Effect of the Surface on the Magnetic Properties of an Electron Gas

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The energy levels of free electrons confined to a finite cylindrical box with a uniform axial magnetic field are obtained by the WKB approximation and used to compute the magnetic susceptibility with Fermi statistics. The usual treatments which neglect the effects of the walls are shown to be justified for both the steady susceptibility and the de Haas van Alphen terms provided the radius of the box is sufficiently large. In the case of the oscillatory terms it is only necessary that the radius of the box exceed the classical orbit radius R_c of an electron having the Fermi energy ζ in the magnetic field. However, there exists a surface correction to the steady susceptibility whose magnitude relative to the Landau value is $(\zeta/\beta H)^{\frac{1}{2}}(R_c/R)$. This surface correction, the existence of which has been previously pointed out by Osborne and Steele, and by Dingle, is shown to be extremely sensitive to the exact boundary conditions at the surface, including both the abruptness of the surface jump in potential and the height of the barrier relative to the Fermi energy. Indeed, the correction term can be either paramagnetic or diamagnetic depending on these details. The form of the WKB approximation appropriate to different boundary conditions is discussed, and a modification of Dingle's theory is presented which may be used to calculate approximately the susceptibility of the system for any value of the ratio R/R_c when the boundary conditions are known.

I. INTRODUCTION

A NUMBER of papers[1–13] have been published in the last twenty years concerning the theory of the magnetic susceptibility of a system of free electrons or of electrons confined to a box, and a variety of elegant methods have been developed. It has not been altogether clear, however, to what extent the walls of the system could be neglected in some of these calculations, and the dependence of the susceptibility on the form of the wall potential has not been adequately investigated. Osborne,[7] Steele,[8] and Dingle,[3,4] have recently given calculations which take the walls into account, but they have arrived at different conclusions concerning the corrections to the susceptibility required by the finite size of the box. Since the walls play an essential role in a box of any size, it seems desirable to have a derivation which shows this explicitly. The author believes that the present treatment offers a clear picture of the physical situation as well as some new results concerning the dependence of the susceptibility upon the size of the box.

It is well known[14,15] that in classical physics the positive moment contributed by electrons that collide with the walls of the system exactly cancels the negative moment of electrons far from the walls. Van Vleck[5] and Teller[6] showed that a similar balancing occurs in quantum mechanics (with a nonzero resultant) and gave arguments to justify the value for the magnetic susceptibility obtained by Landau[9] from the free energy. However, Teller's argument was for an infinite plane wall, and Van Vleck's required the use of the old quantum mechanics, although the details of his arguments are very similar to those used in the present paper. It is not clear to what extent either justifies the more recent calculations by Landau[1] and others of the oscillatory de Haas van Alphen terms. The present work had its origin in an improved derivation for a cylindrical box which made clear this balancing of diamagnetic and paramagnetic states and obtained the usual results for the Landau steady susceptibility and the de Haas van Alphen oscillations provided the box was sufficiently large. It was then found that the WKB approximation could be used to calculate the energies of the electron states whose wave functions were appreciably distorted from free-electron form by the presence of the walls and that from these energies corrections to the total susceptibility could be obtained which were important for smaller boxes. This work was in qualitative agreement with that of Osborne[7] and Steele,[8] who predicted a "surface diamagnetism," and agreed with Dingle's work[4] in the size- and field-dependence of the corrections but disagreed in that Dingle predicted a paramagnetic correction of about one-third the magnitude of our result. We have found that this difference arises from our having determined the energy levels from that form of the WKB phase integral condition which is correct when the potential barrier at the surface rises slowly, whereas Dingle used the form correct when the barrier rises abruptly to infinite height. We have outlined a number of considerations which must determine the correct form of the WKB approximation when we know the form of the surface potential in a real

[1] D. Schoenberg, Proc. Roy. Soc. (London) **A170**, 341 (1939).
[2] E. H. Sondheimer and A. H. Wilson, Proc. Roy. Soc. (London) **A210**, 173 (1951).
[3] R. B. Dingle, Proc. Roy. Soc. (London) **A211**, 500, 517 (1952); **A212**, 38, 47 (1952).
[4] R. B. Dingle, Proc. Roy. Soc. (London) **A216**, 118 (1953).
[5] J. H. Van Vleck, *Theory of Electric and Magnetic Susceptibilities* (Oxford University Press, London, 1932), p. 353 ff.
[6] E. Teller, Z. Physik **67**, 311 (1931).
[7] M. F. M. Osborne, Phys. Rev. **88**, 438 (1952).
[8] M. C. Steele, Phys. Rev. **88**, 451 (1952).
[9] L. Landau, Z. Physik **64**, 629 (1930).
[10] C. G. Darwin, Proc. Cambridge Phil. Soc. **27**, 86 (1930).
[11] R. Peierls, Z. Physik **80**, 763 (1933); **81**, 186 (1933).
[12] M. Blackman, Proc. Roy. Soc. (London) **A166**, 1 (1938).
[13] A more complete bibliography is given in the papers by Dingle.
[14] J. H. Van Leeuwen, Dissertation, Leiden, 1919; Summary in J. phys. et radium **2**, 361 (1921).
[15] Reference 5, Chap. IV.

metal, but since we lack sufficiently detailed information concerning the surface potential we have not attempted to carry through a calculation for any model of a real metal. It appears that surface corrections of the general form predicted should result for any reasonable model, the numerical coefficient and sign depending on the details of the model. Before further calculation is done, it would be desirable to have experimental evidence at hand: if such surface corrections can be located, their sign and magnitude may be of great assistance in our selection of a model of the metal surface and our choice of the best form of the WKB approximation. If no such corrections can be found, we must seek a model that makes the surface effects too small for observation.

Unfortunately, much of the calculation that has gone into this work is too lengthy for publication here, so that frequently only results may be quoted. Most of the analysis has been made available elsewhere.[16]

II. METHODS OF CALCULATING THE MAGNETIC MOMENT

The usual procedure has been to calculate the magnetic moment M from the Helmholtz free energy F by the formula

$$M=-(\partial F/\partial H)_{T,V,N}, \tag{201}$$

where H is the absolute value of the uniform external magnetic field applied to the system, T the absolute temperature, V the volume of the system, and N the total number of electrons present. It is, however, evident that if the electrons are independent, except in so far as they obey the exclusion principle when Fermi statistics are used, then the moment of the system should also be given by the sum of the moments of the individual electron states weighted with the probability that the state is occupied.[5,7] Thus with Fermi statistics we should have

$$M=-\sum_i(\partial\epsilon_i(H)/\partial H)\times\{1+\exp[(\epsilon_i(H)-\zeta)/kT]\}^{-1}, \tag{2.2}$$

where k is the Boltzmann constant and $\epsilon_i(H)$ the energy of the state i, and where ζ is determined by the condition

$$N=\sum_i\{1+\exp[(\epsilon_i(H)-\zeta)/kT)\}^{-1}, \tag{2.3}$$

the sum being taken over all single electron states. On the other hand, the free energy is given by

$$F=N\zeta-kT\sum_i\ln\{1+\exp[(\zeta-\epsilon_i(H))/kT]\}, \tag{2.4}$$

and since by (2.3) $(\partial F/\partial\zeta)=0$, (2.1) and (2.2) give the same result, provided the limits of summation in (2.4) and the degeneracy of states with a common energy (if we should use the index i to label a collection of states with the same energy instead of a single state) do not depend on H.

However, for a system confined by a cylindrical box of cross section A with its axis parallel to the uniform magnetic field, the energies of states unperturbed by the walls are, if we neglect the moment due to spin,

$$\epsilon(n,k_z)=\hbar^2k_z^2/2m+(2n+1)\beta H,\quad n=0,1,2,\cdots, \tag{2.5}$$

where $e\hbar/2mc=\beta$ is the Bohr magneton, and the electronic wave function depends on the position coordinate z along the axis only through the factor $\exp(ik_zz)$. The degeneracy of each such (n,k_z) level is to first approximation[3,8] eHA/hc, if we neglect spin degeneracy. As remarked by Van Vleck[5] and Osborne,[7] if we use only these energy states (2.5) and this degeneracy in (2.2), we find a large negative total moment of magnitude greater than $N\beta$, whereas (2.4) and (2.1) yield the usual Landau result (for $\beta H\ll\zeta$)

$$M=-(4m\beta^2V/h^2)(N\pi^2/9V)^{\frac{1}{3}}H=-N\beta^2H/2\zeta=-\tfrac{1}{3}n(\zeta)\beta^2H, \tag{2.6}$$

plus the periodic de Haas van Alphen terms. Here $n(\zeta)$ is the density of states (including spin degeneracy) in the energy scale at the Fermi level ζ, and the second expression shows (2.6) to be much less in magnitude than $N\beta$. Our first problem is, then, to show that the difference between these methods is removed when we include the positive moments of the boundary states in our summation (2.2).

III. THE BOUNDARY STATES IN THE WKB APPROXIMATION

We consider the Schrödinger equation satisfied by the wave function of a single electron state in a cylindrical box of length L and radius R with its axis parallel to the uniform magnetic field, in which we neglect all interaction between electrons

$$-(\hbar^2/2m)[(\partial^2\psi/\partial z^2)+r^{-2}(\partial^2\psi/\partial\phi^2)+r^{-1}(\partial/\partial r)(r\partial\psi/\partial r)]-i\beta H(\partial\psi/\partial\phi)+(e^2H^2/8mc^2)r^2\psi=E\psi, \tag{3.1}$$

for $r<R$, and the boundary condition $\psi(R)=0$. On separating in cylindrical coordinates, we put

$$\psi=f(r)\exp(ik_zz+is\phi),\qquad \epsilon'=E-(\hbar^2k_z^2/2m)-\beta Hs,\quad s=0,\pm1,\pm2,\cdots, \tag{3.2}$$

and get as the equation for $f(r)$

$$-(\hbar^2/2mr)(\partial/\partial r)(r\partial/\partial r)f(r)+[(\hbar^2s^2/2mr^2)+(e^2H^2r^2/8mc^2)]f(r)=\epsilon' f(r). \tag{3.3}$$

We now make the substitution $r=e^x$, $f(r)=g(x)$, which puts (3.3) in a form suitable for the WKB approxi-

[16] H. Brooks and F. S. Ham, Technical Report No. 169 of Cruft Laboratory, Harvard University, March 10, 1953. This report was published under contract with the Office of Naval Research and has been distributed to the usual recipients of the Cruft Laboratory Reports. The authors have a few extra copies which they will be glad to send upon request. This report has, moreover, been deposited as Document No. 4099 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document number and by remitting $7.50 for photoprints or $2.75 for 35-mm. microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

mation,[17]

$$(\partial^2 g(x)/\partial x^2)+(2m/\hbar^2)[\epsilon' e^{2x}-(\hbar^2 s^2/2m) - (e^2H^2/8mc^2)e^{4x}]g(x)=0. \quad (3.4)$$

This determines ϵ' in terms of s and n through the phase integral condition (after transformation back to r)

$$\int_{r_1}^{r_2}\left[2m\left(\epsilon'-\frac{\hbar^2 s^2}{2mr^2}-\frac{e^2H^2r^2}{8mc^2}\right)\right]^{\frac{1}{2}}dr=(n+\tfrac{1}{2})\hbar\pi, \quad (3.5)$$

where r_1 and r_2 are the two positive zeros of the quantity under the square root, provided $r_2<R$. This condition yields

$$\epsilon'=(2n+|s|+1)\beta H, \quad (3.6)$$

and the energies are given by (2.5). Electronic states with these energy values are not significantly distorted by the container from the free-electron form, and they will be referred to henceforth as "bulk states." If, however, $r_1<R<r_2$, then the upper limit of integration is R, and it is evident that for given n and s, ϵ' will be increased over the value (3.6).[18] These states are appreciably distorted by the wall and will be called "surface states." We note that the quantum numbers n, s, and k_z and the spin orientation completely specify a single state, which according to the exclusion principle can be occupied by no more than one electron.

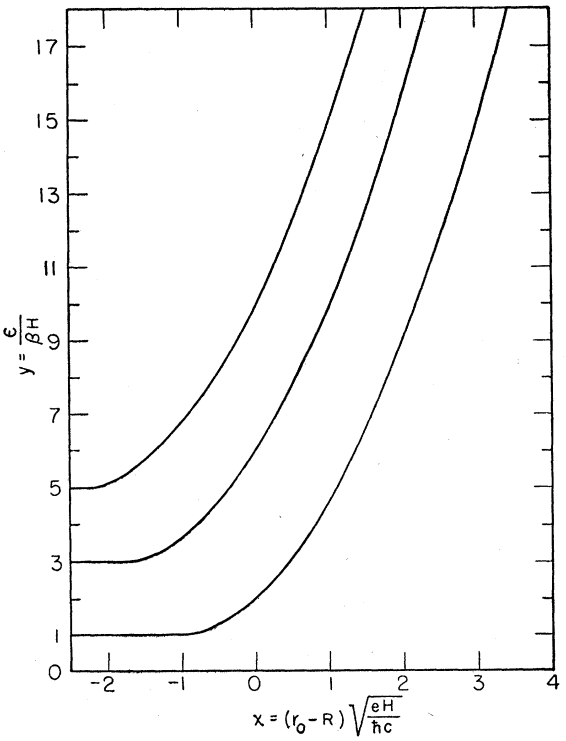

FIG. 1. Energy of surface states for $n=0, 1, 2$.

[17] R. E. Langer, Phys. Rev. **51**, 669 (1937).

[18] When the upper limit is R, the $(n+\frac{1}{2})$ in (3.5) is incorrect. For the present we will continue to use $(n+\frac{1}{2})$ here. The necessary corrections are discussed in Sec. IV.

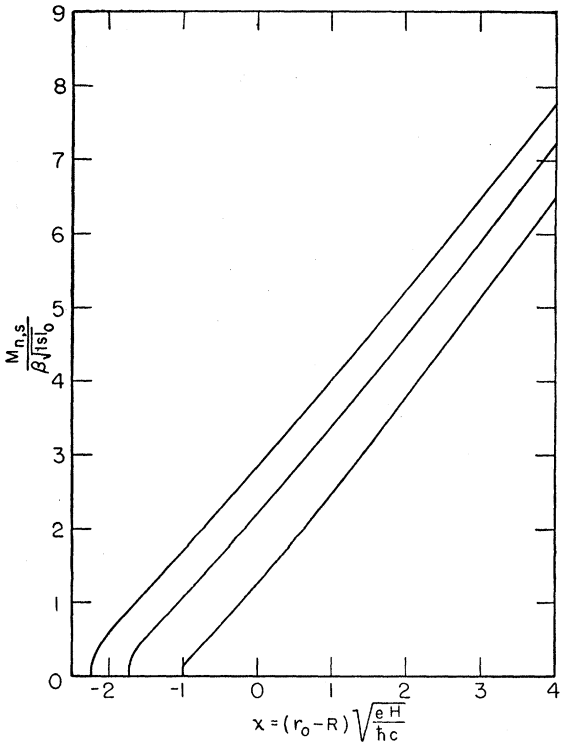

FIG. 2. Moment of surface states for $n=0, 1, 2$.

Evaluation of ϵ' in (3.5) for the surface states has been carried out, and the resulting "transverse energy" $\epsilon=E-\hbar^2 k_z^2/2m$ is plotted in Fig. 1 for $n=0, 1, 2$. Details of this calculation may be found in reference 16 In plotting the figure we have changed the labeling o an electronic state from n, k_z, s to n, k_z, r_0, where $r_0=(2hc|s|/eH)^{\frac{1}{2}}$ is the radius at which the effective radial "potential" $v(r)=(\hbar^2 s^2/2mr^2)+(e^2H^2r^2/8mc^2)$ appearing in (3.3) and (3.5) has its minimum. We notice that for a given n, states with r_0 smaller than a value depending on n and H are bulk states with energies given by (2.5).

The moment of a surface state is given by

$$M_{ns}=-(\partial\epsilon_{ns}/\partial H)_s = [-(\partial\epsilon_{ns}/\partial H)_{r_0}-(\partial\epsilon_{ns}/\partial r_0)_H(dr_0/dH)], \quad (3.7)$$

in which the second term is for surface states very much the larger. Since $(\partial\epsilon/\partial r_0)_H$ is positive, as is seen from Fig. 1, and (dr_0/dH) negative, the moment of a surface state is positive and very large compared to the moment of a bulk state. The relatively few surface states are thus able very nearly to cancel the large negative moment contributed by all the bulk states. M_{ns} is plotted in Fig. 2 for $n=0, 1, 2$. Here $|s|_0=eHA/hc$.

Calculation of the free energy and total moment using these surface states has been carried out for a container whose radius R is much larger than the classical orbit radius $R_c=(c/eH)(2m\zeta)^{\frac{1}{2}}$ of an electron moving in a plane perpendicular to the magnetic field

with energy equal to the Fermi energy ζ of the system. The details of the work are given in reference 16. The result shows that for $R \gg R_c$ the oscillatory part of the moment which accounts for the de Haas van Alphen effect for this model is correctly given by the usual formulas,[1-3] corrections being negligible. The steady part of the moment is found to be

$$M_s = -(0.02652)LR^2(2m/\hbar^2)^{\frac{1}{2}}\beta^2 H\zeta^{\frac{1}{2}} - (0.02293)LR(2m/\hbar^2)\beta^{\frac{3}{2}}H^{-\frac{1}{2}}\zeta^{4/3}, \quad (3.8)$$

in which we neglect small temperature dependent corrections. The first term is the ordinary Landau moment, which dominates provided $R \gg (\zeta/\beta H)^{\frac{1}{2}}R_c$. The second term is a diamagnetic contribution due to the finite size of the container. Other corrections are very much smaller provided $R \gg R_c$. The numerical coefficients in (3.8) have been calculated for the simplified model of spinless electrons (for which no spin degeneracy exists). For a real electron gas we must multiply both terms in (3.8) by two to account for the twofold spin degeneracy of states even if we continue to neglect the contribution by the spin to the total moment. Inclusion of this moment further changes the coefficient of the first term in (3.8) from $2(-0.02652)$ to $4(0.02652)$—the usual Pauli paramagnetism. The second term is unchanged, spin corrections due to the surface states being small if $\zeta \gg \beta H$.

TABLE I. Numerical coefficient of the surface correction term [second term in Eq. (3.8) of text] for various values of the parameter α.

α	Coefficient
0.75	0.00763
0.70	−0.00047
0.65	−0.00770
0.60	−0.01378
0.55	−0.01896
0.50	−0.02293

The expression (3.8) for M_s agrees with the conclusion of Osborne and Steele that the system should show a surface diamagnetism which depends on container dimensions and magnetic field in the same way as the second term of (3.8). A surface correction of this form has also been predicted by Dingle,[4] but he has found that it should be paramagnetic. The origin of this discrepancy is discussed in the next section.

IV. CORRECTIONS FOR WALL THICKNESS

We remarked in a footnote[18] that for surface states the use of $(n+\frac{1}{2})$ in (3.5) is incorrect, yet we have used $(n+\frac{1}{2})$ in obtaining (3.8). The phase integral equation (3.5) with $(n+\frac{1}{2})$ is derived in WKB theory from the requirement that the phase of the oscillatory approximate wave function in the region between the turning points r_1 and r_2 be such that the wave function connects smoothly to a damped exponential in the classically forbidden regions beyond the turning points.[19] In the present problem we imagine our system bounded by a sharp, impenetrable wall at R—that is, we wish to impose the boundary condition $\psi(R)=0$. If the phase of the WKB wave function is chosen so that the wave function vanishes at one of the turning points, theory shows that $(n+\frac{3}{4})$ must replace $(n+\frac{1}{2})$ in (3.5); if the condition must be satisfied at both turning points, $(n+1)$ must be used, with $n=0, 1, 2, 3, \cdots$ as usual. This last form of (3.5) yields the correct eigenvalues for a one-dimensional electron in the potential $V(x)=0$ for $|x|<a$, $V(x)=\infty$ for $|x|>a$. The $(n+\frac{3}{4})$ form of (3.5) yields the exact eigenvalues for a similar problem with $V(x)=\infty$ for $x<0$, $V(x)=kx^2$ for $x>0$. Consequently, if we assume a sharp impenetrable wall in the present magnetic problem [$V(r)=0$ for $r<R$, $V(r)=\infty$ for $r>R$], then we should use $(n+\frac{3}{4})$ in (3.5) when calculating the energies of the surface states.

At first sight one would not expect this change to make much difference, since n is quite large for most of our electron states. However, we have calculated the magnetic moment by using the Poisson sum formula (Dingle I, Appendix) to carry out the sums over the quantum number n, and this formula depends critically on the choice between $(n+\frac{1}{2})$ and $(n+\frac{3}{4})$: with $(n+\frac{1}{2})$ we obtain (3.8); with $(n+\frac{3}{4})$ the correction term in (3.8) becomes paramagnetic. Specifically, the following form of the Poisson sum formula is readily proved:[16] if $0<\alpha<1$,

$$\sum_{n=0}^{\infty} f(n+\alpha) = \sum_{r=-\infty}^{\infty} e^{-2\pi i r\alpha}\int_0^{\infty} f(n)e^{2\pi i n r}dn. \quad (4.1)$$

In Table I we show the value of the coefficient of the second term in (3.8) obtained using various values of α. The value obtained using $\alpha=\frac{3}{4}$ agrees exactly with the coefficient of the leading term in Dingle's result for the surface correction (when our value is multiplied by two to include spin degeneracy).

Thus, the magnitude and sign of the surface corrections depend critically on the choice of α. The same is true of the value of the susceptibility at weak fields, $R \ll R_c$, calculated by Dingle,[4] for as may be seen from his derivation the coefficient of this term depends on the form of the Poisson sum exactly as does the coefficient of Table I. Using $\alpha=\frac{1}{2}$, we should thus obtain a paramagnetism roughly three times the magnitude of the diamagnetism Dingle reports.

For the idealized model using the sharp, impenetrable wall, there is no question but what we should use $\alpha=\frac{3}{4}$, as Dingle has done. However, for an approximate calculation of the susceptibility of the electrons in a real metal, the choice is not at all clear: the rise of potential at the wall is not infinitely sharp and is, moreover, of finite height, so that it is far from obvious that $\alpha=\frac{3}{4}$

[19] L. I. Schiff, *Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1949), p. 186.

is a good choice; yet the wall may be sufficiently sharp so that $\alpha=\frac{1}{2}$ is not sufficiently accurate.

To investigate the question of the best choice of α, we may compare the exact eigenvalues of certain one-dimensional problems with the eigenvalues obtained from a modified WKB phase integral in which α replaces the usual $\frac{1}{2}$ and is determined for each eigenstate such that the WKB eigenvalue agrees with the exact result. First, we consider the effect of having the surface potential barrier of finite height. For the potential

$$V(x)=\begin{cases}\infty, & x<-L\\ 0, & -L<x<0\\ W, & x>0\end{cases} \tag{4.2}$$

the wave function for $-L<x<0$ is, apart from a multiplicative constant, $\psi\sim\sin[k(x+L)]$, where

$$k=\hbar^{-1}(2mE)^{\frac{1}{2}},$$

and E is the energy eigenvalue. For $x>0$ and $E<W$, $\psi\sim e^{-\kappa x}$, $\kappa=\hbar^{-1}[2m(W-E)]^{\frac{1}{2}}$. The eigenvalue E is determined by equating the logarithmic derivatives $(1/\psi)(\partial\psi/\partial x)$ at $x=0$. This yields the equation for E:

$$k\cot(kL)=-\kappa. \tag{4.3}$$

For the WKB result we integrate

$$\int_{-L}^{0}(2mE)^{\frac{1}{2}}dx=(n+\alpha)\hbar\pi, \quad n=0, 1, 2, \cdots \tag{4.4}$$

and obtain $kL=(n+\alpha)\pi$. We regard this as an equation for α, substitute it in (4.3), and obtain

$$\cot(\pi\alpha)=-\kappa/k=-[(W/E)-1]^{\frac{1}{2}}. \tag{4.5}$$

We thus obtain Table II. Here in addition to α we tabulate $\alpha'=\alpha-\frac{1}{4}$. In (4.2) the potential suffers an infinite jump at $x=-L$. Since in the problems mentioned earlier we reduce α by $\frac{1}{4}$ on replacing a sharp barrier by a slowly rising potential, it appears that α' would be a proper choice if in the potential (4.2) we made gradual the potential rise at $x=-L$.

We have also investigated the problem with the potential

$$V(x)=\begin{cases}\infty, & x<-L\\ 0, & -L<x<0.\\ \frac{1}{2}m\omega^2x^2, & x>0\end{cases} \tag{4.6}$$

The detailed calculations may be found in reference 16. The results are given in Table III.

Two other simple problems give further information concerning the proper choice of α in different situations. Table IV summarizes the results for the potential

$$V(x)=\begin{cases}W, & |x|>L/2\\ 0, & |x|<L/2\end{cases}, \tag{4.7}$$

and Table V summarizes those for

$$V(x)=\begin{cases}\frac{1}{2}m\omega^2x^2, & x>0\\ W, & x<0\end{cases}, \tag{4.8}$$

where $W\gg\hbar\omega$.

TABLE II. Tabulation[a] of the parameters α and α' for the one-dimensional potential $V(x)=\infty$, $x<-L$; $V(x)=0$, $-L<x<0$; $V(x)=W$, $x>0$, for various values of the ratio E/W.

E/W	α	α'
$\rightarrow1$	$\rightarrow\frac{1}{2}$	$\rightarrow\frac{1}{4}$
$\frac{3}{4}$	$\frac{2}{3}$	5/12
$\frac{1}{2}$	$\frac{3}{4}$	$\frac{1}{2}$
$\frac{1}{4}$	$\frac{5}{6}$	7/12
$\rightarrow0$	$\rightarrow1$	$\rightarrow\frac{3}{4}$

[a] α is the parameter appearing in the WKB phase integral equation which brings the value of the energy eigenvalue E obtained by the WKB approximation into agreement with the exact value. Also $\alpha'=\alpha-\frac{1}{4}$.

The results of Tables II to V suggest the following behavior of α in the WKB evaluation of the eigenvalues of any differential equation which can be regarded as the Schrödinger equation for a one-dimensional electron confined by two potential barriers: if the barriers rise sharply and are of height W very much greater than the energy E of the eigenstate under consideration, then α is approximately unity; if one of the barriers is made to rise more gradually, α will be diminished somewhat, but it will not fall below roughly $\frac{3}{4}$; if the other barrier is similarly smoothed, α can be diminished further to about $\frac{1}{2}$; if the height W of one barrier is reduced so that E/W approaches unity, α will drop further by as much as about $\frac{1}{2}$; if the second barrier height is similarly reduced, α can drop by an additional $\frac{1}{2}$. The effect on α of making any one of these changes appears to be approximately independent of the other changes, so that the changes in α from these various alterations are roughly additive. It thus appears that if both barriers are gradual and if E/W is only slightly less than unity for both barriers, α can be as low as $-\frac{1}{2}$, provided, of course, that the eigenstate is not the one of lowest energy, since α must always be positive for this state to yield a positive zero-point energy.

In a real metal the energy difference between the Fermi level and the bottom of the conduction band is an appreciable fraction of the difference between the bottom of the band and the top of the surface barrier. We may crudely estimate the "sharpness" of the barrier in terms of Table III by representing the barrier by $\frac{1}{2}m\omega^2(r-R)^2$ and by defining ω in terms of the thickness of the wall region $(r'-R)$ and the Fermi energy ζ.

TABLE III. Tabulation of the parameter α for the one-dimensional potential $V(x)=\infty$, $x<-L$; $V(x)=0$, $-L<x<0$; $V(x)=\frac{1}{2}m\omega^2x^2$, $x>0$, for various values of the ratio $E/\hbar\omega$. For definition of α see footnote to Table II.

$E/\hbar\omega$	α
$\rightarrow\infty$	$\rightarrow\frac{3}{4}$
6	0.750
2	0.753
1	0.743
$\frac{1}{2}$	0.750
1/10	0.838
1/100	0.938
$\rightarrow0$	$\rightarrow1$

TABLE IV. Tabulation of the parameter α for the one-dimensional potential $V(x)=W$, $|x|>L/2$; $V(x)=0$, $|x|<L/2$, for various values of the ratio E/W. For definition of α see footnote to Table II.

E/W	α
$\rightarrow 1$	$\rightarrow 0$
$\frac{3}{4}$	$\frac{1}{3}$
$\frac{1}{2}$	$\frac{1}{2}$
$\frac{1}{4}$	$\frac{2}{3}$
$\rightarrow 0$	$\rightarrow 1$

Setting $\frac{1}{2}m\omega^2(r'-R)^2=\zeta$, we obtain

$$(\zeta/\hbar\omega)=\hbar^{-1}(r'-R)(\tfrac{1}{2}m\zeta)^{\frac{1}{2}}. \tag{4.9}$$

Using $\zeta\sim 10^{-12}$ erg, $(r'-R)\sim 10^{-8}$ cm, and the free-electron mass, we find $(\zeta/\hbar\psi)\sim 1/10$. From Table III we see that this gives us an intermediate value for α, especially since most occupied states have energies below ζ.

It appears from these considerations that for a given model of a real metal we might be able to satisfactorily estimate α as a function of the electron energy E. The calculation of the free energy and magnetic moment is not seriously complicated by the variation of α with E. A derivation based on Dingle's work is sketched in the Appendix, although no attempt is made to obtain a numerical result for any model. A numerical result will evidently depend on the details of the model chosen, and such a calculation would be of especial interest only when and if such size corrections to the susceptibility are located experimentally.

Finally we should remark that we obtain an additional term in the moment of the system if the wall potential is made gradual. To estimate this, we consider the potential

$$V(r)=\begin{cases}\frac{1}{2}m\omega^2(r-R)^2, & r\gtrsim R\\ 0, & r\lesssim R\end{cases}. \tag{4.10}$$

Using the usual WKB analysis (see reference 16), we find that the ratio of this additional term to the usual surface term [the second term in (3.8)] is roughly $(eH/\omega mc)(\zeta/\beta H)^{\frac{1}{2}}$. Estimating ω from wall thickness as above, we find this to be about 10^{-2} or less for reasonable values of the parameters. We may thus infer that for any other form of wall potential confined to a sufficiently thin layer this contribution is negligible.

V. COMMENTS

The assumption has been tacitly made throughout this paper that the WKB approximation determines the energy eigenvalues with sufficient accuracy for the calculation of the surface corrections to the susceptibility. This assumption might be questioned in so far as it is well known that small errors in the eigenvalues can lead to a tremendous error in the calculated value of the susceptibility, and we have seen, moreover, that surface corrections depend critically in their numerical value and sign (though not in order of magnitude) on the choice of α in the WKB phase integral condition. However, the WKB calculation of the eigenvalues is very accurate when the quantum number n is large, as it is in the present problem for the vast majority of states. Moreover, although it is necessary to modify the WKB phase integral condition by choosing the value of $\alpha(E_p)$ appropriate to the given form of the surface potential, it appears from the one-dimensional problems studied above that this choice can be made in a consistent and predictable manner. It seems from these problems and from the procedure outlined in the appendix for calculating the susceptibility once $\alpha(E_p)$ is chosen that it should be possible to calculate the susceptibility for a given surface potential with accuracy of at least ten or twenty percent. Finally, it is reassuring that with the sharp, impenetrable wall $[\alpha(E_p)=\frac{3}{4}]$ Dingle has obtained the same results for small systems ($R\ll R_c$) using perturbation procedures with the exact zero-field wave functions[3] [Proc. Roy. Soc. (London) **A212**, 47 (1952)] that he has obtained with the WKB method.[4]

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APPENDIX

It is quite easy to modify Dingle's analysis[4] to take into account the variation of α with E. Instead of inquiring into the location of the zeros of the wave functions, as Dingle does, we determine the eigenvalues with the modified phase integral condition [from (3.5)]

$$n+1=1-\alpha(E_p)+\left(\frac{2m}{\pi^2\hbar^2}\right)^{\frac{1}{2}}\int_{r_1}^{r_2 \text{ or } R}\times\left[E_p-\beta Hs-\frac{\hbar^2s^2}{2mr^2}-\frac{e^2H^2r^2}{8mc^2}\right]^{\frac{1}{2}}dr. \tag{A1}$$

Here $E_p=E-\hbar^2k_z^2/2m$, the upper limit of integration is the smaller of r_2 or R, and the eigenvalues are determined by the condition that n be a positive integer or

TABLE V. Tabulation of the parameter α for the one-dimensional potential $V(x)=\frac{1}{2}m\omega^2x^2$, $x>0$; $V(x)=W$, $x<0$, for various values of the ratio E/W, where $\hbar\omega\ll W$. For definition of α see footnote to Table II.

E/W	α
$\rightarrow 1$	$\rightarrow\frac{1}{4}$
$\frac{1}{2}$	$\frac{1}{2}$
$\rightarrow 0$	$\rightarrow\frac{3}{4}$

zero. Temporarily confining our attention to two dimensions, as in Dingle's work, we find that the number of states with a given s, given spin orientation, and energies below any arbitrary value of E_p is the largest integer $[n+1]$ less than the quantity (in general not an integer) $(n+1)$ defined for that E_p by (A1). This is obtained from the Poisson sum formula exactly as in Dingle's analysis,

$$[n+1]=-\tfrac{1}{2}+\sum_{P=-\infty}^{\infty}\int_0^{(n+1)} e^{2\pi i x P}dx, \qquad \text{(A2)}$$

and $Z_p(E_p, H)$, the number of states in the two-dimensional system with energies below E_p, is then to sufficient accuracy obtained by inegrating over s and multiplying by two for spin degeneracy. We then follow Dingle exactly in transforming to three dimensions and obtaining $\int_0^E ZdE$.

When in (A1), for particular values of s and E_p, the larger turning point r_2 is less than R, the eigenstates with energies close to E_p are what Dingle calls "exponential states," or "bulk states" in our terminology. For these values of s and E_p, α is then $\frac{1}{2}$. For "surface states" or "trigonometrical states" (Dingle) for which which $r_1<R<r_2$, $\alpha(E_p)$ will depend on the form of the wall potential. It seems reasonable to assume that to sufficient accuracy it will depend only on E_p, and in particular not on s.

Evaluation of terms in $\int_0^E ZdE$ for exponential states is unchanged from Dingle's analysis. For the trig states, we replace Dingle's Eq. (3.4) by (A3), where we use his notation for ease of comparison except in replacing his $\sum_1^{P(E)}1$ by $[n+1]$, the same quantity,

$$[n+1]=\tfrac{1}{2}-\alpha(E_p)+\int_{x_-}^{\lambda}\frac{\{\eta^2 x/\lambda-(l\pm x)^2\}^{\frac{1}{2}}}{2\pi x}dx + \sum_{P=-\infty}^{\infty}{}'\frac{\exp(2\pi i P[1-\alpha(E_p)])}{2\pi i P} \times\exp\left[2iP\int_{x_-}^{\lambda}\frac{\{\eta^2 x/\lambda-(l\pm x)^2\}^{\frac{1}{2}}}{2x}dx\right]. \qquad \text{(A3)}$$

Dingle's calculations of the various integrals may now be used, and we obtain to replace his (3.19), (3.20), (3.21),

$$Z_p(E_p, H)=S'(E_p)(\eta\mp 2\lambda)^{\frac{3}{2}}/\eta^{\frac{1}{2}}, \qquad \text{(A4)}$$

$$S'(E_p)=(-\tfrac{1}{3})!S(E_p)/\pi(12)^{\frac{1}{2}}, \qquad \text{(A5)}$$

$$S(E_p)=2\sum_{P=1}^{\infty}P^{-5/3}\cos(2\pi P\alpha(E_p)+\pi/6). \qquad \text{(A6)}$$

The only change is thus to make S' and S dependent on E_p. Finally, defining $Q'(\eta)=S'(E)$, we obtain to replace Dingle's (3.22) and (3.23),

$$\int_0^E ZdE=-\frac{\pi\hbar^2 L\eta^{10/3}}{2mR^3}\mathbf{K}\left(\frac{2\lambda}{\eta},\eta\right), \qquad \text{(A7)}$$

$$-\tfrac{1}{2}\pi^2\mathbf{K}(a,\eta)=\int_0^1 Q'(\eta t)(t+a)^{\frac{3}{2}}t^{\frac{3}{2}}(1-t^2)^{\frac{1}{2}}dt + \int_a^1 Q'(\eta t)(t-a)^{\frac{3}{2}}t^{\frac{3}{2}}(1-t^2)^{\frac{1}{2}}dt. \qquad \text{(A8)}$$

We finally obtain for the low-temperature steady susceptibility [Dingle (6.5)] per unit volume

$$\chi=-(e^2R^{\frac{1}{2}}E_0^{\frac{3}{2}}/2^{\frac{1}{2}}m^{\frac{1}{2}}c^2\hbar^{4/3})\{\mathbf{K}'(a,\eta_0)+\eta_0^{-\frac{1}{2}}\mathbf{J}'(a)\}, \qquad \text{(A9)}$$

where

$$\mathbf{K}'(a,\eta_0)=-(4/3\pi^2 a)\left\{\int_0^1 Q'(\eta_0 t)(t+a)^{-\frac{1}{2}}t^{\frac{3}{2}}(1-t^2)^{\frac{1}{2}}dt - \int_a^1 Q'(\eta_0 t)(t-a)^{-\frac{1}{2}}t^{\frac{3}{2}}(1-t^2)^{\frac{1}{2}}dt\right\}. \qquad \text{(A10)}$$

The important oscillatory part of the susceptibility for $R>R_c$ is unchanged in this analysis since it arises from the exponential states alone. For $R\ll R_c$ the oscillatory susceptibility will depend on the choice of $\alpha(E_p)$.

Finally, we give in Table VI the values of $S(E)$ for various values of $\alpha(E)$.

TABLE VI. Tabulation of $S(E)$ as a function of the parameter $\alpha(E)$.[a] Values of $S(E)$ are in error by no more than 0.004.

$\alpha(E)$	$S(E)$	$\alpha(E)$	$S(E)$
0.00	3.678	0.50	−1.362
0.05	1.254	0.55	−1.126
0.10	0.204	0.60	−0.824
0.15	−0.496	0.65	−0.456
0.20	−0.986	0.70	−0.028
0.25	−1.312	0.75	0.456
0.30	−1.516	0.80	0.998
0.35	−1.608	0.85	1.592
0.40	−1.612	0.90	2.236
0.45	−1.522	0.95	2.934
		1.00	3.678

[a] $S(E)$ is defined in Eq. (A6) of the Appendix.