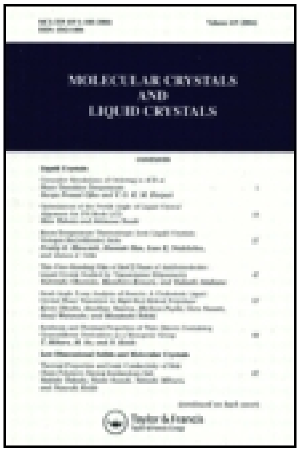

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Casci and Casscf Studies of Dinuclear Transition Metal Systems with Quadruple Metal-Metal Bonds (M=Cr(Ii), Mo(Ii))

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CASCI AND CASSCF STUDIES OF DINUCLEAR TRANSITION METAL SYSTEMS WITH QUADRUPLE METAL-METAL BONDS (M=Cr(II), Mo(II))

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Abstract The complete active space (CAS) configuration interaction (CI) and CASSCF calculations for naked Cr(II)-Cr(II) (**1**) and Mo(II)-Mo(II) (**2**) dimers were carried out in order to examine the reliability of the previous MO-theoretical results obtained by the *ab initio* UHF and DFT methods. From the CASCI and CASSCF calculations, it was concluded that the formal bond orders (one σ, two π, and one δ bonds) are reduced to the effective ones due to the strong correlation and also that the valence-bond (VB) like model such as the Heisenberg model works well in **1**. The effective exchange integrals (J_{ab}) calculated for the system were compatible with the experimental results available. On the other hand, the σ and π bonds in **2** were strong, showing that the MO picture is reliable. The δ bond of **2** was calculated to be rather weak, although it is stronger than that of **1**. The CASCI and CASSCF results support the previous UHF and DFT results for **1** and **2**.

INTRODUCTION

The quadruple metal(M)-metal(M) bonds (M = Cr(II), Mo(II), *etc.*) have attracted continuous interest. Previously[1] we have investigated the nature of the quadruple metal-metal bonds of the naked Cr(II)-Cr(II) (**1**) and Mo(II)-Mo(II) (**2**) dimers under the spin-unrestricted Hartree-Fock (UHF) and density functional (DFT) methods. The effective exchange interaction in **1** was found to be weaker than that of **2** and thereby the multiple bond of **1** was expected to have much larger broken-symmetry (BS) character than that of **2**. Although the *ab initio* UHF and DFT calculations were useful for qualitative MO theoretical descriptions of the multiple metal-metal bonds in these systems,[2-4] the UHF and DFT solutions for the low-spin (LS) state often resulted in the so-called spin contamination errors.[5-6] Thus, for more refined investigation of **1** and **2**, the spin-restricted multiconfiguration approach such as the configuration interaction (CI) calculation is desirable.[6-8] As an extension of the previous work,[1] we here perform the complete active space (CAS) CI calculations of **1** and **2** by using the UHF natural orbitals (UNO).[6-8] The CASSCF calculations of **1** and **2** are successively carried out in order to confirm the UNO CASCI results. The total energies of the excited high-spin (HS) states for **1** and **2** are also calculated by the UNO CASCI and CASSCF methods. The energy splittings between the spin multiplets by these methods are compared with those by the previous approximate spin-projected UHF and DFT methods in combination with the Heisenberg model.[9-12] Implications of the calculated results are discussed in terms of molecular design of new d-d conjugated systems.

THEORETICAL BACKGROUNDS

(A) Determinations of UNO and CAS

Several theoretical aspects are briefly described in this section. Theoretically, the use of the natural orbitals are desirable for rapid convergence of the CI descriptions of the quadruple metal-metal bonds of **1** and **2**. As a direct extension of previous UHF and DFT calculations of **1** and **2**, we here employ the approximate natural orbitals and their occupation numbers[6] of these solutions, which are obtained by diagonalyzing the first-order density matrices,

$$\rho(1,1') = \sum_{i=1}^{m} n_i \phi_i(1)\phi_i(1'), \qquad (1)$$

where ϕ_i and n_i denote, respectively, the i-th UNO and its occupation number. As illustrated in Figure 1, the UNOs are classified from the occupation numbers into three different groups; (1) core orbitals with $n_i = 2.0$, (2) active orbitals where $0.0 < n_i < 2.0$, and (3) virtual orbitals with $n_i = 0.0$. Therefore, the complete active space (CAS) among UNOs can be easily determined for a property under consideration. The full CI wave function Ψ within the UNO CAS is called UNO CASCI one,

$$\Psi = \Sigma\, C_i \Phi_i \qquad (i = 1 \sim \text{full}), \qquad (2)$$

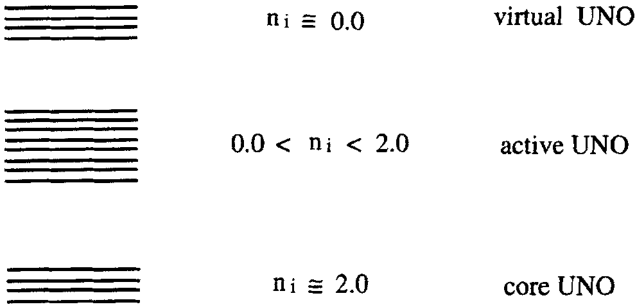

FIGURE 1 Classification of UNOs into three groups with their occupation numbers.

where C_i and Φ_i denote the UNO CASCI coefficient and configuration state function respectively. The reoptimization of the UNO and CASCI coefficients by the multiconfiguration (MC) SCF technique provides the CASSCF solution. The CASCI and CASSCF calculations of **1** were carried out by using Tatewaki-Huzinaga basis set [533(21)/53(21)/(41) + diffuse d(α = 0.0912)][13] which is supplemented by the 4p-AO with the same exponent as that for the 4s-AO. This triple zeta basis set is abbreviated as BSI. On the other hand, the Tatewaki-Huzinaga basis set [43333/4333/43], which is abbreviated as BSII, was used for **2**.

(B) Comparisons between the occupation numbers by UNO CASCI and CASSCF

The occupation numbers n_i of UNO for **1** were calculated by using the low-spin (LS) UHF/BSI solution. Judging from the n_i values in Equation (1), the eight active orbitals and eight electrons {8, 8} were at least necessary for the CASCI and CASSCF calculations of **1**. Here, the UNO CAS {8, 8} was utilized for the CASCI calculations and was also used as the trials for the CASSCF calculations. Tables I and II summarize, respectively, the occupation numbers of UNOs by UNO CASCI {8, 8} and those by CASSCF {8, 8}. From Tables I and II, the following conclusions were drawn:

(1) The occupation numbers of the eight natural orbitals obtained for the low-spin (LS) state by the UNO CASCI {8, 8} calculations are close to the corresponding values by the CASSCF {8, 8} calculations. This indicates that the UNOs are good trial orbitals for the CASSCF calculations and the UNO CASCI can be used instead of CASSCF if the latter calculation is often impossible for larger systems.

(2) The occupation numbers of the σ-, π- and δ-bonding orbitals for **1** are 1.45, 1.36,

TABLE I Occupation numbers of the eight natural orbitals for **1** by UNO CASCI {8, 8}.

R(Å)	σ	$\pi(\pi_\perp)$	δ	δ^*	$\pi^*(\pi^*_\perp)$	σ^*
2.000	1.432	1.347	1.072	0.928	0.654	0.568
2.015	1.421	1.333	1.068	0.932	0.667	0.579
2.389	1.235	1.126	1.018	0.982	0.874	0.765
2.500	1.198	1.097	1.013	0.987	0.903	0.802
3.000	1.086	1.031	1.003	0.997	0.969	0.914
3.500	1.033	1.010	1.001	0.999	0.990	0.967

TABLE II Occupation numbers of the eight natural orbitals for **1** by CASSCF {8, 8}.

R(Å)	σ	$\pi(\pi_\perp)$	δ	δ^*	$\pi^*(\pi^*_\perp)$	σ^*
2.000	1.449	1.359	1.075	0.925	0.641	0.550
2.015	1.437	1.344	1.070	0.930	0.656	0.562
2.389	1.239	1.127	1.018	0.982	0.873	0.761
2.500	1.201	1.097	1.013	0.987	0.903	0.799
3.000	1.087	1.031	1.003	0.997	0.969	0.913
3.500	1.033	1.010	1.001	0.999	0.990	0.967

and 1.08 even at the interatomic distance R = 2.00 Å. The bond orders are significantly reduced even for the σ– and π–orbitals because of the d-d electron repulsion. The bond order for the δ-bond of **1** is almost zero.

(3) The occupation numbers of the σ- and π-bonding orbitals for **1** decrease with the increase of the interatomic distance R, and they become smaller than 1.2 if R exceeds 2.5 Å.

The conclusions (1)-(3) by UNO CASCI and CASSCF are consistent with previous UHF and DFT results for the bonding property of **1**, suggesting that UHF and DFT methods are applicable to larger d-d conjugated systems for qualitative discussion.

DIRECT EXCHANGE COUPLINGS IN DINUCLEAR METAL-METAL SYSTEMS

(A) Calculation of J_{ab} by UHF and DFT

The preceding results clearly indicate that the valence bond (VB) or localized picture is useful for qualitative understanding of the bonding property of **1**. As we reported previously, the UHF and DFT molecular orbitals for the up- and down-spins were largely localized on the left and right Cr(II) ions, respectively. When the energy difference between the ground and excited higher spin states becomes small, the populations of the higher spin states become significant at finite temperature. This situation is the paramagnetic state described by the Heisenberg model.

We have already calculated the direct effective exchange integrals (J_{ab}) for **1** by using an approximate spin-projection (AP)[10] procedure for the UHF and DFT solutions,

$$J_{ab}(\mathrm{AP\ X}) = [E(LS)-E(HS)] / [\langle S^2\rangle(HS)-\langle S^2\rangle(LS)], \quad (3)$$

where the E(Y) and S^2(Y) denote, respectively, the total energy and total spin angular momentum for the spin state Y. X denotes the UHF or DFT method. Equation (3) was derived under the assumption that the energy splittings for the spin multiplets are well described by the Heisenberg model as illustrated in Figure 2, and these energy levels are equally applicable to the spin multiplets involved in the low-spin UHF and UBLYP solutions, where UBLYP denotes the spin-unrestricted Kohn-Sham (UKS) B-LYP (DFT) solution.[14-15] The reliability of the Equation (3) was already examined in the case of the triplet methylene dimer by using the CASSCF calculations in relation to the molecular design of organic ferromagnets. In order to confirm the previous AP UHF and DFT calculations of J_{ab} values for **1**, the computations of the total energies of the pure spin states are desirable.

(B) Calculation of J_{ab} by UNO CASCI and CASSCF

In order to examine the reliability of the spin multiplet splittings by the Heisenberg model, the J_{ab} values for the direct exchange coupling between the Cr(II) ions were calculated from total energies E(Z) by UNO CASCI and CASSCF methods as follows:

$$J_{ab}(1) = (E(S) - E(Q)) / 6 \quad (4a)$$
$$J_{ab}(2) = (E(T) - E(Q)) / 4 \quad (4b)$$
$$J_{ab}(3) = (E(S) - E(T)) / 2 \quad (4c)$$

where S, T and Q (= Z) denote, respectively, the singlet, triplet and quintet states as illustrated in Figure 3. From Figure 3, if these J_{ab} values are nearly equal, *i.e.*, $J \cong J_{ab}(1) \cong J_{ab}(2) \cong J_{ab}(3)$, the spin multiplet splittings should be close to those of the Heisenberg model. Tables III and IV summarize the $J_{ab}(1)$, $J_{ab}(2)$, and $J_{ab}(3)$ values obtained for **1** by CASCI and CASSCF {8, 8} methods. From Tables III and IV, the

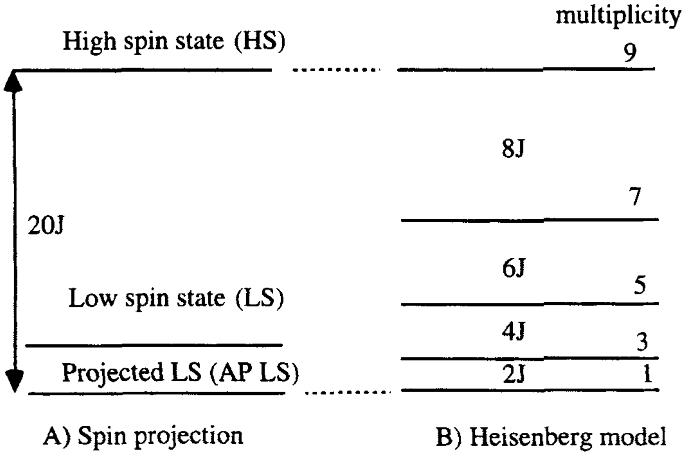

FIGURE 2 The energy diagrams used for the derivation of Equation (3) (see text).

following notices are available:

(1) All the $J_{ab}(n)$ values are negative in sign, being independent of the computational methods employed. The direct exchange interaction between Cr(II) ions is antiferromagnetic in accordance with the experimental results.

(2) The magnitudes of the $J_{ab}(n)$ (n = 1-3) values by UNO CASCI and CASSCF are almost equal to each other at each interatomic distance. Therefore, the UNO CASCI can be used as an alternative to CASSCF in order to calculate the $J_{ab}(n)$ (n = 1-3) values of relatively large systems.

(3) The absolute values of $J_{ab}(1)$, $J_{ab}(2)$, and $J_{ab}(3)$ at each geometry by UNO CASCI and CASSCF are similar to each other, indicating that the energy splittings coincide with those predicted by the Heisenberg model. Thus, the model proved reliable for **1**.

(4) The absolute $J_{ab}(1)$ value by UNO CASCI at each geometry is always larger than that of AP UHF, where the J_{ab} value is calculated by the energy difference between the HS (s = 4) and LS (s = 0) states as illustrated in Figure 2. This implies that the correlation correction for the UHF solution by the Møller-Plesset (MP) and/or coupled-cluster (CC) methods is required for the quantitative purpose.

(5) The absolute $J_{ab}(1)$ value by CASSCF at each geometry is not so different from that of AP DFT (UKS BLYP), although the AP DFT value is calculated by the energy difference between the HS (s = 4) and LS (s = 0) states. However, the DFT values are quite larger than the corresponding CASSCF values in the intermediate

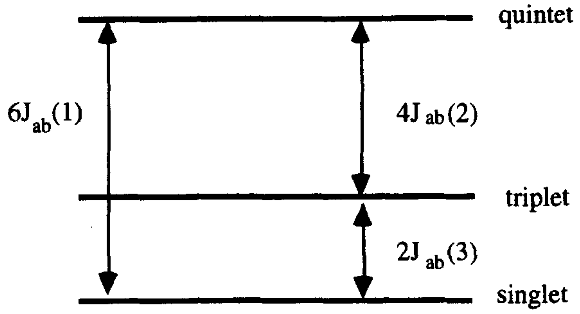

FIGURE 3 Energy diagrams used for the calculations of J_{ab} values by the UNO CASCI and CASSCF methods.

TABLE III $J_{ab}(n)$ (n=1-3) of **1** by UNO CASCI (BSI).

R(Å)	$J_{ab}(1)$	$J_{ab}(2)$	$J_{ab}(3)$	J_{ab}(AP UHF)
2.000	-805.9	-803.6	-810.5	-565.5
2.015	-752.3	-749.2	-758.3	-535.5
2.389	-156.2	-156.0	-156.7	-136.0
2.500	-100.5	-100.5	-100.5	-88.8
3.000	-13.00	-13.01	-13.00	-12.0

TABLE IV $J_{ab}(n)$ (n=1-3) of **1** by CASSCF (BSI).

R(Å)	$J_{ab}(1)$	$J_{ab}(2)$	$J_{ab}(3)$	J_{ab}(AP DFT)
2.000	-832.6	-824.1	-849.4	-891.4
2.015	-776.2	-767.4	-793.7	-850.2
2.389	-158.2	-157.1	-160.3	-279.5
2.500	-101.5-	-101.0	102.5	-202.8
3.000	-13.07	-13.02	-13.18	-7.4

region; $2.3 < R < 2.5$ Å. The same tendency was also obtained in the case of the DFT calculations of dimers of nitroxides.

The UNO CASCI calculations for **2** were carried out to calculate the J_{ab} values by using Equation 4. Table V summarizes the calculated J_{ab} (n = 1-3) values in addition to the corresponding UHF results.[1] From Table V, conclusions are as follows:

(1) The calculated $J_{ab}(n)$ (n = 1-3) values for **2** are largely negative in the region; R < 2.5 Å, showing that **2** is diamagnetic in nature.

(2) The absolute $J_{ab}(1)$, $J_{ab}(2)$ and $J_{ab}(3)$ values for **2** are quite different from each other in the region; R < 2.5 Å, in sharp contrast to those of **1**. The energy splittings among the singlet (S), triplet (T) and quintet (Q) states are quite different from those by the Heisenberg model.

(3) The absolute $J_{ab}(1)$, $J_{ab}(2)$ and $J_{ab}(3)$ values for **2** are almost equivalent in the region; R > 2.5 Å. The multiplet splittings become close to the Heisenberg type.

COMPARISONS BETWEEN THE THEORETICAL AND EXPERIMENTAL VALUES

The magnitude of the calculated J_{ab} values for **1** and **2** decreases with the increase of the interatomic distance (R) as shown in Tables III-V. The J_{ab} values could be fitted with the single exponential function,

$$J_{ab} = -p \exp(-qR), \tag{5}$$

where p and q are the fitting parameters. Figure 4 shows variations of the J_{ab} (1) value by CASSCF and J_{ab} values by UHF and DFT (BLYP) with R (Å). The experimental J_{ab} values for the binuclear Cr(II) complexes reported by Cotton *et al.*[16-17] were also shown in Figure 4. The calculated J_{ab} values for **1** decrease with R in an exponential manner. The experimental values by Cotton *et al.* coincide with this tendency, although the magnitude of the observed J_{ab} values are larger than the calculated ones, which were attributed to neglecting the contributions from ligands (L).

CONCLUDING REMARKS

Both the UNO CASCI and CASSCF methods are effective for the theoretical elucidation of the bonding properties of the direct exchange-coupled **1** and **2**. The energy splittings among the ground singlet, excited triplet, and quintet states for these species were also calculated by these methods. The calculated results are consistent with the experimental results.[16,17] The effective exchange interaction for the Cr(II)-Cr(II) system (**1**) is much weaker than that of Mo(II)-Mo(II) (**2**). The valence-bond (VB) like model such as the Heisenberg model fits to **1**, though it does not hold good for **2**.

TABLE V $J_{ab}(n)$ (n = 1-3) of **2** by UNO CASCI(BSII).

R(Å)	$J_{ab}(1)$	$J_{ab}(2)$	$J_{ab}(3)$	J_{ab}(APUHF)
2.0000	-5841.5	-7098.8	-3326.8	-3224.9
2.0981	-4425.1	-5375.5	-2524.3	-2444.2
2.1208	-4136.0	-5014.3	-2379.3	-2290.7
2.5000	-1097.5	-1156.2	-980.1	-737.8
3.0000	-147.2	-147.3	-146.8	-132.9
3.5000	-17.23	-17.24	-17.19	-17.21

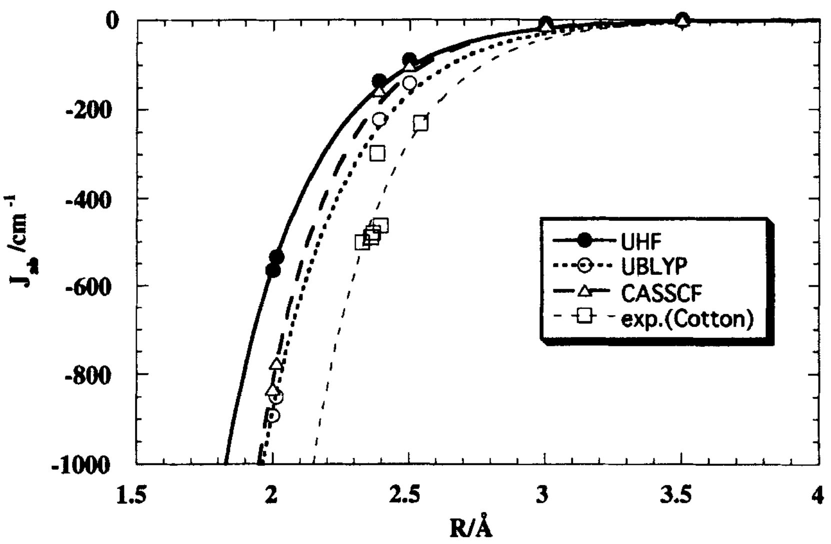

FIGURE 4 Variations of of the J_{ab} values obtained by the *ab initio* calculations and the experiments with the Cr(II)-Cr(II) distance (R).

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