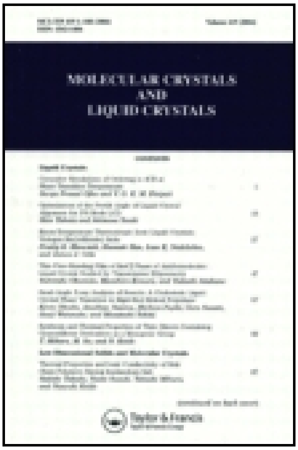

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Theoretical Studies on Magnetic Interactions of Dichromium Tetraacetate by Using Hybrid Density Functional Method

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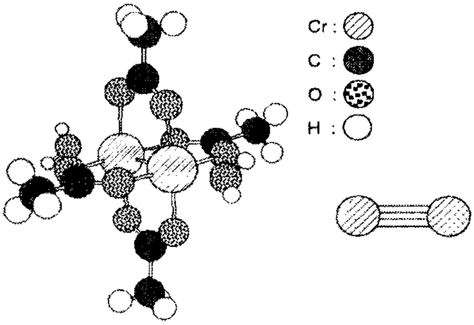
The hybrid parameters of the density functional theory (DFT) for the open shell system in terms of the effective exchange integrals (J_{ab}). By using the parameters, J_{ab} value for $Cr_2(O_2CCH_3)_4(H_2O)_2$ are calculated and Cr-Cr direct exchange interaction are estimated by using DFT natural orbital (DNO) CAS CI method.

Keywords: Dichromium tetraacetate; quadrupoleple bond; effective exchange integrals; Hybrid Density Functional method

INTRODUCTION

Dichromium(II) complexes are interesting because of quadruple Cr-Cr bond, magnetic properties, and so on. Especially, dichromium tetraacetate dihydrate $Cr_2(O_2CCH_3)_4(H_2O)_2$ (**1**) as shown in FIGURE 1, which exhibits temperature-dependent paramagnetism, is a fundamental substance to investigate effective exchange interactions of those systems. Many experimental studies on this compound have been performed, but



1 (a)

2 (b)

FIGURE 1. (a) Full model of dicromium tetraacetate dihydrate $Cr(II)_2(O_2CCH_3)_4(H_2O)_2$ **1**. (b) Cr(II) dimer model **2**.

post Hartree-Fock (HF) calculations are difficult because the system is far large. On the other hand, the density functional theory (DFT) are applied to the large-sized molecules in recent years. DFT has the advantage that the exchange-correlation effects are taken at a lower computing cost. It has been used for theoretical study of magnetic interactions in transition metal complexes. In general, J_{ab} value of the open shell systems, however, are estimated too negative value by using usual BLYP and B3LYP methods, because BLYP and B3LYP are optimized for closed shell systems [6].

In this work, we determined the parameter sets for open shell systems and estimate direct exchange interaction effect by CAS CI [8,8] calculations using DNO.

THEORETICAL BACKGROUND

Within the Kohn-Sham equation [1], total energy of the system is expressed as eq.(1)

$$E = E^T + E^V + E^J + E^{XC} \tag{1}$$

where E^T is the kinetic energy, E^V is the nuclear-electron potential energy, E^J is the electron-electron coulomb energy and E^{XC} is the exchange-correlation energy, respectively. And we generalize the exchange-correlation terms as follows:

$$E^{XC} = c_1 E_X^{HF} + c_2 E_X^{Slater} + c_3 \Delta E_X^{Becke88} + c_4 E_C^{VWN} + c_5 \Delta E_C^{LYP} \tag{2}$$

where E_X^{HF} is HF exact exchange, E_X^{Slater} is Slater's DFT exchange [2], $\Delta E_X^{Becke88}$ is Becke's 1988 correction function to Slater's exchange [3], E_C^{VWN} is Vosko, Wilk and Nusair 1980 correlation functional [4] and ΔE_C^{LYP} is Lee, Yang, Parr correlation correction [5], respectively.

We determined the mixing coefficients (c_i) of each functional by fitting J_{ab} values of our methods to those of UCCSD(T) at naked Cr dimer model (**2**). Next, the J_{ab} value of **1**, with the experimental geometry, was calculated by using the same parameter sets. In those calculations, We use Heisenberg model (eq. 3) and size-consistent spin projection (eq. 3) to estimate J_{ab}[6].

$$H = -2\sum J_{ab}\mathbf{S_a} \bullet \mathbf{S}_b \tag{3}$$

$$J_{ab} = \left({}^{LS}E - {}^{HS}E\right) \Big/ \left({}^{HS}\langle s^2\rangle - {}^{LS}\langle s^2\rangle\right) \tag{4}$$

Each calculations are performed by the use of Tatewaki-Huzinaga MIDI [7] plus Hays' diffuse d-basis set [8]: (533(21)/53(21)/(41)) for Cr and 6-31+G* basis sets for other atoms. Gaussian94 program pacage [9] and HONDO95 program pacage [10] are used for those calculations .

TABLE 1 (a) Each hybrid parameter and J_{ab} value for full model **1**
(b) J_{ab} value for naked Cr dimer model **2**

parameter sets					(a)	(b)	methods
c_1	c_2	c_3	c_4	c_5	(cm^{-1})	(cm^{-1})	
0.0	1.0	1.0	1.0	1.0	-1042	-302	UBLYP
0.2	0.8	0.72	1.0	0.81	-733	-402	UB3LYP
0.5	0.5	0.5	1.0	1.0	-520	-299	UB2LYP
0.5	0.5	0.5	1.0	0.0	-466	-258	UB2VWN
0.5	0.5	0.0	1.0	0.0	-493	-253	US2VWN
1.0	0.0	0.0	0.0	0.0	-281	-151	UHF
						-210	UCCSD(T)
					-490		exp.

RESULT AND DISCUSSION

Each parameters and the results are shown in TABLE 1. UB2LYP, UB2VWN and US2VWN in the table are our new parameter sets. Those reproduced not only J_{ab} value of UCCSD(T) method for **2** but also the experimental J_{ab} value for **1**, while usual BLYP and B3LYP indicate too negative values. We performed another attempt to investigate effects of axial ligands, and CAS CI calculation by using natural orbitals obtained by our DFT parameter sets. The shifts of the J_{ab} value when axial ligands are changed are shown in TABLE 2. All axial ligands behave σ-type contribution to the complex. Our methods are also valid to estimate the

TABLE 2 The shifts of J_{ab} value with the change of axial ligand

J_{ab}(noH_2O)	J_{ab}(H_2O)	J_{ab}(NH_3)	J_{ab}(PH_3)	*cf*
(cm^{-1})	(cm^{-1})	(cm^{-1})	(cm^{-1})	
-467	-520	-530	-502	UB2LYP
-419	-466	-478	-453	UB2VWN
-440	-493	-503	-479	US2VWN
-250	-281	-289	-277	UHF

TABLE 3 J_{ab} value for **1** calculated by DNO CAS CI [8,8]

method	J_{ab}
UB2LYP-NO	-327
UB2VWN-NO	-331
US2VWN-NO	-327
UHF-NO(UNO)	-301

(In cm^{-1})

effects by change of ligand. TABLE 3 is the results of DNO CAS CI [8,8] calculation. Unrestricted HF natural orbital (UNO) CAS CI and other related calculations such as CAS SCF or CAS PT2 and so on, were attempted at several models and made sure of its effectiveness [10]. Our approach which use DNO active space, however, has not been investigated well. It is interesting from the point of view of its effectiveness to inspect this method. The natural orbitals are selected as the view point of magnetic interest, that is $\sigma^2\pi^2\pi^2\delta^2\delta^*\pi^*\pi^*\sigma^*$ which have mainly metal d character. Those are the most important orbitals related with Cr-Cr direct interaction. In the other words, this CAS calculations are indicating J_{ab} value brought by Cr-Cr direct interaction. Therefore the difference between TABLE 1 and TABLE 3 is the effect of the throughbond interactions. For example, 193 cm^{-1} is the throughbond effect calculated by UB2LYP method. As the result of those analysis, it is brought to light that the most effective interaction between Cr atoms is the Cr-Cr direct interaction.

SUMMARY

In this study, we determined the mixing coefficients of DFT and HF in terms of the effective exchange integrals (J_{ab}). Judging from these results, this approach is available for the Cr-acetate complexes and other related substances, *i.e.*, Cu-acetate, Zn-acetate and so on. Furthermore, since this method can estimate approximative J_{ab} value of large system with lower computing cost, it is able to be applied to large size strong correlating systems. To investigate relations between hybrid parameters and J_{ab} value in the systematic way, this methods will become more useful methods.

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