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2013 Chinese Phys. B 22 096801

(http://iopscience.iop.org/1674-1056/22/9/096801)

Chin. Phys. B Vol. 22, No. 9 (2013) 096801

RAPID COMMUNICATION

Interaction and local magnetic moments of metal phthalocyanine and tetraphenylporphyrin molecules on noble metal surfaces*

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(Received 19 May 2013; revised manuscript received 21 May 2013)

In order to understand the Kondo effect observed in molecular systems, first-principles calculations have been widely used to predict the ground state properties of molecules on metal substrates. In this work, the interaction and the local magnetic moments of magnetic molecules (3d-metal phthalocyanine and tetraphenylporphyrin molecules) on noble metal surfaces are investigated based on the density functional theory. The calculation results show that the d_{z^2} orbital of the transition metal atom of the molecule plays a dominant role in the molecule–surface interaction and the adsorption energy exhibits a simple declining trend as the adsorption distance increases. In addition, the Au(111) surface generally has a weak interaction with the adsorbed molecule compared with the Cu(111) surface and thus serves as a better candidate substrate for studying the Kondo effect. The relation between the local magnetic moment and the Coulomb interaction U is examined by carrying out the GGA+U calculation according to Dudarev's scheme. We find that the Coulomb interaction is essential for estimating the local magnetic moment in molecule–surface systems, and we suggest that the reference values of parameter U are 2 eV for Fe and 2–3 eV for Co.

Keywords: magnetic molecule, local magnetic moment, Kondo effect

PACS: 68.43.Fg, 68.35.Dv, 68.37.Ef

DOI: 10.1088/1674-1056/22/9/096801

1. Introduction

Recently, the Kondo effect has been investigated in molecule–surface systems – magnetic molecules/atoms adsorbed on noble metal surfaces – with the aid of scanning tunneling microscopy/spectroscopy (STM/STS) techniques.[1–10] The local density of states (LDOS) obtained by STS will be modified by the many-body Kondo resonance states, which appear as a Fano line shape[11,12] (Kondo peak or dip) near the Fermi level. The half-width of the peak (or dip) corresponds to the Kondo temperature T_K. Thus, the very first step of detecting the Kondo effect is to distinguish the Kondo signal from STS, but this is not easily done in experiments. One difficulty arises from the fact that the signal of the Kondo resonance states can be disturbed by a couple of factors, like the inelastic electronic tunneling, phonon-assisted processes,[13] local orbital signals,[7] etc., which would greatly affect the Kondo temperature estimation. The other difficulty is that the coupling environment (e.g., mixing effect and on-site correlation[14]) on the surfaces is distinct from that in bulk. Consequently, it is difficult to directly compare the Kondo temperatures measured in surface systems with those measured in bulk systems. For instance, Fe doped in bulk Au shows a Kondo temperature 1 K.[15] However, it is reported that the Fe impurity on Au(111) shows a Kondo temperature as high as 300 K.[5] It is hard to judge whether the discrepancy is caused by the changing of the environment or even whether the measured signals in STS are not caused by the Kondo effect at all.

In experiment, the best thing one can do currently is to carry out the STS measurements with varying temperature or varying magnetic field.[3] However, these methods are only applicable for low-T_K systems. Because when temperature is increased for a high-T_K system, the molecules intensely diffuse over the substrate before the Kondo signals disappear due to the thermal fluctuation, making the STS measurement entirely impossible. In order to understand the STS data correctly, density functional theory (DFT) calculations have been widely used to explain the experimental observed appearance or disappearance and the high or low T_K of the Kondo effect for magnetic molecules on metal substrates.[5–7] The first issue that most works focus on is whether the local magnetic moment exists when the magnetic molecule is adsorbed on the substrate, which is the key element for the confirmation of the Kondo effect. However, some conflicting understandings remain. One example is about the Kondo quenching in CoPc on Au(111). The system has been previously investigated by STS,[7] and it was found that the Kondo effect does not occur. The author further carried out DFT calculations and found that the adsorption on Au(111) would totally quench the local magnetic moment, which is normally seen as a prerequisite for the Kondo effect to occur. However, a later DFT study[16] with a more realistic model casted doubts on the viewpoint, pointing

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* Project supported by the National Natural Science Foundation of China (Grant No. 51210003) and the National Basic Research Program of China (Grant Nos. 2011CB921702 and 2011CB808401).

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out that the local magnetic moment of Co is largely sustained after adsorption. The calculation in Ref. [7] seems questionable, because non-physical limitation is imposed on the surface atoms. The second issue is the coupling strength between the molecule and the substrate.[17] It is known that the Kondo temperature T_K normally increases as the coupling strength increases. A deep investigation of the coupling strength helps estimate the Kondo temperature reasonably. Therefore, a correct understanding for magnetic molecules on noble metal surfaces, including the coupling strength and the preservation or disappearance of magnetic moment, is of great importance and needs more effort.

In this work, we focus on magnetic molecules, 3d-metal phthalocyanine (MPc) and tetraphenylporphyrin (TPP-M) (M = Fe, Co), adsorbed on noble metal surfaces (Cu(111) and Au(111)), theoretically investigating the interaction between the molecule and substrate based on the first-principles methods. We find that the d_{z^2} orbital of the transition metal (TM) atom of the molecule plays a dominant role in the molecule–surface interaction and the adsorption energy exhibits a simple declining trend as the adsorption distance increases. In addition, Au(111) is a better candidate substrate for studying the Kondo effect. The GGA+U calculations show that the Coulomb interaction is essential for estimating the local magnetic moment in molecule–surface systems and that the local magnetic moment reappears when the local Coulomb interaction is added.

2. DFT calculation details

We carry out a first-principles study on MPc and TPP-M (M = Fe, Co) on Cu(111) and Au(111) surfaces. The molecular structures are shown in Figs. 1(a) and 1(b). The aim is to obtain the adsorption energy $E_{\rm ad}$, density of states (DOS), and the local magnetic moment after the molecule is adsorbed on the substrate. In addition, we discuss the relation between the local magnetic moment and the Coulomb interaction U by using the GGA+U calculations. DFT calculation details are as follows. A single MPc or TPP-M (M = Mn, Fe, Co) molecule is put on a 3-layer 7×8 Cu(111) or Au(111) slab to simulate an isolated molecule adsorbed on the substrate. The calculation is based on Vienna *Ab-initio* Simulation Package (VASP) code. Spin-polarized Perdew-Wang 91 (PW91) exchange correlation functional[18] and PAW pseudopotentials[19] are employed. For each molecule on the substrate, two configurations are examined (see Figs. 1(c) and 1(d)), and each setup is relaxed until the net forces are less than 0.02 eV/Å, except that the atoms in the bottom layer are fixed.

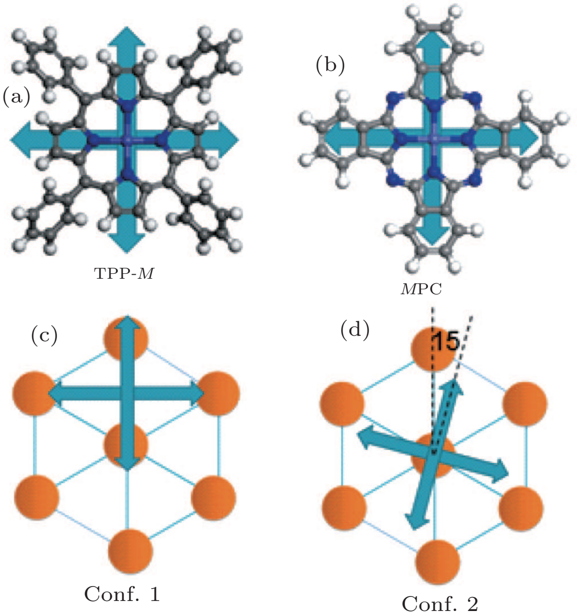

Fig. 1. (color online) (a) and (b) Structures of TPP-M and MPc molecules (grey: carbon, white: hydrogen, blue: nitrogen, the transition metal is at the center). (c) and (d) Two configurations examined (the circles represent the atoms on the substrate).

3. Results and discussion

The adsorption energy $E_{\rm ad}$ is listed in Table 1. The adsorption energy is defined as $E_{\rm ad} = E_{\rm mol} + E_{\rm sub} - E_{\rm mol+sub}$, where $E_{\rm mol}$ is the energy of an isolated molecule, $E_{\rm sub}$ is the energy of a pure metal substrate, and $E_{\rm mol+sub}$ is the energy of the molecule–substrate combined system.

Table 1. The adsorption energy $E_{\rm ad}$, local magnetic moment M, and adsorption distance $d_{\rm TM}$ for MPc and TPP-M on Au or Cu surface. The accuracy of DFT is about 10 meV, U is in the order of 1 eV, thus the accuracy of the local magnetic moment is ~ 0.01. The numbers in parentheses are the local magnetic moments of the isolated molecules. Here $d_{\rm TM}$ is defined as the average vertical distance from the central TM atom in the molecule to the substrate.

	Conf.	$E_{\rm ad}$/eV	$M/\mu_{\rm B}$	$d_{\rm TM}$/Å
FePc@Cu(111)	1	0.486	0.91 (2.00)	2.8
	2	0.384	1.69 (2.00)	3.3
CoPc@Cu(111)	1	0.756	0.00 (1.00)	2.9
	2	0.735	0.00 (1.00)	3.0
FePc@Au(111)	1	0.374	2.01 (2.00)	3.6
	2	0.415	2.05 (2.00)	3.4
CoPc@Au(111)	1	0.413	0.62 (1.00)	3.6
	2	0.428	0.58 (1.00)	3.4
TPP-Fe@Cu(111)	1	0.229	0.00 (2.00)	2.8
	2	0.335	1.96 (2.00)	3.8
TPP-Co@Cu(111)	1	0.381	0.12 (1.00)	3.2
	2	0.180	0.22 (1.00)	3.3
TPP-Fe@Au(111)	1	0.294	2.33 (2.00)	4.2
	2	0.277	2.31 (2.00)	4.1
TPP-Co@Au(111)	1	0.293	1.07 (1.00)	3.8
	2	0.305	1.21 (1.00)	4.1

MPc and TPP-M molecules on Au(111) and Cu(111) surfaces belong to the weak interaction type and all $E_{\rm ad}$ are below 1 eV. It is noticed that $E_{\rm ad}$ on Au(111) is generally smaller than that on the Cu(111) surface. For instance, CoPc on Cu(111) has an E_{ad} around 0.7 eV, while it is about 0.4 eV on Au(111). In addition, TPP-M molecules generally have smaller E_{ad} than MPc molecules on the same metal surface. In our investigated systems, the E_{ad} of TPP-M ranges from 0.20 eV to 0.35 eV, while that of MPc ranges from 0.40 eV to 0.75 eV. The adsorption distance d_{TM} is larger in TTP-M than that in MPc. This is due mainly to the fact that MPc has a flat and rigid skeleton, lying parallel to the substrate. In contrast, the TPP-M molecule contains internal rotation freedoms due to the four benzene rings on the corner, which tends to lie with an angle to the substrate. Consequently the TPP-M molecule is propped up and the TM atom is relatively far away from the substrate. The E_{ad} of magnetic molecules on a metal surface consists of two parts. The first part is contributed by the interaction between the molecular skeleton (the molecule excluding the central TM atom) and the metal surface, the skeleton–surface part. The second part is from the interaction between the TM atom and the metal surface, the TM–surface part. Given a specific molecule, it is reasonable to assume that the skeleton–surface part is a constant, and the differences in adsorption energies with various central TMs are mainly due to the TM–surface part. Therefore, the adsorption energy E_{ad} serves as a measure of the coupling strength between the TM atom and the substrate.

We plot E_{ad} vs. adsorption distance d_{TM} in Fig. 2. In our calculation, two configurations of each molecule–surface system are examined (Fig. 1). Each data point of E_{ad} is the stable one selected from the two examined configurations. Note that E_{ad} is closely related to d_{TM}, generally following a declining trend as d_{TM} increases; while E_{ad} is not directly related to the type of the molecular skeleton. This means that the only relevant characteristic of the molecular skeleton is how far it holds the TM atom away from the substrate. Consequently, it is helpful, at least within our examined systems, to neglect the complexities of the molecular structures and merely see the molecule as an effective force lifting the TM atom.

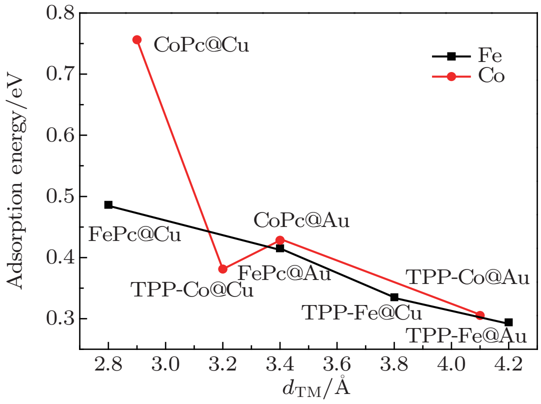

Fig. 2. (color online) Adsorption energy E_{ad} vs. adsorption distance d_{TM}. The red line is for CoPc and TPP-Co on different surfaces, and the black line is for FePc and TPP-Fe on different surfaces. The adsorption energy generally follows a declining trend with adsorption distance d_{TM} increasing.

To further understand the interaction between the molecule and the substrate, we examine the projected DOS (PDOS) onto the central TM atom. For instance, the PDOS for TPP-Co adsorbed on Cu(111) and Au(111) surfaces is presented in Fig. 3. Generally speaking, the TM–substrate coupling broadens the molecular energy level. The PDOS shows that the adsorption has mainly modified the d_{z^2} orbital (Fig. 3(a)), as d_{z^2} is almost doubly occupied after the adsorption (Fig. 3(a)), while the energy of the other d orbitals are almost unchanged (Figs. 3(b)–3(d)).

When the molecule is on the Cu(111) surface, similar with being on Au(111), the modification of PDOS mainly occurs for the d_{z^2} orbital (see Fig. 3(a)). Compared with Au(111), Cu(111) modifies the PDOS of the TM atom more intensely. In experiment, it is difficult to measure the local magnetic moment after the molecule being adsorbed on the surface, thus one often has to assume that the local magnetic moment is equal to that of the isolated molecule, which is justifiable only for weak-interaction systems. Thus researchers prefer a weak-interaction system for studying the Kondo effect. Our results show that the Au(111) surface is generally a better candidate than Cu(111).

Based on the above calculation results, we arrive at two conclusions: first, Cu(111) has a stronger interaction with adsorbed molecules compared with Au(111); second, the interaction is mainly due to the overlap of the d_{z^2} orbital with the substrate. From these two conclusions, we obtain a simplified picture, which provides a qualitative guideline to understand what is happening in molecule–surface systems. As the spatial distribution of d_{z^2} is right above and underneath the TM atom, which is perpendicular to the molecular plane, it is less affected by the ligands (in this case, the molecular skeleton). Thus the d_{z^2} orbital can be viewed as a nearly free orbital. When the molecule approaches the Au (or Cu) surface, it is essentially a process of d_{z^2} approaching the orbitals of the Au atoms (mainly the s and d_{z^2} of the closest Au atom due to the similar symmetry). The distance to the substrate determines the extent of orbital overlap and thus determines the interaction strength. Consequently, the dominant role of the d_{z^2} orbital leads to a simple declining tendency as the adsorption distance increases. We also notice that there is an exception for the declining rule, that is, CoPc on Au(111) ($d_{\mathrm{TM}} = 3.4$ Å) is more stable than TPP-Co on Cu(111) ($d_{\mathrm{TM}} = 3.2$ Å). The abnormality is mainly due to the difference of radial distributions between Au and Cu atoms. As the radius of Au is larger than that of Cu, the d_{z^2} overlap of CoPc on Au is larger than that of TPP-Co on Cu. Therefore, the dominant factor changes to the radius of substrate atoms when two adsorption distances are close to each other.

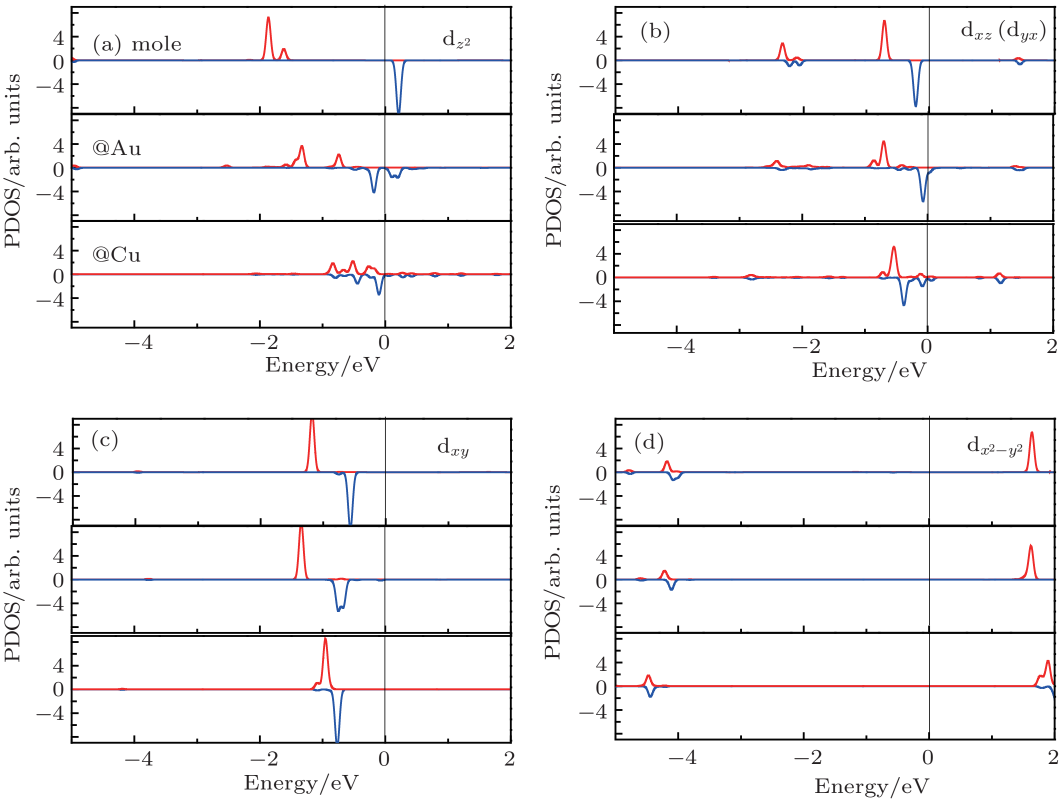

Fig. 3. (color online) PDOS for TPP-Co: (a) d_{z^2}, (b) d_{xz}, (c) d_{xy}, (d) $d_{x^2-y^2}$. For each figure, the first row is the PDOS of the isolated TPP-Co molecule; the second and the third rows are PDOS of TPP-Co on Au(111) and Cu(111) surfaces, respectively. The color (red and blue) distinguishes the two spin directions. The Fermi energy has been shifted to zero.

Generally speaking, a stronger TM–substrate interaction leads to a greater broadening of the molecular energy level and thus leads to a higher Kondo temperature. Because the half-width of the molecular energy level is related to the mixing parameter V in the Anderson model,[14] from which one can readily estimate the Kondo temperature.[12] Therefore, for the strong-interaction systems (e.g., CoPc on Cu(111)), we expect a higher T_K than that in weak-interaction systems (e.g., FePc on Au(111)).

There is also an important controversy about the bare local magnetic moment for the molecule adsorbed onto the metal surface. It probably originates from the distinct methods used in modeling the substrate.[7,16] In the present work, we focus on the problem from a different viewpoint. Coulomb interaction U is a significant parameter greatly affecting the orbital arrangements above ε_F. As we know, GGA (also LSDA) tends to underestimate the band gap (the energy difference between the highest occupied states and the lowest empty states). In present case, the TM–substrate interaction broadens the energy level, and some tails of the broadened empty d orbitals of the minor spin may go under the Fermi level, leading to an underestimate of the local magnetic moment. The GGA+U is a scheme of adding a correcting term to the pure GGA correlation functional, equivalently adding a repulsion energy between the d orbitals of TM. The Coulomb interaction strength is specified by input parameter U. The parameter can be estimated by experiments or first-principles calculations, and a proper U would correct the underestimated local magnetic moment in pure GGA. Here, we discuss U in detail by performing GGA+U calculations according to Dudarev's scheme.[20] The result is plotted in Fig. 4.

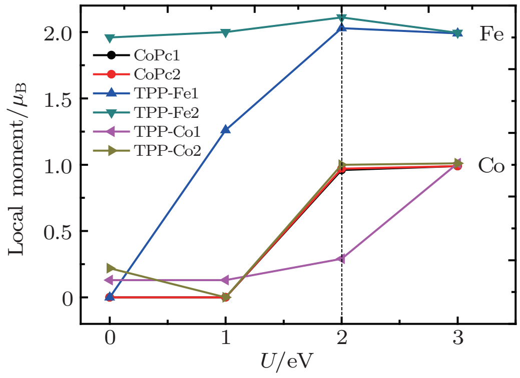

Fig. 4. (color online) Relation between the local magnetic moment and the Coulomb interaction parameter U. All the molecules indicated are on Cu(111) surfaces. The parameter is sampled with 1 eV energy space. The number after the system (e.g., CoPc1, TPP-Fe2) indicates the configuration.

The local magnetic moment increases (but not consistently) with the parameter U increasing. The GGA+U calculation shows that the Coulomb interaction correction is important for molecule–surface systems. It turns out that a small U (about 1 eV) leads to the local magnetic moment increasing from 0 to $1.2\mu_B$ for TPP-Fe on Cu(111). This indicates that the quenching of the local magnetic moment is probably due to an underestimation of the Coulomb interaction. In addition, we find that for each TM species the parameter U has a specific threshold value, above which the local magnetic moment is stable, insensible to any further increase of U. In this work, the threshold values obtained are 2 eV for Fe and 2–3 eV for Co. It was reported from experiments that the reference values of U are 1–2 eV and 3 eV for Fe and Co, respectively.[21–23] Our results are consistent with the previous work. Thus, the Coulomb interaction is essential for estimating the local magnetic moment using first-principles methods. According to our results, the proper values for Fe and Co are 2 eV and 3 eV, respectively. It should be emphasized that U is an effective parameter affected by the conditions of environmental screening. For example, U of TM's d orbital is relatively small in metals due to the screening effect, while it is larger in the isolated state. Thus the reference value mentioned here is applicable merely to TM doped into organic molecules.

4. Conclusion

We have studied the adsorption energies and local magnetic moments of magnetic molecules adsorbed on metal surfaces. We showed that the adsorption energy follows a simple declining trend as the adsorption distance increases. Au(111) interacts with adsorbed molecules weakly compared with Cu(111) and thus may be a better candidate for studying the Kondo effect. In addition, we found that the quenching of local magnetic moment is probably caused by the underestimation of the Coulomb interaction and suggested that the reference values of U are 2 eV for Fe related systems and 2–3 eV for Co related ones. These results provide a guidance for magnetic molecules on noble metal surfaces (Au(111) and Cu(111)), including how to determine the coupling strength and correctly calculate the magnetic moment of the molecules on surfaces, which is important in molecular spintronics.

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