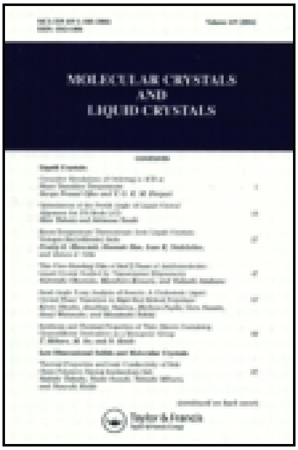

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Ab Initio mo Calculations of Superexchange Integrals For Transition-Metal Fluorides: MFM^{3+} (M=Cu(?), Ni(II) and Mn(II)). Active Control of the Magnetic States

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AB INITIO MO CALCULATIONS OF SUPEREXCHANGE INTEGRALS FOR TRANSITION-METAL FLUORIDES: MFM^{3+} (M=Cu(II), Ni(II) and Mn(II)). ACTIVE CONTROL OF THE MAGNETIC STATES

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Abstract Ab initio UMP calculations were carried out for binuclear transition-metal fluorides in order to elucidate variations of the superexchange integrals with intermetallic distances. It was shown that the antiferromagnetic superexchange integrals calculated for tricentric systems MFM^{+3} (M=divalent ions) by the approximately spin-projected UMPn (n= 1 - 4) method with the triple zeta basis set are about -134, -22 and -1 cm^{-1} in the cases of Cu(II), Ni(II) and Mn(II), respectively. These are consistent with the experimental results available. The hole-or electron doping into antiferromagnetic systems is also discussed in relation to previous proposals to obtain the switching type molecular magnets controlled by thermal, photochemical, electrochemical and other techniques.

INTRODUCTION

There have been many experimental and theoretical studies of copper oxides and related antiferromagnetic solids after the discovery of the high T_c superconductivity[1] in the hole or electron doped states of the former species. We have carried out ab initio unrestricted Hartree-Fock (UHF) calculations of several tricentric transition metal systems; M1-X-M2 (M1, M2=Cr, Mn, Fe, Co, Ni, Cu divalent ions; X= O^{2-}, F^- etc, for elucidation of the sign and magnitude of the indirect exchange coupings between transition-metal ions through anions X.[2-5] Computational results have indicated that the orbital symmetry rules[6] are applicable to qualitative explanations of the sign of the so-called superexchange integrals (J_{ab}) between M1 and M2. They were also elucidated possible organic analogs (π-R• systems)[3] for copper oxides and many other d-π electronic systems which are interesting from the spin fluctuation mechanism for the high-Tc superconductivity.[7,8] Very recently, the orbital symmetry rules were applied to molecular design of new types of ferromagnetic or ferrimagnetic polymers composed of heteropoly transition-metal tetrathiolates.[9,10]

The common features in the electronic states of the above species are of high sensitivity for various external parameters such as hole concentration, electronic field, photoexcitation, etc. We have already discussed possible variations of the electronic states induced by hole or electron doping into antiferromagnetic species.[2-5] However, previous computations[2-5] were limited to the unrestricted Hartree-Fock (UHF)-type and the Hubbard model. Apparently, more reliable computations are inevitable for further discussions of possible electronic states. Here, as a continuation of previous work,[2-5] the UHF Mϕller-Plesset perturbation (UMP) calculations of tricentric systems: MFM^{+3} (M=Cu(II), Ni(II) and Mn(II)) are performed in order to elucidate the effect of electron correlation correction on the sign and magnitude of J_{ab} values of these systems. Implications of the calculated results are discussed in relation to possible modifications of antiferromagnets into ferro-, ferri-, and other magnetic materials by electron or hole doping, photoexcitation, external mgnetic field etc.[2-5]

THEORETICAL CALCULATIONS

(A) Antiferromagnetic Orbital Interactions

First, let us consider the molecular structures of the clusters examined here. FIGURE 1 illustrates the two-dimensional antiferromagnetic sheet, which is involved in K_2CuF_3, K_2NiF_4etc. These systems are isoelectronic to La_2CuO_4, the precursor of the high T_c superconductor.[1] As previously,[2] we extracted the linear binuclear systems; MXM (M=Cu(II), Ni(II) and Mn(II)) as the model clusters.

The extended Hückel calculations were carried out for the Cu(II)-Cu(II) and Cu(II)FCu(II) systems in order to elucidate the orbital interaction schemes between Cu(II).[11] FIGURE 2 illustrates the orbital energy diagrams and related symmetry-adapted orbitals. This orbital picture is reliable if the energy gap between symmetric (S) and second antisymmetric (A_2) orbitals is sufficiently large. However, because of the near degeneracy between them , the orbital mixing occurs in the UHF approximation, giving the different-orbitals for different spins (DODS) as follows[11]

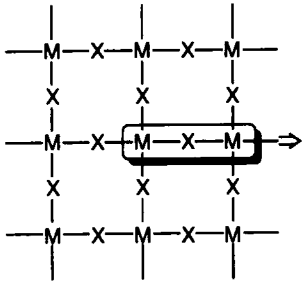
$$\psi\,(\text{up spin}) = \cos\theta\ \phi(S) + \sin\theta\ \phi(A_2) \qquad (1a)$$

$$\psi\,(\text{down spin}) = \cos\theta\ \phi(S) - \sin\theta\ \phi(A_2). \qquad (1b)$$

From FIGURE 2, the DODS MO are symmetry-broken and are essentially localized on the left and right transition metal ions, respectively. The singlet-coupled state of these magnetic DODS orbitals is responsible for the antiferromagnetically exchange-coupled state of the Cu(II) ion at the zero-temperature.[2-5]

(B) Effective Exchange Integrals

The magnetic orbitals have tails on the central fluoride anion, which is responsible for the superexchange interaction. The effective exchange interactions (J_{ab}) between



K_2CuF_3, K_2NiF_4, K_2MnF_4, La_2CuO_4

Model Extraction	magnetic active orbitals
$Cu(II)^{2+}$-F^--$Cu(II)^{2+}$	d_{x2-y2}
$Ni(II)^{2+}$-F^--$Ni(II)^{2+}$	d_{x2-y2}, d_{xy}
$Mn(II)^{2+}$-F^--$Mn(II)^{2+}$	d_{all}

FIGURE 1. 2-D antiferromagnetic planes and the model clusters

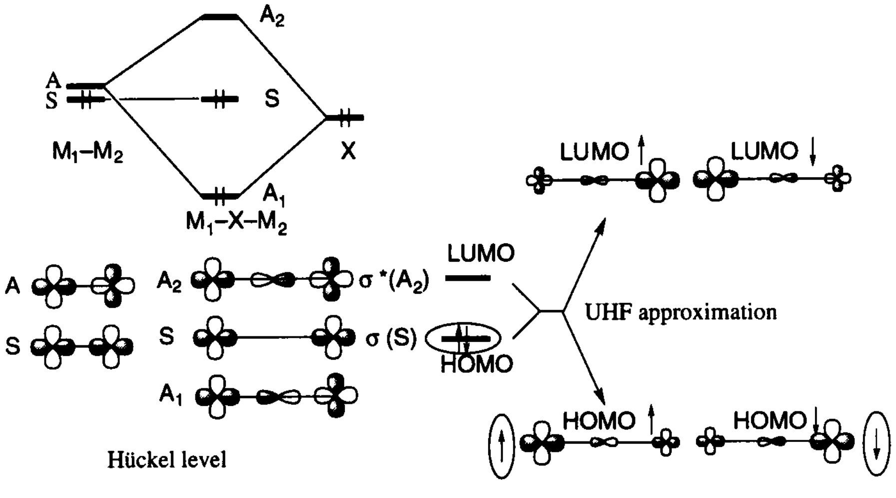


FIGURE 2. Orbital interaction diagrams in the Cu(II)-Cu(II) and Cu(II)FCu(II) systems at the spin restricted and unrestricted levels.

the magnetic orbitals can be described by the Heisenberg model. The J_{ab} values were easily calculated by the approximate spin-projected UMP (APUMP) scheme obtained by the combination of the UMP method and Heisenberg model (HB) as shown previously[11,12]

$$J_{ab}(APUMPn)=\frac{{}^{HS}E_{UMPn}-{}^{LS}E_{UMPn}}{{}^{HS}<S^2>_{UMPn}-{}^{LS}<S^2>_{UMPn}} \tag{2}$$

where ${}^{X}E_{UMPn}$ and ${}^{X}<S^2>_{UMPn}$ denote, respectively, the total energy and total angular momentum for the spin state X by the UMPn method.

The Eq. (2) was applied to calculations of J_{ab} values for binuclear systems; MFM^{3+} (M=Cu(II), Ni(II) and Mn(II)) by the use of the Tatewaki-Hujinaga[13] MIDI plus Hays' diffuse d-basis sets: (533(21)/53(21)/411) for transition metal ions and MIDI plus diffuse sp-orbitals for fluoride anion.[2-5,11] The functional behaviors of the calculated J_{ab} values with respect to the M-F distance were similar in the three different systems examined here. As an example, FIGURE 3 illustrates variations of the J_{ab} values calculated for Cu(II)-F-Cu(II)$^{3+}$ by changing the copper-fluroride distance R(X-F).

From FIGURE 3 and the abbreviated FIGURES, the following conclusions are drawn:

(1) The J_{ab} values calculated MFM^{3+} (M=Cu(II), Ni(II) and Mn(II)) are negative (antiferromagnetic) by all the computational methods employed.

(2) The magnitude of the J_{ab} values by APUMPn (n=1 - 4) decrease with the increase of R(X-F) in an exponential manner.

(3) The magnitude of the J_{ab} values are sensitive to the correlation corrections.

(C) Potential Curves

The total energies of MFM^{+3} (M=Cu(II), Ni(II) and Mn(II) were calculated by the APUMPn method using the aforementioned triple-zeta basis set. The functional behaviors of the potential curves with respect to the M-F distance were similar in the three different systems. As an example, FIGURE 4 illustrates the potential curves obtained for Ni(II)-F-Ni(II) by APUMPn (n=1 - 4) changing the Ni(II)-F distance. From FIGURE 4 and the abbreviated FIGURES, the shapes of the potential curves are not so different among the levels of the correlation corrections by APUMPn. However, the optimum M(II)-F distances become slightly longer with the increase of the perturbation corrections, but they are about 1.9 Å at the APUMP4 level.

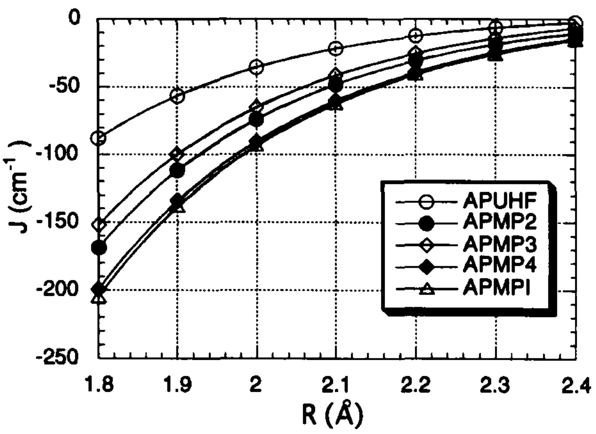


FIGURE 3. Jab values for Cu(II)FCu(II) with the intermetallic distances

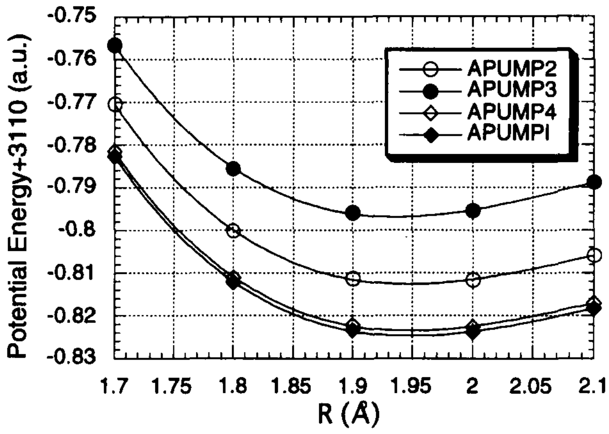


FIGURE 4 Potential curves calculated for Ni(II)FNi(II) by the APUMPn method.

RESULTS AND DISCUSSIONS

(A) Superexchange Integrals

The superexchange integrals (J_{ab}) in K_2CuF_3, K_2NiF_4 solids have been determined by several experimental techniques.[14] Therefore, we here compare the calculated J_{ab} values with the experimental ones. TABLE I summarizes the J_{ab} values calculated at the optimized M(II)-F distances by APUMPn (n=1-4).

From TABLE I, the following conclusions are drawn:

(1) The optimum J_{ab} values by APUHF are -56, -12 and -1 cm^{-1}, respectively, for Cu(II), Ni(II) and Mn(II) (=M) in the MFM^{+3} system.

(2) The optimum J_{ab} values by APUMP4 are -134 and -22 cm^{-1}, respectively, for Cu(II) and Ni(II) (=M) in the MFM^{+3} system.

(3) The calculated values by APUMP4 are consistent with the experimental values available:[14] -132, -36 and -3 cm^{-1} for K_2CuF_3, K_2NiF_4 and K_2MnF_4, respectively.[14] This implies that the cluster model is reliable for computations of the J_{ab} values.[2-5]

The above conclusions (1)-(3) supported previous calculated results on the basis of the UHF calculations.[2-5] This in turn indicates that previous theoretical proposals[2-5,10] for new d-π systems and organic analogs to copper oxides are still reasonable after the correlation corrections by the MPn method as described below.

(B) Control of Magnetic Properties by External Fields

Recently we have discussed possibilities of active controls of electronic of properties molecule-based magnetic materials by external fields in relation

TABLE I. Comparison between the observed and calsulated effective exchange integrals[a)] for transition-metal halides.

structure[b)]	Jab	Jobs
$Cu^{+2}F^{-1}Cu^{+2}(K_2CuF_3)$	-56(APU) -111(APUMP2) -99(APUMP3) -134(APUMP4) -138(APUMPI)	-132
$Ni^{+2}F^{-1}Ni^{+2}(K_2NiF_4)$	-12(APU) -20(APUMP2) -19(APUMP3) -22(APUMP4) -23(APUMPI)	-36
$Mn^{+2}F^{-1}Mn^{+2}(K_2MnF_4)$	-0.9(APU)	-2.9

a) cm^{-1},b) corresponding solids are given in parenthes.

to their potential applications to advanced technologies.[2-5,10,15-20] Concernig with these applications, there are several reasons why antiferromagnetic solids such as K_2CuF_3 and La_2CuO_4 are interesting and important:

(1) Electronic structures of these species are often sensitive to external variables (doping of hole or electron, pressure, temperature,[9] external electronic and magnetic fields, photoexcitation etc) and the variations with such parameters are nonlinear in many cases as illustrated in FIGURE 5.

(2) Control of magnetic and opt-magnetic[21] properties with the above variables are key issue for molecule-based magnetic materials.

FIGURE 5 illustlates the bistability expected in several natural and artificial magnetic systems.[15] The bistability is indeed crucial in relation to active controls (or switching) of electronic,[2-5] magnetic[15-19] and optical[21] properties of molecule-based materials in general. It is also crucial for constructions of electronic devices, biomimenic systems[9] etc.

In order to obtain new magnetic materials, we have examined doping of electron or hole into antiferromagnetic solids[2-5], electron-transfers between high-spin molecules and spacers induced by the external variables,[15-19] spin crossover between the high- and low-spins by the external magnetic fields[20] as illustrated in FIGURE 6.

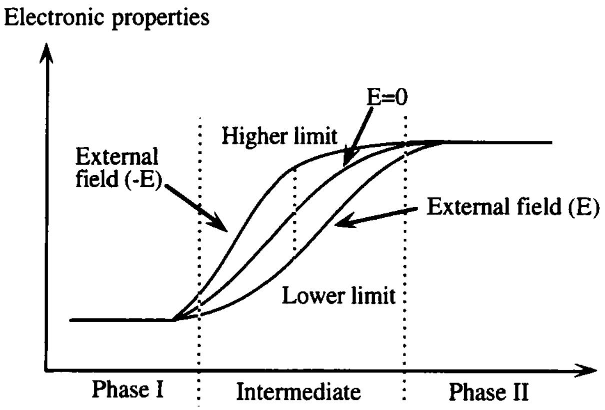


FIGURE 5. Control of electronic, magnetic, and optical properties of molecule-based materials by external parameters (see text). Switchings by external fields are feasible in the intermediate regime generated by several techniques.

From FIGURE 6, the following notices are available:

(A) The antifrromagnetic insulator may be converted into ferrimagnetic insulator or metal by oxidation (or reduction) of transition-metal ions by several techniques.[2-5, 10]

(B) The antifrromagnetic insulator may be converted into ferrimagnetic insulator or metal by charge transfer between transition-metal ions by several techniques.[5,16-19]

(C) The antifrromagnetic spin coupling may be converted into ferromagnetic spin coupling by hole doping at anionic site X by several techniques.[2-5,9,10]

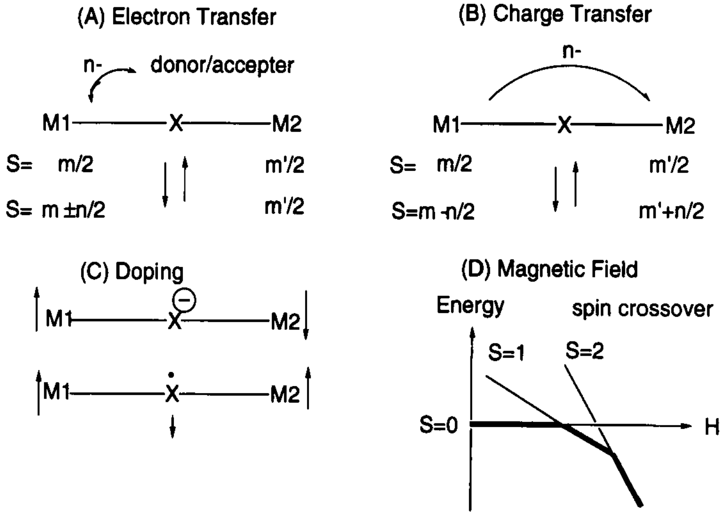


FIGURE 6 Switchings of the spin states and spin alignments by several techniques

(D) The spin crossover (spin flop) between the low- and high-spin states may be induced by the external magnetic field.[20,22]

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