Density Functional Calculations of Magnetic Exchange Interactions in Polynuclear Transition Metal Complexes

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Two effective computational approaches for the study of magnetic exchange interactions in large molecules are discussed and tested on a number of model systems, namely, broken-symmetry (BS) and single-determinant (SD) models. Both methods are based on the density functional theory (DFT) but exploit different approximations to deal with multiconfigurational problems. Our results show that the BS model provides semiquantitative results for widely different situations, such as metal−radical interactions and metal−metal interactions mediated by inert organic bridges. Although more refined (and expensive) methods are needed for truely quantitative work, the BS/DFT approach provides a very useful tool for the rationalization of magneto−structural correlations and for the comparison of different bonding situations in large systems involving transition metal atoms.

Introduction

The experimental investigation of exchange interactions between magnetic centers in molecular or solid state systems constitutes one of the main research topics in modern chemistry. In solid state inorganic chemistry, magneto−structural correlations are widely used to interpret the magnetism of solids and to develop synthetic strategies affording compounds with expected magnetic properties.[1] In bioinorganic chemistry, the understanding of the magnetic interactions between metal centers provides information about the coordination environment and permits assessments regarding the geometry of active sites in enzymes.[2] In the last few years, a number of magnetic systems containing organic free radicals (such as nitroxide derivatives) and paramagnetic transition metal ions have been synthesized as possible precursors for ferromagnetic materials.[3]

Exchange-coupled systems are characterized by the presence of a manifold of states of different total spins, nearly degenerate in the absence of spin−orbit coupling and of magnetic fields, populated at room temperature. Understanding the electronic origin of these spin states has long been a challenge for theoretical chemists and physicists. The first theoretical interpretation of the magnetic properties of exchange-coupled systems dates back to 1963, when Anderson[4] proposed a model for magnetic properties of insulators. In 1975 and 1976, Hay, Thibeault, and Hoffmann[5] and Kahn and Briat[6] adapted the Anderson model to molecular systems. This latter formalism (*orbital model of exchange interaction*) is still widely applied to rationalize the magnetic properties of molecules and to derive qualitative magneto−structural correlations in bridged binuclear transition metal systems using semiempirical quantum chemical calculations.[1] In extended systems, the exchange interactions between nearest neighbors are stronger than those between more distant magnetic centers and determine the short-range electron correlation and the low-dimensional magnetic behavior. The *magnetic electrons* are rather well localized onto single paramagnetic centers in the so-called *magnetic orbitals*. The interactions between the magnetic orbitals therefore govern the onset of the exchange interactions. The latter are determined by two main factors: the exchange energy between electrons of equal spin, which favors a parallel alignment of the spins between two adjacent centers (the so-called *potential exchange* in the Anderson theory[4]), and the overlap between the magnetic orbitals, which gives rise to a transfer of electron density between the paramagnetic centers and favors the antiparallel alignment of the spins (the so-called *kinetic exchange* in the Anderson theory[4]). The interaction between magnetic orbitals can be direct (*direct exchange interaction*) or can occur *via* ligand-centered orbitals (*superexchange interaction*). Qualitatively, the exchange interactions can be understood in terms of *exchange pathways*, which connect the magnetic and ligand orbitals interacting by symmetry, and can be regarded as the

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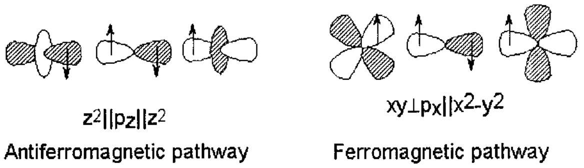
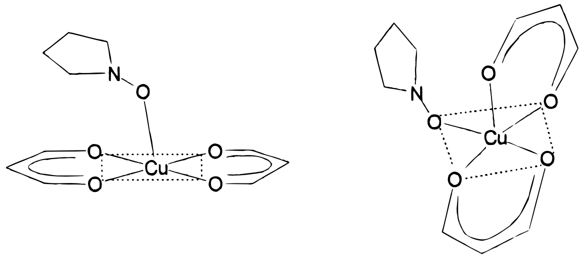
Scheme 1



highways for the propagation of the correlation between the magnetic electrons. An example of exchange pathways is shown in Scheme 1. Examination of the exchange pathways arising from several different metal−ligand conformations led Goodenough and Kanamori to develop the qualitative rules[7] that aided experimentalists for many years and were recovered by the orbital model of the exchange interaction.[5,6] Quantitative calculations of the magnetic exchange interactions require an accurate description of the multiplet structure of the molecules for the ground and the lowest excited states. This task can be accomplished by starting from the conventional Hartree−Fock (HF) molecular orbital theory and using extensive configuration interaction (CI) to correlate the magnetic electrons. By use of the pseudopotential approach to incorporate the effect of core electrons, rather large molecules can be treated at the *ab initio* level. Following the pioneering work of De Loth *et al.*,[8] a series of papers appeared dealing with the calculation of the singlet−triplet splitting in binuclear copper(II) complexes.[9] Complete active-space (CAS) multiconfigurational calculations have been used to describe the exchange interactions in a series of oxo-bridged complexes.[10] According to the increasing complexity of the wave functions, a number of exchange pathways have been recognized as important in transmitting the exchange interactions, such as double-spin polarization and charge transfer contributions. In 1979, Noodleman and Norman[11] suggested a formalism based on a broken spin and space symmetry single-determinant wave function for describing the low-spin state, which accounts for a large part of the electron correlation.[12] This formalism has been widely used within density functional theory (DFT)[13] and applied to clusters[14] as large as $[Fe_4S_4R_4]^{n\pm}$. A few HF calculations have been also reported.[15]

Until recently, less attention has been devoted to the exchange interactions between transition metal ions and free organic radicals[16] (nitroxide derivatives in most cases) where the magnetic orbitals can be described as follows. One orbital is mainly localized on the metal center, usually coming from antibonding interactions with surrounding diamagnetic ligands, whereas the other orbital is localized on the paramagnetic ligand center, usually a π^* orbital of a nitroxide group. The interaction occurs *via* the formation of a bond between the metal and the radical. This situation is opposite to that commonly found for polynuclear transition metal complexes, where the exchange interactions are generally propagated through diamagnetic bridging ligands, and can be viewed as weak bonding interactions between the metal centers, on which the unpaired electrons are mainly localized. Despite this difference in the electronic origin, the magnetic effects are always due to the presence of different spin multiplets, populated at room temperature. Depending on the relative orientation of the radical and the transition metal, a strong bonding interaction can result (usually with the oxygen of a nitroxide group of the radical), leading to the stabilization of a nonmagnetic singlet state. On the other hand, when the magnetic orbitals are nearly orthogonal, a magnetic spin state becomes lower in energy than the singlet state. Two classical geometric situations leading to different magnetic behaviors are shown in the Chart 1. Only a few calculations, based on a limited CI expansion, have been performed on these systems. It has been suggested that the mechanism of propagation of the magnetic interactions depends on the value of exchange integrals and on spin polarization mechanisms through a d_{z^2} orbital orthogonal to the magnetic metal orbital.[17]

Chart 1



In almost all the cases considered so far, the *ab initio* methods have been found to correctly describe either weak bonding interactions between metal ions or bonding between transition metals and organic radicals. The computed energy sequence of the spin multiplets agrees well with the experimental data. However, calculations involving transition metal ions, even using pseudoptentials to account for the core electrons, are lengthy and are not, therefore, well suited for comparison between different geometric situations to afford magneto−structural correlations. The use of the broken-symmetry (BS) approach greatly reduces the computational effort. In this respect, worth mentioning is the series of papers by Rappé *et al.*,[15] comparing *ab initio* full CI and HF-BS calculations. The systems so far studied have been the model species HHeH, $[HFH]^-$, $Cl_3Ti{-}O{-}TiCl_3$, and $[Cl_3Fe{-}O{-}FeCl_3]^{2+}$. The first two systems are very questionable from a chemical viewpoint but offer the opportunity to be treated at any level of accuracy and to model weak bonding interactions between 1s electrons on the H centers mediated by s and p electrons of the He and F atoms, respectively. The main conclusion of Rappé *et al.*[15] was that the HF-BS approach is capable of giving results surprisingly close to those obtained by large-CI calculations.

We felt it important to organize the different theoretical approaches used for the quantitative study of the exchange interactions by including DFT calculations, which are becoming very powerful tools in computational quantum chemistry of large

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systems. Also we wished to treat in the same framework transition metal clusters and transition metal complexes bound to organic radical systems with the aim of searching for a computational model which could account for exchange interactions having different electronic origins. The approaches we will apply and compare are the BS formalism and the direct calculation of the multiplet structure using the single-determinant (SD) technique. The latter approach was developed by C.D.,[18] using the principles of Ziegler *et al.*,[19] and has been applied[20] to the calculation of the multiplet structure of the excited states of $[Ru(bpy)_3]^{2+}$. To the best of our knowledge, this is the first time that this approach has been applied to the calculation of the multiplet structure arising from magnetic exchange interactions. Since our aim is to study model systems as near as possible to real chemical systems, we will focus our attention on exploiting the applicability of DFT. Results of *ab initio* CI and CAS-SCF calculations will be taken as references in cases where experimental data are not available.

The paper is divided into three main sections. In the first section, a brief outline of the computational methods, especially BS and SD formalisms, is given. In the second section, the results obtained with the different methods for the simple model systems H−He−H and H_2NO-H are presented and compared. In the third part, the same computational tools are applied to more realistic systems: different structures of the $[Cu_2Cl_6]^{2-}$ complex and the $[(acac)_2Cu(ONH_2)]$ model system. The systems studied in the second section represent the simplest models of weak bonding interactions: H−He−H and, for long H−O distances, $H-ONH_2$ models for the interaction between a 1s orbital and a π^* orbital orthogonal to it. $3d-\pi^*$ orbital interactions are considered for the more complex model $[(acac)_2Cu(ONH_2)]$, in which the axial nitroxide radical is approximated with the simplest possible nitroxide, namely ONH_2. $[Cu_2Cl_6]^{2-}$ complexes can be considered as classical examples of exchange interactions between transition metal ions and have been the object of extensive experimental and theoretical investigations;[21] therefore, they appear to be a challenging test case for any calculation on magnetic exchange.

Methods of Calculation[22]

The calculation of the low-lying energy levels in exchange-coupled systems requires the evaluation of the energies of all the spin states resulting from different occupations of a set of one-electron levels. This means that a multideterminant wave function in needed. Since, in addition, the energy spacing of the multiplets is of the order of kT, the electron correlation can play a dramatically important role. Multiconfigurational wave functions can be handled at the *ab initio* level only with large computational costs. Therefore, large molecular systems can be treated only as single-point runs and magneto−structural correlations on real chemical substances are generally prohibitive. Much effort has thus been devoted to develop a post-HF computational formalism based on an efficiently truncated CI expansion.[8] Alternatively, use is made of the density functional (DFT) formalism, which is expected to be reliable because the exchange and the correlation contributions to the electronic energy are naturally incorporated into the functionals of the electron density.[13] Such an approach also offers the advantage of drastically reducing the computational costs.

Broken-Symmetry Formalism. The BS formalism, widely used for quantitative calculations of the exchange-coupling constants in polynuclear transition metal complexes, has been reviewed several times.[13,14] In this formalism, a one-to-one correspondence is established between the energy of a Slater determinant built up with orbitals localized on different centers and bearing electrons with opposite spin and the energy of a microstate with $M_s = 0$ computed using the effective Heisenberg−Dirac−Van Vleck spin Hamiltonian

$$H = J\mathbf{S}_1\cdot\mathbf{S}_2 \quad (1)$$

where J is related to the multiplet energy splitting according to

$$J = \frac{E(S) - E(S-1)}{S} \quad (2)$$

In (2), $E(S)$ represents the energy of a state with total spin S. Equation 1 is widely used to reproduce experimental data, and J is known as the *magnetic exchange-coupling constant*. For a binuclear system of spin $S_1 = S_2$, the energy of the BS state is a weighted average of the energies of pure-spin multiplets and J can be obtained from the equation

$$J = \frac{E(S_1 + S_2) - E(\mathrm{BS})}{2S_1S_2} \quad (3)$$

where E(BS) is the energy of the broken-symmetry determinant. The term *broken-symmetry state* means that a localized solution of the spin states is usually obtained by using an electronic symmetry lower than the actual geometric symmetry. The use of eq 3 reduces the calculation of the multiplet structure in a binuclear system to the calculation of the total energies of two Slater determinants, one representing the state with the highest spin multiplicity and the other a state with $M_s = 0$ built from wave functions localized onto the different metal centers. Using spin projection techniques, it has been shown that E(BS) accounts for most of the electronic correlation for the singlet state, like, for example, ligand spin polarization effects.[23] The actual form of eq 3 has been shown to be valid when the overlap integral, S_{12}, between the magnetic orbitals is small ($S_{12}{}^2 << 1$), which is likely to be the case for weakly bonded paramagnetic moieties. A more general formula has been derived[11a] for any value of S_{12}, which shows that eq 3 can lead to an overestimation of the J values as large as 50% when $S_{12} = 1$. By using (3), one is therefore always overestimating the value of J. In the BS model, the high-spin state is completely uncorrelated and its energy is usually taken from spin-unrestricted calculations.

Single-Determinant Formalism. The calculation of the multiplet splitting using single determinants is discussed in detail elsewhere.[15,19] Following these results, it is possible to replace the energy of a single determinant by the corresponding statistical energy as obtained in DF theory. In the case of symmetrical molecules with degenerate orbitals, the individual multiplet states arising from an open-shell configuration cannot, in general, be expressed by a single determinant. That is, DF calculations do not yield multiplet energies directly. One uses then irreducible tensor operators and the Wigner−Eckart theorem to describe the multiplet manifold. This allows one to write the energy of a multiplet arising from a given configuration as a weighted sum of single-determinant energies.[15,19] Following this line of thought, one can exploit symmetry to the largest possible extent in order to simplify the

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[22] See the abbreviation paragraph at the end of the paper for the explanation of the symbols used.
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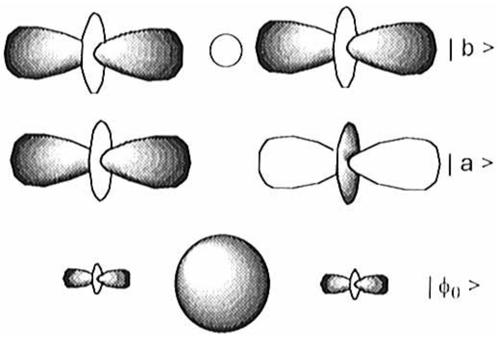
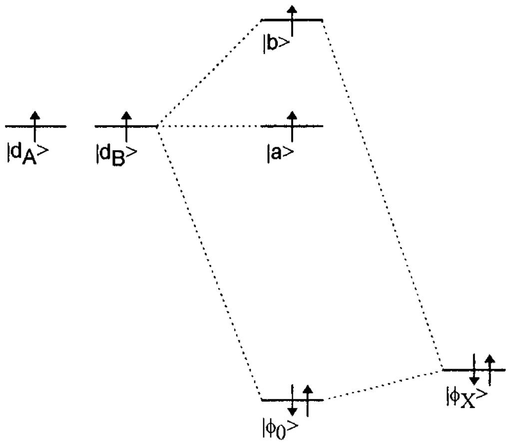
Scheme 2



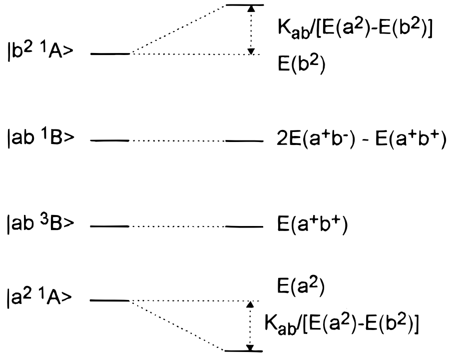
Scheme 3



relation between the multiplet splitting and single-determinant energies and thus keep computational effort to a minimum.

The calculation of the exchange-coupling constant, J, is essentially an extension of the multiplet calculations to exchange-coupled systems. We give next a short description of the method.

Consider the coupling of two magnetic orbitals via a single bridge atom, like that shown in Scheme 2, and the corresponding MO diagram shown in Scheme 3. For only the HOMO and LUMO (or SOMO in the triplet state) orbitals, the following four multiplets arise: $|a^2\ {}^1A\rangle$, $|ab\ {}^1B\rangle$, $|ab\ {}^3B\rangle$, $|b^2\ {}^1A\rangle$. Assuming that $|a\rangle$ and $|b\rangle$ do not belong to the same irreducible representation, the following energy diagram is obtained:



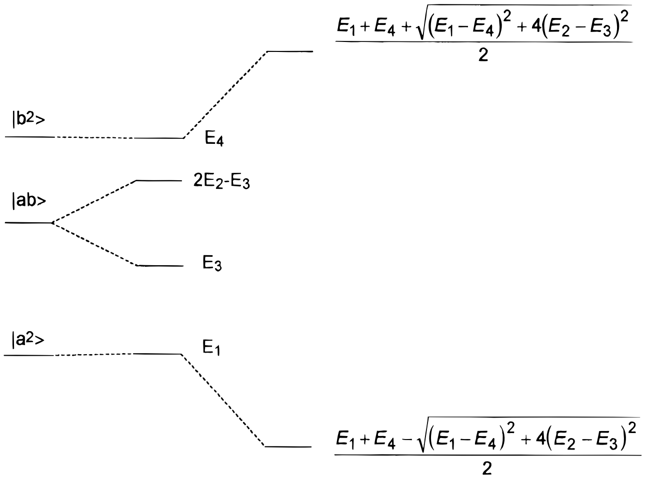
where the superscripts + and − label the spin of the electron and E indicates the energy of a single Slater determinant. The above considerations are not limited to the orbital interactions shown in Scheme 3, but are valid in general when we are considering two magnetic electrons (active electrons) in two molecular orbitals (active orbitals), $|a\rangle$ and $|b\rangle$. Using the approach described in ref 15, the energies of the following single determinants are to be evaluated:

$$E_1 = E\left(\left|a^{\uparrow}a^{\downarrow}\right|\right), E_2 = E\left(\left|a^{\uparrow}b^{\downarrow}\right|\right), E_3 = E\left(\left|a^{\uparrow}b^{\uparrow}\right|\right), E_4 = E\left(\left|b^{\uparrow}b^{\downarrow}\right|\right)$$

Moreover, the exchange integral K_{ab} can be obtained directly from the energy difference between ^1B and ^3B according to

$$K_{ab} = \frac{E\left({}^1B\right) - E\left({}^3B\right)}{2} = E\left(\left|a^{\uparrow}b^{\downarrow}\right|\right) - E\left(\left|a^{\uparrow}b^{\uparrow}\right|\right) = E_2 - E_3$$

Hence, we obtain the energies of the complete multiplet pattern as



The exchange-coupling constant, J, is obtained from the energy difference of the two lowest lying multiplets.

The orbital situation shown above is typically encountered in oligonuclear transition metal complexes. When the interaction between a transition metal complex and an organic radical is considered, the ^1A states correspond to charge transfer states in which one unpaired electron is transferred to the organic radical from the metal and *vice versa*. Therefore, these states are higher in energy than the B states, which become the low-lying multiplets.

Actual calculations of the single-determinant energies can be performed by using a transition state procedure in which the active orbitals are all equally populated or separately converging each determinant and computing the difference between the total energies (ΔSCF). The two procedures have been found to yield comparable results in previous cases, but in the following, we will apply only the ΔSCF procedure, which, although more expensive, appears more theoretically sound. Although this formalism can be used within any single-determinant theory, we have used only the DFT approach, as implemented in the Amsterdam density functional (ADF) code.[24] In all cases, triplet state energies have been computed by an unrestricted approach, since it is well-known that spin contamination is negligible in DFT.[25]

Multideterminant Formalism. From a formal point of view, an open-shell singlet must be described by at least a two-determinant wave function. Although a closed-shell singlet is correctly described by a single Slater determinant, the contribution of the next biexcited singlet state is of fundamental importance when weak bonding interactions have to be considered. In such circumstances, a CAS(2,2) approach is the simplest general-purpose recipe. At the same time, spin

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contamination is often quite strong in the UHF wave functions of triplet states.[25] As a consequence, these have been described either by an ROHF procedure or by spin projection on the UHF solution (PUHF). Starting from a converged CAS computation, dynamic correlation is introduced by multireference Møller−Plesset perturbation theory (orthogonal valence bond Møller−Plesset 2, OVB-MP2),[26] available in the Gaussian 94 series of programs.[27] However, the results obtained for the smallest model systems (*vide infra*) show an oscillatory behavior of the perturbative contribution to the energy with the number of active orbitals included in the CAS. Although reliable results are obtained when all the valence orbitals are used in the CAS, this approach becomes prohibitive for systems containing transition metal ions. As a consequence, for the larger systems the electron correlation was accounted for by a CAS calculation followed by a second-order CI calculation including a reduced number of external orbitals. The orbitals to be included in the calculations were selected by projecting the most significant atomic orbitals onto the molecular orbitals issued from the CAS step. Further details will be given for any particular case. It was shown in several papers that the QCISD(T) method,[28] although based on a single-reference formalism, is able to recover a large part of the nondynamic correlation. As a consequence, we performed some computations also by this method. Finally, some attempts to reach the full-CI limit for small systems were performed by the CIPSI algorithm.[29] In this method, a multireference space is progressively enlarged to include all the configurations whose interaction with those already present in the variational space is larger than a given threshold. In a second step, dynamic correlation is computed by a second-order barycentric Møller−Plesset treatment. Reducing the threshold for inclusion in the variational space, it is possible to monitor the convergence of the computations. All the configurations were taken into account variationally in the case of H−He−H, whereas the threshold was reduced up to convergence of the results in the case of H_2NO−H, where core electrons of N and O were not introduced into the correlation treatment.

The H−He−H and H_2NO−H Models

The one-electron orbital scheme describing the H−He−H system is shown in Figure 1. The multiplet structure arises from the distribution of four electrons in three orbitals. The low-lying singlet is $^1\Sigma_g{}^+$, and the triplet is $^3\Sigma_u{}^+$. The singlet−triplet separations (ST) computed for three H−He distances using *ab initio* and DFT methods are reported in Table 1.

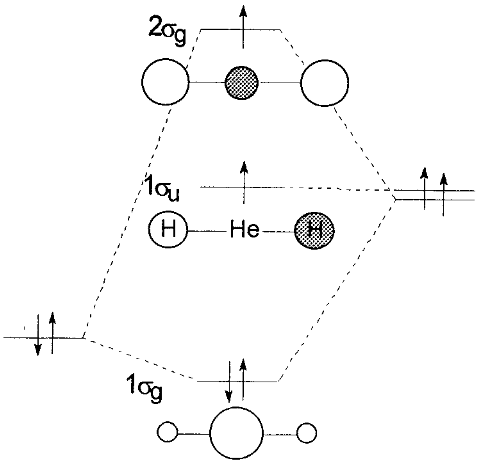

Figure 1. One-electron orbital scheme for the H−He−H model system.

Table 1. Singlet−Triplet Separations (cm^{-1})[a] Computed for H−He−H at Different H−He Distances

	H−He distances (Å)		
method of calcn	1.25	1.625	2.00
	Ab Initio		
CAS(2,2)	4204	476	48
OVB-MP2(2,2)	4358	420	26
CAS(4,3)	4294	484	46
OVB-MP2(4,3)	4530	492	48
QCISD(T)	4928	790	202
RU-BS	4298	526	60
PU-BS	4580	554	60
full CI	4860	544	50
	DFT		
Xα-BS	6004	646	58
LDA-BS	12432	760	158
BP-BS	10529	1268	134
Xα-SD	5631	745	64
LDA-SD	9050	1553	183
BP-SD	7799	1170	123

[a] The reported values are $E(^3\Sigma_u) - E(^1\Sigma_g)$. Positive values indicate that the singlet is the ground state. The abbreviations are explained in the text.

Ab initio calculations on the H−He−H system were performed with the programs GAMESS,[30] Gaussian 94,[27] and HONDO-CIPSI[31] using a 6-311G** basis set. DFT calculations were performed using the ADF program package[24] with Slater triple-ζ functions to represent the s orbitals of the hydrogen and helium atoms. The exponents of the functions are those given in the ADF database. The full-CI calculations compare well with the values reported[15b] by Hart et al.: 4782, 530, and 52 cm^{-1} for H−He distances of 1.25, 1.625, and 2.00 Å, respectively. The slight discrepancy between our values and those of Hart et al. (∼2%) is probably due to the difference between the basis functions used. The BS calculations at the HF level give results which nicely compare with the full-CI ones. As already noted,[15b] the difference between the two methods more severely affects the singlet−triplet splitting at long distances. This is indicative of a larger influence of the correlation on these values. Reasonably good agreement with the full-CI results is obtained also with the CAS(2,2) calculations, showing that this relatively simple approach is still able to include the largest part of the electron correlation. The second-order perturbation corrections (OVB-MP2) do not correctly take into account the dynamic correlation except when the full-valence active space (CAS(4,3)) is used. As mentioned above, this procedure becomes prohibitive for larger systems and has, therefore, been replaced by a reduced second-order configuration interaction (SOCI) on the computed CAS wave

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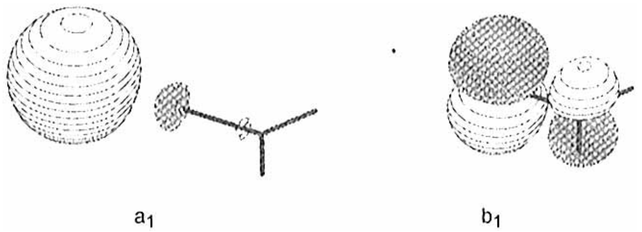

Figure 2. Schematic drawing of the frontier orbitals for the H_2NO-H model system.

functions. From another point of view, the QCISD(T) single-reference approach gives very good results at an H−He distance of 1.25 Å, but its performance strongly degrades at longer distances. Although this is probably connected to the onset of strong spin contamination in the UHF reference function, we refrain from applying approximate spin projection procedures[32] to post-HF computations due to the lack of generality and to their questionable theoretical foundation. As a consequence, no further QCISD(T) computations were performed.

DFT calculations were performed by the BS and the SD approaches using several different functionals. It is worth noting that the two approaches are equal when the magnetic orbitals are orthogonal to each other and localized onto different magnetic centers, as in the case of the H_2NO-H model. Xα is the local functional[33] which approximates the exchange energy and does not contain any correlation correction. The results reported in Table 1 show that $^1\Sigma_g^+$ is the ground state, in agreement with the *ab initio* results, and also that the singlet−triplet energy gap (ST) has the correct order of magnitude. Including correlation at both the local[34] (WVN) and nonlocal[35] (Becke−Perdew) levels of approximation leads to a much larger stabilization of the singlet state toward the triplet state.

For the H−He−H model, we can conclude that the BS approach, at either the HF or the DFT-Xα level, yields results in fair agreement with those of full-CI calculations.

Ab initio calculations on H_2NO-H were performed with a 6-311G basis set. DFT calculations were done with Slater triple-ζ functions for the valence orbitals. The 1s core orbitals of N and O were kept frozen. When the O−H distance is sufficiently large that the overlap between the 1s orbital of H and the appropriate 2p orbital of O is negligible, HOMO and LUMO orbitals are shown schematically in Figure 2. The calculations were performed in C_{2v} symmetry on the geometry optimized in the triplet state, keeping the O−H distance fixed at $d_{OH} = 1.9$ Å and the N−O−H angle fixed at $\alpha_{NOH} = 180°$. The optimized geometric parameters are $d_{NH} = 0.98$ Å, $d_{NO} = 1.38$ Å, and $\alpha_{HNO} = 114.4°$.

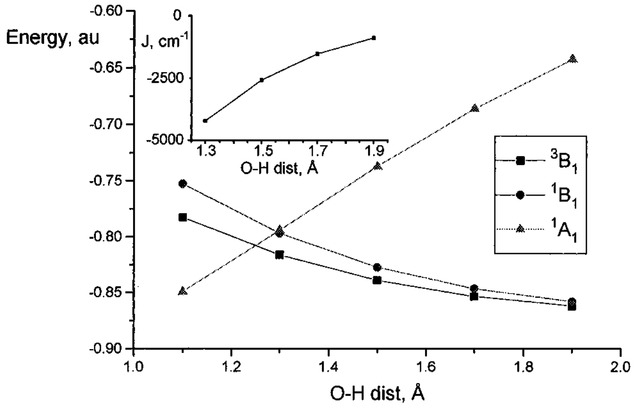

Figure 3. Dependence of the total energies of the three lowest electronic states of H_2NO-H on the O−H distance. The insert shows the corresponding variation of *J* (see text).

Table 2. Singlet−Triplet Separations (cm^{-1})^a Computed for H2NO−H with an O−H Distance of 1.9 Å

method of calcn	$E(^3B_1) - E(^1B_1)$	method of calcn	$E(^3B_1) - E(^1B_1)$
	Ab Initio		
CAS(2,2)/ROHF	−884	SOCI(6,4,8)	−970
RMP2	−2149	full CI	−962
CAS(6,12)	−972		
	DFT		
Xα-SD	−931	BP-SD	−668
LDA-SD	−840		

^{a} The following abbreviations are used here: RMP2 = $E(^3B_1)$ and $E(^1B_1)$ obtained from restricted open-shell MP2 calculations; SOCI-(n,a,e) = second-order CI calculation on an active space of *a* active orbitals and *e* empty orbitals with *n* active electrons (this corresponds to a CAS(n,a) calculation followed by a CISD calculation including *e* virtual orbitals).

In the triplet state, the HOMO and LUMO orbitals are singly occupied. The b_1 orbital can be clearly assigned to an N−O π* orbital. The a_1 orbital is mainly localized on the 1s orbital of H, with a small contribution from an sp hybrid of O. This view of the magnetic orbitals indicates that the exchange interaction is propagated through the exchange pathway 1s $\parallel$ sp $\perp$ π*. This pathway is expected to be ferromagnetic as long as the sp and π* orbitals are orthogonal. Placing two electrons in the a_1 and b_1 orbitals gives rise to four states (C_{2v} symmetry): $^3B_1$, $^1B_1$, and two $^1A_1$. The two $^1A_1$ states represent, at large distances, charge transfer states in which the electrons are localized on the H atom or in the π* orbital and are, therefore, expected to be at higher energy as compared to $^3B_1$ and $^1B_1$. The variation of the relative energies of the three lower lying multiplets, obtained by CAS(2,2)/ROHF calculations, as a function of the O−H distance is shown in Figure 3. At distances longer than 1.3 Å, the $^3B_1$ state becomes the ground state with $^1B_1$ as the next excited state. The computed variation of the singlet−triplet splitting, $J = E(^3B_1) - E(^1B_1)$, is shown in the inset of Figure 3. At 1.9 Å, the two levels are close in energy, and this geometric conformation was used to more accurately investigate the influence of the computational model on the singlet−triplet energy gap. The results of *ab initio* and DFT calculations are collected in Table 2. All the models agree on placing the $^3B_1$ state lowest in energy. Electron correlation was included in the HF formalism by using second-order CI calculations on triplet and singlet ROHF references. Also, we chose a subspace of the entire electronic space which includes the 1s orbital of H and the 2p orbitals of O (12 basis functions from the contraction of 20 Gaussian primitives). Using this space as the complete active space, we performed a CAS(6,12) calculation and further a second-order CI calculation taking as reference states those coming from a minimum CAS(6,4) calculation (SOCI(6,4,8)). The results of all the calculations compare well with the CIPSI result, which should be very close to a full-CI valence computation. Also, the uncorrelated ROHF calculations differ only by 8% from the CIPSI result, showing that, in the present case, the electronic correlation gives only small corrections to the ST splitting. These contributions can, however, become important when smaller ST splittings are to be computed.

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Table 3. Singlet−Triplet Separations (cm^{-1}) Computed for $[Cu_2Cl_6]^{2-}$

method of calcn	φ (deg) 0°	45°	70°
	Ab Initio		
LOC[a]	36	−58	87[b]
DELOC[a]	6	−47	75[b]
BS	1620	1331	1901
	DFT		
XαSW-BS[c]	198	−210	113
Xα-BS	122	−309	72
LDA-BS	362	−246	191
BP-BS	256	−200	109
Xα-SD	−41	−437	−106
LDA-SD	160	−374	45
BP-SD	−35	−402	−145
experiment	0 to 40[d]	−80 to −90[e]	

[a] Reference 9. [b] Computed for $\varphi = 90°$. [c] Reference 21. [d] Reference 38. [e] Reference 39.

DFT calculations, performed using the SD model, also agree well with the CIPSI value. The best agreement is obtained by using the Xα functional. Inclusion of correlation reduces the ST gap, indicating that the singlet state is more influenced than the triplet.

The $[Cu_2Cl_6]^{2-}$ and $[(acac)_2Cu-ONH_2]$ Cases

$[Cu_2Cl_6]^{2-}$ complexes have long been used as test examples for magneto−structural correlations. Several correlations between the measured exchange-coupling constants and geometric parameters have been established experimentally.[36] The first quantitative calculations of the exchange-coupling constants as a function of geometric parameters date back to 1986 and were based on the Xα-SW formalism.[21] In these calculations, the effect of the tetrahedral distortion of the $CuCl_4$ plane on the magnetic properties was reproduced. More recently, a series of papers appeared dealing with the calculation of the dependence of the exchange-coupling constants on a larger series of structural parameters.[9] These calculations, based on a variational CI calculation of the ST splitting at the *ab initio* level of approximation, give figures in very good agreement with the experimental data. The essential features of the method[9a] are the direct calculations of the ST energy gap through a perturbative expression which avoids the calculation of a small number from large total energies and the use of the so-called ST splitting observable-dedicated molecular orbitals in the CI procedure.[9a] The results of these calculations, relevant for the present work, are collected in Table 3, and we will use these results as "exact results" to compare with other calculations. The effects of the core orbitals of copper and chlorine on the valence electrons were approximated by pseudopotentials. In Table 3, two series of results are presented corresponding to the use of localized (LOC) or delocalized (DELOC) molecular orbitals. The ST splittings computed in the two cases differ significantly, especially for the planar conformation, $\varphi = 0°$.

The model complex and the relevant geometric parameters are shown in Figure 4. DFT calculations were performed using the ADF program package with double-ζ functions for the copper and chlorine atoms. The core orbitals up to 2p for copper and chlorine were kept frozen. The ST splittings computed using the SD and BS approaches are collected in Table 3. In the same table, BS calculations at the HF level of approximations are also reported. These calculations were performed with the Gaussian 94 package[27] using the Hay−Wadt optimized basis set for coppers and terminal chlorine atoms.[37] The core orbitals were treated by using the appropriate pseudopotentials.[37] The bridging chlorines were treated using a 6-311G all-electron basis set. A p polarization function with an exponent of $\zeta = 0.06$ was applied to all the chlorines. In order to obtain a better localization of the molecular orbitals into the magnetic orbitals of the broken-symmetry state, it was necessary to reduce the covalency of the copper−chlorine bond by removing part of the electronic charge from the chlorines. This was achieved by adding two Na^+ ions at a distance of 3.0 Å from each copper along the Cu−Cu direction. An STO-3G basis was applied to each Na atom. Test calculations were performed at $\varphi = 0°$ without the Na atoms and showed a variation smaller than 5% in the computed ST splitting.

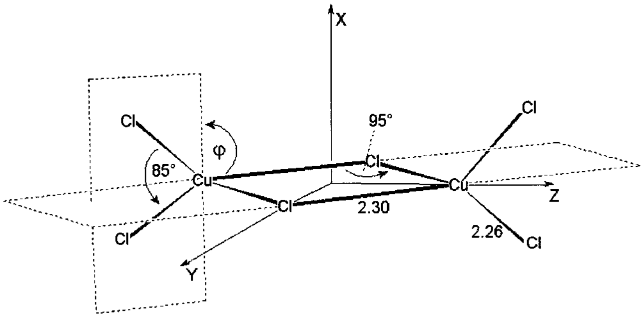

Figure 4. Schematic drawing and main geometric parameters of $[Cu_2Cl_6]^{2-}$ complexes.

The reference *ab initio* results,[9] shown in Table 3, were obtained using a CI expansion on the reference determinants obtained from an active space built up from the HOMO and LUMO. These calculations agree well with the experimental data. In particular, the observed change of coupling from anti- to ferromagnetic on varying the φ angle from 0 to 45° is reproduced and the order of magnitude of the ST splitting is obtained. It is be relevant to remark at this point that the geometric parameters which influence the ST splitting are numerous and in any calculations one always uses some idealization in the geometry of the model molecule. One cannot therefore expect a full quantitative agreement with the experimental data. In the present case, for example, the α bridge angle was held fixed at 95° (which corresponds to an average value of the angles seen in the crystal structures)[38,39] irrespective of the value of φ. In order to verify if a simple model can be applied to $[Cu_2Cl_6]^{2-}$, we performed HF calculations using the BS approach, which succeeded in reproducing the ST splitting in the model H−He−H case. The computed values of the ST splitting are very different from the experimental data even qualitatively (see Table 3), since they do not reproduce the observed variation of sign, the singlet state always being much more stabilized than the triplet state. These results are rather surprising, since the HF-BS approach has been successfully applied to monobridged oxygen complexes to reproduce the antiferromagnetic ground state.[15] The CAS(2,2) approach, which was found to underestimate the ST splitting in the

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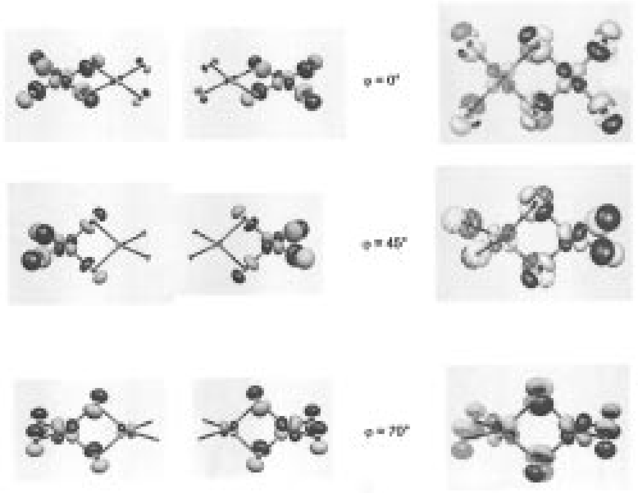

Figure 5. Isodensity surfaces ($\psi = 0.07$ (e bohr^{-3})$^{1/2}$) of the magnetic orbitals of $[Cu_2Cl_6]^{2-}$ obtained from Xα-BS calculations at different φ values (see Figure 4). Left: separate magnetic orbitals. Right: a representative view of the overlap between the magnetic orbitals.

H−He−H model, gives degenerate singlet and triplet states for $[Cu_2Cl_6]^{2-}$. For $\varphi = 0°$, inclusion of correlation by single and double excitations from the CAS wave functions into the virtual orbitals gave an ST splitting of -14 cm^{-1}. These results are in agreement with the calculations of Fink et al.[10] on a number of model complexes. These authors found that CASSCF or valence CI calculations are not able to reproduce the magnitude of the magnetic exchange-coupling constants, which requires the use of more time-consuming multireference CEPA calculations.[40]

DFT calculations (see Table 3) performed in the BS formalism reproduce the correct ordering of the singlet and triplet states. The absolute value of the ST splitting is larger than the experimental values and the reference *ab initio* results. The scattered-wave (SW) result[21] and the Xα-LCAO result are comparable and can also be considered in fair agreement with the reference values. Inclusion of correlation *via* the correlated functionals induces a larger stabilization of the singlet state with respect to the triplet state and causes a larger ST separation when $S = 0$ is the ground state. The poorest agreement with the exact values is obtained by the SD method. The LDA-SD calculations are better than the BS ones in the antiferromagnetic cases, whereas the opposite is true in the ferromagnetic situation corresponding to $\varphi = 45°$. In this model, the singlet state is not sufficiently stabilized with respect to the triplet. As a conclusion, we can say that the BS approach seems in this case to account for a large part of the correlation of the singlet state while the SD model does not. Better results would be expected if some of the dynamic correlation of the triplet state could be included.

The use of the BS orbitals allows an easy visualization of the exchange pathways within the active electron approximation of the exchange interaction. The magnetic orbitals of $[Cu_2Cl_6]^{2-}$ computed in the Xα-BS formalism are shown in Figure 5 (left) for $\varphi = 0$, 45, and 70°. These are magnetic orbitals mainly localized on one half of the dimeric molecule. Spin-up electrons are represented on the left-hand side of each diagram. Spin density is transferred from one center to the other by two main mechanisms: the direct contribution (atomic orbitals of the other center directly contribute to the magnetic orbital) and the superexchange (spin density is transferred to the common bridging ligands). The superexchange contribution is more relevant for $\varphi = 0$ and 70° and favors an antiferromagnetic alignment of the spins. The angular variation of the superexchange contributions is better visualized in the right part of Figure 5 in which the magnetic orbitals have been allowed to overlap. For $\varphi = 45°$, the bridging orbitals are nearly orthogonal and favor a ferromagnetic interaction.

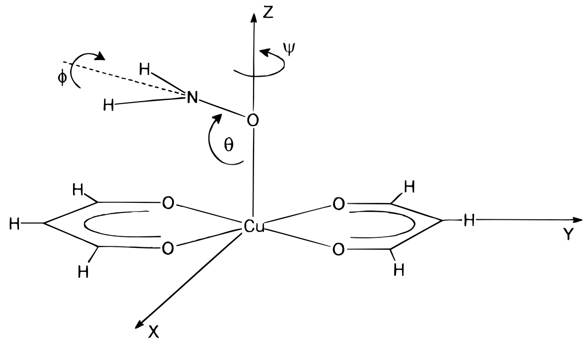

Figure 6. Schematic drawing and main geometric parameters for $[(acac)_2Cu{-}ONH_2]$.

Table 4. Singlet−Triplet Separations (cm^{-1}) Computed[a] for $[(acac)_2Cu{-}ONH_2]$

method of calcn	$E(^3A'') - E(^1A'')$	method of calcn	$E(^3A'') - E(^1A'')$
	Ab Initio		
CAS(2,2)/ROHF	−52.4	SOCI(8,2,8)[b]	−50.3
SOCI(0,2,94)	−48.5		
	DFT		
Xα-SD	−180	BP-SD	−169
LDA-SD	−171		
experiment[c]	−10 to −70		

[a] $\psi = 90°$ was used in all the calculations. [b] The 18 orbitals included in the SOCI calculations are the valence 3d orbitals on copper and the valence 2p orbitals on the oxygen atom of the radical. [c] Reference 16.

The $[(acac)_2Cu{-}ONH_2]$ complex is a model for a classical series of compounds containing a transition metal ion bound to a nitroxide radical.[16] The coordination environment of the transition metal ion (in the present, case copper(II)) is modeled by an acetylacetonate ligand (real compounds generally use the hexafluoro derivative). The nitroxide ligand is represented by the simplest model radical $H_2NO^{\bullet}$ already used in the literature.[17] The geometric arrangement and the Cartesian reference system are shown in Figure 6.

Ab initio calculations were performed using Hay−Wadt pseudopotentials[37] for copper and for the oxygen and the carbon atoms of the acetylacetonate ligands, while all electrons were kept for the nitrogen, oxygen, and hydrogen atoms of the radical. The basis sets were (9s,5p)/[4s,2p] for the N and O atoms of the radical, (4sp)/[2sp] for the C and O atoms of the ligands, and (3s,2p,5d)/[2s,2p,2d] for Cu. The H atoms were treated using a (4s)/[2s] basis set. The entire orbital space consists of 136 contracted functions. DFT calculations were performed using double-ζ Slater orbitals with the standard exponents available in the ADF program package. The results of the calculations performed at $\psi = 90°$ (C_s symmetry) are collected in Table 4. The effect of the electron correlation on the computed ST splitting was investigated by correlating the two active electrons in the HOMO and LUMO orbitals with all the virtual electrons through an SOCI(2,2,94) calculation. The ST gap actually computed, -48.5 cm^{-1}, is very close to that obtained by a simple CAS(2,2)/ROHF calculation, -52.4 cm^{-1}, indicating that, as already noted for the simple $H_2NO{-}H$ model, nondynamic electron correlation is playing only a minor role in the exchange interaction. A more complete CI approach was

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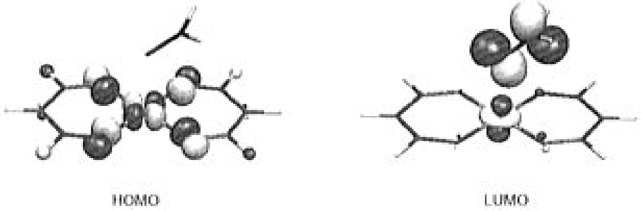

Figure 7. Isodensity ($\psi = 0.07$ (e bohr^{-3})$^{1/2}$) surfaces of the magnetic orbitals of $[(acac)_2Cu-ONH_2]$ obtained from Xα-SD calculations.

Table 5. Singlet−Triplet Separations (cm^{-1}) Computed for $[(acac)_2Cu-ONH_2]$ at different ψ Angles

method of calcn	ψ (deg) 0°	ψ (deg) 45°
Ab Initio		
CAS(2,2)/ROHF	−53.0	−49.2
DFT		
Xα-SD	−184	−190
LDA-SD	−174	−179
BP-SD	−173	−178

developed using as active orbitals all the 3d orbitals on Cu (six in the Cartesian representation used in GAMESS[30]) and the 2p orbitals of the O atom of the nitroxide radical. This yields an 18-orbital basis space in which we performed an SOCI(18,10,8) calculation. The results of these calculations gave an ST splitting of −50.3 cm^{-1}, which must be regarded as the most accurate result.

DFT calculations give an ST splitting larger than that obtained by the *ab initio* methods, but in any case always with the triplet state as the ground state. CAS(2,2)/ROHF and DFT calculations were also performed for $\psi = 0$ and 45° (Table 5). In all cases, a ferromagnetic ground state was computed and the ST splitting was almost constant with the ψ angle, in agreement with the experimental observations.

A perspective drawing of the HOMO and LUMO orbitals (SOMOs in the triplet state) is shown in Figure 7. The HOMO is an antibonding Cu−O orbital mainly localized on the $3d_{xy}$ metal orbital, while the LUMO is essentially formed by an N−O π^* orbital almost equally delocalized on the N and O atoms. A significant contribution to the LUMO comes from the $3d_{z^2}$ orbital perpendicular to the CuO_4 plane. This orbital is responsible for a transfer of electron density from the radical to the metal, suggesting the following ferromagnetic pathway for the exchange interaction: $3d_{xy} \perp 3d_{z^2} \parallel \pi^*$.

Conclusions

The performance of two formalisms developed for calculating multiplet energies, namely, the broken-symmetry valence-bond and the single-determinant approach, has been investigated on model compounds representing two limiting examples of exchange interactions. In the H−He−H and $[Cu_2Cl_6]^{2-}$ cases, the exchange interactions are propagated *via* diamagnetic ligands bridging two paramagnetic centers (superexchange). For the H_2NO-H and $[(acac)_2Cu-ONH_2]$ models, the exchange interactions are propagated through a direct mechanism involving interactions between orthogonal orbitals favoring a parallel alignment of the unpaired spins. In the latter cases, we have shown through *ab initio* calculations that nondynamic electron correlation plays only a minor role in determining the value of the exchange-coupling constant. In agreement with previous findings, the opposite situation is encountered in the $[Cu_2Cl_6]^{2-}$ system. DFT models have been found to correctly reproduce the sign of the exchange-coupling constants in all cases, but they are not reliable for a quantitative estimation of the absolute values.

It is difficult at this point to indicate a general strategy for predicting the magnetic behavior of exchange-coupled systems, since a post-HF calculation of the electron correlation is generally too costly to be applied to real systems and DFT models, which can easily handle large aggregates of atoms, give only approximate values of the exchange-coupling constants which can differ by up to 100% from the actual value. The best strategy to follow in the future is probably to use DFT models for scanning geometric variations over a rather wide range of parameters and then accurately compute the multiplet structure with post-HF methods only in selected areas of interest.

Abbreviations. The following abbreviations are used throughout the paper: CAS(n,m) = complete active-space multiconfigurational SCF calculation involving a set of m orbitals with n electrons;[41] CASPT2(n,m) = MP2-level electron correlation correction to the CAS(n,m) energy;[42] QCISD(T) = quadratic CI calculation including single and double substitution with a perturbative inclusion of triple substitutions;[28] RU-BS = broken-symmetry calculation using the ROHF energy for the triplet state; PU-BS = broken-symmetry calculation using the energy of the triplet state obtained by spin projection from a UHF calculation; CISD = configuration interaction calculation with single and double excitations; Xα = exchange functional[33] with an empirical α coefficient equal to 0.7; LDA = local-density approximation to the exchange correlation;[34] BP = Becke−Perdew gradient corrected exchange-correlation functional;[35] Xα-BS, LDA-BS, BP-BS = broken-symmetry calculations using the various functionals.

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