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Magnetic anisotropy in 5d transition metal–porphyrin molecules*

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Single molecule magnets (SMMs) with large magnetic anisotropy energy (MAE) have great potential applications in magnetic recording. Using the first-principles calculations, we investigate the MAE of 5d transition metal–porphyrin-based SMMs by using the PBE and PBE + U with different U values, respectively. The results indicate that W–P, Re–P, Os–P, and Ir–P possess the considerably large MAE among 5d TM–P SMMs. Furthermore, the MAE of 5d TM–P can be facilely manipulated by tensile strain. The reduction of the absolute value of MAE for Ir–P molecule caused by tensile strain makes it easier to implement the writing operation. The decreasing of the occupation number of minority-spin channels of Ir-$d_{x^2-y^2}$ orbital leads the MAE to decrease when the tensile strain increases.

Keywords: the first principle calculations, single molecule magnets, magnetic anisotropy

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1. Introduction

Single molecule magnets (SMMs) have evoked a great deal of study interest for their potential applications in high-density information storage,[1,2] quantum computing,[3,4] spintronics,[5–8] and spin dynamics combined with logic operation design.[9] Nevertheless, the major obstacle to develop SMM molecular devices is the low blocking temperature T_B. The T_B is a threshold temperature for holding their spin orientations against thermal fluctuations.[10] The T_B can be related to E_A, V, and k_B by $T_B \sim E_A V/25k_B$, where E_A is the energy barrier between easy magnetization direction and hard magnetization direction, V is the sample volume, and k_B is the Boltzmann constant. Then it is crucial to search for the SMMs with the large magnetic anisotropy energy (MAE) and to explore the high-density spintronic devices for data storage.

Recent studies suggest that the transition metal–phthalocyanine-based (TM–Pc) materials possess colossal MAE.[11–13] Compared with TM–Pc molecules, the transition metal–porphyrin molecules (TM–P) have similar structure, thermal stability, and electronic properties, and thus the TM–P-based materials may also bring away very large MAE. However, most of studies focused the biological significance, catalytic capabilities, and optoelectronic applications of TM–P,[14–20] only a small number of studies were devoted to the magnetic properties of 3d TM–P molecules.[21,22] Among all TM–P molecules, 5d TM–P molecules are very good candidates with giant MAE because of the strong spin–orbit coupling (SOC).

On the other hand, there is also a fundamental dilemma in data storage applications. A large anisotropy is needed to stabilize a magnetic bit against thermal perturbation, nevertheless, and a low anisotropy is desired for magnetization reversal during information writing. To compromise this contradiction, different approaches such as strain and electric field have been proposed to manipulate the MAE in writing information.[23–27] In this paper, we investigate the electronic and magnetic properties of 5d TM–P molecules and the manipulation of MAE for iridium–porphyrin-based (Ir–P) SMM by biaxial tensile strain based on the first-principles calculations. We find that W–P, Re–P, Os–P, and Ir–P possess the considerable MAE and the magnitude of MAE can be manipulated by the biaxial tensile strain. The calculated density of states shows that the occupation number of the minority spin channels of Ir-$d_{x^2-y^2}$ orbital decreases with the increase of the biaxial tensile strain, which leads the MAE to decrease. Therefore, the TM–P (W–P, Re–P, Os–P, and Ir–P) SMM should be considered as a high-density magnetic storage unit.

2. Methods

The first-principles calculations are performed in the framework of the spin-polarized density functional theory (DFT) calculations by using the projector augmented wave (PAW)[35,36] as implemented in the Vienna *ab initio* simulation package (VASP) code.[37] The exchange–correlation in-

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teractions are described in a generalized gradient approximation (GGA)[38] and Hubbard U in the form of the Perdew, Burke, and Ernzerh (PBE) functional. The plane-wave basis sets with cut-off energy of 500 eV are used for expanding the Kohn–Sham orbitals.[35,36] The equilibrium geometries are obtained when the atomic forces are smaller than 0.010 eV/Å. The MAE value is evaluated by implementing SOC in VASP in a noncollinear mode[39] and it is defined as the difference in energy between in-plane ([100]) and out-of plane ([001]) magnetization directions (MAE $= E[001] - E[100]$). During the calculation of MAE, the geometric, electronic, and magnetic degrees of freedom are relaxed simultaneously until the change in total energy between successive iteration steps is smaller than 10^{-7} eV. All calculations are performed with a cubic box of 25 Å in side length, and a single $\boldsymbol{k}$ point (Γ point) is used for integrating the Brillouin zone (BZ).

To test the accuracy of our theoretical predictions, we investigate the stability of the magnetic configurations by using HSE06. We calculate the Ir–P molecule with doublet, quartet, sextet, octuplet, and decuplet by using HSE06. The calculated results indicate that the structure with low spin multiplet is most stable, which is consistent with the result from the GGA. Considering the reliability of the calculation results and computation efficiency, we study the structure and magnetic properties of TMP by the GGA method. To further verify the reliability of our calculated results, we also optimize the structure of Ir–P by the CI method in Gaussian 09[40] and find that the lowest energy structure of Ir–P is also planar structure, which is in agreement with that obtained by GGA. Finally, we investigate the MAE of 5d transition metal–porphyrin by using GGA$+U$ with U value being 1 eV, 2 eV, and 3 eV, and the obtained results are also in agreement with the results obtained by GGA.

3. Structure and magnetic properties of 5d TM–P molecule

Figures 1(a) and 1(b) show the top view and side view of stable structure of the 5d TM–P molecule, respectively. The most stable geometry of 5d TM–P molecules is a planar structure, which is similar to the structure of 5d transition metal–porphyrin.[28] In all planar molecules, the TM atom is located in the center of vacancy formed by four N atoms. Figure 2(a) shows the variation of total magnetic moment of 5d TM with composition in TM–P molecules for U being 0 eV, 1 eV, 2 eV, and 3 eV, respectively. Without applying U value, the total magnetic moment of 5d TM–P molecules gradually increases with increasing the atomic number and reaches a maximum value 4.0 μ_B at W–P molecule, then decreases linearly to 0.37 μ_B at Pt–P molecule. Subsequently, the total magnetic moment of Au–P again increases to 1.0 μ_B. The imposed U values do not change the magnetic moment of 5d TM–P molecules except for Pt–P. To further investigate the origin of magnetic moment of 5d TM-P molecules, figures 1(c) and 1(d) display the spin density isosurface of Ir–P molecule. One can see that the spin densities of Ir–P molecule are mainly located on the Ir–d orbitals, indicating that the magnetic moment of Ir–P molecule primarily comes from the Ir atom, which is applicable to other 5d TM–P molecules.

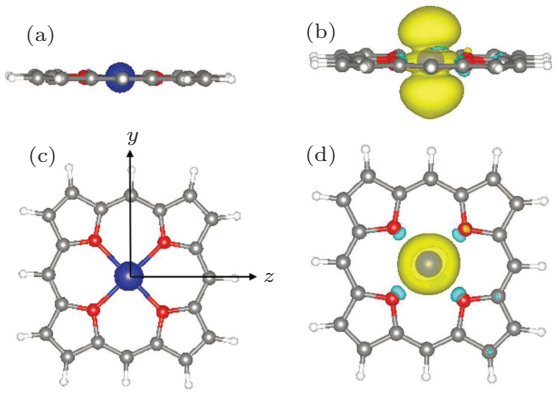


Fig. 1. Structure and isosurface of spin density of Ir–P molecule: [(a), (c)] side view and [(b), (d)] top view, with gray, red, and blue balls denoting C, N, and TM atoms, respectively.

To obtain high-T_B materials, we investigate the MAE of 5d TM–P molecules. Figure 2(b) shows the MAE with TM in 5d TM–P molecules with U value being 0 eV, 1 eV, 2 eV, and 3 eV, respectively. Without U, we find that the MAE of 5d TM–P molecule displays the oscillation, forming a peak and a valley at W–P and Ir–P, respectively. The MAE of peak position is positive, meanwhile the MAE of valley is negative. The positive MAE indicates that the easy magnetization axis is perpendicular to the molecule plane, whereas the negative MAE shows that the easy magnetization direction is parallel to the molecule plane. In most cases the MAE is positive, only Os–P, Ir–P, and Au–P system possess negative MAE. The MAE value of W–P and Re–P are about 26 meV and 20.8 meV, respectively. And the values of MAE for Os–P and Ir–P reach 24.9 meV and 62.9 meV, respectively. The 5d orbitals are spatially more extended than the 3d and 4d orbitals, so their U values should be smaller than those of 3d and 4d orbitals.[29] Then figure 2(b) only gives the MAE of 5d TM–P molecules with U value being 0 eV, 1 eV, 2 eV, and 3 eV, respectively. One can find that the U value has a strong effect on the magnitude of MAE but does not affect the trend of MAE for 5d TM–P. And the W–P, Re–P, Os–P, and Ir–P still possess the large MAE among 5d TM–P. The very large MAE of TM–P (W–P, Re–P, Os–P, and Ir–P) single-molecule indicates that these systems can be used as a unit for magnetic storage.

It is also important to study the relationship between the MAE and the orbital moment anisotropy (OMA,[30] $\Delta M_L[0\ 0\ 1] - M_L[1\ 0\ 0]$), since both of them arise from the SOC.[31–34] As is well known, the TM atoms in TM–P molecule play a dominant role in determining the MAE, figure 2(c) also displays the OMA of TM for TM–P molecules

as a function of 5d-TM atom with U value being 0 eV, 1 eV, 2 eV, and 3 eV, respectively. As shown in Fig. 2(c), the OMA for each of Re–P, Os–P, and Ir–P is larger than that of other 5d TM–P molecules, which suggests that the large OMA induces a large MAE. The corresponding relationship between the MAE and the OMA is established in most situations except the case where the large spin magnetic moment causes a large MAE for W–P.

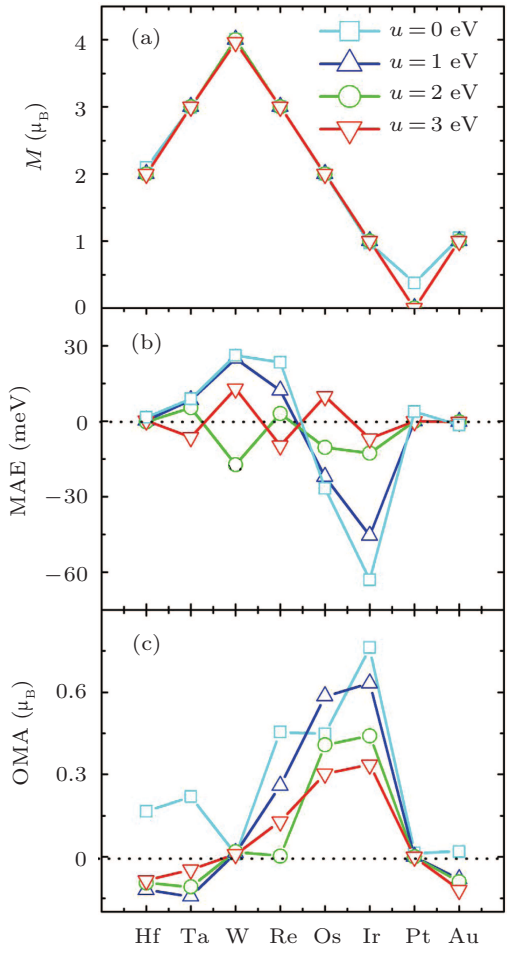


Fig. 2. Magnetic properties of metal–porphyrin (TM–P) molecules as a function of 5d-TM atom with U being 0 eV, 1 eV, 2 eV, and 3 eV, respectively, showing (a) total magnetic moment, (b) MAE, and (c) OMA of TM atoms.

4. Biaxial tensile strain manipulation of MAE in Ir–P molecule

To solve the fundamental dilemma in data storage applications, we now investigate the manipulation of MAE for Ir–P molecule by applying biaxial tensile strain without U. Figure 3 gives the MAE of Ir–P molecule as a function of biaxial tensile strain, and with its inset displaying the direction of biaxial tensile strain. We find that the biaxial tensile strain can regulate the magnitude of MAE, but cannot change the easy magnetization direction of Ir–P molecule. In a range of 2%–10% strain, the absolute value of MAE is always smaller than that without strain. The value of MAE abruptly decreases to 15.69 meV under a biaxial strain of 2%. Continually increasing the tensile strain from 2% to 6%, the value of MAE is fluctuated with 16 meV. With 6%–10% strain being applied, the absolute value of MAE gradually increases again and reaches 32.2 meV and 40.7 meV at 8% and 10% strains, respectively. Although the absolute value of MAE increases from 6% to 10% strain, the value of MAE under tensile strain is usually smaller than that without strain, especially in the range of 2%–6%. The reduced MAE of Ir–P molecule at tensile strain may solve the dilemma in data storage applications. Exerting a tensile strain within the scope of 2%–6% on the Ir–P, its MAE becomes $\sim$ 16 meV, which is easy to implement the writing operation. The large absolute value of MAE will make the storage information stable when the tensile strain is withdrawn. Experimentally, when placed on the surface of material, the free Ir-P molecule may be stretched or compressed, which causes a tensile stress or compressive stress. Then we manipulate the strain on the molecule by placing the different stresses on the substrate.

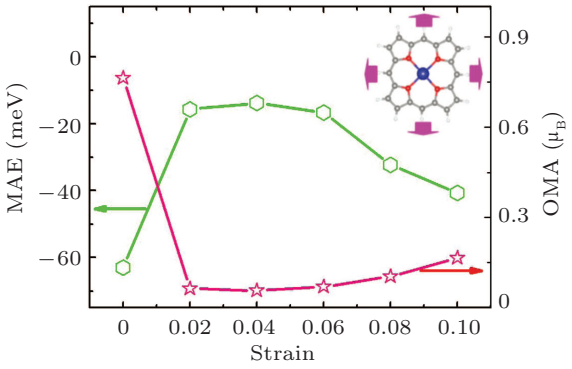


Fig. 3. MAE (green line) and OMA (red line) of TM atom of Ir–P molecule as a function of biaxial tensile strain, respectively.

5. Origin of tunable MAE by biaxial tensile strain

We now explore the mechanism of MAE for TM–P molecule. To understand the origin of MAE in electronic structure, we analyze the projected density of states (PDOS) of Ir–d molecule under 0% and biaxial tensile strain of 2% through the second-order perturbation theory[30]

$$E_x - E_z \approx \xi^2 \left[\sum_{u,o} \frac{|\langle o|L_z|u\rangle|^2}{E_u - E_o} - \frac{|\langle o|L_x|u\rangle|^2}{E_u - E_o} \right], \qquad (1)$$

where o and u denote the occupied and unoccupied valance states, respectively, and L_x, L_y, and L_z are the orbital angular momentum operators. According to Eq. (1), the most dominant contributions to MAE come from the states near the E_F, and its behavior is substantially determined by the denominator. As presented in Fig. 4, for Ir–P molecule, most states near the E_F contributing to MAE are d_{xy}, d_{xz}, and $d_{x^2-y^2}$. The magnetization direction is primarily determined by the SOC of d_{xy} with $d_{x^2-y^2}$ state through L_z operator, and then the easy magnetization axis is parallel to the Ir–P molecule plane. The hard magnetization direction comes from the coupling between d_{xy}

and d_{xz} states through L_x operator. Since the minority-spin unoccupied $d_{x^2-y^2}$ state density is much larger than the d_{xz} state density, Ir–P molecule possesses giant MAE. When 2% of the biaxial tensile strain is applied, the $d_{x^2-y^2}$ state shifts toward high energy. The difference in energy between d_{xy} and $d_{x^2-y^2}$ state becomes large, which leads the E_z to decrease, and then the difference in energy between $E_x - E_z$ decreases as indicated from Eq. (1). Because the minority-spin unoccupied $d_{x^2-y^2}$ state density is still larger than the d_{xz} state density, the easy axis of Ir–P molecule does not change under 2% of the biaxial tensile strain.

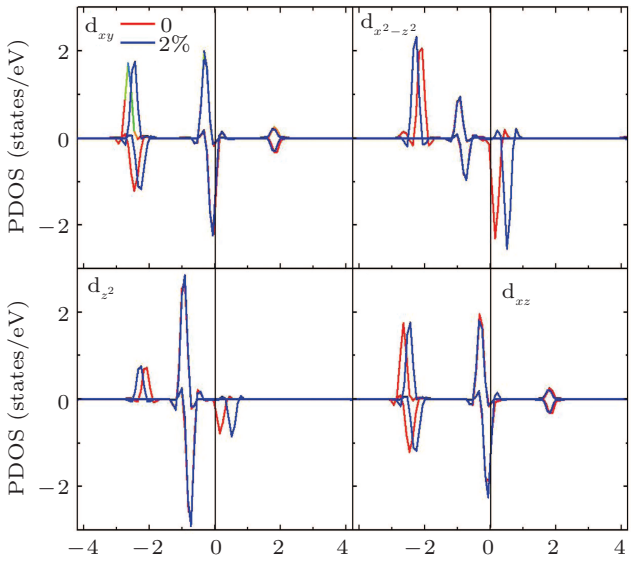


Fig. 4. Projected local density of states (PDOS) of Ir-5d in Ir–P molecule under 0% (red line) and 2% (blue line) of biaxial tensile strain, respectively.

Finally, we investigate the effect of biaxial tensile strain on OMA. Figure 3 displays the OMA of Ir–P molecule as a function of biaxial tensile strain. The OMA is the largest (0.762 μ_B) under no biaxial tensile strain. Under 2% of biaxial tensile strain, the OMA of Ir–P molecule decreases to 0.063 μ_B. With the biaxial tensile strain increasing from 2% to 6%, the OMA changes from 0.056 μ_B to 0.069 μ_B. As the tensile strain continues to increase, the OMA gradually increases. The trend of OMA is almost similar to that of MAE under biaxial tensile strain. Thus, the MAE exhibits approximate linear dependence on the OMA for the TM–P molecules under a biaxial tensile strain.

6. Conclusions

In summary, we have systematically studied the electronic and magnetic properties of 5d TM–P molecules by first-principles calculations and found that W–P, Re–P, Os–P, and Ir–P molecules have giant MAE. Moreover, the absolute value of MAE for Ir–P molecule can be reduced by tensile strain, which makes it easy to implement the writing operation. The decrease of occupation number of minority-spin channels of Ir-$d_{x^2-y^2}$ orbital plays an important role in determining the reduction of MAE of Ir–P molecule while the tensile strain increases.

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