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# Density functional study of tetrahedral manganese clusters

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## Abstract

We have applied the ab initio density functional theory (DFT) based on generalized spin orbital (GSO) for tetrahedral manganese clusters with a noncollinear spin structure. It was found that three-dimensional (3D) spin states become clearly ground-states by all of GSO-localized spin density approximation, GSO-generalized gradient approximation, and GSO-hybrid methods for tetrahedral  $\text{Mn(II)}_4\text{O}_4$ . These results are consistent with the experimental results.

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*Keywords:* Generalized spin orbital; Density functional theory; Tetrahedral manganese clusters; Noncollinear molecular magnetism; Hybrid methods; Three-dimensional spin structure

## 1. Introduction

In the past few decades, multicenter metal clusters have attracted great attentions in relation not only to biomimetic compounds but also to single-molecular magnets (SMMs), both of which the functionality is due to purely the molecular origin [1]. In particular oxo-bridged manganese clusters constitutes an important class among these compounds [2] and are challenging targets of computational chemistry. For instance, the oxo-bridged tetranuclear manganese clusters ( $\text{Mn}_4\text{O}_4$ ) are of great interest as the model complex of the photosynthetic water oxidation center [3]. While some researchers investigated the di- $\mu$ -oxo manganese dimers from the viewpoints of the magnetic properties [4] and catalyzed reactivities [5], the reports of ab initio calculation of tetranuclear clusters are scanty. However, as for SMM of more high-nuclearity clusters, Zeng et al. conducted discrete variational calculations for  $\text{Mn}_{12}\text{Ac}$  and  $\text{Fe}_{11}$  at the localized spin density approximation (LSDA) level and suggested the possibility of intramolecular spin-frustration from the intramolecular effective exchange integrals [6]. Pederson and co-workers have computed the magnetic anisotropic energies of  $\text{Mn}_{12}\text{Ac}$

and  $\text{Mn}_{10}$  [7] clusters using generalized gradient approximation (GGA) solutions for spin-orbit couplings within a perturbational scheme. They showed that the spin-flipped coupling elements contributed significantly to anisotropy barriers in both cases, implying that the spin-canting plays a important role in the intramolecular spin-anisotropy effects although the SMMs have ferrimagnetic structure. Both of these prior results also imply that spin canting is important for the investigation of the ground spin state even though this cluster has an almost ferrimagnetic spin structure. Furthermore, tetranuclear complexes including  $\text{Mn}_4\text{O}_2$  are reported to be SMMs [8,9]. In particular, Carsto et al. [9] pointed out that intramolecular spin-frustrations play a key role to determine the spin states of a  $\text{V}_4\text{O}_2$  cluster which was reported to become a SMM. Previously, the present authors pointed out the possibility of the three-dimensional (3D) spin structure for cubane complexes and other high-nuclearity clusters based on classical Heisenberg (HB) model [10]. Thus, the ab initio treatment for noncollinear magnetism is needed.

While the common spin-unrestricted density functional theory (DFT) [11] can be applied for 1D spin density which we call axial spin density wave (ASDW) and of which example is shown in Fig. 1(A), generalized spin orbital (GSO) treatment of DFT is essential for spin-frustrated systems in which competing exchange interactions lead to an energetically preferred 2D spin

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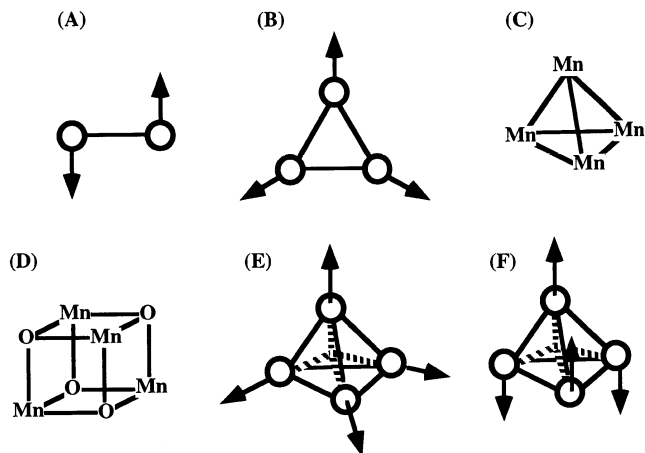


Fig. 1. The collinear (A) and noncollinear (B) spin alignments, the geometries of the tetrahedral manganese cluster (C),  $\text{Mn}_4\text{O}_4$  (D), and noncollinear (TSW) (E) and collinear (ASDW) (F) spin structures of the tetrahedral manganese cluster.

structure, which was noted as the helical spin density wave (HSDW), as shown in Fig. 1(B). Furthermore, for tetrahedral manganese clusters ( $\text{Mn}_4$ ) illustrated in Fig. 1(C) and the cubane type of  $\text{Mn}_4\text{O}_4$  shown in Fig. 1(D), 3D spin structure, which we call the torsional spin wave (TSW) state hereafter, illustrated in Fig. 1(E) is conceivable for tetrahedral ( $T_d$ ) configuration besides ASDW (Fig. 1(F)). By taking GSO-DFT approach presented below, we can describe not only collinear magnetism involving one-dimensional (1D) spin density but also noncollinear magnetism involving two- (2D) or three-dimensional (3D) spin densities. Indeed, we found for hydrogen and chromium clusters that TSWs shown in Fig. 1(E) [12] become ground states by ab initio linear combination gaussian type orbital (LCGTO) GSO-LSDA methods [13]. In this study, we examine ground-states spin structures of GSO-DFT solutions for  $\text{Mn}_4$  and  $\text{Mn}_4\text{O}_4$  having the geometries as in Fig. 1(C) and (D). In addition, we estimate the effective exchange integrals using the HB model scheme [14].

## 2. Theoretical background

In this section, we briefly present the theoretical background of GSO-DFT approach [13,14] used in our study.

The most essential feature of GSO-DFT is the extension of the constrained search region (CSR) for minimizing the Kohn-Sham (KS) energy functional [4], that is employment of  $2 \times 2$  spin density matrix

$$\rho(\mathbf{r}) = \begin{pmatrix} \rho_{\alpha\alpha}(\mathbf{r}) & \rho_{\alpha\beta}(\mathbf{r}) \\ \rho_{\beta\alpha}(\mathbf{r}) & \rho_{\beta\beta}(\mathbf{r}) \end{pmatrix} \quad (1)$$

for the fundamental parameter, instead of  $\rho_\alpha(\mathbf{r})$  and  $\rho_\beta(\mathbf{r})$ , and minimization of KS energy functional over

all non-interacting  $N$ -representable spin density matrices such that

$$E_{\text{KS}} = \min_{T\rho(\mathbf{r})=N} \left\{ T_S[\rho(\mathbf{r})] + \int d\mathbf{r} Tr V_{\text{eff}}(\mathbf{r})\rho(\mathbf{r}) \right\} \\ = \min_{\Phi(\mathbf{r}) \rightarrow N} \langle \Phi | \hat{T}_s + \hat{V}_{\text{eff}} | \Phi \rangle. \quad (2)$$

Here  $T_S[\rho(\mathbf{r})]$  is the kinetic energy functional of an auxiliary non-interacting KS system involving the effective potential, which we denote  $V_{\text{eff}}(\mathbf{r})$ . By introducing an exchange-correlation (XC) functional  $E_{\text{XC}}[\rho(\mathbf{r})]$ , we obtain the following for the set of coupled equations for KS orbitals that construct a KS single-determinant wavefunction,

$$\sum_{\sigma_2} \left[ \delta_{\sigma_1\sigma_2} \left\{ -\frac{\nabla_i^2}{2} + \int d\mathbf{r}' \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \right\} + \frac{\delta E_{\text{XC}}}{\delta \rho_{\sigma_2\sigma_1}}(\mathbf{r}) \right. \\ \left. + V_{\text{ext}}^{\sigma_1\sigma_2}(\mathbf{r}) \right] \psi_i^{\sigma_2}(\mathbf{r}) \\ = \varepsilon_i \psi_i^{\sigma_1}(\mathbf{r}), \quad (3)$$

where  $\sigma_i$  ( $i=1, 2$ ) is a spin variable ( $\alpha$  or  $\beta$ ).

In order to exploit CSR consisting of all non-interacting  $N$ -representable spin density matrices given by Eq. (1), the XC functional of the GSO-LSDA [13–15] expressed by

$$E_{\text{XC}}^{\text{GSO-LSDA}}[\rho_+, \rho_-] \\ = \int d\mathbf{r} (\rho_+(\mathbf{r}) + \rho_-(\mathbf{r})) \varepsilon(\rho_+(\mathbf{r}), \rho_-(\mathbf{r})), \quad (4)$$

must be employed for Eq. (3). The localized up ( $\rho_+$ ) and down ( $\rho_-$ ) spin densities are expressed by using the number density  $n(\mathbf{r})$  and the pauli matrices' vector  $\vec{\sigma}$  as

$$\rho_{\pm}(\mathbf{r}) = n(\mathbf{r}) \pm |Tr \vec{\sigma} \rho(\mathbf{r})|/2. \quad (5)$$

The XC functional depends on the off-diagonal terms of spin density  $\rho(\mathbf{r})$ , such that the KS equations become coupled equations like Eq. (3). The extensions to GGA or hybrid methods with generalized Hartree-Fock are straightforward. For the collinear magnetic systems,  $\rho(\mathbf{r})$  reduces to  $\rho_\alpha(\mathbf{r})$  and  $\rho_\beta(\mathbf{r})$ , and Eq. (3) to two equations for  $\alpha$  and  $\beta$  orbitals, respectively, leading to the standard spin-unrestricted DFT.

We employed the familiar exchange-correlation functionals of three classes: (i) HFS exchange [11] plus the Vosko–Wilk–Nusair fifth (VWN5) correlation functional [16], i.e. SVWN5, as a LSDA, (ii) Becke88 [17]+LYP [18] (BLYP) as a gradient corrected approximation, and (iii) B3LYP [19] as a hybrid approximation. MINI basis sets [20] are used for all calculations. The computational results are presented in the next section.

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