B. Magnetic Moment

In all the work that follows, the magnetic moment will be obtained from the formula[7]

$$M=-(\partial F/\partial H)_{T,V}, \tag{7}$$

where M is the magnetic moment, H is the magnetic field intensity, and V is the volume. We shall only consider systems in which N is held constant so that $E_0(N, H)$ and H can be considered as the variables that determine M. Then Eq. (7) can be written as

$$M=-(\partial F/\partial H)_{E_0}-(\partial F/\partial E_0)_H(dE_0/dH). \tag{8}$$

But from Eqs. (1) and (2) we have

$$(\partial F/\partial E_0)_H=N-\sum_i 1/(1+e^{(E_i-E_0)/kT})=0 \tag{9}$$

so that

$$M=-(\partial F/\partial H)_{E_0}=-(\partial(F-NE_0)/\partial H)_{E_0}. \tag{10}$$

C. Relations to the Theory of Numbers

From Eq. (10) it is clear that we must find F before computing M. But Eq. (5) which is the desired expression for F shows that our immediate aim is to evaluate the function $G(E)$. For the particular problem of the diamagnetism of free electrons, Landau[1] used the Euler-Maclaurin formula for getting $G(E)$. In the course of repeating Landau's calculations, the present author found that the results obtained by using the Euler-Maclaurin formula depended not only on the order of summation over quantum numbers but also on the particular form of the formula. Since it was believed that the theory of physical phenomena should be independent of order of summation, a detailed study was undertaken to resolve the difficulty. It was at this stage that the concepts of number theory were first employed.

Let us suppose that for a particular problem the solution of Schrödinger's equation gives rise to an eigenvalue relation in which the energy levels are expressed as explicit functions of quantum numbers.[8] Then by fixing the energy parameter at E the eigenvalue relation will describe some surface in quantum number space. Now the computation of $G(E)$ resolves itself into the problem of counting the number of quantum states within or on the particular energy surface. This counting is completely analogous to the number theory problem of finding the number of lattice points within a closed surface located in a grid of discrete unit cells. (A lattice point is defined as a point having integers for

[6] This is true when the spin interaction with applied fields is not accounted for. When spin energy is included, one has two independent sums to consider.

[7] This formulation of the magnetic moment follows the development given in Mott and Jones, *Properties of Metals and Alloys* (Oxford University Press, London, 1936).

[8] It will be shown later that the use of the WKB approximation will allow the computation of $G(E)$ even when the eigenvalues are not known as explicit functions of the quantum numbers.

coordinates.) The discreteness of the quantum numbers is sufficient to indicate that there will be corrections to the result obtained by merely computing the volume enclosed by the energy surface.

Lattice point problems have been considered in great detail by mathematicians. The problem of the lattice points of a circle has received particular attention since it is considered the most fundamental as well as the most interesting. Generally the mathematician is more concerned about finding the order of magnitude of the corrections to the number of lattice points than actually getting an explicit relation for the desired total number. Although order of magnitude relations are of value in solid state problems, it was felt more desirable to strive for explicit relations in all cases. Unfortunately we shall see that even in relatively simple quantum-mechanical problems the task of getting an explicit representation for $G(E)$ becomes quite formidable. Number theorists have used a variety of methods in solving lattice point problems. The particular procedure to be used throughout this paper follows closely the work of Kendall[9] on the number of lattice points inside a random oval. Details of the method as applied to quantum mechanics will be given in the text that follows.

III. NO SURFACE EFFECTS (SPINLESS ELECTRONS)

We first consider the magnetic properties of a spinless electron gas enclosed in a box of dimensions L_x, L_y, L_z. This calculation will be restricted to such magnetic field strengths and dimensions of the container as to avoid (seemingly) the need for considering the effect of surface states.

A. Schrödinger Equation

If the applied magnetic field H is along the z axis, the Schrödinger equation for an electron in the box can be written as

$$\frac{1}{2m}\left[-\hbar^2\nabla^2+\frac{e^2A_y^2}{c^2}-\frac{2e\hbar}{ci}A_y\frac{\partial}{\partial y}\right]\psi=E\psi, \tag{11}$$

where $\mathbf{H}=\nabla\times\mathbf{A}$ and we choose $\mathbf{A}=(0, Hx, 0)$. This equation can be separated into two ordinary differential equations if we assume a solution of the form

$$\psi=\phi(x)\zeta(z)e^{2\pi i n_y y/L_y}. \tag{12}$$

Substituting Eq. (12) into Eq. (11) and introducing separation constants gives

$$\frac{-\hbar^2}{2m}\frac{d^2\phi}{dx^2}+\left[\frac{1}{2m}\left(\frac{hn_y}{L_y}-\frac{e}{c}A_y\right)^2-E_1\right]\phi=0, \tag{13}$$

and

$$\frac{-\hbar^2}{2m}\frac{d^2\zeta}{dz^2}-E_2\zeta=0, \tag{14}$$

where $E=E_1+E_2$. The motion in the direction of the field is clearly that of a free particle so that we can immediately write the eigenvalues as

$$E_2=h^2n_z^2/2mL_z^2, \tag{15}$$

if we assume periodic boundary conditions in the z dimension. With this assumption, the quantum number n_z takes on all positive and negative integer values (including zero).

We will now use the WKB approximation to solve for the eigenvalue E_1, since this is the method which will be subsequently applied to estimate the effect of surface states. Equation (13) is the Schrödinger equation of a one-dimensional system with a classical Hamiltonian of the form

$$\mathcal{H}=p^2/2m+U=E_1, \tag{16}$$

where

$$U=\frac{1}{2m}\left(\frac{hn_y}{L_y}-\frac{e}{c}A_y\right)^2. \tag{17}$$

Inserting the value $A_y=Hx$, the classical turning points of the motion become

$$x=\frac{chn_y}{eHL_y}\pm\frac{c}{eH}(2mE_1)^{\frac{1}{2}}. \tag{18}$$

(For symmetry it is convenient to set the origin of coordinates such that the walls are at $\pm L_x/2$.) Using these turning points in the WKB quantum condition

$$\oint p_x dx=(n+\tfrac{1}{2})h \tag{19}$$

leads to the eigenvalue relation

$$E_1=2\beta H(n+\tfrac{1}{2}), \tag{20}$$

where $\beta=e\hbar/2mc$, the Bohr magneton. These levels are recognized as the energy values of a simple harmonic oscillator having a frequency of $eH/2\pi mc$. From Eq. (18) we see that the equilibrium position of the oscillator (center of the orbit) is chn_y/eHL_y and the "orbit radius" is $(c/eH)(2mE_1)^{\frac{1}{2}}$. The eigenvalues given by Eq. (20) are highly degenerate because of the multitude of n_y values that can be assigned (n_y takes on the same range of values as n_z) in the orbit center. In fact, the degeneracy will be fixed by the maximum value that can be assigned to n_y and still have the parabolic potential determine the turning points. For $|n_y|$ greater than this critical value, Eq. (20) will no longer be applicable, since one turning point will then be fixed at $\pm L_x/2$, where the potential is assumed to be infinite. We will now obtain an explicit expression for this degeneracy since this will clarify the approximations to be made. If we fix the value of E_1, the harmonic oscillator solution, Eq. (20), will fail when the condition $U=E_1$ is satisfied simultaneously with the condition that one of the turning points is at $\pm L_x/2$. This leads

[9] D. G. Kendall, Quart. J. Math. (Oxford) 19, 1 (1948).

to the restriction

$$|n_y| \leq |eHL_xL_y/2ch-(L_y/h)(2mE_1)^{\frac{1}{2}}|$$

on n_y. The total degeneracy of the level E_1 is therefore

$$(eHL_xL_y/ch)-(2L_y/h)(2mE_1)^{\frac{1}{2}}. \quad (21)$$

If n_y is allowed to take on values outside of the above range, we would have to obtain a new expression for the eigenvalues.[10] The states resulting from this extension in n_y are our so-called surface states. At this point, we follow Landau[1] in specifying that for sufficiently strong magnetic fields and/or large enough L_x we can neglect the second term in Eq. (21) and designate the degeneracy, D, of the oscillator levels by

$$D=eHL_xL_y/ch. \quad (22)$$

This specification is equivalent to saying that the orbit radius corresponding to energies of the order of the Fermi energy is small compared to the dimension L_x. When E_1 is of order 1 electron volt, this requires

$$HL_x \gg 2c(2mE_1)^{\frac{1}{2}}/e \sim 10. \quad (23)$$

This condition is satisfied even for relatively low fields if we use macroscopic dimensions.

Before proceeding with the calculation of the free energy it should be noted that, in treating the magnetic susceptibility with a classical model, omission of the surface states under any circumstances would lead to a huge diamagnetism.[5] The question therefore arises as to the legitimacy of our neglecting the surface states in the quantum-mechanical case. At this stage, we merely indicate that some compensation was made for omitting the surface states when we increased the degeneracy of the interior states from Eq. (21) to Eq. (22). If this compensation happens to restore the effects of the neglected states, then we have justified the use of the increased degeneracy. Detailed calculations given later in this paper will show that the compensation is fortuitously exact, but without such calculations it is not at all obvious that Landau's argument for neglecting the surface states is valid. An elaboration of this point was believed to be in place since there has appeared in the literature[11] a somewhat misleading qualitative physical explanation to justify Landau's approximation.

Calculation of $G(E)$ and the Free Energy

combining of Eqs. (20) and (15) gives

$$E=h^2n_z^2/2mL_z^2+2\beta H(n+\tfrac{1}{2}). \quad (24)$$

This level is degenerate in the quantum number n_y to the extent D given in Eq. (22). Equations (24) and (22) describe a parabolic cylinder in quantum number space. Our calculation of $G(E)$ is therefore equivalent to the problem of finding the number of lattice points within such a cylinder bounded by the $n=0$ plane. Since the degeneracy is independent of E we need only consider the two-dimensional lattice point problem in the n, n_z plane. In that plane Eq. (24) describes a parabola which is cut off by the line $n=0$. The particular number theory problem of computing the lattice points under such a curve had not been considered at the time this work was initiated. But following the work of Kendall[9] it is possible to obtain here an explicit representation for the number of lattice points. A detailed account of this calculation is given below, since the method employed may be of value in other problems.

Let us allow the parabola in the n, n_z plane to be randomly located but with its axis parallel to the n axis. Then we can write the equation of the parabola as

$$E=A(n_z-\alpha_2)^2+B(n+\tfrac{1}{2}-\alpha_1), \quad (25)$$

where

$$A=h^2/2mL_z^2, \quad B=2\beta H.$$

Now the number of lattice points under this parabola (cut off by the line $n=\alpha_1$) will be periodic in α_1 and α_2 with a periodicity of a single lattice spacing (unity) along either the n or n_z axes. We can therefore represent $G(E)$ as a doubly periodic function in a Fourier series,

$$G(E)=D\sum_{\kappa=-\infty}^{\infty}\sum_{\lambda=-\infty}^{\infty}a_{\kappa,\lambda}e^{2\pi i(\kappa\alpha_1+\lambda\alpha_2)}. \quad (26)$$

The Fourier coefficients $a_{\kappa,\lambda}$ depend upon the parameter E as well as the factors A and B. Before proceeding with the determination of $a_{\kappa,\lambda}$ we must examine the question of where the parabola should be cut off. In the final analysis we must set $\alpha_1=\alpha_2=0$, in order that the parabola given by Eq. (25) be correctly oriented in accordance with the quantum-mechanical requirement specified by Eq. (24). Further, the lowest value of n is supposed to be zero. However, by setting $\alpha_1=0$ and leaving the cutoff of the parabola at $n=0$, the Fourier series will only count one-half of the states along the $n=0$ line. This would be due to the large discontinuity experienced by the number of lattice points as one slides the parabola (along the n axis) so that the cutoff passes through an integer value of n. The Fourier series would then give the average of the two values on either side of the discontinuity. Since the discontinuity would correspond to the number of states along $n=0$, we would be undercounting the states by one-half the amount along that line. In order to avoid this difficulty and still maintain the requirement $\alpha_1=\alpha_2=0$, it is convenient to move the cutoff from $n=0$ to $n=-\frac{1}{2}$. This shift of the cutoff increases the area enclosed by our closed curve but it does not change the number of lattice points. The particular choice of $n=-\frac{1}{2}$ for the cutoff may appear to be arbitrary at this stage, since we could have chosen any value in the range

$$-1<n<0$$

[10] The quantum number n_y can actually take on all integer values in the range $|n_y| \leqslant |eHL_xL_y/2ch+(L_y/h)(2mE_1)^{\frac{1}{2}}|$. We will deal with the complete range further on in this paper.

[11] See, for example, F. Seitz, *Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), p. 585.

without changing the number of lattice points. We shall see that the value $n=-\frac{1}{2}$ simplifies the problem considerably.

Let $G(E)$ also be represented by the sum

$$G(E)=D\sum_{n,n_z} c(n_z-\alpha_2, n+\tfrac{1}{2}-\alpha_1), \tag{27}$$

where $c(u, v)$ = unity or zero according as (u, v) does or does not fall in the range

$$Av^2+Bu\leqq E, \quad u\geqq 0. \tag{28}$$

The summation in Eq. (27) is extended over all lattice points but only a finite number of these contribute non-zero terms. From Eq. (26) and the periodicities in α_1 and α_2, it follows that

$$a_{\kappa,\lambda}=\int_0^1\int_0^1 \frac{G(E)}{D}e^{-2\pi i(\kappa\alpha_1+\lambda\alpha_2)}d\alpha_1 d\alpha_2. \tag{29}$$

If we now make the transformation

$$u=n+\tfrac{1}{2}-\alpha_1, \quad v=n_z-\alpha_2, \tag{30}$$

and use Eq. (27), we get

$$a_{\kappa,\lambda}=(-1)^\kappa\int\int_{Av^2+Bu\leq E} e^{2\pi i(\kappa u+\lambda v)}dudv. \tag{31}$$

Since α_1 and α_2 will both be set to zero and the cutoff will be at $n=-\frac{1}{2}$, it follows from Eq. (30) that the limits of integration in the u, v plane will be

u: from 0 to E/B;

v: from $-(E/A)^{\frac{1}{2}}$ to $(E/A)^{\frac{1}{2}}$.

From Eq. (31) we have

$$a_{\kappa,\lambda}=(a_{-\kappa,-\lambda})^*; \quad a_{\kappa,-\lambda}=(a_{-\kappa,\lambda})^*, \quad \text{and} \quad a_{\kappa,\lambda}=a_{\kappa,-\lambda},$$

so that $G(E)$ can be written as

$$G(E)=D\sum_{\kappa,\lambda=-\infty}^{\infty} a_{\kappa,\lambda}=D[a_{0,0}+2\sum_{\kappa=1}^{\infty}R(a_{\kappa,0})+2\sum_{\lambda=1}^{\infty}R(a_{0,\lambda})+4\sum_{\kappa,\lambda=1}^{\infty}R(a_{\kappa,\lambda})] \tag{32}$$

(where R denotes "the real part of"). Utilizing the symmetry of our boundary curve with respect to v, it follows from Eq. (31) that

$$R(a_{\kappa,\lambda})=(-1)^\kappa\int\int_{Av^2+Bu\leqq E}\cos(2\pi\kappa u)\cos(2\pi\lambda v)dudv. \tag{33}$$

The coefficient $a_{0,0}$ which corresponds to the area of the closed curve is found to be simply

$$a_{0,0}=4E^{\frac{3}{2}}/3BA^{\frac{1}{2}}. \tag{34}$$

(This is the first advantage of having chosen $n=-\frac{1}{2}$ as the cutoff.) For $\kappa\neq 0$, the general coefficient $R(a_{\kappa,\lambda})$ can be expressed as

$$R(a_{\kappa,\lambda})=(-1)^\kappa B^{\frac{1}{2}}U_{\frac{3}{2}}(w, y)/A^{\frac{1}{2}}\pi(2\kappa)^{\frac{3}{2}}, \tag{35}$$

where

$$w=4\pi E/B, \quad y=2\pi\lambda(E/A)^{\frac{1}{2}}, \tag{36}$$

and $U_{\frac{3}{2}}(w, y)$ is the $\frac{3}{2}$ order Lommel function of two variables discussed by Watson[12] in his Bessel function treatise. For $\kappa=0$, we have

$$R(a_{0,\lambda})=E^{\frac{3}{4}}A^{\frac{1}{4}}J_{\frac{3}{2}}(y)/\pi B\lambda^{\frac{3}{2}}, \tag{37}$$

where $J_{\frac{3}{2}}$ is the $\frac{3}{2}$ order Bessel function of the first kind. From the results given above, $G(E)$ can be explicitly expressed as

$$G(E)=\frac{4DE^{\frac{3}{2}}}{3BA^{\frac{1}{2}}}+2D\sum_{\lambda=1}^{\infty}\frac{E^{\frac{3}{4}}A^{\frac{1}{4}}}{\pi B\lambda^{\frac{3}{2}}}J_{\frac{3}{2}}(y)+\frac{2DB^{\frac{1}{2}}}{A^{\frac{1}{2}}\pi}\sum_{\lambda=0}^{\infty}\sum_{\kappa=1}^{\infty}\frac{P_\lambda(-1)^\kappa}{(2\kappa)^{\frac{3}{2}}}U_{\frac{3}{2}}(w, y), \tag{38}$$

where

$$P_\lambda=\begin{cases}1 \text{ for } \lambda=0\\ 2 \text{ for } \lambda\neq 0.\end{cases}$$

The free energy can now be given formally by substituting Eq. (38) into Eq. (5). It is noted that by shifting the cutoff to $n=-\frac{1}{2}$ we have changed E_L from βH to zero. This is very convenient in Eq. (5), since $G(E_L)$ then becomes zero. In fact, this is the second advantage of having chosen $n=-\frac{1}{2}$ instead of some other value for the cutoff. If we now take into account the factor of two due to spin degeneracy, and require $E_0\gg kT$, the free energy can be expressed as

$$F-NE_0=\frac{-16\pi V(2m)^{\frac{3}{2}}E_0^{5/2}}{15h^3}\left[1+\frac{5\pi^2}{8}\left(\frac{kT}{E_0}\right)^2\right]-\sum_{\lambda=1}^{\infty}\frac{4L_xL_y(2m)^{\frac{3}{4}}}{L_z^{\frac{1}{2}}h^{\frac{3}{2}}\lambda^{\frac{1}{2}}}\int_0^\infty E^{\frac{3}{4}}J_{\frac{3}{2}}(y)f(E)dE+\sum_{\lambda=0}^{\infty}\sum_{\kappa=1}^{\infty}P_\lambda(-1)^\kappa\frac{2Ve(2m)^{\frac{1}{2}}\beta^{\frac{3}{2}}H^{5/2}}{\pi^2h^2c\kappa^{5/2}}\times\int_0^\infty U_{\frac{1}{2}}(w, y)\frac{df(E)}{dE}dE. \tag{39}$$[13]

B. Magnetic Moment

The magnetic moment is obtained by substituting Eq. (39) into Eq. (10), and carrying out the indicated differentiation. Since the integrated term and the single

[12] G. N. Watson, *Treatise on The Theory of Bessel Functions* (Cambridge University Press, Cambridge, 1944), pp. 537–550.

[13] It is noted that the terms with $\kappa\neq 0$ have been transformed so as to obtain the derivative of the Fermi function under the integral. The introduction of the 5/2 order Lommel function arises from the relation

$$\int U_{\frac{3}{2}}(w, y)dE=BU_{\frac{1}{2}}(w, y)/2\pi\kappa,$$

which is encountered upon partial integration.

sum on λ in Eq. (39) do not contain H explicitly, they do not contribute anything to the magnetic moment. Differentiating the double sum gives:

$$M=-\sum_{\lambda=0}^{\infty}\sum_{\kappa=1}^{\infty}P_\lambda\frac{(-1)^\kappa 2Ve(2m)^{\frac{1}{2}}\beta^{\frac{1}{2}}}{\pi^2\hbar^2c\kappa^{5/2}}\times\left[\frac{5}{2}H^{\frac{1}{2}}\int_0^\infty U_{\frac{1}{2}}(w,y)\frac{df(E)}{dE}dE\right.$$
$$\times\frac{-\pi\kappa H^{\frac{1}{2}}}{\beta}\int_0^\infty U_{\frac{3}{2}}(w,y)\frac{df(E)}{dE}dE$$
$$\left.\times\frac{-\pi^2\lambda^2\beta H^{5/2}}{\kappa A}\int_0^\infty U_{7/2}(w,y)\frac{df(E)}{dE}dE\right]. \quad (40)$$

The last two integrals in Eq. (40) arise from the relation

$$\partial U_{5/2}(w,y)/\partial H=-\pi\kappa E U_{3/2}(w,y)/\beta H^2 - \pi\lambda^2\beta U_{7/2}(w,y)/\kappa A. \quad (41)$$

Equation (40) is an exact representation of the magnetic moment. But in order to obtain an answer in integrated form, we have to impose some restrictions on the relative magnitudes of E and βH. In addition, we will limit ourselves to the low temperature region.

We now impose the condition

$$E_0\gg\beta H \quad (42)$$

in order to allow the use of the asymptotic expansion of the Lommel function $U_\nu(w,y)$.

1. *Terms with* $\lambda=0$

For purposes of later discussion it is now convenient to break up the sum of Eq. (40) into parts, i.e. $\lambda=0$ and $\lambda\neq0$. For $\lambda=0$, we have the asymptotic expansion[12]

$$U_\nu(w,0)\sim\cos\left(\frac{w}{2}-\frac{\nu\pi}{2}\right)+\sum_{p=0}^{\infty}(-1)^p\Big/\left[\Gamma(\nu-1-2p)\left(\frac{w}{2}\right)^{2p-\nu+2}\right] \quad (43)$$

for $|w|$ large. In our case, Eq. (42) expresses the condition $|w|$ large. Since the series in Eq. (43) is rapidly convergent, we need only retain the first term of the sum. Thus we have

$$U_\nu\left(\frac{4\pi\kappa E}{B},0\right)\sim\cos\left(\frac{2\pi\kappa E}{\beta H}-\frac{\nu\pi}{2}\right)+B^{2-\nu}/[\Gamma(\nu-1)(2\pi\kappa E)^{2-\nu}]. \quad (44)$$

This gives rise to the sum

$$-\sum_{\kappa=1}^{\infty}\frac{(-1)^\kappa 2Ve(2m)^{\frac{1}{2}}\beta^{\frac{1}{2}}}{\pi^2\hbar^2c\kappa^{5/2}}\left[\frac{5}{2}H^{\frac{1}{2}}\int_0^\infty\cos\left(\frac{2\pi\kappa E}{B}-\frac{5\pi}{4}\right)\frac{df(E)}{dE}dE\right.$$
$$\left.+\frac{4\kappa^{\frac{1}{2}}H}{\beta^{\frac{1}{2}}}\int_0^\infty E^{\frac{1}{2}}\frac{df(E)}{dE}dE-\frac{\pi\kappa H^{\frac{1}{2}}}{\beta}\int_0^\infty\cos\left(\frac{2\pi\kappa E}{B}-\frac{3\pi}{4}\right)\frac{df(E)}{dE}dE\right] \quad (45)$$

in the value of M. The second integral of Eq (45) is a standard type Fermi-Dirac integral. At low temperatures we have

$$\int_0^\infty E^{\frac{1}{2}}\frac{df(E)}{dE}dE\cong-E_0^{\frac{1}{2}}\left[1-\frac{\pi^2}{24}\left(\frac{kT}{E_0}\right)^2\right], \quad (46)$$

so that this part of the sum becomes

$$\frac{8Ve(2m)^{\frac{1}{2}}\beta HE_0^{\frac{1}{2}}}{\pi^2\hbar^2c}\left[1-\frac{\pi^2}{24}\left(\frac{kT}{E_0}\right)^2\right]\sum_{\kappa=1}^{\infty}\frac{(-1)^\kappa}{\kappa^2}. \quad (47)$$

But since

$$\sum_{\kappa=1}^{\infty}\frac{(-1)^\kappa}{\kappa^2}=\frac{-\pi^2}{12}, \quad (48)$$

Eq. (47) becomes

$$\frac{-2Ve(2m)^{\frac{1}{2}}\beta E_0^{\frac{1}{2}}H}{3\hbar^2c}\left[1-\frac{\pi^2}{24}\left(\frac{kT}{E_0}\right)^2\right]. \quad (49)$$

This part of the magnetic moment is not periodic in H. In fact, it is identical to the ordinary Landau[1] diamagnetism with the correction due to temperature. The result obtained here agrees with the previous work of Stoner[14] who investigated the temperature dependence of the Landau diamagnetism.

The two other integrals of Eq. (45) give terms in M which are periodic functions of the magnetic field. These integrals can be evaluated by means of contour integration. It is found that their contribution to M is

$$-\sum_{\kappa=1}^{\infty}\frac{(-1)^\kappa 2Ve(2m)^{\frac{1}{2}}\beta^{\frac{1}{2}}}{\pi^2\hbar^2c\kappa^{5/2}}\left[\frac{5\pi^2\kappa kTH^{\frac{1}{2}}\cos\left(\frac{\pi\kappa E_0}{\beta H}-\frac{5\pi}{4}\right)}{2\beta^{\frac{1}{2}}\sinh(\pi^2\kappa kT/\beta H)}\right.$$
$$-\frac{\pi^2\kappa kTH^{\frac{1}{2}}\sin\left(\frac{\pi\kappa E_0}{\beta H}-\frac{3\pi}{4}\right)}{\beta\sinh(\pi^2\kappa kT/\beta H)}$$
$$+\frac{\pi^4\kappa^2(kT)^2\cosh\left(\pi^2\kappa\frac{kT}{\beta H}\right)\sin\left(\frac{\pi\kappa E_0}{\beta H}-\frac{3\pi}{4}\right)}{\beta^2H^{\frac{1}{2}}\sinh^2(\pi^2\kappa kT/\beta H)}$$
$$\left.-\frac{\pi^3\kappa^2kTE_0\cos\left(\frac{\pi\kappa E_0}{\beta H}-\frac{3\pi}{4}\right)}{\beta^2H^{\frac{1}{2}}\sinh(\pi^2\kappa kT/\beta H)}\right]. \quad (50)$$

[14] E. C. Stoner, Proc. Roy. Soc. (London) **A152**, 672 (1935). It is noted that Stoner expresses his result in terms of ϵ_0, the Fermi energy at $T=0°K$ and $H=0$, whereas the E_0 used in the present work is a function of T and H. E_0 can be expressed as a function of ϵ_0, T, H, to bring the two results into coincidence.

If we now invoke our conditions:

$$E_0 \gg kT \quad \text{and} \quad E_0 \gg \beta H,$$

we can neglect the first three terms appearing in the brackets of Eq. (50) compared to the fourth. The significant contribution to M from the terms with $\lambda=0$ therefore becomes (using the definition of β, the Bohr magneton, to transform the nonperiodic term)

$$\frac{-4\pi V(2m)^{\frac{3}{2}}\beta^2 E_0^{\frac{1}{2}}H}{3h^3}\left[1-\frac{\pi^2}{24}\left(\frac{kT}{E_0}\right)^2\right]$$

$$+\sum_{\kappa=1}^{\infty}\frac{(-1)^{\kappa}2\pi kTVe(2m)^{\frac{1}{2}}E_0\cos\left(\dfrac{\pi\kappa E_0}{\beta H}-\dfrac{3\pi}{4}\right)}{\kappa^{\frac{1}{2}}h^2c\beta^{\frac{1}{2}}H^{\frac{1}{2}}\sinh(\pi^2\kappa kT/\beta H)}. \quad (51)$$

2. Terms with $\lambda\neq 0$

Before obtaining the contribution from the terms with $\lambda\neq 0$, we must examine the relative magnitudes of y and w appearing in the argument of the Lommel functions. For $\lambda\neq 0$, we find that $y\sim w$ when $E=E_0$ and $H>10$ gauss (if L_z is of order cm). Therefore, if we require $|w|\gg 1$ in our asymptotic solution, we must simultaneously require $|y|\gg 1$. This situation arises from the physical parameters which determine the argument of the Lommel functions. Unfortunately it also means that we cannot use (without caution) the asymptotic development for $U_\nu(w, y)$ given by Watson,[12] in which only $|w|\gg 1$. When both $|y|\gg 1$ and $|w|\gg 1$ we can use the method of critical points (see the appendix) to get the asymptotic development of $U_\nu(w, y)$. The result is dependent upon the relative magnitudes of y and w. The three expansions for $U_{\frac{1}{3}}(w, y)$ are given below:

$$U_{\frac{1}{3}}(w, y)\sim\begin{cases}\cos\left(\dfrac{w}{2}+\dfrac{y^2}{2w}-\dfrac{3\pi}{4}\right)+\left(\dfrac{2}{\pi}\right)^{\frac{1}{2}}\dfrac{w^{\frac{3}{2}}\cos y}{(w^2-y^2)}, & y<w\\ \dfrac{1}{2}\cos\left(w-\dfrac{\pi}{4}\right)+\dfrac{\cos w}{2^{\frac{3}{2}}\pi^{\frac{1}{2}}w^{\frac{1}{2}}}, & y=w\\ \left(\dfrac{2}{\pi}\right)^{\frac{1}{2}}\dfrac{w^{\frac{3}{2}}\cos y}{(w^2-y^2)}, & y>w.\end{cases} \quad (52)$$

The singular case of $y=w$ is not of great physical significance, since it only occurs at a specific value of H. We are more concerned with the other cases since there H can take on continuous values. Before proceeding to the moments resulting from $\lambda\neq 0$, we note that $y<w$ requires that (for $E=E_0$)

$$\lambda<\kappa hE_0^{\frac{1}{2}}/L_z(2m)^{\frac{1}{2}}\beta H. \quad (53)$$

After carrying out the calculation to get the magnetic moment it is found that only those terms arising from the condition $y<w$ are significant. The specific contribution to M from these terms is

$$-\sum_{\lambda=1}^{\infty}\sum_{\kappa=\kappa L(H,\lambda)}^{\infty}\frac{(-1)^{\kappa}4\pi kTVe(2m)^{\frac{1}{2}}\beta^{\frac{1}{2}}H^{\frac{1}{2}}}{\kappa^{\frac{1}{2}}h^2c}$$

$$\times\left(\frac{2\lambda^2mL_z^2\beta}{\kappa h^2}-\frac{\kappa E_0}{\beta H^2}\right)\frac{\cos\left(\dfrac{\pi\kappa E_0}{\beta H}+\dfrac{2\pi\lambda^2m\beta L_z^2H}{\kappa h^2}-\dfrac{3\pi}{4}\right)}{\sinh(\pi^2\kappa kT/\beta H)}, \quad (54)$$

where $\kappa_L(H, \lambda)$ is the integral part of

$$\lambda L_z(2m)^{\frac{1}{2}}\beta H/hE_0^{\frac{1}{2}}.$$

C. Discussion of the Magnetic Moment

For the case $E_0\gg\beta H$, the magnetic moment is the sum of Eqs. (51) and (54). We have already discussed the nonperiodic term. The remaining terms are all periodic functions of H. We shall separate the discussion of the single sum in Eq. (51) and the double sum in Eq. (54), but we identify the totality of these sums with the experimentally observed de Haas-van Alphen effect.

Consider now the single sum on κ. If we express our result in terms of the magnetization, M/V, then both the amplitudes and frequencies of all the terms in this sum are independent of the dimensions of the box. These terms are identically those found by Landau[2] in his theory of the de Haas-van Alphen effect.

We now examine the double sum in Eq. (54). The fundamental difference between these terms and those of the single sum is that the amplitudes and frequencies are now functions of the dimension L_z. We will now propose an argument[15] to show that the contribution of this double sum can be neglected. Suppose there is an uncertainty δL_z in the dimension L_z. Then in order for the cosine term to have a definite value (when H is fixed), we require that δL_z should not change the phase by more than $\pi/2$. This leads to the condition:

$$\delta L_z<\kappa h^2/8\lambda^2m\beta L_zH. \quad (55)$$

If we set $\lambda=1$ and κ equal to the lowest possible value compatible with Eq. (53), this condition becomes

$$\delta L_z<2^{\frac{1}{2}}h/8m^{\frac{1}{2}}E_0^{\frac{1}{2}}. \quad (56)$$

If we use the free electron value for m and E_0 as 1 ev, this requires

$$\delta L_z<3\times 10^{-8}\text{ cm}.$$

This severe restriction on the uncertainty in L_z cannot be met in a laboratory specimen. Therefore, the cosine term in the double sum will average to very nearly zero. However, as κ grows, the restriction on δL_z becomes less severe. In fact, the above argument fails completely when $\kappa\gg\lambda$. Under such circumstances we have another factor which will nullify the significance of the double

[15] The author wishes to thank Professor M. H. Johnson for suggesting this argument.

sum. It is the damping factor

$$1/\sinh(\pi^2\kappa kT/\beta H).$$

For κ large the damping factor will make the amplitude of the oscillations negligible. As a result of this analysis we can completely neglect the double sum given by Eq. (54). This is equivalent to saying that the "Landau" counting of states leads to no significant size effect in the magnetic moment. This conclusion is consistent with the fact that we did not include any surface states in this part of the calculation.

IV. SURFACE EFFECTS (SPINLESS ELECTRONS)

The results given in Sec. III are dependent on the use of an eigenvalue degeneracy given by Eq. (22). We have already indicated that there is no *a priori* reason for believing that this degeneracy takes proper account of the surface states in a finite container. In this section we will determine the effect of surface states by means of the WKB approximation and number theoretical methods.

A. Distribution Function $G(E)$

The method we shall follow here is different from that used in the previous section where we utilized an eigenvalue relation with an assumed degeneracy. To find the effect of the surface states with such a method would first require an appropriate eigenvalue relation. Although it is possible to accomplish this by means of the WKB approximation, the resulting expression does not give the energy as an explicit function of the three quantum numbers. Because of this difficulty, it is easier to leave the quantum number n in phase integral form and express $G(E)$ as a triply-periodic Fourier series in the quantum numbers. We shall show that such a procedure will allow us to draw certain general conclusions about the magnetic moment of an electron gas in a finite container.

We start with the WKB quantum condition for the motion in the x direction

$$\oint p\,dx=(n+\tfrac{1}{2})h. \tag{57}$$

If we suppose x_1 and x_2 are the classical turning points for a given orbit with energy E_1, we have

$$n=\frac{2}{h}\int_{x_1}^{x_2} p\,dx-\tfrac{1}{2}, \tag{58}$$

where, for our problem,

$$\begin{aligned} p&=[2mE_1-(hn_y/L_y-eHx/c)^2]^{\frac{1}{2}},\\ E&=(h^2n_z^2/2mL_z^2)+E_1. \end{aligned} \tag{59}$$

Our number theory problem is now to count the lattice points within or on the energy surface E in the three-dimensional quantum number space. No assumption is made about a degeneracy. If the counting is done properly, all questions of degeneracy will be automatically answered. Let $G(E)$ be represented by a triply-periodic Fourier series

$$G(E)=\sum_\kappa\sum_\lambda\sum_\mu a_{\kappa,\lambda,\mu}e^{2\pi i(\kappa\alpha_1+\lambda\alpha_2+\mu\alpha_3)}, \tag{60}$$

where α_1, α_2, α_3 correspond to translations along the n, n_y, n_z axes, respectively. In order to avoid a discontinuity in $G(E)$ when α_1, α_2, α_3 are all set to zero we will move the lower limit of n from 0 to $-\frac{1}{2}$. This is done to count all the states in the n_z, n_y plane. Leaving the cut-off plane of the surface at $n=0$ would result in counting only one-half the states in the n_z, n_y plane.

Following the methods in Sec. 3 we find that

$$\begin{aligned} G(E)=a_{0,0,0}&+2\sum_{\kappa=1}^{\infty}R(a_{\kappa,0,0})+2\sum_{\lambda=1}^{\infty}R(a_{0,\lambda,0})\\ &+2\sum_{\mu=1}^{\infty}R(a_{0,0,\mu})+4\sum_{\kappa,\lambda=1}^{\infty}R(a_{\kappa,\lambda,0})\\ &+4\sum_{\lambda,\mu=1}^{\infty}R(a_{0,\lambda,\mu})+4\sum_{\kappa,\mu=1}^{\infty}R(a_{\kappa,0,\mu})\\ &+8\sum_{\kappa,\lambda,\mu=1}^{\infty}R(a_{\kappa,\lambda,\mu}), \end{aligned} \tag{61}$$

where

$$\begin{aligned} R(a_{\kappa,\lambda,\mu})=(-1)^\kappa\iiint_{\tau(p)}&\cos(2\pi\kappa n)\cos(2\pi\lambda n_y)\\ &\times\cos(2\pi\mu n_z)\,dn\,dn_y\,dn_z, \end{aligned} \tag{62}$$

and the integration[16] is over the volume $\tau(p)$, throughout which p is a real number This volume will include both the harmonic oscillator states of Sec. III and our surface states. Consider first the principal coefficient $a_{0,0,0}$ which corresponds to the volume of our energy surface. This coefficient will be by far the largest term in the expansion of $G(E)$. The other terms will represent the number theory corrections to the replacement of a sum by an integral.

1. *The $a_{0,0,0}$ Term*

From Eq. (62) we have

$$a_{0,0,0}=R(a_{0,0,0})=\iiint_{\tau(p)}dn\,dn_y\,dn_z. \tag{63}$$

Integrating first over n, using the upper limit

$$\frac{2}{h}\int_{x_1}^{x_2}p\,dx$$

and the lower limit zero, gives

$$a_{0,0,0}=\frac{2}{h}\iiint_{\tau'(p)}p\,dx\,dn_y\,dn_z, \tag{64}$$

[16] The lower limit for the n appearing in Eq. (62) is zero. This results from the shift in cutoff as explained in Sec. III.

where $\tau'(p)$ is the volume in x, n_y, n_z space throughout which p is real. It is now more convenient to integrate over n_y first. The limits on n_y are determined by the condition $p=0$. This gives the upper (u) and the lower (l) limits

$$\begin{aligned}(n_y)_u &= eHL_yx/hc+(L_y/h)(2mE_1)^{\frac{1}{2}},\\ (n_y)_l &= eHL_yx/hc-(L_y/h)(2mE_1)^{\frac{1}{2}}.\end{aligned} \tag{65}$$

The limits on x are determined by the extreme values of the classical turning points. By assuming an infinite potential at the walls of the box, these limits become

$$(x)_u=\tfrac{1}{2}L_x, \quad (x)_l=-\tfrac{1}{2}L_x. \tag{66}$$

Finally, the limits of n_z are obtained directly from Eq. (59) with E_1 set to zero. This gives

$$(n_z)_u=L_z(2mE)^{\frac{1}{2}}/h, \quad (n_z)_l=-L_z(2mE)^{\frac{1}{2}}/h. \tag{67}$$

Having thus defined $\tau'(p)$, we carry out the integration of Eq. (64) in the order n_y, x, n_z. This gives

$$a_{0,0,0}=4\pi V(2mE)^{\frac{3}{2}}/3h^3, \tag{68}$$

which is exactly the number of states for free electrons in a box without a magnetic field. In fact, Eq. (68) is identical to the result obtained in Sec. III when we modified the degeneracy to eliminate the need for calculating the effects of surface states. To this extent the calculation given here is a justification of Landau's argument. From a physical point of view, our calculation shows that Landau's overcounting of the harmonic oscillator states exactly compensates his neglecting the surface states.

2. *The $a_{\kappa,0,0}$ Terms*

Although the two methods of counting give the same total volume term, it is evident that the corrections will be different. Qualitatively, the energy surface will approach that of Sec. III as H becomes large, since the harmonic oscillator states then comprise the greatest part of the volume. Under such conditions, one might expect that $G(E)$ would be given by Eq. (38) plus higher order corrections. This conclusion could be made still more plausible by allowing the dimension L_x to be large. However, the situation for low fields and finite L_x does not offer any obvious conclusions. Under such conditions the effect of the surface states is emphasized.

From the results given in Sec. III we know that to compute the magnetic moment we need only consider those correction terms in which the frequency of the oscillatory part is not a function of the dimensions of the box. In the present Fourier expansion, this corresponds to using only the terms $R(a_{\kappa,0,0})$. Our immediate task is therefore to calculate those coefficients. It seems plausible that the results of Sec. III should be identifiable in such a calculation. In this sense we have some control on the validity of the analysis. From Eq. (62), we have

$$R(a_{\kappa,0,0})=(-1)^\kappa\int\int_{\tau(p)}\int\cos(2\pi\kappa n)dndn_ydn_z. \tag{69}$$

Integrating first over n, and inserting the limits, gives

$$R(a_{\kappa,0,0})=\frac{(-1)^\kappa}{2\pi\kappa}\int\int_{\tau'(p)}\sin\left(\frac{4\pi\kappa}{h}\int_{x_1}^{x_2}pdx\right)dn_ydn_z. \tag{70}$$

Now we break the integral into two parts corresponding to the oscillator states and the surface states. The division is determined by the value of n_y. In Sec. III we found that for

$$0\leqq|n_y|\leqq\left|\frac{eHL_xL_y}{2hc}-\frac{L_y}{h}(2mE_1)^{\frac{1}{2}}\right|$$

we had oscillator states, but for

$$\begin{aligned}|q|=\left|\frac{eHL_xL_y}{2hc}-\frac{L_y}{h}(2mE_1)^{\frac{1}{2}}\right|&\leqq|n_y|\\ &\leqq\left|\frac{eHL_xL_y}{2hc}+\frac{L_y}{h}(2mE_1)^{\frac{1}{2}}\right|=|r|\end{aligned}$$

we got surface states. For the oscillator states the turning points x_1, x_2 are given by the equations

$$\begin{aligned}x_1&=(hcn_y/eHL_y)-(c/eH)(2mE_1)^{\frac{1}{2}},\\ x_2&=(hcn_y/eHL_y)+(c/eH)(2mE_1)^{\frac{1}{2}}.\end{aligned}$$

For the surface states we have (the subscript s denotes surface)

$$x_{1,s}=x_1, \quad x_{2,s}=\tfrac{1}{2}L_x.$$

Thus Eq. (70) can be written as

$$\begin{aligned}R(a_{\kappa,0,0})=\frac{2(-1)^\kappa}{\pi\kappa}&\int_0^{(L_z/h)(2mE)^{\frac{1}{2}}}\\ &\times\left[\int_0^q\sin\left(\frac{4\pi\kappa}{h}\int_{x_1}^{x_2}pdx\right)dn_y\right.\\ &\left.+\int_q^r\sin\left(\frac{4\pi\kappa}{h}\int_{x_{1,s}}^{x_{2,s}}pdx\right)dn_y\right]dn_z.\end{aligned} \tag{71}$$[17]

If we now impose the restriction $E_0\gg\beta H$, it is possible to obtain the asymptotic value of $R(a_{\kappa,0,0})$. The evaluation of Eq. (71) is dependent on the use of the method of critical points recently introduced by van der Corput.[18] With a plausible interpretation of this method

[17] The factor of 2 appearing in Eq. (71) results from using the symmetry properties of the integral with respect to n_y and n_z to change the limits appropriately.

[18] J. G. van der Corput, Proc. Acad. Sci. (Amsterdam) **51**, 650 (1948).

it is found that

$$R(a_{\kappa,0,0})\sim\Big[(-1)^{\kappa}DB^{\frac{1}{2}}U_{\frac{1}{2}}(w,0)/A^{\frac{1}{2}}\pi(2\kappa)^{\frac{3}{2}}$$
$$-\frac{(-1)^{\kappa}L_yL_z2mE^{\frac{1}{2}}B^{\frac{1}{2}}}{\pi 2^{\frac{1}{2}}\kappa^{\frac{1}{2}}h^2}\cos\left(\frac{w}{2}-\frac{3\pi}{4}\right)$$
$$+\frac{(-1)^{\kappa}L_yL_z2mE^{\frac{1}{2}}B^{\frac{3}{2}}}{h^2\kappa^{5/3}}\left(\frac{\Gamma(5/3)\Gamma(11/12)\pi^{\frac{1}{2}}3^{7/6}}{\Gamma(17/12)4^{5/3}}\right)\Big]. \quad (72)$$

The symbols in Eq. (72) have the same values as in Sec. III. Details on the use of the method of critical points for the evaluation of Eq. (71) are given in the appendix.

B. Magnetic Moment

With the restriction $E_0\gg\beta H$, the magnetic moment resulting from $R(a_{\kappa,0,0})$ is

$$M=\frac{-4\pi V(2m)^{\frac{3}{2}}\beta^2E_0^{\frac{1}{2}}H}{3h^3}\left(1-\frac{\pi^2}{24}\left(\frac{kT}{E_0}\right)^2\right)$$
$$+\sum_{\kappa=1}^{\infty}\frac{(-1)^{\kappa}2\pi kTVe(2m)^{\frac{1}{2}}E_0\cos(\pi\kappa E_0/\beta H-\frac{3}{4}\pi)}{\kappa^{\frac{1}{2}}h^2c\beta^{\frac{1}{2}}H^{\frac{1}{2}}\sinh(\pi^2\kappa kT/\beta H)}$$
$$-\sum_{\kappa=1}^{\infty}\frac{(-1)^{\kappa}2\pi kTL_yL_z2mE_0^{\frac{3}{2}}\cos(\pi\kappa E_0/\beta H-\frac{3}{4}\pi)}{\kappa^{\frac{1}{2}}h^2\beta^{\frac{1}{2}}H^{\frac{3}{2}}\sinh(\pi^2\kappa kT/\beta H)}$$
$$-\frac{L_yL_z2mE_0^{4/3}\beta^{\frac{2}{3}}}{h^2H^{\frac{1}{2}}}\left[1-\frac{2\pi^2}{27}\left(\frac{kT}{E_0}\right)^2\right]$$
$$\times\left(\frac{\Gamma(5/3)\Gamma(11/12)\pi^{\frac{1}{2}}3^{7/6}\zeta(5/3)(2^{\frac{2}{3}}-1)}{2^{7/3}\Gamma(17/12)}\right), \quad (73)^{19}$$

where $\zeta(5/3)$ is the Riemann Zeta-function of argument 5/3. The first and second terms of Eq. (73) give exactly the result obtained in Sec. III (Eq. 51). This identification serves to confirm our conjecture that the size effects might appear as a correction to the previous results. The third and fourth terms of Eq. (73) give the effect of the finite size of the box. It is seen that both the oscillatory and nonoscillatory parts of the moment are affected by size.

The two oscillatory parts of Eq. (73) become of the same order of magnitude when

$$H=H_c\sim 2c(2mE_0)^{\frac{1}{2}}/eL_x \quad (74)$$

(where H_c denotes a critical field strength). This is exactly the field condition below which our solution fails.

The additional nonoscillatory correction is noteworthy since it varies as $H^{-\frac{1}{2}}$. It is a diamagnetic effect which (for specimen dimensions of order cm) is comparable to the Landau diamagnetism at fields below 1000 gauss. Further discussion of this term will be delayed until after we have considered the effect of electron spin.

V. SURFACE EFFECTS (ELECTRONS WITH SPIN)

In the previous sections we accounted for the electron spin by merely introducing a degeneracy of two in the Fermi summations. Actually, the spin will alter the eigenvalues and give rise to the spin paramagnetism. We now complete the present calculation with a consideration of the influence of both the electron spin and the surface states due to a finite container.

A. Distribution Function $G(E)$

Assuming that the total wave function is separable into a product of a spin function and a spatial coordinate function, we can write the electronic eigenvalues as

$$E=An_z^2+E_1\pm\beta H. \quad (75)$$

The function $G(E)$ must now be written as

$$G(E)=G_+(E)+G_-(E), \quad (76)$$

where the $\pm$ subscripts refer to the eigenvalues obtained from Eq. (75) with $\mp\beta H$, respectively.

1. $G_+(E)$

If we move the cut-off plane to $n=-\frac{1}{2}$ (just as for the spinless case in Sec. IV), we get identically the number theory problem considered in Sec. IV with E replaced by $(E+\beta H)$. By designating the spinless distribution function as $G_{\text{n.s.}}(E)$, we can write

$$G_+(E)=G_{\text{n.s.}}(E+\beta H), \quad (77)$$

where $G_{\text{n.s.}}(E)$ is given by Eq. (61). It must be noted that the minimum value of E for which Eq. (77) holds is $-\beta H$. In other words $G_+(-\beta H)=0$.

2. $G_-(E)$

Following the above reasoning, we can write

$$G_-(E)=G_{\text{n.s.}}(E-\beta H), \quad (78)$$

if we move the cutoff again to $n=-\frac{1}{2}$. In Eq. (78) the minimum value of E is βH since $G_-(\beta H)=0$.

B. Free Energy

The free energy for this case is given by

$$F-NE_0=$$
$$-\left(\int_{-\beta H}^{\infty}G_+(E)f(E)dE+\int_{\beta H}^{\infty}G_-(E)f(E)dE\right). \quad (79)$$

[19] The condition $E_0\gg\beta H$ imposes an upper bound on the magnetic field strength. However, it must be emphasized that the result given by Eq. (73) is also dependent on H having a lower bound. Our use of the WKB approximation has not considered states which have turning points determined by the infinite potentials at both walls simultaneously. This imposes the restriction that $H>2c(2mE_0)^{\frac{1}{2}}/eL_x$ for the applicability of Eq. (73).

We transform the first integral by the substitution

$$E+\beta H=\epsilon^+,$$

and the second integral by the substitution

$$E-\beta H=\epsilon^-.$$

This gives

$$F-NE_0=-\left(\int_0^\infty G_+(\epsilon^+-\beta H)f(\epsilon^+-\beta H)d\epsilon^+ + \int_0^\infty G_-(\epsilon^-+\beta H)f(\epsilon^-+\beta H)d\epsilon^-\right). \quad (80)$$

However, from Eqs. (77) and (78), we have

$$G_+(\epsilon^+-\beta H)=G_{\text{n.s.}}(\epsilon^+)$$

and

$$G_-(\epsilon^-+\beta H)=G_{\text{n.s.}}(\epsilon^-),$$

so that we can write

$$F-NE_0=-\left(\int_0^\infty G_{\text{n.s.}}(\epsilon^+)f(\epsilon^+-\beta H)d\epsilon^+ + \int_0^\infty G_{\text{n.s.}}(\epsilon^-)f(\epsilon^-+\beta H)d\epsilon^-\right). \quad (81)$$

In Eq. (81) there is no need to distinguish between ϵ^+ and ϵ^- since they are both integration variables. Hence, we have finally

$$F-NE_0=-\int_0^\infty G_{\text{n.s.}}(\epsilon)[f(\epsilon-\beta H)+f(\epsilon+\beta H)]d\epsilon. \quad (82)$$

If we again restrict our interest to the terms $a_{0,0,0}$ and $R(a_{\kappa,0,0})$ in $G_{\text{n.s.}}(E)$, we can obtain the asymptotic value (when $E_0\gg\beta H$) of the free energy. The methods used for evaluating Eq. (82) have been described in the previous sections and the appendix.

C. Magnetic Moment

After differentiating the resultant expression for the free energy to get the magnetic moment one encounters many factors of the form

$$(E_0\pm\beta H)^{p/q},$$

where p takes on the values 1, 3, 4, 5, while q is 2 or 3. (The combinations occur in such a way that p and q do not contain common factors.) These factors can all be expanded in power series with $(\beta H/E_0)$ as the variable, since in our asymptotic region $\beta H/E_0\ll 1$. After performing these expansions and combining terms, we find that the magnetic moment is

$$\begin{aligned}M=&\frac{4\pi V(2m)^{\frac{3}{2}}\beta^2E_0^{\frac{1}{2}}H}{h^3}\left(1-\frac{1}{24}\left(\frac{\beta H}{E_0}\right)^2-\frac{\pi^2}{24}\left(\frac{kT}{E_0}\right)^2\right)\\&-\frac{4\pi V(2m)^{\frac{3}{2}}\beta^2E_0^{\frac{1}{2}}H}{3h^3}\left(1-\frac{\pi^2}{24}\left(\frac{kT}{E_0}\right)^2\right)\\&+\sum_{\kappa=1}^{\infty}\frac{2\pi kTVe(2m)^{\frac{1}{2}}E_0\cos(\pi\kappa E_0/\beta H-\frac{3}{4}\pi)}{\kappa^{\frac{1}{2}}h^2c\beta^{\frac{1}{2}}H^{\frac{1}{2}}\sinh(\pi^2\kappa kT/\beta H)}\\&-\sum_{\kappa=1}^{\infty}\frac{2\pi kT(2m)L_yL_zE_0^{\frac{1}{2}}\cos(\pi\kappa E_0/\beta H-\frac{3}{4}\pi)}{\kappa^{\frac{1}{2}}h^2\beta^{\frac{1}{2}}H^{\frac{3}{2}}\sinh(\pi^2\kappa kT/\beta H)}\\&-\frac{L_yL_z(2m)E_0^{4/3}\beta^{\frac{2}{3}}}{h^2H^{\frac{1}{3}}}\left[1+\frac{8}{9}\left(\frac{\beta H}{E_0}\right)^2-\frac{2\pi^2}{27}\left(\frac{kT}{E_0}\right)^2\right]\\&\times\left(\frac{\Gamma(5/3)\Gamma(11/12)\pi^{\frac{1}{2}}3^{7/6}\zeta(5/3)(2^{\frac{2}{3}}-1)}{2^{7/3}\Gamma(17/12)}\right). \quad (83)\end{aligned}$$

We shall now identify and discuss each of the five terms which comprise this magnetic moment.

1. The first term is the Pauli spin paramagnetism with higher order temperature and field corrections. (It is noted that the explicit dependence upon temperature and field could be obtained if E_0 were given explicitly in the variables T and H. This could be accomplished through the use of the normalizing condition Eq. (2).)

2. The second term is the ordinary Landau diamagnetism with higher order corrections.

3. The third term is the usual de Haas-van Alphen effect obtained when no surface states are included. It is noted that this part of the moment differs from the spinless case (Secs. III and IV) by having a phase difference of $\pm\pi$ for terms with κ odd. This result is in agreement with the work of Akhieser,[20] Sondheimer and Wilson,[4] and Dingle.[21]

4. The fourth term is the surface state correction to the de Haas-van Alphen effect. It differs from the corresponding term found in Sec. IV by a phase difference of $\pm\pi$ when κ is odd. This correction becomes comparable to the usual de Haas-van Alphen effect when

$$H=H_c\sim 2c(2mE_0)^{\frac{1}{2}}/eL_x. \quad (84)$$

It is re-emphasized here that Eq. (84) expresses the field condition below which the entire solution fails.

5. The fifth term is a nonoscillatory diamagnetic effect arising from the surface states. Since it was also found in Sec. IV we can say that this effect is independent of electron spin. In light of this circumstance we will now focus our attention on this "surface" diamagnetism. For a free electron gas with E_0 of the order of

[20] A. Akhieser, Compt. rend. acad. sci. U.R.S.S. **23**, 874 (1939).
[21] R. B. Dingle, Proc. Roy. Soc. (London) **A211**, 500 (1952).

1 electron volt, the "surface" (s) magnetization is

$$(M/V)_s \sim -10^{-3}/L_x H^{\frac{1}{2}}, \tag{85}$$

while the remaining (r) nonoscillatory magnetization from the Pauli and Landau terms is

$$(M/V)_r \sim 10^{-6} H. \tag{86}$$

For the assumed value of E_0, we also have

$$H_c \sim 10/L_x. \tag{87}$$

From Eqs. (85) and (86) we find that the $|(M/V)_s|$ is about equal to $|(M/V)_r|$ when

$$H = H_0 \sim 3\times 10^2/L_x^{\frac{3}{2}}. \tag{88}$$

In order to comment on the feasibility of finding the surface diamagnetism experimentally, we shall now examine the above quantities for real specimens.

(a) If L_x is of order cm, H_c is of order 10 gauss while H_0 is of order 300 gauss. For 1 cc of material at 300 gauss we would have to be able to measure a magnetic moment of about 10^{-4} cgs unit in order to observe the surface diamagnetism. Although this is feasible experimentally, it is not an easy task.

(b) If L_x were of order 10^{-2} cm, H_c would be of order 10^3 gauss, while H_0 would be of order 6×10^3 gauss. Now we would need to measure moments of about 5×10^{-3} cgs unit in order to observe the surface diamagnetism. Such moments can be measured accurately without elaborate arrangements.

The analysis given above suggests that experiments may be performed to test the theoretical prediction of surface diamagnetism. It would be desirable to use a monovalent metal, such as Cu, Ag, Na, or Au, for such an experiment since these metals are most closely represented by a free electron model. The specimen could be in powder form with individual particles electrically insulated and having dimensions of the order 10^{-2} cm. Finally, the experiment could be performed at room temperature, since even at $T=300°$K the corrections to the moment are small compared to the temperature-independent terms.

The author wishes to thank Professor R. D. Myers for his guidance in this work, and M. F. M. Osborne not only for suggesting the problem but also for many stimulating discussions.

VI. APPENDIX. The Asymptotic Value of $R(a_{\kappa,0,0})$ as Obtained from the Method of Critical Points

A. Transformation of Eq. (71)

We designate by I_1 and I_2 the first and second integrals, respectively, of Eq. (71). Substituting

$$\theta = hn_y/L_y - eHx/c \tag{A1}$$

into I_1 and carrying out the integrations over θ and n_y gives

$$I_1 = \frac{2(-1)^\kappa}{\pi\kappa}\int_0^{(L_z/h)(2mE)^{\frac{1}{2}}}\left(\frac{eHL_xL_y}{2hc} - \frac{L_y}{h}(2mE_1)^{\frac{1}{2}}\right)\times\sin\left(\frac{\pi\kappa E_1}{\beta H}\right)dn_z. \tag{A2}$$

Now consider the first part of this integral. Setting

$$\phi = hn_z/L_z(2mE)^{\frac{1}{2}} \tag{A3}$$

transforms this part to

$$\frac{(-1)^\kappa eHL_xL_yL_z(2mE)^{\frac{1}{2}}}{\pi\kappa h^2 c}\int_0^1 \sin\left[\frac{\pi\kappa E}{\beta H}(1-\phi^2)\right]d\phi. \tag{A4}$$

The value of the integral in Eq. (A4) is given by Watson.[12] In terms of our previously used symbols, Eq. (A4) becomes

$$(-1)^\kappa DB^{\frac{1}{2}}U_{\frac{1}{2}}(w,0)/A^{\frac{1}{2}}\pi(2\kappa)^{\frac{3}{2}}. \tag{A5}$$

If we again use the substitution given by Eq. (A3), the second part of I_1 becomes

$$\frac{-4(-1)^\kappa L_yL_zmE}{\pi\kappa h^2}\int_0^1 (1-\phi^2)\sin\left[\frac{w}{2}(1-\phi^2)\right]d\phi. \tag{A6}$$

The evaluation of this integral will require the use of the method of critical points.

With appropriate transformations, I_2, the second part of Eq. (71) can be put into the form:

$$I_2 = \frac{4(-1)^\kappa L_yL_zmE}{\pi\kappa h^2}\left[\int_0^1\int_0^1 (1-\phi^2)^{\frac{1}{2}}\times\sin\left[\frac{w}{2\pi}(1-\phi^2)\left(\frac{\pi}{2}+f(\tau)\right)\right]d\tau d\phi + \int_0^1\int_0^1 (1-\phi^2)^{\frac{1}{2}}\times\sin\left[\frac{w}{2\pi}(1-\phi^2)\left(\frac{\pi}{2}-f(\tau)\right)\right]d\tau d\phi\right] \tag{A7}$$

where

$$f(\tau) = \tau(1-\tau^2)^{\frac{1}{2}} + \sin^{-1}\tau.$$

We shall use the method of critical points to evaluate both of the double integrals in Eq. (A7).

B. Details of the Method of Critical Points

Consider the general integral

$$I = \int_a^b g(x)e^{iwf(x)}dx, \tag{A8}$$

where a, b, $f(x)$, and $g(x)$ are independent of the

parameter w. It is further assumed that $f(x)$ and $g(x)$ are infinitely often differentiable in the closed interval $a \leqq x \leqq b$. We seek the value of I for $|w| \gg 1$. Van der Corput[18] asserts that the asymptotic character of I is completely determined if the behavior of $f(x)$ and $g(x)$ is given in the vicinity of the critical points.[22] These points are the end points a and b and the points between a and b where the phase $wf(x)$ is stationary. The contribution of each critical point is called the residue at that point. The residue at a critical point ξ can be developed asymptotically in ascending powers of $1/w^{1/m}$, where m is the smallest positive integer such that the m^{th} derivative of $f(x)$ at ξ is not zero. To establish the nature of the residue at ξ we expand $g(x)$ and $f(x)$ in Taylor series around ξ. It can be shown that the complete residue at ξ may be expressed as

$$(\text{Res})_\xi = e^{iwf(\xi)}\left[\frac{C_1}{w^{1/m}}+\frac{C_2}{w^{2/m}}+\cdots+\frac{C_s}{w^{s/m}}+\cdots\right], \quad \text{(A9)}^{23}$$

where

$$C_s=\frac{g^{s-1}(\xi)}{(s-1)!}\left[\frac{m!}{f^m(\xi)}\right]^{s/m}\frac{(s/m)!}{s(-i)^{s/m}} + \frac{i(m+s/m)!}{(m+s)(-i)^{(m+s)/m}}\left(\frac{m!}{f^m(\xi)}\right)^{(m+s)/m} \times \sum_{0<p<s}\frac{g^{p-1}(\xi)f^{m+s-p}(\xi)}{(p-1)!(m+s-p)!}. \quad \text{(A10)}^{24}$$

Let us now apply this development to the integral $I_{1,2}$ appearing in Eq. (A6). To put it into the desired form, we write

$$I_{1,2}=\mathcal{I}_m\int_0^1 g(\phi)e^{iwf(\phi)}d\phi, \quad \text{(A11)}$$

where

$$g(\phi)=(1-\phi^2)^{\frac{1}{2}}, \quad f(\phi)=\tfrac{1}{2}(1-\phi^2),$$

and $\mathcal{I}_m$ denotes "the imaginary part of." The critical points are 0 and 1. The point 0 is a stationary phase point as well as an end point. From Eq. (A10) it is found that the residue at the point 0 is

$$(\text{Res})_0=e^{iw/2}\left[\frac{(\frac{1}{2})!(2!)^{\frac{1}{2}}}{w^{\frac{1}{2}}(i)^{\frac{1}{2}}}-\frac{(2!)^{\frac{1}{2}}(\frac{3}{2})!}{w^{\frac{1}{2}}3(i)^{\frac{1}{2}}}\right]. \quad \text{(A12)}$$

Since the function $g(\phi)$ cannot be expanded into a Taylor series around the point 1, we must make an appropriate transformation to get the residue there. If we let

$$(1-\phi^2)^{\frac{1}{2}}=z, \quad \text{(A13)}$$

we would require the residue at $z=0$. The transformed integral is

$$\int_0^1 \frac{z^2}{(1-z^2)^{\frac{1}{2}}}\exp(iwz^2/2)dz, \quad \text{(A14)}$$

so that we can now expand our functions around $z=0$. Carrying out the details of expansion leads to

$$(\text{Res})_{z=0}=(\text{Res})_{\phi=1}=2(2!)^{\frac{1}{2}}(\tfrac{3}{2})!/w^{\frac{1}{2}}3(-i)^{\frac{1}{2}}. \quad \text{(A15)}$$

By neglecting the terms $O(1/w^{\frac{1}{2}})$, and taking the imaginary part of the residue, we get

$$I_{1,2}\sim(\pi)^{\frac{1}{2}}\cos(\tfrac{1}{2}w-\tfrac{3}{4}\pi)/(2w)^{\frac{1}{2}}. \quad \text{(A16)}$$

We now consider the double integrals in Eq. (A7). The general philosophy in handling double integrals is to apply the previous development twice. There are additional features which make the double integration more complicated, but rather than discuss them generally we shall note them in solving the specific examples. We designate by $I_{2,1}$ and $I_{2,2}$ the first and second double integrals in Eq. (A7). Then $I_{2,2}$ can be written as

$$I_{2,2}=\mathcal{I}_m\int_0^1\int_0^1 g(\phi,\tau)e^{iwF(\phi,\tau)}d\tau d\phi, \quad \text{(A17)}$$

where

$$g(\phi,\tau)=(1-\phi^2)^{\frac{1}{2}},$$
$$F(\phi,\tau)=[(1-\phi^2)/2\pi][\tfrac{1}{2}\pi-\tau(1-\tau^2)^{\frac{1}{2}}-\sin^{-1}\tau].$$

The critical points here are first the points within the region of the integration where the phase $wF(\phi,\tau)$ is stationary, i.e., where the $\partial F/\partial\phi=\partial F/\partial\tau=0$; then the vertices of the boundary of the region; finally those boundary points are critical where $F(\phi,\tau)$, taken along the boundary curve, is stationary. For our integral $I_{2,2}$ the following points (infinite in number) are critical:

$$\phi=0, \quad \tau=0$$
$$\phi=1, \quad 0\leqq\tau\leqq1$$
$$0\leqq\phi\leqq1, \quad \tau=1.$$

To get the residue at the point $(0,0)$ we expand $g(\phi,\tau)$ and $F(\phi,\tau)$ in double Taylor series around that point. Substituting these expansions into the integrand gives

$$(\text{Res})_{0,0}=e^{iw/4}\int_0^\infty\int_0^\infty\left(1-\frac{\phi^2}{2}-\cdots\right) \times\exp\left\{iw\left[-\frac{\tau}{\pi}-\frac{\phi^2}{4}+\cdots\right]\right\}d\tau d\phi. \quad \text{(A18)}^{25}$$

[22] This condition on $f(x)$ and $g(x)$ is weaker than the requirement that $f(x)$ and $g(x)$ be infinitely often differentiable in the closed interval $a\leqq x\leqq b$. In practice we use the weaker condition for the evaluation of integrals.

[23] Van der Corput gives this form for the residue without showing the explicit values of $C_1, C_2, \cdots$.

[24] In getting Eq. (A10) we have assumed that ξ is the lower bound of the interval. If ξ were an interior point or the upper bound of the interval, the value of C_s would be changed to the extent of a factor of 2 or the inclusion of a negative sign.

[25] The extension to infinity for the upper limits of both integrations is justified here since the major contribution of the double integral is around $(0,0)$. Details on this point can be found in van der Corput's paper.

Integrating first on τ and keeping only the largest terms gives

$$(\mathrm{Res})_{0,0}=\frac{\pi e^{iw/4}}{iw}\int_0^\infty\left(1-\frac{\phi^2}{2}-\cdots\right)\times\exp\left\{iw\left[-\frac{\phi^2}{4}-\cdots\right]\right\}d\phi. \quad \text{(A19)}$$

We now integrate over ϕ to get

$$(\mathrm{Res})_{0,0}=\frac{\pi e^{iw/4}}{iw}\left[\frac{(\frac{1}{2})!}{w^{\frac{1}{2}}(i/4)^{\frac{1}{2}}}\right]. \quad \text{(A20)}$$

Thus, this residue is $O(1/w^{\frac{3}{2}})$.

Next we consider the residue from the points $0\leqq\phi\leqq1$, $\tau=1$. The function $F(\phi,\tau)$ cannot be expanded in a Taylor series around any point having $\tau=1$. Therefore, we must resort to a suitable transformation to accomplish the calculation. If we let

$$\sin^{-1}\tau=\theta, \quad \text{(A21)}$$

we would require the residue from the points $0\leqq\phi\leqq1$, $\theta=\pi/2$. By expanding the functions in the integrand around $\theta=\pi/2$, we can express the residue from this entire boundary [designated as $(\mathrm{Res})_{b_1}$] as

$$(\mathrm{Res})_{b_1}=\int_0^1\int_0^\infty(1-\phi^2)^{\frac{1}{2}}\left(\Theta-\frac{1}{3!}\Theta^3-\cdots\right)\times\exp\left\{i\frac{w(1-\phi^2)}{2\pi}\left[\frac{4}{3!}\Theta^3+\cdots\right]\right\}d\Theta d\phi, \quad \text{(A22)}$$

where

$$\Theta=\tfrac{1}{2}\pi-\theta.$$

The integration over Θ follows from the general development for single integrals. If we keep only the largest term of the resulting expansion, the residue is

$$(\mathrm{Res})_{b_1}=\frac{(\frac{2}{3})!(3\pi)^{\frac{2}{3}}}{w^{\frac{2}{3}}2(-i)^{\frac{2}{3}}}\int_0^1\frac{d\phi}{(1-\phi^2)^{1/6}}. \quad \text{(A23)}$$

The integral in Eq. (A23) is a standard type, so that the final result can be written as

$$(\mathrm{Res})_{b_1}=\frac{(\frac{2}{3})!(3\pi)^{\frac{2}{3}}\pi^{\frac{1}{2}}\Gamma(11/12)}{w^{\frac{2}{3}}(-i)^{\frac{2}{3}}4\Gamma(17/12)}. \quad \text{(A24)}$$

This residue is $O(1/w^{\frac{2}{3}})$.

Using a similar analysis we find that the residue from the boundary $\phi=1$, $0\leqq\tau\leqq1$ is $O(1/w^{\frac{2}{3}})$. The complete evaluation therefore shows that the largest term in $I_{2,2}$ is given by the imaginary part of Eq. (A24), which is $O(1/w^{\frac{2}{3}})$.

The integral $I_{2,1}$ can be evaluated by the same procedure as given above. It is found that the largest term for this integral is $O(1/w^{7/6})$. Combining the results of the two integrations, we find that

$$I_2\sim(3\pi)^{7/6}\Gamma(5/3)\Gamma(11/12)/8\Gamma(17/12)w^{\frac{2}{3}}. \quad \text{(A25)}$$

The sum of Eqs. (A5), (A16), and (A25) is the value for $R(a_{\kappa,0,0})$ given by Eq. (72).