Effect of the Electron Correlation on the Multiplet Structure of the $(3d)^2$ Configuration of Ti III and Cr V*

RAYMOND W. MIRES AND CHUN C. LIN†
Department of Physics, University of Oklahoma, Norman, Oklahoma
(Received 26 November 1963)

The effect of the electron correlation of the two valence electrons has been investigated for atoms with $(1s)^2$ $(2s)^2$ $(2p)^6$ $(3s)^2$ $(3p)^6$ $(3d)^2$ ground configuration. The atom is taken as a two-electron system with each electron moving in a Hartree-Fock type effective potential. A correlation factor $(1+cr_{12})$ is inserted in the wave function of each of the multiplet members obtained from the Hartree-Fock type one-electron orbitals, and the values of c are determined by the variation method. The use of the correlated wave function has improved, though overcorrected, the multiplet spacings of both Ti III and Cr V.

I. INTRODUCTION

IN the theory of multiplet structure of a two-electron configuration such as $(3d)^2$, the wave functions of various terms are usually taken as the Clebsch-Gordan type combination of products of one-electron orbitals.[1,2] The multiplet spacings are found to depend on, in the case of $(d)^2$, two Slater-Condon integrals. The usual procedure is to treat these integrals as adjustable parameters chosen to fit the experimental values of the levels. In this manner, reasonable agreement with experiment generally can be obtained, and the "empirical" values of the Slater-Condon integrals for the transition elements in various stage of ionization have been given in the literature.[3]

The Slater-Condon parameters can be calculated, in principle, from the wave function of the $3d$ electrons. It is well known that if the usual Slater orbitals are used as the $3d$ atomic wave function, the calculated Slater-Condon parameters are substantially smaller than the empirical values.[4] Satisfactory agreement with experimental values is obtained for the Slater-Condon parameters calculated from hydrogen-like wave functions only when a certain set of empirical rules of the effective nuclear charge is used.[5] A more accurate way to calculate these parameters is to use the Hartree-Fock $3d$ functions and indeed this has been done for many transition elements. It was found that the calculated multiplet spacings are considerably larger than the experimental values.[2] The discrepancy here can be ascribed to the configuration interaction. Each term in $(3d)^2$ interacts with the terms of the same symmetry in the upper configurations, and due to the different degree of interaction, the upper members of the $(3d)^2$ multiplet will be pushed down more than the lower ones, resulting in smaller multiplet spacings. However, a detailed calculation of the configuration interaction is very difficult, because of the large number of excited configurations which must be taken into consideration.

In this paper, we shall seek to improve the calculation of the multiplet structure from the approach of electron correlation. A correlation factor of the form $(1+cr_{12})$ will be inserted in the wave functions which were obtained from linear combinations of products of one-electron orbitals, and the parameter c is determined from the variation method. The accuracy of this method depends on the choice of the variational function, and the use of a simple form $(1+cr_{12})$ is, of course, not expected to lead to results as accurate as those derived from a detailed configuration interaction analysis. However, with the proper approximation our variational approach can be formulated in a rather simple manner and does not involve a great deal of numerical computation. The results of this calculation show an improvement over the case of the uncorrelated Hartree-Fock functions.

II. GENERAL FORMULATION

In order to simplify the numerical computation, we shall introduce the approximation of replacing the atom by a two-electron system with each electron moving in an effective potential $V(r)$ which includes the effect of the inner core. The use of this core model amounts to neglecting *part* of the interplay between the valence and the core electrons. The detailed approximate nature of the core model will be discussed in the next section in connection with the Hartree-Fock procedure. The Hamiltonian is now written as (in atomic units)

$$H=-\tfrac{1}{2}\nabla_1^2+V(r_1)-\tfrac{1}{2}\nabla_2^2+V(r_2)+(1/r_{12}). \quad (1)$$

The zeroth-order approximation consists of taking the wave function as a product of the one-electron wave functions ϕ_{nlm} which are the eigenfunctions of the operator H_1 and H_2, i.e.,

$$H_i\phi_{nlm}(\mathbf{r}_i)=[-\tfrac{1}{2}\nabla_i^2+U(r_i)]\phi_{nlm}(\mathbf{r}_i) =E_{nlm}{}^0\phi_{nlm}(\mathbf{r}_i), \quad (2)$$

$$\phi_{nlm}(r_i\theta_i\varphi_i)=R_{nl}(r_i)Y_{lm}(\theta_i\varphi_i).$$

* Supported by the Texas Instruments, Incorporated and by the U. S. Office of Naval Research.
† Alfred P. Sloan Foundation Fellow.
[1] E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge University Press, London, 1951).
[2] J. C. Slater, *Quantum Theory of Atomic Structure* (McGraw-Hill Book Company, Inc., New York, 1960), Vol. I.
[3] W. M. Cady, Phys. Rev. **43**, 322 (1933); M. A. Catalan and M. T. Antunes, Z. Physik **102**, 432 (1936); M. A. Catalan and F. Rohrlich, and A. G. Shenstone, Proc. Roy. Soc. (London) **A221**, 421 (1954); L. E. Orgel, J. Chem. Phys. **23**, 1819 (1955); M. Ostrofsky, Phys. Rev. **46**, 604 (1934); Y. Tanabe and S. Sugano, J. Phys. Soc. Japan **9**, 766 (1954).
[4] D. A. Brown, J. Chem. Phys. **28**, 67 (1958).
[5] N. F. Lane and C. C. Lin, Ann. Phys. (N. Y.) **20**, 234 (1962).

Here $U(r)$ differs from $V(r)$ in that the former has included the screening effect of one electron on the other. For the case of two equivalent electrons, the composite two-electron wave functions are obtained by forming linear combinations of the products of ϕ according to the Clebsch-Gordan coefficients

$$\psi_{LM}(1,2)=\sum_{m_1} C_{m_1,M-m_1}{}^{Lll}\phi_{nlm_1}(1)\phi_{nl,M-m_1}(2)$$
$$=R_{nl}(1)R_{nl}(2)\sum_{m_1} C_{m_1,M-m_1}{}^{Lll}\times Y_{lm_1}(\theta_1\varphi_1)Y_{l,M-m_1}(\theta_2\varphi_2). \quad (3)$$

To take the electron correlation into consideration, we shall modify the wave function in Eq. (3) into the form

$$N^{-1/2}\psi_{LM}(1,2)(1+cr_{12}), \quad (4)$$

where N is the normalization constant and c is to be determined by the variation method and is, of course, dependent on L. It can be readily shown that the appended wave functions in (4) are still eigenfunctions of L^2 and L_z with the same eigenvalues as the original functions $\psi_{LM}(1,2)$. One can then multiply the orbital functions in (4) by the appropriate spin functions for two-electron systems (singlet and triplet) to form the composite antisymmetric wave functions which are eigenfunctions of L^2, L_z, S^2, and S_z. Since no spin interaction terms were included in Eq. (1), the calculated energies do not depend explicitly on the spin functions and thus the spin part of the wave functions will be omitted in the following calculations. The energy is

$$W=(\psi(1+cr_{12})|H|\psi(1+cr_{12}))/N$$
$$=(\psi|(1+cr_{12})H(1+cr_{12})|\psi)/N. \quad (5)$$

The numerator can be considered as the diagonal matrix element of the operator

$$\bar{H}=H+c(r_{12}H+Hr_{12})+c^2r_{12}Hr_{12}$$

with the original uncorrelated wave functions in Eq. (3) as the basis. The last term can be simplified in the following way. Let us write the total Hamiltonian as

$$H=H_1+H_2+H', \quad (6)$$

where H', according to Eqs. (1) and (2), is

$$H'=(1/r_{12})+V(r_1)-U(r_1)+V(r_2)-U(r_2). \quad (7)$$

For two equivalent electrons we have

$$\langle r_{12}Hr_{12}\rangle=2\langle r_{12}H_1r_{12}\rangle+\langle r_{12}H'r_{12}\rangle. \quad (8)$$

From the property of the Laplacian operator it can be shown that

$$r_{12}H_1r_{12}=r_{12}{}^2H_1-1-r_{12}\nabla_1r_{12}\cdot\nabla_1. \quad (9)$$

Upon expanding the last term as

$$r_{12}\nabla_1r_{12}\cdot\nabla_1=\tfrac{1}{2}\nabla_1r_{12}{}^2\cdot\nabla_1$$
$$=\tfrac{1}{2}\nabla_1(r_1{}^2+r_2{}^2-2r_1r_2\cos\theta_{12})\cdot\nabla_1, \quad (10)$$

it is apparent that the $\cos\theta_{12}$ term vanishes as one integrates over the angular coordinates of the electron 2. It follows that

$$\langle r_{12}\nabla_1r_{12}\cdot\nabla_1\rangle=\langle\tfrac{1}{2}\nabla_1r_1{}^2\cdot\nabla_1\rangle=\left\langle r_1\frac{\partial}{\partial r_1}\right\rangle$$
$$=\int_0^\infty R_{nl}(1)r_1\frac{\partial}{\partial r_1}R_{nl}(1)r_1{}^2dr_1$$
$$=\frac{1}{2}\int_0^\infty\left[\frac{\partial}{\partial r_1}(r_1{}^3R_{nl}{}^2)-3r_1{}^2R_{nl}{}^2\right]dr_1=-\tfrac{3}{2}. \quad (11)$$

In a similar way we can show that

$$\langle r_{12}{}^2H_1\rangle=\langle(r_1{}^2+r_2{}^2-2r_1r_2\cos\theta_{12})H_1\rangle=2\langle r_1{}^2H_1\rangle. \quad (12)$$

Substitution of Eqs. (9), (11), and (12) into (8), results in

$$\langle r_{12}Hr_{12}\rangle=4\langle r_1{}^2H_1\rangle+1+\langle r_{12}H'r_{12}\rangle. \quad (13)$$

Also, since the eigenfunctions of H_1 are used as the basis, we have

$$\langle r_{12}H_1\rangle={}_1r\langle H_{12}\rangle=E_{nlm}{}^0\langle r_{12}\rangle. \quad (14)$$

By means of Eqs. (13) and (14), $\langle\bar{H}\rangle$ can be rewritten as

$$\langle\bar{H}\rangle=\langle H+2c(2r_{12}H_1+r_{12}H')$$
$$+c^2(4r_1{}^2H_1+r_{12}H'r_{12}+1)\rangle. \quad (15)$$

The normalization constant is

$$N=(\psi(1+cr_{12})|\psi(1+cr_{12}))=1+2c\langle r_{12}\rangle+2c^2\langle r_1{}^2\rangle. \quad (16)$$

The energies of each member of the multiplet associated with the ground configuration can be obtained by minimizing

$$W=\langle\bar{H}\rangle/N \quad (17)$$

with respect to c using the proper zeroth-order function according to Eq. (3) for a given L as the basis.

III. CORRELATED HARTREE-FOCK FUNCTIONS

So far we have not specified the choice of the potential functions $V(r)$ and $U(r)$ as introduced in Eqs. (1) and (2). The best way to obtain $V(r)$ is from the Hartree-Fock self-consistent field (SCF) functions of the inner electrons. Watson[6] has given extensive tabulation of the SCF wave function for the first-row transition elements. Our discussion here will be confined to the case of $(3d)^2$ although extension to other configurations with two equivalent electrons can be easily made.

Let us denote by inner core electrons those in the closed shell $(1s)^2\cdots(3p)^6$. The equation for the radial part of the SCF function of the $3d$ electrons is[2]

$$\left\{-\frac{1}{2}\frac{d}{dr_1}\left(r_1{}^2\frac{d}{dr_1}\right)-\frac{Z}{r_1}+\frac{3}{r_1{}^2}+\frac{1}{r_1}\left[\sum_{nl=1s}^{3p}N(nl)Y_0(nl,3d;r_1)\right.\right.$$
$$+\frac{1}{2\sqrt{5}}\sum_{nl=1s}^{3p}\frac{N(nl)}{(2l+1)^{1/2}}\sum_k c^k(20;l0)Y_k(nl,3d;r_1)$$
$$\left.\left.\times\frac{R_{nl}(r_1)}{R_{3d}(r_1)}\right]+\frac{1}{r_1}\sum_k a^{(k)}Y_k(3d,3d;r_1)\right\}R_{3d}(r_1)$$
$$=-\epsilon_{3d}R_{3d}(r_1), \quad (18)$$

where $N(nl)$ is the number of electrons in the (nl) closed shell, Z is the nuclear charge of the atom, $c^k(lm;l'm')$ are integrals involving the normalized associated Legendre functions $\Theta_{lm}(\theta)$, i.e.,

$$c^k(lm:l'm')=\left(\frac{2}{2k+1}\right)^{1/2}\int_0^\pi \Theta_{k,m-m'}(\theta)\Theta_{lm}(\theta) \times\Theta_{l'm'}(\theta)\sin\theta d\theta, \quad (19)$$

and

$$Y_k(nl,n'l':r_1)=r_1^{-k}\int_0^{r_1} R_{nl}(r_2)R_{n'l'}(r_2)r_2^{k+2}dr_2 +r_1^{k+1}\int_{r_1}^{\infty} R_{nl}(r_2)R_{n'l'}(r_2)r_2^{-k+1}dr_2. \quad (20)$$

The terms inside the square bracket in Eq. (18) represent the potential of the electric field generated by the inner core electrons. Thus, we may identify the effective potential $V(r)$ due to interaction of the inner core electrons as

$$V(r)=-\frac{Z}{r}+\frac{1}{r_1}\Bigg[\sum_{nl=1s}^{3p} N(nl)Y_0(nl,3d;r_1) +\frac{1}{2\sqrt{5}}\sum_{nl=1s}^{3p}\frac{N(nl)}{(2l+1)^{1/2}}\sum_k c^k(20;l0) \times Y_k(nl,3d;r_1)\frac{R_{nl}(r_1)}{R_{3d}(r_1)}\Bigg]. \quad (21)$$

The last term in the left-hand side of Eq. (18) is the result of the screening of one $3d$ electron on the other. The values of $a^{(k)}$ vary depending on whether we choose to minimize in the SCF procedure a particular multiplet level (unrestricted Hartree-Fock functions) or the weighted average of all the multiplets of the $(3d)^2$ configuration (restricted function).[6] In the former case, we have

$$a_L{}^{(k)}=\sum_{m_1m_1'} C_{m_1M-m_1}{}^{Lll}C_{m_1',M-m_1'}{}^{Lll} \times c^k(lm_1;lm_1')c^k(l,M-m_1';l,M-m_1) \quad (22)$$

and, for the latter,

$$a_c{}^{(0)}=1, \quad a_c{}^{(2)}=a_c{}^{(4)}=-2/63. \quad (23)$$

In this paper we shall use only the restricted SCF functions,[6] because in order to demonstrate the effect of the electron correlation on the multiplet spacing, one should use the same zeroth-order radial function for all five terms of $(3d)^2$.

Solutions of Eq. (18) have been given by Watson for several atomic ions with $(3d)^2$ configuration.[6] We shall now identify Eq. (18) with Eq. (2) and therefore obtain $U(r)$ as

$$U(r)=V(r)+r^{-1}\sum_k a_c{}^{(k)}Y_k(3d,3d;r), \quad (24)$$

with $V(r)$ given by Eq. (21). The one-electron functions ϕ are taken as Watson's analytic SCF orbitals.

We are now ready to introduce the correlation factor $(1+cr_{12})$ as described in Eq. (4). At this point, the approximation which is inherent with the "core" picture, must be made. The potential functions $V(r)$ and $U(r)$ are determined from the SCF orbitals of inner core electrons which in turn depend on the wave function of the $3d$ electrons. Thus, when the correlation factor is appended to the wave function of the two valence electrons, the SCF orbitals of the inner electron, and therefore $U(r)$ and $V(r)$, will change accordingly. In this work we shall ignore such a change in the functional forms of $U(r)$ and $V(r)$. This is the approximation involved in the core model which was referred to at the beginning of Sec. II.

Combination of Eqs. (6), (7), and (24) gives

$$H=H_1+H_2+H'; \quad H'=(1/r_{12})-\mathfrak{U}(r_1)-\mathfrak{U}(r_2), \quad (25)$$
$$\mathfrak{U}(r_i)=r_i^{-1}\sum_k a^{(k)}Y_k(3d,3d;r_i).$$

In order to reduce Eq. (15) to a more specific form, it is noted from Eqs. (25) that

$$\langle H\rangle=-2\epsilon+\langle 1/r_{12}\rangle-2\langle\mathfrak{U}(r_1)\rangle, =-2\epsilon+\sum_k a^{(k)}F^{(k)}(3d,3d)-2\langle\mathfrak{U}(r_1)\rangle, \quad (26)$$

where

$$F^{(k)}(3d,3d) =\int\int\frac{r_<^k}{r_>^{k+1}}|R_{3d}(r_1)R_{3d}(r_2)|^2r_1^2r_2^2dr_1dr_2. \quad (27)$$

Next r_{12} will be expanded by the Legendre polynominals as

$$r_{12}=\sum_k Q_k(r_<,r_>)P_k(\cos\theta_{12}), \quad (28)$$

$$Q_k(r_<,r_>)=\frac{r_<^{k+2}}{(2k+3)r_>^{k+1}}-\frac{r_<^k}{(2k-1)r_>^{k-1}}, \quad (29)$$

where $r_<$ and $r_>$ are the lesser and greater of r_1 and r_2. From Eq. (15) we can write

$$\langle\bar{H}\rangle=-2\epsilon+\sum_k a_L{}^{(k)}F^{(k)}(3d,3d)-2\langle\mathfrak{U}(r_1)\rangle -2c[2\epsilon\sum_k a_L{}^{(k)}M^{(k)}(3d,3d) +2\sum_k a_L{}^{(k)}R^{(k)}(3d,3d)-1] -c^2[4\epsilon\langle r_1^2\rangle-\sum_k a_L{}^{(k)}M^{(k)}(3d,3d) +2\langle r_1^2\mathfrak{U}(r_1)\rangle+2\langle r_1^2\rangle\langle\mathfrak{U}(r_1)\rangle-1], \quad (30)$$

where

$$M^{(k)}(nl,nl)=\int\int Q_k(r_<,r_>)|R_{nl}(r_1)R_{nl}(r_2)|^2 \times r_1^2r_2^2dr_1dr_2, \quad (31)$$

[6] R. E. Watson, Solid State and Molecular Theory Group, MIT, Cambridge, Massachusetts, Technical Report No. 12, 1959 (unpublished).

TABLE I. Comparison of the multiplet energies calculated with and without correlation for Ti III.

Level	c	Calculated energy (a.u.) No corr.	With corr.	Energy diff. (cm^{-1})
^3F	0.0704	−0.677022	−0.681043	882
^1D	0.1779	−0.626789	−0.647514	4548
^3P	0.1982	−0.616256	−0.639331	5064
^1G	0.2450	−0.598432	−0.631686	7298
^1S	0.5873	−0.482976	−0.627349	31686

Spacing	Obs. (cm^{-1})	Calculated (cm^{-1}) No corr.	with corr.	Deviation (%) No corr.	with corr.
^1D–^3F	8473	11025	7359	+30.1	−13.1
^3P–^3F	10570	13337	9155	+26.2	−13.4
^1G–^3F	14398	17249	10833	+19.8	−24.8
^1S–^3F	14053 (?)	42588	11784	···	···

$$R^{(k)}(nl,nl)=\int\int Q_k(r_<,r_>)\mathcal{U}(r_1)\,|\,R_{nl}(r_1)R_{nl}(r_2)\,|^2 \times r_1^2r_2^2dr_1dr_2. \quad (32)$$

The expression for the energy which is to be minimized is

$$\begin{aligned}W=&-2\epsilon+\{\textstyle\sum_k a_L{}^{(k)}F^{(k)}(3d,3d)-2\langle\mathcal{U}(r_1)\rangle\\&-2c[2\textstyle\sum_k a_L{}^{(k)}R^{(k)}(3d,3d)-1]\\&-c^2[-\textstyle\sum_k a_L{}^{(k)}M^{(k)}(3d,3d)+2\langle r_1{}^2\mathcal{U}(r_1)\rangle\\&+2\langle r_1{}^2\rangle\langle\mathcal{U}(r_1)\rangle-1]\}\\&\times[1+2c\textstyle\sum_k a_L{}^{(k)}M^{(k)}(3d,3d)+2c^2\langle r_1{}^2\rangle]^{-1}. \quad (33)\end{aligned}$$

Tables I and II show the results of the correlation coefficients and the multiplet spacings of the correlated wave functions as compared with experimental data[7] for Ti III and Cr V.

The simple correlation factor has improved considerably, though overcorrected, the calculated spacings of $^1D-{}^3F$ and $^3P-{}^3F$ in both Ti III and Cr V. The deviation of the ^1G–^3F, however, is larger with the correlated functions than with the uncorrelated ones. The experimental term value of the $(3d)^2\,{}^1G$ state for Cr V was obtained by extrapolation[7] and the uncertainty involved in this procedure could be responsible for this anomaly. In the case of Ti III, no immediate explanation can be given for the large deviation of the ^1G state.

The correlation coefficients and thus the energy suppression due to the correlation effect for the five members of $(3d)^2$ increase in the same order as the energy. Also, the correlation coefficients for Ti III and Cr V are nearly equal to each other. It is interesting to note that in the calculation of the correlation energy using $(1+cr_{12})$ for the $(1s)^2$ configuration of the isoelectronic sequence He, Li^+, Be^{2+}, ···, O^{6+}, the values of c obtained by the variational method are of nearly the same magnitude for the entire series.[8] Also, it was found that in the He sequence the simple $(1+cr_{12})$ correlation factor accounts for about half (or less) of the difference between the energies calculated from the product-type functions and the experimental energies.[8] Of course, for the helium-like atoms, one is dealing with the total energies rather than the energy spacings within a multiplet. However, these results do give some rough indications as to the degree of improvement on the multiplet spacings that can be reasonably expected from the $(1+cr_{12})$ appendage.

The two main approximations employed in this calculation are the choice of a simple correlation factor $(1+cr_{12})$ and the core model, and are presumably responsible for the major part of the discrepancy from the experimental term values. To improve the calculation, a two-parameter correlation form such as $[1+cr_{12}+c'(r_1-r_2)^2]$ may be used. Also, one can abandon the core approximation and repeat the SCF calculation using the correlated wave function for the two valence electrons to determine the improved wave functions of the inner core. This would result in a change of the effective potential $V(r)$. Examination of Eq. (30) shows that the multiplet spacings depend mainly on the radial part of the SCF function of the $(3d)$ electron, but do not contain $V(r)$ explicitly. Although $R_{3d}(r)$ is affected by $V(r)$, one may expect that the change in multiplet spacings produced by such a variation of $V(r)$ will not be a serious one. Finally, there is the question of the importance of the correlation terms between the valence electrons and the core electrons which have not been considered in this work. The inner-outer correlation is expected to have more influence on the absolute shifts of the energy of the entire $(3d)^2$ group than on the spacings between the components. In the absence of detailed calculations of the inner-outer correlation, no estimate can be given for the change of the multiplet

TABLE II. Comparison of the multiplet energies calculated with and without correlation for Cr V.

Level	c	Calculated energy (a.u.) No corr.	With corr.	Energy diff. (cm^{-1})
^3F	0.0725	−0.934298	−0.938856	1000
^1D	0.1797	−0.861935	−0.885135	5092
^3P	0.1951	−0.847776	−0.873253	5592
^1G	0.2416	−0.821558	−0.858753	8163
^1S	0.5544	−0.655069	−0.783719	28235

Spacing	Obs. (cm^{-1})	Calculated (cm^{-1}) No corr.	with corr.	Deviation (%) No corr.	with corr.
^1D–^3F	13200	15882	11790	+20.3	−10.7
^3P–^3F	15500	18989	14398	+22.5	− 7.1
^1G–^3F	[22060][a]	24744	17581	+12.2	−20.3
^1S–^3F	···	61284	34049	···	···

[a] Obtained by extrapolation (see Ref. 7).

[7] C. E. Moore, Nat. Bur. Std. (U.S.), Circ. No. 467.

[8] G. R. Ellison, Masters thesis, University of Oklahoma, 1963 (unpublished).

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

ACKNOWLEDGMENTS

The authors wish to thank Dr. K. Hijikata for suggesting the application of electron correlation to the multiplet structure calculation and for many enlightening discussions. We are also indebted to Dr. Turner Hasty and D. R. Powell for their assistance and continual interest in this work.

PHYSICAL REVIEW VOLUME 134, NUMBER 2A 20 APRIL 1964

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

LIONEL FRIEDMAN†
University of Pittsburgh, Pittsburgh, Pennsylvania

(Received 22 October 1963; revised manuscript received 30 December 1963)

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

I. INTRODUCTION

THE purpose of this paper is to present the results of some investigations concerning the steady diamagnetic susceptibility of "small" systems of electrons. A "small" system is defined as one whose characteristic linear dimensions (L) are very much less than the average radii (R_c) of the classical electronic orbits[1] in an applied dc magnetic field. In treating this problem, it is customary to idealize[2] the real physical situation to that of a free-electron gas confined to a box. The surface of the box is then represented by a simple, and analytically tractable, potential barrier. The use of such a model seems justifiable in view of the fact that the very existence and order of magnitude of size corrections for small systems have not been definitely established. These are, indeed, the subjects of the present paper.

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

The present paper began with an investigation of such effects by means of a detailed examination of a very simple geometrical model: namely, a plane-parallel slab, small (in the previously defined sense) in one dimension (at the boundaries of which the wave function is assumed to vanish), and satisfying periodic boundary conditions along the other two transverse dimensions. Such a geometry had been considered earlier by Papapetrou[5] who obtained just the Landau result[6] for a degenerate electron gas. In addition to confirming his calculation by an alternate procedure and obtaining

* This work was supported in part by the U. S. Air Force Office of Scientific Research, Grant No. AF 196-63.

† Present address: RCA Laboratories, Princeton, New Jersey. The author would like to thank RCA Laboratories for the opportunity of completing this work.

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

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

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

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

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