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Excitation Energy Dedicated Molecular Orbitals. Method and Applications to Magnetic Systems

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This paper proposes a general strategy to define molecular orbitals which are especially adapted to the calculation of the energy difference between two states. These orbitals are shown to be eigenvectors of blocks of the difference between the density matrices relative of the two states. They may be used for rational enlargement of the active space in CASSCF calculations or for truncations of the configuration interaction space. Several examples show the relevance of the method to identify the few molecular orbitals of a bridge between magnetic centers which play a role in the spin coupling mechanism.

1. Introduction

Accurate ab initio calculations of excitation energies on rather large organic molecules and organometallic complexes are highly desirable but face problems of size of the configuration interaction step. A similar difficulty is met in solid state physics, when quantum chemical calculations on embedded clusters, pieces of a periodic lattice, are performed to determine the effective interactions between sites, such as the effective exchange in magnetic materials, or the effective hopping in doped systems.

In general, a zero-order description of the excitation between two states Ψ_1 and Ψ_2 is possible using a common set of molecular orbitals and concerning a few number of electrons in a limited number of orbitals. This description is obtained, for instance, by a state average CASSCF calculation, the complete active space (CAS) involving these active electrons and orbitals. The active orbitals are usually located around the Fermi level, or may be concentrated on atomic orbitals of metal atoms. Several examples may be considered, for instance:

(i) an optical $\pi \rightarrow \pi^*$ excitation on a conjugated organic system surrounded by large saturated substituents,

(ii) the singlet to triplet excitation energy in a dinuclear complex with unpaired electrons on the metallic centers and large bridging and external ligands, which fix the effective magnetic coupling between the metal atoms,

(iii) the effective transfer integral between two equivalent centers A and A′, i.e., the resonance between $A^{+}\cdots A'$ and $A\cdots A'^{+}$, appearing as the half of the difference between the g and u doublet states. These electron (or hole) carriers may be connected through large ligands as well.

The transition energies given by the limited CASSCF calculations are usually far from the desired accuracy. For instance, for singlet−triplet excitation energies in magnetic binuclear complexes (case ii), the CASSCF estimation is typically 25% of the experimental value.[1−7] This means that the inactive electrons and inactive orbitals actually play a role in the accurate evaluation of the energy difference. To go further, the size of the CAS in the CASSCF calculation may be increased. But it is not easy to select rationally the enlargement of the CAS, and its dimension may become prohibitive before giving an accurate value of the transition energy. Another solution consists in performing single and double substitutions (involving inactive occupied and virtual molecular orbitals (MOs)) on the top of the small CAS, resulting in a CAS-SDCI calculation. The size consistency of these treatments may be ensured by an appropriate dressing of the diagonal elements.[8,9] If N_{CAS} is the size of the CAS and n_{o} and n_{v} are respectively the number of occupied and virtual inactive orbitals, the size of the CI matrix scales as $N_{\mathrm{CAS}}n_{\mathrm{o}}^{2}n_{\mathrm{v}}^{2}$. A rational smaller CI expansion is that of the difference dedicated CI (DDCI) method,[10] which discards the purely inactive double excitations of the CAS-SDCI, its length scaling as $N_{\mathrm{CAS}}n_{\mathrm{o}}n_{\mathrm{v}}^{2}$. The direct CI codes[11,12] handle typically up to 10^7 determinants, but this limit is rapidly reached, even from very moderate CAS, when large basis sets and large ligands are considered.

On the other hand, if the excitation concerns a region A of the system, the electrons and MOs of a region B very far from A will not play a role in the excitation. However, the canonical orbitals may be strongly delocalized on regions A and B. The use of localized orbitals is not very convenient for the transition energy calculations, and it may destroy the symmetry of the MOs. Notice that in such a problem $A\cdots B \rightarrow A^{*}\cdots B$ the CASSCF enlargement may bring the active orbitals on B, if the correlation on B is important, while they play no role on the $A \rightarrow A^{*}$ excitation energy.

Hence a procedure that would define the inactive orbitals (occupied and virtual) having the largest participation to the excitation energy would be welcome. In the recent past, two papers have proposed a perturbative procedure to define "dedicated inactive MOs".[13−15] The proposal was quite general, introducing "observable dedicated MOs" (see also ref 16), where the observable may be a dipole moment, a nuclear coupling

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constant, or a transition energy. The method is perturbative and based on the diagrammatic expansion (in terms of Feynman's diagrams) of the desired observable.

The present work will show the following:

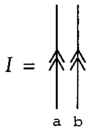
(i) For excitation energies between the states Ψ_1 and Ψ_2 the dedicated MOs are the eigenvectors of blocks of the difference between the density matrices of the two states, R_1-R_2.

(ii) The most-involved dedicated MOs (i.e., those having the largest differential occupation numbers in absolute value) concentrate the physical contributions to the transition energy, providing either rational criteria for enlarging the CAS or the possibility of rational truncations of the CAS-SDCI or CAS-DDCI by freezing the least participating MOs (i.e., those whose differential occupation numbers are closer to zero).

2. Method: Relevance of the Difference of Density Matrices

2.1. Derivation. Let us consider a CAS space, S, defining a *core* with occupied inactive orbitals $\{i,j,...\}$, a set of active MOs, $\{a,b,...\}$, with variable occupation numbers, and virtual MOs, $\{r,s,...\}$. The vacuum state is taken as the *core*, so that the determinants $\{I,J,...\}$ of the CAS may be represented by a set of ascending propagation lines with two arrows. For instance, for two electrons, see Scheme 1.

SCHEME 1



The eigenvectors of the state m may be written as

$$\Psi_m = \Psi_m^{(0)} + \Psi_m^{(1)} + \Psi_m^{(2)} + ... \quad (1)$$

where

$$|\Psi_m^{(0)}\rangle = \sum_{I\in S} c_{mI}|I\rangle \quad (2)$$

is the CAS component, and

$$|\Psi_m^{(1)}\rangle = \sum_{\alpha\notin S} c_{m\alpha}^{(1)}|\alpha\rangle \quad (3)$$

is the outer space component, the determinants of which are labeled α, β, ...

If $\Psi_m^{(0)}$ is the zero-order wave function, the first-order correction to the wave function $\Psi_m^{(1)}$ may be written as

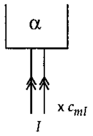
$$\Psi_m^{(1)} = \sum_{\alpha\notin S} \frac{|\alpha\rangle\langle\alpha|H|\Psi_m^{(0)}\rangle}{E_m^0 - E_\alpha^0} = \sum_{\alpha\notin S}\sum_{I\in S} \frac{|\alpha\rangle\langle\alpha|H|I\rangle c_{\mathrm{mI}}}{E_m^0 - E_\alpha^0} \quad (4)$$

and the second-order energy $\epsilon_m^{(2)}$ is

$$\epsilon_m^{(2)} = \sum_{\alpha\notin S} \frac{\langle\Psi_m^{(0)}|H|\alpha\rangle\langle\alpha|H|\Psi_m^{(0)}\rangle}{E_m^0 - E_\alpha^0} = \sum_J \sum_I \sum_{\alpha\notin S} c_{mI}c_{mJ} \frac{\langle J|H|\alpha\rangle\langle\alpha|H|I\rangle}{E_m^0 - E_\alpha^0} \quad (5)$$

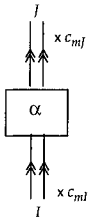
These contributions of the wave function may be represented as in Scheme 2:

SCHEME 2



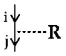
and the contributions of the energy as in Scheme 3:

SCHEME 3



Let us consider now a matrix element of the block of the density matrix between occupied orbitals, concerning, for instance, the operator $a_j^\dagger a_i = \rho_{ij}$, which contributes to the ij matrix element of the density matrix. This operator is diagrammatically represented as in Scheme 4:

SCHEME 4



The contribution of $\Psi_m^{(0)}$ to the block between occupied MOs of the density matrix

$$R_{\mathrm{occ},m}^0 = \langle\Psi_m^{(0)}|R_{\mathrm{occ}}|\Psi_m^{(0)}\rangle \quad (6)$$

is diagonal, with occupation numbers equal to two. The modifications come from the outer space components of the wave function up to the second order in the operator correlation expansion:

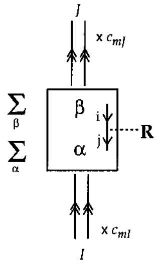
$$R_{\mathrm{occ},m} = R_{\mathrm{occ},m}^0 + \langle\Psi_m^{(0)}|R_{\mathrm{occ}}|\Psi_m^{(1)} + \Psi_m^{(2)}\rangle + \langle\Psi_m^{(1)} + \Psi_m^{(2)}|R_{\mathrm{occ}}|\Psi_m^{(0)}\rangle + \langle\Psi_m^{(1)}|R_{\mathrm{occ}}|\Psi_m^{(1)}\rangle \quad (7)$$

The second and third terms are zero since the CAS and outer space determinants cannot be connected by the operator ρ_{ij}. Hence, the modifications of the R_{occ} block of the density matrix come entirely from $\langle\Psi_m^{(1)}|R_{\mathrm{occ}}|\Psi_m^{(1)}\rangle$:

$$R_{ij,m} = \sum_{J\in S}\sum_{\beta\notin S}\sum_{I\in S}\sum_{\alpha\notin S} c_{mJ}c_{mI} \frac{\langle J|H|\beta\rangle\langle\beta|a_j^\dagger a_i|\alpha\rangle\langle\alpha|H|I\rangle}{(E_m^0 - E_\beta^0)(E_m^0 - E_\alpha^0)} \quad (8)$$

which can be pictured as in Scheme 5:

SCHEME 5



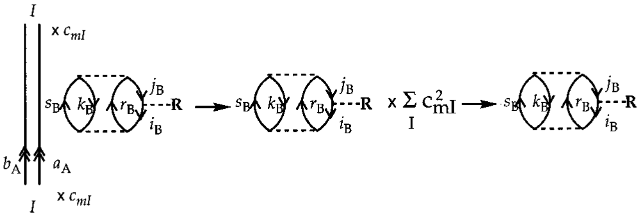
This is nothing but the insertion of the ρ_{ij} operator in the inactive propagation lines of the second-order energy diagrams.

The diagonal term $R_{ii,m}$ measures the degree of participation of the orbital i to the correlation energy of the state m. By introducing the off-diagonal elements, $R_{ij,m}$ and diagonalizing $R_{\mathrm{occ},m}$, a hierarchy of quasi-natural occupied MOs is obtained, those with lowest occupation numbers having the largest contribution to the correlation energy.[17]

If one is only interested in the energy difference between Ψ_m and Ψ_n, the contribution $\epsilon_m^{(2)} - \epsilon_n^{(2)}$ appears as the difference of diagrams and the participation of an orbital i in this difference will be measured by the difference of the corresponding elements $R_{ii,\mathrm{m}} - R_{ii,\mathrm{n}}$ of the density matrices of the two states. The participation of the orbitals in the energy difference is given by the difference of the density matrices, and by diagonalizing $\Delta R_{\mathrm{occ}} = R_{\mathrm{occ},m} - R_{\mathrm{occ},n}$, energy difference dedicated MOs are obtained. The "implication numbers", which are the eigenvalues of ΔR_{occ}, may be positive or negative. The dedicated MOs whose implication numbers have the largest absolute values are the orbitals which have the largest contributions to the energy difference. Those with zero as implication number do not contribute to the excitation energy. The preceding derivation is immediately transposed to the block of the density matrix between virtual orbitals.

It is easy to show that the method avoids the involvement of orbitals which do not participate to the excitation process for physical reasons. For instance, in a supermolecular A...B problem in which A and B do not interact, for an excitation located on A, i.e., from $|\Psi_{m,\mathrm{AB}}\rangle = |\Psi_m^{\mathrm{A}}\rangle\cdot|\Psi_0^{\mathrm{B}}\rangle$ to $|\Psi_{n,\mathrm{AB}}\rangle = |\Psi_n^{\mathrm{A}}\rangle\cdot|\Psi_0^{\mathrm{B}}\rangle$, in the m state density matrix important contributions between occupied orbitals i_{B} and j_{B} on the fragment B may appear coming from double excitations on B, which may be important if B is strongly correlated (Scheme 6):

SCHEME 6



Among the most participating natural orbitals for state m, there are probably some orbitals on B which actually do not play any role in the excitation energy. By considering the difference of the density matrices $R_{\mathrm{occ},m} - R_{\mathrm{occ},n}$, these contributions cancel and the orbitals on B will have a null implication number.

The present derivation generalizes two previous works, which had proposed dedicated MOs for the treatment of diradicalar problems (i.e., the determination of the magnetic coupling between two sites)[13,14] and for mixed-valence compounds (i.e., the evaluation of the transfer integral between two sites).[15] These works had given specific perturbative derivations from localized descriptions and had not established the relationship with the difference of density matrices.

The proposal can be applied as well to determine ionization potentials. A common set of MOs is obtained; either by a state average or by considering the eigenvectors of the sum of the two density matrices of the two states, the MOs are partitioned into three sets (occupied inactive, active, and virtual inactive). After that the diagonalization of the blocks of the difference of the density matrices relative to the occupied or to the virtual inactive MOs provides the orbitals which have the largest participation to the ionization energy.

2.2. Practical Use of the Dedicated MOs. *1. Rational Enlargement of the Complete Active Space*. Let us consider a problem where a specific CAS has been defined. If one performs a post-CASCI calculation, either perturbative or variational, the diagonalization of the occupied and virtual blocks of the difference of the density matrices of the two states furnishes dedicated MOs, the most implicated orbitals being those with the largest absolute implication numbers. These orbitals can be introduced in an enlarged CAS. The post-CASCI calculation can be repeated from that rationally enlarged CAS.

2. Truncated Variational Treatments. Let us consider two levels of post-CASCI calculations, a level 1 and a more sophisticated (and therefore more expensive) level 2. The dedicated MOs can be extracted from a calculation on level 1 and a subset of the most implicated dedicated MOs can be extracted. The level 2 treatment can be applied on the configurations which only involve the selected MOs, the rest being treated at level 1. Let us give a few examples:

Level 1 can be a CAS-SDCI calculation and level 2 a CAS-SDTQCI calculation.

Level 1 can be a CAS-SCI calculation, which takes into account all the dynamical repolarization effects of the different valence configurations. Level 2 may be a CAS-SDCI or a CAS-DDCI treatment.

Level 1 may be a CASPT2 and level 2 a CAS-SDCI or a CAS-DDCI calculation.

3. Numerical Illustrations

To illustrate the performance of excitation energy dedicated MOs, two examples have been taken, one corresponding to a dinuclear magnetic complex, namely two Cu atoms bridged by an oxalato ligand, the second one concerning a bimetallic fragment of the $\mathrm{La}_{2-x}\mathrm{Sr}_x\mathrm{CuO}_4$ compound, typically representative of the high-T_c superconductor materials. The collective electronic properties of these materials are usually interpreted from the knowledge of two local bicentric interactions, namely the magnetic coupling, J, which permutes the opposite spins on two adjacent metallic atoms, and the electron transfer integral, t, which moves the hole (in the case of doping) from one metallic atom to the in-plane neighbors.[18]

In both systems, the Cu atoms bear an unpaired electron (or a hole in the doped system), and both the magnetic interaction and the electronic coupling between the two metallic centers can be obtained from the spectrum of the bimetallic cluster, as the energy difference between the lowest singlet and triplet states for J[19] (where J is negative in the case of an antiferromagnetic coupling) and as the half of the energy-difference between the doublet$_{\mathrm{g}}$ and the doublet$_{\mathrm{u}}$ states for t.[20] The active orbitals with fluctuating spin or fluctuating electronic population are easily determined by performing either the calculation of the triplet state or a state average CASSCF calculation. However, the mechanism of the magnetic or electronic coupling goes through determinants which involve charge transfer processes from the ligand to the metal atoms. The role of the ligands is different in the two problems. For the magnetic exchange between the two Cu atoms, the ligand−metal charge transfer states represent intermediates and the process is dynamical, and it cannot go through an improvement of the active magnetic orbitals.[21−23] For the doped system and the hopping integral t, the hole centered on the Cu atoms is partly delocalized on the bridging ligand and its delocalization is mainly static, and it can be incorporated through a Cu(3d)−O(2p) hybridization of the active orbitals.[21,22]

All the calculations concerning the determination of the starting MOs (restricted open-shell Hartree−Fock calculation on the triplet state or a state-average CASSCF calculation) have been performed by using the MOLCAS 4.1 package.[24] The CASDI[11] and the DDCI-SCIEL[12] programs have been used in the CI calculations.

3.1. Nature of the Most-Implicated MOs and Enlargement of the CAS. The determination of the MOs of the ligand, which play this crucial role in the physical mechanism, is far from being trivial. The canonical orbitals, which are strongly delocalized, are not suited for this mechanism, since a large number of these orbitals would be involved. The use of the present strategy provides a set of occupied MOs of the bridge, which concentrate the electron or the spin transfer mechanisms, even starting from the strictly minimal CAS, containing one or two electrons in two active orbitals, and a rather limited CI calculation, such as a CAS + single excitations.

The relevance of the bridging ligand centered MOs will be demonstrated by comparing the excitation energy obtained from an enlarged CAS, containing the two active orbitals and the most involved occupied dedicated MOs and the single excitations on the top of this CAS, with the experimental coupling constant or with the results of a much larger CI obtained from the minimal CAS by a DDCI expansion.

Complementary information can be obtained by analyzing the wave function of the ground state of the system, comparing the role played by these bridge-centered MOs.

3.1.1. High-T_c Superconductors: Magnetic Coupling and Hopping Integral. The $La_{2-x}Sr_xCuO_4$ system has been previously studied in order to extract the magnetic coupling and hopping integral between neighbor Cu sites.[21,22] As has been shown, both magnetic and hole transfer processes can be adequately treated by means of ab initio CI calculations on properly embedded clusters. Since both phenomena are essentially localized on the CuO_2 planes, a binuclear cluster of formula Cu_2O_7, containing the nearest in-plane oxygen neighbor atoms and properly embedded in the Madelung field of the infinite crystal, has been used to model the system. Extended CI calculations of DDCI-type starting from the minimal CAS (two electrons in two orbitals for J extraction, and one electron in two orbitals for the hole-doped system), the size of which is around half a million of determinants, have provided an accurate value of J (−138 meV versus the well-established experimental values of −128 ± 6 meV,[25] −134 ± 5 meV[26−28]). For t, there is no direct experimental estimation, but a value of around −0.5 eV is generally accepted,[29] to be compared with the ab initio evaluation of −0.55 − 0.58 eV.[21,22] These large CI calculations will be considered as our benchmark, regarding both the excitation energy and the physical content of the wave function.

The MOs dedicated to the magnetic exchange have been determined in a very cheap way, from a CAS + single excitations (CAS-SCI) from the minimal CAS (two orbitals and one electron for t or two electrons for J). The J value obtained from this reduced CI calculation is rather poor (only a 60% of the experimental value), but it is sufficient to provide relevant dedicated MOs, as will be seen below.

Figure 1 shows the two magnetic active orbitals (Figure 1, a and b) and the two most-implicated inactive occupied dedicated MOs for the magnetic coupling. As expected, the orbital with the largest implication number ($n_i = 0.96 \times 10^{-3}$) corresponds to the 2p orbital of the bridge oxygen atom, with tails on the outer-oxygen atoms, directed toward the metal atoms (Figure 1c). The second most-involved MO ($n_i = 0.24 \times 10^{-3}$) is a linear combination of 2p oxygen orbitals with an important contribution of the 2s orbital of the central oxygen atom (Figure 1d). Two other dedicated occupied MOs presenting a nonnegligible implication number are the in-phase and out-of-phase combination of the d_{z^2} orbital of the Cu atoms. Regarding virtual orbitals, the most-implicated MOs are centered on the bridging oxygen atom with a local 3s ($n_i = 0.24 \times 10^{-3}$) or 3p ($n_i = 0.60 \times 10^{-3}$) character. They are completely different from the canonical MOs of the small CASSCF calculation (two electrons in two orbitals). It is worth to notice that these dedicated MOs have a large projection onto the active space obtained from a large CASSCF (10e/12MOs) calculation.

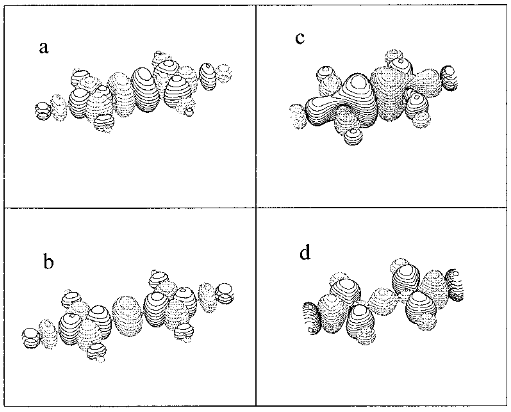


Figure 1. Most implicated dedicated MOs for La_2CuO_4 system: (a) and (b) are the active magnetic orbitals, (c) and (d) are the most participating ligand-centered inactive occupied orbitals of symmetry ungerade and gerade, respectively.

TABLE 1: Magnetic Coupling Values for the La_2CuO_4 System at Different Levels of Calculation and Different CAS[a,b]

type of CI	J (meV)	C_I/C_N	C_{CT}/C_N
CAS(2/2)-CI	−30	0.0389	0.0
CAS(6/4)-CI	−31	0.0418	0.0078
CAS(6/6)-CI	−46	0.0501	0.0331
CAS(2/2)-SCI	−83	0.0867	0.0414
CAS(6/4)-SCI	−150	0.1312	0.2269
CAS(6/6)-SCI	−153	0.1320	0.2283
CAS(2/2)-DDCI	−138	0.1146	0.2013
exp	−128 ± 6,[25] −134 ± 5[26−28]		

[a] C_I/C_N and C_{CT}/C_N represent, respectively, the ionic/neutral and charge-transfer/neutral configuration ratio of the wave function of the singlet ground state. [b] CAS (m/n) corresponds to m electrons in n MOs.

Table 1 shows the results obtained from various CAS-CI as well as larger CI calculations (CAS-SCI and DDCI). Enlarging the CAS by adding the two most-implicated occupied MOs, i.e., incorporating the charge transfer from the oxygen atoms to the magnetic orbitals, a CAS-SCI calculation can be performed, which now includes the dynamical relaxation and polarization of the ligand to metal charge transfer configurations (LMCT), and the final result of that inexpensive calculation (26×10^3 determinants) provides a value of $J = -150$ meV, in good agreement with our “benchmark” calculation (DDCI on the top of the minimal CAS), which involves 5×10^5 determinants and gives $J = -138$ meV. Adding the two most implicated virtual MOs (6e/6MOs CAS) no longer significantly changes the results of the CAS-SCI ($J = -153$ meV).

The values obtained for the magnetic coupling can be related to the physical content of the wave functions, also reported in Table 1. Let us call a and b the local magnetic orbitals, and l the doubly occupied bridging orbitals involved in the ligand to metal charge transfer. The a and b orbitals are given by a $\pi/4$

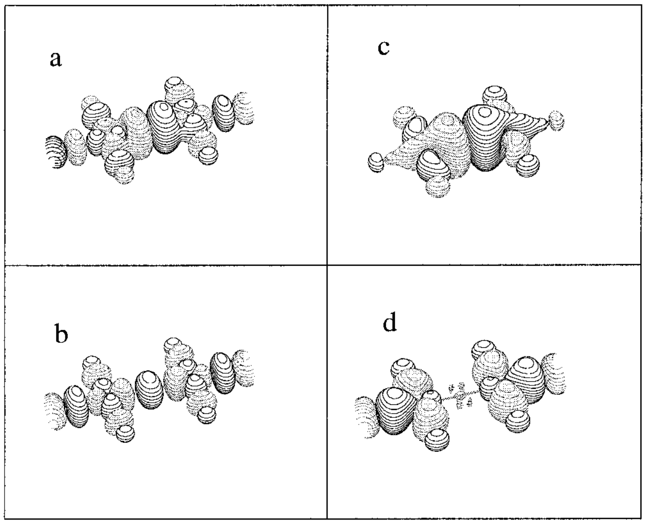


Figure 2. Most implicated hole-transfer dedicated MOs for $La_{2-x}Sr_xCuO_4$ system: (a) and (b) are the active hole-transfer orbitals, (c) and (d) are the most participating ligand-centered inactive occupied orbitals of symmetry ungerade and gerade, respectively.

rotation of the symmetry-adapted orbitals pictured in Figure 1, *a* and *b*, while the *l* MO is drawn in Figure 1c. The three dominant valence-bond (VB) configurations of the singlet state are

$$\text{neutral:}\quad \psi_N = |l\bar{l}(a\bar{b} + b\bar{a})|/\sqrt{2}$$

$$\text{ionic:}\quad \psi_I = |l\bar{l}(a\bar{a} + b\bar{b})|/\sqrt{2}$$

$$\text{charge transfer:}\quad \psi_{CT} = |a\bar{a}(l\bar{b} + b\bar{l}) + b\bar{b}(l\bar{a} + a\bar{l})|/2$$

and the content of the ground state wave function: $\psi_S = C_N\psi_N + C_I\psi_I + C_{CT}\psi_{CT} + ...$ can be analyzed from the ratios C_I/C_N and C_{CT}/C_N. Comparing with the values given by our best CI ($C_I/C_N = 0.11$ and $C_{CT}/C_N = 0.20$), the CAS values are significantly underestimated, i.e., there is a lack of electron delocalization at this level, resulting in an underestimation of the antiferromagnetic character. Going to the CAS-SCI level on the top of the small CAS increases these ratios and pushes J to −88 meV, but misses the dynamical polarization of the charge transfer states. Incorporating these configurations in the CAS and performing a CAS-SCI calculation will introduce these physical effects and results in a simultaneous improvement of J, C_I/C_N, and C_{CT}/C_N. Hence, the bridging dedicated MOs concentrate the zero-order physics responsible for the magnetic coupling.

Regarding the doped system (Figure 2), and using hole-adapted active MOs (with an important mixing of Cu(3d) and O(2p) orbitals, Figure 2, a and b), the same type of calculation (single excitations on the top of the one electron in two MO CAS) gives hole-adapted difference-dedicated MOs. The most participating MO ($n_i = 0.66 \times 10^{-2}$) is a 2p orbital located on the bridging oxygen atom with ungerade symmetry (Figure 2c), as expected, while the following one ($n_i = 0.44 \times 10^{-2}$) is of gerade symmetry, with large components on the 2p orbitals of the external ligands and on the 3d orbitals of Cu atoms (Figure 2d). The small CAS-CI value of t is −0.729 eV, much larger than our best estimate, $t = -0.587$ eV given by the full DDCI expansion (2.8×10^5 determinants) from this CAS. Adding the two most implicated occupied MOs to the CAS (now 5e/4MOs) and performing a CAS-SCI calculation (4×10^4 determinants) provides a satisfactory value of $t = -0.578$ eV.

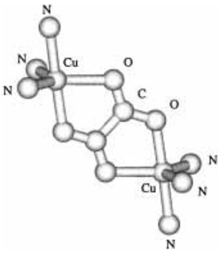


Figure 3. Schematic representation of the $[(NH_3)_6Cu_2(\mu\text{-}C_2O_4)]^{2+}$ complex, where N corresponds to NH_3 groups.

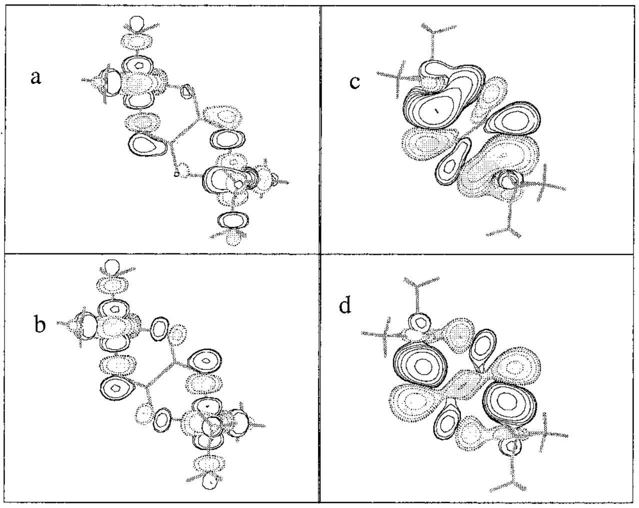


Figure 4. Most implicated magnetic dedicated MOs for the $[(NH_3)_6\text{-}Cu_2(\mu\text{-}C_2O_4)]^{2+}$ complex: (a) and (b) are the active magnetic orbitals, (c) and (d) are the most participating ligand-centered inactive occupied orbitals of symmetry ungerade and gerade, respectively.

3.1.2. Oxalato-Bridged Copper Dinuclear Complexes. The structural dependence of the coupling constant found in a series of $[L_3Cu(\mu\text{-}C_2O_4)CuL_3]^{2+}$ complexes, where L is an external ligand of aminic type that has been replaced by NH_3 groups, has been previously studied at the DDCI level.[23] We have considered here one of the compounds of formula $[(Et_5\text{-dien})_2Cu_2(\mu\text{-}C_2O_4)](BPh_4)_2$, Et_5dien = 1,1,4,7,7-pentaethyldiethylenetriamine. The geometry has been crystallographycally established and the magnetic coupling has been found −9.27 meV.[30,31] A representation of this model is plotted in Figure 3. In this system, the magnetic orbitals are the symmetric and antisymmetric combinations of Cu d_{z^2} type orbitals, directed along the apical bond between the copper atom and one of the oxygen atoms of the oxalato ligand, as pictured in Figure 4 (a and b). In such a complex, with remote magnetic centers and a polyatomic ligand, the identification of the ligand-centered MOs which play a role in the magnetic coupling is not intuitive and the dedicated MOs procedure may help in their definition. The J value calculated at DDCI2 level, which is a reduced space with respect to DDCI, containing all the single and double excitations involving at least two active electrons, is −4.55 meV, far to the experimental value. The complete DDCI calculation on the top of the minimal CAS (two active electrons in two magnetic orbitals) may be considered as a benchmark calculation. It includes 2.7×10^6 determinants, and gives −11.08 meV, in good agreement with the experimental estimation. This calculation is invariant under rotation of the occupied MOs but is very expensive. It contains the whole physics but it does not permit to isolate the role of the ligands.

Dedicated MOs have been obtained from the minimal CAS-(2e/2MOs)-SCI, which gives a very poor value of the coupling

TABLE 2: Magnetic Coupling Values for the $[(NH_3)_6Cu_2(\mu\text{-}C_2O_4)]^{2+}$ Complex at Different Levels of Calculation and Different CAS[a]

type of CI	J (meV)	C_I/C_N
CAS(2/2)-CI	−0.82	0.0064
CAS(6/4)-CI	−0.84	0.0065
CAS(2/2)-SCI	−2.20	0.0127
CAS(2/2)-DDCI2	−4.55	0.0132
CAS(6/4)-SCI	−11.20	0.0376
CAS(2/2)-DDCI2+LMCT*S	−10.58	0.0406
CAS(2/2)-DDCI	−11.08	0.0356
exp	−9.27[30,31]	

[a] CAS (6/4) corresponds to *m* electrons in *n* MOs.

TABLE 3: Effect of the Truncation of the DDCI Space in the Magnetic Coupling Value and in the Components of the Ground State Wave Function for the La_2CuO_4 System[a]

% space DDCI	J (meV)	C_I/C_N	C_{CT}/C_N
100	−138	0.1146	0.2013
53	−134	0.1160	0.1971
27	−140	0.1192	0.1967
12.5	−138	0.1169	0.1911
1.8	−111	0.1011	0.1498
exp	−128 ± 6,[25] −134 ± 5[26−28]		

[a] C_I/C_N and C_{CT}/C_N represent, respectively, the ionic/neutral and charge-transfer/neutral configuration ratio of the wave function of the singlet ground state.

constant $J = -2.2$ meV, only the 20% of the experimental value. The two most participating occupied MOs ($n_i = 0.72 \times 10^{-4}$ and 0.29×10^{-4}) have the expected bridging character, since they are combinations of σ oxygen-lone pairs, belonging to the same irreducible representations as the magnetic ones. These orbitals are plotted in Figures 4c and 4d.

To test the relevance of these two most implicated MOs in the ligand to metal charge-transfer mechanism, single CI has been performed on the top of the enlarged CAS(6e/4MOs) giving a satisfactory value of the coupling constant $J = -11.20$ meV for a much reduced CI expansion (10^5 determinants).

An alternative solution consists in adding to the DDCI2 space all the single excitations on a reduced number of ligand to metal charge-transfer configurations (DDCI2+LMCT*S in Table 2). This procedure gives a value of −10.58 meV for the magnetic coupling, close to the preceding value. Both results are in good agreement with the benchmark DDCI result with a much smaller (4%) CI size. Similar results ($J = -9.47$ meV) had been obtained previously with the same type of CIs, using bridging ligand MOs coming from extended CASSCF calculations, for instance 10 electrons in 10 orbitals.[23] The dedicated MOs have the advantage of avoiding the convergence difficulties of the large CASSCF calculations.

3.2. Truncation of CI Expansions. As previously mentioned, the inactive dedicated MOs with implication numbers closest to zero should play a negligible role in the excitation energy. Whatever the level of the CI treatment, it is worth comparing the truncated versus the nontruncated CI results.

An increasing number of the least implicated MOs (both occupied and virtual) have been frozen, using different types of CI expansions. The results appear in Table 3 and Figure 5 for the magnetic coupling and in Figure 6 for the hopping integral in the $La_{2-x}Sr_xCuO_4$ system, and in Table 4 and Figure 7 for the magnetic coupling in the oxalato−Cu(II) complex.

An efficient definition of the dedicated MOs should provide a selection of the most implicated MOs sufficient to approach, at a given CI level, the result of the same type of CI, running on all the MOs. For the La_2CuO_4 system, this has been tested on the CAS-SCI level for the small CAS (2e/2MOs), which only gives a 60% of the experimental J value, and on the DDCI calculation on the same CAS, which gives a value of −138 meV, in good agreement with the experimental estimate, and it is considered as our reference calculation. A “strong” freezing of the least implicated MOs, resulting in a drastic truncation of the CI space to 20% of its total size already gives a value of J

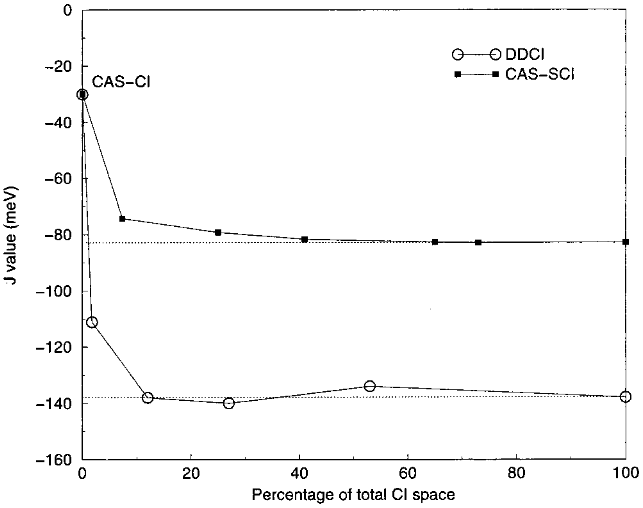


Figure 5. Effect of the truncation of the CI space on the value of the magnetic coupling J in the La_2CuO_4 system. Two CI levels on the top of the small CAS (2e/2MOs) have been considered: CAS-SCI (squares) and DDCI (dots). The value obtained for a space of 0% of the total one corresponds to the diagonalization of the CI matrix on the basis of the determinants of the CAS.

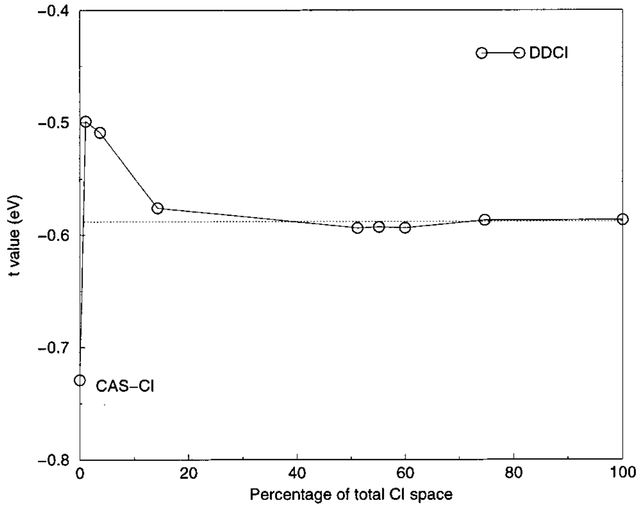


Figure 6. Effect of the truncation of the DDCI space on the value of the hopping integral t in the $La_{2-x}Sr_xCuO_4$ system. A small CAS (1e/2MOs) has been used. The value obtained for a space of 0% of the total DDCI corresponds to the diagonalization of the CI matrix on the basis of the determinants of the CAS.

TABLE 4: Effect of the Truncation of the DDCI Space in the Magnetic Coupling of the $[(NH_3)_6Cu_2(\mu\text{-}C_2O_4)]^{2+}$ Complex

% space DDCI	J (meV)	% space DDCI	J (meV)
100	−11.08	8	−8.22
67	−11.10	1	−4.94
42	−11.14	exp	−9.27[30,31]
20	−11.17		

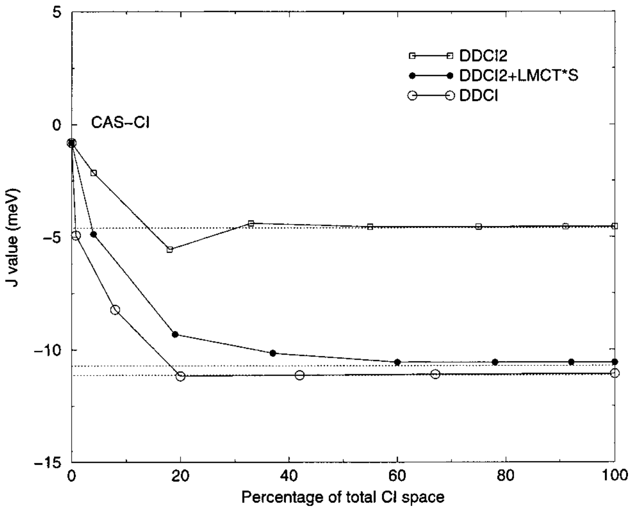


Figure 7. Effect of the truncation of the CI spaces on the value of the magnetic coupling *J* in the $[(NH_3)_6Cu_2(\mu\text{-}C_2O_4)]^{2+}$ complex: (open squares) DDCI2, (dashed dots) DDCI2+LMCT*S, and (open dots) DDCI spaces.

in good agreement with that obtained from the corresponding total CI space. This agreement is not fortuitous since, as it appears in Table 3, the weights of the leading VB configurations are stable, and already correct for severely truncated CI spaces (∼10% of the total size).

The same behavior is obtained regarding the calculation of the effective hopping integral in the doped system. The minimal CAS-CI overestimates its value (−0.729 eV) and truncations to the CI size of about 20% of the total DDCI size are sufficient to obtain an accurate value of t (-0.59 ± 0.02 eV).

The results on the $[(NH_3)_6Cu_2(\mu\text{-}C_2O_4)]^{2+}$ complex show the same trend. The effects of the truncation of the DDCI space on the exchange coupling are reported in Table 4. As previously indicated, DDCI2 results are poor, but the comparison is possible within the same type of CI procedure. By freezing 50% of the MO set, the CI space is truncated to around 30% of the total size but is able to give 96% of the magnetic coupling. Figure 7 shows that for three types of CI calculations (DDCI2, DDCI2+LMCT*S and DDCI) the results are stable when the percentage of determinants of the CI space goes beyond a 30% threshold.

These results show that it is possible to use the dedicated MOs to reduce considerably the size of the CI expansions in a rational manner, without a significant loss of accuracy.

4. Conclusions

The benefit of using natural orbitals to concentrate the CI expansion of a state is well-known. This interest is not purely academic since approximate natural orbitals may be calculated through a low cost procedure (low order perturbative expansion, for instance) before performing a variational CI, which may eventually freeze the orbitals with largest (∼2.0) and smallest (∼0.0) occupation numbers. Average density matrices, summed over a few eigenstates of interest, are sometimes used. It is possible to iterate the CI natural orbitals procedure to obtain results which become independent of the choice of the starting MOs. This idea has been exploited[5,21,22,32] in the recent past for the difference-dedicated CI procedure,[10] a CAS-SDCI truncated to the double excitations which contribute to the transition energies at second order of perturbation. The iterative DDCI method improves greatly the active orbitals, involved in the transition.

The use of the eigenvectors of difference of density matrices is less frequent. It has been used to identify the nature of the hole created by a doping in the spin lattices of a high-T_c superconductor.[22] Another application has used this strategy to produce quasidiabatic MOs for the diabatization of potential energy surfaces.[33] In both cases, the attention was concentrated on the active MOs.

The present work proposes to use this idea to produce, after a preliminary definition of a CAS space containing the dominant physics of the excitation, the inactive orbitals (occupied and virtual) which have the largest contributions to the excitation energy. These orbitals may be calculated from a post-CASCI calculation of very moderate cost, such as the CAS + single CI. As illustrated on a series of examples, concerning the magnetic coupling and the electron transfer process in dinuclear complexes, the nature of the most implicated MOs is physically meaningful for the excitation involving changes (spin or charge) on the active remote sites. The most implicated MOs concentrate on the bridging ligands with significant tails on the external ligands. These MOs may be incorporated in a rationally enlarged CAS. Even when a moderate CI is performed on the top of this enlarged CAS (for instance, CAS + single CI) accurate values of the transition energies have been obtained.

An alternative use consists, oppositely, in freezing the least implicated occupied and virtual MOs. If a large CI from the minimal CAS, as a CAS-SDCI or a CAS-DDCI, is performed, the freezing of these nonparticipating MOs has negligible effect on the transition energy. As shown in the numerical examples a very large reduction of the computational effort is possible when using the difference-dedicated MOs. The present development concentrates on a particular transition involving two states. It is possible to consider independently a series of transitions $\Psi_m \rightarrow \Psi_n$ in a pairwise manner. If one prefers to calculate simultaneously a set of transitions from the lowest state $|\Psi_0 \rightarrow \Psi_m, m = 1, N\}$, it is possible to calculate

$$\langle\Psi_0|R|\Psi_0\rangle - \frac{\sum_{m=1,N}\langle\Psi_m|R|\Psi_m\rangle}{N} \qquad (9)$$

and its eigenvectors. Of course, the relevance of the so-obtained difference-dedicated MOs may be problematic, if the physical content of the various excited states is deeply different, and the pairwise procedure is recommended, Ψ_0 being calculated each time with transition-specific MOs.

This work shows that the consideration of eigenvectors of the difference between density matrices is both physically enlightening and practically efficient.

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