Single-molecule spin orientation control by an electric field

Yachao Zhang^{a)}

Guizhou Provincial Key Laboratory of Computational Nano-Material Science, Guizhou Education University, Guiyang 550018, China

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We report the effects of an electric field E on the spin orientations of nickelocene (Nc) deposited on the Cu surfaces by means of first-principles calculations. We employ the Hubbard- U corrected van der Waals density functional to take into account the strong correlation effects of the localized $3d$ electrons and the non-covalent binding involved in the molecule-surface coupling. We show that the deposited Nc molecule can switch between in-plane (in small E -field) and perpendicular magnetization (in large E -field). We find that the significant charge transfer between the molecule and the metallic surface plays a dominant role in the spin reorientation transition. From an electronic structure perspective, the shift in the Fermi level enhances the coupling between the occupied and unoccupied Ni- $3d$ states of different spin states, which tends to facilitate the perpendicular magnetic anisotropy. These findings shed some light on the electrical control of the magnetic anisotropies of single-molecule magnets on metal surfaces. *Published by AIP Publishing.* [<http://dx.doi.org/10.1063/1.4983697>]

I. INTRODUCTION

The electrical control of magnetism is of crucial importance for its applications.^{1–3} However, it is extremely challenging to address the spin states of a single-molecule deposited on the surfaces that are attractive for the miniaturization of magnetoelectronic devices^{4–7} and for quantum computations due to their long coherence time.⁸ First, the molecules may lose their magnetic behaviors when attached to solid state substrates or electrodes even though the molecules seem to be structurally preserved.⁹ Second, the adsorption configurations of the molecules are in some cases not desirable due to their self-assembly or molecule-surface interactions.¹⁰ Further, the characterization of local magnetism at the single-molecule level is still not a simple task.^{11–13}

In particular, for single-molecule magnets (SMMs) featured by large molecular spin moments and high magnetic anisotropy barriers (MABs),¹⁴ few studies have been carried out to address the manipulation of their magnetic behaviors. From the technological point of view, it is desirable to increase the MAB to better stabilize the magnetic moments against thermal fluctuations as well as quantum tunneling.¹⁵ While previous studies have found that an external electric field E can modify the MAB of some surface-supported molecules including Fe_4 ¹⁶ and FePc ,¹⁷ there is still a limited understanding of how the spin orientations of these individual molecules can be manipulated via their interactions with the electrons.

The purpose of this study is to present a clear insight into the mechanism of the electrical control of the molecular spin orientations by electronic structure calculations including the effects of the strong correlation and the non-covalent molecule-surface coupling that were not well considered in previous theoretical studies.^{18,19} The ground state spin orientations of

a uniaxial system are usually characterized by the magnetic anisotropy energy (MAE).^{20,21} Here the MAE is defined as the energy it takes to rotate the spin S from a perpendicular to a parallel orientation in the z -axis,

$$\text{MAE} = E_{\theta=0} - E_{\theta=\pi/2}, \quad (1)$$

where θ is the magnetization angle. Thus, the positive and negative values of the MAE indicate the in-plane and perpendicular magnetic anisotropies, respectively. In magnetic materials, the MAE is primarily governed by the relativistic spin-orbit coupling (SOC) and the electrostatic crystal-field interactions. To determine the MAE reliably with first-principles approaches, one should tackle the SOC in an effective way^{22–24} and describe accurately the strong correlation effects in the magnetic centers^{20,25} and the van der Waals (vdW) interactions involved in the molecule-surface binding.²⁶ Recently, we have proposed a Hubbard- U corrected vdW density functional (vdW-DF + U) that can incorporate the strong correlation effects of the localized electrons and the non-covalent interactions in a first-principles way and can provide an improved description of the molecular spin on surfaces.²⁷

In this work, we demonstrate, through the vdW-DF + U calculations, that it is possible to control the spin orientations of a nickelocene (Nc hereafter) molecule deposited on Cu surfaces (Cu(100) and Cu(111)) with an external electric field. We monitor the variation of the MAE of the deposited Nc under the influence of an electric field and find that the MAE changes from positive to negative when the field is increased, indicating that the Nc molecule exhibits an in-plane to perpendicular magnetization transition. We attribute the spin reorientation transition to the significant charge transfer between the molecule and the surface. Besides, we also explain the mechanism in terms of the shift in the Fermi level.

This paper is organized as follows. In Sec. II, we present the computational setup in detail. In Sec. III, we show the magnetic anisotropy of the Nc molecules and the influence of

^{a)}Electronic mail: yachao.zhang@pku.edu.cn

an external electric field and propose the underlying electronic origin in terms of charge transfer and the variations of the electronic states near the Fermi level. Sec. IV is devoted to a short summary of these findings.

II. COMPUTATIONAL SETUP

We simulate the surface-supported molecule with a slab model which consists of a four-layer substrate with a 4×4 supercell in the lateral plane and a $20 \text{ \AA}$ vacuum space. The atoms in the substrate are fixed during the geometry optimization based on the Broyden–Fletcher–Goldfarb–Shanno algorithm (BFGS) method, and the parameter controlling force convergence for the structural relaxation is set to $0.04 \text{ eV/\AA}$. Besides, a dipole correction is applied to cancel the artificial electric field induced by the asymmetric slab model.

We perform all calculations with the GPAW package,²⁸ which is a real-space implementation of the projector augmented wave (PAW) method.²⁹ Since the spin-orbit coupling is dominated by the regions near the nuclei, only contributions from inside the PAW augmentation sphere are considered. In the package, the spin-orbit correction to the total electronic energy is evaluated by a nonself-consistent diagonalization of the spin-orbit term v^{SO} on the basis of the scalar-relativistic Kohn-Sham eigenstates $|\psi_{nk\sigma}\rangle$,³⁰ which are provided by a standard spin-polarized calculation. The spin-polarized density functional calculations are carried out based on the vdW-DF proposed by Dion and co-workers,³¹ and the Hubbard- U parameter accounting for strong correlations of Ni-3d electrons is set to 1.5 eV , which has proved to be optimal for metallocene molecules.²⁷ We adopt the linear combinations of atomic orbitals (LCAOs) mode with a polarized double- ζ (DZP) basis set in the representation of wavefunctions and employ a $4 \times 4 \times 1$ k -mesh to sample the Brillouin-zone. The smearing of the electronic occupations is performed using a Fermi-Dirac distribution at an electronic temperature of 1000 K .

III. RESULTS AND DISCUSSION

A. Magnetic anisotropy of nickelocene

We begin the analysis by presenting the structural properties of our model system, the Nc molecule deposited on the Cu(100) and Cu(111) surfaces. Nc is a uniaxial double-decker molecule (inset in Fig. 1) that consists of a magnetic center Ni (with a $3d^8$ electronic configuration) sandwiched by two cyclopentadienyl (C_5H_5 , denoted Cp) ligands. We restrict our study on the “flat” lying adsorption configuration where the Cp rings are parallel to the substrate. This bonding orientation has been shown by an experiment to be able to preserve the magnetic properties of the Nc molecule on Cu surfaces.³² Upon deposition, the molecule is somewhat distorted. On both surfaces, the distances from Ni to the top Cp ring (d_{top}) become slightly shorter than those of the bottom ring (d_{bot}) which is attached to the substrate (Table I). The distortion is caused by the molecule-surface interactions in a similar manner to that in the ferrocene/Cu(111) system.¹⁸ Nevertheless, the overall molecular deformation is

FIG. 1. (a) Contour plot of the total anisotropy energy E_{aniso} of Nc as a function of the polar angle θ and the azimuthal angle ϕ . (b) Fitting of the lowest-order uniaxial anisotropy model $E_{\text{aniso}} = K \sin^2 \theta$ to the calculated results, where K is the first uniaxial anisotropy constant. The magnetic anisotropy energy (MAE) is given by $-K$. Inset: the molecular structure and spin orientation of Nc.

not significant in which the variation of metal-ligand distances is within $0.01 \text{ \AA}$.

Here we mention that the preservation of the molecular structure should be ascribed largely to the physisorption of the Nc molecule on Cu surfaces. It has been demonstrated that the ferrocene (Fc) molecules can be kept stable and they form ordered molecular layers on the Cu(111) surface through a nondissociative physisorption.³⁴ For the Nc/Cu(100) or Cu(111) system, the predicted molecule-surface distances ($d_{\text{mol-surf}} > 3 \text{ \AA}$) are consistent with those of the Fc/Cu(111) model system.³⁴ It indicates that the nature of the Nc-surfaces binding should be of physisorption like in Fc/Cu(111).³⁵ Besides, we note that there are only tiny differences between the two substrates regarding molecular geometries and binding energies E_b (Table I), indicating that the two surfaces provide quite a similar local chemical environment for the adsorbed Nc.

TABLE I. Optimized distances between Ni and the top (bottom) Cp ring d_{top} (d_{bot}) and molecule-surface distances ($d_{\text{mol-surf}}$), binding energies E_b , and MAE of the isolated and adsorbed Nc.

	iso mol	Cu(100)	Cu(111)
d_{top} ($\text{\AA}$)	1.89	1.88	1.88
d_{bot} ($\text{\AA}$)	1.89	1.89	1.89
$d_{\text{mol-surf}}$ ($\text{\AA}$)		3.10	3.12
E_b^a (eV)		2.23	2.14
MAE (meV)			
This work	1.16	1.12	1.14
Reference	1.54 ^b and 1.35 ^c	1.27 ^b	

^a $E_b = E_{\text{Nc}} + E_{\text{surf}} - E_{\text{Nc/surf}}$.

^bReference 32.

^cReference 33.

Then we investigate the magnetic anisotropy of the Nc molecule. We present the total anisotropy energy (E_{aniso}) surface in the coordinates of the polar and azimuthal angles θ and ϕ in Fig. 1(a). It shows that the energy surface reaches a minimum at $\theta = \pi/2$ at any ϕ values from 0 to 2π , which means that the easy-axis lies in the xy -plane, and the molecule exhibits a perfect in-plane magnetic anisotropy. We evaluate the MAE by a curve fitting based on the lowest-order uniaxial anisotropy model $E_{\text{aniso}} = K \sin^2 \theta$ (Fig. 1(b)). The MAE value (Table I) is given by $-K$ and agrees well with the reported results,^{32,33} especially the one provided by the constraint density functional theory.³³

It is worth mentioning that the magnitude of the MAE per unit cell is typically measured in meV or even in μeV in real materials, and the states near the Fermi level contribute mostly to the magnetic anisotropy of the system. For this reason, we need appropriate parameters to converge the calculations. Here we use the Nc/Cu(100) model system to check the convergence of the results with respect to the k -point sampling and electronic temperature T in Fermi-Dirac smearing (Table II). It shows that the resulting MAE is not sensitive to the k -mesh parameter, while considerably influenced by the electronic temperature larger than 1000 K. Therefore, the parameters employed ($4 \times 4 \times 1$ k -mesh and $T = 1000$ K) can ensure the convergence and efficiency of our calculations.

Upon deposition, the MAE is slightly decreased compared to that in the free molecule, and the decrease is a bit more pronounced on Cu(100) than that on Cu(111) (Table I). Because $d_{\text{mol-surf}}$ is shorter and E_b is larger in Nc/Cu(100) than that in Nc/Cu(111), the Nc-Cu(100) binding should be somewhat more stronger than the Nc-Cu(111) binding. As a result, the MAE will be decreased to a larger extent when the molecule binds more strongly to the surfaces. Meanwhile, we note that according to the theoretical studies by Ormaza *et al.*,³² the MAE of Nc is decreased by more than 17% on the Cu(100) surface, which is much more significant compared to our results (Table I). This phenomenon should result from the discrepancy in describing the molecule-surface interactions. In their work, $d_{\text{mol-surf}}$ is predicted to be 2.35 Å, which is 0.75 Å shorter than that in our model and suggests a typical chemisorption. The chemical bondings at the interfaces can considerably modify the magnetic properties of the adsorbates.³⁶ In contrast, we carefully take into account the vdW interactions in our calculations and predict a physisorption which would not disturb the magnetic behaviors drastically.

TABLE II. Convergence test of the calculated MAE with respect to k -point sampling and the electronic temperature T in Fermi-Dirac smearing using Nc/Cu(100) as a model system.

k -mesh ^a	MAE (meV)	T (K) ^b	MAE (meV)
$1 \times 1 \times 1$	1.13	300	1.08
$2 \times 2 \times 1$	1.15	500	1.10
$4 \times 4 \times 1$	1.12	1000	1.12
$6 \times 6 \times 1$	1.11	2000	1.38
$8 \times 8 \times 1$	1.14	3000	1.57

^aTested at $T = 1000$ K.

^bTested with a $4 \times 4 \times 1$ k -mesh.

B. Effects of an electric field

To explore the influence of the electric field E on the ground state spin orientations of Nc, we switch on a field along the surface normal and monitor the variation of the MAE (Fig. 2). Overall, the MAE of the deposited Nc tends to be decreased upon increasing the field pointing either upwards ($E > 0$) or downwards ($E < 0$). We see that the downward field has a more dramatic impact on the magnetic anisotropy than the upward one. In particular, the MAE changes from positive to negative when the magnitude of the downward E is larger than 1.0 V/Å on both surfaces, while for the upward field, the critical value to change the sign of the MAE is a little larger on the Cu(111) surface than that on Cu(100) due to a small difference in the molecule-surface binding strength. These results show that the ground state molecular spin can be turned from an in-plane to a perpendicular direction to the substrate in a sufficiently large electric field. In contrast, for the isolated Nc molecule, the MAE remains almost unaltered when E is imposed. Therefore, the effects of an electric field on the magnetic anisotropy of a molecule depend critically on the molecule-substrate interactions in the same way as in the manipulation of the low-spin to high-spin transition of the Fc molecule.¹⁸

We should emphasize that the effects of the electric field are investigated with frozen geometries. We note that the applied field at the interface can modify the structural properties of the molecular adsorbate. For Nc/Cu(100), when an electric field of -0.2 V/Å is applied, the molecule-surface distance is shortened by 0.01 Å, and the distance between Ni and the top Cp ring d_{top} is increased by 0.02 Å compared to that in the zero field, while d_{bot} remains unaltered. It has been shown that the variation of the adsorption configurations can significantly affect the transport properties³⁷ and the magnetic behaviors of the molecular adsorbate.^{38,39} However, due to the physisorption nature of Nc on Cu surfaces, the small changes in the molecular geometries cannot alter the ground state in-plane spin orientation that is stabilized by a MAE larger than 1.0 meV. Meanwhile, it is interesting to note that the critical value of the electric field which induces the spin reorientation transition may be decreased because

FIG. 2. Variation of the MAE of the isolated (iso mol) and surface (Cu(100) and Cu(111)) supported Nc under the influence of an electric field E . Positive and negative MAEs indicate the in-plane and perpendicular magnetic anisotropies, respectively.

the applied field can effectively enhance the molecule-surface coupling.

C. Origin of the spin reorientation transition

In order to understand the electronic origin of the manipulation of spin orientation, we exploit the charge transfer between Nc and Cu(100) by Bader charge analysis (Fig. 3(a)). It shows that in the zero field, no noticeable charge transfer Δn can be observed. This phenomenon should be a confirmation of the physisorption at the interface where the electronic states from the molecule and the substrate practically do not overlap.³⁵ When an electric field is turned on, some amount of charge transfer occurs. The upward field tends to remove some electrons from the molecule ($\Delta n > 0$), while the downward field tends to transfer some electrons into the molecule from the substrate ($\Delta n < 0$). The magnitude of Δn is slightly larger in the upward field than that in the downward field at the same E value, indicating that it is a bit more difficult to add electrons to Nc than to the subtract electrons from the molecule deposited on the Cu surfaces. This difference can be explained from the variation of the electron density $\Delta\rho$ (see the inset in Fig. 3(a)) caused by the electric field. It shows that the upward field removes electrons mainly from the top Cp ring, while the downward field adds electrons into both the top Cp ring and the magnetic center, where the strong Coulomb correlation tends to prevent electron pairing in the localized $3d$ orbitals.⁴⁰ Therefore, for the Nc molecule with more than

FIG. 3. (a) Charge transfer Δn between the molecule and the Cu(100) surface induced by the electric field E . Positive and negative values of Δn refer to the electron subtraction and addition in the molecule, respectively. Inset: the charge density difference $\Delta\rho = \rho_{E=\pm 2.0} - \rho_{E=0.0}$ with an isosurface value of $0.005 e/\text{bohr}^3$. (b) The MAE of Nc and Nc/Cu(100) as a function of charge transfer Δn . Inset: the electronic configuration of the ground state Nc.

a half-filled $3d$ shell, the electron addition is somewhat more difficult than the electron subtraction.

For the purpose of identifying the role of a charge transfer, we employ the isolated Nc molecule as a model system and explore the variation of MAE upon charging of the molecule (Fig. 3(b)). We find that both electron addition and subtraction can considerably decrease the MAE when Δn is smaller than 1.0, which is the maximum value of charge transfer between the Nc and Cu surfaces under the applied field. Particularly, the negative Δn that can be induced by the downward E causes a more significant change in the MAE than the positive Δn that can be induced by the upward E . This trend is well in agreement with the MAE- Δn relationship found in the surface-supported Nc (Fig. 3(b)). These results indicate that the charge transport should play a dominant role in controlling the molecular spin orientations. Recently, a theoretical study has shown that the magnetization direction of the $\text{Eu}_2(\text{C}_8\text{H}_8)_3$ molecule can be manipulated by changing the oxidation state of the molecule, emphasizing the importance of charge transport on the magnetic anisotropy.²⁰

Previous studies have found that the electron transport properties of surface-supported metallocene molecules including Nc^{41,42} and Fc⁴³ can be manipulated by tailoring the molecule-surface contacts. Considering the close interplay between the electron transport and the internal spin degrees of freedom,^{44–46} one can expect to observe a transport induced spin reorientation transition in a two-probe device involving the Nc molecule.

It should also be noted that excess charge transfer can destroy the partially filled electronic configuration of the magnetic center and thus will suppress the magnetic anisotropy (Fig. 3(b)). When two electrons are added ($\Delta n = -2.0$), the $3d$ orbitals become fully occupied, and the magnetism disappears. At $\Delta n = 2.0$, two electrons from the $d_{xz,yz}$ orbitals are removed, and the electronic structure will resemble that of Fc, which is a singlet molecule in the ground state.⁴⁷ Besides, it is worth pointing out that the electron addition or subtraction process can be conveniently controlled by a gate voltage in electronic devices.^{16,48} Consequently, the identified magnetoelectric effect of Nc should be promising for future applications in molecular spintronics.

Finally, we examine the variation of the projected density of states (PDOSs) of Ni- $3d$ orbitals (Fig. 4) to understand the spin reorientation transition from an electronic structure

FIG. 4. Projected density of states (PDOSs) of the Ni- $3d$ orbitals of Nc deposited on Cu(100) in different fields. Positive and negative values of PDOS indicate majority- and minority-spin states, respectively. The Fermi level E_F is set to 0.0 eV.

perspective. For uniaxial systems, the MAE is dominated by second-order effects in the perturbative expansion,²³ which can be effectively estimated by the coupling between the majority- and minority-spin states near the Fermi level E_F .^{33,49} Previous studies have found that the electric field can modify the magnetic anisotropy by changing the electronic states near E_F .^{17,50} Here for our system, the Fermi level is shifted in the electric field. We see that in the downward field ($E < 0$), E_F is shifted toward higher energy, such that the lowest unoccupied molecular orbital (LUMO), the minority-spin $d_{xz,yz}$ state, becomes partially filled. In the upward field ($E > 0$), E_F is shifted toward lower energy, and the highest occupied molecular orbital (HOMO), the majority-spin $d_{xz,yz}$ state, becomes partially empty. In both cases, the size of the energy gap between the majority-spin and minority-spin $d_{xz,yz}$ states is decreased, thus enhancing the coupling between these two sets of states, which has been shown to contribute to the perpendicular magnetic anisotropy in metallocene molecules³³ and should be responsible for the spin orientation transition in the Nc molecule.

IV. CONCLUDING REMARKS

In summary, we have studied the effects of an electric field on the magnetic anisotropy of the Nc molecule deposited on the Cu(100) and Cu(111) surfaces by electronic structure calculations. We consider the strong correlation of the $3d$ electrons and the dispersion interactions at the molecule-surface interface using the vdW-DF + U approach. We find that on both surfaces the molecule can exhibit an in-plane to perpendicular magnetization transition in a sufficiently large field. We show that the charge transfer at the interface plays an active role in the electrical manipulation of the molecular spin orientation. Besides, we explain the electronic origin of the spin reorientation transition in terms of the energy shift in the Fermi level, which enhances the coupling between the $3d_{xz,yz}$ orbitals of different spin states. This study provides some physical insights into the electrical control of the magnetic anisotropies of the molecular magnets adsorbed on metallic surfaces.

Finally, we should point out that we have performed the investigations of the influence of the electric field with frozen geometries that are obtained in the absence of the applied field. However, when an electric field is imposed, there are notable changes in the molecular structures as well as the molecule-surface distance, which would somewhat modify the magnetic behaviors of the molecular adsorbate. Therefore, the effects of an applied electric field on the adsorption configurations should deserve some further systematic studies.

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