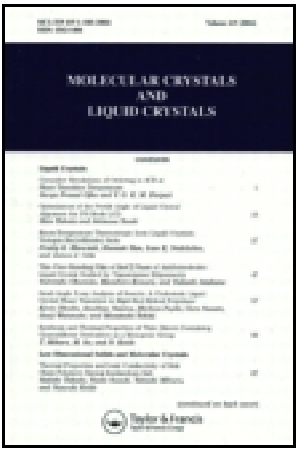

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Theoretical Study on the Magnetic Interaction for Manganese Oxides

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Theoretical Study on the Magnetic Interaction for Manganese Oxides

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The unrestricted Hartree-Fock (UHF) and hybrid density functional theory (HDFT) calculations have been carried out for manganese oxides. In order to elucidate magnetic properties of the species, the effective exchange integrals (J_{ab}) have been obtained by the total energy difference between the highest and lowest spin states. The natural orbital analysis has also been performed for elucidation of symmetry and occupation numbers of the magnetic orbitals.

Keywords: HDFT, superexchange interaction, manganese oxides, effective exchange integrals

INTRODUCTION

The LSDA approximation often breaks down for strong correlation systems such as La_2CuO_4. The SIC and LDA+U approaches have been proposed for improvement of the approximation[1]. Recently, the utility of HDFT is also pointed out for such systems[2]. In our previous work [3, 4], we have reoptimized the mixing coefficients of the HDFT approach to magnetic clusters in order to improve the calculated results for the copper halides, nickel halides, copper oxides and nickel oxides. It was found that HDFT such as UB2VWN, US2VWN and UB2LYP provided proper results for these compounds.

In this study, we here examine MnO [5,6] and putative La_2MnO_4 for comparison with La_2MO_4 ($M=Cu^{2+}$, Ni^{2+}) [4]. We have constructed the simple linear cluster models (M-O-M, M-O-M-O-M) for MnO and ring cluster model (M_4O_4) for La_2MO_4 ($M=Cu^{2+}$, Ni^{2+}) as shown in FIGURE 1. For computations of cluster models, UHF and three types of Half and Half (HH)-DFT (UB2VWN, US2VWN and UB2LYP) have been employed to obtain the effective exchange integrals using several computational schemes with spin projection. In order to clarify the magnetic interactions, we have also calculated spin densities, charge densities and natural orbitals. The full geometry optimizations were performed by each broken symmetry method.

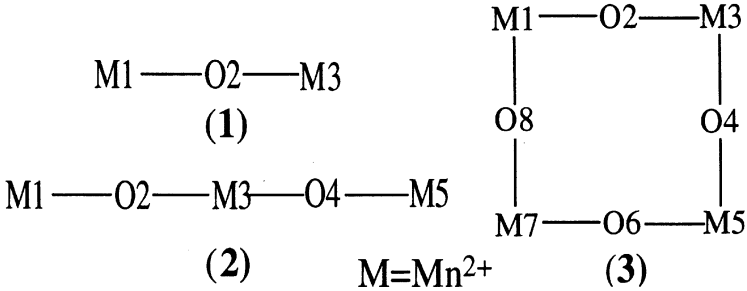

FIGURE 1 Model clusters (**1**, **2**) of MnO and that (**3**) of putative La_2MnO_4

THEORETICAL BACKGROUND

Computation of effective exchange integrals (J_{ab})

Magnetic properties of transition metal complexes and/or clusters have been investigated by the Heisenberg-type spin coupling Hamiltonian

$$\mathbf{H}(HB) = -\sum_{ab} 2J_{ab}\mathbf{S}_a \bullet \mathbf{S}_b, \qquad (1)$$

where J_{ab} is the orbital-averaged effective exchange integral between the a-th and b-th metal sites with spin operators $\mathbf{S}_a$ and $\mathbf{S}_b$. Ab initio calculations of J_{ab} are classified into two types. One is the spin-symmetry adapted (SA) perturbational and configuration interaction (CI) approach. It is desirable for quantitative computations of J_{ab}, but it is hardly applicable to transition-metal complexes because of high computational costs. In fact, twenty active orbitals and twenty active electrons {20, 20} are at least necessary for CI of Mn_4O_4. The other is the broken-symmetry (BS) approach, which is often used for such systems because of lower computational costs, though the spin contamination problem occurs in the low-spin (LS) state. As shown in eq. (2) , J_{ab} values by our approximate spin projection (AP) procedure have been reasonable values for copper oxides and nickel oxides [4].

$$J_{ab} = \frac{{}^{LS}E(X) - {}^{HS}E(X)}{{}^{HS}\langle S^2 \rangle - {}^{LS}\langle S^2 \rangle}, \tag{2}$$

where ${}^{Y}E(X)$ and ${}^{Y}\langle S^2 \rangle$ denote, respectively, total energy and total spin angular momentum for the spin state Y by the method X (=UHF, UDFT, etc). In this study, we use this scheme in obtaining J_{ab} values of manganese oxides.

Computational methods

Computational methods employed here are unrestricted Hartree Fock method (UHF) and hybrid-DFT methods (UB2VWN, US2VWN and UB2LYP). In the hybrid-DFT calculations, exchange-correlation potentials are generally defined by

$$E_{XC}=C_1E_X^{HF}+C_2E_X^{Slater}+C_3\Delta E_X^{Becke88}+C_4E_C^{VWN}+C_5\Delta E_C^{LYP}, \tag{3}$$

where the third and fourth terms mean Becke's exchange correlation involving the gradient of the density and Vosko, Wilk and Nusair (VWN) correlation functional, respectively, and the last term is the correlation correction of Lee, Yang and Parr (LYP) which includes the gradient of the density. C_i (i=1 to 5) are the mixing coefficients.

The parameter sets (C_1, C_2, C_3, C_4 and C_5) are (0.5, 0.5, 0.5, 1.0 and 0.0) for UB2VWN, (0.5, 0.5, 0.0, 1.0 and 0.0) for US2VWN and (0.5, 0.5, 0.5, 1.0 and 1.0) for UB2LYP. Tatewaki-Huzinaga MIDI plus Hay's diffuse basis sets are used for manganese atom and 6-31G* basis set is used for oxygen. All calculations were performed by using Gaussian94 program package [7].

RESULTS AND DISCUSSIONS

In order to understand the magnetic interaction of manganese oxides, we have calculated effective exchange integrals (J_{ab}). Table I summarizes the J_{ab} values for $Mn^{2+}OMn^{2+}$ (**1**), $Mn^{2+}OMn^{2+}OMn^{2+}$ (**2**) and $Mn^{2+}{}_4O_4$ (**3**). This table shows that cluster models have antiferromagnetic interactions (J_{ab} <0) because of superexchange interactions.

Table I. Effective exchange integrals (J_{ab})[a] calculated for manganese oxides

Model	UHF	UB2VWN	US2VWN	UB2LYP
MnOMn (**1**)	-2.69	-32.1	-38.3	-32.8
MnOMnOMn (**2**)	-2.95	-26.4	-32.6	-28.3
Mn_4O_4(**3**)	-8.88	-27.1	-35.3	-28.9

[a] J_{ab} are shown in cm^{-1}

We can obtain MO-theoretical explanation of magnetic interaction for the manganese oxide clusters by the natural orbital (NO) analysis. Here, we only discuss about the shapes and occupation numbers of NOs

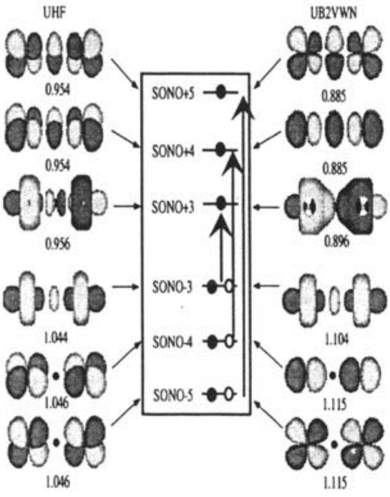

FIGURE 2
Natural Orbitals of (**1**)

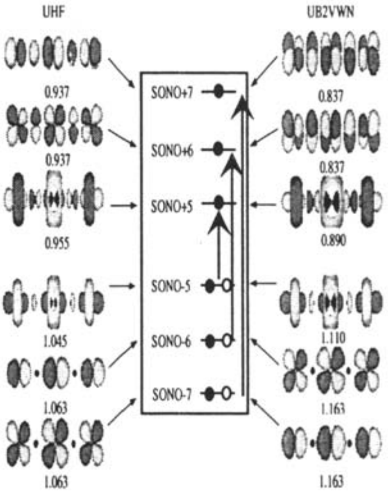

FIGURE 3
Natural Orbitals of (**2**)

by UHF and UB2VWN methods, since other HH-type DFT methods provide similar results.

FIGURE 2 and FIGURE 3 show the shapes and occupation numbers of singly occupied NO (SONO) for manganese oxides **1** and **2** by UHF and UB2VWN, respectively. It is found that SONOs by both methods are delocalized over the cluster and two types of superexchange interaction exist. For example of **2**, SONO±5 have σ-type interaction between $d_{x^2-y^2}$ orbital of manganese sites and p_x orbital of oxygen sites. SONO±6 and SONO±7 show π-type interaction between d_{xy} and d_{zx} orbital of manganese sites and p_y and p_z orbital of oxygen sites.

Table II summarizes the spin density populations in the low spin states (**2** and **3**) and the charge density populations are given in parenthesis. The calculated spin moment for **2** is in good agreement with the experimental value for MnO (4.79)[5]. The sign of spin densities for the nearest manganese ions is opposite, showing the antiferromagnetic spin correlation. The charge transfer from oxygen to manganese sites is seen because of superexchange interaction.

Table II. Spin (charge)[a] densities of manganese oxides (**2** and **3**) by UHF and UB2VWN

		site number[b]							
Model	Methods	M1	O2	M3	O4	M5	O6	M7	O8
2	UHF	4.96	0.04	-5.00	0.04	4.96			
		(1.52)	(−1.16)	(1.28)	(−1.16)	(1.52)			
	UB2VWN	4.79	0.15	-4.87	0.15	4.79			
		(1.42)	(−1.00)	(1.17)	(−1.00)	(1.42)			
3	UHF	5.02	0.00	-5.02	0.00	5.02	0.00	-5.00	0.00
		(1.12)	(−1.12)	(1.12)	(−1.12)	(1.12)	(1.12)	(−1.12)	(1.12)
	UB2VWN	4.87	0.00	-4.87	0.00	4.87	0.00	-4.87	0.00
		(1.00)	(−1.00)	(1.00)	(−1.00)	(1.00)	(1.00)	(−1.00)	(1.00)

[a] charge density populations are given in parenthesis.

[b] the site numbers are shown in FIGURE 1

CONCLUDING REMARKS

By using effective exchange integrals and the shape of natural orbitals and their occupation numbers, we have investigated the magnetic interactions of manganese oxides. We have concluded as follows; (i) the HDFT (UB2LYP etc) is applicable to manganese oxide clusters (ii) model clusters have the antiferromagnetic interactions via superexchange interaction, in agreement with the AF II phase of MnO (iii) superexchange mechanisms are divided into two classes; σ-type SE and π-type SE interactions.

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