Bosons as the Origin for Giant Magnetic Properties of Organic Monolayers

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Recently, unusual giant magnetic properties were found experimentally in some organized organic monolayers adsorbed on solid substrates. A model is presented which explains the observed phenomenon. The model is based on the special properties of electrons transferred from the substrate to the layer as a result of the adsorption process. Triplet pairing of those electrons is forced by the special 2D properties of the organic layer. Such pairs are confined within domains in the organic layer and their quantum statistics provide a model that explains the unique magnetization as well as all other features of the experimental observations. The model suggests the possible existence of Bose-Einstein condensation at room temperature on the scale of the domains.

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The motivation for the present considerations is the need to explain giant magnetization which was observed in organic monolayers made from diamagnetic molecules adsorbed on diamagnetic substrates. It appears *ex nihilo,* when certain organic molecules are self-assembled as monolayers on solid substrates. So far, this type of magnetism was observed for organic thiols adsorbed on gold [1] and organic acids adsorbed on GaAs surfaces [2]. Some of the films studied show very high specific magnetization, up to hundreds of Bohr magnetons per adsorbed molecule, with no saturation up to a field of 1 T. The magnetic susceptibility is highly anisotropic with the highest response along the axis perpendicular to the surface and shows almost no temperature dependence down to a few degrees Kelvin. The organic layers for which magnetization was observed are characterized by a transfer of electrons from the substrate to the layer occurring upon adsorption [3,4]. The most striking phenomenon which challenges explanation is the magnetization of hundreds of Bohr magnetons per adsorbed molecule. Both the size of magnetism and the large anisotropy point to surface orbital magnetism [5] as a possible explanation for the phenomenon. However, simple orbital magnetism would require angular momenta of several hundreds for electrons within molecules, thus necessitating inconceivably high kinetic energy (e.g., about 400 eV for a $l = 100$ state with molecules of 1 nm radius).

The model presented here deals with some special physical properties of the electrons that were transferred from the substrate and reside on the layer. It is shown that the lowest energy state of these electrons is reached by pairing to triplets, namely, forming boson pairs. Such pairs are confined within domains in the organic layer. Their quantum statistics as triplet bosons provides a model which explains well the experimental observation.

The organic monolayer can be imagined as a 2D lattice of dipolar amphiphilic molecules adsorbed on a metal substrate so that all the positive poles point away from the substrate. These molecules are typically long with their long axis almost perpendicular to the substrate. In the adsorption process, electrons from the metal are transferred to the layer and neutralize the positive poles, thus, drastically reducing the large electrostatic energy of the dipole layer [4,6]. This process results in a very thin reversed dipolar layer on the interface between the substrate and the organic layer with substantially reduced free energy. The gain in energy due to the transfer of a single electron per molecule can be up to several tens of eV. This subject was addressed before both experimentally and theoretically [3,4,6]. Interestingly, the topology of such "brushlike" structures was suggested [7] to induce low dimensional electronic Bose-Einstein condensation.

Since the molecules are originally with "closed shells" and have typically low electron affinity, the transferred electrons necessarily occupy negative ion states which are with large radius around the long molecular axis. In particular, for the organized monolayer, the Pauli principle excludes their location near the molecular axes. Thus, those transferred electron are "squeezed" on a two dimensional network of borders between the molecules. They reside in the vicinity and on the plane of the positive poles (see the illustration in Fig. 1). The nature of this network of transferred electrons is the focus of the current model.

Assuming a single transferred electron for each attached molecule, a 2D lattice could be considered with a single molecule at each unit cell. The effective single electron periodic potential must include large exchange terms due to the virtual overlap of electrons on the borderlines of the cells (Fig. 1). To explicitly include such terms, it is preferred to consider a larger unit cell which includes $2N$ transferred electrons and $2N$ molecules. A reasonable approximation is to add an additional repulsive energy, E_r, to the binding of each molecule due to the pair of overlapping electrons on the borderlines, as shown in

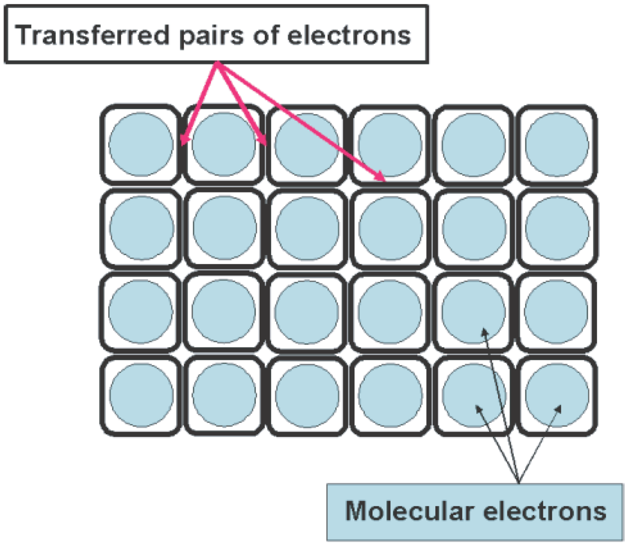

FIG. 1 (color online). Schematic view of the locations of the transferred electrons on the plane of the positive poles of the attached molecules, away from the molecular electrons.

Fig. 1. The electrostatic repulsion between those two border-squeezed electrons favors the triplet configuration for each pair of electrons. This is because the triplet amplitude vanishes smoothly at zero distance between the electrons. The corresponding zero amplitude of the singlet is at a finite separation between the electrons. Calculations of E_r on a single segment of intermolecular dimension at different (narrow) effective radii along the borderline are shown in Fig. 2, illustrating that the singlet state is higher in energy than the triplet state by many eV. It is important to realize that the system described is different from any common bond in a molecular system. Here, the transferred electrons must reside between the molecules while in a typical molecular bond only a small portion of the total charge is located on the bond between the nuclei. This difference causes the triplet state to be the ground state here while in many molecular systems the singlet is the ground state. Hence, the adoption of the transferred electrons configuration in Fig. 1 forces a paired electrons many body (of transferred electrons) state. Namely, to a good approximation, the many body state is of bosons. As such, the minimal 2D unit cell is of two molecules and Bloch single boson solutions are appropriate. Thus, the periodic solutions within a cell of the various order parameters are accompanied with almost continuous phases along the 2D space, allowing for low energy collective phenomena.

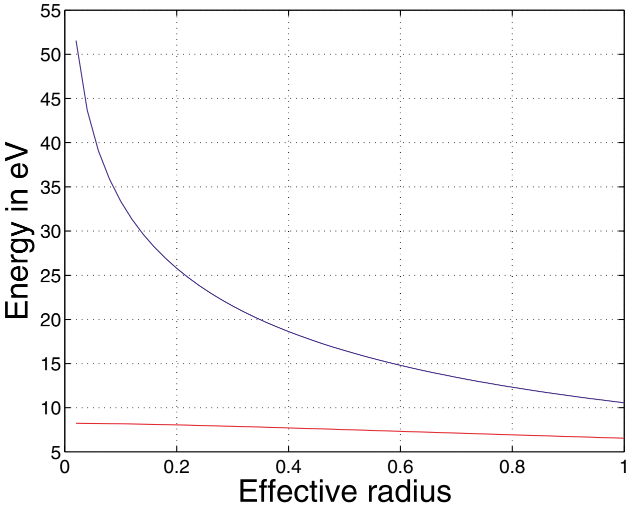

FIG. 2 (color online). Singlet (above) and triplet (below) energies are shown in a 5 Å segment as a function of the effective radius (in Å) of the segment.

The number of triplet pairs is half the number of attached molecules (on the order of $10^6\mu^{-2}$). The connectivity of pairs amplitude along the borderlines between molecules ensures a long range spin magnetism with a very high critical temperature. The planarity suggests a preferred direction, z, which is chosen to be perpendicular and pointing away from the substrate. Experimentally, domains are formed during the adsorption process with dimensions between 0.05–1μ [8]. It is assumed that the shape of the domains is molded by the chemistry of attachment and once the molecules are adsorbed, the domains do not change upon cooling or upon changing magnetic field. According to the above arguments, within each domain the spin direction is highly correlated.

Beyond the spin, another degree of freedom of each pair of electrons is the orbital angular momentum l. The requirement for antisymmetry for a pair of triplet electrons allows only for odd integers: $l = 1, 3, \ldots$. Assuming noninteracting bosons on a circular domain, the lowest energy modes associated with the internal angular momentum degree of freedom of the electron pairs are a discrete set of "drum" modes. Those include angular momentum modes with energies which correspond to rotations around the domain axis.

Consider an effective magnetic field H perpendicular to the surface. This magnetic field is composed of an external field and the internal field due to average neighboring magnetization. The energy of a single pair of electrons in the effective magnetic field, within a domain of radius ξ and area $A = \pi\xi^2$, is given by the eigenvalues of the following Hamiltonian:

$$\mathcal{H} = T + \mu_B l_z H, \tag{1}$$

where μ_B is the electronic magnetic moment Bohr magneton, and T is the kinetic energy, with l dependent energies,

$$E_l(H) = \frac{\hbar^2 l^2}{4m_0\xi^2} + \mu_B l H = \frac{\hbar^2}{4m_0\xi^2}[(l-\lambda)^2 - \lambda^2], \tag{2}$$

where λ is the classical angular momentum that minimizes the energy. Defining an energy factor (domain's rotational constant)

$$\varepsilon = \frac{\hbar^2}{4m_0\xi^2}, \tag{3}$$

there are various ways to express λ, such as

$$\lambda = -\frac{\mu_B H}{2\varepsilon} \tag{4}$$

and

$$\lambda = -2\frac{AH}{\Phi_0} = -2\frac{\Phi}{\Phi_0}, \tag{5}$$

with $\Phi_0 = hc/e$. The physical minimum energy is at an odd integer l_λ which is closest to λ. When the flux in the domain changes by one unit of Φ_0, the ground state angular momentum of each triplet pair changes by two.

When H_T is the field in Tesla and ξ_μ is the radius of the domain in microns then

$$|\lambda| = 1520 H_T \xi_\mu^2. \tag{6}$$

Hence, in the presence of a magnetic field, each triplet-pair boson possesses an extraordinarily high angular momentum. For a given domain size, the effective magnetic field defines a ground state with an odd internal angular momentum l_λ for the triplet pairs, so that l_λ is as close as possible to λ. The parameter λ is proportional to the effective magnetic field and the area A of the domain [Eqs. (4) and (5)].

From the above discussion and according to Eq. (6), the average contribution of each triplet pair to the magnetization is λ Bohr magnetons, assuming a unit g factor for electronic orbital motion.

Any number of bosons can occupy each state of the transferred electrons within a domain provided that the total number of bosons is half the number of transferred electrons within that domain. Therefore, the free energy in a domain is given by [9]

$$g = \beta^{-1}\sum_l \ln(1 - e^{-\beta(E_l - \mu)}), \tag{7}$$

where μ is the chemical potential, corresponding to the average number, $\langle N \rangle$, of triplet pairs in the domain

$$\langle N \rangle = -\frac{\partial g}{\partial \mu} = \sum_l \frac{e^{-\beta(E_l-\mu)}}{(1 - e^{-\beta(E_l-\mu)})} = \sum_{n=1}^{\infty}\sum_l e^{-n\beta(E_l-\mu)}. \tag{8}$$

Consider the contribution of $n - 1$ bosons separately

$$G_n = \sum_l e^{-n\beta(E_l-\mu)} = e^{n\beta(\mu+\varepsilon\lambda^2)} F_n, \tag{9}$$

such that

$$\langle N \rangle = \sum_{n=1}^{\infty} G_n, \tag{10}$$

and to each $n - 1$ bosons, the contribution of different angular momenta l

$$F_n = \sum_l e^{-n\beta\varepsilon(l-\lambda)^2}. \tag{11}$$

Equation (11) can be approximated using two limits, resulting in two regimes. In the first, the sum over the Gaussian functions can be approximated by an integral, provided that $\sigma > 2$, where

$$2\sigma^2 = (n\beta\varepsilon)^{-1} \tag{12}$$

with a result

$$F_n = \sqrt{2\pi}\sigma, \tag{13}$$

which is independent of λ, thus, independent of H. Equation (12) defines a critical index

$$n_c = \frac{1}{8\beta\varepsilon}, \tag{14}$$

such that for $n < n_c$ the condition $\sigma > 2$ is fulfilled. The critical index can be quantified by

$$n_c = 570 T_K \xi_\mu^2, \tag{15}$$

where T_K is the temperature in degrees Kelvin.

The contribution of $n \le n_c$ to $\langle N \rangle$ is given by

$$\langle N \rangle_n = \sqrt{8\pi n_c}\sum_{n=1}^{n_c}\frac{e^{n\beta(\mu+\varepsilon\lambda^2)}}{\sqrt{n}}. \tag{16}$$

Since at a given temperature, many l states contribute to the domain's boson population, this regime is called "normal" and the participating bosons are referred to as "normal bosons." The average number of normal bosons in the domain, $\langle N \rangle_n$, depends on H only through the chemical potential dependence on λ, namely, $\mu' = \mu + \varepsilon\lambda^2$.

For $\mu' = 0$, the sum in Eq. (16) can be approximated by $2\sqrt{\pi n_c}$ which limits $\langle N \rangle_n$, at low temperatures, to be a negligible fraction of $\langle N \rangle$.

In the second limit, for $\sigma < 2$, Eq. (11) is a sum of almost nonoverlapping Gaussian functions. It can be approximated by a single Gaussian where only one l_λ contributes. When the ground state is described by a large fraction of bosons occupying a single state, then that fraction is called a condensate. Since for $n > n_c$ all bosons with l_λ contribute to the ground state, then, if the corresponding fraction of $\langle N \rangle$ is significant, a condensate condition is achieved.

For each $n - 1$ boson, the single Gaussian contribution is

$$F_n = e^{-n\beta\varepsilon(l_\lambda-\lambda)^2}, \tag{17}$$

where l_λ is the odd integer which is the closest to λ. Therefore

$$G_n = e^{n\beta\{\mu+\varepsilon[\lambda^2-(l_\lambda-\lambda)^2]\}} \tag{18}$$

and its sum up to $n \to \infty$ converges only if $\mu < -\varepsilon[\lambda^2 - (l_\lambda - \lambda)^2] \le -\varepsilon\lambda^2$. For $\lambda \gg 1$, $\lambda^2 - (l_\lambda - \lambda)^2$ can be replaced by λ^2. Thus, the contribution to $\langle N\rangle$ by the condensed boson phase is given by

$$\langle N\rangle_c = \frac{e^{n_c\beta(\mu+\varepsilon\lambda^2)}}{1 - e^{\beta(\mu+\varepsilon\lambda^2)}}. \tag{19}$$

In each domain, the pairs condense at the corresponding l_λ level. The value of l_λ increases by 2 when the flux through the domain changes by Φ_0, and the dependence on H of the average number of condensed bosons is only through $\mu' = \mu + \varepsilon\lambda^2$.

The convergence of $\langle N\rangle_c$ requires $\mu' < 0$. As mentioned above, under such conditions $\langle N\rangle_n$ of Eq. (16) is limited to a much smaller number of pairs than expected for regular domain sizes. This is easily realized for low temperatures. Thus, at room temperature and below, the very existence of a condensate phase requires that most of the available pairs in the domain will be in this state.

The arguments so far indicate that almost all the bosons are in a condensate within each domain. Therefore, to a good approximation, the effective field is simply the external magnetic field. For the magnetic properties, both $\langle N\rangle_n$ and $\langle N\rangle_c$ and therefore also the sum $\langle N\rangle = \langle N\rangle_n + \langle N\rangle_c$ depend on the magnetic field only through $\mu' = \mu + \varepsilon\lambda^2$. Since

$$\langle N\rangle = -\frac{\partial g}{\partial\mu}, \tag{20}$$

then the magnetization of the domain is given by

$$\begin{aligned} M &= -\frac{\partial g}{\partial H} = 2\lambda\frac{\partial\lambda}{\partial H}\varepsilon\langle N\rangle = -\mu_B\lambda\langle N\rangle \\ &= 2\langle N\rangle\mu_B^2 H\frac{m_0}{\hbar^2}\xi^2. \end{aligned} \tag{21}$$

Each pair of electrons contributes $|\lambda|$ Bohr magnetons to the magnetic moment, independently of temperature. This is a direct result of the condensed boson character of the transferred electrons.

The specific magnetization for each molecule in units of Bohr magnetons M_{Bohr} is given by

$$M_{\mathrm{Bohr}} = \frac{1}{2}\frac{\mu_B H}{\varepsilon}. \tag{22}$$

Rather than being a result of competition between the magnetic energy $\mu_B H$ and kT, as in ordinary paramagnetic material, here M_{Bohr} is given by the ratio of the electronic magnetic energy and the domain's rotational constant ε. Hence, the average magnetization per molecule depends on the size of the domain.

The system reaches saturation when the maximum angular momentum $l = L_M$, within a domain, is achieved. The maximum depends on the Fermi energy of the electrons in the substrate and is estimated as $L_M \approx 2000\xi_\mu$. Therefore, in a layer with a variety of domain sizes, very small domains are saturated at relatively low magnetic fields. This explains the curvature of some magnetization plots obtained for different samples.

Three conditions are required for observing the triplet pairing and its boson condensation consequences: substantial charge transfer, close packing of the organic molecules in an organized manner, and "squeezing" of the extra electrons between the molecules of the organic layer. The last condition means that in the case of amphiphilic molecules, the headgroup that binds the molecule to the surface must be of the same size (or smaller) when compared with the "tail." Otherwise, the distance between the tails is relatively large and the transferred electrons are not forced to be in the triplet state.

In conclusion, a theory which recognizes the triplet boson character of the layer of transferred electrons explains the *ex nihilo* magnetization of organic monolayers on solid substrates, its magnitude, anisotropy, and temperature independence. The huge paramagnetic character of the transferred electron layer is comparable to the opposite sign diamagnetism of superconductors. In superconductors, the angular momentum of the center of mass motion of Cooper pairs contributes to diamagnetism while in the present case the internal angular momentum within the pair is responsible for the paramagnetism. The freezing of the center of mass motion of the triplet pairs makes the state of the transferred electrons different from other known condensation phenomena.

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