

Comments on the orbital magnetic susceptibility of electrons confined by smooth potentials*†

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Jennings and Bhaduri have recently derived an expression for the zero-field limit of the orbital magnetic susceptibility for a Maxwell-Boltzmann gas of electrons confined by a smooth potential. Their expression for the susceptibility, which represents the two lowest-order terms in its expansion in powers of Planck's constant, is shown to be, for a certain class of potentials, the two lowest-order terms in its high-temperature expansion as well.

Jennings and Bhaduri¹ have recently derived an expression for the orbital-magnetic susceptibility in the zero-field limit for a Maxwell-Boltzmann gas of electrons confined by a smooth potential. They find

$$\chi = \chi_L \left[1 - \frac{\hbar^2 \beta^2}{60m} \int \left(\frac{\partial^2 U}{\partial x^2} + \frac{\partial^2 U}{\partial y^2} \right) e^{-\beta U} d^3r / \int e^{-\beta U} d^3r \right], \tag{1}$$

where χ_L is the Landau susceptibility per particle given by $\chi_L = \frac{1}{3}\beta(e\hbar/2mc)^2$ and U is the potential. They state that Eq. (1) is the high-temperature expression for the susceptibility. While this is plausible, and is true for a certain class of potentials, they show only that Eq. (1) represents the first two terms in the expansion of the susceptibility in powers of Planck's constant. Since the integrals exhibited in Eq. (1) are functions of temperature, it is not obvious that Eq. (1) represents the lowest-order terms in the expansion of the susceptibility in inverse temperature. As a result of examining the same problem, I derived, independently, the expression for the susceptibility given in Eq. (1) and also succeeded in proving that for a certain class of potentials, Eq. (1) does, in fact, represent the first two terms in the expansion of the susceptibility in inverse temperature.² Hence, one can say that the leading term in the expansion for the susceptibility in powers of Planck's constant is also the infinite-temperature limit for the susceptibility, provided certain restrictions on the potential are met.

We require that the potential become positively infinite as configuration-space variables become infinite. This ensures that the electrons remain confined to some region of space. We also require that the potential has no poles other than the pole at infinity. Write the potential as

$$U(r, \theta, \varphi) = \sum_{n=1}^N f_n(\theta, \varphi) r^n,$$

where $f_n(\theta, \varphi)$ is positive definite. The proof may be extended to a larger class of potentials²; for

example,

$$U(x, y, z) = \sum_{n,l,m}^{N,L,M} a_{nlm} x^n y^l z^m,$$

where $n + l + m \leq N, L, M$ with N , the maximum value of n ; L the maximum value of l ; M , the maximum value of m ; and a_{N00} , a_{0L0} , and a_{00M} are positive definite.

We proceed with the outline of a derivation of the expression for the zero-field high-temperature-limit orbital magnetic susceptibility. Take the susceptibility to be given by

$$\chi = -\lim_{B \rightarrow 0} \frac{\partial^2 F}{\partial B^2},$$

where F is the free energy. Express the magnetic vector potential in the Landau gauge $\vec{A} = -B(y, 0, 0)$. After expanding the partition function to second order in field strength, performing the operations indicated to obtain χ , and using an expression developed by Goldberger and Adams³ to manipulate exponential operators in traces, one has that

$$\chi = \frac{e^2}{2Mc^2 Z_0} \left(\text{Tr} y^2 e^{-\beta \mathcal{H}_0} - \frac{\beta}{2M} \text{Tr} \int_0^1 ds p_x y e^{-(1-s)\beta \mathcal{H}_0} p_x y e^{-s\beta \mathcal{H}_0} \right), \tag{2}$$

where \mathcal{H}_0 , the zero-field Hamiltonian, is given by $\mathcal{H}_0 = T + U$ and $Z_0 = \text{Tr} e^{-\beta \mathcal{H}_0}$. The above expression for the susceptibility is quite similar to two expressions for the susceptibility already extant in the literature. Kubo's⁴ equation (6.1) is essentially the same as the above—the difference is that he used the symmetric gauge rather than the Landau gauge. Jennings and Bhaduri's¹ expression (A1) may be transformed into Kubo's expression by cyclically permuting exponential operators and changing variables of integration.

Taking the trace over plane waves and commuting $p_x y$ through $e^{-(1-s)\beta \mathcal{H}_0}$ one has

$$\chi = \frac{e^2}{2Mc^2 Z_0} \int_{\mathbf{K}} \int_{\mathbf{r}} e^{i\mathbf{K}\cdot\mathbf{r}} \left(y^2 - \frac{\beta}{2M} \int_0^1 p_x y \left\{ p_x y - (1-s)[\beta\mathcal{C}_0, p_x y] + \frac{(1-s)^2}{2} [\beta\mathcal{C}_0, (\beta\mathcal{C}_0, p_x y)] + \dots \right\} e^{-\beta\mathcal{C}_0} e^{-i\mathbf{K}\cdot\mathbf{r}} d^3K d^3r. \right. \quad (3)$$

Next, one develops the Wigner-Kirkwood⁵ expansion of $e^{-\beta\mathcal{C}_0}$ [i.e., $e^{-\beta U}(1 - \beta^2[T, U] + \dots)e^{-\beta T}$], where the terms denoted (\dots) are various combinations of commutators of the T and U operators. Finally, one proceeds to evaluate the commutators, carry out the indicated differentiations and perform integrations over s and \mathbf{K} space. One is then left with an expansion in \hbar , whose coefficients are integrals over configuration space of functions of temperature and the potential U . The exact form of the coefficients is unimportant for the purpose of this argument since we shall assume that the expansion in positive powers of Planck's constant has already been achieved. We are concerned here only with finding the relation-

ship between \hbar and β .

We shall first assume that the potential is homogenous of degree N ; this restriction will later be lifted. Make the following transformations:

$$\vec{r} \rightarrow \vec{r}' = \beta^{1/N} \vec{r}, \quad (4a)$$

$$\vec{p} \rightarrow \vec{p}' = (\beta/2M)^{1/2} \vec{p} = -i\lambda\beta^{1/N} \nabla', \quad (4b)$$

$$U' = \beta U, \quad (4c)$$

$$T' = \beta T = -\lambda^2 \nabla'^2 = -\lambda^2 \beta^{2/N} \nabla'^2, \quad (4d)$$

where λ is the thermal De Broglie wavelength given by $\lambda = (\hbar^2 \beta / 2M)^{1/2}$. With the above transformations we may rewrite the susceptibility as

$$\chi = \left(\frac{e^2}{2Mc^2 Z_0} \right) \beta^{-2/N} \left(\text{Tr} y'^2 e^{-\mathcal{C}'_0} + \lambda^2 \beta^{2/N} \text{Tr} \int_0^1 ds \frac{\partial}{\partial x'} y' e^{-(1-s)\mathcal{C}'_0} \frac{\partial}{\partial x'} y' e^{-s\mathcal{C}'_0} \right). \quad (5)$$

Wherever $-i\hbar$ appeared in the expansion of Eq. (3) as the result of evaluating commutators, the factor $-i\lambda\beta^{1/N}$ now appears. For example,

$$[\vec{p}, x] = -i\hbar \rightarrow [\vec{p}', x'] = -i\lambda\beta^{1/N}.$$

Now, except for the overall multiplicative factor of $\beta^{2/N}$, the only place where β occurs is with \hbar in the combination $\lambda\beta^{1/N}$. Hence an expansion in powers of \hbar is also an expansion in powers of $\lambda\beta^{1/N}$.

Next proceed to complete the proof by considering potentials which are not homogenous. We do this by comparing the temperature dependence of a typical term in the expansion of the susceptibility when the potential is homogenous to that same term when the potential is nonhomogenous. Take the potential to be given by

$$U(r, \theta, \varphi) = \sum_{n=1}^N f_n(\theta, \varphi) r^n. \quad (6)$$

Next, make the transformations (4a)–(4d) as in the homogenous case. We may then write the transformed potential

$$U' = \beta U = f_N(\theta, \varphi) r'^N + \sum_{n=1}^{N-1} f_n(\theta, \varphi) \beta^{(N-n)/N} r'^n.$$

The first of two terms is independent of tempera-

ture and is the only term that would appear if the potential were homogenous of degree N ; the second term contains only positive powers of β . It follows that the leading temperature dependence of any term in the high-temperature expansion of the susceptibility, for a potential of the form given by Eq. (6), vanishes no slower with β than that same term does when the potential is homogenous of order N . This would indicate that for a potential of the form given by Eq. (6) that \hbar and β appear in the expansion of the susceptibility in the combination $\hbar^2 \beta^{1+1/N}(1 + \dots)$ where (\dots) denotes terms of order greater than 0 in β , but this is not so. It could happen that the leading term in β (the only term present if the potential is homogenous) for some typical term in the expansion of the susceptibility vanishes when integrated over configuration space. In such a case the relationship of \hbar and β would be given by $\hbar^2 \beta^{1+\epsilon+1/N}(1 + \dots)$, where $\epsilon > 0$ and (\dots) denotes terms of order greater than 0 in β . Thus we have that \hbar and β always occur in the combination $\hbar^2 \beta^{1+\epsilon+1/N}(1 + \dots)$, where (\dots) denotes terms of order greater than 0 in β and $\epsilon \geq 0$. We have then that a term of order \hbar^{2N} in Planck's constant is also a term of order at least $\beta^{1+1/N}$ in inverse temperature.

It is tempting to try to extend the validity of Eq. (1) to the case of hard-wall potentials (i.e., the po-

tentials confining the electrons are infinitely deep square-well-type potentials). This one may not do. Consider a potential of the form $U(r) = U_0(r/r_0)^n$, where r_0 is some constant and n is some positive integer. For such a potential the second term in Eq. (1) becomes $(\hbar^2\beta/30M)(\beta U_0/r_0)^{2/n}g(n)$, where $g(n) = n(n-1)\Gamma[(n-1)/n]/\Gamma(1/n)$. If we set $n=2$, we recover Jennings and Bhaduri's result for the isotropic harmonic oscillator; and, indeed, for any finite value n , Eq. (1) is a valid expression for the susceptibility. Equation (1), however, is not valid for the infinite square-well case. (If we take the $n \rightarrow \infty$ limit, the potential above becomes an infinite square well, but for large n the second term in Eq. (1) becomes proportional to n^2 and so diverges as $n \rightarrow \infty$.) The infinite square-well case for certain geometries has been studied elsewhere.^{2,6} It is found that the susceptibility may

be written $\chi = \chi_L[1 + O(\hbar\beta^{1/2})]$, not $\chi = \chi_L[1 + O(\hbar^2\beta)]$, as is indicated by the form of the correction term in Eq. (1). Evidently the operations of taking the trace and passing to the limit $n \rightarrow \infty$ may not be interchanged.

I have derived the expression for the two lowest-order terms in the expansion of the susceptibility in powers of Planck's constant for a smooth potential which is bounded. This expression is identical to Eq. (1). Bounded potentials more accurately represent the surface potential seen by an electron in a metal than do unbounded potentials. The calculation of the susceptibility is more lengthy when the potential U is a bounded potential; for such potentials one may not always cyclically permute operators in traces.² If one may not cyclically permute operators in traces, one may not use Eq. (2) as the expression for the susceptibility,

but the more complicated expression

$$\chi = \frac{e^2}{2Mc^2Z_0} \left(\text{Tr} \int_0^1 ds e^{-(1-s)\beta\mathcal{H}_0} y^2 e^{-s\beta\mathcal{H}_0} - \frac{\beta}{M} \int_0^1 s_1 ds_1 \int_0^1 ds_2 e^{-(1-s_1)\beta\mathcal{H}_0} p_x y e^{-s_1 s_2 \beta\mathcal{H}_0} \right). \quad (7)$$

One may not cyclically permute the exponential operators, if the potential is bounded. I have not, however, succeeded in proving that Eq. (1) is also the first two terms in the high-temperature expansion of the susceptibility though such a conclusion seems probable. One may use such bounded potentials to describe finitely deep potential wells. If the number of such wells is finite then the second-order term in Eq. (1) vanishes by phase-space considerations when integrations are taken over all space—this is equivalent to saying that electrons at a high temperature do not feel a finite number of finitely deep potentials in infinite space. However, if the density of such potential wells is finite, then the second-order term in Eq. (1) does not vanish. Hence, one would expect that Eq. (1) describes the contribution to the susceptibility due

to impurity atoms in solids or due to alloying of solids. Equation (1) agrees with a theorem by Kohn and Lumming⁷ which states that for weak potentials the correction to the zero-field susceptibility is second order in the potential strength.

In closing, I would like to point out that one should be able to construct similar proofs for the relation between \hbar and β for other thermodynamic quantities when classical statistics and potentials which are smooth and increase without bound as configuration-space variables increase without bound are involved.

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