Model Calculation of Size Effects in Orbital Magnetism

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(Received 15 March 1991)

Size effects in the orbital magnetic susceptibility of small metallic systems are investigated by considering some simple model systems. The atomlike properties at low temperatures gradually evolve towards a diamagnetism close to the bulk Landau value at high temperatures, with only small size-dependent deviations. For k_BT smaller than the energy-level spacing, the susceptibility of an ensemble average of different particles is expected to show orbital paramagnetism. This mechanism is proposed as an explanation for the observations of Kimura and Bandow.

PACS numbers: 75.20.En, 35.20.My, 36.40.+d

Under the influence of a magnetic field the electrons in a metal are constrained to move on cyclotron orbits. This motion results in a small magnetic response, known as Landau diamagnetism. What happens when we decrease the size of the system or, alternatively, lower the field to the point where the cyclotron orbit radius R_c grows larger than the size of the system L?

Since the appearance of Landau's original paper [1], many workers have considered this question (e.g., see Denton [2] and references therein). In general, boundaries were found to have a small effect in the range of validity of the calculations (large quantum numbers), but the results all differ from Landau's result by at least a numerical factor. Landau diamagnetism seems to survive, at least qualitatively, for $L/R_c \rightarrow 0$, and apparently does not hinge on the existence of Landau orbits. More recently, both Robnik [3] and Altshuler, Gefen, and Imry (AGI) [4] predicted a paramagnetic correction for decreasing L. Speculations of giant diamagnetism [5], but also giant paramagnetism [6], have appeared. Here, we study the limit $L/R_c = 0$ by explicit calculation of the simplest possible models by which it is possible to demonstrate many effects, often predicted by more complicated models. We distinguish three kinds of size effects: (a) At temperatures T large compared to the energy-level spacing Δ/k_B a susceptibility close to the Landau value is obtained (deviations only a few percent) in both the degenerate and nondegenerate limits, even for just a few electrons in the box. The deviations are of the order of the surface corrections predicted by Robnik [3]. (b) For $k_BT/\Delta < 1$ there is only a lower bound to the susceptibility, set by the diamagnetic term. This lower bound is realized in spherical closed-shell clusters, as predicted by Kresin [7]. A large paramagnetism is found in systems with (near-)degenerate levels at the Fermi energy E_F. (c) Ensemble averages of particles with a distribution in size or structure can show a large orbital paramagnetism. This was also found for the diffusive regime by AGI [4]. We propose that this new size effect may describe the hitherto unexplained paramagnetism in small Mg particles reported by Kimura and Bandow [8].

The Hamiltonian of any system is modified by a magnetic field according to

$$\mathcal{H} = \mathcal{H}_0 + \frac{e}{2m_e} B \mathcal{L}_z + \frac{e^2}{8m_e} B^2 r_\perp^2 . \quad (1)$$

Here we have taken the field along the z axis, the symmetric gauge for the vector potential $\mathbf{A} = \frac{1}{2}\mathbf{B}\times\mathbf{r}$, and $r_\perp^2 = x^2 + y^2$. We ignore the spin of the electrons throughout. For high fields the last two terms lead to Landau quantization of the energy spectrum. Here, however, we are interested in the low-field limit so that these terms can be considered as small perturbations. The term in the z component of the angular momentum $\mathcal{L}_z$ produces paramagnetism: For a spherical system $\mathcal{L}_z$ is diagonal and we have a Zeeman splitting of the degenerate levels, resulting in a Curie-like paramagnetic susceptibility. In general, $\mathcal{L}_z$ is not diagonal, and the term is treated in second-order perturbation, known as van Vleck paramagnetism,

$$\chi_{\mathrm{vV}} = + \frac{\mu_0 e^2}{2m_e^2 \Omega} \sum_{k \neq 0} \frac{|\langle \psi_0 | \mathcal{L}_z | \psi_k \rangle|^2}{E_k - E_0} , \quad (2)$$

with Ω the volume of the system. Note that χ_{vV} increases for decreasing energy-level separation, i.e., for increasing system size. The last term in (1) produces Larmor diamagnetism in atoms, and is proportional to the square of the wave-function radius, and thus is also large for larger systems. The two large contributions approximately cancel, as will be shown below.

The simple model system that we will consider first is a sphere with infinite potential walls. The energy levels in a magnetic field are given by $E_{nlm}(B) = E_{nl}(0) + m\mu_B B + \alpha_{nlm} B^2$; m are the $\mathcal{L}_z$ eigenvalues and $\alpha_{nlm} B^2$ is the expectation value of the last term in (1). Inserting this energy in the grand canonical partition function, one can derive an expression [9] for the susceptibility at $B = 0$,

$$\chi = \frac{\mu_0}{\Omega} \sum_{nlm} f_0 \left[(1 - f_0) \frac{m^2 \mu_B^2}{k_B T} - 2\alpha_{nlm} \right] . \quad (3)$$

The first term in (3) is Curie-like at low temperatures; the last term is the temperature-independent diamagnetism. The factors f_0 and $1 - f_0$ describe the temper-

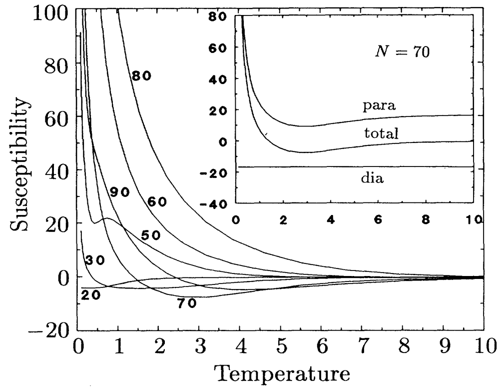

FIG. 1. The orbital susceptibility as a function of T for a spherical potential well, filled with N electrons; the number N is indicated for each curve. Inset: The two paramagnetic and diamagnetic contributions separately for $N=70$. The units for χ and T are $\mu_0 e^2/4\pi m_e a$ and $\hbar^2/2m_e a^2 k_B$, respectively, where a is the radius of the sphere.

ature-dependent occupation of the (n,l) quantum numbers, where $f_0(E_{nl},T)$ is the Fermi distribution at $B=0$. For a closed system the correct way would be to start from the canonical ensemble; however, we will concentrate on the high-temperature side $k_BT>\Delta$, where the distinction with the grand canonical ensemble vanishes. The α_{nlm} can be expressed in analytical form [9] and then it is straightforward to evaluate (3) numerically. The calculation was performed for all levels up to $2\times10^4\hbar^2/2m_e a^2$, with a the radius of the sphere, which involves n and l values up to 45 and 145, respectively. The chemical potential was adjusted at each temperature to keep N constant to within 10^{-5}.

Figure 1 shows the evolution of χ as a function of k_BT/Δ for various numbers of electrons N in a spherical box. $N=20$ is a closed-shell configuration, which is diamagnetic at low T. For the other examples we find a fast decay of χ with T, much faster than $1/T$. The inset shows, for $N=70$, how the paramagnetic term evolves from low-temperature Curie-like paramagnetism to a constant value at high T. This behavior is analogous to the high-temperature Pauli spin susceptibility for a degenerate electron gas. Here the orbital paramagnetism is almost exactly compensated by the temperature-independent diamagnetism. It is not obvious from Eq. (3) that the few paramagnetic terms near E_F that contribute to χ should compensate for all the diamagnetic terms below E_F. This compensation, however, is not exact, as is seen from the enlarged scale in Fig. 2. There is a residual diamagnetism which tends to a constant for high T and N. The vertical scale is normalized to the Landau expression for the diamagnetism of the degenerate free-electron gas,

$$\chi_L=-\mu_0\mu_B^2 n/2E_F \tag{4}$$

which is about $-0.128N^{1/3}$ on the scale of Fig. 1. Here

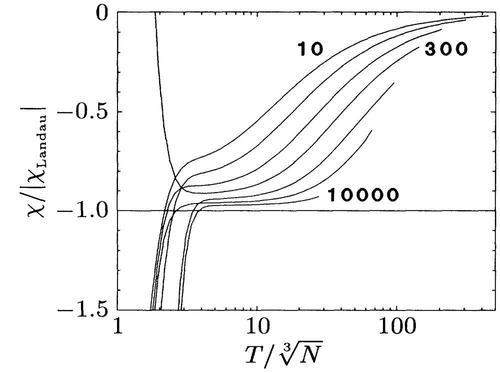

FIG. 2. The results of Fig. 1 normalized to the absolute value of the bulk Landau susceptibility for $N=10$, 30, 100, 300, 1000, 3000, and 10000. Note that the temperature is scaled by $N^{1/3}$ (see text).

E_F is the Fermi energy, n is the electron density, and $\mu_B=e\hbar/2m_e$. For low N and even higher temperatures, we observe a drop in the magnitude of χ. From Fig. 3 one observes that we are now in the nondegenerate limit of Landau diamagnetism,

$$\chi_L=-\mu_0\mu_B^2 n/3k_BT\,. \tag{5}$$

Indeed, for low N the condition $k_BT>\Delta$ soon implies $k_BT>E_F$. For low N the agreement with the bulk χ_L is almost exact; for higher N the temperature is in between the degenerate and nondegenerate limits resulting in deviations from the $1/T$ behavior. The plateaus in Fig. 2, though, are systematically above -1, with growing deviations for smaller N. This is the first size effect that we observe, and this was predicted by Robnik [3]. However, his results seem to overestimate the effects, in particular for the nondegenerate case. It seems that most of the deviations can be accounted for by a size correction to the Fermi energy [10], which enters χ through (4).

Note that the temperature scale in Fig. 2 is divided by $N^{1/3}$, showing that the onset of Landau diamagnetism for

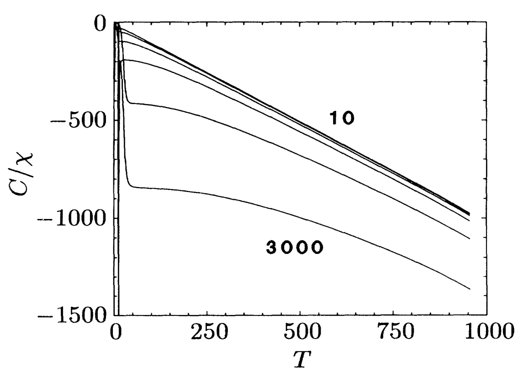

FIG. 3. The inverse susceptibility for the spherical well, normalized to C, with $\chi_L=-C/T$, the bulk Landau value, Eq. (5). $N=10$, 30, 100, 300, 1000, and 3000.

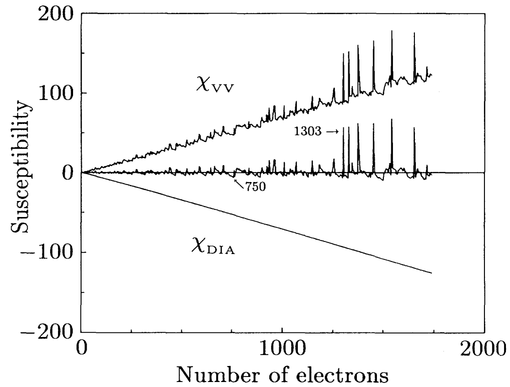

FIG. 4. The orbital susceptibility for a rectangular box at $T=0$ as a function of the number of particles in the box. The diamagnetic and paramagnetic contributions approximately cancel. Here the ratio of sizes along the x and y axes is $L_1/L_2=\sqrt{1.1}$. The units for χ are $\mu_0 e^2/m_e L_1$.

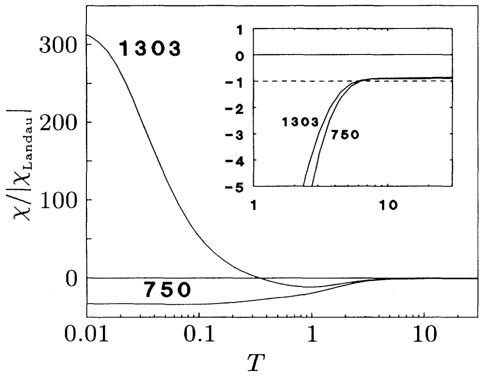

FIG. 5. Temperature dependence for $N=750$ and $N=1303$ (first high paramagnetic excursion in Fig. 4) of the rectangular box. Inset: Representation of how the bulk Landau value is approached.

the spherical system scales roughly with this factor. The underlying idea is that the scale for smoothing out the level-density fluctuations is not Δ, but $E_{n+1,l}-E_{n,l}$.

A realistic model for small particles will in general not be spherical. In order to illustrate that the results are not very sensitive to the special symmetry of the problem, we present a similar calculation for a rectangular box (some details can be found in Ref. [11]). Figure 4 shows the $\chi_{\rm dia}$ and $\chi_{\rm VV}$ terms separately (for a particular choice of gauge [11]) at $T=0$ as a function of the number of electrons. It demonstrates that in this case there is already approximate cancellation at $T=0$. The erratic structure on $\chi_{\rm VV}$ is due to the fluctuations in the energy-level spacing at E_F. The length of the sides of the box are chosen unequal in order to avoid degeneracies in this case. Figure 5 again shows how a steady diamagnetism survives at high temperatures. The large paramagnetism for $N=1303$ is a result of a small energy separation to the next level [Eq. (2)], and for k_BT larger than this energy the behavior for these near-degenerate levels is identical to that of the degenerate levels in Fig. 1.

We stress that this is a $B=0$ result and that we have made no assumptions on the physical size of the system. The size enters through the temperature scale and through N, which is commonly proportional to the volume. Size effects in orbital magnetism are, therefore, not a function of L/R_c, but rather of k_BT/Δ.

Although most systems are not perfectly spherical, the large diamagnetic susceptibilities for closed-shell configurations may be observed in size-selected clusters of alkali particles in vapor jets as predicted by Kresin [7]. The effect is limited, though, by the temperature, $k_BT<\Delta$. At room temperature the maximum diamagnetic susceptibility will be observed for particles of about 100 atoms.

For a general shape of small particles any sign and value above the diamagnetic curve in Fig. 4 is possible, and no definite trend as a function of particle size is expected [11]. However, for a distribution of particle sizes, the high paramagnetic excursions of Fig. 4 do not average out, as is shown in Fig. 6. For sufficiently wide distributions the result is always paramagnetic and may be much larger than $|\chi_L|$. This result is analogous to the predictions of AGI for the diffusive regime: When decreasing the particle size for *fixed temperature*, χ should increase from χ_L to a paramagnetic value, when an ensemble average of different particles is considered. Such effects may have been observed by Kimura and Bandow [8]. Their's is perhaps the only direct observation of the Kubo size effect for the spin susceptibility. At the same time they find an increase in the paramagnetic background for smaller particles, which has remained unexplained so far. Their estimate of the average Δ for the smallest particles is higher than 800 K [12]. This is sufficiently high to allow observation of orbital paramagnetism at room tem-

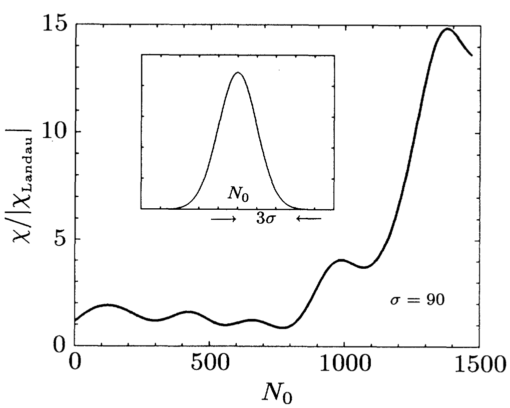

FIG. 6. Average susceptibility of a Gaussian distribution of boxes with different N values, of width $\sigma=90$, as a function of the center of the distribution N_0.

perature and the size of the effect can easily be accounted for. For particles larger than 100 Å the level spacing Δ is small enough that the bulk Landau value is expected in the experimental range of temperatures, in agreement with the observations. However, the observed temperature dependence for fixed particle size is weaker than expected from this simple model. For a detailed comparison a more realistic model of level distribution should be considered.

It is necessary to comment briefly on the relation between this work and that of AGI [4], since the approach is very different. We consider only simple, perfectly integrable model systems as opposed to the statistical treatment of diffusive particles in AGI. Further, AGI consider field-dependent effects at finite temperature, where we study only the $B=0$ limit. The results presented in Figs. 4 and 6 are exact and only when the temperature dependence of the susceptibility is calculated we make an approximation in using the grand canonical ensemble. This results in small errors in $\chi(T)$ for $k_BT < \Delta$; however, qualitatively the results are correct. For $k_BT > \Delta$ the results are *quantitatively* correct. In contrast to speculations of AGI, the results for the diffusive and integrable problems are not very different. In both cases a delicate balance between paramagnetic and diamagnetic contributions exists, with a residual paramagnetism at low temperatures when averaging over a set of particles. In AGI the average is taken over distributions of scattering centers; here we average over particle sizes. The very fact that both studies find qualitatively the same results suggests that the effect is very general, and independent of the model considered.

Finally, we would like to point out that the cancellation of the large paramagnetic and diamagnetic terms, that is found throughout, is required by the correspondence principle. For any classical system the Bohr–van Leeuwen theorem [13] maintains that the orbital moment is zero. At $k_BT \gg \Delta$ the quantization is washed out and the classical result should be obtained. The reason for χ_L to persist is discussed very clearly by Robnik [3]. The χ_L, Eq. (4), does not depend directly on the size of $\hbar$, but the quantum nature enters via the existence of a Fermi energy. Indeed, for $k_BT > E_F$ Eq. (5) applies, which vanishes as $\hbar^2$.

This work is part of the research program of the Leiden Materials Research Center (WFMO) and the Stichting voor Fundamenteel Onderzoek der Materie (FOM) and was made possible by financial support from the Nederlandse Organisatie voor Wetenschappelijk Onderzoek (NWO). One of us (J.M.v.R.) has profited from discussions with Professor David Shoenberg and Dr. Israel Vagner.

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