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Restricted Ensemble-Referenced Kohn−Sham versus Broken Symmetry Approaches in Density Functional Theory: Magnetic Coupling in Cu Binuclear Complexes[†]

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Abstract: The performance of density functional theory in estimating the magnetic coupling constant in a series of Cu(II) binuclear complexes is investigated by making use of two open shell formalisms: the broken symmetry and the spin-restricted ensemble-referenced Kohn−Sham methods. The strong dependence of the calculated magnetic coupling constants with respect to the exchange-correlation functional is confirmed and found to be independent of whether spin symmetry is imposed or not. The use of a method which guarantees the spin state does not improve the correlation with the experiment and indeed shows some worsening due to an overestimation of the ferromagnetic interactions. However, with the present exchange-correlation functionals, a rather systematic deviation is found. Therefore, it would be possible to develop improved density functionals which will allow for a rigorous treatment of open shell systems in density functional theory.

1. Introduction

The Kohn−Sham (KS) implementation[1] of density functional theory (DFT)[2] has no doubt become the standard electronic structure method in computational chemistry as well as computational materials science.[3−6] Successful applications of DFT in chemistry are very broad covering, among others, molecular structure, thermochemistry, reactivity in organic, inorganic and organometallic chemistry, interpretation of infrared spectra, prediction of nuclear magnetic resonance shielding, core level binding energies,[7−9] and, more recently, interpretation of optical spectra.[10] Likewise, there are numerous examples of successful applications of DFT in condensed matter and surface science.[3] The prediction of crystal structures, the reconstruction of complex surfaces, the structure of chemisorbed molecules, and the reaction mechanisms of chemical reactions mediated by surfaces can be mentioned in this respect along with the broad field of applications emerging from coupling of DFT with molecular dynamics which in itself generated a new field usually termed ab initio simulations.[11]

The basis of the Kohn−Sham method is the existence of a reference system of noninteracting electrons with the density identical to that of the real physical system. The existence of such a reference system is usually taken for granted although there is a large body of literature dealing with this important problem. In the original KS formulation, the density of the reference system is written as a Slater determinant with identical spatial part for the alpha and beta spin orbitals and for an even number of electrons resulting in a closed shell electronic structure. For stable molecules and nonmagnetic solids having precisely a closed shell electronic structure this is a very reasonable choice which indeed imposes spin symmetry. In the case of radicals and

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other magnetic systems the closed shell *Ansatz* cannot be used and different alternatives have been proposed, with the spin-unrestricted or spin-polarized version of the KS implementation (UKS) being almost universally used in this case.[12,13]

The UKS implementation is very similar to the Unrestricted Hartree Fock (UHF) method proposed earlier by Pople and Nesbet[14] and by Berthier.[15] For many years, the UHF method was the most common approach to the open shell problem in quantum chemistry, and in the late 1970s and early 1980s it was implemented in almost all semiempirical and ab initio Hartree−Fock computational codes. The periodic formulation of the UHF method was also developed and later coded into the CRYSTAL suite of programs.[16] However, many numerical applications of UHF to different systems soon encountered certain problems, mainly related to the so-called spin contamination arising from the fact that the corresponding UHF wave function is not an eigen function of the square of the total spin operator. These difficulties led quantum chemists to seek for alternatives to UHF within the different orbitals for different spins scheme; we mention here extended Hartree−Fock[17−19] and similar formalisms. However, these methods appeared to be very complex and not very accurate because of the lack of the dynamic electron correlation. Hence, the UHF approaches were almost abandoned, and the problems encountered by these methods were solved by making use of the more advanced wave function theory (WFT) methods of electronic structure such as the multiconfigurational self-consistent field (MCSCF), the configuration interaction (CI) methods, or the coupled cluster (CC) approaches.[20] Notice, however, that these methods demand a huge increase in the computational complexity and an enormous computational cost. In principle, numerical accuracy up to a predefined threshold can be achieved by these sophisticated wave function based methods. In practice, however, even with the present day available supercomputers, very accurate calculations can be carried out in systems containing a rather limited (∼10−20) number of atoms. Clearly, density functional methods do not face these limitations, because the electron correlation is implicitly introduced through the exchange-correlation functional. However, one must be aware of the possible artifacts arising from the fact that, while the real system of interacting electrons possesses the well-defined spin symmetries, the UKS noninteracting reference system does not.

In the case of radicals or open shell systems with a high spin open shell ground state, the UKS approach is almost free of problems, at least judged from the numerical success evidenced in many applications. The problems remain, however, when the system of interest exhibits a low spin ground state or when the property of interest concerns energy differences involving both high and low spin states. This is the case of biradicals and, also, of a broad class of systems such as di- or polinuclear complexes with open shell transition-metal atoms; the same problem appears when computing various spectral terms of a given atomic or molecular multiplet state. A practical solution to the problem of computing the energy of low spin states for transition-metal dinuclear complexes has been given by Noodleman[21,22]

in the framework of UHF and of SCF-Xα methods. An independent, closely related, method was also proposed by Yamaguchi in the framework of UHF.[23] These practical approaches are all based on the use of broken symmetry (BS) solutions which do not necessarily represent the desired state but the energy of which can be related to the desired spin state through spin symmetry considerations, such as the Slater sum rule as applied by Ziegler, Rauk, and Baerends,[24] through projection techniques, such as the methods of Noodleman[21,22] and Yamaguchi,[23] or through the appropriate mapping approach.[25,26] In this context it is also worth pointing out the pioneering calculations of Bagus and Bennet[27] on the energies of atomic multiplets in the framework of SCF-Xα.

The broken symmetry approaches provide a way to bypass the problem of dealing with low spin states in the UKS calculations; however, the problem itself still remains. The origin of the problem is in the neglect of spin symmetry requirement in the wave function of the noninteracting reference system employed in the KS self-consistent approach. This problem has attracted the attention of many theoretical groups, and a number of well-defined procedures have been proposed. Thus, new Kohn−Sham procedures within strict spin-restricted formalism have been proposed which result in a proper description of open shell states where the total spin quantum numbers (S and S_z) are well defined, for instance, the spin-Restricted Ensemble-referenced Kohn−Sham (REKS) method of Filatov and Shaik,[28,29] which is, in its spirit, similar to the well-known CASSCF approach. The CAS-DFT approach[30] has been also formulated where the nondynamic electron correlation effects and the proper spin symmetry are introduced through the CASSCF wave function and the dynamic electron correlation is taken over by a suitable correlation functional. The problem of CAS-DFT lies, however, in the double counting of correlation effects, which are implicitly incorporated via the density functional and are explicitly treated by the WFT method. The time dependent DFT formalism[31−33] does also treat spin symmetry correctly, but its current implementation cannot be applied to the problem of magnetic coupling where the low spin ground state possesses strong multireference character and requires the inclusion of doubly excited configurations for its proper description. Hence, the REKS approach seems to be the most appropriate spin restricted KS method which can be applied to the study of magnetic coupling in this kind of systems.

In the present work, we extend our previous studies about the REKS description of magnetic systems[34,35] to a new series of large Cu binuclear complexes, which cover a broad range of physical situations, from strongly antiferromagnetic coupling to ferromagnetic interactions. In doing so one must be aware of the strong dependence of the magnitude of the calculated magnetic interaction on the exchange-correlation functional employed in the calculations. In particular, we recall the dramatic effect of the amount of the Fock exchange in the HF/DFT hybrid functionals.[36−38] Indeed, by tuning this parameter one can obtain almost any a priori desired result. This criticism does not, by any means, pretend to invalidate the high quality research in this field and the meaningful

magneto-structural correlations derived from these calculations. We just want to stress the weakness of the present approaches and, hence, stimulate further research work in the development of new and improved density functionals. In any case, this discussion makes it clear that the predictive capability of DFT approaches with regard to the quantitative prediction of magnetic coupling in this type of systems is limited. Therefore, the aim of the present work is not to reproduce the experimental values but to examine the performance of the REKS approach and, for a series of density functionals, compare the results predicted by this more physically grounded formalism with those obtained by means of a more pragmatic broken symmetry approach.

2. Density Functional Description of Open Shell Electronic States in Magnetic Systems

Many magnetic systems exhibit localized magnetic moments at a given atom—or group of atoms—with unpaired electrons. Hence, an effective magnetic moment, S_i, which depends on the actual electronic configuration of the magnetic center, can be associated with this center to rationalize the magnetic properties of these systems. Various interactions between these localized magnetic moments are possible which give rise to an interesting magnetic behavior and define the observed magnetic properties. These interactions are usually described with the help of the phenomenological Heisenberg—Dirac—van Vleck (HDVV) Hamiltonian which provides the simplest physical model for the description of magnetic coupling (or exchange coupling) in a broad class of chemical compounds including organic biradicals, inorganic complexes, and ionic solids. This Hamiltonian describes the isotropic interaction between localized magnetic moments S_i and S_j as

$$\hat{H}^{HDVV} = -\sum_{i>j} J_{ij}\hat{S}_i \cdot \hat{S}_j \qquad (1)$$

where the J_{ij} constant controls the magnitude and type of interaction between S_i and S_j localized spin moments. In eq 1, a positive value of J_{ij} corresponds to a ferromagnetic interaction. The HDVV Hamiltonian can be rigorously derived from the effective Hamiltonain theory. This is an effective Hamiltonian which describes the low-energy spectrum arising from the interactions between S_i and S_j. These interactions are of quantum mechanical nature, and, in general, they are much stronger than the classical interactions between magnetic dipoles.

For the simplest problem of two electrons in two atomic orbitals, such as in a Cu dinuclear complex, it follows that the lowest energy electronic states are a singlet, S, and a triplet, T. These states are the eigenstates of the HDVV Hamiltonian, and the magnetic coupling constant can be obtained as in eq 2.

$$J = E(S) - E(T) \qquad (2)$$

Assuming that the HDVV Hamiltonian effectively describes the low-energy spectrum of these systems, a one-to-one correspondence between the eigenstates of the HDVV Hamiltonian and those of the exact nonrelativistic Hamiltonian must exist. In particular, notice that the lowest

eigenstates of the exact Hamiltonian are also a singlet S and a triplet T. The one-to-one correspondence between the eigenfunctions of the HDVV and those of the exact Hamiltonian follows from the fact that both Hamiltonians commute with the total spin operators.

In practice, however, the eigenfunctions of the exact Hamiltonian are not known, and a suitable approximation is generally used. Within the spin-restricted description of the relevant electronic states, the one-to-one correspondence mentioned above is imposed by construction. In the simplest case of two electrons in two atomic orbitals (i_A and j_B), one can choose a delocalized description and construct two molecular orbitals of g (even) and u (odd) symmetry. The lowest singlet state is multireference in nature and involves a variable mixing of the two resulting closed shell determinants which, for a given set of g and u molecular orbitals, is optimal for the variational two by two configuration interaction *Ansatz*. Alternatively, one can choose to continue using the localized description, and, in this case, several single Slater determinants can be constructed. Thus, one has the ferromagnetic solution, |FM>,

$$|FM > = |....i_A j_B > \qquad (3)$$

which corresponds to the $M_S = 1$ (or $M_S = -1$) component of the triplet state T, and two broken symmetry solutions

$$|BS1 > = |....i_A \bar{j}_B > \qquad (4)$$

and

$$|BS2 > = |....\bar{i}_A j_B > \qquad (5)$$

which can be combined to yield the $M_S = 0$ component of the triplet T or the singlet S thus preserving the space and spin symmetry. In practice, one can choose to work with only one of the two broken symmetry solutions and variationally optimize the orbitals with respect to it. The resulting wave function does not have spin and space symmetry and does not represent any electronic state of the exact Hamiltonian. Nevertheless, one can relate the expectation energy of the broken symmetry solution to that of the singlet state by an appropriate mapping. This is the basis of the broken symmetry approach proposed by Noodleman[21,22] and Yamaguchi et al.[23] Hence, it is easy to show that

$$J = E(S) - E(T) = \frac{2(E(BS) - E(FM))}{1 + < i'_A | j'_B >^2} \qquad (6)$$

where "i'_A" and "j'_B" stand for the self-consistent localized orbitals on magnetic centers A and B, and $< i'_A | j'_B >$ corresponds to the overlap integral between these magnetic orbitals. It has been shown that this overlap integral is usually less than 0.1,[25] and, therefore, the denominator in eq 6 does not significantly deviate from unity.

In the standard Kohn—Sham implementation of density functional theory, the reference state is a single determinant state, and, hence, the only way to get an estimate of the magnetic coupling constant is the computation of the |FM> and |BS> single determinant state through eq 6 and neglecting the overlap term. On the other hand, in the spin-

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restricted ensemble-referenced Kohn−Sham (REKS) method, employed in the present study, a completely different strategy is used which is based on the ensemble approach to density functional theory. Within the standard Kohn−Sham procedure to DFT, it is tacitly assumed that *any* physical density can be represented by a single Slater determinant constructed from the N lowest eigenfunctions of a certain Hamiltonian which describes a system of noninteracting particles moving in potential V_s (pure state V-representability). However, already in the early works on Kohn−Sham DFT, it was realized that such a representation can not be the most general one, and it was suggested to employ the ensemble density (weighted sum of the densities of several states) to represent the physical density (density of a system of interacting particles).[39,40] The rigorous proof that any physical density can be represented by an ensemble of densities, as in eq 7, has been provided by Lieb[41] and Englisch and Englisch.[42]

$$\rho(\mathbf{r}) = \sum_i w_i \rho_i(\mathbf{r}) \qquad (7)$$

Within the Kohn−Sham approach, the ensemble representation translates to the fractional occupation numbers of the Kohn−Sham orbitals, that is

$$\rho(\mathbf{r}) = \sum_k n_k |\phi_k(\mathbf{r})|^2 \qquad (8)$$

where the occupation numbers n_k vary between 0 and 2. In spite of its formal exactness, the ensemble representation was considered to be of a purely academic interest until its practical validity was demonstrated in the first principles numeric Kohn−Sham simulations of the exact densities for a number of strongly correlated systems carried out by Baerends et al.[43] and Ullrich et al.[44] Together with the theoretical arguments, these results show unambiguously that the ensemble representation is of immediate practical relevance and that it is the only *rigorous* representation for the density of a strongly correlated system of electrons.

The practical implementation of the ensemble approach to DFT was hindered by the absence of approximate density functionals conforming to the ensemble densities. The REKS method[29] was designed to fill this gap in computational DFT. The method combines the ensemble representation for the density with certain ideas from wave function theory (WFT) for constructing the energy functional for ensemble densities. Therefore, the method shares some features of the multireference approaches in WFT, and the nomenclature developed for the complete active space (CAS)SCF methods is applicable to REKS as well. Thus, in the REKS(2,2) (two active electrons in two active orbitals) method, the density is represented as an average over densities of two configurations: one with doubly occupied KS orbital $\phi_r(\mathbf{r})$ and another with doubly occupied orbital $\phi_s(\mathbf{r})$, where $\phi_r(\mathbf{r})$ and $\phi_s(\mathbf{r})$ can be the HOMO and the LUMO in the conventional single determinant KS calculation. The inactive core KS orbitals are occupied with 2 electrons each, and the ground state density is given as in eq 9.

$$\rho^{\mathrm{REKS}}(\mathbf{r}) = \left(\sum_k^{core} 2|\phi_k(\mathbf{r})|^2\right) + n_r|\phi_r(\mathbf{r})|^2 + n_s|\phi_s(\mathbf{r})|^2 \quad (9)$$

The total ground state energy for a state with two fractionally occupied KS orbitals is represented as a weighted sum of the KS energies of the individual configurations $E^{\mathrm{KS}}(...\phi_r^2...)$ and $E^{\mathrm{KS}}(...\phi_s^2...)$ and a coupling term which is expressed as a linear combination of the KS energies of the singly excited configurations generated within the same (2,2) active space, see eq 10.

$$E^{\mathrm{REKS(2,2)}} = \frac{n_r}{2}E^{\mathrm{KS}}(...\phi_r^2...) + \frac{n_s}{2}E^{\mathrm{KS}}(...\phi_s^2...) +$$
$$f(n_r,n_s)\Big[E^{\mathrm{KS}}(...\phi_r\phi_s...) -$$
$$\frac{1}{2}E^{\mathrm{KS}}(...\phi_r\overline{\phi_s}...) - \frac{1}{2}E^{\mathrm{KS}}(...\overline{\phi_r}\phi_s...)\Big] \quad (10)$$

Thus, the energy of the ensemble state is represented as an ensemble of the energies of individual states (microstates) where each microstate is assumed to be pure state V-representable. Each of the microstates can be viewed as a weighted sum of a number of the real physical states, in the same way that a broken spin-symmetry state can be viewed as a sum of the true singlet and triplet states. Therefore, eq 10 is based on model considerations similar to those used in the works of Ziegler et al.[24] and von Barth.[13] Note, however, that the total energy in eq 10 is minimized with respect to the KS orbitals and their fractional occupation numbers. As it has been demonstrated by Staroverov et al.,[45] within the finite basis set, the optimization of the total energy with respect to the orbitals is equivalent to the optimization with respect to the KS potential. Therefore, this orbital optimization procedure is a valid implementation of the KS scheme for an orbital-dependent density functional.

The factor $f(n_r,n_s)$ in front of the last term in eq 10 can be derived from the following considerations. In the case of (near) degenerate active orbitals $\phi_r(\mathbf{r})$ and $\phi_s(\mathbf{r})$, where the occupation numbers are $n_r \approx n_s \approx 1$, the factor $f(n_r,n_s)$ is given by eq 11, which is the same as in the CASSCF(2,2) energy functional.

$$f(n_r,n_s) = (n_r n_s)^{1/2} \qquad (11)$$

In such a case, nearly all the correlation energy taken into account via the functional form (10) corresponds to the nondynamic correlation energy. In the situation where there is a substantial energy gap between $\phi_r(\mathbf{r})$ and $\phi_s(\mathbf{r})$ and one of the occupation numbers is nearly zero and another is nearly two ("normal" single reference case), the factor $f(n_r,n_s)$ should satisfy eq 12 which can be obtained from analysis of the energy functional in DFT with the fractional occupation numbers (DFT-FON) method.[46]

$$f(n_r,n_s) = (n_r n_s) \qquad (12)$$

In this regime, the energy functional (10) with the factor (12), no extra correlation energy is taken into account *explicitly*, via the functional form (10), and the double counting of the correlation energy is suppressed.

In the first implementation of the REKS method, a geometric average of the two asymptotes (11) and (12) was taken for the factor $f(n_r,n_s)$ in eq 10; see eq 13

$$f^{REKS}(n_r,n_s) = (n_r n_s)^{3/4} \qquad (13)$$

This choice provides a reasonable account of the nondynamic electron correlation combined with the sufficient suppression of the double counting of the dynamic correlation, as was confirmed in comparisons of the REKS results for "normal" single-reference states with the results from the conventional single-reference KS method.

Recently, another algebraic expression for the factor $f(n_r,n_s)$, which interpolates between the asymptotic regimes (11) and (12), was suggested. This expression, eq 14,

$$f^{REKS(new)}(n_r,n_s) = [n_r n_s]^{(1-1/2n_r n_s+\delta/1+\delta)}; \quad \delta = 0.4 \quad (14)$$

satisfies the condition (11) in the vicinity of the orbitally (near) degenerate state and provides a better suppression of the double counting of the dynamic electron correlation in the "normal" state; a detailed description of this new formula and the choice of the parameters in it will be given elsewhere. This is evidenced by the results of the calculations for the planar and the 90°-twisted ethylene carried out with the use of the old formula (13), with the new formula (14) and (for the planar ethylene) with the standard closed-shell single-reference KS approach (RKS). Calculations employing the 6-311(d,p) basis set together with the B3LYP density functional and the geometries optimized with the RKS method for the planar ethylene and with the old REKS method for the twisted ethylene give total energies of $E^{RKS} = -78.6139345$ au, $E^{REKS} = -78.6145855$ au, and $E^{REKS(new)} = -78.6139726$ au for the planar geometry. Thus the new formula (14) provides considerably better elimination of the double counting of the dynamic electron correlation in the "normal" state. The old REKS formula (eq 13) "overshoots" the total energy by 0.408 kcal/mol, whereas with the new formula as in eq 14 the REKS energy differs from the RKS one by 0.024 kcal/mol only. This implies that the effect of the double counting of the dynamic correlation should not be observed in practical calculations. For the orbitally degenerate state of 90°-twisted ethylene, both formulations of REKS, the old and the new one, yield total energies of -78.5064634 au and -78.5064635 au, respectively, which are practically identical. The advantage of the new formula (14) will become obvious later on when discussing the singlet−triplet separations in binuclear metal complexes.

The fractional occupation numbers in REKS are analogous to the natural orbital occupation numbers in conventional wave function multireference methods. Thus, one can analyze the REKS density and energy in similar terms as in conventional WFT. Because of the variational nature of the REKS energy functional, the one-electron properties, including the energy gradient, can be straightforwardly obtained from its density matrix. The feasibility of the REKS method makes it an attractive alternative to conventional multiref-erence methods in WFT, in particular, when large molecular systems, such as those studied in the present work, are considered. Moreover, because the REKS method belongs

to the class of spin-restricted methods, it does not experience difficulties with the spurious spin-contamination which plagues spin-unrestricted (DFT or not) calculations. This however implies that, in the calculation of singlet−triplet energy separations, the triplet state energy should be calculated with the use of the spin-restricted method as well. Thus, the spin-restricted open-shell KS (ROKS) method is employed in the present work for the calculation of these differences in connection with the REKS method.

3. Computational Details

For each one of the different systems described in the next section, we have computed the magnetic coupling constant with the use of both, the broken symmetry UKS and the REKS/ROKS, approaches discussed above. The extended basis sets are employed which consist of the 6-3111+G basis set on Cu and the 6-31G* basis set on the remaining atoms. Several exchange-correlation functionals are examined which start from quite opposite extremes. At one extreme, we have the Hartree−Fock method which uses the exact nonlocal exchange and neglects the electron correlation effects (except for a part of nondynamical correlation introduced through the spin polarization). At the other extreme, there lies the Local Density Approximation (LDA) which employs local exchange and correlation functionals. However, because this approach fails to describe most magnetic systems, it is not considered here. Hence, the pure DFT method chosen in this work is the gradient-corrected BLYP density functional obtained by using the Becke (B) exchange[47] and the Lee−Yang−Parr (LYP) correlation functional[48] which is based on the original work of Colle and Salvetti on the correlation factor.[49,50] Next, we explore a couple of hybrid HF/DFT functionals which incorporate a certain amount of the Fock exchange. These are the BH&HLYP[51] and B3LYP func-tional[52] which both use the Becke gradient corrected exchange and the LYP correlation functionals and mix in 50% and 21% of the Fock exchange, respectively.

The broken symmetry UKS and ROKS computations have been carried out using the Gaussian03[53] package, and the REKS calculations have been carried out with the CO-LOGNE2005 code.[54]

4. Selected Reference Systems: Structure and Exchange Constants

In order to investigate the effect of spin symmetry require-ments on the predicted magnetic coupling constants of real systems as well as to further analyze the performance of the different exchange-correlation functionals, a set of binuclear Cu complexes covering a broad range of J values, ranging from strong ferro- to strong antiferromagnetic couplings, has been chosen. This set of molecules has been selected according to the following criteria: (i) In order to minimize the zero field splitting effects which can be problematic in a nonrelativistic approach, as the one used here, we have exclusively considered binuclear copper(II) complexes; (ii) The simplicity of the molecular structure with a moderate number of atoms (in some systems, the large innocent groups have been substituted by simpler groups); (iii) A wide diversity of bridging ligands; (iv) The crystalline structure

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Table 1. Cambridge Structural Database Notation, Chemical Formula, Magnetic Coupling Constant, and References for Experimental Structure and/or Magnetic Data of the Six Compounds Studied in the Present Work

CCDC refcode	chemical formula	J (cm^{-1})	ref
YAFZOU	[{Cu(phen)}$_2$(μ-AcO) (μ-OH)](NO$_3$)$_2 \cdot$H$_2$O	111	56
XAMBUI	[{Cu(dpt)}$_2$\{μ-O$_2$C-(η^5-C$_5$H$_4$)Fe(η^5-C$_5$H$_5$)\}$_2$] (ClO$_4$)$_2$	2	57
PATFIA	[{Cu(dmen)}$_2$\{μ-OMe\}\{μ-O$_2$C-(η^5-C$_5$H$_4$)Fe(η^5-C$_5$H$_5$)\}] (ClO$_4$)$_2$	-11	58
CAVXUS	[{Cu(petdien)}$_2$(μ-C$_2$O$_4$)](PF$_6$)$_2$	-19	59, 60
CUAQAC02	[{Cu(H$_2$O)}$_2$(μ-AcO)$_4$]	-286	61
BISDOW	[{Cu(bpy)(H$_2$O)(NO$_3$)}$_2$(μ-C$_2$O$_4$)]	-382	62

is well characterized experimentally, even with the positions of H atoms well determined. The resulting set of structures, together with the corresponding standard abbreviations as in the Cambridge Structural Database,[55] which will be used henceforth, is listed in Table 1. The relevant experimental data has been taken from refs 56−62, and the compounds are sorted in the order of decreasing J values.

In order to avoid mixing structural and electronic effects, the crystallographic structures for which the magnetic parameters have been measured have been used without further optimization. In BISDOW we excluded the nitrate ligands since it has been found that these do not significantly affect the calculated coupling constant values. Following the previous work, all ferrocenecarboxylate ligands in XAMBUI and PATFIA complexes have been replaced by formiate groups.[57,58]

In the following we provide a short description of the more salient features of each of these compounds.

YAFZOU shows a triplet ground state, and its structure contains a dimeric Cu(II) cation where the metal ions are bridged by a hydroxo and a carboxylato ligands. Two terminal 1,10-phenantroline ligands configure an essentially square planar coordination geometry for each copper atom. The resulting core geometry leads to a strong ferromagnetic coupling which agrees with the well studied magnetostructural correlation for this kind of heterobridged complexes.[58,63−65]

XAMBUI contains a centrosymmetric dicopper(II) cation which consists of two [Cu(dpt)] fragments (dpt = dimethylpropilenetriamine) bridged by two ferrocenecarboxylato ligands in *syn,anti* binding, which form a core consisting of a six-membered ring in a chair conformation. Copper atoms are in a square-pyramidal coordination, with parallel basal planes, where each carboxylate group is bonded to a basal position of one copper and one apical position of the other. This disposition makes the magnetic orbitals parallel, which obscures the superexchange pathways, thus resulting in a very weak ferromagnetic coupling.

PATFIA consists of two Cu(II) ions bridged by one methoxo and one ferrocenecarboxylato group. The coordination sphere of each copper ion is completed by one bidentate chelating ligand (dmen = N,N-dimethylethylenediamine), resulting in a slightly distorted square planar environment. In this compound the methyl group of the bridge is close to the Cu−O(CH$_3$)−Cu core plane, leading to an antiferromagnetic coupling.

CAVXUS contains a binuclear cation where the copper atoms are bridged through an oxalato bis-chelating ligand.

The coordination environment is completed by a tridentate N,N,N′,N″,N″-pentaethyldiethylenetriamine (petdien) ligand resulting in a pronounced trigonal bipyramidal (pentacoordinated) character. The deviation from the square planar to the trigonal bipyramidal geometry results in a reduction of the antiferromagnetic coupling, as shown by Kahn and co-workers.[60]

The CUAQAC02 complex is the well-known copper(II) acetate which consists of two copper ions bridged by four acetate groups in a paddle-wheel core. The coordination environment of the metal ions is square-planar pyramid, with a water molecule in the apical position. This system has been studied by many groups either experimentally or theoretically and is one of the best known models for fundamental magnetic studies.[66]

BISDOW consists of a centrosymmetric binuclear neutral molecule where the two copper ions are bridged by an oxalato bis-chelating anion. Coplanar to the bridge there are two terminal 2,2′-bipyridine chelating ligands, providing a basic square planar environment for the copper atoms. In addition, a nitrate anion and a water molecule coordinate each metal center at longer distances, thus completing a 4 + 1+1 coordination mode. The influence of these groups on the magnetic coupling is negligible, especially for the weakest nitrate ligands, at 2.75 Å bond distance.

5. Results and Discussion

The results for the six compounds described above, and summarized in Table 2, confirm previous findings[25,34−38] reviewed at length recently[26] but also add some new, interesting and somehow unexpected features. First, let us concentrate on the predictions of the broken symmetry approach for the different methods described in section 3. The most evident trend is that HF largely underestimates the magnitude of the magnetic coupling constant, whereas a pure DFT method such as the gradient corrected BLYP largely overestimates it. The prediction of the two hybrid methods represents a general improvement although some necessary remarks will be raised in the forthcoming discussion. Except for the very weakly antiferromagnetic PATFIA compound, all methods correctly predict the ferro- or antiferromagnetic character. This is quite an unexpected conclusion, especially for the HF method since, at first sight, one would expect the nature and the extent of electronic correlation effects to be different for the different compounds. However, previous analyses of the electronic correlation effects based on accurate configuration interaction wave functions reveal a common origin of the most important terms,[67,68] confirming earlier analysis based on perturbation

Table 2. J Values (in cm^{-1}) Using Spin Unrestricted and Restricted Formalisms for the Different Binuclear Copper Complexes Studied in This Work

compound [J exptl]	method	broken symmetry $J = 2(E(\text{BS}) - E(\text{T}))$	REKS/ROKS $J = \Delta E_{ST}$ REKS	REKS (new)
YAFZOU	HF	+37	+18	+18
[+111 cm^{-1}]	BH&HLYP	+91	+89	+87
	B3LYP	+194	+269	+264
	BLYP	+261	+462	+447
XAMBUI	HF	+0.1	+0.1	+0.04
[+2.5 cm^{-1}]	BH&HLYP	+0.7	+1.0	+0.75
	B3LYP	+3.9	+7.0	+6.2
	BLYP	+24	+32	+31
PATFIA	HF	+16	+11	-0.2
[-11 cm^{-1}]	BH&HLYP	+9.0	+78	+32
	B3LYP	-61	+247	+139
	BLYP	-493	+105	-55
CAVXUS	HF	-1.0	-0.5	-1.1
[-19 cm^{-1}]	BH&HLYP	-5.3	0.3	-3.4
	B3LYP	-21.2	19.6	+3.3
	BLYP	-83.3	+83.1	+27.4
CUAQAC02	HF	-39	-12	-20
[-286 cm^{-1}]	BH&HLYP	-132	-47	-91
	B3LYP	-429	-158	-285
	BLYP	-1121	-595	-774
BISDOW	HF	-49	-17	-30
[-382 cm^{-1}]	BH&HLYP	-160	-68	-135
	B3LYP	-634	-224	-429
	BLYP	-2299	-1164	-1361

Figure 1. Experimental versus HF, BH&HLYP, and B3LYP calculated broken symmetry values of the magnetic coupling constant of the six compounds studied in the present work. The experimental versus experimental plot is also drawn for reference. Values for the corresponding correlation factors are given in eqs 15−17.

theory.[66] Therefore, one can conclude that for strongly ferro- or antiferromagnetic compounds, even the HF method will predict a qualitatively correct magnetic description although it is not clear that this simple approach will be able to make good predictions about the magneto-structural correlations. For weakly antiferromagnetic compounds such as PATFIA it is likely that HF will make a wrong prediction. Notice, however, that the situation for weakly ferromagnetic compounds is different since HF predicts the right ferromagnetic character of XAMBUI. This is because direct exchange, explicitly accounted for in the HF method, makes a very important contribution to ferromagnetic interactions.

A more quantitative picture can be found by inspecting the correlation between the experimental and calculated values (Figure 1) which, for each exchange-correlation potential, is given below
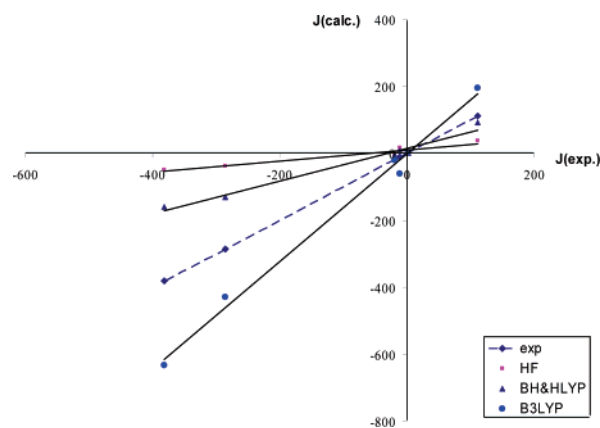
$$J_{\text{calc}}^{\text{HF}} = 0.165\, J_{\text{exp}} + 10.108 \quad \text{with } R^2 = 0.94 \quad (15)$$

$$J_{\text{calc}}^{\text{BH\&H}} = 0.489\, J_{\text{exp}} + 14.896 \quad \text{with } R^2 = 0.98 \quad (16)$$

$$J_{\text{calc}}^{\text{B3LYP}} = 1.608\, J_{\text{exp}} - 1.193 \quad \text{with } R^2 = 0.99 \quad (17)$$

$$J_{\text{calc}}^{\text{BLYP}} = 4.757\, J_{\text{exp}} - 155.08 \quad \text{with } R^2 = 0.91 \quad (18)$$

Equations 16−18 show that all methods including a part of Fock exchange are able to reproduce the experimental trend in a semiquantitative way and, also, that a pure gradient

corrected method such as BLYP leads to a global description which is even worse than the one obtained with the HF method. Moreover, the independent term in eqs 16−18 provides a measure of the limitations of each method. Thus, within the broken symmetry approach, HF and BH&HLYP should not be applied to compounds where the magnetic coupling is antiferromagnetic and of the order of 10−15 cm^{-1} because they will predict a ferromagnetic behavior. The fact that HF and BH&HLYP underestimate the magnitude of the magnetic coupling constant is also clear from the values of the slope of the straight lines in eqs 15 and 16 which is significantly smaller than 1. Notice also that the correlation improves with decreasing the amount of Fock exchange, the 21% included in the B3LYP functional being close to an optimum value, at least for the list of compounds studied in the present work. This can be deduced from the small value of intersect with the J_{calc} axis. However, the slope of the linear regression suggests that the broken symmetry B3LYP predicts J values which are clearly too large. Assuming, with no theoretical justification,[26,34,35] that the energy of the broken symmetry solution is an estimate of the energy of the open shell singlet state will lead to a slope of ~0.8, closer to the desired value but still with an average 20% error. Therefore, the good correlation found for hydroxo- and alkoxo-bridged Cu(II) binuclear complexes[69] and some other binuclear complexes does not seem to hold when the magnetic coupling spans a wide range of values and when the nature of the bridging ligands is also of increased complexity.[70] Here, it is worth pointing out recent studies on magnetic solids evidencing that the proper choice of Fock exchange is less universal than desired and therefore is dependent on the type of system. In fact, previous calculations have shown that at least for NiO[71] and cuprates[68,72] the best percentage of Fock exchange is ~35%.

The results obtained from the broken symmetry approach evidence once again the strong dependence of the magnetic coupling constant on the exchange-correlation functional.[34−38] One can, of course, still argue that the good correlation for the B3LYP results is indicative of the suitability of this

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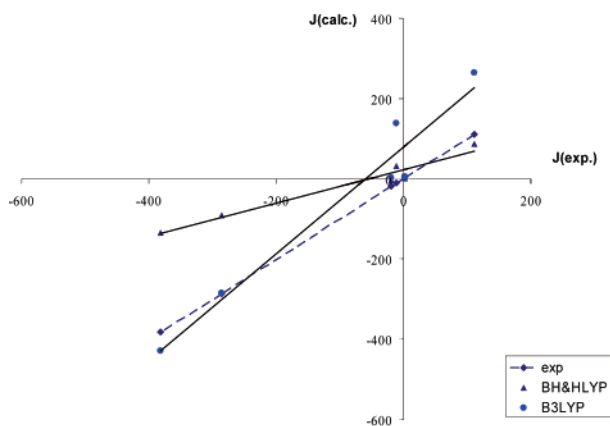*J. Chem. Theory Comput., Vol. 3, No. 3, 2007* **771**

Figure 2. Experimental versus BH&HLYP and B3LYP calculated ROKS/REKS(new) (cf. eq 14) values of the magnetic coupling constant of the six compounds studied in the present work. The experimental versus experimental plot is also drawn for reference. Values for the corresponding correlation factors are given in eqs 19 and 20.

functional to describe magnetic interactions in these systems. This is even more the case if one decides to neglect spin symmetry considerations and take the broken symmetry energy as that of the singlet state and compute J using eq 2 instead of eq 6. This line of reasoning is only based on numerical arguments[69,70] and lacks fundamental theoretical support.[34,35] A better assessment of the reliability of the existing exchange-correlation functionals in the description of the magnetic coupling can be made by using a method which does not rely on the broken symmetry approach and, therefore, does allow one to avoid referring to the expectation value of the square of the total spin operator which is not really defined within the framework of DFT since it is a two-electron operator. This is because in DFT, the density, and not the N-electron wave function, is the main mathematical object, and one can claim that the Kohn−Sham determinant is just a construct to get the density. However, in such a case one can only use DFT to get the energy of the ground state without any information about its spin state. This point of view will, of course, restrict the use of DFT to ground state properties only, and prediction of magnetic coupling constants will not be possible. The spin-Restricted Ensemble-referenced Kohn−Sham (REKS) method described in section 2 offers a theoretically well-grounded alternative since it ensures that the final density for the antiferromagnetic state arises from a singlet state. Using the ROKS procedure for the triplet state permits one to compute J as in eq 2, that is using exactly the same mapping that one would use when aiming to compute J from a wave function approach.

Now, let us focus on the results for the magnetic coupling of the compounds in Table 1 as predicted from the ROKS/REKS formalism and using different correlation functionals. As in the case of the broken symmetry results, a more quantitative picture can be found by inspecting the correlation between the experimental and calculated values (Figure 2) which, for the two hybrid exchange correlation potentials, is given by eqs 19 and 20 below.

$$J_{calc}^{BH\&H} = 0.415 \, J_{exp} + 22.204 \quad \text{with } R^2 = 0.96 \quad (19)$$

$$J_{calc}^{B3LYP} = 1.328 \, J_{exp} + 79.087 \quad \text{with } R^2 = 0.95 \quad (20)$$

From results in Table 2 and the correlation in eqs 19 and 20 it is clear that the use of a formalism which is rigorously spin restricted does not largely improve the results. This is contrary to what is expected and to what is commonly found when using wave function formalism. The direct conclusion is therefore that the exchange-correlation functionals investigated are not capable of correctly describing open shell systems. This is confirmed by the analysis of the results obtained using the HF exchange potential (and no correlation potential) in the ROKS/REKS formulas. The predicted ROHF/REHF magnetic coupling constants are smaller in absolute value than those predicted using the broken symmetry approach. This is because the broken symmetry approach introduces an uncontrolled amount of dynamic electron correlation through spin polarization,[73] and, hence, the UHF broken symmetry results are usually very similar to those obtained through a Complete Active Space Configuration Interaction wave function. However, in the ROKS/REKS formalism the amount of dynamical correlation is minimized to avoid a double counting since this has to be introduced by the correlation functional. Using the REKS formula as in eq 13 or 14 leads to a similar qualitative description (Table 2). A somewhat better correlation between the experimental and the calculated results is obtained using the new REKS formula as in eq 14. Since the BLYP results are always grossly overestimated (by a factor of ∼3) we will focus in the results corresponding to the BH&HLYP and B3LYP hybrid functionals which are summarized in Figure 2. This plot is qualitatively similar to Figure 1, and the slope of the straight lines (0.415 and 1.328) is very similar to the values in eqs 16 and 17 for the broken symmetry calculations. However, the linear regression lines appear to be somewhat displaced to the left with a concomitant increase in the intercept to the J_{calc} axis. This is a clear indication that when used in rigorous spin restricted formalism the BH&HLYP and B3LYP exchange-correlation functionals tend to grossly overestimate the ferromagnetic component of the magnetic coupling.

A clear conclusion of the above discussion is that, for a given exchange-correlation functional, the scale factor between experimental and either broken symmetry or ROKS/REKS values is almost the same, provided the latter are displaced to the origin of coordinates. A corollary of the conclusion above is that eq 6 must be used when employing the broken symmetry approach, otherwise the scale factor between experimental and calculated values corresponding to a given functional will be method dependent. To summarize, broken symmetry and ROKS/REKS lead to similar descriptions although with the present functionals the latter exhibits a trend to overestimate the ferromagnetic interactions. However, the fact that the deviation is rather systematic opens the possibility for the development of improved functionals which will allow for a rigorous treatment of open shell systems in density functional theory.

6. Conclusions

In this work we have investigated the performance of two different formalisms to describe open shell systems in density functional theory by analyzing the calculated magnitude of the magnetic coupling constant in a series of Cu(II) binuclear complexes. The two open shell formalisms are the broken symmetry approach, where the spin symmetry requirements are neglected, and the restricted ensemble Kohn−Sham method, where the spin symmetry is fully taken into account. The series of compounds includes both ferro- and antiferromagnetic compounds and cover a broad range of values.

The present study confirms the strong dependence of the calculated magnetic coupling constant with respect to the exchange-correlation functional. This is found to be a general conclusion which does not depend on whether spin symmetry is imposed or not. All methods, including HF and gradient corrected functionals, are capable of properly describing the main trends, especially for compounds with large values of the magnetic coupling constants. However, the HF method largely underestimates this property, whereas pure density functional largely overestimates it. The use of hybrid functionals improves both the correlation between calculated and experimental values and the quantitative agreement with the experiment. However, even the hybrid B3LYP functional is shown to be unable to accurately predict magnetic coupling constant in different families of compounds.

The use of a method which guarantees the correct spin state does not improve the correlation with respect to experiment and indeed shows some worsening due to an overestimation of the ferromagnetic interactions. However, for a given exchange-correlation functional, the scale factor between experimental and either broken symmetry or ROKS/REKS values is nearly the same although only if a displacement of the coordinate origin is carried out for the latter. This fact provides further support to the argument about the use of proper mapping to obtain meaningful values of the magnetic coupling constant even if the final results may not be in numerical agreement with experiment due to the above-mentioned dependence of the calculated value on the exchange-correlation functional.

To conclude, the spin unrestricted broken symmetry and spin restricted ROKS/REKS approaches lead to similar descriptions of the magnetic coupling constants. However, in the latter case and with the present exchange-correlation functionals, a rather systematic deviation is found. Therefore, it would be possible to develop improved functionals which will allow for a rigorous treatment of open shell systems in density functional theory. In this sense, a particularly promising approach could be the use of the recently proposed local hybrid functionals[74] which for the prediction of thermodynamic data have very recently proven to be competitive with other hybrid functional such as B3LYP.[75] Clearly, the performance of such new functionals in the description of magnetic coupling needs to be explored.

References

(1) Kohn, W.; Sham, L. *Phys. Rev.* **1965**, *140*, A1133.

(2) Hohenberg, P.; Kohn, W. *Phys. Rev.* **1964**, *136*, B864.

(3) For reviews on DFT methods, see for example: (a) Parr, R. G.; Yang, W.; Density-Functional Theory of Atoms and Molecules. In *International Series of Monographs on Chemistry*; Oxford University Press: New York, 1989; Vol. 16. (b) *Density Functional Methods in Chemistry*; Labanowski, J. K., Andzelm, J. W., Eds.; Springer: Heidelberg, 1990. (c) *Modern Density Functional Theory-A Tool For Chemistry in Theoretical and Computational Chemistry*; Seminario, J. M., Politzer, P., Eds.; Elsevier: Amsterdam, 1995; Vol. 2. (d) *Chemical Applications of Density Functional Theory*; Laird, B. B., Ross, R. B., Ziegler, T., Eds.; ACS Symposium Series 629, American Chemical Society: Washington, DC, 1996. (e) *Electronic Density Functional Theory, Recent Progress and New Directions*; Dobson, J. F., Vignale, G., Das, M. P., Eds.; Plenum Press: New York, 1998. (f) Gill, P. In *Encyclopedia of Computational Chemistry;* Schleyer, P. V. R., Allinger, N. L., Clark, T., Gasteiger, J., Kollman, P. A., Schaefer, H. F., III, Schreiner, P. R., Eds.; Wiley: Chichester, U.K., 1998; Vol. 1, p 678.

(4) Fulde, P. *Electron Correlations in Molecules and Solids*; Springer-Verlag: Berlin and Heidelberg, 1995.

(5) Koch, W.; Holthausen, M. C. *A Chemist's Guide to Density Functional Theory*; Wiley-VCH Verlag GmbH: Weinheim, 2000.

(6) Payne, M. C.; Teter, M. P.; Allan, D. C.; Arias, T. A.; Joannopoulos, J. D. *Rev. Mod. Phys.* **1992**, *64*, 1045.

(7) *Recent Developments and Applications of Modern Density Functional Theory (Theoretical and Computational Chemistry)*; Seminario, J. M., Ed.; Elsevier: Amsterdam, 1996.

(8) *Density Functional Theory of Molecules, Clusters and Solids (Understanding Chemical Reactivity)*; Ellis, D., Ed.; Springer: Berlin, 2002.

(9) *Principles and Applications of Density Functional Theory in Inorganic Chemistry I (Structure and Bonding)*; Kaltsoyannis, N., McGrady, J. E., Eds.; Springer: Berlin, 2004.

(10) *Time-Dependent Density Functional Theory (Lecture Notes in Physics)*; Marques, M. A. L., Ullrich, C. A., Nogueira, F., Rubio, A., Burke, K., Gross, E. K. U., Eds.; Springer: Berlin, 2006.

(11) Martin, R. M. *Electronic Structure: Basic Theory and Practical Methods*; Cambridge University Press: Cambridge, 2004.

(12) Gunnarsson, O.; Lundqvist, B. I. *Phys. Rev. B* **1976**, *13*, 4274.

(13) Von Barth, U. *Phys. Rev.* A **1979**, *20*, 1693.

(14) Pople, J. A.; Nesbet, R. K. *J. Chem. Phys.* **1954**, *22*, 571.

(15) Berthier, G. *J. Chim. Phys. Biol.* **1954**, *51*, 363.

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(16) Saunders, V. R.; Dovesi, R.; Roetti, C.; Orlando, R.; Zicovich-Wilson, C. M.; Harrison, N. M.; Doll, K.; Civalleri, B.; Bush, I.; D'Arco, Ph.; Llunell, M. *CRYSTAL2003 User's Manual*; University of Torino: Torino, 2003.

(17) Löwdin, P. O. *Phys. Rev.* **1955**, *97*, 1509.

(18) Löwdin, P. O. *Rev. Mod. Phys.* **1960**, *32*, 328.

(19) Mayer, I.; Ladik, J.; Biczo, G. *Int. J. Quantum Chem.* **1973**, *7*, 583.

(20) Jensen, F. *Introduction to Computational Chemistry*; John Wiley & Sons: Chichester, 2002.

(21) Noodleman, L. *J. Chem. Phys.* **1981**, *74*, 5737.

(22) Noodleman, L.; Davidson, E. R. *Chem. Phys.* **1986**, *109*, 131.

(23) Yamaguchi, K.; Jensen, F.; Dorigo, A.; Houk, K. N. *Chem. Phys. Lett.* **1988**, *149*, 537.

(24) Ziegler, T.; Rauk, A.; Baerends, E. J. *Theor. Chim. Acta* **1977**, *43*, 261.

(25) Caballol, R.; Castell, O.; Illas, F.; Malrieu, J. P.; Moreira, I. de P. R. *J. Phys. Chem. A* **1997**, *101*, 7860.

(26) Moreira, I. de P. R.; Illas, F. *Phys. Chem. Chem. Phys.* **2006**, *8*, 1645.

(27) Bagus, P. S.; Bennet, B. I. *Int. J. Quantum Chem.* **1975**, *9*, 143.

(28) Filatov, M.; Shaik, S. *Chem. Phys. Lett.* **1998**, *288*, 689.

(29) Filatov, M.; Shaik, S. *Chem. Phys. Lett.* **1999**, *304*, 429.

(30) Gräfenstein, J.; Cremer, D. *Chem. Phys. Lett.* **2000**, *316*, 569.

(31) Gross, E. K. U.; Kohn, W. *Adv. Quantum Chem.* **1990**, *21*, 255.

(32) Cassida, M. In *Recent Advances in Density Functional Methods*; Chong, E. D., Ed.; World Scientific: Singapore, 1995; Vol. I.

(33) Stratmann, R. E.; Scuseria, G. E.; Frisch, M. J. *J. Chem. Phys.* **1998**, *109*, 8218.

(34) Illas, F.; Moreira, I. de P. R.; Bofill, J. M.; Filatov, M. *Phys. Rev. B* **2004**, *70*, 132414.

(35) Illas, F.; Moreira, I. de P. R.; Bofill, J. M.; Filatov, M. *Theor. Chem. Acc.* **2006**, *116*, 587.

(36) Martin, R. L.; Illas, F. *Phys. Rev. Lett.* **1997**, *79*, 1539.

(37) Illas, F.; Martin, R. L. *J. Chem. Phys.* **1998**, *108*, 2519.

(38) Ciofini, I.; Illas, F.; Adamo, C. *J. Chem. Phys.* **2004**, *120*, 3811.

(39) Gilbert, T. L. *Phys. Rev. B* **1975**, *12*, 2111.

(40) Valone, S. M. *J. Chem. Phys.* **1980**, *73*, 1344, 4653.

(41) Lieb, E. H. *Int. J. Quantum Chem.* **1983**, *24*, 243.

(42) Englisch, H.; Englisch, R. *Phys. Stat. Sol. (B)* **1984**, *123*, 711; *124*, 373.

(43) Schipper, P. R. T.; Gritsenko, O. V.; Baerends, E. J. *Theor. Chem. Acc.* **1998**, *99*, 329.

(44) Ullrich, C. A.; Kohn, W. *Phys. Rev. Lett.* **2001**, *87*, 093001.

(45) Staroverov, V. N.; Scuseria, G. E.; Davidson, E. R. *J. Chem. Phys.* **2006**, *124*, 141103.

(46) Wang, S. G.; Schwarz, W. H. E. *J. Chem. Phys.* **1996**, *105*, 4641.

(47) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(48) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

(49) Colle, R.; Salvetti, O. *Theor. Chim. Acta* **1975**, *37*, 329; **1979**, *53*, 55.

(50) Colle, R.; Salvetti, O. *J. Chem. Phys.* **1993**, *79*, 1404.

(51) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 1372.

(52) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098.

(53) *Gaussian 03 (Rev. B.04)*; Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Ragha-vachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. Gaussian Inc.: Pittsburgh, PA, 2003.

(54) Kraka, E.; Gräfenstein, J.; Filatov, M.; Polo, V.; Wu, A.; He, Y.; Olsson, L.; Konkoli, Z.; He, Z.; Gauss, J.; Reichel, F.; Cremer, D. *COLOGNE2005*; Göteborg University: Göteborg, 2005.

(55) Allen, F. H. The CSD System: The Cambridge Structural Database: A quarter of a million crystal structures and rising. *Acta Crystallogr., Sect. B: Struct. Sci.* **2002**, *B58*, 380−388. Bruno, I. J.; Cole, J. C.; Edgington, P. R.; Kessler, M.; Macrae, C. F.; McCabe, P.; Pearson, J.; Taylor, R. Con-Quest: New software for searching the Cambridge Structural Database and visualizing crystal structures. *Acta Crystallogr., Sect. B: Struct. Sci.* **2002**, *B58*, 389.

(56) Tokii, T.; Hamamura, N.; Nakashima, M.; Muto, Y. *Bull. Chem. Soc. Jpn.* **1992**, *65*, 1214.

(57) López, C.; Costa, R.; Illas, F.; Molins, E.; Espinosa, E. *Inorg. Chem.* **2000**, *39*, 4560.

(58) López, C.; Costa, R.; Illas, F.; de Graaf, C.; Turnbull, M. M.; Landee, C. P.; Espinosa, E.; Mata, I.; Molins, E. *Dalton Trans.* **2005**, 2322.

(59) Sletten, J. *Acta Chem. Scand. A* **1983**, *37*, 569.

(60) Julve, M.; Verdaguer, M.; Gleizes, A.; Philoche-Levisalles, M.; Kahn, O. *Inorg. Chem.* **1984**, *23*, 3808.

(61) de Meester, P.; Fletcher, S. R.; Skapski, A. C. *J. Chem. Soc., Dalton Trans.* **1973**, 2575.

(62) Castillo, O.; Muga, I.; Luque, A.; Gutierrez-Zorrilla, J. M.; Sertucha, J.; Vitoria, P.; Roman, P. *Polyhedron* **1999**, *18*, 1235.

(63) Nishida, Y.; Kida, S. *J. Chem. Soc., Dalton Trans.* **1986**, 2633.

(64) McKee, V.; Zvagulis, M.; Reed, C. A. *Inorg. Chem.* **1985**, *24*, 2914.

(65) Chou, Y. C.; Huang, S. F.; Koner, R.; Lee, G. H.; Wang, Y.; Mohanta, S.; Wei, H. H. *Inorg. Chem.* **2004**, *43*, 2759.

(66) de Loth, Ph.; Cassoux, P.; Daudey, P. J.; Malrieu, J. P. *J. Am. Chem.* Soc. **1981**, *103*, 4007.

(67) Calzado, C. J.; Cabrero, J.; Malrieu, J. P.; Caballol, R. *J. Chem. Phys*. **2002**, *116*, 2728.

(68) Calzado, C. J.; Cabrero, J.; Malrieu, J. P.; Caballol, R. *J. Chem. Phys*. **2002**, *116*, 3985.

(69) Ruiz, E.; Alemany, P.; Alvarez, S.; Cano, J. *J. Am. Chem. Soc.* **1997**, *119*, 1297.

(70) Ruiz, E.; Cano, J.; Alvarez, S.; Alemany, P. *J. Comput. Chem.* **1999**, *20*, 1391.

(71) Moreira, I. de P. R.; Illas, F.; Martin, R. L. *Phys. Rev. B* **2002**, *65*, 155102.

(72) Moreira, I. de P. R.; Dovesi, R. *Int. J. Quantum Chem.* **2004**, *99*, 811.

(73) Cremer, D.; Filatov, M.; Polo, V.; Kraka, E.; Shaik, S. *Int. J. Mol. Sci.* **2002**, *3*, 604.

(74) Jaramillo, J.; Scuseria, G. E.; Ernzerhof, M. *J. Chem. Phys.* **2003**, *118*, 1068.

(75) Bahmann, H.; Rodenberg, A.; Arbuznikov, A. V.; Kaupp, M. *J. Chem. Phys.* **2007**, *126*, 11103.