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REGULAR ARTICLE

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The double exchange phenomenon revisited: the $[Re_2OCl_{10}]^{3-}$ compound

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Abstract Correlated ab initio calculations have been performed on the $[Re_2OCl_{10}]^{3-}$ anion. The calculated spectrum does not respect the intervals given by the usually accepted double exchange Hamiltonian. Surprisingly enough the ground-state happens to be of intermediate spin multiplicity (i.e. a quartet) at any level of correlation treatment. A model that combines the Anderson and Hasegawa method and the usually used double exchange one rationalizes the spectrum calculated both by a configuration interaction restricted to the open shell molecular orbitals and at a more correlated level of calculation. An alternative analysis of the double exchange phenomenon, based on a molecular orbital language, is presented. The specific effects of the electronic correlation brought by extended active space and by a difference dedicated configuration interaction are also analyzed.

1 Introduction

The mechanism of double exchange (DE) takes place in mixed valence compounds involving at least two metallic centers having several open shells. The delocalization of the extra electron between the metallic centers that bear these open shells induces a ferromagnetic order. This phenomenon has attracted the interest of physicists and chemists in many different fields. While the DE phenomenon has first been introduced by solid state physicists [1,2], it has then been extensively studied by chemists [3–17]. A number of these DE compounds are also the active centers of ferredoxins and enzymes where they have been found of fundamental importance for their mechanisms of action [18–24].

The magnetic properties of DE-mixed valence clusters are generally rationalized using the model Hamiltonian proposed by Zener [1]. Among these clusters, the homonuclear bimetallic DE compounds (d^n and d^{n+1}) have been investigated in detail (see articles [13,25,26] and references therein). The double exchange interaction doubles the number of spin levels (of total spin S) which are splitted into one symmetric and one antisymmetric spin states ($E(S,\pm)$). Energies of these different states are given by the expression:

$$E(S,\pm) = \pm\frac{t}{S_m + 1/2}(S+\frac{1}{2}) - \frac{J}{2}[S(S+1) - S_m(S_m+1)] \tag{1}$$

where + and − refer to the highest and lowest roots, respectively, of the same spin manifold and S_m is the highest total spin. The second term of Eq. (1) is given by the usual Heisenberg Hamiltonian and includes the exchange isotropic constant J. For an overall antiferromagnetic contribution ($J < 0$), this term lowers the mean energy of the low and intermediate spin states compared to the highest ones. The first term describes the extra electron delocalization between the d^n and d^{n+1} ions and is therefore related to the hopping integral t between the two orbitals sharing this electron. This term is responsible for the stabilization of one of the highest spin states compared to the lowest ones and accounts for the appearance of a high spin ground-state even if the electronic interactions which determine J result in an overall antiferromagnetic contribution ($J < 0$).

Experimentally, in the most favorable cases, it is possible to observe electronic absorption transitions between two states of the same spin multiplicity and hence to determine the parameter B. However, since most of the time one can only measure the energy difference between the ground-state and a few of the low-lying excited states, a direct confrontation of the model with experimental evidence is generally not possible. In recent works, on the $[Ni_2(napy)_4Br_2]^+$ system [27] and on the $[Fe_2(OH)_3(NH_3)_6]^{2+}$ complex [28,29] and in the model case of a lengthened N_2^+ cation [30], it has been pointed out that the calculated spectrum is not rationalizable using the usual double exchange Hamiltonian.

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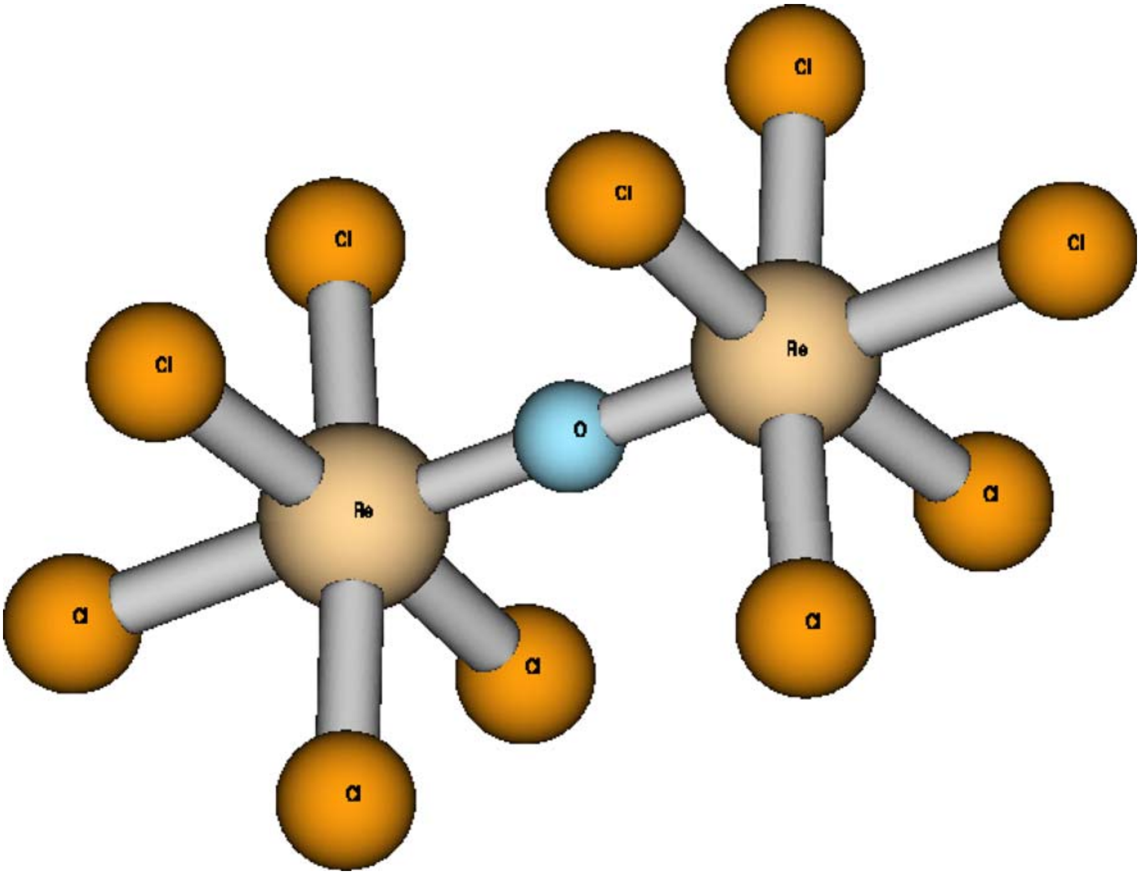

Fig. 1 Schematic view of the $[Re_2OCl_{10}]^{3-}$

It has been shown that an excited local (atomic) state, namely a non-Hund state, plays a crucial role in the stabilization of the low spin states. This non-Hund state is the only antiferromagnetic contribution of the Anderson Hasegawa model. On the contrary it is neglected in the usual DE model in which the antiferromagnetism is attributable to the Heisenberg spin exchange interaction (i.e. to the valence bond (VB) forms in which the atom-centered orbitals are doubly occupied).

The present paper reports a theoretical study of the $[Re_2OCl_{10}]^{3-}$ complex (see Fig. 1). The magnetic moment of this complex is $3.57\mu_B$ at 293 K [31], a moment which would be consistent with an $S = 3/2$ spin ground state. Since this mixed valence compound presents a double exchange phenomenon, one can think that the antiferromagnetic contributions should be very large in order to stabilize a quartet ground state instead of the expected sextet one. This complex is therefore a good candidate in order to quantify the various contributions to antiferromagnetism, namely the usual exchange integral versus the non-Hund atomic states. This study will show that:

(1) the spectrum strongly deviates from the one predicted by the usual model Hamiltonian,
(2) a model already tested in reference [27] and [30] that combines the usual DE model and the Anderson and Hasegawa model reproduces perfectly the calculated spectrum. The leading parameters of this model will be extracted.
(3) surprisingly enough the ground-state is of intermediate spin multiplicity, and this unusual feature is compatible with the proposed modelization.
(4) the oxygen bridge is responsible for both the extra electron transfer and the spin exchange between the unpaired electrons of the two Re atoms.
(5) finally, an unusual approach based on a MO language will be presented, and the role of the non-dynamical and dynamical correlation will be analyzed within this MO picture.

Section 2 gives the spectrum calculated at different levels of correlation and compares it to the predictions of the usual model Hamiltonian.

Section 3 recalls the derivation of the extended model and shows its relevance to interpret the calculated energy spacings.

Section 4 focuses on the discussion of the effect of non-dynamical and dynamical correlation (outside of the minimal active space) on the spectrum.

2 Calculated spectrum of the $[Re_2OCl_{10}]^{3-}$ complex

2.1 Computational details

The complex anion is of D_{4h} symmetry (see Fig. 1). The geometry has been taken from reference [32]. The Re atoms are not located in the Cl planes. The small deviation results in a bond angle O–Re–Cl(*cis*) of 92.7°. The Re–Cl distances are: Re–Cl(*cis*) $= 2.349$ Å and Re–Cl(*trans*) $= 2.379$ Å. Since the ponctual symmetry group D_{4h} was not available in the programs used here, the D_{2h} symmetry has been imposed in the calculations, and the irreducible representations that will be mentionned in this paper will always refer to that symmetry subgroup. Finally let us specify that the Z axis is the intermetallic axis and that X and Y are taken so that they belong to the planes defined by two Cl(*cis*) atoms and the bridging oxygen. Relatisvistic core ab initio model potentials (AIMP) including 62 electrons and the corresponding optimized basis set [33,34] ($3s3p3d1f$ contraction) have been used for the Re atoms. For the O and Cl atoms the following AIMP and corresponding basis sets [35] contractions were used: for O, AIMP (2 electrons) and the corresponding $5s6p1d$ basis set contracted in $2s3p1d$, for Cl, AIMP (10 electrons) and the corresponding $7s7p1d$ basis set contracted in $2s2p1d$.

Calculations have been performed using the MOLCAS package [36] and the CASDI package [37] for the configuration interaction (CI) steps. The computational procedure follows a strategy that has widely been used for the treatment of magnetic systems and is known to provide reliable results [38–40].

As discussed in the next subsections, two types of complete active spaces (CAS) will be considered. The first one, the CAS(5,6), is minimal, it concerns five electrons in six orbitals essentially localized on the Re atoms, and is supposed to contain the essential physics. Then an enlarged CAS(9,8) adds four electrons and the π_u^X and π_u^Y orbitals which are essentially the p_x and p_y orbitals of the oxygen bridge.

The orbitals are optimized for the lowest sextet state at the minimal CAS + single excitations level in an iterative procedure that diagonalizes the density matrix and provides quasi-natural orbitals [41,42]. Then one performs difference dedicated configuration interaction (DDCI) calculations [43] for the lowest states of different spin and space symmetries. The DDCI2 version implies all the singly excited determinants and all the doubles on all the references having up to two inactive occupied orbitals (two holes) or two virtual orbitals (two particles). Some calculations have been performed using the more computationally expensive DDCI3 version in which the two holes and one particule as well as the two particules and one hole excitation processes are added to the previous ones. Most of the here-reported results have been obtained using the enlarged CAS+DDCI2 method where the active space includes the bridging ligand orbitals. It has been shown in previous papers that these results are of the same quality than those obtained at the minimal CAS+DDCI3 level [44,45] or even better when the bridging ligands play an important role in the wavefunction (as it is the case here).

2.2 Confrontation of the DE usual model with the calculated spectrum

Each metallic center is in a slightly distorted octahedric environment, and the rhenium atoms are formally Re(IV) and Re(V), i.e. present d^3 and d^2 configurations, respectively; in the first one, the three t_{2g}-like orbitals are singly occupied while in the second one, there is a hole in one of them. This complex is symmetric due to the strong interaction between the two metallic centers. This interaction goes through the bridging O atom and a monoelectronic picture can easily be provided by explicitly considering the interaction between two $ReCl_5$ subsystems and the orbitals of that oxygen (as shown is Scheme 1). The interaction between the two subsystems $ReCl_5$ leads to four orbitals (of b_{2g}, b_{3g} and b_{3u}, b_{2u} irreducible representations in the D_{2h} symmetry point group) exhibiting a π overlap. These orbitals are essentially built from the d_{xz} and d_{yz} atomic orbitals. Four orbitals (two b_{1g} and two a_u) presenting a δ overlap can be obtained from the d_{xy} atomic orbitals while two other δ-like orbitals of a_g and b_{1u} symmetry result from the $d_{x^2-y^2}$ atomic orbitals interaction. Finally two other orbitals of a_g and b_{1u} symmetries are combinations of the d_{z^2} atomic orbitals and present a σ overlap. Since, the nature of these overlaps partially explains the electronic structure of the complex, let us use the σ, π and δ designation when referring to these orbitals.

The antibonding interaction with the low-lying doubly occupied orbitals localized on the bridging oxygen atom is responsible for the large destabilization of both the π_u orbitals and the σ_g and σ_u orbitals. The final orbital energy ordering, that has first been proposed by Campbell and Clark [46], is the following:

$$\begin{aligned}\pi_g^X(d_{xz}) = \pi_g^Y(d_{yz}) &< \delta_g^{xy}(d_{xy}) \\ &< \delta_u^{xy} < \pi_u^X(d_{xz}) = \pi_u^Y(d_{yz}) \\ \pi_u^X(d_{xz}) = \pi_u^Y(d_{yz}) & \\ &< \sigma_g(d_{z^2});\, \delta_g(d_{x^2-y^2});\, \delta_u(d_{x^2-y^2});\, \sigma_u(d_{z^2})\end{aligned}$$

In order to check this energetic order of the molecular orbitals (MO), we have performed calculations on the sextet states (which are the only spin multiplicity states that can reasonably be described within a single-determinantal description) of different space symmetry, i.e. with a different MO filling. Assuming this energetic order, one obtains two degenerate sextet states ${}^6B_{2g}$ and ${}^6B_{3g}$ in the D_{2h} symmetry subgroup. The corresponding single-determinantal wavefunctions are:

$$^6B_{2g} = |\mathrm{core}.\pi_g^X\pi_g^Y\delta_g^{XY}\delta_u^{XY}\pi_u^Y| \tag{2}$$

$$^6B_{3g} = |\mathrm{core}.\pi_g^X\pi_g^Y\delta_g^{XY}\delta_u^{XY}\pi_u^X| \tag{3}$$

The ${}^6B_{1g}$ state in which both the π_u^X and π_u^Y orbitals are occupied (one of the δ orbitals is empty) lies 2.1 eV above the degenerate ${}^6B_{2g}$ and ${}^6B_{3g}$ states. This result confirms

Table 1 CAS(5,6)CI, CAS(5,6)+DDCI2, CAS(5,6)+DDCI3 and CAS(9,8)+DDCI2 energy spacings in cm^{-1} taking the mean energy of the sextet states as zero of energy

	CAS(5,6)CI	CAS(5,6)DDCI2	CAS(5,6)DDCI3	CAS(9,8)DDCI2
$E(S_g)$	−9737	−7972	−8167	−8239
$E(S_u)$	9737	7972	8167	8239
$E(Q_g)$	−2115	−908	–	−1203
$E(Q_u)$	−11068	−10340	–	−11362
$E(D_g)$	−10345	−9691	–	−10646
$E(D_u)$	−6496	−5770	–	−6572

that the π_u orbitals are higher in energy than the δ orbitals. Another SCF calculation in which the σ_g orbital is occupied and the π_u ones are empty has been performed in order to verify the relative positions of these orbitals. The energy of the corresponding ${}^6A_u$ state is 6.06 eV above the ${}^6B_{2g}$ and ${}^6B_{3g}$, showing that the σ_g orbital is higher in energy than the π_u orbitals. These results are consistent with the proposed energetic ordering of the orbitals in the sextet states, at least for those orbitals that will play a crucial role in the electronic structure of the low energy states. Moreover, these results show that the σ orbitals are high in energy and can therefore be removed from the list of active orbitals. Their low occupation at higher correlated level of calculations confirms this assertion.

Other spin states cannot be described using a single determinant; hence CASCI calculations will be performed using these six active orbitals filled by five electrons (i.e. CAS(5,6)). As well as for the sextet states, all couples of states generated by the same active space, in each spin $S = 1/2$, $S = 3/2$ and $S = 5/2$ subspaces are degenerate. There are two spacially degenerate families of states according to the orbital where the extra electron is delocalized. For the sake of simplicity, we shall only consider the one where the extra electron is delocalized between the d_{yz} atomic orbitals, i.e. where the π_g^Y and π_u^Y orbitals share the extra electron. The full discussion that follows would be applicable to the family of states where the extra electron is delocalized between the d_{xz} atomic orbitals. The hopping between the two d_{yz} atomic orbitals will generate subsets of states of *g* and *u* symmetries which, respectively, belong to the B_{3g} and B_{2u} symmetries.

Calculations of the ground state and the five first excited states (in the considered symmetries) have been performed. The ground state is a quartet state of B_{2u} symmetry consistent with the magnetic properties of $[\mathrm{Re_2OX_{10}}]^{n-}$ anion proposed in references [32,46,47]. The confrontation of the usual DE model with the computed energy spacings has been performed using the spectra computed at various levels of correlation treatment. Table 1 reports the corresponding energy spacings taking the mean energy of the sextet states as zero of energy. Although it was not possible to perform calculations at the minimal CAS+DDCI3 level of correlation for the complete spectrum, the energy of the sextet states (the determination of which requires less determinants) has been computed in order to validate the use of the enlarged CAS+DDCI2 method. As can be seen in Table 1, the computed energy differences between the sextet states compare very well.

Table 2 Parameters *t* and *J* in cm^{-1} obtained using Eqs. (4), (5), (6), (7) and (8) at the CAS(5,6), CAS(5,6)+DDCI2 and CAS(9,8)+DDCI2 levels of correlation

	t_S	t_Q	t_D	J_Q	J_D
CAS(5,6)CI	9737	6715	5774	−2637	−2105
CAS(5,6)+DDCI2	7972	7074	5882	−2250	−1933
CAS(9,8)+DDCI2	8239	7068	6111	−2513	−2152

From the spectrum, we can extract the two basic parameters of the double exchange model Hamiltonian. From the energy difference between the mean value of the sextet states and that of the quartet ones, one can extract the first value of J, denoted as J_Q

$$\frac{E(S_g)+E(S_u)}{2} - \frac{E(Q_g)+E(Q_u)}{2} = \frac{-5J_Q}{2} \tag{4}$$

where *S* and *Q* respectively, stand for sextet and quartet. Similarly, we can extract another value of *J* from the sextet and the doublet states (labeled *D*), let us call it J_D

$$\frac{E(S_g)+E(S_u)}{2} - \frac{E(D_g)+E(D_u)}{2} = \frac{-8J_D}{2} \tag{5}$$

The two calculated values, given in Table 2, differ by 20%. Various estimations of *t*, also given in Table 2, are calculated from the energy differences between states of the same spin multiplicity:

$$E(S_g) - E(S_u) = 2t_S \tag{6}$$

$$E(Q_g) - E(Q_u) = \frac{-4t_Q}{3} \tag{7}$$

$$E(D_g) - E(D_u) = \frac{2t_D}{3} \tag{8}$$

Even if one may consider the deviations between the two estimates of *J* to be acceptable, the discrepancies on the *t* values (around 30% of difference) invalidate the relevance of the usual model Hamiltonian. Such a discrepancy already appeared in the $[\mathrm{Ni_2(napy)_4Br_2}]^+$ system [27]. One can also notice that the discrepancy is somewhat smaller in the correlated calculations. However, model Hamiltonians are simplifications of the CASCI descriptions and should at least reproduce CASCI calculations correctly.

3 A refined model that combines the usual double exchange model and the Anderson Hasegawa model

The derivation of the combined model applied to a case of three open shells per metallic center has been detailed in a model case of double exchange on the N_2^+ molecule [30]. Let us just recall it briefly.

The analysis is performed in terms of atom-centered orbitals. These orbitals are linear combinations of the active g and u orbitals of a given symmetry. From the active orbitals π_g^Y and π_u^Y, essentially built from the d_{yz} orbitals, one may define atom-centered equivalent orbitals of d_{yz} character as

$$a_1 = \frac{\pi_g^Y + \pi_u^Y}{\sqrt{2}} \tag{9}$$

$$a_2 = \frac{\pi_g^Y - \pi_u^Y}{\sqrt{2}} \tag{10}$$

Similarly atom-centered orbitals having a d_{xz} character are given by

$$b_1 = \frac{\pi_g^X + \pi_u^X}{\sqrt{2}} \tag{11}$$

$$b_2 = \frac{\pi_g^X - \pi_u^X}{\sqrt{2}} \tag{12}$$

and the atom-centered orbitals having a d_{xy} character are

$$c_1 = \frac{\delta_g^{XY} + \delta_u^{XY}}{\sqrt{2}} \tag{13}$$

$$c_2 = \frac{\delta_g^{XY} - \delta_u^{XY}}{\sqrt{2}} \tag{14}$$

Let us concentrate on the family of states where the extra electron is delocalized between the d_{yz} atom-centered orbitals, while two electrons are located in the two d_{xz} and two electrons in the d_{xy} atomic orbitals.

The model space on which the zero-order DE Hamiltonian is developed is a restriction of the CAS to the neutral VB determinants (i.e. the $\mathrm{Re}(d^3)\mathrm{Re}(d^2)$ forms) having at most one electron per orbital. Then, among these determinants only those combinations which are products of atomic ground states are kept in the usual model. Since the combined model considered here also considers some of the excited atomic states, let us introduce both the ground and the first excited states of the two Re($d3$) and $\mathrm{Re}(d^2)$ atoms.

The ground state of the atom that does not bear the extra electron (for instance the atom 2) is a triplet according to Hund's rule. Its three S_z components are labeled T_2^-, T_2^0 and T_2^+ where the index 2 refers to the atom 2. Its first excited state is a singlet S_2^0. The space part of these states is a product b_2c_2 of $d_{xz}d_{xy}$ character.

$$T_2^- = |\mathrm{core}.\bar{b}_2\bar{c}_2| \tag{15}$$

$$T_2^0 = |\mathrm{core}.\frac{b_2\bar{c}_2 + \bar{b}_2c_2}{\sqrt{2}}| \tag{16}$$

$$T_2^+ = |\mathrm{core}.b_2c_2| \tag{17}$$

$$S_2^0 = |\mathrm{core}.\frac{b_2\bar{c}_2 - \bar{b}_2c_2}{\sqrt{2}}| \tag{18}$$

The other center (namely 1) bears three electrons and has a quartet ground-state in which the three electrons occupy the three a_1, b_1 and c_1 orbitals. The four corresponding S_z components are labeled $Q_1^{-3/2}$, $Q_1^{-1/2}$, $Q_1^{+1/2}$ and $Q_1^{+3/2}$

$$Q_1^{-3/2} = |\mathrm{core}.\bar{a}_1\bar{b}_1\bar{c}_1| \tag{19}$$

$$Q_1^{-1/2} = |\mathrm{core}.\frac{(\bar{a}_1\bar{b}_1c_1 + a_1\bar{b}_1\bar{c}_1 + \bar{a}_1b_1\bar{c}_1}{\sqrt{3}}| \tag{20}$$

$$Q_1^{+1/2} = |\mathrm{core}.\frac{\bar{a}_1b_1c_1 + a_1\bar{b}_1c_1 + a_1b_1\bar{c}_1}{\sqrt{3}}| \tag{21}$$

$$Q_1^{+3/2} = |\mathrm{core}.a_1b_1c_1| \tag{22}$$

The first excited states of atom 1 are the following ${}_1D_1^{1/2}$ and ${}_2D_1^{1/2}$ doublets

$${}_1D_1^{1/2} = |\mathrm{core}.\frac{a_1b_1\bar{c}_1 - a_1\bar{b}_1c_1}{\sqrt{2}}| \tag{23}$$

$${}_2D_1^{1/2} = |\mathrm{core}.\frac{2\bar{a}_1b_1c_1 - a_1b_1\bar{c}_1 - a_1\bar{b}_1c_1}{\sqrt{6}}| \tag{24}$$

When only considering the atomic ground state in the model space, (i.e. in the usual Zener DE Hamiltonian), one obtains six eigenstates in the $S_z = 1/2$ subspace: a sextet S_g, a quartet Q_g and a doublet D_g of B_{3g} symmetry and a sextet S_u, a quartet Q_u and a doublet D_u of B_{2u} symmetry. By taking into account only the monoelectronic hopping integral $t_{a_1a_2} = t$, their respective energies are:

$$E(D_g) = \frac{-t}{3} \tag{25}$$

$$E(Q_g) = \frac{2t}{3} \tag{26}$$

$$E(S_g) = -t \tag{27}$$

$$E(D_u) = \frac{t}{3} \tag{28}$$

$$E(Q_u) = \frac{-2t}{3} \tag{29}$$

$$E(S_u) = t \tag{30}$$

As already shown in papers [27,30] and also considered by Anderson and Hasegawa [2], other products of neutral VB states basically involving the same determinants directly interact with the Zener model space. These functions are product of the ground state of one Re atom by one of the two first excited non-Hund states of the other Re atom. Due to large interactions between the Zener model space and symmetry adapted combinations of the ${}_2D^{1/2}$ atomic non-Hund state, a variational treatment is recommended [15]. The refined spectrum of the six variationally calculated eigenstates S_g^{var}, S_u^{var}, Q_g^{var}, Q_u^{var}, D_g^{var} and D_u^{var} of the $S_z = 1/2$ subspace presents different energy spacing. If one calls ΔE the excitation energy from the atomic quartet ground state to the atomic non-Hund doublet state, the energy of these eigenstates are given by

$$E(D_g^{\text{var}}) = \frac{\Delta E - \sqrt{\Delta E^2 + 4t(t + \Delta E/3)}}{2} \tag{31}$$

$$E(D_u^{\text{var}}) = \frac{\Delta E - \sqrt{\Delta E^2 + 4t(t - \Delta E/3)}}{2} \tag{32}$$

$$E(Q_g^{\text{var}}) = \frac{\Delta E - \sqrt{\Delta E^2 + 4t(t - 2\Delta E/3)}}{2} \tag{33}$$

$$E(Q_u^{\text{var}}) = \frac{\Delta E - \sqrt{\Delta E^2 + 4t(t + 2\Delta E/3)}}{2} \tag{34}$$

Let us notice that in cases where $\Delta E < 2t$, a simple perturbative treatment of the atomic non-Hund states would be valid.

In the studied complexes, the orbitals that are responsible for the electron transfer are of π symmetry. Concerning the spin exchange, the two other π symmetry orbitals are also involved. We can therefore anticipate that due to the large effective transfer integrals (that goes through the oxygen $2p$ orbitals) in this symmetry, the effect of the spin coupling between the electrons occupying the orbitals b_1 and b_2 must be taken into account. The contribution of the c_1 and c_2 orbitals is probably less important (the corresponding δ overlap being very small) but can also be considered in an overall antiferromagnetic spin exchange integral. Each couple of electrons (in the π and δ orbitals) contributes to the antiferromagnetism by two different quantities. The first contribution is coming from the neutral VB determinants involving a doubly occupied b_1 or b_2 (respectively c_1 or c_2) such as $|\text{core}.a_1c_1b_2\bar{b}_2\bar{c}_2|$ (respectively $|\text{core}.a_1b_1\bar{b}_2c_2\bar{c}_2|$). The second contribution is coming from singly ionic VB determinants of $\text{Re}(d^1)\text{Re}(d^4)$ nature such as $|\text{core}.a_1b_1\bar{b}_1c_1\bar{c}_2|$ which are higher in energy than the previous neutral ones. It is possible to consider a single global antiferromagnetic coupling J ($J < 0$) that takes into account all these contributions perturbatively. Its effect on the spectrum results in the following Heisenberg energy lowerings:

$$\delta E_S = 0 \tag{35}$$

$$\delta E_Q = \frac{5}{2}J \tag{36}$$

$$\delta E_D = 4J \tag{37}$$

In order to see wether this model describes correctly the calculated spectrum, the three parameters t, ΔE and J appearing in the combined model have been optimized. Of course the number of equations (6) is higher than the number of parameters, and one can appreciate the reliability of both the model and the extracted parameters by recalculating the final energies of the six states from the expressions:

$$E(S_g^F) = t \tag{38}$$

$$E(S_u^F) = -t \tag{39}$$

$$E(Q_g^F) = \frac{\Delta E - \sqrt{\Delta E^2 + 4t(t - 2\Delta E/3)}}{2} - \frac{5}{2}J \tag{40}$$

Table 3 Parameters of the variational model in cm^{-1} and percentage of error in energy on the full spectrum

	t	J	Δ	%error
CASCI	9737	−1007	15523	1.1
CAS(5,6)DDCI2	7972	−1293	19433	1.6
CAS(9,8)DDCI2	8239	−1533	21296	2.0

$$E(Q_u^F) = \frac{\Delta E - \sqrt{\Delta E^2 + 4t(t + 2\Delta E/3)}}{2} - \frac{5}{2}J \tag{41}$$

$$E(D_g^F) = \frac{\Delta E - \sqrt{\Delta E^2 + 4t(t + \Delta E/3)}}{2} - 4J \tag{42}$$

$$E(D_u^F) = \frac{\Delta E - \sqrt{\Delta E^2 + 4t(t - \Delta E/3)}}{2} - 4J \tag{43}$$

The optimized parameters are given in Table 3 as well as the percentage of error on the energies. This error has been calculated as the difference between the computed energies and the analytically calculated ones (from the extracted parameters and expressions 38 to 43) divided by the spectrum width. The comparison of these energies with the numerically CAS(5,6)CI computed ones (see Table 1) shows that an agreement within 2% of error is obtained. Notice that the ratio $|t/\Delta E|$ is approximately equal to 0.63 in the studied system so that the variational treatment of the non-Hund state effect is necessary here. This result shows that the term additional to the usual model due to the contribution of the non-Hund states plays a crucial role in the stabilization of the low and intermediate spin multiplicity states. As occured in the previously studied $[\text{Ni}_2(\text{napy})_4\text{Br}_2]^+$ compound, this effect brings an important contribution to the antiferromagnetism. However, the parameters $J = 1533\,\text{cm}^{-1}$ that come from the neutral determinants with atom-centered orbital double occupancies and the singly ionic determinants is non-negligible, contrarily to what occurs in the $[\text{Ni}_2(\text{napy})_4\text{Br}_2]^+$ compound in which the hopping integral (involving a δ overlap) that determines the J value is negligible. This can easily be understood since the spin coupling integral J is essentially governed by the delocalization between the b_1 and b_2 orbitals. This effect is proportional to the square of the hopping integral t' between these orbitals which is approximatively t, the overlap between these orbitals being of π nature as well as the overlap between the a_1 and a_2 orbitals.

4 A molecular orbital approach: role of the non-dynamical and dynamical correlation

While the combined here-proposed model has been analytically derived starting from atomic-centered orbitals and ground and excited atomic states, the full *ab initio* study has been performed using symmetry-adapted MOs. Elementary zeroth-order descriptions using delocalized MOs are based on the prevalence of a single-determinantal wavefunction that is delocalized over the whole complex and that partially forgets the spin and charge atomic orders. Of course, such a monoelectronic approximation is not relevant for a realistic description of strongly correlated systems like magnetic systems. A more realistic approach consists in performing a CASCI calculation in which the charge and spin fluctuation are optimized in a certain number of orbitals, namely the active orbitals. In order to confront the atomic states approach and the MO approach, the most adequate single-determinantal wavefunctions for the six studied states will be introduced and the role of the non-dynamical correlation will be analyzed in the first subsection. Then, since a quantitative treatment of magnetic systems constituted of transition metal compounds requires also the inclusion of correlation beyond the minimal CAS, a specific analysis will be devoted to that kind of contributions.

4.1 Non-dynamical correlation brought by the minimal CASCI

In order to understand the effect of the correlation inside the minimal CAS, let us look at the different bonds involved in the studied system in both the VB and the symmetry-adapted MO languages. As already said in a previous section, the atom-centered orthogonal orbitals l and r localized, respectively, on the left and right metallic atoms and obtained by linear combinations of the g (gerade) and u (ungerade) MOs of a specific bond are:

$$l = \frac{g+u}{\sqrt{2}} \tag{44}$$

$$r = \frac{g-u}{\sqrt{2}} \tag{45}$$

In the MO language the non-correlated single-determinantal wavefunction corresponding to a singlet arrangement of two electrons in the molecular orbital g (if g is of lower energy than u) is:

$$\phi_0 = |\text{core}.g\bar{g}| = |\text{core}.\frac{1}{2}(l\bar{l} + r\bar{r} + l\bar{r} + r\bar{l})| \tag{46}$$

where the weight of the ionic VB forms $l\bar{l}$ and $r\bar{r}$ is equal to the weight of the neutral VB forms $l\bar{r}$ and $r\bar{l}$. The effect of the non-dynamical correlation brought by a CAS in which the other spin and space compatible determinant $\phi_0' = |\text{core}.u\bar{u}|$ is considered as a reference result in a wavefunction Ψ in which the weights of the neutral and ionic VB forms are no more constrained to be equal

$$\Psi = \lambda|\text{core}.g\bar{g}| - \mu|\text{core}.u\bar{u}| = \frac{(\lambda+\mu)}{2}|\text{core}.(l\bar{r} + r\bar{l})| + \frac{(\lambda-\mu)}{2}|\text{core}.(l\bar{l} + r\bar{r})| \tag{47}$$

where λ and μ are the (CAS) optimized positive coefficients. The situation of two strongly correlated electrons (unpaired) is described by a Ψ wavefunction in which the coefficients λ and μ are equal (or almost equal) in absolute value, i.e. where the weight of the neutral VB forms is close to 1. In such a case the antiferromagnetic contribution is 0 or negligible. In the MO picture, another way of looking at the effect of non-dynamical correlation is to compare the occupation of the g and u orbitals. The uncorrelated situation corresponds to two electrons in the g orbital and zero electron in the u orbital while the most correlated situation is obtained for one electron in both orbitals (and a prevalence of the neutral VB forms). One should of course notice that when the two electrons are in a triplet spin arrangement (ferromagnetic interaction), the Ψ wavefunction can be reduced to a single determinant

$$\Psi = |\text{core}.gu| = |\text{core}.lr| \tag{48}$$

The following analysis is made in terms of differential occupation of the g and u orbitals and will consider the three following subsystems of the complex MOs:

- the δ subsystem which is constituted of the two δ_g and δ_u orbitals essentially spanned on the d_{xy} orbitals of the Re atoms. The main contributions to the correlated wavefunctions are brought by determinants in which the two shared electrons are in a singlet configuration in the D_g state with almost equal coefficients on $\delta_g\bar{\delta}_g$ and $\delta_u\bar{\delta}_u$ and in a triplet configuration $\delta_g\delta_u$ in all the other states. This δ bond is therefore the most correlated one, since it is almost uniquely spanned by neutral VB forms. Hence, the corresponding exchange interaction is close to zero and this subsystem does not contribute significantly to the antiferromagnetism. For a sake of simplicity this interaction will be discarded in the next discussion. The only point to keep in mind is that the total symmetry of that subsystem is singlet gerade in the D_g state while it is triplet ungerade in all the other states in the correlated wavefunctions. As it will be shown later, the choice between these two bielectronic states is governed by the possible energetic preferences of the two other subsystems.
- the π^X subsystem (which contains two electrons) is constituted of the two π_g^X and π_u^X orbitals essentially spanned on the d_{xz} orbitals of the Re atoms. The interaction between these two atom-centered orbitals is quite important as it will be shown in the following discussion and the most adequate non-correlated wavefunction would be spanned on a determinant built on the $\pi_g^X\bar{\pi}_g^X$ form traducing the partial covalency of the π^X subsystem. One should of course notice that this subsystem is responsible for the usual antiferromagnetic contribution.
- the π^Y subsystem which is constituted of the two π_g^Y and π_u^Y orbitals essentially spanned on the d_{yz} orbitals of the Re atoms. This subsystem accepts the extra electron. For spin and space symmetry requirements, the studied states will have either the extra electron in the π_g^Y orbital or in the π_u^Y one. Of course, one can already anticipate that since the π_u^Y orbital is higher in energy than the π_g^Y one, the effect of both non-dynamical and dynamical correlations will be crucial in those states for which the π_u^Y orbital is occupied.

Let us now compare the difference of population of the orbitals g and u of the three subsystems in the (most adequate) single-determinantal wavefunctions and in the CASCI wavefunctions. The differencial populations for all the studied states are reported in Table 4.

Concerning the sextet states, both wavefunctions are restricted to single determinants in the minimal CAS, and the role of the non-dynamical correlation is therefore zero. These determinants are $|\text{core}.\delta_g\delta_u\pi_g^X\pi_u^X\pi_g^Y|$ for the S_g state and $|\text{core}.\delta_g\delta_u\pi_g^X\pi_u^X\pi_u^Y|$ for the S_u one. Of course, for spin reasons the bielectronic states in both the δ and π^X subsystems are ungerade triplet states and there is, therefore, no antiferromagnetic contribution. The extra electron is constrained to occupy the π_g^Y orbital in the S_g state and the π_u^Y orbitals in the S_u one. This accounts for the energetic ordering of the two states.

In the quartet states, the alignment of three spins requires a triplet arrangement either in the δ or π^X subsystems. As already noticed, since the δ subsystem is highly correlated, the choice of a singlet or a triplet bielectronic state in that subsystem, must not have any consequence on the stability of the considered states. On the contrary, a singlet arrangement in the π^X subsystem would lead to more stable solutions than a triplet arrangement. Hence, the most adequate single-determinantal wavefunctions of the quartet states Q_u and Q_g will, respectively, be $|\text{core}.\delta_g\delta_u\pi_g^X\bar{\pi}_g^X\pi_g^Y|$ and $|\text{core}.\delta_g\delta_u\pi_g^X\bar{\pi}_g^X\pi_u^Y|$. Contrarily to the sextet wavefunctions, these two states will take benefit of the non-dynamical correlation.

Concerning the Q_u state, the essential effect of the non-dynamical correlation is to reduce the occupation of the π_g^X orbital compared to the π_u^X one. This result reflects the fact that the π^X bond is partially correlated i.e. the weight of the ionic VB forms must be reduced in the correlated wavefunction. One should also notice that the differential occupation of the π_g^Y and π_u^Y orbitals is the largest one (in comparison to all the other states) which accounts for the stability of that peculiar state.

In the correlated Q_g state, two dramatical effects can be identified:

(1) the first one is a higher occupation of the π_g^Y orbital compared to the π_u^Y one

(2) the second one is the large decrease of the occupation of the π_g^X orbital.

Actually the first effect is correlated to the second one. The occupation of the π_g^Y orbital stabilizes the state by a quantity proportional to t and is therefore the leading stabilizing factor. The only spin and space compatible determinants in which the π_g^Y orbital is occupied have open shells in the π^X subsystem with a dominant weight (0.83) of neutral VB forms in that specific subsystem. In other words, in order to maintain the extra electron in the π_g^Y orbital, this state must sacrifice part of the partial covalency in the π^X subsystem.

Concerning the doublet states, the single-determinantal wavefunctions contain one unpaired electron. This requires that the bielectronic states in both the δ and π^X subsystems are gerade singlet states. The corresponding determinants are, respectively, $|\text{core}.\delta_g\bar{\delta}_g\pi_g^X\bar{\pi}_g^X\pi_g^Y|$ for the D_g state and $|\text{core}.\delta_g\bar{\delta}_g\pi_g^X\bar{\pi}_g^X\pi_u^Y|$ for the D_u state.

In the D_g state, the non-dynamical correlation revises the weight of the neutral and ionic VB forms, but one should note that the covalency of the π^X bond is more important than in all the other states. This result is consistent with a more important antiferromagnetic contribution (in the usual acception). The extra electron is essentially localized in the π_g^Y orbital as expected.

Surprisingly enough, in the correlated D_u state, the π_g^Y orbital is also more populated than the π_u^Y one. This reversion of the differential population in the π^Y subsystem is made possible for space symmetry reason by the appearance of an ungerade triplet bielectronic state in the δ subsystem.

These results show that the main role of the non-dynamical correlation is to give the flexibility to the different wavefunctions to choose the adequate bielectronic states in the δ and π^X subsystems in order to maximize the population of the π_g^Y orbital. As a consequence, the states in which the non-dynamical correlation plays the largest role are those in which the π_u^Y orbital is occupied in the single-determinantal wavefunction.

This analysis which proposes an understanding of the different wavefunctions in terms of correlated bonds between the two Re atoms is quite unusual for double exchange systems. It is nevertheless compatible with the usual interpretation. Indeed, in the usual analysis the electronic order induced by the double exchange phenomenon is governed by the interactions between the lowest atomic states. The energetic ordering of these atomic states is governed by the Hund's rule. When looking carefully at the correlated wavefunctions of the different states, it appears that the role of the non-dynamical correlation that essentially kills the ionic VB forms is also to restaure the electronic charge and spin atomic orders. For instance, in the Q_g state, the determinant that prevails in a single-determinantal description is coupled with another determinant ($\phi_1 = |\text{core}.\delta_g\delta_u\pi_g^X\pi_u^X\bar{\pi}_g^Y|$ through an integral which is proportional to the monocentric exchange integral that is responsible for the atomic spin order (Hund's rule). Although it will not be developed further here, one could check that the same interaction is responsible for the

Table 4 Difference of populations of the g and u orbitals in the three subsystems (see text) in the six studied states calculated for a non-correlated (single determinantal) wavefunction (I) , at the (minimal) CASCI level (II) and at the enlarged CAS+DDCI2 level (III) of correlation

States	(I)			(II)			(III)		
	π^y	π^x	δ	π^y	π^x	δ	π^y	π^x	δ
S_u	−1	0	0	−1	0	0	−0.585	0.030	0.001
Q_g	−1	2	0	0.321	0.522	0.001	0.210	0.500	0.001
S_g	1	0	0	1	0	0	0.825	−0.003	0.0001
D_u	−1	2	2	0.604	1.054	0.012	0.585	1.141	0.010
D_g	1	2	2	0.807	1.134	0.032	0.734	1.187	0.040
Q_u	1	2	0	0.889	1.017	0.007	0.800	1.165	0.035

correlation in the D_u state. Finally, we have seen in the previous section that the electronic interactions partially destroy the spin and charge atomic orders of the Re atoms in the complex. This bonding effect is responsible for the role of the non-Hund atomic states. We can see here that starting from an MO description of the complex, the non-dynamical correlation partially restaures the atomic charge and spin orders. It is interesting to note that, while leading to the same chemical and physical interpretation, these two descriptions start from a completely different point of view, the second one being more common in chemistry.

4.2 Correlation beyond the minimal CAS

Let us now consider the correlation effect beyond the CASCI. This contribution is taken into account when enlarging the CAS and by DDCI calculations. One way to evaluate the correlation effects brought by extended CI beyond the minimal CAS consists in measuring the projection of the extensively correlated vectors onto the minimal CAS. These results, reported in Table 5, show that the S_u state is the most correlated vector which results in a dramatic reduction of the t parameter. Three kinds of effects susceptible of modifying the minimal CASCI previously discussed spectrum can be identified:

(1) The inclusion of dynamical correlation through the participation of singly and some of the doubly excited determinants in the wavefunction is responsible for the relaxation of ionic VB forms [48]. This results in an increase of the difference of population of the π_g^X and π_u^X orbitals in the π^X subsystem (see Table 4). The largest occurrence of a π_g^X double occupation in the correlated wavefunction confirms a partial covalency of the π^X bond. It is correlated with a smaller occupation of the π_g^Y orbital compared to the π_u^Y one except in the case of the S_u state for which, as expected, the essential role of the dynamical correlation is to permit the occupation of the π_g^Y orbital.

(2) The specific effect of the non-active $d_{x^2-y^2}$ and d_{z^2} empty orbitals localized on the Re atoms. As already seen in the $[Ni_2(napy)_4Br_2]^+$ compound the low lying empty orbitals on the metal are partially populated at the correlated level of treatment. These effects are taken into account in the correlated calculations reported here. In order to identify the orbitals that participate to this stabilization, we have calculated the natural orbitals and looked at their occupation numbers. It appears that an orbital essentially spread on the $d_{x^2-y^2}$ orbitals has an occupation close to 0.01 electron (in all the states) while another orbital essentially spread on the d_{z^2} orbitals has an occupation number of 0.005 electron. This correlation effect seems to be non-differential since these orbitals play an identical role on all the studied states. Hence, these effects will not be discussed further here.

Table 5 Projections (P) of the correlated wavefunctions onto the minimal CAS subspace and occupation numbers, respectively, n_y and n_x of the p_y and p_x orbitals of the oxygen atom and depopulation (X) of these atomic orbitals

States	P	n_y	n_x	X
S_u	0.705	1.797	1.934	0.269
Q_g	0.807	1.878	1.941	0.181
S_g	0.825	1.869	1.958	0.173
D_u	0.828	1.894	1.944	0.162
D_g	0.831	1.890	1.946	0.163
Q_u	0.835	1.894	1.946	0.160

(3) Both the spin coupling and the delocalization of the extra electron involve hopping through the oxygen bridging ligand. The implication of the oxygen ligand in both the extra electron transfer and the spin exchange can be directly appreciated by looking at the weight of the oxygen orbitals in the magnetic orbitals. In the π_u^Y and π_u^X orbitals, the respective weight of the p_y and p_x orbitals of the oxygen is important. The π_u^Y orbitals is represented in Fig. 3. Of course, for symmetry reasons the π_g orbitals are not developped on the oxygen bridge. The corresponding metal-ligand binding orbitals (having a ligand character) are essentially developped on the p_y and p_x orbitals. Even if their tails on the metals are quite important, let us call these orbitals p_y and p_x for the sake of simplicity. As already noticed on several studied magnetic compounds, a correct treatment of the processes of spin coupling and of delocalization of the extra electron requires at least an enlarged CAS+DDCI2 procedure that also includes these two orbitals in the active space. The diagonal elements of the density matrix (i.e. the population of these orbitals) calculated for the correlated vectors are significantly lower than 2. These results are reported in Table 5. The p_y orbital which is of the same symmetry as the d_{yz} orbitals bearing the transferable electron is the most depopulated. It is responsible for the jump of the transferable electron from one Re to the other. Similarly, the p_x orbital which is of the same symmetry as the d_{xz} orbitals of the Re atoms is involved in the spin exchange of the two electrons of the π^X subsystem. One should note that the oxygen does not bear any orbital of the same symmetry as those of the δ subsystem which is consistent with the fact that this subsystem is the most correlated. It is interesting to notice that the total depopulation of these oxygen orbitals is correlated with the values of the projections of the various states onto the CAS, confirming that this phenomenon is responsible for the most important part of the correlation effect. In particular, the S_u state is widely stabilized by the interaction with determinants in which the excitations imply these orbitals. The corresponding determinants are $|p_y\pi_g^Y\bar{\pi}_g^Y\delta_g\delta_u\pi_u^Y|$ and $|p_y\pi_g^Y\delta_g\delta_u\pi_u^Y\bar{\pi}_u^Y|$ and their respective coefficients in the correlated wavefunction are 0.29 and 0.16.

5 Conclusion

This paper reports an ab initio study of the low energy spectrum of the $[Re_2OCl_{10}]^{3-}$ complex. It has been shown that

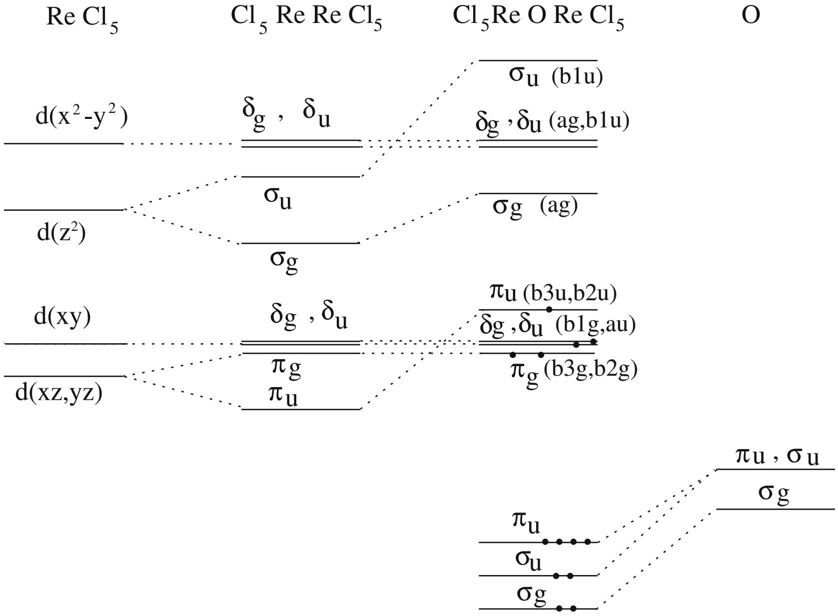

Fig. 2 Orbital energy ordering proposed by Campbell and Clark [46] and compatible with the calculations reported here. The irreducible representations (in the D_{2h} symmetry point group) to which belong the orbitals built from the d metallic orbitals are given in parentheses

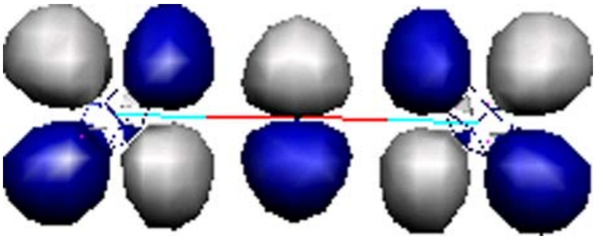

Fig. 3 π_u^Y orbital optimized for the S_g state

the calculated spectrum strongly deviates from the one predicted by the usual model Hamiltonian of double exchange. A recently proposed refined model that combines the Anderson and Hasegawa model [2] and the usual DE model reproduces very well the energy spacings calculated here. From a qualitative point of view, the interpretation of the antiferromagnetic contribution is deeply different in the Anderson Hasegawa model and in the usual DE model. Indeed, while it was entirely attributed to the delocalization in the two subsystems bearing two electrons in the usual model, it is due to the delocalization of the transferable electron (through the participation of the non-Hund atomic states) in the Anderson Hasegawa model. In the complex studied here, an important part of the antiferromagnetism is due to the non-Hund state. Such a work rehabilitates the suggestion of Anderson and Hasegawa [2] who attributed the entire antiferromagnetic contribution to this process. In the studied compound, nevertheless, the usual antiferromagnetic mechanism is also responsible for a significant part of the stability of the non-highest spin states. It should be noted that the contributions of the two mechanisms to the global antiferromagnetism are of comparable amplitude and both of them must be taken into account. The overlap between the orbitals of the π_Y subsystem that bears the transferable electron is exactly the same as the overlap between the orbitals of the π_X subsystem that bears two electrons. Of course, the δ overlap being very weak, the corresponding antiferromagnetic contribution is negligible.

It has been shown that compared to the usual model, the combined model that introduces the non-Hund states increases the left–right circulation of the electrons and therefore the covalency. In both models, the analytic development starts from atomic states (which are ruled by the Hund's rule) and determines the electronic structure by introducing bonding interactions. Another approach based on an MO language has been presented. It is interesting to note that it starts from an opposite point of view. While the basic single-determinantal description starts from MOs in which the bonding character is exaggerated, the non-dynamical correlation restaures partially the spin and charge atomic order. The role of non-dynamical and dynamical correlation beyond the CAS reincreases somewhat the covalency through the participation of the occupied orbitals of the oxygen ligand. This effect which stabilizes considerably the S_u state dramatically reduces the parameter t.

Finally, one of the interesting features of this peculiar complex is the unusual ordering of the spin states. While the double exchange complexes usually have a ground state of the highest spin multiplicity, the antiferromagnetism is sufficiently large in the $[Re_2OCl_{10}]^{3-}$ to generate a spectrum in which both the Q_u and D_g states are below the expected S_g one. Such an ordering of the states should confer to that complex singular thermodynamic magnetic properties.

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