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Ab Initio CI Determination of the Exchange Coupling Constant of Doubly-Bridged Nickel(II) Dimers

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Ab initio DDCI2 (difference-dedicated configuration interaction) calculations are performed on the exchange coupling constant of the doubly-bridged Ni(II) complexes $[Ni(en)_2Cl]_2^{2+}$ and $[Ni(terpy)(N_3)]_2^{2+}$, which are modeled by substituting the external ligands with ammonia groups. The variational CI space is selected on the grounds of the effective Hamiltonian theory and includes all the second-order contributions to the difference between the lowest quintet, triplet, and singlet states. Both complexes are found to be ferromagnetic, with coupling constants of 1.8 and 21.1 cm^{-1}, in good agreement with the experiment. A transformation of the molecular orbitals is also proposed for large systems, enabling the molecular orbital set to be significantly truncated—as well as the file of two-electron integrals and the DDCI2 space—with no loss of efficiency.

1. Introduction

Weak interactions in polynuclear metal systems with unpaired electrons leading to small energy splittings and their ferromagnetic or antiferromagnetic character have been widely studied in recent years. Biradical systems such as some Cu(II) (d^9) dimer complexes, with carboxylate, hydroxo, or halide bridges,[1] are simple examples, with one well-localized unpaired electron on each metal center, resulting in a small singlet−triplet energy gap, the sign of which depends on the ligands and on the metal coordination among other factors. Several bridged binuclear complexes of a more complex electronic structure have also been synthesized and their magnetic behaviors analyzed in the last two decades. Dimers with Ni(II) (d^8),[2−4] V(III) (d^2), and Cr(III) (d^3)[5] have been described, as well as some polynuclear complexes.[6] Most of these complexes are antiferromagnetic.

The spin interaction in these systems is usually described using the phenomenological Heisenberg Hamiltonian

$$H_{ex} = -2\sum_{i<j} J_{ij} S_i S_j$$

where S_i, S_j are local total spin operators and J_{ij} the exchange parameters. The summation may in general be limited to the pairs of nearest neighbors. The energy levels are thus expressed as functions of the exchange parameters, and by a fit of the magnetic susceptibility versus the temperature curve, the exchange parameters are evaluated from the experiment. A negative value of the coupling constant indicates antiferromagnetic coupling and has been attributed by Anderson[7] to indirect coupling through the bridge ligands or a superexchange mechanism. For dimers with total spin S_1 at each magnetic center, the possible states have total spin $S = 0, 1, ..., 2S_1$ and the difference between energy levels is given by

$$E(S) - E(S-1) = -2JS$$

From a quantum chemical point of view, in an early work Hay et al.[8] presented a semiquantitative approach to the exchange coupling in copper dimers which was based on an orbital analysis. Although successful qualitative predictions have been made from this method or related ones,[9] nonempirical calculations are needed to obtain quantitative estimations, especially for systems such as Ni(II) or Cr(III) complexes, since the complexity of the electronic structure and of the prediction of magnetic properties quickly increases with the number of unpaired electrons on the metal center as well as with the number of paramagnetic centers.

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A few quantitative approaches to the problem have been proposed. Noodleman[10] developed a formalism based on unrestricted Hartree−Fock (UHF) broken-symmetry calculations, which was applied to polynuclear sulfur-bridged iron complexes.[11] Doubly-chloride-bridged copper dimers[12] and oxo-bridged titanium dimers[13] have also been studied using the same procedure. A second-order perturbative development of the CI expansion was proposed by de Loth et al.[14] for biradical systems, and it was applied to several bridged copper dimers[15] with little computational effort. Although there was good agreement in most cases, some important higher order effects appeared to be neglected. On the basis of the same perturbative considerations, we recently presented a variational method for the *ab initio* calculation of the exchange coupling constant of biradical systems. When this method was applied to dihalide-bridged copper dimers[16,17] or to nitroxide biradicals,[18] a good quantitative agreement with experimental results was obtained. The method, which was recently generalized to apply to magnetic exchange interactions in polynuclear systems[19] is based on the definition of a minimal model space. In the framework of the quasi-degenerate perturbation theory, a set of determinants contributing to the energy splitting is then established on the basis of a second-order development of the corresponding effective Hamiltonian. This set of determinants is then treated variationally. The model space in these magnetic problems is a subspace of the complete active space (CAS) generated by the *n* unpaired electrons in *n* orbitals, and the determination of the exchange coupling can be considered as a particular case of the more general scheme of specific CI for determining energy differences[20] that we have called the difference-dedicated configuration interaction (DDCI) method. Since some additional restrictions appear in the exchange coupling treatment, we have labeled this particular CI as DDCI2. The method will be briefly reviewed in section 2.

Ab initio CI calculations of superexchange coupling on systems with more than two unpaired electrons are rather scarce. Very recently, multireference coupled electron pair approximation (MR-CEPA) calculations on oxygen-bridged binuclear complexes of Ni(II)[21] and of Ti(III), V(III), and Cr(III)[22] were reported. The aim of the present study is to show the efficiency of the DDCI2 method in two Ni(II) dimers, with the representative bridging ligand chloride or azide in the end-on coordination mode. Ferromagnetic interactions prevail in these complexes, while with other types of bridges such as oxalate[4j,k] or squarate[4l] the interaction is antiferromagnetic. The exchange coupling constants of two doubly-bridged complexes have been determined: the bis(μ-chloro) complex $[Ni(NH_3)_4Cl]_2^{2+}$ (**1a**) (Figure 1) and the bis(μ-azido) complex $[Ni(NH_3)_4(N_3)]_2^{2+}$ (**2a**) (Figure 2). These two complexes reproduce the experimental geometry of the Ni_2X_2 core (X being the bridging ligand halide or azide) of the complexes $[Ni(en)_2Cl]_2^{2+}$ (**1b**)[2] and $[Ni(terpy)(N_3)]_2^{2+}$ (**2b**),[3] and the external ligands have been replaced by NH_3 groups. The aim of these calculations is to prove that the methodology used is able to produce close agreement with experimental results and therefore may be used to predict the trend of the coupling in unknown systems.

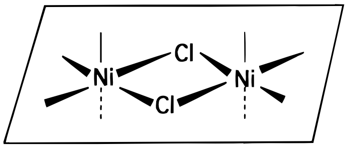

Figure 1. Simplified geometry of the complex $[Ni(NH_3)_4Cl]_2^{2+}$ (**1a**).

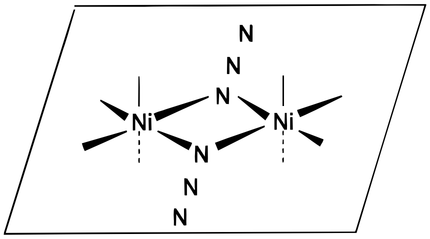

Figure 2. Simplified geometry of the complex $[Ni(NH_3)_4(N_3)]_2^{2+}$ (**2a**).

Although the size of the DDCI2 space increases only with the square of the size of the atomic basis set, when the number of unpaired electrons rises, the DDCI2 space can increase considerably, depending on the symmetry point group of the molecule and on the size of the basis set. On the other hand, if we want to calculate the exchange coupling in complexes with a higher number of magnetic centers, the full transformation of the atomic two-electron integrals to molecular integrals can exceed storage capabilities. The MO set has to be truncated to solve both problems. Natural orbitals (NO) have been extensively used as a rational way of performing this truncation in order to concentrate the CI expansion. Following the same strategy, in previous works[16,23] we have described a perturbative method to obtain observable-dedicated MOs (DMOs) that has proved to be efficient. In section 3, we will extend this procedure to obtain exchange coupling dedicated MOs (EC-DMOs), which will permit the magnetic exchange coupling to be calculated in systems with extended ligands or with a high number of unpaired electrons.

The results for the two Ni(II) model dimers $[Ni(NH_3)_4Cl]_2^{2+}$ (**1a**) and $[Ni(NH_3)_4(N_3)]_2^{2+}$ (**2a**) are reported in section 4. The efficiency of both combined methods, DDCI2 and the transformation into exchange coupling dedicated orbitals, is shown. Some concluding remarks are given in section 5.

2. The DDCI2 Method To Evaluate the Exchange Coupling Constant

The DDCI2 method was first derived to evaluate singlet-triplet (S−T) gaps in biradical systems and was then generalized for problems with *n* unpaired electrons in *n* orbitals. If a, b, c, d, ... are the singly-occupied orbitals, the corresponding space configuration may be written as [core]abcd.... The determinants

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$\{\Phi_I\}$ belonging to the configuration only differ in their spin distribution. Their number is $\binom{n}{n/2}$ if n is even. For four electrons, for instance, there are six determinants:

$$|\mathrm{ab\bar{c}\bar{d}}|,\ |\mathrm{a\bar{b}c\bar{d}}|,\ |\mathrm{\bar{a}bc\bar{d}}|,\ |\mathrm{a\bar{b}\bar{c}d}|,\ |\mathrm{\bar{a}b\bar{c}d}|,\ |\mathrm{\bar{a}\bar{b}cd}|$$

These six neutral valence bond determinants generate a model space, S, which is a subspace of the (4,4) CAS. The spectrum of the magnetic states may be obtained by diagonalizing the effective Hamiltonian built on that model space. In the framework of the quasi-degenerate perturbation theory at the second-order level, the elements of the effective Hamiltonian may be written

$$\langle\Phi_I|H_{\mathrm{eff}}^{(2)}|\Phi_J\rangle = \langle\Phi_I|H|\Phi_J\rangle + \sum_{\Phi_\alpha \notin S} \frac{\langle\Phi_I|H|\Phi_\alpha\rangle\langle\Phi_\alpha|H|\Phi_J\rangle}{E_J^0 - E_\alpha^0}$$

When the off-diagonal terms $\langle\Phi_I|H_{\mathrm{eff}}^{(2)}|\Phi_J\rangle$ are considered, Φ_I and Φ_J necessarily differ by at least two spin orbitals. The determinants $\{\Phi_\alpha\}$ which are obtained by a single-excitation or a double-excitation process interact with both Φ_I and Φ_J and may at most involve two degrees of freedom, i.e. two inactive occupied MOs p and q, $\Phi_\alpha = D^{+}_{pq\rightarrow ab}|\Phi_I\rangle$, two inactive virtual MOs i and j, $\Phi_\alpha = D^{+}_{ab\rightarrow ij}|\Phi_I\rangle$, or one occupied and one virtual inactive MO, $\Phi_\alpha = D^{+}_{pa\rightarrow bj}|\Phi_I\rangle$.

As far as the diagonal elements are concerned, it has been proved[19] that all substitutions involving more than two inactive MOs simply shift all the energies by the same amount, provided that for the zeroth-order Hamiltonian H^0

$$H^0 = \sum_{I \in S} E_I^0 |\Phi_I\rangle\langle\Phi_I| + \sum_{\alpha \notin S} E_\alpha^0 |\Phi_\alpha\rangle\langle\Phi_\alpha|$$

a Møller−Plesset type definition is chosen.

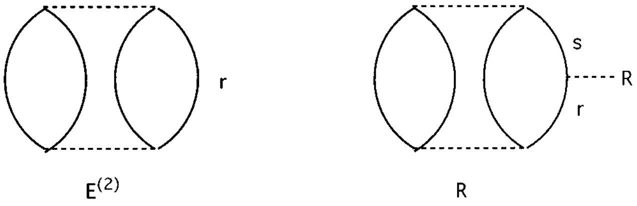
The generators and the set of excited determinants interacting with them, involving at least two active MOs, define a CI space, and instead of using the perturbative development, this space may be diagonalized to incorporate higher order effects and to avoid the problem of intruder states. In order to make this CI space invariant under rotations of the MO set, the model space should be extended to the CAS and all the excited determinants obtained from the CAS by single and double substitutions involving at most two inactive orbitals (occupied or virtual) should be included in the CI space. This extension adds a few determinants which are not strictly necessary for the calculation of the second-order effective Hamiltonian, but it ensures the invariance of the DDCI2 space and therefore enables us to work with symmetry-adapted MOs, which reduces the file of two-electron integrals as well as the dimension of the DDCI2 space. The value of the coupling constant is given by the difference between two roots.

The physical effects that are considered in the DDCI2 treatment include all the effects up to the second order as discussed by de Loth et al.:[14,15] potential exchange, kinetic exchange, dynamic spin polarization, and charge transfer, as well as polarization of the ionic forms. The variational treatment, however, introduces higher order effects, among which are the contributions enabling the relaxation of the ionic forms that appear at the fourth order.

The number of the determinants in the DDCI2 space is proportional to $Mn_o^2n_v^2$, where M is the number of the determinants of the CAS, n_o is the number of inactive occupied MOs, and n_v is the number of inactive virtual MOs. While the number of active electrons remains small, the size of the DDCI2 space remains manageable, since it only increases with the square of the basis set dimension. But with increasing numbers of unpaired electrons, the size of the DDCI2 space may become too large. Moreover, the file of two-electron integrals may also become very large depending on the ligands. In order to work within manageable CI space sizes as well as the file of molecular integrals, it may be desirable to truncate the MO set.

3. Truncation of the Set of Molecular Orbitals: Exchange Coupling Dedicated Molecular Orbitals

It is well-known that SCF MOs are an inadequate starting point for making good estimations of the correlation energy when the MO set has to be truncated, since ordering the orbitals according to their eigenvalues is not a good criterion, particularly for virtual MOs, to estimate their contribution to the correlation energy. Less arbitrary choices, such as natural orbitals (NOs), are needed for this purpose. Ever since Löwdin's proposal long ago,[24] they have constantly proved their usefulness. There are many possible ways of obtaining NOs, and of these, a low-order perturbative construction of the one-particle density matrix is a simple and inexpensive technique.[25] By using a diagrammatic representation, the elements of the density matrix are obtained from the second-order diagrams of the correlation energy by introducing an interaction line with the $R = a_s^+a_r$ operator on the propagation lines of the Feynman diagrams, where a^+ and a are the creation and annihilation operators, respectively



We have proposed a generalization of this strategy to obtain observable-dedicated MOs[23] (DMOs), since any observable may be calculated perturbatively as a sum of diagrams. The procedure consists of the perturbative construction at the lowest order of a *participation matrix*, analogous to the one-particle density matrix, but including the contributions to the observable. The eigenvalues, that we have called *participation numbers*, may be associated with the contribution of the corresponding eigenvectors to the observable, and thus may be used as a criterion for truncating the new molecular orbital set. The efficiency of these DMOs has been proved for several applications, in particular for determining energy differences, such as dissociation energies,[23] or more recently electronic coupling in electron-transfer problems.[26] The method has also been used for determining the S−T gap in biradical systems.[16] The transformed MOs have good convergence properties for the evaluation of the observable, which permit the size of the file of molecular integrals and of the CI space to be considerably reduced. The purpose of the present work is to generalize the procedure for more complex magnetic problems, such as the calculation of the exchange coupling constant of Ni(II) dimers, and to prove its efficiency. Since the S−T splitting in biradicals is the simplest example of exchange coupling, we will first review the procedure for this simple case.

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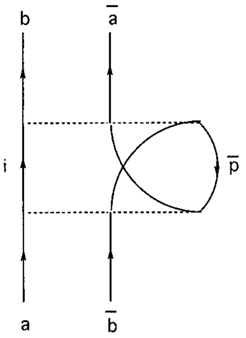
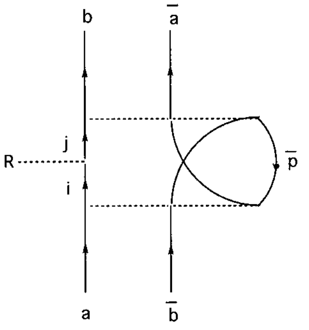
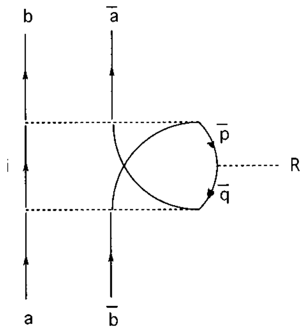
3.1. S−T Gap Dedicated Molecular Orbitals. The diagrams associated with the observable are in this case all the second-order energy contributions to the S−T gap. Since the model space is limited to the two neutral VB determinants associated with the singly-occupied orbitals a and b, $|a\bar{b}|$ and $|\bar{a}b|$, as discussed above, the only contributions to the energy difference come from the off-diagonal elements of the effective Hamiltonian. As an example, for a double excitation on the generator $|...p\bar{p}q\bar{q}a\bar{b}|$ (p, q are doubly occupied inactive MOs) of the type $\Phi_\alpha = |...p\bar{a}q\bar{q}i\bar{b}|$ (i is a virtual MO), i.e. a double spin polarization process, the second-order diagrams are of the type



The detailed second-order contributions to the S−T gap in biradicals as well as their diagrammatic transcription have been given by de Loth et al.[14] The (r,s) element of the S−T participation matrix is obtained simply by introducing an interaction line with the $R = a_r^+a_s$ operator on either the hole or particle propagation lines:



contribution to R_{ij}



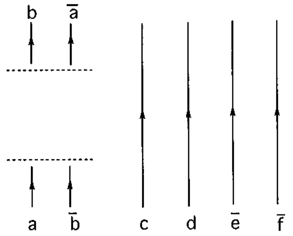
contribution to R_{pq}

So as not to change the zeroth-order description, the unitary transformation of the MOs is performed inside the subset of inactive occupied MOs, on one hand, and of virtual MOs, on the other. Both blocks of the participation matrix are diagonalized separately. The eigenvectors associated with the largest absolute values of the roots are the new MOs which most contribute to the S−T gap, or ST-DMOs.

It is important to point out that only a small part of the two-electron molecular integrals are affected by this transformation, since the interactions between the model space determinants and the significant excitations involve at most two inactive orbitals. Only the $\langle mn||rs\rangle$ (m, n = a, b; r, s are all MOs) integrals are needed, which are easily stored in six matrices of the atomic basis set dimension.

3.2. Molecular Orbitals Dedicated to Exchange Coupling. The procedure can be generalized quite easily, by taking into account some simple considerations. Two types of situations appear in the off-diagonal elements of the effective Hamiltonian:

(i) The determinants Φ_I and Φ_J differ by two active spin orbitals. The only possibility of keeping the remaining $n - 2$ propagation lines unchanged occurs when the difference consists of the spin inversion of an $a\bar{b}-\bar{a}b$ type pair



Thus the diagrams are the same as for the 2-electron case, for all the possible pairs of active orbitals and all the permutations of α and β spins in the remaining propagation lines. So the contributions of each pair are multiplied by a factor $\binom{n-2}{(n-2)/2}$. The contribution to a matrix element is obtained by adding the contributions of each pair.

(ii) The determinants Φ_I and Φ_J differ by four active spin orbitals. The intermediate determinants in this case necessarily belong to the CAS. Since only active orbitals are concerned, the diagrams do not contribute to the blocks of the participation matrix we are interested in.

The participation matrix can be easily constructed by looping on all the pairs of active orbitals. Since only the $\langle mn||rs\rangle$ integrals (m, n = active MOs; r, s = all MOs) are needed for each pair, the same partial transformation of the molecular integrals and the storage in six matrices for each pair of active MOs may be used.

The diagonalization of the participation matrix by blocks of occupied {p} and virtual {i} MOs provide new subsets of occupied {p′} and virtual {i′} MOs. The roots with largest absolute values are associated with the transformed orbitals which most contribute to the exchange coupling (EC-DMOs). Thus the participation numbers provide a logical way of truncating the EC-DMO set with no loss of important physical effects. The active set of MOs remains unchanged, and the unitary transformation of the occupied and virtual MOs keeps the energy obtained by diagonalizing the whole DDCI2 space invariant.

The calculation procedure of the exchange coupling constant can be schematized in the following steps: (1) SCF calculation; (2) localization of the active MOs; (3) partial transformation of the 2-electron integrals since all the integrals needed concern two active orbitals; (4) perturbative construction of the exchange coupling participation matrix and diagonalization of both occupied and virtual MO blocks; (5) ordering of the eigenvectors of each subset according to their participation and the truncation of the EC-DMO set to obtain a 2-electron integral file and/or a reasonably sized DDCI2 space; (6) complete transformation of the 2-electron integrals with the truncated set of EC-DMOs; (7) generation of the DDCI2 space (depending on the point group of the molecule, different DDCI2 subspaces according to different irreducible representations, IR) and diagonalization; (8) calculation of the coupling constant from the energy difference.

4. Results

The structural and magnetic properties of Ni(II) dimers with two halide or azide bridging ligands have been the object of many studies.[2−4] It appears, in general, that the coupling constant strongly depends on the structural parameters, the Ni−Ni distance and the bridge angle, Ni−X−Ni. The type of coordination of the Ni atom or the nature of the external ligands seems to have slight influence on the coupling, provided they keep their σ-donor character. The two complexes studied here,

$[Ni(en)_2Cl]_2^{2+}$ (**1b**)[2] and $[Ni(terpy)(N_3)]_2^{2+}$ (**2b**),[3] have been reported to be ferromagnetic, although the first one has a small coupling constant *J*. The calculations were performed on two model complexes, $[Ni(NH_3)_4Cl]_2^{2+}$ (**1a**) (Figure 1), and $[Ni(NH_3)_4(N_3)]_2^{2+}$ (**2a**) (Figure 2), where the geometry of the Ni−(μ-X)$_2$−Ni unit, with X = Cl^- or N_3^-, was taken from the crystallographic data for **1b** and **2b**, respectively, and the external ligands were modeled by ammonia groups to maintain the coordination surrounding of the metal. It should be pointed out that the use of model ligands is unavoidable if high-level calculations are to be performed using a reasonable amount of computer memory and time, as other authors have already mentioned.[21,22] We will first report the results obtained in the full DDCI2 calculation of the coupling constants of complexes **1a** and **2a** (Figures 1 and 2). These results will then be used as a benchmark to analyze the convergence of the truncation procedure.

4.1. Computational Details. All calculations were performed with a [3s,2p,2d] basis set for the Ni atoms, two different basis sets of double ζ (DZ) and double ζ plus polarization (DZP) quality for the bridge atoms Cl and N, and a SZ basis set for external NH_3 groups. An additional diffuse s function was added ($\zeta = 0.05$) to the CI basis set. Core potentials were used in all calculations.[27,28] A restricted open-shell SCF (OSRHF) calculation was performed for the highest multiplicity, a quintet state, of the complex. The resulting MOs were used in the 2-electron integral transformation. The DDCI2 space was then generated. The transition energies were obtained from differences of the eigenvalues corresponding to the most stable quintet, triplet, and singlet states, and the exchange coupling constant were evaluated from the differences of the corresponding eigenvalues of the Heisenberg Hamiltonian: $E(S{=}2) - E(S{=}1) = -4J$, $E(S{=}1) - E(S{=}0) = -2J$. Both differences will be calculated to verify the validity of this approximation.

As far as the geometry is concerned, in both models the experimental geometry of the metal−bridge ligand−metal unit was closely reproduced. The geometry of this unit is heavily dependent on the external ligands and counterions, and it is well-known that the coupling constant is very sensitive to geometry changes. The use of model compounds in this type of calculation justifies the fact that no optimization is performed.

4.2. Exchange Coupling Constants for the Complexes $[Ni(NH_3)_4Cl]_2^{2+}$ and $[Ni(NH_3)_4(N_3)]_2^{2+}$. The experimental geometry of the complex $[Ni(en)_2Cl]_2^{2+}$ (**1b**)[2] gives an approximately octahedral nickel environment, with only small distortions in the ethylenediamine ligands In the model complex **1a**, the experimental geometry of the Ni−(μ-Cl)$_2$−Ni unit has been maintained, and the external ligands are modeled through ammonia groups, in an octahedral coordination. Since the Ni−Cl distances differ by about 0.1 Å, the structure belongs to the C_{2h} point group.

The set of MOs was obtained from the open-shell restricted Hartree−Fock (OSRHF) calculation of the quintet state, with two a_g and two b_u active MOs, built from bonding and antibonding combinations of almost pure 3d orbitals of both metal atoms, $3d_{xy}(Ni_1) \pm 3d_{xy}(Ni_2)$ and $3d_{z^2},3d_{x^2-y^2}(Ni_1) \pm 3d_{z^2},3d_{x^2-y^2}(Ni_2)$. The lowest quintet, triplet, and singlet are respectively the ^5A_g, the ^3B_u, and the ^1A_g states. Two different DDCI2 subspaces, one for each IR, are built, the dimensions of which are 117 348 and 117 128 determinants for the A_g and the B_u IR, respectively, with the DZ basis set, and 137 828 and 137 588 with the DZP basis set. As expected, the values of the coupling constants are independent of the roots chosen to evaluate them. Small coupling constants were found, $J = 1.1$ cm^{-1} in DZ and $J = 1.8$ cm^{-1} in DZP basis sets, respectively, and were in good agreement with the experimental value[2] of 3.5 cm^{-1}.

In the $[Ni(terpy)(N_3)]_2^{2+}$ (**2b**)[3] complex, the coordination of the azide anion is of the end-on type. From the crystallographic data, in the Ni−(μ-N_3)$_2$−Ni unit the Ni−Ni distance is 3.27 Å and the Ni−N−Ni angle 101.3° and the structure has an inversion center. Since the Ni−N(azido) distances are slightly different and the out-of-plane distortion of the azido groups is about 30°, the structure of the unit is centrosymmetric. In the model **2a**, the external ligands were substituted by ammonia groups. In order to reduce the size of the calculation, the Ni−N distances were symmetrized in the model, and all the remaining structural parameters of the Ni−(μ-N_3)$_2$−Ni unit were taken from the crystallographic data. Two different structures were considered. The first one, in which the Ni−(μ-N_3)$_2$−Ni unit is planar, belongs to the D_{2h} point group and gives a simplified model which verifies at low computational cost that the value of the coupling constant is independent of the roots considered. As in the previous case the singly-occupied MOs given by the OSRHF calculation are bonding and antibonding combinations of d_{xy} orbitals of the metal atoms, of b_{2u} and b_{1g} symmetries, and of $3d_{z^2},3d_{x^2-y^2}$ orbitals, of a_g and b_{3u} symmetries. The lowest quintent, triplet, and singlet states are respectively the ^5A_g, $^3B_{3u}$, and ^1A_g states. The dimensions of the A_g and the B_{3u} DDCI2 subspaces are 96 808 and 96 432 determinants, respectively, with the DZ basis set and 136 648 and 136 248 determinants with the DZP basis set. The calculated constants are again quite similar with both basis sets, 13.3 and 14.0 cm^{-1}, and as expected are independent of the pair of roots chosen.

The second geometry, which belongs to the C_{2h} point group, is closer to the experimental one. The out-of-plane distortion of the azido groups was introduced, and the positions of the ammonia ligands were distorted from the octahedral coordination according to the experimental geometry. The above results show that the basis set does not greatly influence the value of the coupling constant, and therefore only the DZ basis set is used in this case. Since the D_{2h} calculation showed the trend expected from the Heisenberg Hamiltonian, only the spaces with the highest spin, corresponding to ^5A_g and ^3A_u, were diagonalized, giving a coupling constant of 21.1 cm^{-1}, in excellent agreement with the experiment, $J = 20$ cm^{-1}. Moreover, these two calculations show that, to obtain a reasonable estimate of the coupling constant, the role of the out-of-plane distortion is not crucial since the sign and the order of the magnitude are preserved.

The ferromagnetic character of both compounds at the DDCI2 level of calculation arises from complex contributions of different signs: the potential exchange and the kinetic exchange introduced by Anderson[7] and discussed by Hay et al.,[8] the contributions due to double-spin polarization, charge transfer, or polarization of the ionic forms, as well as higher order contributions. The value of the coupling constant obtained at the zeroth order, i.e. the value obtained by diagonalizing the CAS, may help us to interpret the results. The zeroth-order coupling constants are significantly positive in both molecules, which indicates that the antiferromagnetic kinetic exchange contribution is less important than that of the ferromagnetic potential exchange, since only these two contributions are included at this level of calculation. The sign of the remaining effects is not easily predictable. In the present case, these effects

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(27) (a) Barthelat, J. C.; Durand, Ph. *Gazz. Chim. Ital.* **1978**, *108*, 225. (b) Pelissier, M.; Durand, Ph. *Theor. Chim. Acta* **1980**, *55*, 43.

(28) The calculations were made with the PSHF-CIPSI package written by J. P. Daudey, J. P. Malrieu, D. Maynau, M. Pelissier, F. Spiegelmann, R. Caballol, S. Evangelisti, F. Illas, J. Rubio. Generation of the DDCI-DDCI2 space program was written by O. Castell.

Table 1. Convergence of the Coupling Constant against the Fraction of MOs Kept in the DDCI2 Space in Complex **2a**[a]

% selected MOs	n_{det}	*f*(DMOs)	*f*(CMOs)
48	21 784	1.07	0.41
57	34 044	1.14	0.78
72	51 496	1.00	0.82
77	57 128	1.00	0.35
94	84 720	1.00	1.15
100	96 808	1.00	1.00

[a] *f* is the ratio between the *J* corresponding to the considered fraction of MOs and the *J* corresponding to the complete set of MOs. DMOs: exchange coupling dedicated MOs. CMOs: canonical MOs. The size n_{det} of the corresponding A_g subspace is also indicated.

appear to be globally slightly antiferromagnetic, since they reduce the value of the *J* from the CAS value.

4.3. Reduction of the DDCI2 Space: Use of Exchange Coupling Dedicated MOs. To test the performance of this MO truncation technique, which enables the coupling constant to be calculated in greater systems than the present Ni(II) binuclear complexes, we performed the MO transformation in both complexes. The first step, as described above, is to localize the active MOs, by simply performing a $\pi/4$ rotation. After partial transformation of the 2-electron integrals, the EC-DMOs are obtained by diagonalizing the participation matrix and ordered according to the absolute values of the eigenvalues.

Since the value of the coupling constant is greater for complex **2a**, it is easier to analyze the performance of the transformation technique from the convergence of the values of the coupling constants, and we will discuss this first.

Let us give an illustration of the effect of transforming the MOs. Figure 3 plots the isodensity curves of the most participating virtual EC-DMO belonging to the b_{1g} IR (part a) and the closest canonical antecedents (parts b and c) for complex **2a**. The main effect is the concentration of the density in the bridge region, as well as near the magnetic centers, at the expense of the external ligands. The effect of the transformation on the occupied subset is less significant. Comparable conclusions emerged from the preliminary calculations on the biradical $[Cu_2Cl_6]^{2-}$ complex.[16]

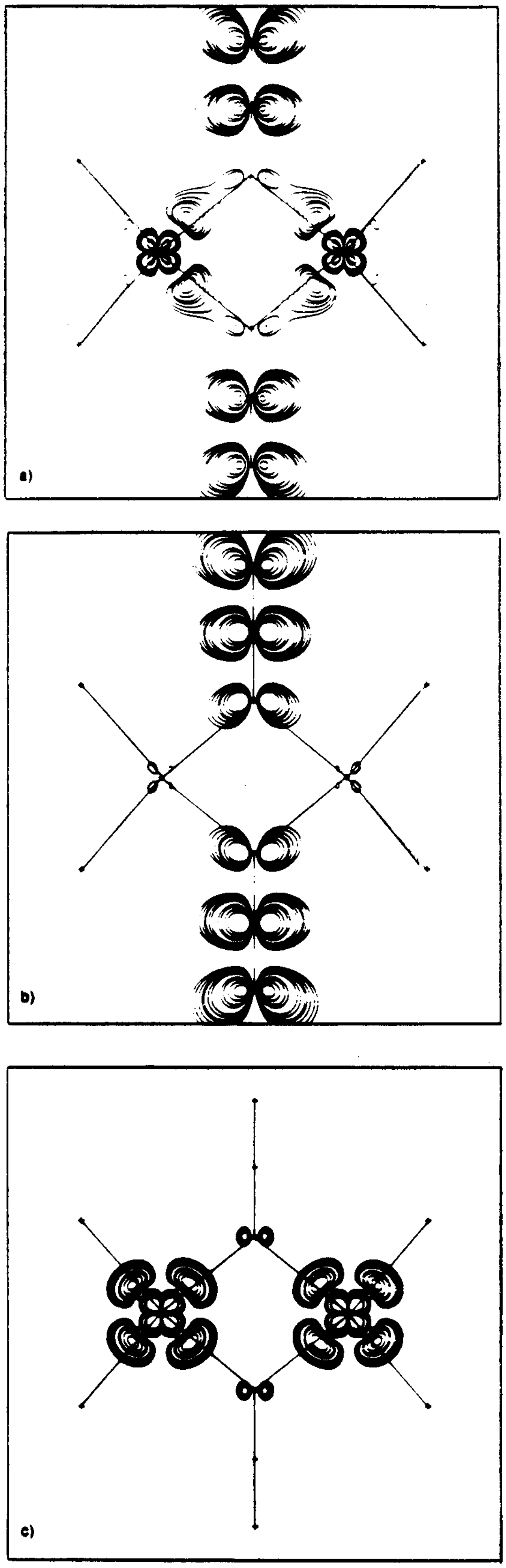

Figure 3. Isodensity curves of the virtual EC-DMO with greatest participation number of b_{1g} symmetry (a) and the closest canonical antecedents (b, c) for **2a** (*xy* plane).

In order to analyze the convergence of the coupling constant values, different truncations from different thresholds of the participation numbers were performed. Five different EC-DMO subsets were selected, by freezing the MOs with absolute values of the participation numbers lower than 10^{-4}, 5×10^{-4}, 10^{-3}, 5×10^{-3}, and 10^{-2}, respectively. Then for each subset the DDCI2 spaces belonging to the different IR were built and diagonalized, and the coupling constant was determined. For the sake of comparison, equivalent spaces were generated with the canonical MO set by freezing the same number of molecular orbitals for each IR. The coupling constant was then calculated for both types of MOs. Table 1 shows the convergence of the procedure against the percentage of EC-DMOs kept in the selection. The size of the A_g subspace is also indicated. It is evident from the comparison that, with about 70% of the MO set, the total convergence of the value of the coupling constant is reached when the transformed orbitals are used, while there are considerable instabilities with the canonical set even when a high number of MOs is included. The important consequences of this are the reduction in the dimension of the DDCI2 space to about 50%, as well as the decrease in the size of the file of the 2-electron molecular integrals to about 30%. The same behavior is shown by complex **1a**, as shown in Figure 4, which plots the convergence of the coupling constant against the percentage of selected MOs. As in two active electron systems,[16] the use of the EC-DMOs permits the dimension of the DDCI2 space to be reduced by half with no loss of accuracy.

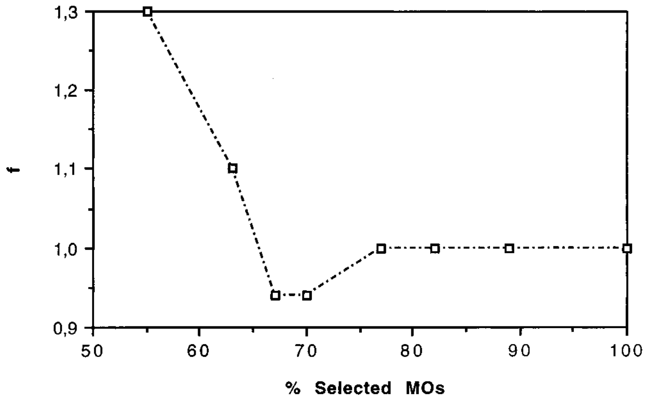

Figure 4. Convergence of the coupling constant against the percentage of transformed MOs for **1a**. *f* is the ratio between the *J* corresponding to the considered fraction of MOs and the *J* corresponding to the complete set of MOs.

5. Conclusions

The results show that the DDCI2 method provides accurate estimations of the magnetic exchange coupling constants, and in the least favorable case the value only differs by 6 cm^{-1} from the reported experimental value, estimated from the magnetic susceptibility−temperature curves. The sign and the magnitude of the coupling are correctly predicted, even in the case of very weak coupling, as in the dichloride-bridged complex. When compared with the few accurate calculations that have been published on similar systems, the DDCI2 results appear to be excellent. Since the size of the CI space increases only with the square of the dimension of the basis set, the method appears to be less expensive than other high-level CI treatments.

The second important feature is that the EC-DMOs and the participation numbers associated with them provide a good criterion for truncating the molecular basis set with no loss of accuracy in the determination of the exchange coupling parameter. The efficiency of the transformation has already been shown in biradical systems, but the generalization to more complex magnetic problems involving a large number of heavy atoms and/or active electrons has more impact, since increasing basis sets and CI spaces are involved and the manageability limits of the problem are rapidly reached. The combination of this truncation technique and the DDCI2 method provides a powerful tool for treating magnetic problems. Work is in progress on the structural dependence of the coupling constant of both diazido-bridged Ni(II) and dihydroxo-bridged Cr(III) binuclear complexes.

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