JOURNAL OF APPLIED PHYSICS **113**, 17E130 (2013)

# Magnetism and multiplets in metal-phthalocyanine molecules

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(Presented 15 January 2013; received 1 November 2012; accepted 12 December 2012; published online 21 March 2013)

Magnetism and multiplets for metal-phthalocyanine (MPc) molecules with transition-metals (M) of Mn and Co were investigated based on the constraint density functional theory calculations by imposing density matrix constraint on the *d*-orbital occupation numbers. For the MnPc, the ground state is found to be the $^4\mathrm{E}_\mathrm{g}$ state with the perpendicular magnetic anisotropy with respect to the molecular plane, while for the CoPc, the ground state is the $^2\mathrm{A}_{1\mathrm{g}}$ state with a planar magnetic anisotropy. © *2013 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4795742]

## I. INTRODUCTION

Transition-metal phthalocyanine (MPc), which forms a planar organic molecule with a transition-metal atom (M), is a promising material in applied and industrial fields, since a variety of electric, optical, and magnetic properties with the high chemical and physical stabilities can be designed by substituting the transition-metal in the MPc.[1–5] Moreover, a challenge to miniaturize devices for novel magnetic applications now extends to treating an extreme limit of the single molecule. Importantly, the property of the MPc is governed by the electronic structure, so-called multiplet, which arises from the *d*-orbitals localized at the transition-metal atom. It is, thus, of importance to understand the multiplet structures of the MPc.

However, the ground state of the multiplets is still debated despite extensive experimental and theoretical investigations spanning decades. For examples, for the FePc, experiments[6–9] have individually proposed the $^3\mathrm{E}_\mathrm{g}$ and either $^3\mathrm{B}_{2\mathrm{g}}$ or $^3\mathrm{A}_{2\mathrm{g}}$ state, and even the density functional theory (DFT) calculations have predicted contradictory.[2,10–14] For the MnPc, the multiplet for ground state has been suggested either $^4\mathrm{E}_\mathrm{g}$ or $^4\mathrm{B}_{2\mathrm{g}}$ state,[11,15,16] and for the CoPc, the $^2\mathrm{E}_\mathrm{g}$ or $^2\mathrm{A}_{1\mathrm{g}}$ state.[11,13] For this, we previously proposed a constraint DFT approach, implemented in the full-potential linearized augmented plane-wave (FLAPW) method,[17] by imposing density matrix constraints on the *d*-orbitals occupation numbers, and our total energy calculations demonstrate that for the FePc, there are three stationary states of the $^3\mathrm{E}_\mathrm{g}$, $^3\mathrm{B}_{2\mathrm{g}}$, and $^3\mathrm{A}_{2\mathrm{g}}$ symmetries and that the ground state is the $^3\mathrm{A}_{2\mathrm{g}}$ state with a planar magnetic anisotropy (MA). Here, we extend our DFT investigations for the MnPc and CoPc, and we demonstrate that for the MnPc (CoPc), the ground state is the $^4\mathrm{E}_\mathrm{g}$ ($^2\mathrm{A}_{1\mathrm{g}}$) state with the out-of-plane (planar) MA.

## II. MODEL AND METHOD

An isolated molecule of the MPc has the simple planar structure shown in Fig. 1(a), where the transition-metal (M) ion located at the center of the molecule has $\mathrm{D}_{4\mathrm{h}}$ site symmetry. In the forms, as shown in Fig. 1(b), a ligand-field splits the *d*-orbitals into three singlets ($d_{\mathrm{xy}}$, $d_{\mathrm{z2}}$, and $d_{\mathrm{x2\text{-}y2}}$) and one doublet ($d_{\mathrm{xz+yz}}$). Ignoring the high lying $d_{\mathrm{x2\text{-}y2}}$ orbital that bonds to the four outer N ions, three multiplets $^4\mathrm{A}_{1\mathrm{g}}$ ($d_{\mathrm{xy},\uparrow}$, $d_{\mathrm{z2},\uparrow}$, $d_{\mathrm{xz+yz},\uparrow}{}^2$, $d_{\mathrm{z2},\downarrow}$), $^4\mathrm{B}_{2\mathrm{g}}$ ($d_{\mathrm{xy},\uparrow}$, $d_{\mathrm{z2},\uparrow}$, $d_{\mathrm{xz+yz},\uparrow}{}^2$, $d_{\mathrm{xy},\downarrow}$), and $^4\mathrm{E}_\mathrm{g}$ ($d_{\mathrm{xy},\uparrow}$, $d_{\mathrm{z2},\uparrow}$, $d_{\mathrm{xz+yz},\uparrow}{}^2$, $d_{\mathrm{xz+yz},\downarrow}$) for MnPc, where the majority-spin states except the $d_{\mathrm{x2\text{-}y2}}$ orbital are fully occupied, is approximately constructed, and two multiplets $^2\mathrm{A}_{1\mathrm{g}}$ ($d_{\mathrm{xy},\uparrow}$, $d_{\mathrm{z2},\uparrow}$, $d_{\mathrm{xz+yz},\uparrow}{}^2$, $d_{\mathrm{xy},\downarrow}$, $d_{\mathrm{xz+yz},\downarrow}{}^2$) and $^2\mathrm{E}_\mathrm{g}$ ($d_{\mathrm{xy},\uparrow}$, $d_{\mathrm{z2},\uparrow}$, $d_{\mathrm{xz+yz},\uparrow}{}^2$, $d_{\mathrm{xy},\downarrow}$, $d_{\mathrm{z2},\downarrow}$, $d_{\mathrm{xz+yz},\downarrow}$) for CoPc when no spin-orbit coupling (SOC) is considered.

As the model of the MPc, we adopted a monolayer slab with infinite vacuum on both sides, and a large in-plane lattice constant of 27 a.u. and atomic positions given by experiments[18,19] were employed.

Calculations were performed in the scalar relativistic approximation (SRA), i.e., excluding the SOC, based on the generalized gradient approximation (GGA)[20] for exchange-correlation, by using the FLAPW method with film geometries by including fully the additional vacuum regions outside of a single slab.[21,22] The LAPW basis with cutoffs of $|\mathbf{k}+\mathbf{G}| \leq 3.6$ a.u.$^{-1}$ and muffin-tin (MT) sphere radii of 2.3 a.u. for transition metal (Mn and Co), 1.2 a.u. for N and C, and 0.8 a.u. for H were used. Lattice harmonics with angular momenta up to $l = 8$ for Mn and Co, 6 for N and C, and 4 for H are employed to expand the charge density, potential, and wave functions.

To constraint electronic configurations of multiplet structures in the MPc without a loss of the site symmetry, we introduce an appropriate total energy functional with constraint fields,

$$E[\rho(\mathbf{r})] = E_{\mathrm{GGA}}[\rho(\mathbf{r})] + \sum_{mm'} \mu^{\alpha}_{mm'}(n^{\alpha}_{mm'} - N^{\alpha}_{mm'}), \qquad (1)$$

where $E_{\mathrm{GGA}}[\rho(\mathbf{r})]$ is the usual total energy functional of the GGA, $n^{\alpha}_{mm'}$ is a density matrix of *d*-orbitals of an atom $\alpha$, and $N^{\alpha}_{mm'}$ is an occupation number that should be constrained. In the LAPW basis, $n^{\alpha}_{mm'}$ is given by the projection of the wave function onto the $Y_{lm}$ subspace[23] as

$$n^{\alpha}_{mm'} = \sum_{k,b} f_{k,b}\langle\Phi_{k,b}|\hat{P}^{\alpha}_{mm'}|\Phi_{k,b}\rangle, \qquad (2)$$

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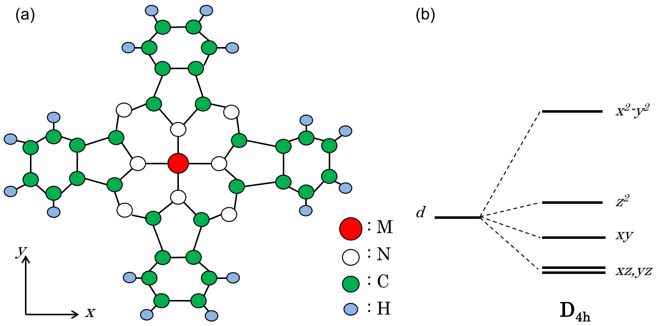

FIG. 1. (a) Atomic structure of MPc molecule. Large closed circle (red) represents a transition-metal (M) ion located at the center of the molecule, which has $D_{4h}$ site symmetry. (b) Energy level splitting for $M^{2+}$ with a $D_{4h}$ site symmetry in MPc.

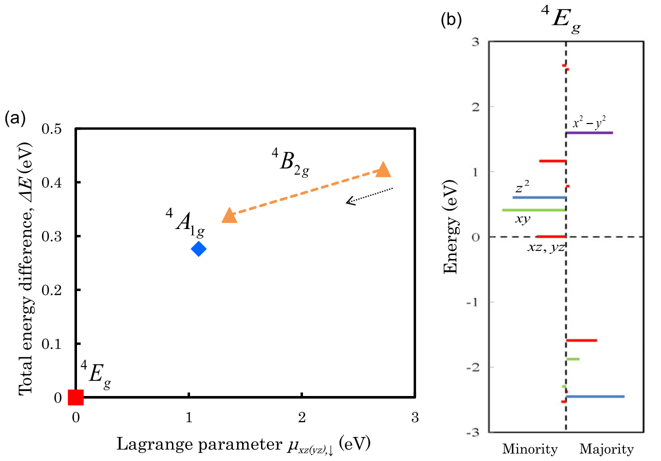

FIG. 2. (a) Calculated total energy difference, $\Delta E$, with respect to the constraint field, $\mu_{xz(yz),\downarrow}$, for MnPc, where the other $\mu_n$'s are set to zero. Closed square, rhombus, and triangle indicate solutions of $^4E_g$, $^4A_{1g}$, and $^4B_{2g}$ states, respectively, obtained by self-consistent calculations. (b) Multiplet structures of the $^4E_g$ state for the MnPc at zero constraint field. Bars (in color) represent weights of *d*-orbital contribution in muffin-tin Mn sphere. Negative and positive energies indicate occupied and unoccupied orbitals, respectively.

$$\hat{P}^{\alpha}_{mm'} = |u^{\alpha}_l Y_{lm}\rangle\langle u^{\alpha}_l Y_{lm'}| + \frac{1}{\dot{u}_l\dot{u}_l}|\dot{u}^{\alpha}_l Y_{lm}\rangle\langle\dot{u}^{\alpha}_l Y_{lm'}|, \tag{3}$$

where **k** and $b$ refer to a **k**-point in the Brillouin zone and a band index, respectively. The $f_{k,b}$ is electron occupation (Fermi) function, and $u^{\alpha}_l$ and $\dot{u}^{\alpha}_l$ are the radial wave function and its energy derivative in the basis function. The corresponding Kohn-Sham equation can be written as

$$\left[H_{GGA} + \sum_{mm'} \mu^{\alpha}_{m'm}\hat{P}^{\alpha}_{mm'}\right]\Phi_{k,b} = \varepsilon\Phi_{k,b}, \tag{4}$$

where the constraint term in the Hamiltonian effectively projects out the chosen irreducible representation for the overall wave function, in which one can pick up an electronic configuration of corresponding multiplet. In practice, we specify a set of constraint fields, $\mu^{\alpha}_n$, along directions of the eigenvectors in the $n^{\alpha}_{mm'}$, consistent with the site symmetry. Then, the $\mu^{\alpha}_{mm'}$, which are rotated back from the $\mu^{\alpha}_n$, are introduced into Eq. (4), and the corresponding $n^{\alpha}_{mm'}$ are determined self-consistently. The self-consistent calculations were carried out using the second variation scheme, i.e., the diagonalization of Eq. (4) was carried out in a basis of the eigenfunctions, $\varphi_{\mathbf{k},b}$, of $H_{GGA}$. Full self-consistency was achieved for the density matrix as well as the charge and spin densities. The total energy is calculated using Eq. (1), with $N^{\alpha}_{mm'} = n^{\alpha}_{mm'}$.

To determine the MA, the second variational method[24] for treating the SOC was performed by using the calculated eigenvectors in the SRA, and the MA energy, $E_{MA}$, was determined by the force theorem,[25–27] which is defined as the eigenvalue difference for the magnetization oriented along the planar direction and the out-of-plane direction with respect to the molecule plane.

## III. RESULTS AND DISCUSSION

### A. Mn-phthalocyanine

Calculated total energy differences, $\Delta E$, of the three multiplets of $^4A_{1g}$, $^4B_{2g}$, and $^4E_g$ states for the MnPc with respect to a variation of the constraint field $\mu_{xz(yz),\downarrow}$ are shown in Fig. 2(a), where the constraint is imposed in the occupation number of the $d_{xz(yz),\downarrow}$ orbitals. First, we started self-consistent calculations by using an initial charge density superimposed by those of spherical atoms and with no constraint field, $\mu_{xz(yz),\downarrow} = 0$, as carried out in the standard (usual) self-consistent calculations. We obtained the $^4E_g$ solution [closed square in Fig. 2(a)], where the doublet $d_{xz+yz,\downarrow}$ orbitals located at the top of the valence states are occupied by one electron, as shown in Fig. 2(b). When the constraint field $\mu_{xz(yz),\downarrow}$ is introduced in the positive direction, the multiplet structure changes to the $^4B_{2g}$ state [closed triangle in Fig. 2(a)]. However, as the $\mu_{xz(yz),\downarrow}$ sets to zero (zero constraint field), the system cannot remain in a stationary solution. Also, for $^4A_{1g}$ state, no stationary solution is obtained at zero constraint field. Thus, the ground state may be concluded to the $^4E_g$ state.

For the $^4E_g$ ground state of the MnPc, the calculated $E_{MA}$ has a positive value of 3.5 meV/molecule, indicating that the spin moments energetically favor pointing out-of-plane (out-of-plane MA). According to perturbation theory,[28] the SOC interaction between occupied and unoccupied *d* states with the same (different) *m* magnetic quantum number through the $L_z$ ($L_x$, $L_y$) operator gives a positive (negative) contribution to the $E_{MA}$. Thus, for the $^4E_g$ state, the half-occupied state (the occupied and unoccupied states) in the doublet $d_{xy+yz,\downarrow}$ orbitals ($m = \pm 1$) yields a positive contribution to the $E_{MA}$.

### B. Co-phthalocyanine

Calculated $\Delta E$ with respect to variations of $\mu_{xz(yz),\downarrow}$ for the CoPc are shown in Fig. 3(a). Self-consisted calculations with an superimposed initial charge density and no constraints yield the $^2A_{1g}$ state, where the singlet $d_{xy,\downarrow}$ and doublet $d_{xz+yz,\downarrow}$ orbitals are fully occupied, while the singlet $d_{z2,\downarrow}$ orbital locates in energy above the valence top, as shown in Fig. 3(b). When the negative $\mu_{xz(yz),\downarrow}$ is introduced, the stationary solution of the $^2E_g$ state is obtained, where the two

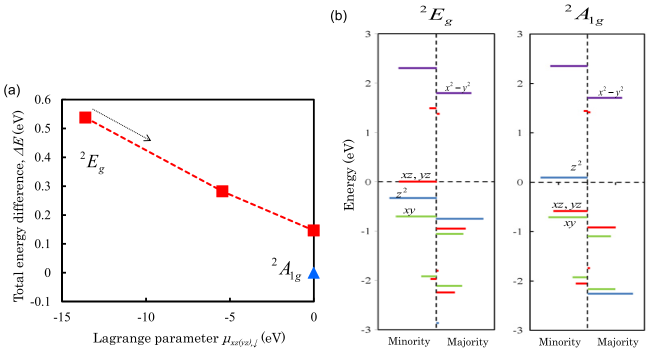

FIG. 3. (a) Calculated total energy difference, $\Delta E$, with respect to the constraint field, $\mu_{xz(yz),\downarrow}$, for CoPc, where the other $\mu_n$'s are set to zero. Closed triangle and square indicate solutions of $^2A_{1g}$ and $^2E_g$ states, respectively, obtained by self-consistent calculations. (b) Multiplet structures of the $^2E_g$ and $^2A_{1g}$ states for CoPc at zero constraint field. Notations are same as in Fig. 2.

singlets $d_{xy,\downarrow}$ and $d_{z2,\downarrow}$ orbitals are fully occupied, and the doublet $d_{xz+yz,\downarrow}$ orbitals are occupied by one electron. The total energy difference indicates that the ground state is the $^2A_{1g}$ state, whose energy is lower than that of the $^2E_g$ state by 150 meV/molecule.

The calculated $E_{MA}$s for the $^2A_{1g}$ and $^2E_g$ states result in $-1.2$ and 14.2 meV/molecule, which indicate the planar and out-of-plane MAs, respectively. The planar MA for ground state of the $^2A_{1g}$ state arises from the SOC between the occupied $d_{xy+yz,\downarrow}$ ($m = \pm 1$) and unoccupied $d_{z2,\downarrow}$ ($m = 0$) orbitals, while the out-of-plane MA for the $^2E_g$ state is due to the SOC in the half-occupied state in the doublet $d_{xy+yz,\downarrow}$ orbitals ($m = \pm 1$).

## IV. SUMMARY

We carried out the first principles calculations with the FLAPW method, based on constraint DFT, to investigate the electronic structures and MA of the multiplets for the MnPc and CoPc. Results predicted that for the MnPc, the ground state is the $^4E_g$ state, in which the easy axis of magnetization favors pointing out of-plane, while there are no stationary solutions of the $^4B_{2g}$ and $^4A_{1g}$ states. For the CoPc, the $^2A_{1g}$ state with the planar MA is the ground state, whose total energy is lower than that of the $^2E_g$ state.

## ACKNOWLEDGMENTS

Work at Mie University was supported by a Grant-in-Aid for Scientific Research (No. 24540344) from the Japan Society for the Promotion of Science, and was performed under the Cooperative Research Program of "Network Joint Research Center for Materials and Devices." Computations were partially performed at ISSP, University of Tokyo.

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