

Gauge Variance of Diamagnetic and Paramagnetic Moments

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Abstract

A simple expression is obtained for the origin dependent change of the gauge variant paramagnetic and diamagnetic components of the electronic orbital magnetic moment. The sum of the two is gauge invariant, as is the total magnetic susceptibility.

A partial proof that the sum of the paramagnetic and diamagnetic susceptibilities of a molecule is invariant under a change of the origin of the vector potential that describes the uniform magnetic field applied to the molecule was given long ago in the book by Van Vleck (1932). However, the issue is one that still attracts attention and a variety of proofs of this theorem continues to appear (Griffith 1961; Geersten 1989). In this note we provide a derivation of the theorem that is applicable not only to the susceptibilities but to the magnetic *moments* themselves. In contrast to former treatments this derivation involves essentially operators alone and therefore is independent of the basis wavefunctions that are used or any particular perturbation scheme. The derivation both gives an explicit expression for the change in the diamagnetic and paramagnetic moments due to a shift of origin and explains naturally an observation of Chan and Das (1962) that the magnitudes of the paramagnetic and diamagnetic moments are smallest when the origin of coordinates is at the centre of charge of the molecule.

We start by considering the situation classically. The orbital magnetic moment \mathbf{m} of a particle with charge e and velocity \mathbf{v} at a distance \mathbf{r} from the origin of coordinates (Fig. 1) is

$$\mathbf{m} = \frac{e}{2} \mathbf{r} \times \mathbf{v}. \quad (1)$$

In an interval of time δt the position vector \mathbf{r} sweeps out an area $\delta \mathbf{S} = \mathbf{r} \times \mathbf{v} \delta t / 2$ so $\mathbf{m} = e d\mathbf{S} / dt$. If the particle moves in a closed orbit of period T then the time average value of the magnetic moment is

$$\bar{\mathbf{m}} = T^{-1} \int_0^T \mathbf{m}(t) dt$$

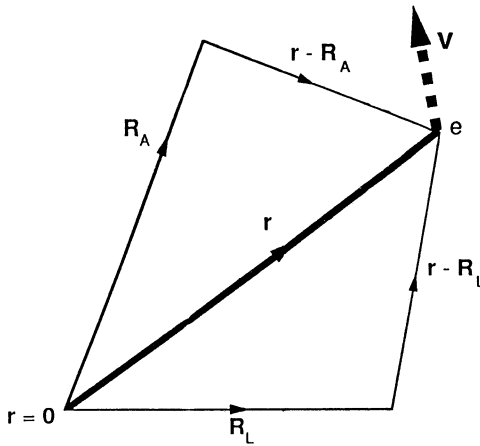


Fig. 1. The particle with charge e and velocity \mathbf{v} is at position \mathbf{r} . In the unprimed system the origin of the vector potential and the point about which the orbital angular momentum is calculated are both at $\mathbf{r} = \mathbf{0}$. In the course of the calculation this point is chosen to be at the centre of charge of the molecule. In the primed system the origin of the vector potential is at \mathbf{R}_A and the point about which the orbital angular momentum is calculated is at \mathbf{R}_L .

or given by the usual expression $\overline{\mathbf{m}} = I\mathbf{S}$, where $I = e/T$ is the current and

$$\mathbf{S} = \oint \mathbf{r} \times d\mathbf{r}/2$$

is the projected area. If now, instead of taking the origin about which the angular momentum is calculated to be at $\mathbf{r} = \mathbf{0}$ we take it at $\mathbf{r} = \mathbf{R}_L$ (Fig. 1), then the magnetic moment in this new (primed) system is $\mathbf{m}' = (\mathbf{r} - \mathbf{R}_L) \times \mathbf{v}e/2$ or

$$\overline{\mathbf{m}'} = \overline{\mathbf{m}} - \frac{e}{2} \mathbf{R}_L \times \int_0^T \mathbf{v}(t) dt. \quad (2)$$

If there is no bulk transport current, so that the integral of $\mathbf{v}(t)$ is zero, it follows that $\overline{\mathbf{m}'} = \overline{\mathbf{m}}$ and the average magnetic moment is independent of the origin of coordinates. An identical result will be found to hold in the quantum mechanical case which we consider next.

It is well known (Aitchison and Hey 1989) that, if the electromagnetic vector potential \mathbf{A} is transformed so that $\mathbf{A} \rightarrow \mathbf{A}' = \mathbf{A} + \nabla\chi$ and the electrostatic potential ϕ changes to $\phi' = \phi - \partial\chi/\partial t$, then the electromagnetic fields \mathbf{E} and \mathbf{B} remain unaltered. The single valued scalar field $\chi(\mathbf{r}, t)$ is known as a gauge field and is proportional to the unit quantum mechanical operator (it is called a c-number). If the wavefunction Ψ of the system that is transformed becomes $\Psi \rightarrow \Psi' = \Psi \exp(i e \chi / \hbar)$, then the transformed Hamiltonian \mathcal{H}' (which involves \mathbf{A}' and ϕ') and wavefunction Ψ' will obey the same time dependent Schrödinger equation as the untransformed system involving \mathbf{A} and ϕ . Physical variables such as the charge and current densities are unchanged. Any operator that represents a physical quantity must be gauge invariant in the sense that the matrix elements of the transformed operator between the transformed states must be independent of the gauge field.

In quantum mechanics the dynamical quantity of importance is not \mathbf{v} but the canonical momentum $\mathbf{p} = m\mathbf{v} + e\mathbf{A}$, where m is the mass of the particle. According to the prescription for quantisation (Dirac 1947) the quantity \mathbf{p} becomes the quantum mechanical operator $-\hbar\nabla$. Accordingly the velocity operator is

$\mathbf{v} = (\mathbf{p} - e\mathbf{A})/m$ and the operator for the orbital angular momentum is

$$\mathbf{m} = \frac{e}{2m} \mathbf{r} \times (\mathbf{p} - e\mathbf{A}). \quad (3)$$

This expression may also be obtained (Stewart 1996) as the derivative $\mathbf{m} = -\nabla_{\mathbf{B}} \mathcal{H}$ with respect to a uniform magnetic field \mathbf{B} of the Hamiltonian $\mathcal{H} = (\mathbf{p} - e\mathbf{A})^2/2m$. It is well known (Aitchison and Hey 1989) that, although the canonical momentum \mathbf{p} is not gauge invariant, the quantity $m\mathbf{v} = \mathbf{p} - e\mathbf{A}$ (commonly called the kinematic momentum) is because the gradient operator acting on the phase of the transformed wavefunction produces a term that cancels that coming from the $e\mathbf{A}$ term. Because \mathbf{r} is also gauge invariant it follows that the orbital magnetic moment of a single particle is gauge invariant too. The gauge part of the phase of the wavefunction of a many particle system may be constructed by adding up the phases of the individual particles and so the same result holds for a many particle system. It is also true that the magnetic moment of the spin is gauge invariant because the spin is not associated with the electromagnetic potentials in non-relativistic theory. Accordingly it follows quite generally that the total magnetic moment of a body is independent of gauge. We ignore the spin in the remainder of this note and consider the orbital moment only.

With a uniform magnetic field $\mathbf{B} = \nabla \times \mathbf{A}$ the conventional choice for the vector potential is $\mathbf{A} = \mathbf{B} \times \mathbf{r}/2$, with \mathbf{B} a c-number, so that the orbital magnetic moment operator \mathbf{m} may be expressed as the sum of two terms

$$\mathbf{m} = \frac{e}{2m} \mathbf{r} \times \mathbf{p} - \frac{e^2}{4m} \mathbf{r} \times (\mathbf{B} \times \mathbf{r}), \quad (4)$$

or $\mathbf{m} = \mathbf{m}^p + \mathbf{m}^d$, where the paramagnetic moment is $\mathbf{m}^p = \mathbf{r} \times \mathbf{p}(e/2m)$ (no assumption is made that the magnetisation associated with it is proportional to the applied field) and the diamagnetic moment is $\mathbf{m}^d = -\mathbf{r} \times (\mathbf{B} \times \mathbf{r})(e^2/4m)$. The diamagnetic moment is quadratic in \mathbf{r} and linear in \mathbf{B} and it may be expressed in matrix form as $m_{\alpha}^d = \Sigma_{\beta} \hat{\chi}_{\alpha\beta}^d B_{\beta}$ where the Greek letters indicate the Cartesian components and, by expansion of the triple vector cross product,

$$\hat{\chi}_{\alpha\beta}^d = -(r^2 \delta_{\alpha\beta} - r_{\alpha} r_{\beta}) e^2/4m, \quad (5)$$

where δ is the Kronecker delta. The quantity $\hat{\chi}_{\alpha\beta}^d$ is an operator; the usual diamagnetic susceptibility (Stewart 1994) is given by its expectation value or thermal statistical average. We shall find that, although the expectation values of the paramagnetic and diamagnetic terms are not generally individually independent of the origins of \mathbf{A} and the point about which the angular momentum is calculated, the sum of them is.

To demonstrate this we calculate the expectation value of the magnetic moment in the primed system in which the origin of the vector potential has been changed from $\mathbf{r} = \mathbf{0}$ to $\mathbf{r} = \mathbf{R}_A$ so that the vector potential is transformed to $\mathbf{A} \rightarrow \mathbf{A}' = \mathbf{B} \times (\mathbf{r} - \mathbf{R}_A)/2 = \mathbf{A} - \mathbf{B} \times \mathbf{R}_A/2$. The gauge field is found by a trivial integration to be $\chi(\mathbf{r}, t) = -(\mathbf{B} \times \mathbf{R}_A) \cdot (\mathbf{r} - \mathbf{C})/2$, where \mathbf{C} is any vector in real space that does not depend on \mathbf{r} . The origin about which

the magnetic moment is calculated is also changed to \mathbf{R}_L so the magnetic moment \mathbf{m} transforms to $\mathbf{m}' = \mathbf{m}^{\text{p}'} + \mathbf{m}^{\text{d}'}$ where $\mathbf{m}^{\text{p}'} = (\mathbf{r} - \mathbf{R}_L) \times \mathbf{p}e/2m$ and $\mathbf{m}^{\text{d}'} = -(\mathbf{r} - \mathbf{R}_L) \times \{\mathbf{B} \times (\mathbf{r} - \mathbf{R}_A)\}e^2/4m$. The latter may be expressed as

$$\mathbf{m}^{\text{d}'} = \mathbf{m}^{\text{d}} - \{\mathbf{R}_L \times (\mathbf{B} \times \mathbf{R}_A) - \mathbf{r} \times (\mathbf{B} \times \mathbf{R}_A) - \mathbf{R}_L \times (\mathbf{B} \times \mathbf{r})\}e^2/4m. \quad (6)$$

We next calculate the result of the paramagnetic term acting on the transformed wavefunction

$$\mathbf{m}^{\text{p}'}\Psi' = -(\mathbf{r} - \mathbf{R}_L) \times \nabla\{\Psi \exp(i e\chi/\hbar)\}(i e\hbar/2m).$$

Noting that the gradient acts on both the phase and on Ψ and using the chain rule for differentiation we obtain for this quantity $(e/2m)\exp(i e\chi/\hbar) \times (\mathbf{r} - \mathbf{R}_L) \times \{\mathbf{p} - (\mathbf{B} \times \mathbf{R}_A)e/2\}\Psi$. If we now take the thermal statistical average of $\mathbf{m}^{\text{p}'}$ by taking the expectation values in the states Ψ' we obtain

$$\langle \mathbf{m}^{\text{p}'} \rangle = \langle \mathbf{m}^{\text{p}} \rangle - \mathbf{R}_L \times \langle \mathbf{p} \rangle e/2m + \{\mathbf{R}_L \times (\mathbf{B} \times \mathbf{R}_A) - \langle \mathbf{r} \rangle \times (\mathbf{B} \times \mathbf{R}_A)\}e^2/4m, \quad (7)$$

where $\langle O \rangle$ indicates the thermal statistical average of any operator O at temperature T which is $\text{Trace}\{O \exp(-\mathcal{H}/kT)\}/\text{Trace}\{\exp(-\mathcal{H}/kT)\}$, where k is Boltzmann's constant. If the thermal average of equation (6) is now added to (7) we get

$$\langle \mathbf{m}' \rangle = \langle \mathbf{m} \rangle - \mathbf{R}_L \times \langle \mathbf{p} - e\mathbf{A} \rangle e/2m, \quad (8)$$

which is the quantum analogue of equation (2). If the gauge invariant quantity $\langle \mathbf{p} - e\mathbf{A} \rangle = m\langle \mathbf{v} \rangle$ is zero, which it will be if there is no bulk transport current (a transport current is not consistent by Maxwell's equations with a uniform magnetic field), then $\langle \mathbf{m}' \rangle = \langle \mathbf{m} \rangle$ and the total orbital magnetic moment is independent of the changes of origin. It follows that the magnetic moment of an assembly of independent atoms is equal to the sum of their individual magnetic moments.

At zero temperature the calculation of the diamagnetic susceptibility requires only a ground state expectation value to be taken but the paramagnetic susceptibility is harder to obtain as it must be calculated by second order perturbation theory which requires the excited states of the molecule to be known. Because of this it is sometimes useful to calculate the diamagnetic and paramagnetic moments separately. The question then arises of how to combine individual moments arising from atoms situated at different origins. This may be answered most simply by choosing the origin of the unprimed system to be at the centre of charge of the atom so that $\langle \mathbf{r} \rangle = \mathbf{0}$. Equation (7) is further simplified by noting that $\langle \mathbf{p} \rangle = \mathbf{0}$. Although \mathbf{p} is a gauge dependent quantity the gauge field is zero in the unprimed system in which $\langle \mathbf{p} \rangle$ is calculated and so for an atom, for example, the average value of \mathbf{p} is well defined. Equations (6) and (7) then become

$$\langle \mathbf{m}^{\text{d}'} \rangle = \langle \mathbf{m}^{\text{d}} \rangle - \mathbf{R}_L \times (\mathbf{B} \times \mathbf{R}_A)e^2/4m, \quad (9a)$$

$$\langle \mathbf{m}^{\text{p}'} \rangle = \langle \mathbf{m}^{\text{p}} \rangle + \mathbf{R}_L \times (\mathbf{B} \times \mathbf{R}_A)e^2/4m. \quad (9b)$$

The correction for change of origin is linear in \mathbf{B} and is only non-zero when both \mathbf{R}_L and \mathbf{R}_A are non-zero. It has no component along \mathbf{R}_L and is zero if \mathbf{B} is parallel to \mathbf{R}_A or if \mathbf{R}_L is orthogonal to both \mathbf{R}_A and \mathbf{B} . The most usual case to be considered is when the properties of several atoms are referred to the same origin so that $\mathbf{R}_A = \mathbf{R}_L = \mathbf{R}$. In this case the correction is quadratic in \mathbf{R} . This provides an explanation for the observation of Chan and Das (1962) that the magnitudes of both their calculated paramagnetic and diamagnetic susceptibilities were least when the origin was at the centre of charge and varied quadratically with distance away from it. The interpretation of equations (9) in this situation is as follows. The α Cartesian component of the quantity $\mathbf{R} \times (\mathbf{B} \times \mathbf{R})e^2/4m$ is given by $\sum_{\beta} B_{\beta}(R^2\delta_{\alpha,\beta} - R_{\alpha}R_{\beta})e^2/4m$. If the diamagnetic susceptibility were calculated with respect to an origin at \mathbf{R} then it would be given by replacing \mathbf{r} in (5) with $(\mathbf{r} - \mathbf{R})$. This would result in a susceptibility operator of $-\{(\mathbf{R} - \mathbf{r})^2\delta_{\alpha,\beta} - (\mathbf{r} - \mathbf{R})_{\alpha}(\mathbf{r} - \mathbf{R})_{\beta}\}e^2/4m$. Since we have chosen $\langle \mathbf{r} \rangle$ to be zero the cross terms in this expression vanish and the result is equal to the sum of the two terms in (9a). The second term in (9b) is needed to ensure the gauge invariance of the total magnetic moment. It is clear that in general the paramagnetic and diamagnetic parts of the orbital moment have no meaning on their own, only their sum has. Similar arguments may be applied to the chemical shift.

Acknowledgment

Dr Richard Bramley is thanked for useful discussions.

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