

Multiconfigurational Perturbation Theory: An Efficient Tool to Predict Magnetic Coupling Parameters in Biradicals, Molecular Complexes, and Ionic Insulators

Coen de Graaf, Carmen Sousa, Ibério de P. R. Moreira, and Francesc Illas*

Departament de Química Física i Centre Especial de Recerca en Química Teòrica, Universitat de Barcelona, C/Martí i Franquès 1, 08028 Barcelona, Spain

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The performance of the complete active space second-order perturbation theory (CASPT2) to accurately predict magnetic coupling in a wide series of molecules and solid state compounds has been established. It is shown that CASPT2, based on a reference wave function that only includes the effects described by the Anderson or Hay–Thibeault–Hoffmann model, correctly reproduces all experimental trends. For a complete quantitative agreement with experiment (or with accurate results arising from the difference dedicated configuration interaction method), it is necessary to include effects that go beyond the Anderson model in the reference wave function. The CASPT2 method is computationally less demanding than CI based methods and, hence, allows us to extend the study of magnetic coupling parameters to larger molecules or systems with elevated spin moments. Moreover, CASPT2 provides a reliable and accurate alternative to density functional based methods that require the use of a broken symmetry approach.

Introduction

The theoretical study of exchange interactions in molecular complexes or solid state compounds has become a rapidly expanding field over the past few years. In the first place, theoretical investigations have been applied to interpret the vast amounts of (new) experimental data related with, for example, the antiferromagnetism in high T_c superconductors,¹ the design of molecular magnets,^{2–5} or the magnetism of metal centers in enzymes.^{6–8} Second, the developments in modern electronic structure theory allowed theoreticians to construct accurate computational schemes, which are indispensable for the study of magnetic interactions because of the small energy differences involved in such processes.

The roots of the theoretical investigations of the magnetic interactions go back to the work of Anderson and Nesbet in the late 1950s, who developed a framework in which (anti)-ferromagnetism can be qualitatively understood.^{9–11} The magnetic coupling was interpreted as a sum of the direct exchange K and the Anderson delocalization term. The first term arises from the interaction between the mutual orthogonal open shell or magnetic orbitals in a local representation and always results in a ferromagnetic contribution. The second term arises from the interaction of the neutral reference configuration with the ionic ones, i.e., those configurations in which an electron is transferred from one magnetic center to the other. This term gives an antiferromagnetic contribution to the overall magnetic interaction. The Anderson model has been proven to be very successful in predicting the sign of the magnetic interaction but is too crude a model to quantitatively reproduce the magnitude of the magnetic coupling. Whereas the analysis of Anderson and Nesbet was basically developed within the field of solid-state magnetism, in the middle of the 1970s, Kahn and Briat¹² and Hay, Thibeault, and Hoffmann (HTH)¹³ discussed the equivalent of this qualitative model for molecular complexes. From the HTH model, very valuable information about the magnetostructural correlations can be derived, but it fails to give quantitative results. Hence, a more quantitative description of the magnetic coupling mechanisms is desirable to be able to

give reliable predictions of magnetic interactions of new and potentially very interesting materials.

Ab initio electronic structure calculations provide a natural approach to investigate the magnetic interactions in molecular complexes or solid state compounds in a more detailed way. Under the assumption of a common orbital part, the energy eigenvalues of the total Hamiltonian can be directly mapped onto the eigenvalues of the well-known Heisenberg Hamiltonian for a two-center problem: $\hat{H} = -J\hat{S}_1\cdot\hat{S}_2$. This offers a way to apply standard quantum chemical techniques for the calculation of electronic energies to magnetic coupling problems. Early ab initio calculations for KNiF_3 by Wachters and Nieuwpoort confirmed the ideas of the Anderson model.¹⁴ However, because of the limited computational resources available at that time, they could not go beyond this level. Almost 10 years later, an important contribution to the field was made by de Loth and co-workers.¹⁵ They described a computational scheme to improve the Anderson or HTH model by second-order perturbation theory, in which only those determinants that contribute to the energy difference of two states of interest are included in the first-order wave function. The relative importance of the different second-order terms (kinetic exchange, double spin polarization, charge transfer, etc.) were studied and compared to the terms arising from the Anderson model.

The work of de Loth et al. initiated a research line aimed at the development of an ab initio computational scheme that gives an accurate description of the magnetism in molecular complexes and solid-state compounds. In a study of the singlet–triplet splitting of dichloro- and difluoro-bridged Cu(II) dimers, Broer and Maaskant introduced the concept of treating the determinants that contribute to the energy difference in a variational way.¹⁶ This configuration interaction approach was given a more firm basis by Miralles et al., who introduced the basic concepts of the difference dedicated CI (DDCI) method.^{17,18} They derived a selection criterion based on a second-order effective Hamiltonian and discussed the effect of the different types of single and double excitations out of a complete active space formed by the open-shell orbitals and unpaired electrons. It was shown that a large part of the external determinants only shift the diagonal matrix elements of the effective Hamiltonian

* To whom correspondence should be addressed.

and hence are irrelevant to the computation of the energy difference. Over the past few years, this method has been shown to perform extraordinarily well in the study of magnetic coupling parameters in molecular complexes^{19–21} and solid-state compounds.^{22–24} In the next section, we give a short outline of the DDCI method and its different variants used nowadays.

A somewhat different strategy to improve the Anderson or HTH model is supplied by unrestricted Hartree–Fock (UHF) and density functional theory (DFT). Because it is in general not possible to express the spin eigenfunctions with a single Kohn–Sham determinant, the mapping procedure described above for the spin-restricted *ab initio* methods cannot be applied. However, the broken symmetry approach of Noodleman and Davidson provides an alternative way to derive magnetic coupling parameters.^{25–27} This approach relates the eigenvalues of the Ising Hamiltonian to the energy eigenvalues of spin symmetry broken solutions. The large advantage of DFT is that it is computationally much less demanding than the DDCI method mentioned above and, hence, can be applied to study large molecular complexes without the need to approximate the real structure by a model.^{28–32} On the other hand, there seems to be no consensus about the details of the relation between the magnetic coupling constant J and the energy difference of the spin symmetry broken states. A large amount of articles have been published on this subject, and at least three slightly different ways exist to perform the mapping.^{29,33–41}

In this paper, we apply a computational scheme that avoids the problems with the mapping procedures of the spin-unrestricted methods but is not as computationally demanding as the DDCI methods. For this purpose, we present the results of the calculations of the magnetic coupling constants in a wide variety of molecular complexes and solid-state compounds using the complete active space second-order perturbation theory (CASPT2) methodology developed by Andersson and co-workers^{42,43} and extensively applied to study the spectroscopy of organic and inorganic molecules in great detail.^{44–47} The method takes a complete active space self-consistent field (CASSCF) wave function that contains the essential physics as zeroth-order wave function and estimates the remaining part of the (mainly) dynamical electron correlation effects by second-order perturbation theory. For magnetic problems, a typical active space would contain the open-shell orbitals and the unpaired electrons, i.e., including the effects described by the Anderson model. In the subsequent CASPT2 step, all valence electrons are correlated to account for the effects discussed by de Loth et al. To obtain more reliable results, it is possible to include some effects that go beyond the Anderson model in the CASSCF wave function to ensure a variational and, hence, more accurate treatment of such effects. Again, CASPT2 accounts for the remaining electron correlation effects but now takes a much longer CASSCF wave function as reference.

The paper is organized as follows: in the subsequent section, we give a short outline of the main points of the DDCI and CASPT2 approaches. Thereafter, we compare the CASPT2 method to DDCI results and/or experimental data in three different kind of systems: an extensive series of ionic insulators, some molecular complexes, and a few biradicals. The systems have been chosen to explore the whole range of magnetic behavior exhibited by these three classes of compounds: from strongly antiferromagnetic to ferromagnetic interactions, including organic and inorganic molecules with different types of magnetic orbitals (*s*-like or *p*-like versus *d*-like), interactions between different transition metals with magnetic moment S varying from $1/2$ to $5/2$ (Cr, Mn, Fe, Ni, and Cu), a range of

different geometries; and interactions with and without bridging ligands. Each subsection first gives some information about the material model, basis sets, and other computational details and then discusses the results obtained. Finally, we summarize the most important conclusions in the last section of the paper.

Computational Methods

DDCI. As already mentioned in the Introduction, the difference dedicated CI scheme is based on the understanding that many external determinants contribute equally to the correlation energy of the electronic states involved in the process under study. Therefore, a selection is made and only those determinants are included that contribute to the energy difference between the states. First, an uncontracted list of determinants is constructed by single and double replacements from the determinants in the reference space, usually a CAS that represents the Anderson model. Thereafter, a selection is made based on arguments from quasidegenerate second-order perturbation theory. For a system with two unpaired electrons, it has been proven that in case of a degenerate reference space only the determinants $|K\rangle$ that fulfill the condition

$$\frac{\langle I|\hat{H}^{(0)}|K\rangle\langle K|\hat{H}^{(0)}|J\rangle}{E_0 - E_K} \neq 0 \quad (1)$$

(where $|I\rangle$ and $|J\rangle$ are two different determinants from the reference space) contribute to the energy difference of the states involved.⁴⁸ It can be easily shown that this condition selects determinants involving at most two orbitals outside the CAS. The complete diagonalization of the resulting CI matrix is usually referred to as DDCI2.

Although, for almost any real system, the selection condition does not apply strictly, the DDCI2 method gives very reasonable results for magnetic interaction problems. However, it has been shown recently that adding some well-defined set of determinants to the wave function gives an important contribution to the energy difference between the states of interest.^{23,49} These extra determinants involve at most three orbitals external to the CAS; the resulting method is labeled DDCI3.

Calzado et al.⁴⁹ and Cabrero et al.¹⁹ have recently analyzed the effect of adding the extra determinants on top of DDCI2 and concluded that the main contribution arises from the relaxation of the determinants connected to the ligand to magnetic center charge-transfer (CT) excitations. These CT excitations are already included in the DDCI2 wave function, but their contribution remains rather small because the wave function lacks flexibility to account for the large orbital relaxation effects accompanying CT excitations.^{50–52} The inclusion of single excitations with respect to these CT excitations at the DDCI3 level lowers the CT excitations in energy and, hence, largely enhances the contribution of these determinants to the wave function. The DDCI3 calculations reported in this paper have been performed with the CASDI suite of programs.⁵³

CASPT2. The partition of the Hamiltonian proposed by Møller and Plesset gives rise to a very successful and efficient method to treat electron correlation effects in systems that can be described by a single reference wave function. However, for a multireference wave function, the Møller and Plesset division can no longer be made, and an alternative choice of $\hat{H}^{(0)}$ is needed. One such scheme is CASPT2. We will briefly resume the most important definitions of the theory, but the reader is referred to the original articles for a more extensive description of the method.^{42,43,54} The reference wave function is a CASSCF wave function that accounts for the largest part of the nondy-

namical electron correlation. The zeroth-order Hamiltonian is defined as follows and reduces to the Møller and Plesset operator in the limit of zero active orbitals:

$$\hat{H}^{(0)} = \sum_{pq\sigma} f_{pq\sigma} \hat{E}_{pq} \quad \text{with} \quad f_{pq\sigma} = -\langle 0 | [[\hat{H}, \hat{a}_{q\sigma}^\dagger], \hat{a}_{p\sigma}] | 0 \rangle \quad (2)$$

where $|0\rangle$ is the CASSCF reference wave function and \hat{E}_{pq} is the usual excitation operators. Alternative formulations of the zeroth-order Hamiltonian have been given by Andersson to treat closed-shell-dominated and open-shell-dominated reference wave functions in a more balanced way.⁵⁴ In the context of this work, we will apply the g1 correction to $\hat{H}^{(0)}$ to calculate the singlet–triplet splitting for some biradicals that have a leading configuration of the singlet with closed shell character, whereas the triplet state is characterized to a large extent with an open shell configuration. Note that, for magnetic interactions between localized spin moments, all states that arise from the different spin couplings have open-shell character, and hence, we will use the unmodified $\hat{H}^{(0)}$ as given by eq 2 in these cases.

As in any perturbational scheme based on Fock-type zeroth-order Hamiltonians, configurations can appear in the first-order wave function with an expectation value of $\hat{H}^{(0)}$ that is very close to (or even lower than) the expectation value of the reference wave function. This can lead to very small (or even negative) energy denominators both in the expressions for the second-order correction to the energy $E^{(2)}$ and the coefficients of the configurations in the first-order wave function $C^{(1)}$ and cause a breakdown of the perturbation treatment of the electron correlation. In general, this problem does not appear for the electronic states that are needed to compute the magnetic coupling parameter. Nevertheless, we have found a breakdown of the perturbation in one case, see the biradicals section. The best way to solve this problem is to include the trouble-causing configuration in the CASSCF wave function. However, it often happens that the state that causes the breakdown does not have a large interaction matrix element with the reference state, and therefore, it is not very important to obtain a good estimate of the second-order energy. On the basis of this observation, Roos and Andersson introduced an alternative solution to the intruder state problem, namely, the so-called level-shift technique.⁵⁵ Here, all configurations in the first-order wave function are shifted to higher energy by an arbitrary μ in this way avoiding the destructive influence of the intruder state. Once the zeroth-order Hamiltonian has been diagonalized, a correction is applied for the appearance of the level shift in the denominators of the expressions for $E^{(2)}$. This level shift method has been successfully applied to a wide variety of problems in the field of spectroscopy⁵⁶ and can be considered as a pragmatic solution to the intruder state problem inherent to perturbation theory. All CASSCF/CASPT2 calculations presented here have been done with MOLCAS 4 (ref 57).

Results

Ionic Insulators. A crystal is a macroscopic object built from a very large number of atoms, which makes a theoretical or computational treatment of the electronic structure of the crystal as a whole impossible. For this reason, it is inevitable to introduce approximations in the calculational scheme. A very natural simplification is the introduction of translational symmetry by imposing periodic boundary conditions, leading to the band theory of electrons moving in a periodic potential. A different approach is to model the crystal by a small number of atoms of the real crystal and embed this so-called cluster in a potential that mimics the rest of the crystal. This approximation

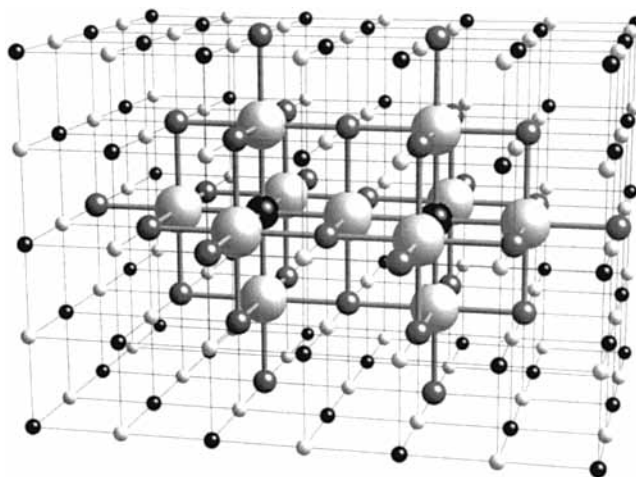


Figure 1. Ni₂O₁₁ cluster embedded in TIPs and point charges. Thick lines connect cluster atoms, whereas thin lines connect point charges and TIPs. Black large spheres are Ni ions, large light spheres represent O, and dark gray spheres represent the Ni ions included in the cluster with TIPs. The small dark and white spheres are positive or negative point charges (not all charges are shown).

is known as the embedded cluster model approach, and the large advantage of this method with respect to band structure calculations is that the description of the electronic structure is easily extended beyond the one-electron model by including electron correlation effects with standard quantum chemical methods, e.g., the ones discussed in the previous section. There exists a substantial amount of evidence that modeling the crystal with a relatively small cluster does not introduce serious artifacts into the calculation of the magnetic interaction parameters. Both the comparison with band structure calculations at the Hartree–Fock level^{58–61} and the extension of the cluster with additional magnetic centers⁶² show that a properly embedded cluster of two magnetic centers extended with the ligands that complete the metal coordination accurately models the crystal.

In the present study, we apply the embedded cluster approach to calculate the magnetic interaction parameter with DDCI3 and CASPT2 to transition-metal (TM) compounds that show a wide variety of magnetic behavior. The series contains the cubic TM monoxides MnO and NiO; the perovskites La₂NiO₄, La₂CuO₄, K₂NiF₄, KNiF₃, and K₂FeF₄; the distorted perovskites KCuF₃ and K₂CuF₄; and the spin-chain compound Sr₂CuO₃. In all of these compounds, magnetic interactions along a linear TM–L–TM (L = ligand; O or F) bond occur, and this magnetic interaction is referred to as J_1 . In addition, other important interactions are found in some of the compounds considered here. In particular, for NiO, we calculate the nearest neighbor interaction J_2 , which occurs along a Ni–O–Ni bond of 90°, and for the spin-chain compound Sr₂CuO₃, we calculate the interchain interaction J_\perp . This interaction is not mediated by a ligand and is thus expected to be rather small.

Figure 1 shows the embedded TM₂L₁₁ cluster to calculate J_1 in NiO. This cluster is representative for the calculation of J_1 in all compounds, except Sr₂CuO₃, for which a Cu₂O₇ cluster is used. J_2 (NiO) is extracted from a Ni₂O₁₀ cluster, and J_\perp (Sr₂CuO₃) is extracted from a Cu₂O₈ cluster. The embedding of these clusters is provided by a set of point charges that reproduce the Madelung potential in the cluster region⁶³ and a set of total ion potentials (TIP's) that account for the short-range repulsion between the O²⁻ or F⁻ anions in the cluster and their nearest neighbors.⁶⁴ For all materials, the experimental geometry has been used to construct the cluster model. In both the DDCI3 and CASPT2 calculations, we use one-electron basis sets of the

TABLE 1: CASSCF, CASPT2, and DDCI3 Magnetic Coupling Parameters (in meV) for a Family of Ionic Insulators^a

compound		small CAS			large CAS		exp.	ref
		CASSCF	CASPT2	DDCI3	CASSCF	CASPT2		
MnO	J_1	-0.44	-1.31				-1.7	86, 87
K ₂ FeF ₄	J_1	-0.45	-1.04				-1.35	88, 89
KNiF ₃	J_1	-2.51	-6.72	-7.61	-2.97	-6.99	-7.40	90
K ₂ NiF ₄	J_1	-2.70	-7.25	-7.65	-3.18	-7.53	-7.90/-9.15	91
KCuF ₃	J_1	-7.05	-20.9	-28.8	-9.18	-22.8	-31.6/-33.8	92-94
K ₂ CuF ₄	J_1	0.33	0.65	2.07	0.59	0.74	1.41/1.83	95, 96
NiO	J_1	-4.99	-16.3	-16.4	-6.44	-17.7	-19	97, 98
	J_2	0.50	1.33	1.88	0.93	1.95	-	-
La ₂ NiO ₄	J_1	-8.79	-26.4	-26.9	-11.5	-28.8	-31	99
La ₂ CuO ₄	J_1	-40.0	-113	-150	-67.9	-139	-128/-134	100-102
Sr ₂ CuO ₃	J_1	-44.4	-177	-246	-86.8	-260	-246	103, 104
	J_{\perp}	-0.02	-1.09	-0.44	-0.12	-2.00	-	-

^a The small CAS only contains the unpaired electrons and the magnetic orbitals localized on the metal centers. The large CAS extends the smaller one with a set of occupied ligand orbitals and one virtual for each (singly or doubly) occupied orbital in the leading configuration state function. Calculated values are compared to available experimental data (references for experimental data are given in the last column).

atomic natural orbital (ANO) type. The final contracted basis set has (5*s*, 4*p*, 3*d*) functions for the TM, (4*s*, 3*p*, 1*d*) for the bridging ligands, and (3*s*, 2*p*) for the other ligands included in the cluster model.^{65,66} Previous applications have shown that a further enlargement of these basis sets does not significantly affect the calculated *J* values.⁶⁷⁻⁶⁹

We now turn to the discussion of the results in Table 1, which lists CASSCF, CASPT2, and DDCI3 *J* values. In the first place, it can be readily seen that the CASSCF values obtained from the small CAS, which is the ab initio equivalent of the Anderson model, reproduce the experimentally observed trends. The sign of the interaction is recovered in all cases, and the relative magnitude of the interactions in the different compounds is also reproduced. The only obvious disagreement with experiment is the absolute magnitude of the interaction, which is far too small in all cases. In line with the discussion of the external electron correlation effects outlined above, CASPT2 and DDCI3 significantly improve the calculated *J* values. The comparison of the DDCI3 values with experiment is (as expected)^{23,49,70} very satisfactory, and hence, the method can provide a quantitative prediction of *J* for materials for which experimental data is absent, scarce, or contradictory.^{24,70,71}

On the other hand the CASPT2 values still show a significant deviation from the experimental and/or DDCI3 values. It is clear that the second-order treatment of the external correlation effects largely improves the Anderson model, but some higher order effects must be included in order to reproduce the DDCI3 values. One way to do this is to go to higher-order perturbation theory, e.g., by applying the CASPT3 method proposed by Werner.⁷² Alternatively, the active space can be extended to include the higher order coupling between external determinants that is missing in the CASPT2 based on the small CAS.⁷³ The effect of the ligand-to-metal CT excitations is accounted for more accurately by adding the ligand orbitals involved in the superexchange interaction to the active space. However, such an active space does not provide any improvement of the results,⁷³ because of the very small interaction matrix elements between the unrelaxed CT configurations and non-CT configurations.^{52,69} To supply the resulting wave function with enough flexibility to account for the large orbital relaxation effects accompanying these CT excitations,⁵⁰⁻⁵² the active space is further augmented with a set of virtual orbitals chosen according to a well-defined physical criterion. For the interactions along linear TM-L-TM bonds, the large active space simply contains the magnetic orbitals centered on the metals, the ligand-2*p_σ* orbital, and for each occupied orbital a virtual orbital of the same symmetry character. In the case of the 90° TM-L-TM bond, the same procedure has been followed: first adding the

ligand-2*p_x* and ligand-2*p_y* orbitals to the active space and then doubling it with the pertinent virtual orbitals. To obtain correctly converged orbitals for the cuprates (copper oxides), it turned out that the active space must be extended with the Cu-3*d_{z²}* orbitals and their correlating counterpart. The natural occupation numbers of these orbitals in the final CASSCF wave function remain close to 2 or 0, but their inclusion in the active space greatly improves the convergence. Finally, note that the larger active space in the calculation of J_{\perp} (Sr₂CuO₃) only contains the magnetic orbitals and the corresponding virtual orbitals because of the lack of a bridging ligand in this case.

With this larger active space, we observe an increase in the magnitude of the CASPT2 values compared to those obtained with the smaller active space. However, these changes are rather small for all compounds except for the cuprates, for which a substantial improvement of the calculated *J* is observed. It is well-known that the CT excitation from O²⁻ to Cu²⁺ lies much lower in energy than the corresponding excitation in the nickel compounds or copper fluorides. Hence, it is not surprising that the copper oxide compounds exhibit a stronger magnetic coupling, which is only correctly reproduced by CASPT2 when the reference wave function allows for an extensive treatment of the instantaneous relaxation of the CT configurations. For the Ni compounds and copper fluorides, these effects are less important, and the difference between the CASPT2 results obtained with the large CAS and those from the small CAS is much smaller than for the cuprates.

For MnO and K₂FeF₄, the recipe of extending the CAS cannot be applied because the small active space already contains a large number of orbitals. Because of the high net spin moment on these transition metals, all TM-3*d* orbitals need to be included in the minimal CAS. The resulting active space of 10 orbitals with 10 (Mn) or 12 (Fe) electrons is simply too large to be duplicated. However, in these compounds, the contribution of the CT excitations is expected to be at least as small as those for the nickel compounds and copper fluorides.⁷⁴ This explains why a quantitative agreement with the experiment is already found with the small CAS. Combined with the fact that the DDCI3 selection criterion results in an unfeasible large CI wave function, we conclude that the CASPT2 method is an interesting alternative approach to study the magnetic interactions in compounds containing magnetic centers with *S* > 1.

Molecular Complexes. The theoretical study of magnetic interactions in molecular complexes makes it possible to access information difficult to extract from the experiment. An interesting example is the exploration of the magnetostructural correlations of a molecule. To derive these correlations, it is necessary to perform a whole series of calculations at different

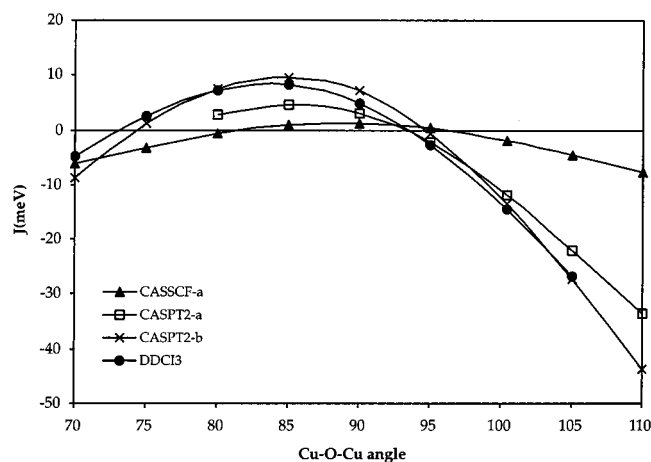


Figure 2. Variation of the magnetic coupling parameter J in the Cu_2Cl_6 molecule with the bridging $\text{Cu}-\text{Cl}-\text{Cu}$ angle θ . The triangles represent the CASSCF results with the small CAS (two orbitals with two electrons). The open circles give the CASPT2 results based on the small CAS, the crosses correspond to those obtained with CASPT2 using the large CAS as reference wave function, and the filled circles give the DDCI3 results.

geometries, and therefore, the computational method applied should not only be very accurate but also rather efficient. To investigate the performance of the CASPT2 method to extract magnetostructural correlations, we have taken the widely studied Cu_2Cl_6 molecule in a planar conformation in which two chlorine atoms form a double bridge between the two coppers. We have studied the correlation of J with variations in the bridging $\text{Cu}-\text{Cl}-\text{Cu}$ angle θ , keeping the $\text{Cu}-\text{Cl}$ distances fixed. For this purpose, two active spaces have been considered that are constructed following the same procedure outlined for the cuprates described above, i.e., two orbitals with two electrons for the small CAS and 10 orbitals with 10 electrons for the large CAS. For all Cl atoms in the molecule, a $(5s, 4p, 1d)$ contraction has been used, where the Cu basis is identical to that used for the cuprates. The geometry of the molecule has been optimized by CASSCF applying the small CAS.

Figure 2 compares the CASPT2 results to DDCI3, which we consider to be our benchmark calculation. It is clear that the small CAS curve (results marked with triangles) only provides a qualitative indication of the magnetostructural correlations. The variation of J with θ is too small, which results in a very flat curve. CASPT2 (open squares) clearly enhances the dependency of J on θ , but the first-order wave function is largely affected by intruder states for small angles. These intruder states cannot be removed by the level shift technique discussed in the previous section. However, the DDCI3 curve (circles) is satisfactorily reproduced by CASPT2 based on the large CAS (crosses) over the whole interval of θ , providing a relatively cheap way to access the magnetostructural correlations in medium sized molecules with a wave function based method.

The second molecular system for which a comparison between CASPT2 and DDCI3 has been made is the $(\text{NH}_3)_3-\text{Cu}-(\mu-\text{O})_2-\text{Cu}-(\text{NH}_3)_3$ model complex (see Figure 3; the geometry has been taken from ref 75). In a DFT study of this model, Ruiz et al. found that it exhibits a surprisingly strong ferromagnetic coupling, and for this reason, it was proposed as an interesting candidate for a building block in the construction of new ferromagnetic materials.⁷⁵ For this molecule, we establish whether the CASPT2 method is able to reproduce such strong ferromagnetic coupling, and we perform an explicit study of the basis size dependency of the magnetic coupling parameter

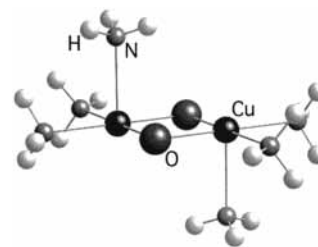


Figure 3. $(\text{NH}_3)_3-\text{Cu}-(\mu-\text{O})_2-\text{Cu}-(\text{NH}_3)_3$.

TABLE 2: Comparison of CASSCF, CASPT2, and DDCI3 Magnetic Coupling Parameters (in meV) of $(\text{NH}_3)_3-\text{Cu}(\text{II})(\mu-\text{O})(\mu-\text{O})\text{Cu}(\text{II})-(\text{NH}_3)_3^a$

basis set	small CAS			large CAS	
	CASSCF	CASPT2	DDCI3	CASSCF	CASPT2
A	6.45	29.3	46.1	12.5	41.5
B	6.74	29.4		13.5	45.8

^a Basis A consists of a $(5s, 4p, 3d)$ basis for Cu, a $(4s, 3p)$ basis for O, a $(3s, 2p)$ basis for N, and a $(2s)$ basis for H. Basis B extends A with an f function for Cu, a d function for O, and a p function for H. The N basis is augmented to $(4s, 3p, 1d)$.

calculated with this second-order perturbation theory scheme. Table 2 compares the CASPT2 results with those obtained by a DDCI3 calculation. We observe a similar behavior as for the strongly antiferromagnetic couplings in the cuprates (cf. Table 1); CASPT2 based on the CAS small only qualitatively reproduces the DDCI3 number, but the extension of the active space in the preceding CASSCF calculation with ligand orbitals and virtuals brings the two methods in quantitative agreement. Furthermore, we observe a rather weak dependence on the size of the basis set. The difference between basis A (triple- ζ valence (TZV) for Cu and O and double- ζ valence (DZV) for the NH_3 groups) and basis B (TZV + polarization for Cu, O, and N and DZV + polarization for H) only weakly affects the calculated J values. Note that the DDCI3 calculation with the larger basis becomes rather demanding, whereas the CASPT2 calculation can be performed in a straightforward way.

Finally, we focus our attention on the magnetic interactions in binuclear complexes containing metal centers with an elevated spin moment, i.e., $S > 1$. For this purpose, we have taken a series of Cr(III) dimers with different bridging ligands. To explore the possibilities of CASPT2 to predict the relative strength of the magnetic interactions in these compounds, we have selected three doubly bridged chromium dimers from a study by Gafford et al.⁷⁶ The general formula of these molecules is $\text{tpma}-\text{Cr}-(\mu-\text{R}_1)(\mu-\text{R}_2)-\text{Cr}-\text{tpma}$, with tpma being tris(2-pyridylmethyl)amine. We have studied the variants with a double OH bridge, with an O and OH bridge, and finally the combination of O with HCO_2 as bridging ligands. Because these molecules have rather voluminous ligands, a modeling has been invoked for this part of the molecule to reduce the computational cost. For this reason, the real tpma ligands have been replaced by four NH_3 groups. Geometries have been optimized at the CASSCF level applying the minimal CAS. The geometries of the $\text{Cr}-(\mu-\text{R}_1)(\mu-\text{R}_2)-\text{Cr}$ fragments are in reasonable agreement with the data given by Gafford et al. for the complete molecules. Figure 4 shows the final structure for the $(\text{NH}_3)_4-\text{Cr}-(\mu-\text{O})(\mu-\text{HCO}_2)-\text{Cr}-(\text{NH}_3)_4$ molecule. In addition, we have calculated the magnetic interaction for the singly bridged Cr dimer reported by Pedersen,⁷⁷ which shows a much larger coupling than the doubly bridged complexes.

The minimal CAS now contains the six unpaired electrons (three per Cr atom) and six orbitals. The application of the DDCI3 selection criterion results in a huge CI wave function

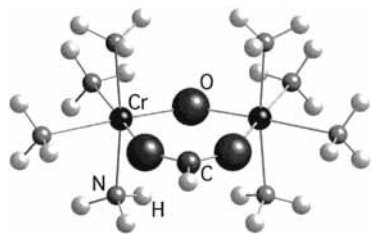


Figure 4. $(\text{NH}_3)_4\text{-Cr}-(\mu\text{-O})(\mu\text{-HCO}_2)\text{-Cr}-(\text{NH}_3)_4$.

TABLE 3: CASSCF and CASPT2 Magnetic Coupling Parameters (in cm^{-1}) of the Doubly Bridged Binuclear Cr(III) Complex $(\text{NH}_3)_4\text{-Cr(III)}(\mu\text{-R}_1)(\mu\text{-R}_2)\text{Cr(III)}-(\text{NH}_3)_4$ for Four Different Combinations of Bridging Ligands

R_1	R_2	$\angle\text{Cr-R}_1\text{-Cr}$	CASSCF	CASPT2	exp. ^{76,77}
OH^-	OH^-	107.7°	-2.37	-17.8	-31.4
O^{2-}	OH^-	108.9°	-1.67	-52.0	-137
O^{2-}	HCO_2^-	139.6°	-32.1	-126	-186
O^{2-}	O^{2-}	178.8°	-54.4	-206	-450

and, except for small basis sets with very few virtual orbitals, is practically impossible. However, CASPT2 offers a relatively cheap and rather precise way to study the magnetic interactions in these compounds as has already been observed above for the ionic insulators containing Mn^{2+} or Fe^{2+} ions. Although the large number of open-shell orbitals makes it impossible to extend the active space with relaxed CT configurations, CASPT2 based on the small CAS already gives a very reasonable description of the magnetic interactions.

The results in Table 3 show that CASPT2 correctly reproduces the relative strength of the experimental magnetic coupling parameters. A direct correlation is observed between J and the angle of the R_1 ligand with the two metal centers: the larger this angle, the larger the magnetic coupling parameter. This confirms the suggestion of Gafford et al. that the magnetic coupling between Cr atoms occurs basically along the $\text{Cr-R}_1\text{-Cr}$ superexchange path. The difference in absolute values between the theoretical and experimental estimates is probably a combination of three factors. First, there is the fact that the reference wave function does not include the important ligand-to-metal CT configurations, and therefore, some electron correlation effects are not properly treated by CASPT2. Second, the limited treatment of the electron correlation in the geometry optimization tends to give too long bond lengths. A more extensive treatment would shorten them, and consequently, stronger magnetic interactions would be obtained. Finally, the modeling of the tpma ligand by NH_3 groups could be somewhat too crude⁷⁸ and should be improved to get better agreement with the experiment. With the present computational resources, only the first point cannot be circumvented within the CASSCF/CASPT2 approach; the other two could be improved in a more detailed study of these compounds.

In summary, the CASPT2 method is able to correctly describe ferromagnetic and antiferromagnetic couplings in some illustrative examples of molecular complexes. It gives quantitative results for molecules containing magnetic centers with a small magnetic moment and allows a qualitative study of the magnetic coupling for systems with larger number of unpaired electrons.

Biradicals. The CH_2 , CHF, CF_2 , CHCF_3 , and SiH_2 biradicals have been chosen to start with because they have been widely studied and can be considered as benchmark systems as far as the calculation of singlet–triplet splitting is concerned.^{54,79–81} Notice, however, that the singlet–triplet splitting in these molecules does not involve the calculation of the interaction between two localized spatially separated spin moments. Here, we investigate the convergence of the CASPT2(g1) singlet–

triplet splitting with the size of the active space and compare the results with the DDCI3 values. For this purpose, three different CASSCF wave functions have been used as reference wave functions for the perturbation calculation. In the first place, a minimal CAS that only contains two electrons and the two orbitals involved in the transition will be referred to as small CAS. This wave function is also used as a reference in the DDCI3 calculations. Second, we apply an active space that includes (most of) the valence orbitals and the corresponding number of electrons and is referred to as medium CAS. For CH_2 , CHF, CF_2 , and SiH_2 , the CAS corresponds to a real valence CAS (considering the F-2s orbital as a core orbital), but in the case of CHCF_3 , such a space would become prohibitively large, and a selection of the most relevant orbitals has been made by performing a restricted active space SCF (RASSCF) calculation in the complete valence space. A more detailed description of this strategy to select a well-balanced complete active space is given in ref 82. The exact specification of the medium CAS for the five molecules considered here is as follows: CH_2 and SiH_2 , six orbitals and four electrons; CF_2 , 10 orbitals and 12 electrons; CHF, eight orbitals and 12 electrons; and CHCF_3 , 10 orbitals and eight electrons. The third active space (large CAS) extends the medium CAS with a set of virtual orbitals to ensure a variational treatment of the most important part of the electron correlation effects. The final size of the large CAS for all molecules is thirteen orbitals with the same number of electrons as in the medium CAS. ANO basis sets are applied using a $(3s, 2p)$ contraction for H, $(5s, 4p, 2d)$ for C and F, and $(5s, 4p, 3d)$ for Si.^{60,76} The geometries of the molecules have been taken from ref 81.

The tendency in the singlet–triplet splitting is rather similar for all molecules. On the basis of the minimal active space, CASPT2(g1) correctly predicts the singlet or triplet to be lowest in energy, and the splitting between the two states is of the order of the experimental splitting (cf. Table 4). However, in agreement with the findings of García et al.,⁸¹ the DDCI3 splittings are clearly more accurate and are all within 2 kcal/mol of the experimental values. To obtain a similar accuracy with the CASSCF/CASPT2(g1) approach, the medium CAS is not sufficient. The calculated singlet–triplet splittings become closer to the DDCI3 values, but still significant differences are found. Only by applying the large CAS as a reference wave function for CASPT2(g1) does the singlet–triplet splittings essentially coincide with those obtained from DDCI3 and the experimental values. The values reported in Table 4 are only moderately dependent on the size of the one-electron basis set. Reducing the basis set for all atoms with one function for each l value changes the singlet–triplet splitting by not more than 2 kcal/mol, both for CASPT2(g1) and DDCI3.

In contrast to the biradicals discussed so far, spatially well-separated spin moments are found in α -*n*-dehydrotoluenes and biverdazyl radicals, and hence, ferromagnetic or antiferromagnetic behavior can be observed in these molecules. The magnetic interactions of α -4-dehydrotoluene and 1,1',5,5'-tetramethyl-6,6'-dioxo-3,3'-biverdazyl (see Figure 5) chosen here as representative examples of biradicals have been studied before with DDCI2 (α -dehydrotoluene)⁸³ and DFT (biverdazyl radical).⁸⁴ Both molecules imply a rather large number of one-electron basis functions, which makes the application of DDCI3 rather expensive and, in the case of the variant of the biverdazyl radical chosen here, almost impossible at present without turning to model structures. The geometry of α -4-dehydrotoluene has been taken from the DDCI2 study,⁸³ and that of the biverdazyl radical has been taken from X-ray data.⁸⁵

TABLE 4: CASSCF, CASPT2, and DDCI3 Singlet–Triplet Splittings (in kcal/mol) for a Series of Biradicals^a

	small CAS			medium CAS		large CAS		exp. ⁸¹
	CASSCF	CASPT2	DDCI3	CASSCF	CASPT2	CASSCF	CASPT2	
CH ₂	24.82	17.70	11.19	10.50	11.45	10.07	10.62	9.1
CHF	4.26	-3.89	-14.10	-22.95	-5.95	-17.51	-13.41	-11.4/-14.6
CF ₂	-34.12	-43.00	-56.69	-55.60	-47.50	-60.26	-53.44	-56.7
CHCF ₃	25.02	19.24	11.35	5.84	10.85 ^b	5.59	10.99	
SiH ₂	-5.15	-13.35	-18.38	-17.91	-18.52	-17.84	-19.04	-18.0/-21.0

^a The small CAS refers to the minimal active space of two orbitals with two electrons. The medium CAS contains (most of) the valence orbitals and electrons. The large CAS includes an additional set of virtual orbitals (more details are given in the text). ^b With a level shift of 0.05 Hartree.

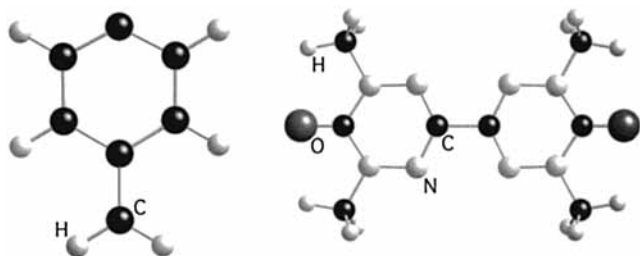


Figure 5. α -4-dehydrotoluene and 1,1',5,5'-tetramethyl-6,6'-dioxo-3,3'-biverdazyl.

TABLE 5: CASSCF, CASPT2, and DDCI3 Magnetic Coupling Parameters (in kcal/mol) for the α -4-Dehydrotoluene and 1,1',5,5'-Tetramethyl-6,6'-dioxo-3,3'-biverdazyl Biradicals^a

	basis	small CAS			large CAS		exp. ^{83,85}
		CASSCF	CASPT2	DDCI3	CASSCF	CASPT2	
dehydro-toluene	A	1.86	4.25	4.96	6.12	6.04	
	B	1.85	4.23		8.44	5.54	3–5
biverdazyl	A	-1.43	-3.50		-3.31	-2.64	-2.2

^a The small CAS only contains the unpaired electrons and the magnetic orbitals. The large CAS includes all important valence orbitals selected by RASSCF calculations and the corresponding electrons extended with a set of virtual orbitals. Basis A uses a (4s, 3p, 1d) contraction for N and all C's except those of the methyl groups in the biverdazyl radical, for which a (3s, 2p) contraction is used. For O, a (3s, 2p, 1d) basis set is applied, and for H, a (2s) basis set is applied. Basis B: C (5s, 4p, 2d) and H (3s, 2p).

Table 5 lists the magnetic interaction parameter J for two different active spaces and gives an indication of the basis set dependency of this parameter in the case of the dehydrotoluene radical. The two active spaces are constructed following the procedure discussed before for the other biradicals, that is to say two orbitals with two electrons for the small CAS and 12 orbitals with 14 electrons for the large CAS, selecting the most important valence orbitals by RASSCF calculations. For the dehydrotoluene molecule, both of the CASPT2 and DDCI3 estimates are within 2 kcal/mol of the experimental value. For the larger biverdazyl radical also, rather good agreement with the experimental data is obtained at all levels of theory, although, especially, the CASPT2 based on the larger CAS is in excellent agreement with the -2.2 kcal/mol measured experimentally. Note that the effect on J of extra basis functions is negligible; J is affected by not more than 0.5 kcal/mol for the CASPT2 based on the large CAS.

Conclusions

The magnetic coupling parameters in a series of compounds have been calculated to establish the performance of CASPT2 and to compare to the experiment and to results arising from the DDCI method. The latter method has been shown recently to give excellent estimates of the magnetic coupling parameters in an extensive series of compounds, including organic biradi-

cals, binuclear complexes, and ionic insulators containing transition metals. The only drawback of the DDCI method is the relatively large computational cost, which becomes prohibitive in many interesting systems. The CASPT2 method has been shown to be a promising alternative to DDCI to study magnetic coupling parameters. Moreover, because of its relatively low computational cost, CASPT2 also provides a clean alternative to the use of density functional theory based methods which require the use of a broken symmetry approach and exhibit a strong dependence of the results on the particular functional applied.³⁶ Close agreement between CASPT2 and either experiment or DDCI is obtained provided that the zeroth-order wave function accounts for two basic mechanisms, namely, the Anderson superexchange and, in part, the instantaneous relaxation of the ligand-to-metal CT configurations. For compounds with magnetic centers with $S \leq 1$, these wave functions can be constructed in a straightforward way. However, for larger spin moments, the inclusion of the relaxation of the charge transfer configurations in the reference wave function is not trivial. Nevertheless, we found that CASPT2 based on a reference wave function that only includes the Anderson superexchange mechanism reproduces all experimental trends very well. This allows us to extend the ab initio investigations of the magnetic coupling to more complicated cases such as those involving more than two magnetic centers and/or elevated total spin moment. We conclude that the CASPT2 method is a general, fast, and rather precise method to study magnetic coupling in biradicals, molecular complexes, and ionic insulators.

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