

## 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,  $\xi$ , 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.

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