Unconventional magnetism in small gold organic molecules

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We present a theoretical study of the magnetic properties of dicyclopentadienyl metallocene and phthalocyanine molecules, that contain the transition metal atoms M = Fe, Co, Ni, Cu, Zn, Ir, Pt and Au. Our most important prediction is that gold and copper molecules are magnetic. We find that the magnetism of these molecules is fairly unconventional: the gold atom itself is weakly magnetic or even non-magnetic. Its role is rather to induce magnetism in the surrounding carbon and nitrogen atoms, producing a sort of spin density wave.

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The efforts devoted in the past few years to fabricate and characterize new nano-scale objects have helped to uncover a wealth of fascinating geometric, mechanical, electronic, magnetic, optical or dissipative properties, that are brought about in many cases by the laws of quantum physics. More specifically, the multidisciplinary field of Nanomagnetism aims at the fabrication of devices with tailored magnetic properties. Indeed, there exists an intense activity in the microscopic community to extend its reach to the nanoscale, by reducing the size of their room-temperature magnetic dots well below the 100 nm mark. Gold nanoparticles of diameters in the 2 nanometer range have been found recently to show room-temperature magnetism, when capped with organic molecules[1, 2, 3]. Interestingly, the experiments have found that the magnetism of these nanoparticles is localized at their surface, where Au atoms are in chemical contact with the capping molecules. The different experiments produce different estimates for the spin moments $M_S$ of the surface gold atoms, which vary from 0.002 to 0.3 $\mu_B$[4], but they agree on the very high value of the magnetic anisotropy energy (MAE), which is of about 0.4 eV/atom. Huge orbital moments $M_L$ at the surface gold atoms have been proposed to exist and originate that large MAEs[4], but the actual measured moments seem to be modest, of order $M_L/M_S \sim 0.15[1, 3]$. 

Molecular magnets are in some ways superior to nanoparticles, since they have a well defined number of atoms with precise chemical identities, and do not suffer from particle number dispersion. Further, molecules are not so prone to conformational changes, since these require breaking a sizable number of covalent bonds, as opposed to the metallic bonds of atomic clusters. Finally, the chemical activity of molecules can be engineered by oxidation or reduction, or by the attachment of end groups. Molecular magnets containing single Rare-Earth ions have been studied in the past[4, 5], but late 5d elements like iridium, platinum or gold are possibly better candidates for room-temperature magnetism since these are heavier elements, which means that they have higher Spin-Orbit coupling constants. Our previous calculations for platinum dimers found MAEs of the order of 0.1 eV/atom[7], which are consistent with the experimental values in gold nanoparticles referred above.

We present here a detailed theoretical study of the magnetism of two popular organic molecules, metallocenes and phthalocyanines. Metallocenes, denoted MCP$_2$, are organometallic molecules that contain two cyclopentadienil rings Cp, which sandwich a transition metal atom M. Metallic phthalocyanines, denoted MPc, are macrocyclic molecules that have an alternating nitrogen atom-carbon atom ring structure, and contain a metal atom M in its center, which bonds with the four isodindole nitrogen atoms. We have used the third row elements Fe, Co, Ni, Cu and Zn, and the fifth row elements Ir, Pt and Au as the metallic atom M. The axial symmetry of these molecules produces a crystal field at the metal ion position which leads to expect that Fe and Zn molecules have a net zero spin, that Co, Ir, Cu and Au molecules have spin 1/2, and that Co and Pt molecules have spin 1. Our simulations confirm these guesses except for Pt molecules, that have a spinless ground state. Interestingly, we find that gold molecules have a finite spin 1/2, but that the distribution of magnetic moments across gold molecules is not conventional. The gold atoms produce a sort of spin density wave such that the surrounding carbon or nitrogen atoms are also magnetized, showing a spin-density-wave pattern, with almost collinear orientations. The gold atom itself contributes about 15 % of the total spin moment of the molecule in orocene, while it is unmagnetized in the phthalocyanine. The orbital moments are between three and thirty times smaller that the spin moments. We have checked that all the spin 1/2 molecules show zero magnetic anisotropy as they should[13]. The spin-1 Ni molecules also show very small anisotropies, which was expected because of its small Spin Orbit coupling constant.

The structural and electronic properties of metallocene and possibly also of phthalocyanine molecules in the gas and crystalline phases are well captured by density functional theory (DFT)[8]. We have therefore carried the simulations with the molecular dynamics SIESTA suite[9], which uses norm-conserving pseudopotentials and a basis set of localized atomic-like wave functions. We have used a triple-zeta doubly polarized basis set for transition metal ions (Fe, Co, Ni, Cu, Zn, Ir, Pt and Au), and a double-zeta polarized basis set for the carbon, nitrogen and hydrogen atoms. We have checked explicitly that our simulation boxes for metallocenes, having 20 Å of lateral size, where large enough to avoid spurious boundary effects of the electric field. For the larger phthalocyanine
molecules, the boxes were cuboids of size 28x28x20 Å³. We have used a very fine grid for the real space integrals to ensure that egg-box effects were absent. We found it essential to set a rather strict tolerance of $5 \times 10^{-4}$ eV/Å in the force relaxation procedure of the atoms, in order to escape from local minima of the energy landscape. We took between 5 and 10 different initial seeds for the geometry/spin arrangements in our sampling of the Hilbert space of each quantum system to ensure that we would reach the ground state configuration. We have confirmed that the Local Density and the Generalized Gradient approximations (LDA and GGA, respectively)\cite{11,12} shed the same results for the ground state and first excited isomers of all the molecules, with only small quantitative differences. We have also double-checked our results for gold molecules with the alternative code QUANTUM ESPRESSO\cite{12}, which uses ultra-soft pseudopotentials and a plane-wave basis set.

Figs. 1(a) and 1(b) show the eclipsed and staggered geometrical structures of metallocene molecules, which have the standard $\eta^5$ coordination, whereby the central metal ion bonds with all five carbon atoms in each ring. There exist other possible geometrical arrangements, where the rings are displaced laterally, or even tilted, so that only one, two or three carbons in each ring bond to the metal ion; the coordination is called $\eta^{1,2,3}$, accordingly. All of the metallocenes that we have simulated have been synthesized, except for AuCp$_2$, and possibly CuCp$_2$. Their geometrical structures for the gas phase have been determined experimentally for Fe, Co, Ni and Zn\cite{14,15}. Detailed quantum chemistry simulations of the geometry and total spin of isolated Fe, Co, Ni, Cu and Zn metallocenes have been performed\cite{8,16,17,18}, which agree with the experimental data. Our results both for the geometry and the spin ground state, which are summarized in Table I, agree in detail with the available experimental and theoretical data.

We select the cobalt, copper and gold metallocenes for a closer inspection of the magnetic phenomena of these molecules. The rationale behind our choice is the following. First, the three molecules have the same spin ($S=1/2$) because of the axial crystal field of the molecule, so that their magnetic properties can be meaningfully compared. Second, cobalt is a strong ferromagnet, while copper and gold have a noble metal electronic shell structure. Third, gold has more delocalized s-wave functions, so it is expected to show a weaker magnetism.

Fourth, we wish to understand better the magnetic properties of small gold molecules in view of the recent experiments mentioned above\cite{1,2,3}. We plot in Fig. 2(a) a schematic view of the geometrical structure and atomic spin moments of CoCp$_2$. We have found that the most stable isomer has basically $D_{5h}$ symmetry, with small Jahn-Teller distortions, which favor $\eta^2$ coordination. More important for the present discussion is the crude size of the atomic moments in the molecule, which the figure shows to be localized in the cobalt atom.

Table I indeed shows that Co carries 75% of the total moment of the molecule ($M_{Co} = 0.75\mu_B$). Notice that the $\eta^1 - \eta^2$ coordination is reflected in the small moment of two of the carbon atoms in each carbon ring. One of the two atom rings in the $D_{5d}$ geometry CuCp$_2$ has been displaced and shows $\eta^3$; the other ring shows a much more slight displacement, which leads to $\eta^1$ coordination, as we show in Fig. 2(b). Furthermore, the two rings are not coplanar. The magnetic configuration of this molecule is rather interesting. The transition metal atom has a much lower magnetic moment, which amounts to only 20% of the total moment of the molecule, see Table I.

Fig 2(b) shows that the magnetization of the carbon atoms follows a non-monotonic dependence with the distance to the copper atom, which is reminiscent of a sort of spin-density wave. Indeed, two of the carbon atoms in the displaced ring have spin moments of 0.25 $\mu_B$, while the other three are very weakly magnetized ($M \sim 0.02\mu_B$). A similar situation happens in the other ring, where two carbon atoms have sizable magnetizations of about 0.13$\mu_B$, while the moments of the other three are tiny. This unconventional behavior is more apparent in AuCp$_2$, that we show in Fig. 2(c). The two cyclopentadienyl rings are displaced in opposite directions by the same distance, which leads to $\eta^2 - \eta^3$ coordination. The two rings are coplanar in this case, which makes a much more symmetric molecule than CuCp$_2$. The figure clearly indicates that two carbon atoms in each ring have a much larger magnetization ($0.21\mu_B$) than the one shown by the central gold atom ($0.13\mu_B$). The magnetization profile shows a more pronounced non-monotonic behavior than CuCp$_2$: the two carbon atoms in each ring which are directly bonded to the gold atom are unmagnetized, while the carbon atom furthest apart

![FIG. 1](Color online) (a) eclipsed, and (b) staggered, geometries of metallocene molecules, showing $\eta^5$ coordination; (c) phthalocyanine molecule.

| Molecule | Exp. geometry | Our geometry | $M_T$ ($\mu_B$) | $M_M$ ($\mu_B$) |
|----------|----------------|---------------|-----------------|-----------------|
| FeCp$_2$ | Eclipsed $\eta^2$ | Agree | 0.0 | 0.0 |
| CoCp$_2$ | Eclipsed $\eta^{1,2}$ | Agree | 0.99 | 0.75 |
| NiCp$_2$ | Eclipsed $\eta^2$ | Agree | 1.99 | 1.22 |
| CuCp$_2$ | Not synthesized | Staggered $\eta^2 - \eta^2$ | 0.99 | 0.22 |
| ZnCp$_2$ | Staggered $\eta^1 - \eta^2$ | Agree | 0.0 | 0.0 |
| IrCp$_2$ | Not available | Eclipsed | 0.95 | 0.50 |
| PtCp$_2$ | Not available | Staggered $\eta^1 - \eta^1$ | 0.0 | 0.0 |
| AuCp$_2$ | Not synthesized | Staggered $\eta^1 - \eta^1$ | 0.99 | 0.13 |
shows antiparallel magnetization. This suggests even more strongly than in the CuCp$_2$ case that we are facing with a spin-density wave profile.

We note that we have used a Mulliken population analysis to draw the above conclusions on the magnetism of metallocene molecules. To dispel fears on the possible inaccuracies of this analysis, we have estimated also the atomic charge and spin moments by integrating the charge and spin densities inside spheres centered in each atom, for a number of different integration radii, that we show in Fig. 3(a). We find that the spin density curves show plateaus for radii slightly larger than the inter-atomic distances. The values of the spin moments at these plateaus coincide almost quantitatively with the estimates provided by the Mulliken analysis. The plateaus are not present for the atomic charges, apart from a small shoulder in the case of gold. To understand better the spatial distribution of the integrands, we plot in Figs. 3(b) and (c) the density iso-contours. The charge iso-contours show the charge conjugation appropriate to the covalent $\pi$ chemical bond among the $p_z$ orbitals in the carbon rings. This is the reason why the integrated charges of the carbon atoms do not show plateau behavior. In contrast the charge about the central gold atom has a spherical shape, which points towards a more ionic character of the gold-carbon bond. This is also reflected in the shoulder referred above. The spin iso-contours have a lobular structure. The four lobes that appear for Au correspond to the $d_{z^2}$ orbital, which is the most directly involved in the gold-carbon chemical bond responsible for the $\eta^2$ coordination. The lobular structure of the carbon atoms corresponds to the $p_z$ orbitals; the lobes point slightly towards the adjacent carbon atoms, which indicates a larger delocalization due to the conjugation present in the ring. We note that the atoms that showed antiparallel spin moments in each ring in Fig. 2(c), show here a negative spin density. The localization of the spin density in the orbitals making up the chemical bonds in the molecule, together with the non-uniform variation of the atomic moments strongly suggest again that the spin landscape in this molecule corresponds to a static spin density wave originated by the presence of the gold atom.

We finally note that the magnetic moments are essentially collinear. We have also computed the expectation value of the atomic orbital moments, which we find to be 0.02-0.03 $\mu_B$ at the gold atom, and below 0.001 $\mu_B$ at most for the surrounding carbon atoms (as otherwise expected since the spin orbit coupling constant is only large for Au). We therefore find that the ratio $M_L/M_S$ is of the order 0.2-0.3 at most. This conclusion agrees with the experimental results for gold nanoparticles.[1, 5]

The above trends on the magnetic behavior of metallocenes can be generalized to other organic molecules containing transition metal ions, like phthalocyanines. We have found that the geometry of these molecules does not change during the force relaxation cycle, and only the positions of the central atoms are slightly modified. Cobalt, copper and gold phthalocyanines (CoPc, CuPc and AuPc, respectively) all have spin 1/2 and zero magnetic anisotropy, as we desired. We have therefore chosen to plot in Fig. 4 our results for molecules laying in the $XY$ plane, with spins oriented along the $z$-axis for CoPc and CuPc; for AuPc in contrast, we found it more illustrative to plot a case where the spins were oriented in the plane of the molecule, and along the x-axis for AuPc. We find that the atomic spin moments are very strongly localized at the cobalt atom for CoPc, but that they are spread towards the neighboring nitrogen atoms in CuPc. Gold ph-
thalocyanine is specially interesting again. The spin moments are spread at the central core and all along the benzene rings in one of the arms of the molecule, while the moments of the central gold atom and of the benzene rings at the other arm are negligible. Hence, the spin configuration in the ground state breaks the $C_{4v}$ symmetry of the molecule down to $C_2$. We stress that the role of this atom seems to produce a spin-density wave, magnetizing its surrounding atoms. As in gold metallocene, we find that the orientation of the magnetic moments in AuPc is collinear to a first approximation. Interestingly, we have found slight non-collinearities when we orient the spins in the plane of the molecule, as is apparent in Fig. 4(c). In contrast, the non-collinearities dissipate when the orientation of the atomic spins is perpendicular to that plane.

We finally wish to pay a closer look at the spin-density profile of AuCP$_2$ and AuPc. We plot to this end the spin density in one of the cyclopentadynyl rings of orocene, in Fig. 5(a). We find that this density is largely spread throughout the ring, as opposed to being strongly localized about the carbon atoms, and shows wide regions of opposite charge. We plot in Fig. 5(b) the charge density of AuPc, which shows the covalency of the benzene rings, and the more ionic character of the bonds linking nitrogen and gold atoms. Fig. 5(c) shows a lateral view of the spin density in AuPc, which indicates that the magnetization is localized in the $p_z$ nitrogen and carbon orbitals. A top view of the molecule in Fig. 5(d) indicates that the spin density is also delocalized in this molecule, showing small regions of negative spin surrounded by much larger regions where the spin density is positive.

As a summary, we find that small gold organic molecules show unconventional magnetic features. We find that the role of the gold atom is to magnetize the surrounding atoms, while displaying themselves small or even negligible magnetic moments. The magnetization pattern shows a spin-density wave behavior, whereby the spin profile is fairly delocalized across the molecule, and presents regions with positive and with negative spin density. We find that the orientation of the spins might be parallel or anti-parallel, but is collinear to a first approximation. We also find that the orbital moments are much smaller that the spin moments.

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