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ON THE DIAMAGNETISM OF FREE ELECTRONS

by

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ABSTRACT

ON THE DIAMAGNETISM OF FREE ELECTRONS

The effect of proximity to an infinite potential wall boundary on the eigenvalues of single particle free electron states in a magnetic field is calculated. A general method for calculating the number of states below a specified energy is described and the diamagnetic susceptibility is calculated for three approximations. It is found that the Landau approximation gives surprisingly good results considering its simplicity. A classification of much of the important work in this subject is presented in the introduction, and a possible discrepancy in the usual applications of the WKB approximation is discussed in an appendix.

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THE DIAMAGNETISM OF FREE ELECTRONS

INTRODUCTION

How can the effect of the boundaries on the free electron diamagnetism be calculated? Bohr[1] and van Leeuwen[2] have shown that classical statistical mechanics gives no magnetic behavior for a free electron gas. In any finite container the magnetic moment of all the electrons whose orbits are entirely inside the box exactly cancels an equal and opposite magnetic moment due to those electrons whose orbits intersect the boundaries.[3] Thus the effect of the boundary seems to be quite important in determining the behavior of a free electron gas. In fact, if the boundary is not considered properly, an erroneously large diamagnetism results, which in several cases has been interpreted as an explanation for the Meissner effect associated with super conductivity.[4] However, Landau[5] found that since the orbital motion of the electron in a magnetic field is periodic, the component of the energy in the plane normal to the field is quantized in units of $2\mu H$ where $\mu = e\hbar/2mc$ is the Bohr magneton. This quantization of the energy led to only a small diamagnetism when the boundary conditions were chosen so that the centers of the electron orbits are required to remain inside a large, but finite container.

Landau's treatment of the boundary conditions seemed so crude that many other attempts were made to improve the accuracy of his work.[6] Essentially two different approaches were used for the

calculation of the magnetization of a system of free electrons obeying Fermi statistics confined in a finite box. The first defines the magnetization in terms of the magnetic moment due to the current density at each point in the container. Teller,[7] van Vleck,[8] Papapetrou,[9] and Linhard[10] use this approach by computing the net current at each point in the container. This superposition of currents from the different states gives zero at all points far from the walls. It also gives zero near the wall if classical statistics is used and the electrons are allowed a continuous range of energy. However, the discrete allowed energies of quantum statistical mechanics, with careful consideration of the electrons striking the boundaries, leads to the small but finite "Landau" diamagnetism. The difficulty of the first approach resolves itself into the determination of the wave functions and the corresponding currents near the walls, whereas the second approach requires only the energy eigenvalues.

Most workers have chosen the second approach using the magnetization

$$M = \sum_i \left(-\frac{\partial E_i}{\partial H}\right) \frac{1}{1 + e^{(E_i - \eta)/kT}}$$

computed by means of the Helmholtz free energy,

$$F = N\eta - \int_0^\infty Z(E,H) \frac{1}{1 + e^{(E-\eta)/kT}} \, dE$$

through the relation,

$$M = -\left(\frac{\partial F}{\partial H}\right)_{T,V} .$$

The essential difficulty of this method lies in the calculation of the function, Z(E,H), the number of single particle states in the

system below an energy, E, for a magnetic field, H, which appears in the free energy. The operator methods of Peierls,[11] and Saénz and O'Rourke,[12] and the density-matrix approach of Sondheimer and Wilson[13] improve the calculation of the sum and arrive at expressions for the function, Z(E,H), which are exact in the mathematical sense that no other approximations are used other than the assumption that the Landau boundary condition or its equivalent is valid. In these calculations, there is no convenient way of considering any but the simplest boundary conditions.

The most direct approach to the influence of various types of boundary conditions on the electrons near the walls of the box requires the eigenvalues of the solutions of the Schrödinger equation for a free electron in a magnetic field with the boundary conditions on the electron wave functions given at the edges of the box. The number of states function, Z(E,H), is then found by summing over the eigenvalues in the whole range of possible quantum numbers prescribed by the boundary conditions.

Landau achieved this result by assuming that the eigenvalues do not depend on the position of the center of the electron orbit with respect to the boundary, requiring only that the centers remain inside the box. (This condition or its equivalent is inherent in the work of all the previously mentioned authors). The first two terms of an Euler-Maclaurin expansion[14] were used to approximate the sum over quantum numbers in obtaining the

constant "Landau" diamagnetism, whose magnitude turns out to be exactly one-third the Paul spin paramagnetism.[15] Landau and Peierls[16] later applied the Poisson summation formula[17] to the sum over quantum numbers in the calculation of the function, Z(E,H), and obtained an oscillatory behavior which is qualitatively similar to that observed experimentally by de Haas and van Alphen.[18]

Dingle,[19] Ham,[20] and Lifshitz and Kosyvich[21] use the WKB approximation to find the eigenvalues as a function of the position of the electron orbital center with respect to the boundary, the magnetic field, and the quantum numbers, and then used the Poisson summation formula to evaluate Z(E,H). Osborne[22] and Steele[23] use the WKB approximation and number theoretical methods to obtain essentially the same results. A possible discrepancy in the WKB approximation will be discussed in an appendix.

Minnaja[24] and the present author attempt to calculate the eigenvalues more exactly for an infinite potential wall at the boundaries of the box, and show that the crude boundary condition applied by Landau gives values for Z(E,H) that are really very close to what would be obtained by an exact solution of the boundary value problem with an infinite wall.

The present paper presents a general method for taking explicit account of the effects of the wall of the box on the free electron diamagnetism in terms of the functional dependence of the energy eigenvalues on the position of the orbital center relative to

the walls. These eigenvalues are then used to calculate the number of states, $Z(E,H)$, in quantum number space with energy less than E, by means of the Euler-Maclaurin expansion. Using Fermi statistics, the Helmholtz free energy, F, is calculated from $Z(E,H)$. The magnetization and the susceptibility then follow directly from the free energy.

Consideration of the free electron case permits good approximate calculations which may be extended to more realistic models which would consider the effects of (a) the lattice field, (b) the Coulomb interaction between the electrons, (c) collisions of the electrons with phonons and with impurities, and (d) the scattering properties of the surface.

DETERMINATION OF EIGENVALUES

The simplest and most direct way to calculate the effect of the boundary on the susceptibility, χ, of a system of free electrons in a magnetic field, H, comes from the statistical mechanical relation between the magnetization,

$$M = -\left(\frac{\partial F}{\partial H}\right)_{T,V}$$

and the Helmholtz free energy,

$$F = N\eta - \int_0^\infty Z(E,H)\,\frac{1}{1+e^{(E-\eta)/kT}}\,dE .$$

The Fermi energy, η, is defined either in terms of the total number of electrons in the system,[25]

$$N = \int_0^\infty \left(\frac{\partial Z}{\partial E}\right)_H \frac{1}{1+e^{(E-\eta)/kT}}\,dE$$

or by the relation

$$\left(\frac{\partial F}{\partial \eta}\right)_{T,V,H} = 0$$

which are equivalent statements.

The above definition of the magnetization in terms of the free energy is equivalent to the definition in terms of the individual magnetic moments of the electron states. To show this, write

$$M = -\left(\frac{\partial F}{\partial H}\right)_{T,V} = -\left(\frac{\partial F}{\partial H}\right)_{T,V,\eta} - \left(\frac{\partial F}{\partial \eta}\right)_{T,V,H}\left(\frac{\partial \eta}{\partial H}\right)_{T,V}$$

but since

$$\left(\frac{\partial F}{\partial \eta}\right)_{T,V,H} = 0$$

we have

$$M = -\left(\frac{\partial F}{\partial H}\right)_{T,V,\eta} = \int_0^\infty \left(\frac{\partial Z}{\partial H}\right)_{T,V,E} \frac{1}{1+e^{(E-\eta)/kT}}\,dE .$$

We may also write

$$\left(\frac{\partial Z}{\partial H}\right)_{T,V,E} = -\left(\frac{\partial Z}{\partial E}\right)_{T,V,H}\left(\frac{\partial E}{\partial H}\right)_{T,V,Z}$$

but $\left(\frac{\partial Z}{\partial E}\right)_{T,V,H} dE$ is just the density of states function used to transform

the sum to an integral, so that

$$M = \sum_i \left(-\frac{\partial E_i}{\partial H}\right)_{T,V} \frac{1}{1 + e^{(E_i - \eta)/kT}}$$

The number of states, Z(E,H), below an energy, E, is obtained by summing all those electron eigenstates in quantum number space with an energy less than E in a magnetic field, H. The required energy eigenstates come from the solutions of the Schrödinger equation for a free electron in a magnetic field when the appropriate boundary conditions on the electron wave functions are considered.

In order to solve the Schrödinger equation, the Hamiltonian of an electron in an electromagnetic field may be written

$$\mathcal{H}(\vec{p},\vec{q},t) = \frac{1}{2m}\left[\vec{p} - \frac{e}{c}\vec{A}(\vec{q},t)\right]^2 + e\,\varphi(\vec{q},t)$$

in Gaussian units. In a more realistic model the potential, φ, would include the periodic lattice field as well as other effects. Here, the potential is assumed to be zero everywhere except outside the box in the x-direction where it is infinite, that is,

$$\varphi(\vec{q},t) = 0 \quad |x| < \frac{L_1}{2} \;, \quad \varphi(\vec{q},t) \to \infty \quad |x| > \frac{L_1}{2} .$$

A uniform magnetic field, H, along the z-direction may be obtained without loss of generality by choosing the vector potential,

$$\vec{A}(\vec{q},t) = (0, Hx, 0).$$

The relation between magnetic induction and the vector potential,

$$\vec{B} = \nabla \times \vec{A}$$

then yields the external induction

$$\vec{B} = \hat{K} H$$

as required. The electrons themselves contribute a term, χH, to the internal induction

$$B' = H(1 + 4\pi\chi)$$

The susceptibility, χ, is of the order of 10^{-6} cgs units, thus this contribution is neglected here, although Linhard[26] and Klein[27] consider this question some in detail.

By replacing the momentum, p, by its equivalent quantum mechanical operator, $\frac{\hbar}{i}\frac{\partial}{\partial q}$, the classical Hamiltonian is taken over into quantum mechanics as the Schrödinger equation for energy characteristic states as follows:

$$\mathcal{H}\psi = -\frac{\hbar^2}{2m}\left[\frac{\partial^2\psi}{\partial x^2} + \left(\frac{\partial}{\partial y} - i\frac{eH}{\hbar c}x\right)^2\psi + \frac{\partial^2\psi}{\partial z^2}\right] = E\psi.$$

This equation may be separated by choosing solutions of the following form:

$$\psi(x,y,z) = u(x)\, e^{ik_y y + ik_z z}.$$

Solutions of this type permit periodic boundary conditions to be applied in the y,z-directions with propagation vector components

$$k_y = \frac{2\pi l}{L_2}, \quad k_z = \frac{2\pi m}{L_3}$$

where l,m are integers.[28] The equation for U(x) then becomes

$$\frac{d^2u}{dx^2} + \left[\frac{2m}{\hbar^2}E - k_z^2 - \left(k_y - \frac{eH}{\hbar c}x\right)^2\right]u = 0$$

which is the equation for a simple harmonic oscillator with center at $x_0 = \frac{\hbar c}{eH}k_y$. The solutions of this equation must then satisfy the applied boundary conditions, the simplest of which are that the solutions, U(x), be zero at the boundary,[29] that is,

$$u(x) = 0, \quad x = +\frac{L_1}{2}, -\frac{L_1}{2}.$$

To facilitate the mathematical consideration of this problem, perform the following transformations:

$$\lambda = \frac{E}{\mu H} - \frac{\hbar c}{e H} k_z^2$$

where $\mu = e\hbar/2mc$ is the Bohr magneton and

$$\zeta = \sqrt{\frac{eH}{\hbar c}}\,(x_0 - x) \,.$$

The sign of ζ (Greek Zeta) is chosen so that the eigenvalues, λ_ν, can be expressed in terms of the variables

$$\zeta_0 = \sqrt{\frac{eH}{\hbar c}}\,(x_0 - \tfrac{L}{2}) \quad , \quad \zeta_1 = \sqrt{\frac{eH}{\hbar c}}\,(x_0 + \tfrac{L}{2})$$

which are proportional to the distance of the center of the electron orbit, x_0, from the respective boundaries, $+\frac{L}{2}$, and $-\frac{L}{2}$. After making the required transformation, the resulting equation is

$$\frac{d^2u(\zeta)}{d\zeta^2} + (\lambda - \zeta^2)\,u(\zeta) = 0 \,.$$

The boundary conditions usually applied to the harmonic oscillator equation require that the solutions, $u_\lambda(\zeta)$, approach zero as ζ approaches plus or minus infinity. This is equivalent to requiring that

$$\zeta_0 \to -\infty \quad , \quad \zeta_1 \to +\infty$$

that is, that the center of the electron orbit be far from both boundaries. These solutions are obtained by transforming to a new dependent variable

$$v(\zeta) = u(\zeta)\, e^{\frac{1}{2}\zeta^2}$$

The derivatives are

$$u' = (v' - \zeta v)\, e^{-\frac{1}{2}\zeta^2}$$

and

$$u'' = (v'' - 2\zeta v' + \zeta^2 v - v)\, e^{-\frac{1}{2}\zeta^2}$$

Thus

$$u'' + (\lambda - \zeta^2)\, u = 0$$

transforms to

$$v'' - 2\zeta v' + (\lambda - 1)\, v = 0$$

among whose solutions are the Hermite polynomials, $H_n(\zeta)$, with eigenvalues, $\lambda = 2n+1$. Thus for a box which is infinitely large in the x-direction (such that I_1 approaches infinity and x_0 approaches zero, because x_0 must be far from either boundary), the proper orthonormal electron wave functions are

$$u_\lambda(\zeta) = \{2^n n!\, \sqrt{\pi}\}^{-\frac{1}{2}}\, e^{-\frac{1}{2}\zeta^2}\, H_n(\zeta).$$

For a box that is large but finite in the x-direction, the set of zero-order eigenvalues $\{2n+1\}$ approximate the actual eigenvalues,[30] λ_ν, extremely well, as long as the distance from the center of the electron orbit, x_0, to either boundary, $x = \pm \frac{L_1}{2}$, is much greater than the classical radius of the electron orbit, $r = \frac{mcv}{eH}$. Since the electron wave function has an inflection point, $u'' = 0$, at the radius of the electron orbit, it is sufficient to require that the inflection point lie well inside the boundary. This is equivalent to the conditions

$$\lambda - \zeta_0^2 >> 0, \qquad \lambda - \zeta_1^2 >> 0.$$

The solutions proportional to the Hermite polynomials are also the correct ones whenever the boundary of the box happens to fall exactly on a zero of a Hermite polynomial, since the condition that

$$u_\lambda(\zeta) = 0$$

at the boundary is satisfied. A graph of the behavior of the eigenvalues, $\lambda_\nu(\zeta_0)$, as a function of the boundary parameter, ζ_0 (the position of the center relative to the boundary) may be constructed from a table of the zeros of the Hermite polynomials,[31] which are circled in the graph (Figure I). Only within the graph of the classical turning points, $\lambda = \zeta_0^2$, is there any great deviation from the zero-order eigenvalues.[32]

Further solutions of the equation

$$u'' + (\lambda - \zeta^2) u = 0$$

are obtained by transforming to the independent variable

$$\xi = \zeta^2 .$$

The derivatives are

$$\frac{dV}{d\zeta} = \frac{dV}{d\xi}\frac{d\xi}{d\zeta} = 2\xi^{\frac{1}{2}}\frac{dV}{d\xi}$$

and

$$\frac{d^2V}{d\zeta^2} = \frac{d^2V}{d\xi^2}\left(\frac{d\xi}{d\zeta}\right)^2 + \frac{dV}{d\xi}\frac{d^2\xi}{d\zeta^2} = 4\xi\frac{d^2V}{d\xi^2} + 2\frac{dV}{d\xi} .$$

Thus

$$\frac{d^2V}{d\zeta^2} - 2\zeta\frac{dV}{d\zeta} + (\lambda - 1) V = 0$$

transforms to

$$\xi\frac{d^2V}{d\xi^2} + \left(\frac{1}{2} - \xi\right)\frac{dV}{d\xi} - \left(\frac{1-\lambda}{4}\right) V = 0 .$$

The confluent hypergeometric equation[33]

$$z\frac{d^2F}{dz^2} + (\gamma - z)\frac{dF}{dz} - \alpha F = 0$$

is satisfied by the functions

$${}_1F_1(\alpha; \gamma; z) = 1 + \frac{\alpha}{\gamma}z + \frac{\alpha(\alpha+1)}{\gamma(\gamma+1)}\frac{z^2}{2!} + \cdots$$

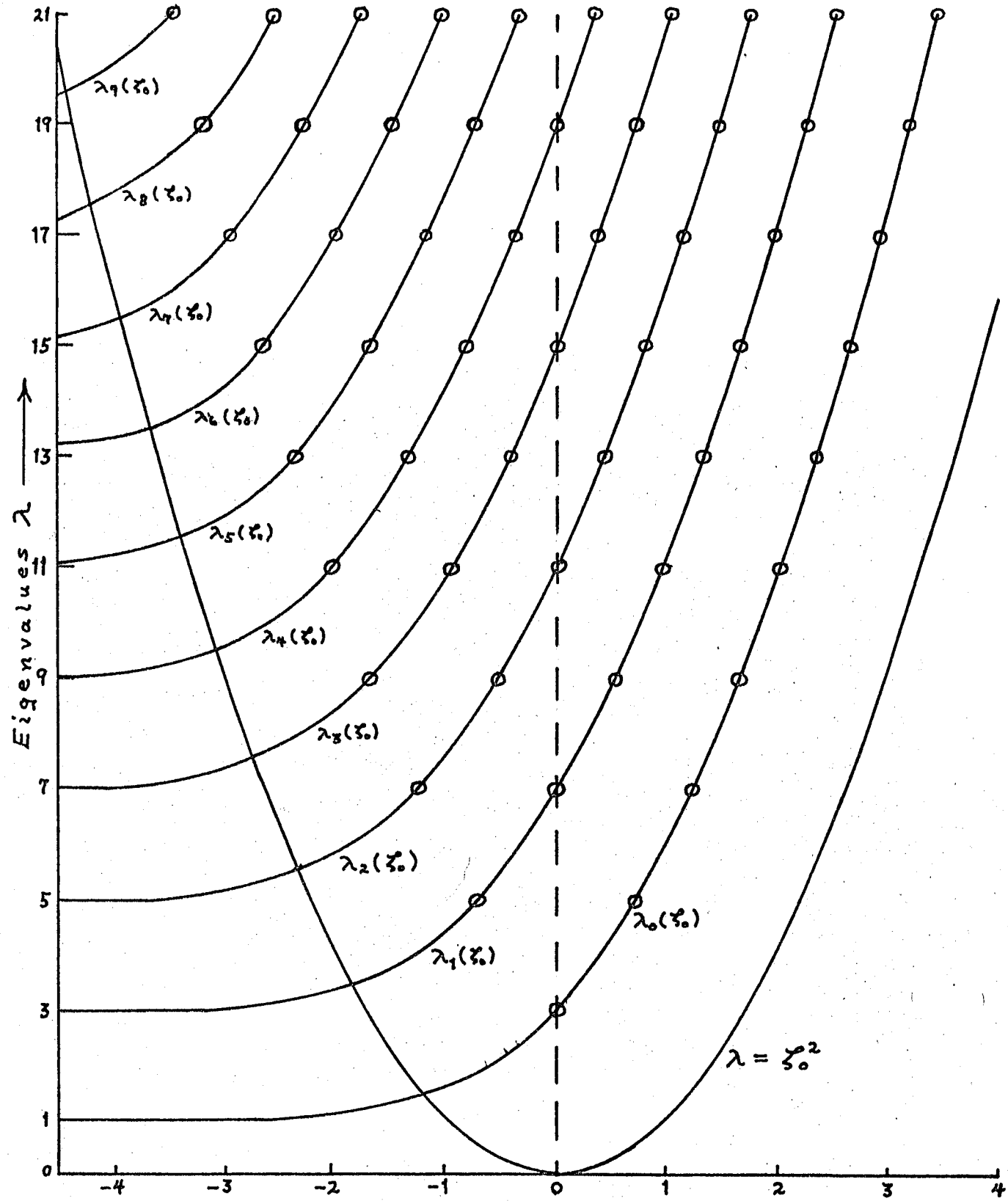
21
19
17
15
13
11
9
7
5
3
1
0
Eigenvalues λ
$\lambda_9(\zeta_0)$
$\lambda_8(\zeta_0)$
$\lambda_7(\zeta_0)$
$\lambda_6(\zeta_0)$
$\lambda_5(\zeta_0)$
$\lambda_4(\zeta_0)$
$\lambda_3(\zeta_0)$
$\lambda_2(\zeta_0)$
$\lambda_1(\zeta_0)$
$\lambda_0(\zeta_0)$
$\lambda = \zeta_0^2$
-4
-3
-2
-1
0
1
2
3
4
Boundary Parameter ζ_0 ⟶

Figure I

and

$$z^{1-\gamma}\ {}_1F_1(\alpha-\gamma+1;\ 2-\gamma;\ z)\,.$$

Thus the general solution of

$$u'' + (\lambda - \zeta^2)\,u = 0$$

may be written as

$$u_\lambda(\zeta) = e^{-\frac{1}{2}\zeta^2}\left\{ A\ {}_1F_1\left(\tfrac{1-\lambda}{4};\ \tfrac{1}{2};\ \zeta^2\right) + \zeta\, B\, {}_1F_1\left(\tfrac{3-\lambda}{4};\ \tfrac{3}{2};\ \zeta^2\right)\right\}.$$

The two constants A and B permit the function to satisfy two independent boundary conditions.[34]

For simplicity, the box is treated as if it were a potential well in the x-direction with the potential growing to infinity outside the boundaries at $x = \pm \frac{L_1}{2}$, so that the electron wave function, $u_\lambda(\zeta)$, must be zero outside the box. Thus the boundary conditions are

$$u_\lambda(\zeta_0) = 0 \quad , \quad u_\lambda(\zeta_1) = 0$$

that is,

$$A\ {}_1F_1\left(\tfrac{1-\lambda}{4};\ \tfrac{1}{2};\ \zeta_0^2\right) + \zeta_0\, B\, {}_1F_1\left(\tfrac{3-\lambda}{4};\ \tfrac{3}{2};\ \zeta_0^2\right) = 0$$

and

$$A\ {}_1F_1\left(\tfrac{1-\lambda}{4};\ \tfrac{1}{2};\ \zeta_1^2\right) + \zeta_1\, B\, {}_1F_1\left(\tfrac{3-\lambda}{4};\ \tfrac{3}{2};\ \zeta_1^2\right) = 0$$

two homogeneous algebraic equations in the two constants A and B. The negative of the ratio of the coefficients yields

$$-\frac{A}{B} = \frac{\zeta_0\, {}_1F_1\left(\frac{3-\lambda}{4};\ \frac{3}{2};\ \zeta_0^2\right)}{{}_1F_1\left(\frac{1-\lambda}{4};\ \frac{1}{2};\ \zeta_0^2\right)} = \frac{\zeta_1\, {}_1F_1\left(\frac{3-\lambda}{4};\ \frac{3}{2};\ \zeta_1^2\right)}{{}_1F_1\left(\frac{1-\lambda}{4};\ \frac{1}{2};\ \zeta_1^2\right)}$$

a transendental equation for the eigenvalues, $\lambda_\nu(\zeta_0, \zeta_1)$, in terms of the two voundary parameters ζ_0 and ζ_1.

A further simplification results if the assumption[35] is made that the length, L_1, of the box in the x-direction and the magnetic field, H, are large enough so that any electron feels the influence of only one boundary at a time, that is

$$L_1 > r_{max} = \frac{c}{eH}\sqrt{2m\eta}$$

where η is the Fermi energy, about 10 eV. This is equivalent to the box being larger than the diameter of the biggest electron orbit, or

$$(\zeta_1 - \zeta_0)^2 = \frac{eH}{\hbar c} L_1 > \lambda_{max} .$$

Since both boundaries influence the eigenvalues, $\lambda_\nu(\zeta_0, \zeta_1)$, in the same way, it is sufficient to consider the electron center, x_0, as being close to only one boundary, say, $x = +\frac{L_1}{2}$. Thus ζ_1 may be treated as if it were very large while ζ_0 is small in comparison. The asymptotic expansion of the confluent hypergeometric function gives

$${}_1F_1(\alpha;\gamma;z) \sim \frac{\Gamma(\gamma)}{\Gamma(\alpha)} e^z z^{\alpha-\gamma}\{1 + O(1/|z|)\}, \quad z \to \infty,$$

thus as $\zeta_1^2 \to \infty$,

$${}_1F_1\left(\tfrac{1-\lambda}{4}; \tfrac{1}{2}; \zeta_1^2\right) \sim \frac{\Gamma(1/2)}{\Gamma\left(\frac{1-\lambda}{4}\right)} e^{\zeta_1^2} \zeta_1^{-\frac{\lambda+1}{2}}$$

and

$$\zeta_1\, {}_1F_1\left(\tfrac{3-\lambda}{4}; \tfrac{3}{2}; \zeta_1^2\right) \sim \frac{\Gamma(3/2)}{\Gamma\left(\frac{3-\lambda}{4}\right)} e^{\zeta_1^2} \zeta_1^{-\frac{\lambda+1}{2}}$$

so that

$$-\frac{A}{B} \sim \Gamma(3/2)\,\Gamma\left(\tfrac{1-\lambda}{4}\right) / \Gamma(1/2)\,\Gamma\left(\tfrac{3-\lambda}{4}\right).$$

This choice of $-\frac{A}{B}$ makes the electron wave function go to zero as approaches negative infinity, that is

$$u_\lambda(\zeta) \to 0, \quad \zeta \to -\infty .$$

The eigenvalue equation then becomes

$$\Gamma\left(\tfrac{1-\lambda}{4}\right) {}_1F_1\left(\tfrac{1-\lambda}{4}; \tfrac{1}{2}; \zeta_0^2\right) - 2\zeta_0 \Gamma\left(\tfrac{3-\lambda}{4}\right) {}_1F_1\left(\tfrac{3-\lambda}{4}; \tfrac{3}{2}; \zeta_0^2\right) = 0$$

and the electron wave functions may be written as

$$U_\lambda(\zeta) = Ce^{-\frac{1}{2}\zeta^2}\left\{\frac{\Gamma(1/2)}{\Gamma\left(\frac{3-\lambda}{4}\right)} {}_1F_1\left(\tfrac{1-\lambda}{4}; \tfrac{1}{2}; \zeta^2\right) - \frac{2\zeta\Gamma(1/2)}{\Gamma\left(\frac{1-\lambda}{4}\right)} {}_1F_1\left(\tfrac{3-\lambda}{4}; \tfrac{3}{2}; \zeta^2\right)\right\}$$

which is proportional to the Weber function[36]

$$D_p(z) = e^{-\frac{1}{4}z^2}\left\{\frac{\sqrt{\pi}}{\Gamma\left(\frac{1-p}{2}\right)} {}_1F_1\left(-\tfrac{p}{2}; \tfrac{1}{2}; \tfrac{z^2}{2}\right) - \frac{z\sqrt{2\pi}}{\Gamma\left(-p/2\right)} {}_1F_1\left(\tfrac{1-p}{2}; \tfrac{3}{2}; \tfrac{z^2}{2}\right)\right\} 2^{\frac{1}{2}p}$$

where $\lambda = 2p+1$ and $z = \zeta\sqrt{2}$, which satisfies the Weber equation

$$\frac{d^2}{dz^2} D_p(z) + \left(p + \tfrac{1}{2} - \tfrac{1}{4}z^2\right) D_p(z) = 0 .$$

The eigenvalue equation above is equivalent to finding the zeros of the Weber function, $D_p(z) = 0$, which may be done numerically in a number of different ways.

This is the crux of the problem because there is no known[37] explicit expression for the eigenvalues, $\lambda_\nu(\zeta_0)$, as a function of the boundary parameter, ζ_0, or for thezeros, Z, of the Weber function in terms of the parameter, p. In this paper, an approximation is used which is comparatively close to the actual eigenvalues. The eigenvalues may be calculated numerically from the eigenvalue equation above, or the asymptotic expansions[38] of the Weber functions may be used to obtain approximate results. For the electron orbit center, x_0, outside the box, that is, for positive values of ζ_0, the asymptotic expansion is

$$U_\lambda(\zeta_0) \sim e^{-\frac{1}{2}\zeta_0^2}\, \zeta_0^{\frac{\lambda-1}{2}} \left\{1 - \frac{(\lambda-1)(\lambda-3)}{(4\zeta_0)^2} + \frac{(\lambda-1)(\lambda-3)(\lambda-5)(\lambda-7)}{2!\,(4\zeta_0)^4} + \cdots\right\} .$$

The implicit equation for the eigenvalues in terms of the boundary parameter,

$$1 - \frac{(\lambda-1)(\lambda-3)}{(4\zeta_0)^2} + \frac{(\lambda-1)(\lambda-3)(\lambda-5)(\lambda-7)}{2!(4\zeta_0)^4} - \ldots = 0$$

is asymptotic in the sense that if a finite number of terms are retained, the roots of the resulting polynomial approximate the required eigenvalues to a certain accuracy which increases as the boundary parameter, ζ_0, goes to infinity or as the eigenvalues approach an odd integer (corresponding to the Hermite polynomial eigenvalues) but decreases as more terms are used in the polynomial.[39] If the eigenvalue is an odd integer, the implicit equation terminates to a polynomial which is equivalent to a Hermite polynomial of the same eigenvalue. The implicit equation gives good results for $\lambda < 4t-1$ when the approximation is terminated after the t-th term. The $(t+1)$-th term then gives an estimate of the error while the sum of the following terms diverges.

For large negative values of ζ_0, that is, for the center of the electron orbit well inside the boundary, the asymptotic expansion of the Weber function is

$$U_\lambda(\zeta_0) \sim e^{-\frac{1}{4}\zeta_0^2}\,\zeta_0^{\frac{\lambda-1}{2}}\left\{1 - \frac{(\lambda-1)(\lambda-3)}{(4\zeta_0)^2} + \frac{(\lambda-1)(\lambda-2)(\lambda-5)(\lambda-7)}{2!(4\zeta_0)^4} - \ldots\right\}$$
$$- \frac{\sqrt{2\pi}}{\Gamma(\frac{1-\lambda}{2})}\, e^{\pi i \frac{\lambda-1}{2}}\, e^{\frac{1}{4}\zeta_0^2}\,\zeta_0^{-\frac{\lambda+1}{2}}\left\{1 + \frac{(\lambda+1)(\lambda+3)}{(4\zeta_0)^2} + \ldots\right\}.$$

Using the fact that $2\delta = \lambda - 2\nu - 1$ will be small in comparison to unity, set $U_\lambda(\zeta_0) = 0$ and approximate

$$\Gamma(\tfrac{1-\lambda}{2}) = \Gamma(-\nu-\delta) \sim -\frac{(-1)^\nu}{\nu!\,\delta} = \frac{2(-1)^{\nu+1}}{\nu!(\lambda-2\nu-1)}$$

Using only the first term in each of the brackets, an approximation[40] to the eigenvalues

$$\lambda_\nu(\zeta_0) \sim 2\nu + 1 + \frac{2^{\nu+2}}{\nu!\sqrt{\pi}}\,|\zeta_0|^{2\nu+1}\, e^{-\zeta_0^2}$$

is obtained which is good for $\zeta_0 < -\sqrt{2\nu+1}$. This approximation is asymptotic in the same sense as the preceding.

CALCULATION OF THE NUMBER OF STATES, Z(E,H)

Now calculate the number of states, Z(E,H), below an energy, E, by counting the number of points in quantum number space, (λ_ν, K_y, K_z), contained in the volume bounded by the constant energy surface

$$E = \lambda_\nu(\zeta_0)\mu H + \frac{\hbar^2}{2m} K_z^2$$

(an inverted parabolic cylinder with its axis parallel to K_y), and the K_y, K_z-plane. The quantum states will lie on the eigenvalue surfaces, $\lambda_\nu(\zeta_0)$, and are uniformly distributed when projected on the K_y, K_z-plane. Since L_2 and L_3 are relatively large, the sums over K_y and K_z may be approximated by integrals.[41] Therefore, a good approximation to the required total number of states, Z(E,H), is obtained by summing over the index, ν, all the areas (projected on the K_y, K_z-plane) enclosed by the intersection of the eigenvalue surfaces with the constant energy cylinders, as illustrated in Figure II. If the sum over ν were replaced by an integral, then there would be no magnetic effect whatsoever,[42] because it is contained entirely in the terms which give the difference between the sum and the integral over quantum numbers.

The intersection of the constant energy surface

$$E = \mu H \lambda_\nu(\zeta_0) + \frac{\hbar^2}{2m} K_z^2$$

with the eigenvalue surfaces, $\lambda_\nu(\zeta_0)$, is obtained by solving for the variable

$$K_z = \frac{\sqrt{2m}}{\hbar} \sqrt{E - \mu H \lambda_\nu(\zeta_0)}.$$

The boundary parameter

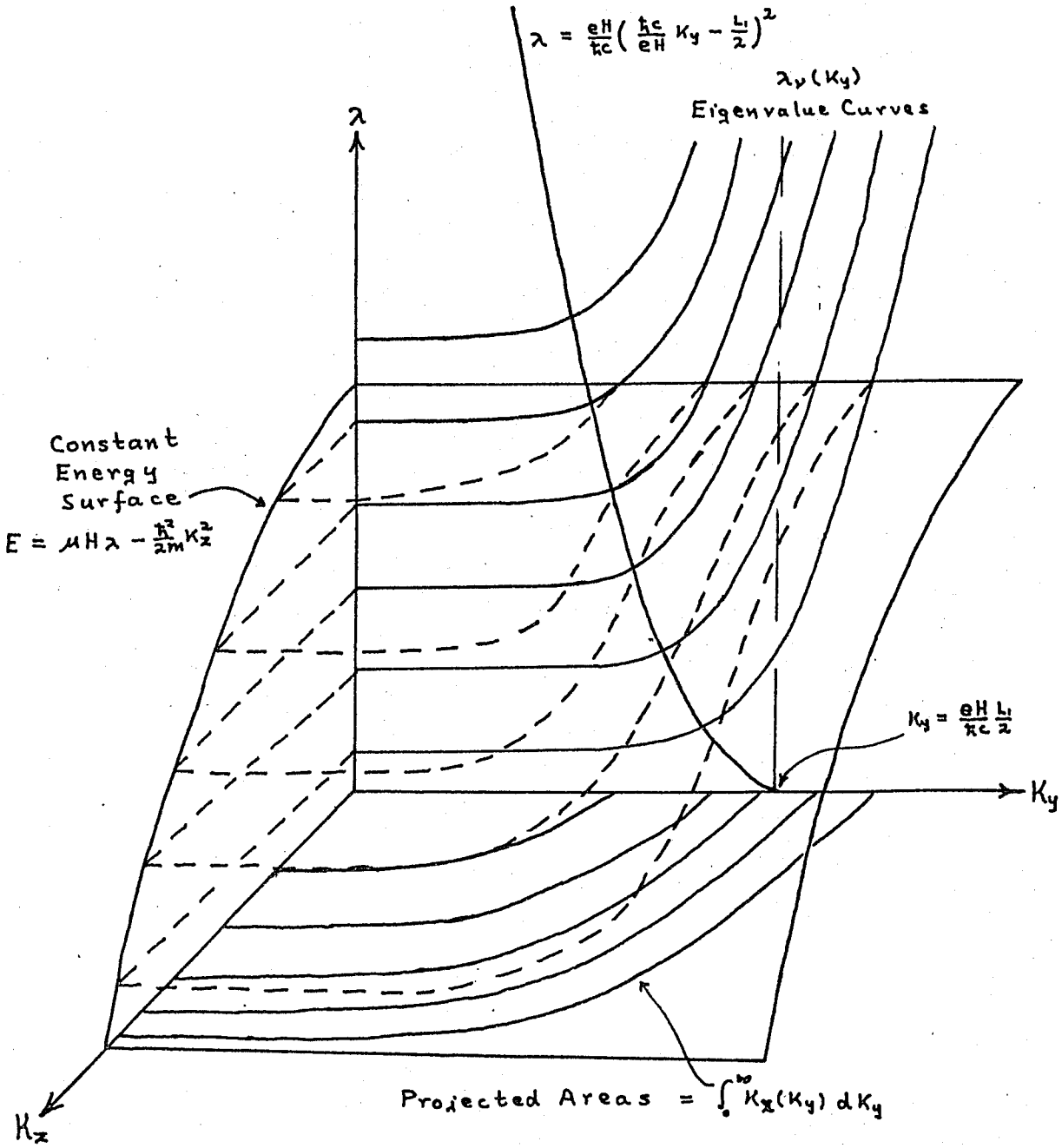
$\lambda = \frac{eH}{\hbar c}\left(\frac{\hbar c}{eH} K_y - \frac{L_1}{2}\right)^2$
$\lambda_\nu(K_y)$
Eigenvalue Curves
λ
Constant
Energy
Surface
$E = \mu H \lambda - \frac{\hbar^2}{2m} K_z^2$
$K_y = \frac{eH}{\hbar c}\frac{L_1}{2}$
K_y
K_z
Projected Areas $= \int_0^\infty K_x(K_y)\, dK_y$

Figure II

$$\zeta_0 = \sqrt{\frac{eH}{\hbar c}}\left(x_0 - \frac{L_1}{2}\right) = \sqrt{\frac{\hbar c}{eH}}K_y - \sqrt{\frac{eH}{\hbar c}}\frac{L_1}{2}$$

depends on K_y, as does the eigenvalue curves

$$\lambda_\nu(\zeta_0) \longrightarrow \lambda_\nu(K_y)$$

and

$$K_z(\zeta_0) \longrightarrow K_z(K_y).$$

The area enclosed by the intersection when projected on the K_y,K_z-plane is obtained by taking the real part of the integral of the function

$$K_z(K_y) = \frac{\sqrt{2m}}{\hbar}\sqrt{E - \mu H \lambda_\nu(K_y)}$$

with respect to K_y from zero to infinity,

$$A = \mathcal{R}e \int_0^\infty K_z(K_y)\, dK_y .$$

The number of states function,

$$Z(E,H) = 4\,\frac{L_2}{2\pi}\frac{L_3}{2\pi}\,\mathcal{R}e\left\{\sum_{\nu=0}^{\infty}\int_0^\infty \frac{\sqrt{2m}}{\hbar}\sqrt{E-\mu H\lambda_\nu(K_y)}\,dK_y\right\}$$

is then obtained by multiplying the area, A, by the density of states in the K_y- and K_z-directions, $\frac{L_2}{2\pi}$ and $\frac{L_3}{2\pi}$, and summing over the index, ν, with a factor of 4 because the area, A, refers to only one quadrant. Only the real part, $\mathcal{R}e$, of the complex quantity in the brackets is of physical interest since this represents possible states in quantum number space. Elimination of the imaginary contribution is accomplished by summing ν and integrating K_y over such ranges as the radical $\sqrt{E - \mu H \lambda_\nu(K_y)}$ remains real, that is,

$$\{E - \mu H\, \lambda_\nu(K_y)\} \geq 0 .$$

The notation and computation is simplified by choosing dimensionless variables as follows:

$$\varepsilon = E/2\mu H , \qquad K_y = \sqrt{\frac{eH}{\hbar c}}\zeta_0 - \frac{eH}{\hbar c}\frac{L_1}{2} .$$

The number of states function may then be written as

$$Z(E,H) = \frac{L_2 L_3}{\pi^2}\frac{eH}{\hbar c}\,\mathrm{Re}\left\{\sum_{\nu=0}^{\infty}\int_{-\sqrt{\frac{eH}{\hbar c}}\frac{L_1}{2}}^{\infty}\sqrt{2\varepsilon-\lambda_\nu(\zeta_0)}\,d\zeta_0\right\}.$$

Three approximations to the eigenvalue curves, $\lambda_\nu(\zeta_0)$, will be considered. In order to obtain the major terms in each of these approximations, the sum over the index, ν, will be replaced by the Euler expansion[43] as follows:

$$\sum_{n\le a}^{b} f(n+\tfrac{1}{2}) = \int_a^{b+1} f(x)\,dx - \frac{1}{24}f'(x)\Big|_a^{b+1} + \dots$$

where a and b are not necessarily integers.

In the first approximation, Landau assumed only that the center of the electron orbit, x_0, must remain inside the boundaries at $x=\pm\frac{L_1}{2}$, that is, $\zeta_{0\,max}=0$, and that the eigenvalues are constant $\lambda_\nu(\zeta_0)=2\nu+1$, independent of the boundary parameter. This gives for the number of states

$$Z_1(E,H) = \frac{L_2 L_3}{\pi^2}\frac{eH}{\hbar c}\,\mathrm{Re}\left\{\sum_{\nu=0}^{\infty}\sqrt{2\varepsilon-2\nu-1}\int_{-\sqrt{\frac{eH}{\hbar c}}\frac{L_1}{2}}^{\infty}d\zeta_0\right\}$$
$$= \frac{L_1 L_2 L_3}{2\pi^2}\left(\frac{eH}{\hbar c}\right)^{3/2}\sum_{\nu=0}^{\nu<\varepsilon-1/2}\sqrt{2\varepsilon-2\nu-1}\,.$$

The sum may be approximated as follows:

$$\sum_{\nu=0}^{\nu<\varepsilon-1/2}\sqrt{2\varepsilon-2\nu-1} = \int_0^{\varepsilon+1/2}\sqrt{2}\sqrt{\varepsilon-x}\,dx - \frac{\sqrt{2}}{24}\frac{d}{dx}(\varepsilon-x)^{1/2}\Big|_0^{\varepsilon-1/2}+\dots$$
$$= \frac{1}{3}(2\varepsilon)^{3/2} - \frac{1}{24}(2\varepsilon)^{-1/2}+\dots$$

The contribution at the upper limit in the approximation is pure imaginary and is therefore neglected. Thus the Landau approximation to the number of states may be written as

$$Z_1(E,H) = \frac{L_1 L_2 L_3}{2\pi^2}\left(\frac{eH}{\hbar c}\right)^{3/2}\left\{\frac{1}{3}(2\varepsilon)^{3/2} - \frac{1}{24}(2\varepsilon)^{-1/2}+\dots\right\}.$$

The second approximation[44] suggests that since the eigenvalues increase as the orbit center approaches the boundary,

the electron states are, in effect, pushed away from the boundary. This situation may be represented by allowing the eigenvalues to remain constant, as in the Landau approximation, but requiring that no electron state shall be allowed within some fraction of the classical radius from the boundary, that is, $\zeta_{0\,max} = -\sqrt{2\nu+1}$. The electron states which would have been in the boundary region are replaced at the top of the electron sea effectively raising the Fermi level. This type of approximation yields a number of states function as follows:

$$Z_2(E,H) = \frac{L_2 L_3}{\pi^2}\frac{eH}{\hbar c}\,\mathrm{Re}\left\{\sum_{\nu=0}^{\infty}\sqrt{2\varepsilon-2\nu-1}\int_{-\sqrt{\frac{eH}{\hbar c}}\frac{L_1}{2}}^{-\sqrt{2\nu+1}} d\zeta_0\right\}$$

$$= \frac{L_1 L_2 L_3}{2\pi^2}\left(\frac{eH}{\hbar c}\right)^{3/2}\left\{\sum_{\nu=0}^{\nu<\varepsilon-1/2}\sqrt{2\varepsilon-2\nu-1} - \frac{2}{L_1}\sqrt{\frac{\hbar c}{eH}}\sum_{\nu=0}^{\nu<\varepsilon-1/2}\sqrt{2\varepsilon-2\nu-1}\sqrt{2\nu+1}\right\}.$$

The first sum is identical to the Landau approximation, while the second sum is approximated as follows:

$$\sum_{\nu=0}^{\nu<\varepsilon-1/2}\sqrt{2\varepsilon-2\nu-1}\sqrt{2\nu+1} = 2\int_0^{\varepsilon+1/2}\sqrt{\varepsilon-x}\sqrt{x}\,dx + \dots$$

Only the integral approximation to the sum is retained in this case since only the major correction term is desired, which is then multiplied by a factor $\frac{2}{L_1}\sqrt{\frac{\hbar c}{eH}}$ which is of the order of 10^{-5} when $L_1 \sim 1$ cm and $H \sim 10^4$ gauss. If the transformation $x = \varepsilon y$ is made and the imaginary contribution neglected, then the integral becomes

$$2\varepsilon^2\int_0^1 (1-y)^{1/2}\,y^{1/2}\,dy = 2\varepsilon^2\,\frac{\Gamma(3/2)\,\Gamma(3/2)}{\Gamma(3)} = \frac{\pi}{4}\varepsilon^2.$$

Therefore the second approximation to the number of states function is

$$Z_2(E,H) = \frac{L_1 L_2 L_3}{2\pi^2}\left(\frac{eH}{\hbar c}\right)^{3/2}\left\{\frac{1}{3}(2\varepsilon)^{3/2} - \frac{1}{24}(2\varepsilon)^{-1/2} - \frac{\pi}{2L_1}\sqrt{\frac{\hbar c}{eH}}\,\varepsilon^2 + \dots\right\}.$$

In the third approximation, an attempt is made to represent the actual eigenvalue curves, $\lambda_\nu(\zeta_0)$, by assuming that

the eigenvalues are essentially constant, $\lambda_\nu(\zeta_0) = 2\nu+1$, up to the point $\zeta_0 = -\sqrt{2\nu+1}$ and are close to the function

$$\lambda_\nu(\zeta_0) = 2\nu+1 + (\zeta_0 + \sqrt{2\nu+1})^2$$

for $\zeta_0 \geq -\sqrt{2\nu+1}$. The number of states function is then given by the following

$$Z_3(E,H) = \frac{L_2 L_3}{\pi^2}\frac{He}{\hbar c}\mathrm{Re}\left\{\sum_{\nu=0}^{\infty}\left[\sqrt{2\varepsilon-2\nu-1}\int_{-\sqrt{\frac{eH}{\hbar c}}\frac{L_1}{2}}^{-\sqrt{2\nu+1}} d\zeta_0 + \int_{-\sqrt{2\nu+1}}^{\sqrt{2\varepsilon-2\nu-1}-\sqrt{2\nu+1}} \sqrt{2\varepsilon-2\nu-1-(\zeta_0+\sqrt{2\nu+1})^2}\, d\zeta_0\right]\right\}.$$

The first integral is identical to that of the second approximation. By transforming to the variable

$$y = (\zeta_0+\sqrt{2\nu+1})^2/(2\varepsilon-2\nu-1) \quad , \quad d\zeta_0 = \tfrac{1}{2}\sqrt{2\varepsilon-2\nu-1}\; y^{-1/2}\, dy$$

the second integral becomes

$$\tfrac{1}{2}(2\varepsilon-2\nu-1)\int_0^1 (1-y)^{1/2}\, y^{-1/2}\, dy = \tfrac{1}{2}(2\varepsilon-2\nu-1)\frac{\Gamma(3/2)\Gamma(1/2)}{\Gamma(2)} = \frac{\pi}{4}(2\varepsilon-2\nu-1).$$

The sum of this term may then be approximated by an integral as follows:

$$\sum_{\nu=0}^{\nu<\varepsilon-1/2}(2\varepsilon-2\nu-1) = 2\int_0^{\varepsilon+1/2}(\varepsilon-x)\,dx = \varepsilon^2 - 1 \;.$$

Thus the number of states function is

$$Z_3(E,H) = \frac{L_1 L_2 L_3}{2\pi^2}\left(\frac{eH}{\hbar c}\right)^{3/2}\left\{\frac{1}{3}(2\varepsilon)^{3/2} - \frac{1}{24}(2\varepsilon)^{-1/2} - \frac{\pi}{2L_1}\sqrt{\frac{\hbar c}{eH}} + \dots\right\}$$

where the ε^2 contributions from the two integrals have cancelled identically, leaving only a very small contribution which is independent of ε. This result indicates that the Landau approximation is remarkably good considering its simplicity.

The magnetization is

$$M = \int_0^\infty \left(\frac{\partial Z}{\partial H}\right)_{T,V,H}\frac{1}{1+e^{(E-\eta)/kT}}\,dE.$$

Substituting $\varepsilon = E/2\mu H$, the number of states functions become

$$Z_1(E,H) = \frac{L_1L_2L_3}{2\pi^2}\left(\frac{e}{\hbar c}\right)^{3/2}\left\{\frac{1}{3}\left(\frac{E}{\mu}\right)^{3/2} - \frac{1}{24}\left(\frac{E}{\mu}\right)^{-1/2}H^2 + \cdots\right\}$$

$$Z_2(E,H) = \frac{L_1L_2L_3}{2\pi^2}\left(\frac{e}{\hbar c}\right)^{3/2}\left\{\frac{1}{3}\left(\frac{E}{\mu}\right)^{3/2} - \frac{1}{24}\left(\frac{E}{\mu}\right)^{-1/2}H^2 - \frac{\pi}{8L_1}\sqrt{\frac{\hbar c}{e}}\left(\frac{E}{\mu}\right)^{2}\frac{1}{H} + \cdots\right\}$$

$$Z_3(E,H) = \frac{L_1L_2L_3}{2\pi^2}\left(\frac{e}{\hbar c}\right)^{3/2}\left\{\frac{1}{3}\left(\frac{E}{\mu}\right)^{3/2} - \frac{1}{24}\left(\frac{E}{\mu}\right)^{-1/2}H^2 - \frac{\pi}{2L_1}\sqrt{\frac{\hbar c}{e}}H + \cdots\right\}.$$

The three approximations are taken together to show the parallel development. The partial differentials of the number of states functions with respect to the magnetic field are therefore

$$\left(\frac{\partial Z_1}{\partial H}\right)_{T,V,N} = -\frac{L_1L_2L_3}{24\pi^2}\left(\frac{e}{\hbar c}\right)^{3/2}\sqrt{\frac{\mu}{E}}\,H + \cdots$$

$$\left(\frac{\partial Z_2}{\partial H}\right)_{T,V,N} = -\frac{L_1L_2L_3}{2\pi^2}\left(\frac{e}{\hbar c}\right)^{3/2}\left\{\frac{1}{6}\sqrt{\frac{\mu}{E}}\,H - \frac{\pi}{8L_1}\sqrt{\frac{\hbar c}{e}}\left(\frac{E}{\mu}\right)^{2}\frac{1}{H^2} + \cdots\right\}$$

$$\left(\frac{\partial Z}{\partial H}\right)_{T,V,N} = -\frac{L_1L_2L_3}{2\pi^2}\left(\frac{e}{\hbar c}\right)^{3/2}\left\{\frac{1}{6}\sqrt{\frac{\mu}{E}}\,H - \frac{\pi}{2L_1}\sqrt{\frac{\hbar c}{e}} + \cdots\right\}$$

The temperature-independent contribution to the boundary effect is indicated by the zero-temperature approximation,[45] so that the Fermi function,

$$f(E) = \frac{1}{1 + e^{(E-\eta)/kT}}$$

may be represented by a step function, that is

$$f(E) = 1 \quad E < \eta\,, \qquad f(E) = 0 \quad E > \eta\,.$$

Therefore the magnetizations are written as

$$M_1 = -\frac{L_1L_2L_3}{24\pi^2}\left(\frac{e}{\hbar c}\right)^{3/2}\mu^{1/2}\,H\int_0^{\eta}E^{-1/2}\,dE = -\frac{L_1L_2L_3}{12\pi^2}\left(\frac{e}{\hbar c}\right)^{3/2}\sqrt{\mu\eta}\,H$$

$$M_2 = -\frac{L_1L_2L_3}{2\pi^2}\left(\frac{e}{\hbar c}\right)^{3/2}\left\{\frac{1}{6}\sqrt{\mu\eta}\,H - \frac{\pi}{24L_1}\sqrt{\frac{\hbar c}{e}}\,\eta^3\,(\mu H)^{-2}\right\}$$

$$M_3 = -\frac{L_1L_2L_3}{2\pi^2}\left(\frac{e}{\hbar c}\right)^{3/2}\left\{\frac{1}{6}\sqrt{\mu\eta}\,H + \frac{\pi}{2L_1}\sqrt{\frac{\hbar c}{e}}\,\eta\right\}.$$

Therefore, the susceptibilities per unit volume are

$$\chi_1 = \frac{1}{V}\frac{M_1}{H} = -\frac{1}{12\pi^2}\left(\frac{e}{\hbar c}\right)^{3/2}\sqrt{\mu\eta}$$

$$\chi_2 = \frac{1}{V}\frac{M_2}{H} = -\frac{1}{2\pi^2}\left(\frac{e}{\hbar c}\right)^{3/2}\left\{\frac{1}{6}\sqrt{\mu\eta} - \frac{\pi}{24L_1}\sqrt{\frac{\hbar c}{e}}\left(\frac{\eta}{H}\right)^{3}\frac{1}{\mu^2}\right\}$$

$$\chi_3 = \frac{1}{V}\frac{M_3}{H} = -\frac{1}{2\pi^2}\left(\frac{e}{\hbar c}\right)^{3/2}\left\{\frac{1}{6}\sqrt{\mu\eta} - \frac{\pi}{2L_1}\sqrt{\frac{\hbar c}{e}}\,\frac{\eta}{H}\right\}.$$

Therefore, the first term is the Landau diamagnetic term

$$\chi_1 = -\frac{e^2}{12\pi^2\hbar c^2}\sqrt{\frac{\eta}{2m}} = -\frac{\mu^2}{12\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\eta^{1/2}$$

or if the first approximation to

$$\eta = \frac{\hbar^2}{2m}\left(\frac{6\pi^2 N}{V}\right)^{2/3}$$

is substituted, the result is

$$\chi_1 = -\frac{1}{3}\mu^2\,\frac{2m}{\hbar^2}\left(\frac{6\pi^2 N}{V}\right)^{1/3}.$$

The correction terms in the latter approximations have the correct qualitative dependence on the size of the box and on the magnetic field that one would expect, that is, the correction terms get larger as the box gets smaller and also as the magnetic field decreases because of the dependence on $1/L$ and $1/H$. These approximations are valid only in the case of very high fields. Landau's work is rigorously correct in the case of infinite magnetic field while the correction terms derived here are attempts to evaluate the deviations for finite fields. It is questionable whether the correction terms have any physical significance[46] since it appears that they are results of the approximations used and not of any real, observable effect.

* *

I would like to acknowledge the help and encouragement that Dr. W. V. Houston has given to me by suggesting this problem and assisting me in all phases of its development.

Appendix I : Comments

The majority of the papers listed in the notes are on deposite in Physics Department Heaps Library at Rice University under the title, "Photocopies of papers related to the boundary effect on the diamagnetism of free electrons."

Papers of historical interest are recorded in Notes 6 and 47. Since these papers are rarely referred to in the literature, it is felt advisable to note them here so that they may not be overlooked.

Several of the latter reviews on the subject of the electron theory of metals are recorded in Note 48.

Only a sample of the extensive russian literature on this subject is recorded in Notes 21 and 49.

Appendix II : WKB Approximation

It is the purpose of the appendix to point out a possible discrepancy in the usual applications of the WKB approximation to the calculation of the boundary effect on free electron diamagnetism. The eigenvalue curves calculated from the WKB approximation, shown in Figure III, give an excellent approximation to the actual eigenvalue curves on the right-hand side of the graph. But the WKB approximation gets worse and worse as one goes to the left-hand side of the graph, until the WKB curves terminate at the inner classical turning point with zero slope and infinite higher derivitives. All the workers who use the WKB approximation (see p.4) then asume that the eigenvalues are constant to the left of the inner classical turning point and essentially ignore the gap in the eigenvalue curves which gives rise to a correction to the magnetization proportional to $H^{-1/3}$ the reciprocal of the cube root of the magnetic field. Dingle (Note 19, paper VI, p.468) uses the curves as shown and obtains a positive contribution to the magnetization, that is, a paramagnetic correction to the susceptibility. Steele[23] essentially moves the eigenvalue curves down bodity until they join onto the constant eigenvalue curves at the inner classical turning point and obtains a negative contribution to the magnetization or a diamagnetic correction to the susceptibility. Ham[20] includes a factor, α, which essentially moves the curves up or down at will. Dingle's results are obtained when $\alpha = 3/4$ and

Steel's when $\alpha = \frac{1}{2}$. Ham shows a graph of the eigenvalues (Note 20, Figure I, p.1115) equivalent to those used by Steele in his calculations. Lifshitz and Kosyvich[21] use other variable parameters besides the one equivalent to Ham's α, but using a different approach they obtain results identical to those of Ham when the proper values of the parameters are used.

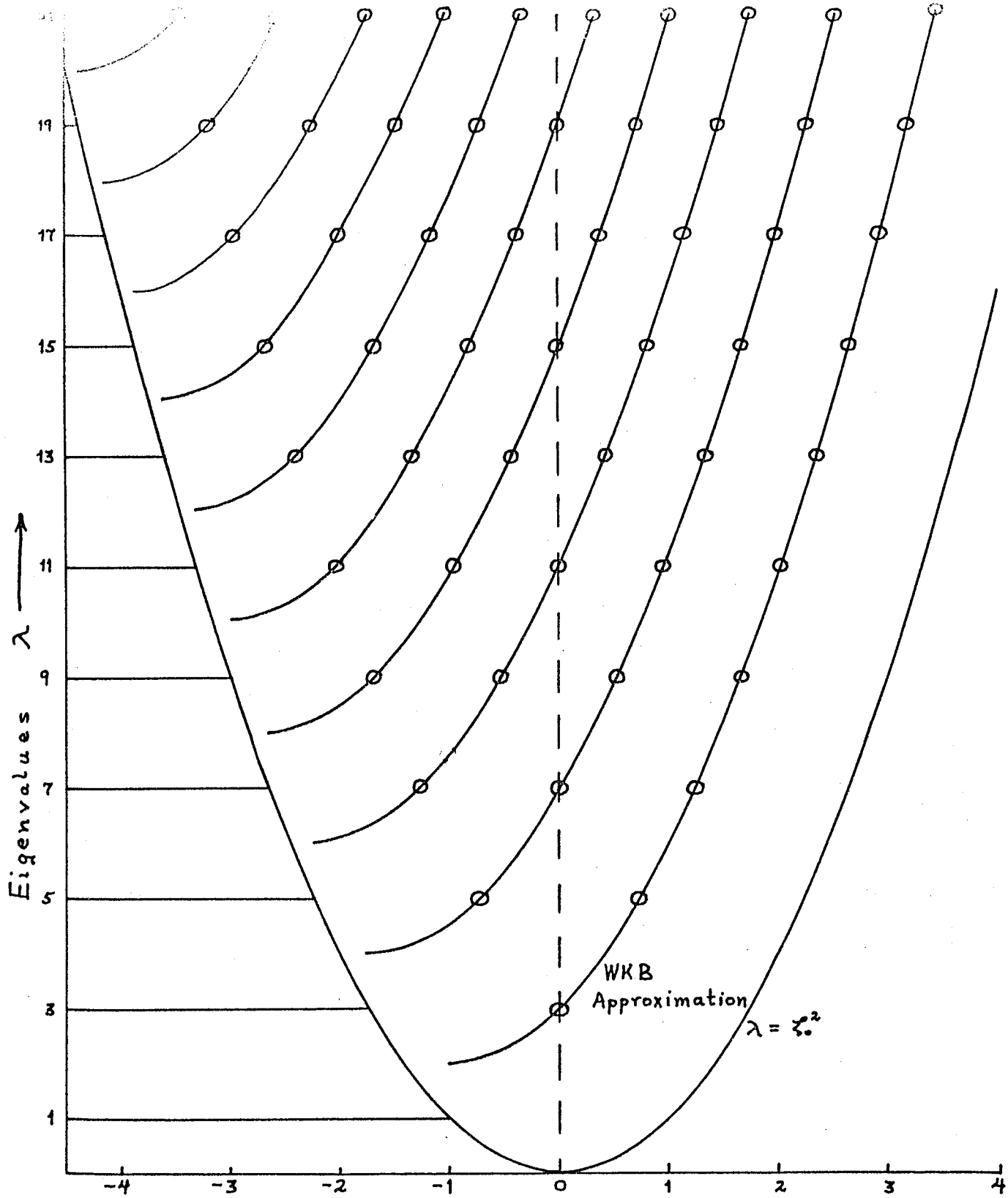
19
17
15
13
11
9
7
5
3
1
Eigenvalues λ
-4
-3
-2
-1
0
1
2
3
4
Boundary Parameter ζ₀
WKB
Approximation
λ = ζ₀²

Figure III

Notes to Page 1

1. Niels Bohr, Dissertation (Copenhagen, 1911). A similar proof is given by J.H.van Vleck, Theory of Electric and Magnetic Susceptibilities (London:Oxford University Press,1932),pp.97-100.

2. J.H.van Leeuwen, Dissertation (Leiden, 1919). A summary is given in Journal de PHysique,II,No.6(1921)361. Proofs are also given by van Vleck,op.cit.,pp.94-97, and by R.E.Peierls, Quantum Theory of Solids (London:Oxford at the Clarendon Press,1955),pp.145-146.

3. A simple, physically intuitive picture is presented by van Vleck,op.cit.,pp.100-102.

4. This seems to have been first suggested by F.Hund,"Rechnungen über das magnetische Verhalten von kleinen Metallstücken bei teifen Temperaturen," Annalen der Physik,XXXII(May 1938)102-114. There is a boundary condition error in A.Papapetrou,"Diamagnetism of electron gas," Zeitschrift für Physik,CVI(1937)9-16; corrected in ibid.,CVII (1937)387-392. This question is also discussed by H.Welker,"Uber ein elektronentheoretisches modell des supraleiters," Sitzungsberichte der Bayerischen Akademie der Wissenschaften,XIV(1938)115-138; summarized in Physikalische Zeitschrift,XXXIX(1938)920-925. The application to superconductivity is considered by William Band,"The occurrence of superconductivity in a collective electron assembly," Physical Review,LXIX(Jan.1946)41;"Superconductivity and magnetic energy between currents," Physical Review,LXIX(March 1946)241; "Diamagnetism and superconductivity," loc.cit.; "Diamagnetism and superconductivity

of a collective electron assembly," Proceedings of the Cambridge Philosophical Society,XLII(Oct.1946)311-327. Some numerical calculations to this effect were done by D.J.Besdin,"The magnetic moment of free electrons," Ph.D. Thesis (Houston, Texas:Rice Institute, May 1950, unpublished); Physical Review,LXXIX(July 1950) 417-418; also with J.H.Robinson,III, Physical Review,~~XCIV~~XCVIII(1954)272. There is an erroneous conclusion in M.F.M. Osborne,"Perfect diamagnetism of free electrons with application to superconductivity," Physical Review,LXXXI(Jan.1951)147-148; corrected in M.F.M.Osborne and M.C.Steele,"Size effects and diamagnetism in finite systems," Physical Review,LXXXVI(April 1952)247. There is a boundary condition approximation error in W.Band,"Low temperature diamagnetism of electrons in a cylinder," Physical Review,XCI(July 1953)249-255; corrected in ibid.,XCIII(Jan.1954)350.

5. L.Landau,"Diamagnetismus der metalle," Zeitschrift für Physik, LXIV(1930)629-637.

6. W.Pauli, among others, realized this and suggested the problem to one of his students, P.Y.Chou,"Diamagnetism of free electrons in metals," Science Reports of the National Tsing Hua University,I(Peiping, China,April 1931). Because all summations were replaced by integrations, a zero result was obtained and erroneously interpreted as due to collisions of electrons with the walls.

7. E.Teller,"Der diamagnetismus von freien elektronen,"

Zeitschrift für Physik,LXVII(1931)311-319.

8. van Vleck,op.cit.,353-359.

9. A.Papapetrou,"Diamagnetism of electron Gas," Zeitschrift für Physik,CXII(1939)587-604.

10. J.Lindhard,"On a free electron gas in static magnetic and electric fields," Arkiv foer Matematic, Astronomi och Fysik,XXXIII (1946)Paper 4, 17pp.

11. R.Peierls,"Zur Theorie des diamagnetismus von Leitungs-electronen," Zeitschrift für Physik,LXXX(1933)763-791; part 2, "... Starke Magnetfelder," ibid.,LXXXI(1933)186-194.

12. A.W.Sáenz and R.C.O'Rourke,"Number of states and the magnetic properties of an electron gas," Reviews of Modern Physics,XXVII,No.4 (1),(Oct.1955)381-398. There are several serious typographical errors in this paper. A corrected reprint may be secured directly from Dr.Saenz, in care of the Radiation Division, Naval Research Laboratory Washington 25, D.C.

13. E.H.Sondheimer and A.H.Wilson,"The diamagnetism of free electrons," Proceedings of the Royal Society of London,CCX-A(1951) 173-169.

14. Van Vleck,op.cit.,p.358. E.C.Stoner,"The temperature dependence of free electron susceptibility,"Proceedings of the Royal

Society of London,CLII-A877(Nov.1935),p.677.

15. W.Pauli,Jr.,"Gas degeneration and paramagnetism," Zeitschrift für Physik,XLI(1927)81-102; ibid.,"Quantum mechanics of the magnetic electron,"XLIII(1927)601-623.

16. See appendix of the following paper for a private communication of Landau, prepared for publication by Peierls. D.Shoenberg, "The magnetic properties of bismuth, III; further measurements on the de Haas-van Alphen effect," Proceedings of the Royal Society of London, CLXX-A942(April 1939)341-364.

17. L.J.Mordell,Poisson's summation formula and the Riemann zeta function," Journal of the London Mathematical Society,IV(1928) 285-291. See also R.Courent and D.Hilbert, Methods of Mathematical Physics,(1st English ed., New York:Interscience Publishers, Inc.,1953) pp.76-77. Used by Peierls, Quantum Theory ...,p.148.

18. W.J.de Haas and P.M.van Alphen,"Dependence of the susceptibility of diamagnetic metals upon the field," Leiden Communications, CCXIIa(1931). Also in K.Akad. Amsterdam. Proc.,XXXIII, No.10(1930)1106-1118.

19. R.B.Dingle,"The diamagnetism of free electrons in finite systems," Physical Review,LXXXII,No.6(June 1951)966. "Some magnetic properties of metals I. General introduction, and properties of large systems of electrons," Proceedings of the Royal Society of London,

CCXI-A1107(March 1952)500-516; ibid.,"II.The influence of collisions on the magnetic behavior of large systems,"pp.517-525; ibid.,"III. Diamagnetic resonance,"CCXII-A1108(April 1952)38-47; ibid., "IV. Properties of small systems of electrons,"pp.47-65; ibid.,"V. Magnetic behavior of a cylindrical system of electrons for all magnetic fields," CCXVI-A1124(Jan.1953)118-142; ibid., "VI. Surface corrections to the Landau diamagnetism and the de Haas-van Alphen effect,CCXIX-A (Oct.1953)463-477; ibid.,"The solution of the Schrodinger equation for finite systems, with special reference to the motion of electrons in Coulomb electric fields and uniform magnetic fields," Proceedings of the Cambridge Philosophical Society,XLIX(1953)103-114; ibid., "Low-temperature diamagnetism of electrons in a cylinder," Physical Review,XCII(Dec.1953)1320.

20. F.S.Ham,"Effect of the surface on the magnetic properties of an electron gas." Physical Review,XCII,No.5(Dec.1953)1113-1119.

21. A.M.Kosevich and I.M.Lifshits,"The de Haas-van Alphen effect in thin metal layers," Soviet Physics JEPT,II,No.4(July 1956)646-649.

22. M.F.M.Osborne,"Number theory and the magnetic properties of an electron gas," Physical Review,LXXXVIII,No.3(Nov.1952)438-451; Summary in "Energy states for a finite cylindrical container in a magnetic field," Proceedings of the International Conference on Low Temperature Physics, (Oxford,Aug.1951)138-139.

23. M.C.Steele,"Application of the theory of numbers to the

magnetic properties of a free electron gas," Physical Review,LXXXVIII, No.3(Nov.1952)451-464; summary in Proceedings of the International Conference on Low Temperature Physics, (Oxford,Aug.1951)137-138.

24. N.Minnaja,"Solution of the Schroedinger equation in a constant magnetic field and diamagnetism," Physica(Netherlands),XXVI,No.10 (Oct.1960)827-833.

25. Throughout this work, the spin of the electrons will be neglected since it does not contribute to the first order terms considered in this problem. To consider the spin, the number of states function, Z(E,H), is merely multiplied by a factor of two, in every case. See reference 45 for higher order terms.

26. O.Klein and J.Lindhard,"Some remarks on the quantum theory of the superconductive state," Reviews of Modern Physics,XVII (April 1945)305-309.

27. O.Klein,"On the magnetic behaviour of electrons in crystals," Arkiv foer Matematic, Astronomi och Fysik,XXXI-A,No.2(1945), paper 12, 15pp.

28. This situation may be realized physically by means of a thin-walled toroid with an axial magnetic field, where the x-direction is taken to be everywhere perpendicular to the walls. The toroid must be large enough so that the curvature may be neglected. This case is discussed by J.M.Ziman, Electrons and Phonons,(Oxford at the

Clarendon Press,1960)pp.18-19.

29. Another simple boundary condition requires the derivative of the function to be zero at the boundary. It is suggested that a linear combination of the eigenvalues of these two types of boundary conditions may be used to fit general experimental results.

30. The eigenvalues, $\lambda_\nu(\xi_0)$, are classified by the number, ν, of zeros or nodes of the function, $u_\lambda(\xi)$, which fall inside the box.

31. The zeros of the Hermite polynomials may be obtained from H.A.Aiken, Tables of the Error Function and of its First Twenty Derivatives, (Cambridge,Mass.:Harvard University Press, 1952), p.xxvii,(Zeros of the derivatives of the error function), by multiplying by the square root of two.

32. For the most part, the curves were drawn in by eye after several points were checked to be certain of the form of the curves. The lower parts of the curves, just outside the $\lambda = \xi_0^2$ graph, were calculated from the exponential approximation to the eigenvalues discussed later in this work.

33. L.J.Slater, Confluent Hypergeometric Functions,(Cambridge, England:University Press, 1960). Herbert Buchholz, Die Konfluente Hypergeometrische Function, (Berlin:Springer-Verlag,1953). U.J. Knottnerus, Approximation formulae for generalized hypergeometric functions for large values of the parameters, (Groningen:J.B.Wolters, 1960).

34. If some boundary condition other than

$$U_\lambda(\zeta) = 0 \quad \text{at} \quad \zeta = \zeta_0, \zeta_1$$

be chosen, then in general some function, $W(\zeta)$, will satisfy an equation of the form

$$W'' + (\lambda - \zeta^2 + V(\zeta))\, W = 0$$

for ζ outside the box, such that

$$W(\zeta) \to 0 \quad \text{as} \quad \zeta \to \pm \infty .$$

The boundary conditions then require that the two functions have equal values and equal slopes at the boundaries. This yields an implicit equation for the eigenvalues, $\lambda_\nu(\zeta_0, \zeta_1)$, a function of the two boundary parameters, ζ_0 and ζ_1, that is, as a function of the position of the orbit center, x_0, relative to the two boundaries.

35. This assumption is not necessary. For small magnetic fields and small containers, the eigenvalues must be found in terms of both boundary parameters. The only alteration is that the lower limit on the sum of states function must be taken as minus infinity and multiplied by a factor of two instead of four.

36. P.S.Epstein, Uber die Beugungan einem ebenem Schirm, Unter Berucksichtigung des Materialeinflusses, (Leipzig:Johann Ambrosius Barth,1914); may be obtained from the University of Illinois Library. L.Fox, "Tables of Weber parabolic cylinder functions and other functions for large arguments," Mathematical Tables,IV,(London:Her Majesty's Stationery Office,1960). I.Ye.Kreyeva and K.A.Karpov,

Tables of Weber functions,I,(New York:Pergamon Press,1961). J.C.P. Miller, Tables of Weber Parabolic Cylinder Functions,(London:Her Majesty's Stationery Office,1955). This reference has an excellent theoretical introduction to the Weber functions.

37. Einar Hille,"On the zeros of the functions of the parabolic cylinder," Arkiv for Matematic, Astronomi och Fysik,XVIII(1924), paper 26, 56pp. A.Erdelyi, et.al., Higher Transcendental Functions, II, (New York:McGraw-Hill,1953),p.126. Miller, op.cit.,p.27, states that he will publish solutions for the zeros of the Weber functions. When he does so, place his expression in the equation for the number of states function on page 17, and grind away. This should give the best approximation to the boundary effect yet calculated.

38. Kireyeva and Karpov, op.cit.,p.ix-xii, and Knottnerus, op.cit.,p.68.

39. One advantage of this approach is that the error obtained in the approximation using a certain number of terms is of opposite sign to that obtained when one more term is included in the approximation, so that good accuracy may be obtained by balancing off the errors in the various approximations.

40. This type of approximation may be done in a number of different ways, examples of which are given in the following work. A.Michels, J. de Boer, and A.Bijl,"Remarks concerning molecular

interaction and their influence on the polarisability," Physica,IV, No.4(Nov.1937)981-994. H.Froehlich,"Solution of Schrodinger equation by pertubation of boundary conditions," Physical Review,LIV,(Dec.1938) 945-947. A.Sommerfeld and H.Welker,"Kunstliche Grenzbedingungen bein Kepler problem" Annalen der Physik,XXXII(1938)56-65. A.Sommerfeld and Hartmann,"Kunstliche Grenzbedingungen in der Wellenmechanick der beschrankte Rotator," Annalen der Physik,XXXVII(1940)333-343. A.C. Auluck and D.S.Kothari,"Quantum mechanics of a bounded linear harmonic oscillator," Proceedings of the Cambridge Philosophical Society,XLI (June 1945)175-179. N.F.Mott and I.N.Sneddon, Wave Mechanics and its Applications,(Oxford:Clarendon Press,1948),p.53. T.T.Kou,"Discussion on the behavior on an electron enclosed in a sphere," Chinese Journal of Physics,VII(April,1949)241-248. C.A.ten Seldam and S.R.de Groot,"On the ground state of a model for compressed helium," Physica, XVIII,No.11(Nov.1952)891-914. J.S.Baijal and K.K.Singh,"The energy levels and transition probabilities for a bounded linear harmonic oscillator," Progress in Theoretical Physics, XIV,No.3(Sept.1955) 214-224. T.E.Hull and R.S.Julius,"Enclosed quantum mechanical systems," Canadian Journal of Physics,XXXIV,No.9(Sept.1956)914-919.

41. If the sum over K_z is not treated as an integral, an oscilatory contribution to the susceptibility, similar to the de Haas-van Alphan effect, is found, whose period depends on the size of the container instead of the magnetic field, although it is doubtful whether this effect can be observed experimentally.

42. A.Sommerfeld and H.Bethe,"Elektronentheorie der Metalle," Handbuch der Physik,XXIV^2 (1933)473ff.

43. K.F.Niessen,"Relation of Dia- and Paramagnetism if an electron gas as a function of the field strenght," Physica, I(July, 1934)783-796; ibid.,"Change of magnetic susceptibility of an electron gas with temperature," pp.979-988.

44. W.V.Houston and E.T.Lane,"Diamagnetism of free electrons," Presented at the Southwest section of the American Physical Society, Austin, Texas, Feb.1961.

45. E.C.Stoner,"The temperature dependence of free electron susceptibility," Proceedings of the Royal Society of London,CLII,No. A877(Nov.1935)672-692.

46. Very little recent experimental work has been done on the size dependence of diamagnetic susceptibility. The following reference reviews early work along these lines, but it is felt that the metal particles must be electrically insulated from each other before an effect is to be expected. This condition is not met in the work referred to in the following. H.Lessheim,"Diamagnetism and Particle Size," Current Science,V,No.3(Sept,1936)119-127; may be obtained at the A.&M. College of Texas Library.

Although, quartz is definitely not a free electron metal, the following workers have found a size dependence of the diamagnetism which can be fitted emperically with a curve which has the proper

dependence on size, that is, on the reciprocal of the length. Y.Shimizu and N.Takatori,"On the size dependency of diamagnetic susceptibility of quartz," Anniversary Volume of Prof.K.Honda, Science Reports of the Tohoku Imperial University, (Sendai, Japan, Oct.1936)306-311.

A size dependent susceptibility is also found in anisotropic crystals by the following worker, but the size dependence is not of the proper form. A.Pacault,"Magnetism of diamagnetic dispersions," Comptus Rendus, CCXXXIV(1952)2169-2171.

47. Historical: D.Iwanenko and L.Landau,"Theory of the magnetic electron, Part I," Zeitschrift für Physik,XLVIII(1928)340-348. Leigh Page,"Deflection of electrons by a magnetic field on the wave mechanics," Physical Review, XXXVI(Aug.1930)444-456. C.G.Darwin,"The diamagnetism of the free electron," Proceedings of the Cambridge Philosophical Society, XXVII(1930)86-90. J.S.Mitchell,"Diamagnetism of free electrons," Philosophical Magazine,XV(April,1933)807-810. L.Posener,"Magnetism of free electrons," Zeitschrift für Physik,LXXV (May, 1932)809-811.T.Takeuchi,"Diamagnetism of the free electron," Proceedings of the Physical and Mathematical Society of Japan, XIII(Oct.1931)267-268.

48. Reviews: A.H.Kahn and H.P.R.Frederikse,"Oscillatory behavior of magnetic susceptibility and electronic conductivity," Solid State Physics, IX(1959)257-291. R.E.Peierls,"Quantum Theory of Solids,"

Theoretical Physics in the Twentieth Century, (New York:Interscience Publishers, 1960),pp.140-160. A.B.Pippard,"Experimental analysis of the electronic structure of metals," Reports of the Physical Society on Progress in Physics,XXIII(1960)176-266.

49. Russian works: I.V.Gorenshtein,"Kinetics of the diamagnetism of free electrons," Zhurnal Eksperimental'noy i Teoreticheskoy Fiziki, XIX,No.8(Aug.1949)pp.164-167. Yu.B.Rumer,"Thermodynamics of the electron gas," ibid.,pp.757-759. G.E.Zilberman,"Magnetic properties of metals at low temperatures," ibid., XXI(1951)1209-1217.