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Local Orbitals for the Truncation of Inactive Space: Application to Magnetic Systems

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A general strategy to reduce the size of the inactive space in extended Configuration Interaction calculations is presented. The approach is based on the use of local orbitals, obtained from a recently reported iterative method. Both occupied and virtual local orbitals are classified according to their topological nature. This criterion permits the elimination of all the orbitals centered on ligands distant from the “interaction area”. This truncation reduces the size of the inactive space considerably and makes feasible calculations otherwise impractical. The procedure is illustrated by the determination of the magnetic coupling constant in two binuclear Cu(II) compounds. The results show that it is possible to recover 95% of the magnetic coupling value with only 10% of the total CI space, pointing to the potentiality of the method. Additionally the local nature of the orbitals provides a way to control the physics of the coupling and to analyze the role of the external ligands in the interaction.

I. Introduction

In the past few years an increasing interest in magnetic systems has been observed, related to improvement of experimental techniques and also to the synthesis and discovery of compounds with interesting properties such as the colossal magnetoresistance present in the manganites[1] or the strong antiferromagnetism observed in the high-T_c superconductor related compounds.[2] From a theoretical point of view, evaluation of the magnetic coupling constants has also made important progress, passing from the qualitative evaluation of the amplitude of J in the 80’s[3−6] to the accurate quantitative determination of its value.[7−18] At this stage, the challenge is not to reproduce experimental data but to interpret and to predict the presence of these kinds of properties. An additional stimulus is going from the binuclear systems to polynuclear ones, which can show both magnetic and electron-transfer properties, as is the case of manganites, high-T_c superconductors, or polyoxometalates.

A general characteristic of these compounds is the presence of several unpaired electrons, distributed in some active orbitals. The ground state has a strong multireference character, and single determinant descriptions such as those reported by density functional theory based methods (DFT), although frequently used, are not really adequate. Among the multireference methods, the Difference Dedicated Configuration Interaction (DDCI) approach[19] has been extensively used recently to determine magnetic coupling constants. This method also has been employed to evaluate the electron-transfer integral t in mixed valence compounds.[11,20−22]

Most of the reported studies deal with the determination of J on binuclear systems. In this case, J can be extracted from the energy difference of the two lowest states of the system. It is also true for the determination of the electronic coupling between two *equivalent* centers. For polynuclear systems (except in the case of high symmetry[23]) and even in the case of the electron transfer between two nonequivalent centers, the DDCI approach must be combined with the effective Hamiltonian theory to evaluate J and t. Two recent examples of the use of this strategy concern the determination of the magnetic coupling and hopping integral between first, second, and third neighbors in hole-doped high-T_c superconductors[24] and the simultaneous evaluation of all the magnetic interactions present in a plaquette of different spin-ladder cuprates.[25]

The method has two limitations: (i) the number of active electrons and/or orbitals and (ii) the size and number of the external ligands. For instance, systems such as the iron−sulfur proteins, containing two or more Fe centers, with five unpaired electrons each (four in the case of mixed valence) are quite difficult to study with this methodology and with CAS-based methods such as CASPT2[26] or NOCI.[27] Indeed, in this situation, most of the references in the CAS carry little weight. Regarding the case of the coupling between two Fe(II) (d^5−d^5) centers, one would expect that all the configurations corresponding to d^{10}−d^0, d^9−d^1, or d^8−d^2 are too high in energy, and then practically would not participate in the description of the ground state. Therefore, it seems more appropriate (and cheaper!) to use a multireference space instead of a complete active space. To select the references a set of local molecular orbitals is necessary.

On the other hand, some approaches, such as the excitation energy dedicated molecular orbitals, have been proposed recently to reduce the number of inactive orbitals. This approach was applied to the evaluation of magnetic and electronic coupling constants.[28−30] These orbitals are the eigenvectors of the density matrix differences of the involved states, and their eigenvalues are related to the degree of participation of the orbital in the energy difference. The orbitals were selected in order of their number of participation, but due to their delocalized nature, it is quite difficult to analyze the physical contributions governing the observable under study.

The aim of this work is to present an alternative approach based on the use of local orbitals and to explore its capability as a tool to reduce the size of the CI expansion and also to

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analyze the physical nature of the magnetic interaction. In a recent work, we presented an iterative method to produce local orbitals in the presence of nondynamical correlation.[31] In such cases, a qualitatively correct description of the wave function requires the use of a Complete Active Space (CAS). Our algorithm is based on the repeated partial diagonalization of the one-electron density matrix obtained from a Single-excitation Configuration Interaction from a CAS space (CAS+S). In this way, a set of natural orbitals very close to the CASSCF orbitals is eventually obtained. The flexibility of the method rests on the possibility of using as reference space a reduced number of configurations instead of the complete active space, depending on the physics of the problem under study. These orbitals can be used for a subsequent CI treatment of the correlation, at both a CAS or a multireference (MR) level.

The method, which is completely general, will be applied here to the determination of the magnetic coupling constant in two systems, both concerning binuclear Cu(II) magnetic systems. Taking advantage of the local nature of the orbitals, it is possible to select the orbitals involved in the CI expansions, using a physical criterion, such as proximity to the active sites, or the orientation with respect to the Cu 3d active orbitals. It is also possible to isolate the most important contributions to J. So, local orbitals can be seen as a tool to analyze the physical factors governing the magnetic coupling.

The method is presented in Section II. The application of this methodology to the determination of the magnetic coupling constant in two binuclear Cu(II) compounds is reported in Section III. Finally, conclusions can be found in Section IV.

II. Theoretical Approaches

A. The Magnetic Coupling Constant and the DDCI Procedure. Magnetic systems are characterized by the presence of unpaired electrons, usually localized on the metal atoms. The properties of the system are governed by the interaction between these unpaired electrons on neighbor centers, which may be viewed as an effective interaction between site-centered spins, and mapped onto a Heisenberg−Dirac−Van Vleck Hamiltonian:[32]

$$\hat{H} = -\sum_{ij} J_{ij}\hat{S}_i\hat{S}_j \tag{1}$$

For two centers with spin $S_z = {}^1/_2$, as the case under consideration, the magnetic coupling constant is related to the energy difference between the singlet and the triplet states:

$$J = E(\mathrm{S}) - E(\mathrm{T}) \tag{2}$$

where J has a negative value if the system is antiferromagnetic (AF) and positive if the triplet is the ground state (ferromagnetic, F). At this point, the Difference Dedicated Configuration Interaction (DDCI) method[19] has been successfully applied recently to evaluate the magnetic coupling, both in molecular systems and in solid-state magnetic materials.[8−13] The key point of the method is that the determinants in the CI expansion have been selected by means of a perturbative criterion, over a reduced number of determinants, corresponding to all the single and double excitations contributing to the energy difference between the states involved in the excitation. This avoids the introduction of all the $(ij) \rightarrow (rs)$ double excitation, i, j being inactive occupied orbitals, and r, s being virtual orbitals, reducing considerably the calculation cost.

As mentioned above, when the complexity of the system increases, the spectrum is not sufficient to evaluate the magnetic coupling constants, and also the wave functions are necessary. In this case, the effective Hamiltonian theory enables us to combine the information contained in both the eigenvalues and the wave functions, and to extract the effective parameters.[23]

B. The Local Molecular Orbitals. Even when the DDCI approach permits an important reduction with respect to the CAS-SD expansion, it could be impracticable for systems containing a large number of electrons and/or orbitals. The object of the present work is to analyze the use of local orbitals as a tool to rationally truncate the inactive space. An iterative scheme to produce CASSCF or quasi-CASSCF orbitals that conserve the physical nature of the original guess orbitals has recently been proposed.[31,33] This procedure is based on an iterative partial diagonalization of the one-body reduced density matrix obtained from a CAS+S wave function. The method has been used to reduce the size of the Multi-Configuration (MC) space,[34] and to converge to a specific minimum among a set of different minima.[35] A brief description of the essential lines of the algorithm is given below.

As is usually done in CAS techniques, the orbitals were partitioned into three classes, i.e., occupied, active, and virtual orbitals. Starting from a CAS-CI wave function, the set CAS+S of single excitations is produced. Single excitations can be performed in two different ways, giving rise to two different variants of the method: (1) uncontracted excitations (i.e., determinants or spin-adapted configurations), obtained by applying the excitation operator $a_i^+ a_j$ (or a spin-adapted combination of excitation operators) to each determinant of the CAS, and (2) internally contracted excitations, obtained by acting with the excitation operator $a_i^+ a_j$ onto the function $|\Psi_{\mathrm{CAS}}\rangle$ as a whole.

A new wave function in the CAS+S space is produced at this point, either with a CI or a perturbational (PT) formalism. The one-body reduced density matrix Γ_1 associated with $|\Psi_{\mathrm{CAS+S}}\rangle$ is then computed. By diagonalizing Γ_1, a new set of orbitals is obtained that can be used to build a new CAS and a new $|\Psi_{\mathrm{CAS}}\rangle$ wave function. The procedure is then iterated until convergence (i.e., orbital or wave function stability) is achieved. If a contracted scheme is used, it can be shown that the final wave function is a CASSCF solution, since the Generalized Brillouin Theorem (GBT)[36,37] has been iteratively realized: the iterated-diagonalization convergence scheme is equivalent to the super-CI approach proposed by Ruedenberg and co-workers in the seventies to perform CASSCF.[38] Because of the GBT, the $|\Psi_{\mathrm{CAS+S}}\rangle$ wave function is identical, at convergence, with the $|\Psi_{\mathrm{CAS}}\rangle$ function, and the result is therefore not dependent on the procedure (CI or PT) used to produce the correction vector. On the other hand, if an uncontracted scheme is used, a set of iterated (approximated) Natural Orbitals (NO) is obtained at convergence, associated with the chosen CAS. It should be noted that in this case, contrary to the previous one, the final orbitals *depend* on the actual procedure used to produce $|\Psi_{\mathrm{CAS+S}}\rangle$ (CI or PT) and, in the case of PT, also on the particular form of PT that is adopted.

The previous scheme produces orbitals that are usually highly delocalized, and that do not have a strong similarity to the initial orbitals. This is because the diagonalization step completely mixes the orbitals within each class. However, one must remember that the whole formalism is invariant under a unitary transformation of the orbitals, which does not mix the orbitals belonging to different classes among themselves. Therefore, it is possible to perform only a *partial diagonalization* of Γ_1, in such a way that this matrix is put into a block-diagonal form, each block being defined by the occupied, active, and virtual

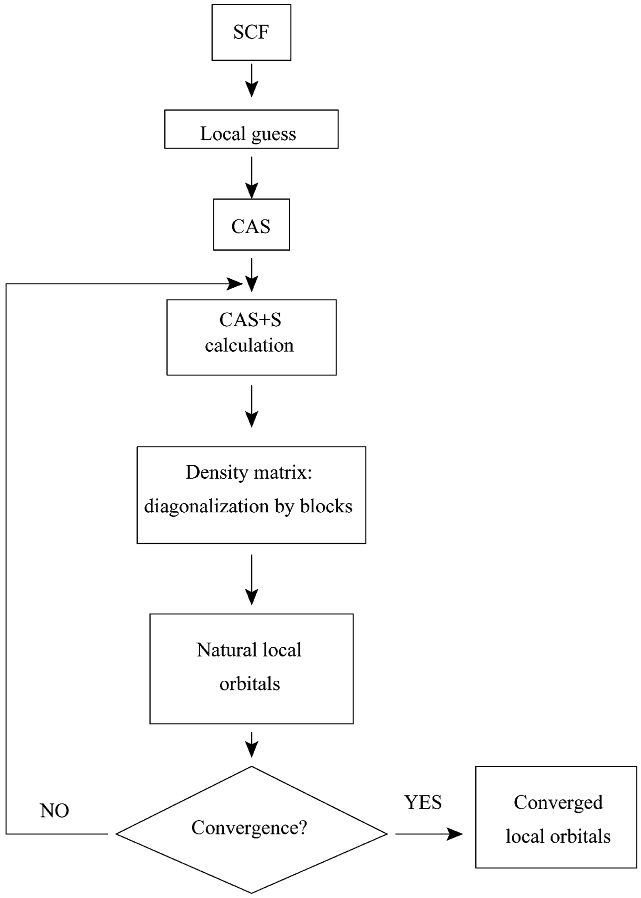

Figure 1. The iterative procedure for obtaining the local orbital set.

orbitals, as in standard CASSCF calculations. In this way, by taking advantage of the unitary invariance of the CASSCF wave function with respect to orbital rotations that are internal to each orbital class, the mixing between the orbitals can be minimized at each iteration. As a result, the orbitals at convergence maintain as far as possible the same nature as the initial orbitals (Figure 1). So, there are two key points: (i) the partial diagonalization that conserves the initial locality of the orbitals and (ii) the definition of the guess of the local orbitals. This *nonautomatic* step requieres a previous knowledge of the basic chemical aspects of the system under study. More details can be found in ref 31.

This formalism is particularly suited to obtain local orbitals in a MR context, a fact that presents a particular interest in reducing the computational effort in the treatment of quasidegenerate systems.[39] At the moment two versions exist: an uncontracted one, based on a CI approach,[31] and a contracted perturbative version.[33] The two versions give extremely similar results, the energy differences being of the order of a fraction of a millihartree for all the systems studied so far.

C. Truncation of the Inactive Space. As mentioned above, the goal of the present work is to take advantage of the local nature of the orbitals to reduce the size of the inactive space. The local orbital set is obtained from low-cost low-level calculations (no more than 20% of the total cost), as discussed in the previous section. The orbitals are then classified according to a topological criterion. All the orbitals external to the "interaction area" are frozen (both occupied and virtuals), and a high-level calculation is now feasible, obtaining accurate values of the observable under study. It is also possible to analyze the role played by a certain ligand, by freezing only those orbitals centered on it. The examples considered here refer to the determination of the magnetic coupling constant in binuclear Cu(II) compounds, but it is a completely general strategy to deal with problems that are usually size-constrained.

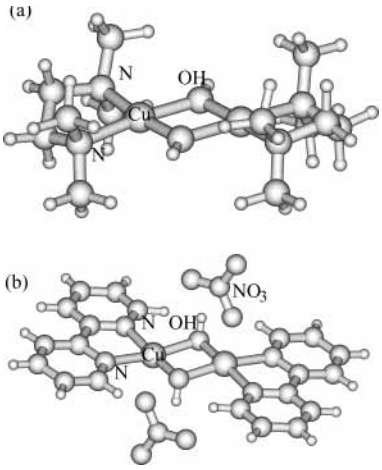

Figure 2. The two μ-hydroxo-bridged Cu(II) complexes under consideration: (a) $[\mathrm{Cu(tmeen)OH}]_2\mathrm{Br}_2$, system A (bromide ions are not included), and (b) $[\mathrm{Cu(bipy)OH}]_2(\mathrm{NO}_3)_2$, system B.

III. Application to Hydroxo-Bridged Cu(II) Binuclear Complexes

To illustrate the procedure, two binuclear Cu(II) complexes with large external ligands have been chosen. There is only one unpaired electron per metallic center, and the J constant can be obtained from the energy difference of the singlet and the triplet states, as shown in eq 2. The procedure is not constrained either to systems with $S_z = {}^{1}/_{2}$ per center or to binuclear complexes. Dealing with binuclear systems with more than one unpaired electron per center, the problem reduces to the calculation of the energies of the corresponding spin functions. For instance, the coupling between two Ni(II) ions in a binuclear complex gives three states (singlet (S), triplet (T), and quintet (Q)). J can be evaluated from the energy difference between two of them: $J = E(\mathrm{S}) - E(\mathrm{T}) = (E(\mathrm{T}) - E(\mathrm{Q}))/2$. Some examples using the DDCI methodology for the determination of J in this kind of systems can be found in recent papers (see, for instance, ref 13). For polynuclear systems, the strategy is still applicable. The extraction of the magnetic coupling constants will be in general more complicated, being necessary the use of the effective Hamiltonian theory.[24,25] It is expected that the truncation of the inactive space by means of the locality criterium has a larger impact in this kind of compounds, which are, in general, too large for a complete extended CI calculation.

A. System Description. Two μ-hydroxo-bridged Cu(II) binuclear complexes have been considered: (i) system A, $[\mathrm{Cu(tmeen)OH}]_2\mathrm{Br}_2$, tmeen = tetramethylethylenediamine, which presents an antiferromagnetic coupling of $-509\ \mathrm{cm}^{-1}$,[40] and (ii) system B, $[\mathrm{Cu(bipy)OH}]_2(\mathrm{NO}_3)_2$, bipy = bipyridine, which has a ferromagnetic coupling of $+172\ \mathrm{cm}^{-1}$.[41] Both of them have been previously studied by means of density functional theory based calculations by Ruiz and co-workers.[16,42] Figure 2 shows a representation of these two compounds. The experimental geometries have been used in both cases.[40,41] In system A, the Cu atoms present a square-planar coordination. The Cu−N, Cu−OH, and Cu−Br distances are respectively 2.03, 1.90, and 4.79 Å, and the Cu−O−Cu angle is 104.1°. In system B, the distance between the N atoms of the bidentate bipyridine ligand and the Cu atom is 2.00 and 1.92 Å for the Cu−OH distance. The Cu−O−Cu angle here is 95.6°. In

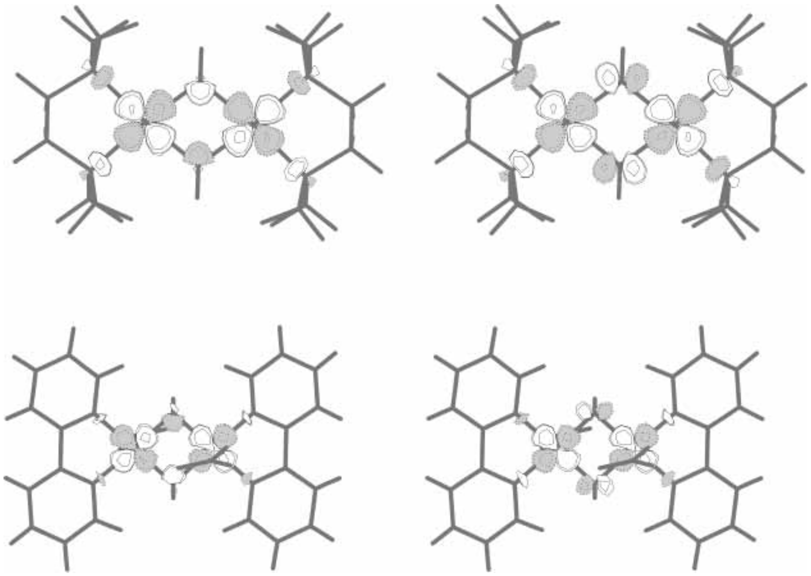

Figure 3. Magnetic active orbitals for system A (on the top) and system B (on the bottom).

contrast to system B, the H atoms of the hydroxo bridges are not in the same plane as the Cu−O−Cu fragment, the out-of-plane H shift being 54°. The out-of-plane displacement of the hydrogen atoms seems to favor the ferromagnetic character of the interaction, as some recent magnetostructural studies have shown.[16,43,44] With regards to the counterion, the distance between one of the oxygen atoms of the nitrate group and the Cu center is 2.38 Å, and the counterion can be considered as an axial ligand, resulting in a square-pyramidal coordination around the Cu centers. For this reason the nitrate groups have been explicitly included in all the calculations.

Different basis sets have been tried out. In all cases the 12 most internal electrons of the Cu atoms have been replaced by the pseudopotentials proposed by Barandiarán and Seijo.[45] Basis I consists of a double-ζ basis set for the Cu atoms[45] (contraction (9s6p6d)/[2s2p2d]), and the ANO-type minimal basis sets for the rest of the atoms[46] (C, O, N: (2s1p), H:(1s)). Basis II is equal to Basis I, except that the contraction employed for O bridge atoms is (3s2p1d) instead of (2s1p). For Basis III, the contraction for the Cu atoms is now (9s6p6d)/[3s3p3d], (3s2p1d) for O and N atoms and (2s1p) for the H of the hydroxo group. The MOLCAS 5.0[47] package has been used to generate the guess orbitals and to evaluate the atomic integrals. SCHMUDORB[48] and CASDI[49] codes have been employed respectively to produce the local set and to perform the diagonalization of the CI matrices.

B. Strategy to Reduce the Space. The procedure starts by establishing the reference value of the magnetic coupling in both systems. We consider that the value provided by the DDCI calculations on the basis of the symmetry-adapted delocalized molecular orbitals is the best available benchmark. In all the calculations the active space is composed of the symmetric (g) and antisymmetric (u) combinations of the d_{xy} Cu orbitals, with a minor contribution coming from the OH bridging groups (Figure 3). The CAS space contains four determinants: $|g\bar{g}\rangle$, $|u\bar{u}\rangle$, $|g\bar{u}\rangle$, and $|u\bar{g}\rangle$. The singlet and triplet wave functions and energies have been obtained from extended CI calculations on the top of this CAS space, J being the energy difference between these two states. Table 1 presents the results concerning system A with a minimal basis set. Two sets of symmetry-adapted delocalized orbitals have been considered: those coming from the triplet state and those obtained from the average of the density matrices of the singlet and triplet states. Regarding the CI expansion, two types of calculations have been performed: (i) CAS+S, with the CI expansion only including all the single-excitations on the top of the determinants of the CAS, and (ii) CAS+DDCI, with all the single and double excitations, except those involving two *holes* (two inactive occupied orbitals) and two *particles* (two inactive virtual orbitals). As has also been reported for other Cu(II) binuclear systems[50] the values obtained for the magnetic coupling are independent of the set of delocalized orbitals, at any level of calculation. With regard to the local orbitals, three sets have been generated, in all cases by means of the uncontracted variational CI version of the localization code: local orbitals (i) from the singlet state, (ii) from the triplet state, and (iii) from the average of the density matrices of the singlet and triplet states. The results are in good agreement with those obtained from delocalized orbitals, independently of the type of local orbitals used and the calculation level.

TABLE 1: Comparison between the Local Set and Delocalized Set for [Cu(tmeen)OH]$_2$Br$_2$, System A, with Minimal Basis Sets (Basis I)[a]

	CAS+S	CAS+DDCI
delocalized, T	−88	−339
delocalized, average S + T	−94	−334
local, T	−88	−324
local, S	−98	−332
local, average S + T	−94	−330

[a] All values in cm^{-1}.

Now the local orbitals are classified according to their nature. For system A (Figure 4), we can distinguish, for instance, the C−H bonds of the CH$_3$ groups, the C−H bonds of the CH$_2$ fragments, and the N−C bonds, where C belongs to the CH$_3$ groups or C is part of the N−C−C−N skeleton. Figure 5 shows some of the local orbitals for system B: the π-type orbitals, the C−H bond orbitals, the C−C in the bipyridine groups, and the orbitals located at the NO$_3$ groups. One may notice that, due to the fact that localization does not forbid the use of the symmetry, what we call local orbitals actually appear on the various equivalent bonds (two or four bonds), and are therefore not really local. Two comments must be made: (i) The relevant locality in our problem is the nature and distance of the local orbitals to the active part of the system. The fact that these orbitals (to be frozen) appear in several places has no consequence. (ii) By symmetric and antisymmetric combinations of

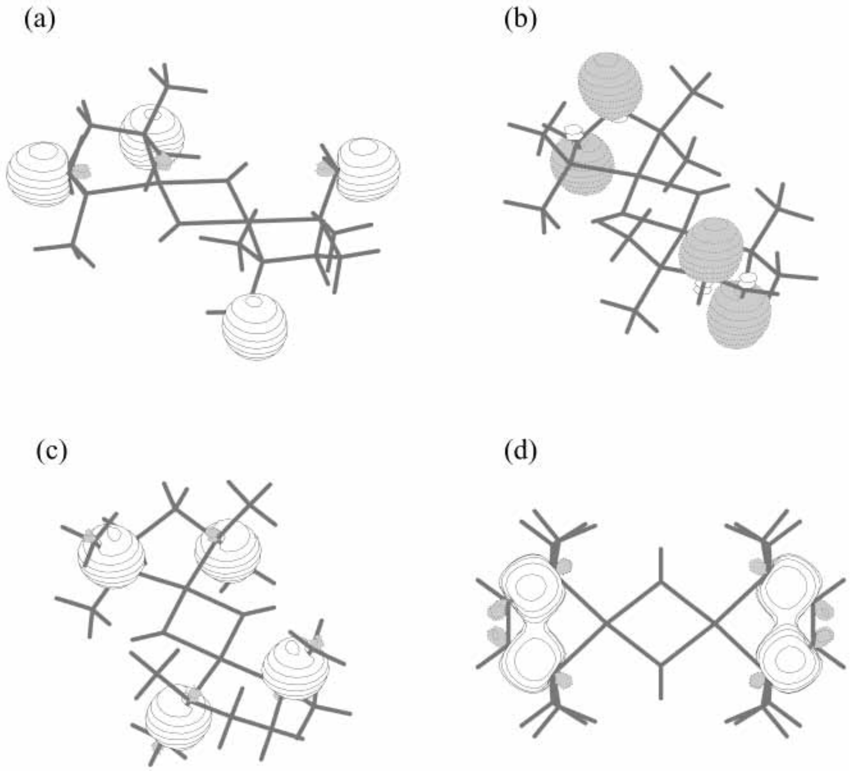

Figure 4. Localized orbitals for system A, minimal basis sets: (a) C−H bonding orbital for CH_3 groups, (b) C−H bonding orbital for CH_2 groups, (c) N−C bonding orbital for N−CH_3 bonds, and (d) N−C bonding orbital for the N−C−C−N skeleton.

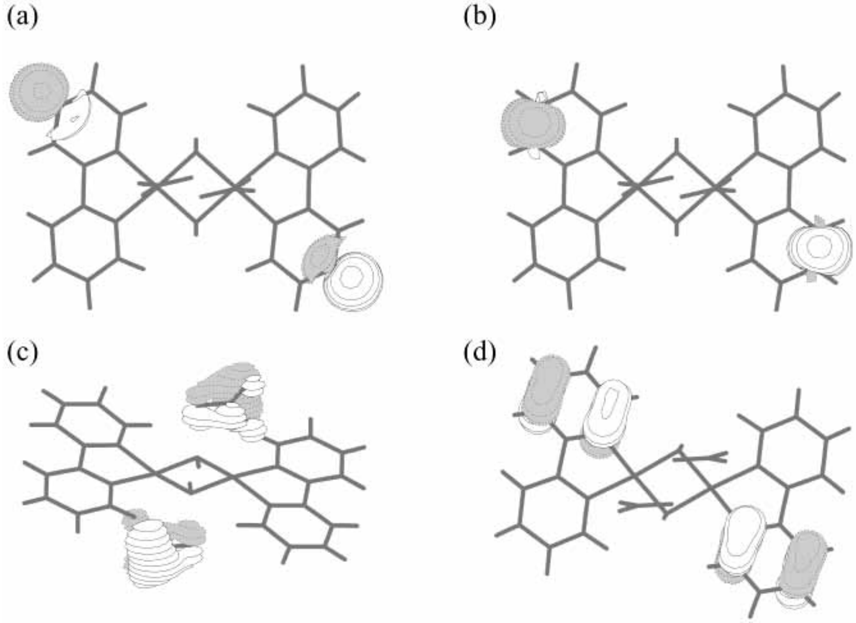

Figure 5. Localized orbitals for system B, minimal basis sets: (a) C−H bonding orbital in bipyridine ligands, (b) C−C bonding orbitals, (c) nitrate group local orbitals, and (d) π-type orbitals in the bipyridine ligands.

these “symmetrical local orbitals”, one would perfectly recover local orbitals, i.e., appearing only at one place in the molecule. Therefore, even if the calculations were done by using the symmetry of the molecule, no information concerning the shape of the local orbitals has been lost.

In the next step, we perform several CAS+DDCI calculations, hereafter referred to as DDCI, freezing in each case a different type of local orbital. Only the values obtained from the average local set are reported. The results (Table 2 and Figure 6 for system A (Basis I), and Table 3 and Figure 6 for system B (Basis II)) show that it is possible to deal with a small fraction of the CI space, recovering at least 90% of the total value of J. For instance, in system A, by freezing all the occupied C−H bonding orbitals 98.5% of the J value is obtained, with only 51% of the original CI space. If the virtual orbitals centered on these bonds are also eliminated, the size of the matrices diagonalized in the CI procedure is only 20% of the original, but the value of J is practically not affected (95% of the total value). By using this topological criterion it is possible to neglect all the orbitals (occupied and virtuals) centered on the N−C and C−H bonds, reducing the CI space to 8% of the complete space, obtaining a J value of -288 cm^{-1}, 87% of the total value.

TABLE 2: Effect of the Truncation of the Average Singlet−Triplet Local Orbital Set on the *J* Value (in cm^{-1}) for [Cu(tmeen)OH]$_2$Br$_2$ (System A), Using the Nature of These Orbitals as Criterion[a]

	% space	*J*	% *J*
complete set	100	−330	100
DDCI space: 1 463 134 det			
frozen occ			
−CH$_3$	62	−332	100
−CH$_3$ and −CH$_2$	51.5	−325	98.5
−CH$_3$, −CH$_2$, and −N−CH$_3$	42	−315	95.4
−CH$_3$, −CH$_2$, −N−CH$_3$, and N−CC−N	37	−311	94.2
frozen occ + vir			
−CH$_3$	33	−321	97.3
−CH$_3$ and −CH$_2$	20	−313	94.8
−CH$_3$, −CH$_2$, and −N−CH$_3$	11	−297	90
−CH$_3$, −CH$_2$, −N−CH$_3$, and N−CC−N	8	−288	87.3

[a] Calculations performed at the DDCI level with minimal basis sets (basis I). See also Figure 6.

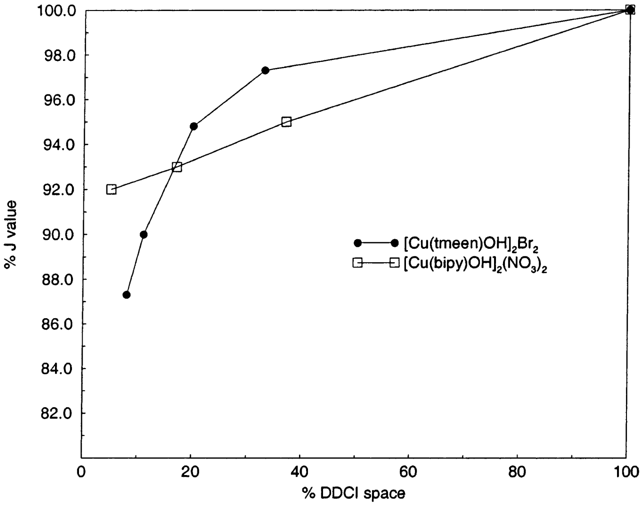

Figure 6. Effect of the truncation of the space on the *J* value for (a) [Cu(tmeen)OH]$_2$Br$_2$, system A (dots), and (b) [Cu(bipy)OH]$_2$(NO$_3$)$_2$, system B (square), both with minimal basis sets.

TABLE 3: Effect of the Truncation of the Average Singlet−Triplet Local Orbital Set on the *J* Value (in cm^{-1}) for [Cu(bipy)OH]$_2$(NO$_3$)$_2$ (System B), Using the Nature of These Orbitals as Criterion[a]

	% space	*J*	% *J*
complete set delocalized		+138	
complete set local	100	+113	100
DDCI space: 6 037 994 det			
frozen occ + vir			
−π, −CH, and 1s	37	+107	95
−π, −CH, −NO$_3$, and 1s	17	+105	93
−π, −CH, −NO$_3$, C−C, and 1s	5	+104	92

[a] Calculations performed at the DDCI level with minimal basis sets (basis II). See also Figure 6.

These results can be improved also by freezing the 1s *core* orbitals. A similar trend is observed for system B (Table 3 and Figure 6). The elimination of all the orbitals with a π-type nature centered on the bipyridine ligand, together with the C−H bonding orbitals and the 1s *core* orbitals, produces a CI space with only 37% of the size of the complete space, but giving 95% of the *J* value. If the orbitals centered on the nitrate groups and the C−C orbitals are also eliminated, the space is just 5% of the total, but the *J* value is still 92% of the total value.

C. Extended Basis Sets. The method at this point seems quite promising, but the results are just qualitative. A quantitative agreement with the experimental values can be obtained by extending the basis sets of the atoms, especially those in the *interaction region*, that is, Cu, OH, and N atoms. Table 4 and Figure 7 correspond to the results obtained after the truncation of the triplet local set for system A with use of Basis III. The improvement of the basis produces a good agreement with the experimental value of the magnetic coupling constant (−509 cm^{-1}) for this system. The size of the complete CI space with use of the extended basis sets is of 4 783 286 determinants. Using the locality of the orbitals as freezing criterion it is possible to recover 93% of the *J* value with only 12% of the total space. As can be seen, elimination of only the methyl groups produces a reduction of 50% in the size of the space without affecting the magnetic coupling constant value. The same behavior is found for system B, as shown in Table 5 and Figure 7. When the basis sets are improved, a quantitative agreement with the experimental data is obtained. In this case, the use of the local orbitals permits the reduction of the CI space up to 7.5% of the initial space, recovering 96.5% of the total value of *J*.

TABLE 4: Effect of the Truncation of the Triplet Local Orbital Set on the *J* Value (in cm^{-1}) for [Cu(tmeen)OH]$_2$Br$_2$ (System A), with Extended Basis Sets (Basis III) at the DDCI Level (See Figure 7)[a]

	% space	*J*	% *J*
exptl value		−509	
complete set delocalized		−500	
complete set local	100	−508	100
DDCI space: 4 783 286 det			
occ + vir			
−CH$_3$	49	−504	99
−CH$_3$ and −CH$_2$	37	−494	97
−CH$_3$, −CH$_2$, and −N−CH$_3$	27	−480	94
−CH$_3$, −CH$_2$, −N−CH$_3$, and −N−C1	23	−471	93
−CH$_3$, −CH$_2$, −N−CH$_3$, −N−C1, and C1−C1	21	−472	93
−CH$_3$, −CH$_2$, −N−CH$_3$, −N−C1, C1−C1, and 1s	12	−473	93

[a] Carbon atom C1 belongs to the N−C−C−N skeleton.

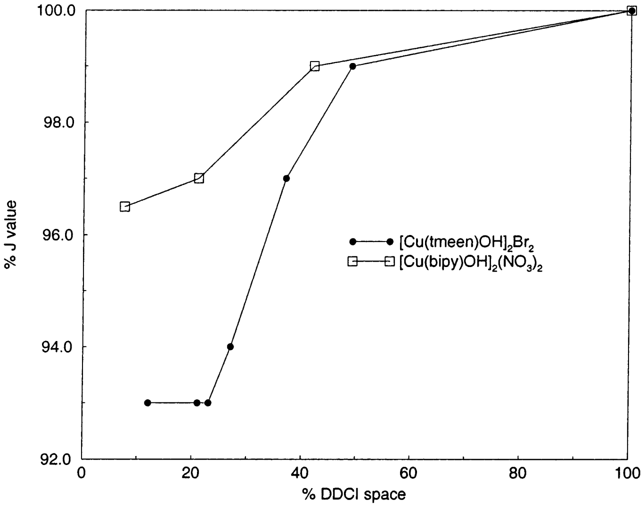

Figure 7. Effect of the truncation of the space on the *J* value for (a) [Cu(tmeen)OH]$_2$Br$_2$, system A (dots), and (b) [Cu(bipy)OH]$_2$(NO$_3$)$_2$, system B (square), both with extended basis sets.

D. Analysis of the Physical Factors. Another potential of the method is the analysis of the factor governing the coupling. In a recent work it was shown that most of the contributions to *J* come from those orbitals placed in the bridging ligands and in the nearest neighborhood of the *interaction region*.[51] Among the excitations included in the DDCI space, those contributing the most to the coupling are those involving a ligand (*l*) to metal

TABLE 5: Effect of the Truncation of the Triplet Local Orbital Set on the J Value (in cm^{-1}) for $[Cu(bipy)OH]_2(NO_3)_2$ (System B), with the Extended Basis Sets (Basis III) at the DDCI Level (See Figure 7)

	% space	J	% J
exptl value:		+172	
complete set delocalized		+159	
complete set local	100	+173	100
DDCI space: 8 555 912 det			
frozen occ + vir			
$-\pi$, $-$CH and 1s	42	+171	99
$-\pi$, $-$CH, $-NO_3$, and 1s	21	+168	97
$-\pi$, $-$CH, $-NO_3$, C$-$C, and 1s	7.5	+167	96.5

(*a* or *b*, the magnetic centers) excitation coupled with a polarization of the electrons of the environment (*h*(hole, occupied) → *p*(particle, virtual)). Also the excitations where a metal-to-ligand excitation is coupled with the polarization of the environment are important. In both cases, to obtain large contributions, the three inactive orbitals, *l*, *h*, and *p* must be centered on the bridging ligands or in atoms not distant from the magnetic centers.

Taking advantage of the localizing procedure, we eliminated all the inactive orbitals placed on the OH bridging ligands. (Notice that the active orbitals present a certain mixing with the OH groups.) For system A, the resulting CI space contains 3 984 498 determinants (83% of the complete space), but the value of J is just -176 cm^{-1}. That shows the different role played by the external and the bridging ligands (the freezing of the CH_3 groups, for instance, produces a space smaller than this one, but the effect on J is negligible). If the inactive occupied orbitals centered on the N atoms oriented toward the Cu centers are also eliminated, the magnetic coupling diminishes again up to a value of -130 cm^{-1}. A similar behavior is found for system B, where the elimination of all the orbitals placed in the OH ligands and the orbitals centered on the N atoms oriented toward the Cu centers (the size of the CI space is 81% of the complete space) gives a value of J of $+30$ cm^{-1}, to be compared to the value of $+173$ cm^{-1} obtained with the complete space.

Finally, we conclude that due to the local character of the interaction, the external ligands play no role in the process, the most important contributions coming from the bridging ligands and the nearest atoms to the magnetic centers. However, some studies based on the density functional theory have found an important effect on the J value depending on the external ligands.[52,53] Probably, these effects can be considered as an artifact due to the highly delocalized nature of the magnetic orbitals in the DFT calculations, completely spread over the whole system.[50]

IV. Conclusions

Two μ-hydroxo bridged Cu(II) binuclear complexes were considered to illustrate the use of the local orbitals as a tool to rationally truncate the inactive space in extended CI calculations. The procedure can be considered as an alternative to the energy excitation dedicated molecular orbitals. The strategy, here employed to reduce the computational cost in the determination of the magnetic coupling constants, is completely general and can be a powerful instrument in those cases where a complete high-level calculation is not practical. It could be useful, for instance, in large systems where only a small fraction of them are directly involved in the process under study. In this case, it is possible to design a strategy where a set of local orbitals is obtained from low-level calculations (available even for large systems), the orbitals located at the inactive regions will be frozen, and only those regions involved in the process will be treated in high-level calculations. In this sense, the procedure could permit one to deal with systems usually reserved to the density functional theory-based methods.

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