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Theoretical Studies of Direct Exchange Couplings Between Transition Metal Ions I. Naked Binuclear Chromium(II) and Molybdenum (II) Systems

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THEORETICAL STUDIES OF DIRECT EXCHANGE COUPLINGS BETWEEN TRANSITION METAL IONS I. NAKED BINUCLEAR CHROMIUM(II) AND MOLYBDENUM (II) SYSTEMS

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Abstract The effective exchange integrals (J_{ab}) and bond orders of naked Cr(II)-Cr(II) and Mo(II)-Mo(II) dimers were calculated by ab initio UHF MO and density functional (DFT) methods. Reduction of formal quadruple bond orders for these species by strong electron correlation effects are examined by these computational procedures. The calculated J_{ab} values are compared with the experimental results for binuclear Cr(II) complexes with different interatomic distances.

INTRODUCTION

The quadruple metal (M)-metal (M) bonds for the $[M_2X_8]^{2n-}$ complexes (M=Cr, Mo, Re, etc) have been extensively investigated by Cotton et al.[1,2] The transition metal ions $[MX_4]^{n-}$ in these dimers are formally regarded as the d^4 configuration with the octahedral (Oh) ligand field. Then the quadruple M-M bonds are described as the $\sigma^2\pi^4\delta^2$ orbital configuration from a simple molecular orbital (MO)-theoretical picture. Very recently, Mashima et al.[3] tried the polymerization of the multiple metal-metal bonds to obtain the extended systems, and actually synthesized the linear tetranuclear Cr(II) and Mo(II) complexes involving these dinuclear transition metal units. The magnetic measurements and solid state NMR spectroscopy of these compounds have revealed

that the direct exchange couplings between the Cr(II) ions are rather weak: the direct exchange integrals (J_{ab}) are in the range; -8 - -80 cm^{-1}.[4] These findings support the VB-like description of the weak Cr(II)-Cr(II) bonds.

As is well known, the multiple metal-metal bonds have been systematically described by the MO theory.[2] The Hückel MO and density functional theories (DFT)[5-7] based on the scattered wave (SW) approximation were heavily utilized for the purpose. On the other hand, the direct exchange couplings between transition metal ions and their superexchange couplings have been described by the VB-like models such as the Heisenberg model in relation to molecule-based magnetism.[8-10] Thus the nature of the metal-metal bonds are variable from the MO-limit (strong covalent bond) to the VB-limit (weak covalent bond), depending on several structural factors and component transition metal ions.[11-13]

From these results, a systematic theoretical study from the MO- to the VB-region is desirable for full understanding of the multiple metal-metal bonds. As our first theoretical step toward these transition metal complexes, the Cr(II)-Cr(II) dimer (**1**) and the Mo(II)-Mo(II) dimer (**2**) without ligands will be examined using the spin-unrestricted Hartree-Fock (UHF) and spin-polarized DFT theories. The different characteristics between these computational methods will be clarified examining the multiple bond orders and the direct exchange integrals (J_{ab}).[8-13]

THEORETICAL BACKGROUNDS FOR BINUCLEAR METAL-METAL SYSTEMS

First, the theoretical background is explained by using the direct exchange-coupled chromium (II) dimer (**1**).[6] The ground state of the divalent chromium ion Cr(d^4) is quintet. Therefore, **1** is regarded as the d^4-d^4 direct exchange-coupled system with a quadruple bond.[1,2] However, the strong electron correlation effect may reduce the formal bond order as in the cases of the direct exchange-coupled manganese dimer and superexchange coupled chromium complexes examined previously.[11] The ab-initio UHF MO calculations of **1** were carried out using Tatewaki-Huzinaga basis set [14] [533(21)/53(21)/(41)+ diffuse d(α=0.0912)] which is supplemented by the 4p-AO with the same exponent as that for the 4s AO. Here, this triple zeta basis set is referred to as BSI. The BSI was also utilized for the unrestricted Kohn-Sham (UKS) calculations by the use of the Becke-Lee-Yang-Parr (B-LYP) functionals.[15,16]

We first examined the highest spin (HS) state. The bonding and antibonding orbitals for the HS (S=4) state of **1** are given by the symmetry-adapted MOs

$$\phi(X) = N [dX(r) + dX(l)], \quad \phi^*(X) = N' [dX(r) - dX(l)] \qquad (1)$$

where N (N') is the normalizing factor and X denotes the d-orbital symmetry, i.e, σ, π_x, π_y, δ_{xy} and δ_{x2-y2}.[1,2] FIGURE 1 illustrates the bonding and antibonding orbitals for each bonding pair at the HS state. They are nearly degenerate in energy at a relatively large interatomic distance or in the strong correlation regime. In this situation, the bonding UHF MOs for the lowest spin LS (S=0) state of **1** are given by the left-right

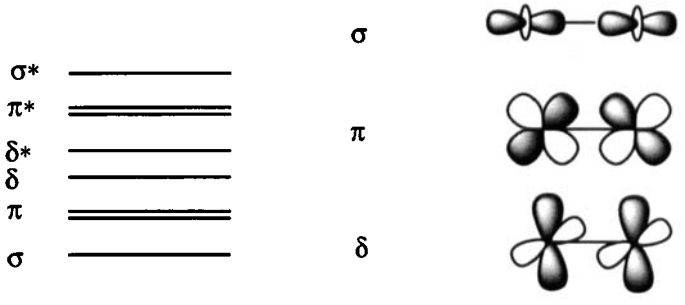

FIGURE 1 The orbital energy levels for the quadruple bond between Cr(II) ions and the orbital shapes for the bonding σ-, π- and δ-orbitals.

split-orbitals, which are described by mixing of the bonding and antibonding MOs in Equation (1) as follows:[13]

$$\psi^{+}(X) = \cos\theta\ \phi(X) + \sin\theta\ \phi^{*}(X) = \cos\omega\ a(r) + \sin\omega\ b(l) \quad (2a)$$

$$\psi^{-}(X) = \cos\theta\ \phi(X) - \sin\theta\ \phi^{*}(X) = \cos\omega\ b(l) + \sin\omega\ a(r) \quad (2b)$$

where θ and ω are the MO- and VB-orbital mixing parameters, while a(r) and b(l) are the localized natural orbitals (LNO) defined at the strong correlation limit ($\theta = 45°$) by

$$a(r) = 1/2\ (\ \phi(X) + \phi^{*}(X)\ ) \quad (3a)$$

$$b(l) = 1/2\ (\ \phi(X) - \phi^{*}(X)\ ) \quad (3b)$$

The LNOs on one site have small tails on the other site, satisfying the orthogonality condition. The molecular orbitals given by Equation (2) are referred to as the different-orbitals for different spins (DODS) MOs[5] for the up- and down-spins for the singlet state of **1**, and these are more or less localized on the left and right chromium atoms, respectively, because of strong electron correlations. FIGURE 2 illustrates these MOs obtained by the ab initio UHF and spin-polarized B-LYP (U-BLYP) calculations. As shown previously,[13] the DODS MOs are reduced to the symmetry-

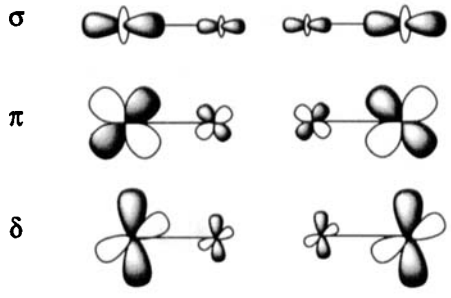

FIGURE 2 The bonding DODS MOs for the up- and down-spins obtained by the UHF and UKS methods.

adapted MOs given by Equation (1) at the weak correlation limit (MO limit) whereas they become equivalent to the LNO by Equation (3) at the VB-limit.

BOND ORDERS FOR DINUCLEAR METAL-METAL SYSTEMS

Since the DODS MOs in FIGURE 2 are more or less symmetry-broken because of the electron repulsion effects, the broken symmetry (BS) character for unstable metal-metal bonds is defined by the weight (D_i) of the doubly excited configuration in the configuration interaction (CI) terminology.[13]

$$y_i = 2\,D_i = = 1 - 2T_i / (1 + (T_i)^2) \quad (4)$$

It is also given by the orbital overlap T_i between the split orbitals i under the UHF and UKS approximations, where the perfect-pairing (PP) approximation is employed.[17] The BS character is the same as the biradical (BR) character for organic BR species. The BS character is rather related to the magnetic property in the case of inorganic complexes or clusters under consideration.

The occupation numbers[13] of UHF and UKS natural orbitals (UNO) in the PP spin-projected UHF (PUHF) or UBLYP solutions are generally given by

$$n_{HO\text{-}i}(PUHF) = [\, n_{HO\text{-}i}(UHF)\,]^2 / (\,1 + (T_i)^2\,) \quad (5)$$

$$n_{LU+i}(PUHF) = [\, n_{LU+i}(UHF)\,]^2 / (\,1 + (T_i)^2\,) \quad (6)$$

where

$$n_{HO\text{-}i}(UHF) = 1 + T_i \quad \text{and} \quad n_{LU+i}(UHF) = 1 - T_i \quad (7)$$

Therefore the effective bond order (BO) for a bond i is defined by

$$BO_i = (n_{HO\text{-}i}(PUHF) - n_{LU+i}(PUHF)\text{-}) / 2 = 2T_i / (1 + (T_i)^2) = 1 - y_i \quad (8)$$

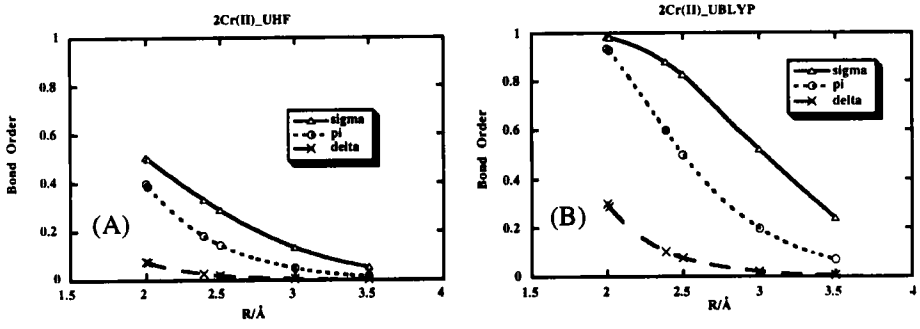

FIGURE 3 The effective bond order of Cr(II)-Cr(II) by the spin -projected UHF (A) and U-BLYP (B) methods.

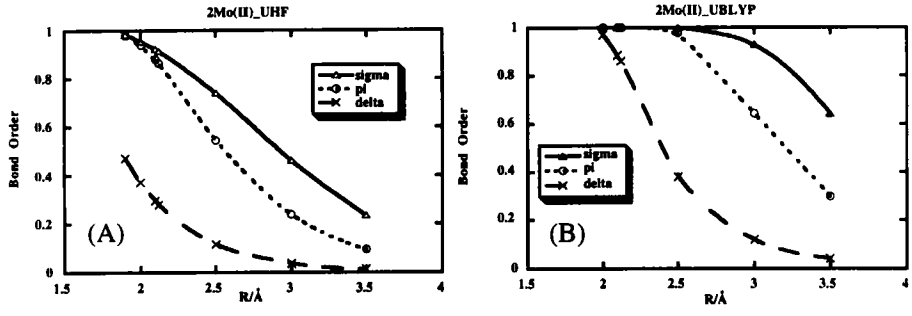

FIGURE 4 The effective bond order of Mo(II)-Mo(II) by the spin-projected UHF (A) and U-BLYP (B) methods (see text).

These formulas were equally used for U-BLYP. [18] From Eq. 8, the formal bond order for the multiple metal-metal bond for dinuclear metal-metal system is reduced to the effective bond order because of the BS character arising from the electron correlation effect. FIGURES 3 and 4 show, respectively, variations of the effective bond orders for **1** and **2** by the UHF and UKS calculations. The triple-zeta BSI and single-zeta basis set (BSII) [43333/4333/43] were use for **1** and **2** , respectively.

From FIGURES 3 and 4, the following notices are available.

(1) The effective bond orders for the d4-d4 exchange-coupled systems are far smaller than the formal value, BO=4, since the δ–δ bond is particularly weak.[1,6]

(2)The effective bond orders are calculated to be relatively small by UHF, whereas such BO reduction is not remarkable in the case of U-BLYP.

(3)The bond orders of the π and σ bonds in Mo(II)-Mo(II) are larger than 0.8 if R<2.5Å , and therefore the metal-metal bonds in the Mo(II)-Mo(II) core are rather stable, compared with those of the Cr(II)-Cr(II) system.

EFFECTIVE EXCHANGE INTEGRALS

Since the Mo(II)-Mo(II) quadruple bonds are usually strong, the ground state of many dimolybdenum complexes involving these cores are diamagnetic in nature.[1-4] On the other hand, several dichromium complexes having the Cr(II)-Cr(II) cores exhibit the temperature-dependent paramagnetism.[1-4] This indicates that the Cr(II)-Cr(II) bonds are weak when the intermetallic distance exceeds 2.0 Å, and therefore the Heisenberg model can be utilized for a VB-like description of them.

As shown previously, the effective direct exchange integrals (J_{ab}) in the Heisenberg model can be calculated for **1** by using an approximate spin-projection (AP)[11] procedure for the UHF and UKS solutions[11,18]

$$J_{ab}(\text{AP-X}) = [E(\text{LS})-E(\text{HS})] / [\ \langle S^2\rangle(\text{HS})-\langle S^2\rangle(\text{LS})\ ](\text{X=UHF, UKS}) \quad (9)$$

where the E(Y) and $\langle S^2\rangle$(Y) denote, respectively, the total energy and total spin angular momentum for the spin state Y. TABLE I summarizes the calculated J_{ab} values for **1**. FIGURE 5 shows variations of the J_{ab} values obtained for the naked Cr(II)-Cr(II) core by the ab initio UHF and DFT/BSI calculations and the experimental J_{ab} values[19,20] for the dichromium complexes with the Cr(II)-Cr(II) distance.

TABLE I The effective exchange integrals J_{ab} (cm^{-1}) of the Cr(II)-Cr(II) dimer by the spin projected UHF and UKS/BSI methods.

R(Å)	AP UH F	AP UBLYP
2.0000	-565.5	-891.4
2.0150	-535.5	-850.2
2.3890	-136.0	-279.5
2.5000	-88.8	-202.8
3.0000	-12.0	-7.4
3.5000	-1.3	-0.0

From TABLE I and FIGURE 5, the following conclusions are drawn:

(1) The effective exchange integrals calculated by both the methods are negative

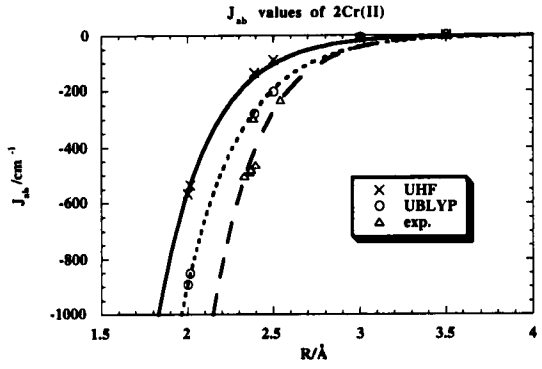

FIGURE 5 Variations of of the J_{ab} values obtained by the ab initio calculations and the experiments with the Cr(II)-Cr(II) distance.

(antiferromagnetic) , showing the covalent bond formation between the chromium ion Cr(II).

(2) The magnitude of the calculated J_{ab} values decrease with the increase of the Cr(II)-Cr(II) distance (R) in an exponential manner.

(3) The magnitude of the J_{ab} values by the UKS DFT method are larger than those of UHF in the small interatomic region (R<2.5 Å), whereas the tendency is reversed if the interatomic distance exceeds a certain limit (R=3 Å).

(4) The absolute values of the experimental J_{ab} values for the binuclear chromium complexes[19,20] are larger than those of the naked cores by DFT. This implies that the ligangds act effectively to enhance the covalent bonding between Cr(II).

CONCLUDING REMARKS

In conclusion the rormal bond order for the multiple metal-metal bond for dinuclear metal-metal systems is reduced to the effective one because of the electron correlation effect. The effective exchange interaction in the Cr(II)-Cr(II) system(**1**) is much weaker than that of Mo(II)-Mo(II) (**2**) and therefore the Cr(II)-Cr(II) multiple bond of **1** has more larger broken-symmetry (BS) character than that of **2**. The effective exchange integrals[19,20] (J_{ab}) observed for chromium complexes with the core **1** were compared with the calculated J_{ab} values. The magneto-structural correlations in these complexes are reasonably understood by the calculated results.

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