

Oscillating spin-density pattern in gold metallocene and phthalocyanine molecules

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We present a theoretical study of the magnetic properties of the spin-1/2 dicyclopentadienyl metallocene (MCp_2) and phthalocyanine molecules that contain the transition-metal atoms $M=Co, Cu, \text{ and } Au$. We find that the spin-density pattern of gold molecules shows a fully delocalized and oscillating behavior. This spin pattern is to be contrasted with the well-known cases of cobalt or iron molecules, where the magnetic moment is strongly localized at the transition-metal ion.

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I. INTRODUCTION

The efforts devoted in the past few years to fabricate and characterize new nanoscale 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 micromagnetic 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 nm range have been found recently to show room-temperature magnetism when capped with organic molecules.¹⁻³ 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 $0.3\mu_B$,³ 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 MAE,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,^{5,6} but late 5d elements such as 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 on the order of 0.1 eV/atom,⁷ which are consistent with the experimental values in gold nanoparticles referred above.

We present here a theoretical study of the spin-density patterns of metallocenes and phthalocyanines molecules con-

taining the transition-metal atoms $M=Co, Cu, \text{ and } Au$. The rationale behind our choice is the following. First, the three molecules have the same spin ($S=1/2$) because of the unpaired electron supplied by the M atom, 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, copper and, to a larger extent, gold, have more delocalized s -wave functions, so it is expected to show a weaker magnetism than the other two. Fourth, we wish to understand better the magnetic properties of small gold molecules in view of the recent experiments mentioned above.¹⁻³

We find that the spin-density pattern of these molecules depends strongly on the identity of the M atom. We find that the atomic moments of cobalt molecules are strongly localized at the cobalt atom. In contrast, the distribution of magnetic moments across gold molecules is very delocalized and shows an oscillatory behavior. The atomic moment at the gold atom in $AuCp_2$ is reduced from one Bohr magneton to $0.13\mu_B$, while in $AuPc$, the atomic moment at the gold atom fully vanishes. We have also found that the spin orientations of all the atomic moments are essentially collinear with only slight noncollinearities. The orbital moments are between three and 30 times smaller than the spin moments.

It is relevant to point out here that the magnetism of cobalt compounds has indeed been studied extensively in the past, both within the physical and the physicochemical communities. The magnetism of copper compounds has also been studied, albeit to a lesser degree. The aspects of the magnetism of gold phthalocyanine and metallocene molecules that we analyze in this paper, to the best of our knowledge, have not been studied before. We have displayed our results on cobalt and copper molecules just to show that there is a gradation in the spin-density pattern which goes from fully localized at the transition-metal atom (for Co) to truly delocalized throughout the molecule for gold molecules. In this last case, the gold atom might become even fully demagnetized, as in gold phthalocyanine. Therefore the spin-density pattern of gold molecules is very different from that found in the extensively studied Fe-, Co-, or Ni-based molecular complexes.

II. COMPUTATIONAL DETAILS

The structural and electronic properties of metallocene molecules in the gas and crystalline phases have been re-

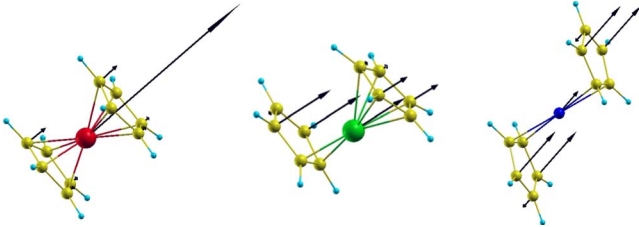


FIG. 1. (Color online) Geometry and atomic spin moments of the most stable isomers of (left) CoCp_2 ; (middle) CuCp_2 ; and (right) AuCp_2 . The atomic spin moments are marked by black arrows, whose size is proportional to the modulus of the moment, and whose direction indicates the orientation of the corresponding atomic spin. Notice that the energy is unaffected by a global spin rotation since the magnetic anisotropy energy is essentially zero in the three molecules. We have chosen to display here a case where the spins are oriented perpendicular to the cyclopentadienyl rings.

ported to be well captured by density-functional theory.⁸ We have double checked that this is the case by carrying out simulations of metallocene molecules containing the transition-metal atoms $M = \text{Fe, Co, Ni, Cu, Zn, Ir, Pt, and Au}$. Our tool has been the molecular-dynamics SIESTA suite,⁹ which uses norm-conserving pseudopotentials and a basis set of localized atomiclike 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, were large enough to avoid spurious boundary effects of the electric field. For the larger phthalocyanine molecules, the boxes were cuboids of size $28 \times 28 \times 20 \text{ \AA}^3$. 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 $5 \times 10^{-4} \text{ eV/\AA}$ 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, respectively,^{10,11} 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,¹² which uses ultrasoft pseudopotentials and a plane-wave basis set. Since both SIESTA and PWSCF take account of the spin-orbit interaction inside the self-consistency cycle, we have also checked that the magnetic anisotropies of these spin-1/2 systems were zero, or better to say, below the accuracy required in our simulations. Indeed, the energy differences of the molecule for different final orientations of the total and the atomic spins of the molecules were of about 0.1 K.¹³

III. DISCUSSION

A. Metallocene molecules

Metallocenes, denoted MCp_2 , are organometallic molecules that contain two cyclopentadienyl rings Cp, which

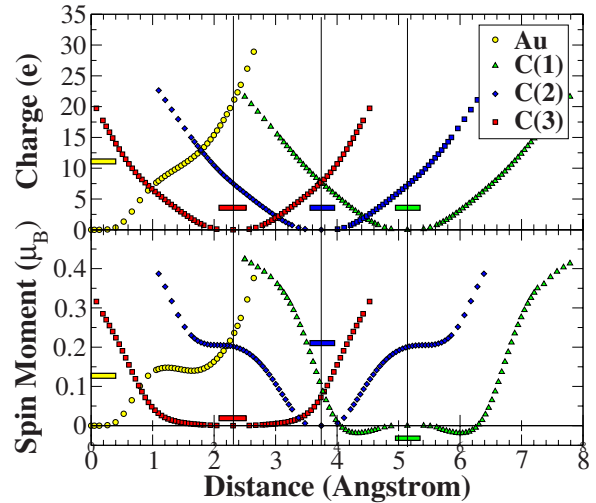


FIG. 2. (Color online) Charge and spin moments in AuCp_2 , estimated by integrating the charge and spin densities on spherical contours. The abscissa in the graph corresponds to an imaginary line that begins at the Au atom, and goes to one of the cyclopentadienyl rings, where it passes first through the closest carbon atom [C(1)], then through the following one [C(2)], and ends up on the farthest [C(3)]. The position of each of these carbon atoms is marked by a vertical line in the graph. The colored rectangular bars indicate the Mulliken population results for the charge and spin moments for each atom. The different data points correspond to increasing integration radii for the spherical integration contours.

sandwich a transition-metal atom M . Figure 1 (left) shows its eclipsed geometrical structure, which has the standard η^5 coordination, whereby the central metal ion bonds with all five carbon atoms in each ring. The staggered configuration corresponds to a rotation of 36° about the molecule axis of one of the carbon rings with respect to the other. 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 . The geometrical structures for the gas phase have been determined experimentally for Fe, Co, Ni, and Zn.^{14,15} Detailed quantum chemistry simulations of the geometry and total spin of isolated Fe, Co, Ni, Cu, and Zn metallocenes have been performed,^{8,16–18} 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 plot in Fig. 1 (left) 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 η^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 ($M_{\text{Co}} = 0.75 \mu_B$). Notice that the $\eta^1 - \eta^2$ coordination is reflected in the small moment of two of the carbon atoms in each carbon ring.

TABLE I. Structural and magnetic properties of the metallocene molecules simulated in this paper. The total spin moment of the molecules is denoted by M_T and is measured in Bohr magnetons. The spin moment of the transition-metal atom M_M is estimated from a Mulliken population analysis and is also measured in Bohr magnetons.

Molecule	Exp. geometry	Our geometry	M_T	M_M
FeCp ₂	Eclipsed η^5	Agree	0.0	0.0
CoCp ₂	Eclipsed $\eta^{1,2}$	Agree	0.99	0.75
NiCp ₂	Eclipsed η^5	Agree	1.99	1.22
CuCp ₂	Not synthesized	Staggered $\eta^2-\eta^5$	0.99	0.22
ZnCp ₂	Staggered $\eta^1-\eta^5$	Agree	0.0	0.0
IrCp ₂	Not available	Eclipsed	0.95	0.50
PtCp ₂	Not available	Staggered $\eta^3-\eta^3$	0.0	0.0
AuCp ₂	Not synthesized	Staggered $\eta^2-\eta^2$	0.99	0.13

One of the two atom rings in the D_{5d} geometry of CuCp₂ has been displaced and shows η^2 coordination; the other ring shows a much more slight displacement, which leads to η^3 coordination, as we show in Fig. 1 (middle). 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 than in the case of CoCp₂, which amounts to only 20% of the total moment of the molecule, see Table I. Figure 1 (middle) shows that the magnetization of the carbon atoms follows a nonmonotonic dependence with the distance to the copper atom. 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 nonmonotonic pattern is more apparent in AuCp₂, that we show in Fig. 1 (right). The two cyclopentadienyl rings are displaced in opposite directions by the same dis-

tance, which leads to $\eta^2-\eta^2$ coordination. The two rings are coplanar in this case, which makes a much more symmetric molecule than CuCp₂. The figure clearly shows 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 an oscillatory behavior: the two carbon atoms in each ring which are directly bonded to the gold atom are almost unmagnetized while the carbon atom furthest apart shows antiparallel magnetization.

We note now that we have used a Mulliken population analysis to draw the above conclusions on the atomic magnetic moments 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. 2. We find that the spin-density curves show plateaus for radii slightly larger than the interatomic 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. This fact indicates that the charge is well delocalized within the two carbon rings and, to a lesser degree, around the gold atom. The lower panel of Fig. 2 illustrates very clearly the oscillatory behavior of the spin-density across AuCp₂.

To illustrate better the spatial distribution of the spin and charge densities, we plot in Figs. 3 the density isocontours. The charge isocontours show the charge conjugation appropriate to the covalent π 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 toward a more ionic character of the gold-carbon bond. This is also reflected in the shoulder referred above. The spin isocontours have a lobular structure. The four lobes that appear for Au correspond to the d_{xy} orbital, which is the most directly involved in the gold-carbon chemical bond responsible for the η^2 coordination. The lobu-

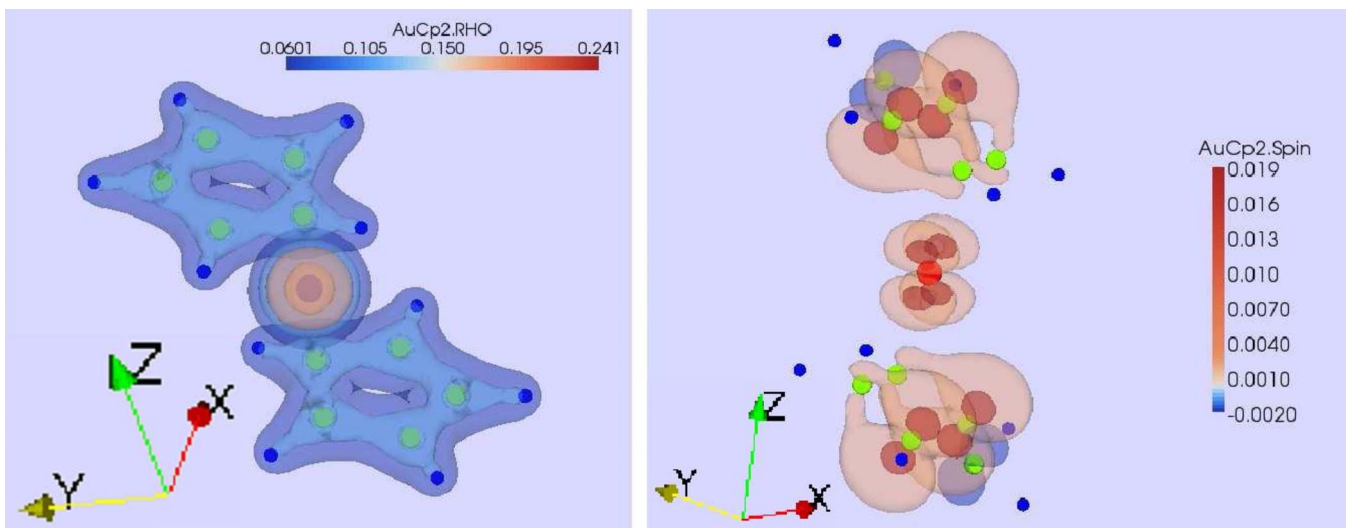


FIG. 3. (Color online) (Left) Charge and (right) spin isocontours in AuCp₂.

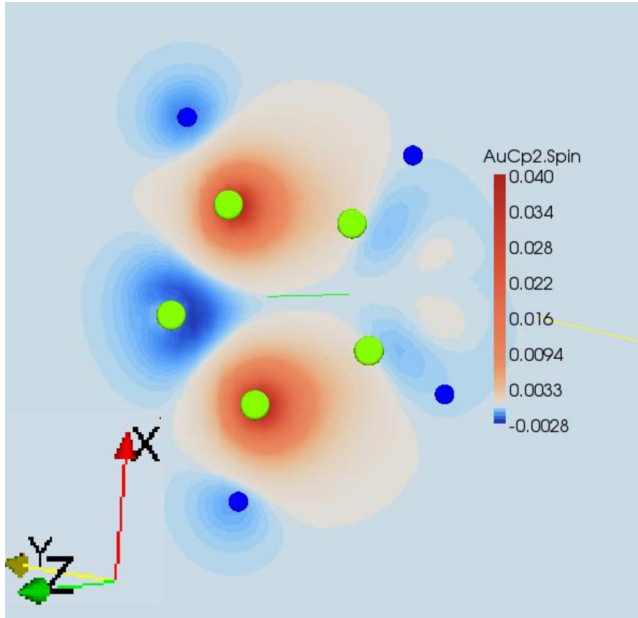


FIG. 4. (Color online) Spin isocontours across one of the carbon rings in AuCp₂.

lar structure of the carbon atoms corresponds to the p_z orbitals; the lobes point slightly toward 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. 1 (right), show here a negative spin density. This is clearly seen in Fig. 4, where we plot the spin density in one of the cyclopentadienyl rings of orocene. This figure illustrates even better that this density is largely spread throughout the ring, as opposed to being strongly localized about the carbon atoms, and shows wide regions of negative spin orientation.

Further insights about the oscillatory spin-density pattern are found by looking at the density of states (DOS) of the molecule, which shows the energy position of the molecular orbitals (MO) of AuCp₂. Figure 5 displays the spin-polarized DOS in a restricted energy window around the Fermi energy (which is set to zero). This figure shows that one can trace a one-to-one correspondence between spin-up and spin-down MO, although each pair is subjected to a different exchange splitting. The unpaired electron of the molecule, responsible for its spin 1/2, is placed at the highest-occupied molecular orbital (HOMO) in Fig. 5, and corresponds to an up-spin orbital. The spin density of the molecule can be written in terms of all the occupied MO of the molecule as

$$\begin{aligned} \sigma(\vec{r}) &= \sum_n |\psi_{n,\uparrow}(\vec{r})|^2 - \sum_{n'} |\psi_{n',\downarrow}(\vec{r})|^2 \\ &= |\psi_{\text{HOMO},\uparrow}(\vec{r})|^2 + n_{\uparrow}(\vec{r}) - n_{\downarrow}(\vec{r}), \end{aligned} \quad (1)$$

where we have split the contribution of the HOMO, which is a positive definite function.

To shed some light on the striking difference between the atomic moments in AuCp₂ and CoCp₂, we have decided to plot $|\psi_{\text{HOMO},\uparrow}(\vec{r})|^2$ for both molecules in Fig. 6. We find that this charge distribution is much more concentrated around

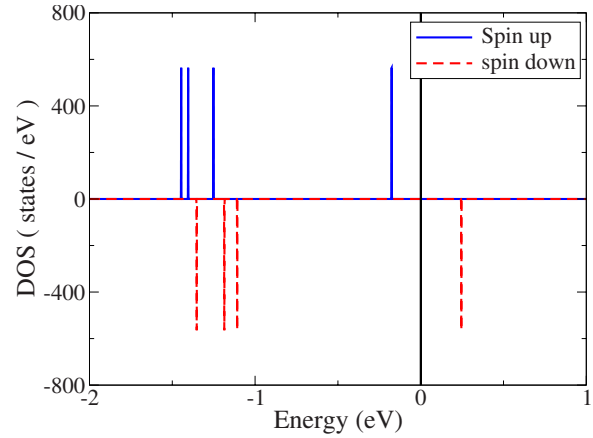


FIG. 5. (Color online) Spin-polarized density of states of AuCp₂ in a restricted energy window around the Fermi energy (which has been set to zero). The figure shows the most relevant molecular orbitals and, in particular, the HOMO and the lowest-unoccupied molecular orbital.

the central transition metal ion for cobaltocene than for AuCp₂, because the $3d$ orbital of cobalt hybridizes less with its surrounding carbon orbitals than the $5d$ orbital of AuCp₂. The HOMO for AuCp₂ is pretty much distributed across the whole molecule, providing therefore a very extended spin distribution. We note that although the integrals over all the space of n_{\uparrow} and n_{\downarrow} are equal, their spatial distribution must be different, if one is to account for the oscillatory behavior of the spin density of AuCp₂, that we have displayed in Fig. 4. This fact can be verified explicitly by plotting separately each of the MO, although these curves are not shown here to avoid cluttering too much the discussion.

We finally note that the magnetic moments are essentially collinear. We have computed the expectation value of the atomic orbital moments, which we find to be $0.02\text{--}0.03\mu_B$ 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 $0.2\text{--}0.3$ at most. This conclusion agrees with the experimental results for gold nanoparticles.^{1,3}

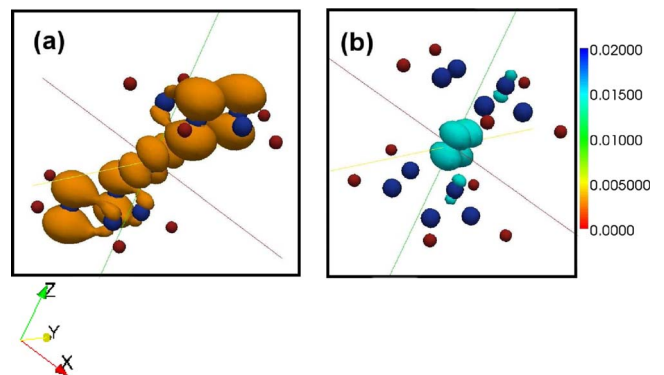


FIG. 6. (Color online) Plot of the spatial distribution of the charge of the HOMO $|\psi_{\text{HOMO},\uparrow}(\vec{r})|^2$ in (a) AuCp₂ and (b) CoCp₂.

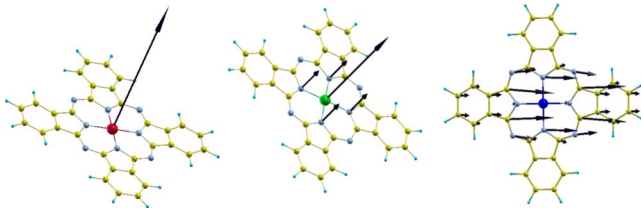


FIG. 7. (Color online) Geometry and atomic spin moments of the most stable isomers of (left) CoPc; (middle) CuPc; and (right) AuPc. The atomic spin moments are marked by black arrows, whose size is proportional to the modulus of the moment, and whose direction indicates the orientation of the corresponding atomic spin. The plane of the CoPc and CuPc molecules is tilted in the figure on purpose. Notice that the spins in AuPc show small noncollinearities.

B. Phthalocyanine molecules

The above trends on the magnetic behavior of metallocenes molecules can be found in other organic molecules containing transition-metal ions, such as phthalocyanines. Metallic phthalocyanines, denoted MPC, are macrocyclic molecules that have an alternating nitrogen atom-carbon atom ring structure, and contain a metal ion M in its center, which bonds with the four isoindole nitrogen atoms. Phthalocyanine molecules were our preferred choice to illustrate the oscillatory behavior of the spin density for the following three reasons. First, they can contain a single transition-metal atom at the center of the molecule, as is the case for metallocene molecules. Second, they are rather dissimilar to metallocenes in other relevant aspects: they have a two-dimensional geometry on the one hand, and on the other the transition-metal ion is bonded to the molecule via chemically active nitrogen atoms. Third, relevant work on the Kondo behavior of cobalt phthalocyanine molecules has appeared in the recent literature,^{19,20} which could be extended to CuPc and AuPc.

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. 7 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, along the x axis. We find that the atomic spin moments are very strongly localized at the cobalt atom for CoPc but that they are spread toward the neighboring nitrogen atoms in CuPc.

Gold phthalocyanine is specially interesting again. The spin moments are spread throughout the central core and all along the benzene rings in one of the arms of the molecule while the atomic moments at the benzene rings in 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 . The moment at the gold atom vanishes in this molecule. Its role is only to provide the extra electron of the molecule and to produce the oscillatory spin-density pattern in the surrounding atoms. It is rather plausible that this anisotropic and oscillatory character of the spin density in AuPc will have a strong impact on the emergence of Kondo features when these molecules are deposited on adequate metallic substrates that do not quench the spin of the molecule.¹⁹

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 noncollinearities when we orient the spins in the plane of the molecule, as is apparent in Fig. 7 (right). In contrast, the noncollinearities disappear when the orientation of the atomic spins is perpendicular to that plane. We plot in Fig. 8 (left) 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. A lateral view of the spin density in AuPc (not shown) indicates that the magnetization is localized in the p_z nitrogen and carbon orbitals. A top view of the molecule in Fig. 8 (right) illustrates again the delocalization of the spin density across the molecule. The figure shows small regions of negative spin surrounded by much larger regions where the spin density is positive.

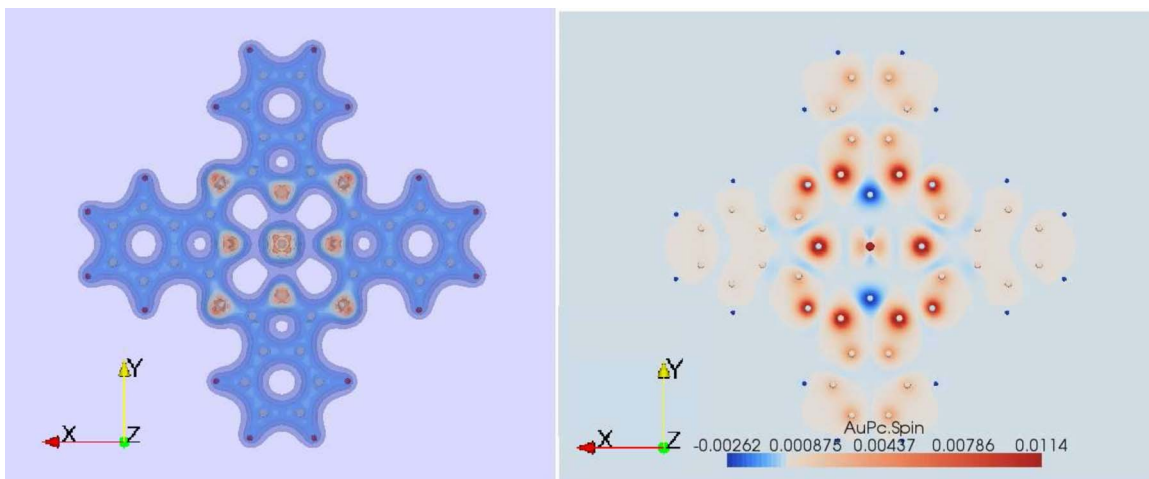


FIG. 8. (Color online) Top view of the (left) charge and (right) spin isocontours in gold phthalocyanine. The color code is such that red (blue) color indicates positive (negative) spin densities. The color intensity indicates how positive or negative is the spin density.

IV. CONCLUSIONS

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 vanishing magnetic moments. The spin-density pattern shows an oscillatory 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 orbital moments are much smaller than the spin moments. Our study should encourage

further efforts in the synthesis and characterization of AuCp₂, and AuPc molecules. It also sheds light on the origin of the magnetism in small gold nanoparticles.¹⁻³

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- ¹Y. Yamamoto, T. Miura, M. Suzuki, N. Kawamura, H. Miyagawa, T. Nakamura, K. Kobayashi, T. Teranishi, and H. Hori, *Phys. Rev. Lett.* **93**, 116801 (2004).
- ²P. Crespo, R. Litrán, T. C. Rojas, M. Multigner, J. M. de la Fuente, J. C. Sánchez-López, M. A. García, A. Hernando, S. Penadés, and A. Fernández, *Phys. Rev. Lett.* **93**, 087204 (2004).
- ³José S. Garitaonandía, Maite Insausti, Eider Goikolea, Motohiro Suzuki, John D. Cashion, Naomi Kawamura, Hitoshi Ohsawa, Izaskun Gil de Muro, Kiyonori Suzuki, Fernando Plazaola, and Teofilo Rojo, *Nano Lett.* **8**, 661 (2008).
- ⁴A. Hernando, P. Crespo, and M. A. García, *Phys. Rev. Lett.* **96**, 057206 (2006).
- ⁵D. Gatteschi, D. Sessoli, and J. Villain, *Molecular Nanomagnets* (Oxford University Press, Oxford, 2006).
- ⁶C. Benelli and D. Gatteschi, *Chem. Rev. (Washington, D.C.)* **102**, 2369 (2002).
- ⁷L. Fernández-Seivane and J. Ferrer, *Phys. Rev. Lett.* **99**, 183401 (2007).
- ⁸M. Swart, *Inorg. Chim. Acta* **360**, 179 (2007).
- ⁹José M. Soler, Emilio Artacho, Julian D. Gale, Alberto García, Javier Junquera, Pablo Ordejón, and Daniel Sánchez-Portal, *J. Phys.: Condens. Matter* **14**, 2745 (2002).
- ¹⁰J. P. Perdew and A. Zunger, *Phys. Rev. B* **23**, 5048 (1981).
- ¹¹J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.* **77**, 3865 (1996).
- ¹²P. Giannozzi, S. Baroni, N. Bonini, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, G. L. Chiarotti, M. Cococcioni, I. Dabo, A. Dal Corso, S. de Gironcoli, S. Fabris, G. Fratesi, R. Gebauer, U. Gerstmann, C. Gougoussis, A. Kokalj, M. Lazzeri, L. Martin-Samos, N. Marzari, F. Mauri, R. Mazzarello, S. Paolini, A. Pasquarello, L. Paulatto, C. Sbraccia, S. Scandolo, G. Sclauzero, A. P. Seitsonen, A. Smogunov, P. Umari, and R. M. Wentzcovitch, *J. Phys.: Condens. Matter* **21**, 395502 (2009).
- ¹³The anisotropy Hamiltonian reduces to a constant for a spin-1/2 system.
- ¹⁴A. Haaland, *Acc. Chem. Res.* **12**, 415 (1979).
- ¹⁵O. G. Garkusha, B. V. Lokshin, and G. K. Borisov, *J. Organomet. Chem.* **553**, 59 (1998).
- ¹⁶Z.-F. Xu, Y. Xie, W.-L. Feng, and H. F. Schaefer, III, *J. Phys. Chem. A* **107**, 2716 (2003).
- ¹⁷K. A. Lyssenko, D. G. Golovanova, and M. Y. Antipina, *Mendeleev Commun.* **13**, 209 (2003).
- ¹⁸Z. Liu, W. Q. Tian, J. Feng, G. Zhang, and W. Li, *J. Mol. Struct.: THEOCHEM* **758**, 127 (2006).
- ¹⁹Aidi Zhao, Qunxiang Li, Lan Chen, Hongjun Xiang, Weihua Wang, Shuan Pan, Bing Wang, Xudong Xiao, Jinlong Yang, J. G. Hou, and Qingshi Zhu, *Science* **309**, 1542 (2005).
- ²⁰C. Iacovita, M. V. Rastei, B. W. Heinrich, T. Brumme, J. Kortus, L. Limot, and J. P. Bucher, *Phys. Rev. Lett.* **101**, 116602 (2008).