

Comment on “Bosons as the Origin for Giant Magnetic Properties of Organic Monolayers”

Vager and Naaman have published an interesting and attractive Letter [1] trying to explain the amazing appearance of giant magnetic properties observed for organic thiols adsorbed on gold [2,3]. Their theory is based upon the following assumptions: (i) the giant magnetic moment is due to transferred electrons from gold to the organic molecules that occupy negative ion states at the interface, with a large radius around the molecular axis, (ii) this magnetic moment has orbital origin, (iii) two border-squeezed electrons form a triplet of spin 1 and consequently the orbital moment should be \hbar times an odd integer, and (iv) the large radius of the orbit is the radius of the domain, ξ , that does not change upon cooling or upon applying magnetic field B , that magnetic field being applied along the z axis, i.e., perpendicular to the orbit and to the interface.

Based on these reasonable statements they considered the L_z dependent Hamiltonian

$$H_o = \frac{L_z^2}{2m\xi^2} - \frac{q}{2m}L_zB. \quad (1)$$

One immediately observes that minimization of the energy eigenvalues with respect to L_z yields the following value for the classical angular momentum at the fundamental state:

$$L_z = \frac{q\xi^2B}{2}, \quad (2)$$

where q and m are the charge ($2e$) and mass ($2m_e$) of the pair of electrons, respectively.

However, the Hamiltonian considered above, (1), missed the diamagnetic term H_d , always present for orbital magnetism and that for this case can be written as

$$H_d = \frac{q^2\xi^2}{8m}B^2. \quad (3)$$

Therefore, the minimum classical eigenvalue of the Hamiltonian $H = H_o + H_d$ that corresponds to $L_z = \frac{q\xi^2B}{2}$ becomes

$$E\left(L_z = \frac{q\xi^2B}{2}\right) = \frac{q^2\xi^2}{8m}B^2 - \frac{q^2\xi^2B}{4m} + \frac{q^2\xi^2}{8m}B^2 = 0. \quad (4)$$

According to relation (4), the total magnetic moment, defined as $-(dE/dB)$, is obviously zero, in contrast with the result obtained in Ref. [1]. The exact compensation of the diamagnetic and paramagnetic terms, described by (4),

reflects for this case the general statement established by the Van Leeuwen [4] theorem. According to this important theorem of classical statistical mechanics, since the orbital magnetic moment is a linear function of the speed of the particles, its thermodynamics equilibrium value is zero. In fact, the result obtained in (4) corresponds to the L value that minimizes the energy of a particle with charge q and original orbital moment L , provided that L modulus can take any value between zero and infinity. Note that the condition for thermodynamics equilibrium at 0 K corresponds to minimum energy.

However, in the framework of quantum mechanics and by considering the discontinuous spectrum of L_z , it can be observed that the magnetic moment at the fundamental state depends on B . For $B = 0$, the diamagnetic or induced orbital moment is zero, whereas due to the antisymmetry requirement the original orbital moment is \hbar , even though classically it would be zero. As B increases, L_z remains constant but the diamagnetic moment increases, up to a field strength at which a new jump of the orbital moment takes place. Therefore, the model, when it includes the diamagnetic term, predicts a periodic dependence of the orbital moment with B in which L modulus varies between \hbar and $-\hbar$. Consequently, the induction of giant moments is far from being clearly explained after taking into account the diamagnetic term.

In summary, a more complete analysis, including the diamagnetic contribution, should be carried out to ascertain whether the assumptions established by Vager and Naaman could be underlying the observed magnetic behavior.

A. Hernando and M. A. García
Instituto de Magnetismo Aplicado
RENFE-UCM
and Departamento de Física de Materiales UCM
Post Office Box 155
Las Rozas
Madrid 28230
Spain

Received 8 August 2005; published 20 January 2006

DOI: [10.1103/PhysRevLett.96.029703](https://doi.org/10.1103/PhysRevLett.96.029703)

PACS numbers: 75.70.-i, 05.30.Jp, 68.18.-g, 73.20.-r

- [1] Z. Vager and R. Naaman, Phys. Rev. Lett. **92**, 087205 (2004).
- [2] I. Carmelli, G. Leituss, Z. Vager, and R. Naaman, J. Chem. Phys. **118**, 10372 (2003).
- [3] P. Crespo *et al.*, Phys. Rev. Lett. **93**, 087204 (2004).
- [4] J. A. Van Leeuwen, J. Phys. Radium **2**, 361 (1921).