Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

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Version of record first published: 18 Oct 2010

To cite this article: Shusuke Yamanaka, Ryo Takeda & Kizashi Yamaguchi (2003): Generalized Spin Orbital Density Functional Study of Multicenter Metal Systems, Molecular Crystals and Liquid Crystals, 379:1, 537-542

To link to this article: http://dx.doi.org/10.1080/713738614

Mol. Cryst. Liq. Cryst., Vol. 379, pp. 537-542

1058-725X/02 $12.00 + .00
DOI: 10.1080/10587250290091010

Generalized Spin Orbital Density Functional Study of Multicenter Metal Systems

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We have firstly developed the ab initio linear combination of gaussian type orbital (LCGTO) program of generalized spin orbital (GSO) density functional theory (DFT) and applied it for multicenter metal clusters with noncollinear spin structures. It was found that two- and three-dimensional spin states become ground-states for Cr_3 (D_{3h}) and Cr_4 (T_d) respectively, indicating importance of GSO treatment of DFT for these clusters.

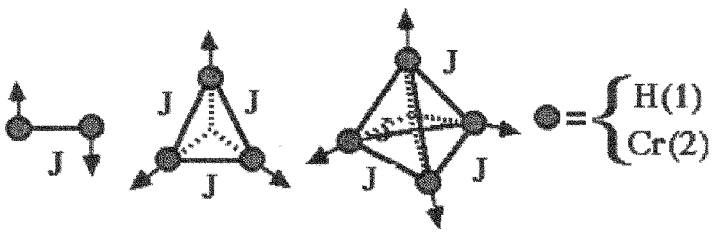
Keywords: Generalized spin orbital density functional theory; multicenter metal clusters; noncollinear molecular magnetism

INTRODUCTION

Noncollinear spin structures have been investigated on the basis of classical Heisenberg (CHB) model[1] and generalized Hartree-Fock (GHF) theory[2]. Nowadays, density functional theory (DFT) has

been developed as an effective theory for metal clusters. In previous studies[3], we have developed the ab initio linear combination of gaussian type orbital (LCGTO) program of generalized spin orbital (GSO) DFT and applied it for noncollinear molecular magnetic systems using localized spin density approximation (LSDA). By taking this approach, 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. While the common spin DFT can be applied for 1D axial spin density wave (ASDW) as shown in Figure 1(A), GSO-DFT is essential for spin-frustrated systems in which competing exchange interactions lead to an energetically preferred 2D helical spin density wave (HSDW) state as shown in Figure 1(B). Furthermore, the torsional spin wave (TSW) state illustrated in Figure 1 (C) is conceivable for tetrahedral (T_d) configuration[1,3]. Indeed, we found for hydrogen clusters that all spin structures shown in Figure 1 (1) become ground states by ab initio GSO-LSDA methods[3].

In this study, we examine ground-states spin structures of GSO-DFT solutions for metal polynuclear chromium clusters having the geometries as in Figure 1 (2). In addition, we estimate the effective exchange integrals (J) using the Heisenberg (HB) model scheme.



(A) (B) (C)

FIGURE 1 The possible spin structures for the low-spin states by the equivalent antiferromagnetic interaction (**J**).

THEORETICAL BACKGROUND

The feature of GSO-DFT is the extension of the constrained search region (CSR), that is, employment of 2×2 spin density matrix $\rho(\mathbf{r})$ to minimize Kohn-Sham (KS) energy such that[4]

$$E_{KS} = \min_{Tr\rho(\mathbf{r})=N} \left\{ T_S[\rho(\mathbf{r})] + \int d\mathbf{r} Tr V_{eff}(\mathbf{r}) \rho(\mathbf{r}) \right\}. \quad (1)$$

Here T_s is the non-interacting kinetic energy involving the effective potential, V_{eff}. This leads to KS equations for GSO's,

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

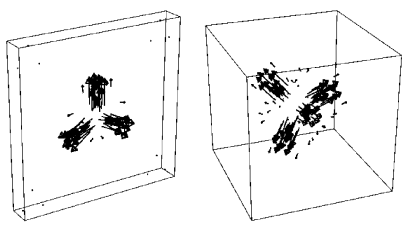
where σ_i (i = 1,2) is a spin variable (α or β). Here, to exploit CSR in (1), the XC functional of the GSO-LSDA[5],

$$E_{XC}[\rho_+, \rho_-] = \int d\mathbf{r} (\rho_+(\mathbf{r}) + \rho_-(\mathbf{r})) \varepsilon(\rho_+(\mathbf{r}), \rho_-(\mathbf{r})), \quad (3)$$

must be used for eq. (2). The localized up (ρ_+) and down (ρ_-) spin densities are given by $\rho_\pm(\mathbf{r}) = n(\mathbf{r}) \pm |Tr \vec{\sigma} \rho(\mathbf{r})| / 2$. All GSO-DFT calculations reported in this paper were carried out based on HFS exchange[3] and the Vosko-Wilk-Nusair fifth (VWN5) correlation functional[6], i.e. SVWN5, with MINI basis sets[7].

RESULTS AND DISCUSSION

We examine chromium clusters illustrated in Figure 1 (2). The interatomic distances are fixed at 2.6 Å. We first calculated the equilateral triangular Cr_3. We found that the HSDW state are more stable than ASDW states by both generalized HFS (GHFS) and GSO-SVWN5 methods as expected. Figure 2 (A) shows the 3D spin density plot for the solution by the GSO-SVWN5 calculation. All spins of three sites, which distribute devotedly on the molecular plane, align with a relative 120° orientation each other. On the other hand, as pointed out for tetrahedral H_4, the CHB model[1] gives the same energies for ASDW, HSDW, and TSW states so that the TSW state is merely one of candidates for the ground-state spin structure. Here we obtained the similar results for Cr_4 (T_d), that is, E(TSW) < E(HSDW) < E(ASDW) by both GHFS and GSO-SVWN5 as we previously presented for H_4 (T_d) [3]. Figure 2 (B) shows the 3D spin density plot of the TSW solution calculated by GSO-SVWN5. At the almost same time that we have reported TSW ground-state solutions for H_4, Hobbs et al. obtained GSO solutions of Cr_4 clusters using the all-electron projector augmented-wave scheme[8].



(A) (B)

FIGURE 2 Spin density plots of (A) Cr_3 (D_{3h}) and (B) Cr_4 (T_d) calculated by GSO-SVWN5

Table 1 lists the effective exchange integral (J) given by $J = \left(E_{LS}^{GSO-DFT} - E_{HS}^{GSO-DFT}\right) \Big/ \left(\left\langle \hat{S}^2 \right\rangle_{HS} - \left\langle \hat{S}^2 \right\rangle_{LS}\right)$ for GHFS and GSO-SVWN5, together with that of GHF for Cr_n (n=2~4). The J's of Cr_n decrease as the number of sites increases as in the case of linear clusters[9].

TABLE 1 Effective exchange integrals (J) (cm^{-1}) for the equilateral Cr_n (n=2~4) clusters

	GHFS	GSO-SVWN5	GHF
Cr_2	-279.6	-430.8	-162.8
Cr_3 (D_{3h})	-270.3	-401.7	-113.7
Cr_4 (T_d)	-210.7	-360.4	-99.73

CONCLUDING REMARKS

In this study, we have found that the HSDW and TSW states are most stable for Cr_3 with D_{3h} symmetry and Cr_4 with T_d symmetry, respectively, by ab initio LCGTO GSO-DFT. These results serve to strength the previous suggestion[3] that the TSW state is plausible for Mn_4O_4 and Fe_4S_4 clusters with the T_d symmetry. Recently, Castro et al.[10] pointed out that intramolecular spin-frustrations play a key role to determine the spin states of a V_4O_2 cluster which was reported to have a butterfly structure and to become a single molecular magnet (SMM). We intend to investigate such multicenter metal clusters based on ab initio GSO-DFT calculations in the future.

Acknowledgements

We thank Dr. Kawakami and Dr. Kiribayashi for setting up the computational environment. This research was supported by the Ministry of Education, Science, Sports and Culture, through a Grant-in-Aid for the Encouragement of Young Scientists (A), No. 13740330.

References

[1.] K. Yamaguchi, *Chem. Phys. Letters*, **30**, 288 (1975).
[2.] K. Yamaguchi and H. Fukutome, *Prog. Theor. Phys*. **54**, 54 (1975).
[3.] S. Yamanaka, et al., *Int. J. Quantum Chem*., **80**, 664 (2000).
[4.] S. Yamanaka, et al., *Int. J. Quantum Chem*., in press.
[5.] U. von Barth et al., *J. Phys. C Solid State Phys*. **5**, 1629 (1972).
[6.] S. H. Vosko, L. Wilk, M. Nusair, *Can. J. Phys*. 58, 1200 (1980).
[7.] S. Hujinaga, Gaussian basis sets for molecular calculations, Elsevier (1984).
[8.] D. Hobbs, G. Kresse, J. Hafner, *Phys. Rev. B*, **62**, 11556 (2000).
[9.] T. Kawakami et al., *J. Mol. Structure (Theochem)* **451**, 89, (1998).
[10.] L. Carsto et al., *J. Am. Chem. Soc.*, **120**, 2365 (1998).