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Magnetic coupling in biradicals, binuclear complexes and wide-gap insulators: a survey of ab initio wave function and density functional theory approaches

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Abstract. State-of-the-art computational approaches to magnetic coupling in biradicals, dinuclear complexes and wide-gap insulators are reviewed with the aim to provide a unified point of view. The most rigorous wave-function-based methods provide an accurate description of magnetic coupling in all these systems, whereas density-functional-based methods within the broken symmetry approach provide an alternative, yet efficient, computational tool. The use of mapping procedures permits the broken symmetry solution to be related to the appropriate spin state. Different arguments are given to show that the neglect of this procedure may lead to values in agreement with experiment, but at the cost of serious contradictions.

Key words: Magnetic coupling – Broken symmetry approach – DFT – UHF – DDCI

1 Introduction

Paramagnetic centres appear rather commonly in many molecules and solids and the magnetic interaction between these centres gives rise to very interesting physical phenomena. This magnetic interaction is usually referred to as magnetic coupling and is of great interest in biradicals [1], dinuclear complexes [2] and ionic solids, in particular, high-temperature superconductor parent compounds [3]. In all these systems, magnetic coupling is usually rationalised in terms of model spin Hamiltonians, the best known and most widely used is the Heisenberg–Dirac–van Vleck (HDVV) Hamiltonian [4, 5], which for two magnetic centres with total net spin S_i and S_j, respectively, is simply given by

$$\hat{H}^{\mathrm{HDVV}} = -J_{ij}\hat{S}_i\hat{S}_j \ , \qquad (1)$$

where J_{ij} is the magnetic coupling constant governing the energy difference between the different spin states and $\hat{S}_i$ and $\hat{S}_j$ are the total spin operators for centres "i" and "j". The choice of the sign in Eq. (1) is such that J_{ij} is positive for a ferromagnetic interaction favouring parallel spins. For an extended solid one must consider that all magnetic centres interact and, hence, it is necessary to consider all possible interactions. However, the magnitude of the magnetic coupling constant decreases exponentially with distance and in many cases it is enough to consider interactions between nearest-neighbour spins only. In this latter case the HDVV may be written as

$$\hat{H}^{\mathrm{HDVV}} = -\sum_{\langle i,j\rangle} J_{ij}\hat{S}_i\hat{S}_j \qquad (2)$$

where the symbol $\langle i,j\rangle$ indicates summation over all i and j neighbouring magnetic centres and J_{ij} is again the Heisenberg coupling constant between "i" and "j" magnetic centres.

Assuming that the magnetic interaction is effectively given by the HDVV Hamiltonian it is possible to extract the magnetic coupling constant from different experiments, such as susceptibility measurements, neutron diffraction or Raman scattering [6]. The experimental values for the magnitude of the magnetic coupling constant cover a broad range, from a few Kelvin in some biradicals and dinuclear complexes [1, 2] to about 1500 K in high-temperature superconductor parent compounds [3]. Attempts to estimate the magnetic coupling constant in all these materials go back to the early days of quantum chemistry. The magnetic coupling in Mn dimer complexes was studied by Nesbet in the early 1960s [7–10]. One of the first applications of the wave-function-based methods of quantum chemistry to the problem of magnetic coupling of an extended system, such as $KNiF_3$, was reported by Wachters and Nieuwpoort in 1972 [11]. These pioneering works used a cluster model for the extended solid together with very approximate wave functions and, although they were unable to reach a quantitative description of magnetic

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coupling, they achieved a remarkable qualitative understanding of such a complex problem.

A more accurate description of magnetic coupling has been possible thanks to recent developments in methods based on configuration interaction (CI) [12–14] and density functional theory (DFT) [15–18]. In the case of CI wave functions the magnetic coupling constant is obtained from energy differences corresponding to pure spin states [19–21] and the only problem is the accurate determination of the proper energies. However, in the case of DFT-based methods one faces additional problems due to the fact that almost all practical implementations of DFT are based on the Kohn–Sham [15] procedure and, hence, on the use of a single Slater determinant to express the electronic density.

The goal of this article is to critically discuss the different procedures that one may find in the literature and to provide a unified point of view of the quantum chemical approach to magnetic coupling in systems that at first sight belong to different research fields. These systems include biradicals, dinuclear complexes and wide-gap insulators. In particular, it will be shown that the use of mapping between the eigenvalues and eigenfunctions of exact and model spin Hamiltonians permits DFT to be used in a way which is fully consistent with the standard wave-function-based quantum chemical approach, whereas significant contradictions may appear when this mapping is not respected.

2 Exact and spin model Hamiltonians, spin eigenfunctions and the mapping strategy

The HDVV model Hamiltonian acts in spin space only and, hence, assumes that the spatial part of the wave functions involved in magnetic coupling is the same for all neutral spin configurations. For two interacting spin moments, i.e. biradicals or dinuclear complexes, the eigenstates of the HDVV can be easily found. Let us first consider the case of two particles with total spin ½ as two hydrogen atoms at a large distance or two effective d^9 Cu^{2+} cations in a dinuclear complex or in a cuprate superconductor parent compound. In this case the spin space has a dimension of 4 and a basis for this space is simply given by $|\alpha\alpha\rangle$, $|\beta\beta\rangle$, $|\alpha\beta\rangle$ and $|\beta\alpha\rangle$. Since the HDVV, the total square spin operator, $\hat{S}^2$, and the z-component of the total spin operator, $\hat{S}_z$, commute with each other it is possible to find a set of eigenfunctions common to the three operators. The eigenfunctions of $\hat{S}^2$ and $\hat{S}_z$ are denoted $|S, M_s\rangle$ and it is straightforward to show that $|1,1\rangle = |\alpha\alpha\rangle$ and $|1,-1\rangle = |\beta\beta\rangle$, whereas $|\alpha\beta\rangle$ and $|\beta\alpha\rangle$, must be combined to yield $|0,0\rangle$ and $|1,0\rangle$. Therefore, the four spin states are grouped in a singlet, $|\mathrm{S}\rangle = |0,0\rangle$, and a triplet, $|\mathrm{T}\rangle$, with its three S_z components. It is a simple exercise to demonstrate that the singlet and triplet states are also eigenfunctions of the HDVV Hamiltonian with energies ¾J and $-$¼J, respectively [22, 23]. Therefore, the magnetic coupling constant is simply given by the energy difference between the singlet and the triplet states. In an ab initio, wave-function-based calculation one commonly applies the exact nonrelativistic Hamiltonian and the two localised spin moments arise from two unpaired electrons in two open shell, or magnetic, orbitals. These two unpaired electrons give rise to a singlet and a triplet state and one can establish a one-to-one correspondence between the ab initio wave functions for the singlet and the triplet and the spin eigenfunctions for the HDVV Hamiltonian. This one-to-one correspondence permits J to be computed from a singlet–triplet energy difference (Fig. 1).

Unfortunately, not all cases are that simple, but the mapping procedure outlined provides a useful guide to the problem of computing magnetic coupling constants. For a somewhat more complicated case, such as two particles with total spin 1, e.g. two effective d^8 Ni^{2+} cations in a dinuclear complex or in a perovskite-like KNiF_3, the dimension of the spin space is 9 and the resulting spin states are the five components ($|22\rangle$, $|21\rangle$, $|20\rangle$, $|2,-1\rangle$ and $|2,-2\rangle$) of a quintet, $|\mathrm{Q}\rangle$, state, the three components of a triplet, $|\mathrm{T}\rangle$, and a singlet, $|\mathrm{S}\rangle$, similar to those described previously. These spin eigenfunctions are also eigenfunctions of the HDVV Hamiltonian with values $-J$, J, and $2J$, respectively [19–21]. The ab initio calculation of such a system involves four open shell orbitals and, again, one can make use of the one-to-one correspondence between the exact and HDVV Hamiltonians to extract J from the appropriate energy differences (Fig. 2). Moreover, this particular case permits the investigation of whether the system under consideration behaves according to the HDVV Hamiltonian because one can extract J from three different mappings.

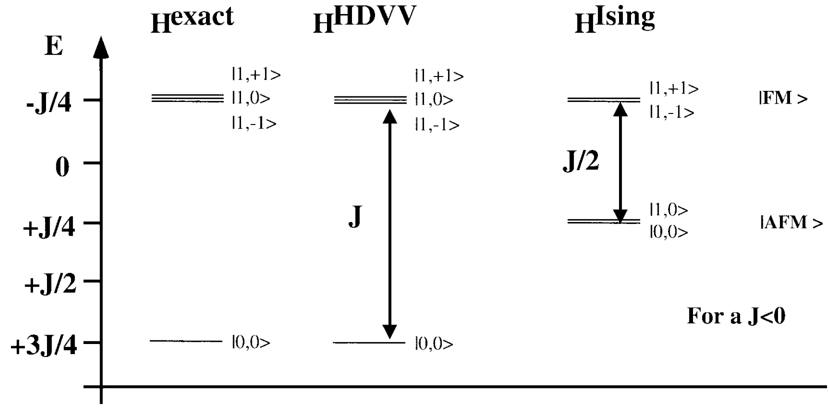

Fig. 1. Energy diagram for the eigenstates of the exact, Heisenberg–Dirac–van Vleck (*HDVV*) and Ising model Hamiltonians for a system of two ½ interacting spins

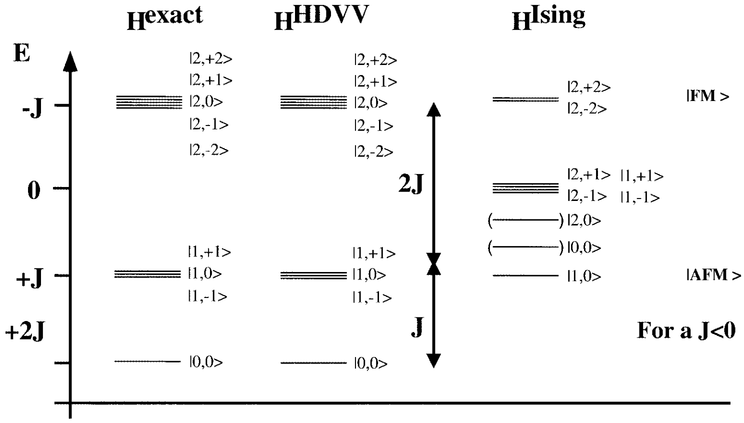

Fig. 2. Energy diagram for the eigenstates of the exact, HDVV and Ising model Hamiltonians for a system of two $S = 1$ interacting spins. States in parentheses indicate that these particular *eigenstates* of the HDVV Hamiltonian are not eigenfunctions of the Ising Hamiltonian, the energy in these cases is just an expectation value

In the case of many magnetic centres it is not always possible to find the eigenfunctions of the HDVV Hamiltonian [22]. This is also the case for periodic systems, where exact solution for HDVV exists for one-dimensional systems only. A common approach to the computation of the magnetic coupling constant for periodic systems is to make use of a simplified version of the HDVV Hamiltonian in which the total spin operators are substituted by the z-component of this operator,

$$\hat{H}^{\text{Ising}} = -J_{ij}\hat{S}_{z,i}\hat{S}_{z,j} \ . \tag{3}$$

The resulting model Hamiltonian is referred to as the Ising model Hamiltonian and has exact solutions for one- and two-dimensional cases only [22] although one can extract J from energy differences between appropriate states [24] by assuming that all interactions are additive. However, these states are not always eigenfunctions of $\hat{S}^2$ and special care is needed when using this approach. The Ising Hamiltonian still commutes with $\hat{S}_z$ so it is possible to use M_s as a quantum number. There are two special eigenstates of this spin Hamiltonian, namely, the one that corresponds to the case of maximum M_s, the so-called ferromagnetic state, and the case of minimum M_s, the antiferromagnetic or Néel state. For an even number of electrons the antiferromagnetic state has $M_s = 0$. The ferromagnetic state, $|\mathrm{F}\rangle$, is always a spin eigenfunction but the single determinantal nature of the antiferromagnetic, state $|\mathrm{AF}\rangle$, prevents this state from being an eigenfunction of the square of the total spin operator, $\hat{S}^2$. For, an infinite system $|\mathrm{AF}\rangle$ cannot be a pure spin state, whereas for dimers one has different situations. In general, the $|\mathrm{F}\rangle$ and $|\mathrm{AF}\rangle$ states are not the only eigenfunctions of the Ising Hamiltonian.

In order to establish comparisons it is interesting to investigate the behaviour of the pure spin eigenfunctions with respect to the Ising Hamiltonian. For the case of two particles with spin ½ it is easy to show that the $|1,1\rangle$ and $|1,-1\rangle$ spin states are also eigenstates of the Ising Hamiltonian with eigenvalue $-\frac{1}{4}J$ as in the Heisenberg Hamiltonian. Both, $|1,1\rangle$ and $|1,-1\rangle$ are representations of the $|\mathrm{F}\rangle$ state and are degenerate with respect to the energy (within the Ising Hamiltonian). Likewise, both $|0,0\rangle$ and $|1,0\rangle$ are eigenfunctions of the Ising model with energy $+\frac{1}{4}J$. This result follows from the fact that $|\alpha\beta\rangle$ and $|\beta\alpha\rangle$ are the eigenfunctions of this model Hamiltonian with $M_s = 0$ and since they are degenerate with respect to the Ising Hamiltonian with the $+\frac{1}{4}J$ eigenvalue, they can be combined to give $|0,0\rangle$ and $|1,0\rangle$ while being eigenfunctions of both operators. From this discussion it is clear that one may take the energy difference between $|1,1\rangle$ (or $|\alpha\alpha\rangle = |\mathrm{F}\rangle$) and $|\alpha\beta\rangle = |\mathrm{AF}\rangle$ and obtain $J/2$ in a straightforward way (Fig. 1). This is precisely the basis of the broken symmetry (BS) approach discussed later and the strategy used in periodic Hartree–Fock calculations with the only difference being that one must take into account the total number of interactions of a given centre [24].

Let us close this section by discussing the energy expectation values for the Ising Hamiltonian of the pure spin states that arise for the case of two particles with total spin 1. This example will be of crucial importance in the forthcoming discussion about the DFT approach to magnetic coupling. Notice that, in this case, M_s is the only good quantum number. Seven of the nine spin states are also eigenstates of the Ising Hamiltonian. These are the two different $|\mathrm{FM}\rangle$ states ($|2,2\rangle$ and $|2,-2\rangle$) with energy $-J$, the $|2,-1\rangle$, $|2,1\rangle$, $|1,1\rangle$ and $|1,-1\rangle$ states with energy equal to zero and the $|1,0\rangle$ state with energy $+J$. Moreover, this last state is degenerate with the proper $|\mathrm{AFM}\rangle$ state and, hence, the energy of the $|1,0\rangle$ state with respect to the HDVV Hamiltonian is equal to that of the $|\mathrm{AFM}\rangle$ state for the Ising Hamiltonian. This is in contrast with the case of two spin ½ particles where the expectation value of the HDVV and Ising Hamiltonians for the combinations of the two representations of the $|\mathrm{AFM}\rangle$ state do not coincide (Fig. 1). The remaining two spin states ($|2,0\rangle$ and $|0,0\rangle$) are not eigenfunctions of the Ising Hamiltonian because they correspond to combinations which are not degenerate with respect to this Hamiltonian. For these two states the energy expectation values are $J/3$ and $2J/3$, respectively (Fig. 2). The interesting point from this algebraic analysis is that for the case of two interacting spin ½ particles, there is no way to combine the two representations of the $|\mathrm{AFM}\rangle$ state that give equal energies within the HDVV and Ising Hamiltonians, whereas for the case of two spin 1 particles the two representations of the $|\mathrm{AFM}\rangle$ state can be combined in a spin state of triplet multiplicity (in the case of using a spin polarized formalism the $|\mathrm{AFM}\rangle$ state will be almost a pure spin state, cf. Sect. 4) which is eigenstate of both, HDVV and Ising, Hamiltonians, with the same energy and the same expectation value for $\hat{S}^2$. Later we will show that these two results lead to important conclusions regarding the use of the broken symmetry approach to magnetic coupling.

3 The wave function approach

The mapping between the eigenstates of the exact and HDVV Hamiltonians permits magnetic coupling constants to be obtained for the wave-function-based approach by simply computing the energies of the appropriate spin state or, more precisely, the energy differences between these states. However, the often small values of the magnetic coupling constants and the very complex physical mechanisms governing their magnitude make this calculation rather difficult. In fact, the simplest ab initio wave function that may deal with pure spin eigenfunctions is the one derived from the restricted open shell Hartree–Fock (ROHF) method. For the case of two unpaired electrons in two orthogonal, symmetry-adapted, molecular orbitals, φ_i and φ_j, it is straightforward to show that the triplet–singlet difference is just $2(\varphi_i\varphi_j|\varphi_j\varphi_i)$ or twice the exchange integral involving the open shell orbitals. Since this is a two-electron repulsion integral, and hence is positive, one finds that the triplet state is always favoured, i.e. the well-known Hund rule. The only physical mechanism included in the ROHF wave function is the direct exchange and, accordingly, it is unable to predict antiferromagnetism. This result led Anderson [25, 26] to propose the well-known superexchange mechanism, which essentially adds to the ROHF wave function the configurations in which the two electrons occupy either φ_i or φ_j. In the language of modern quantum chemistry this is just a complete-active-space CI (CASCI) wave function with two active electrons in two active orbitals. Since the CASCI wave function is invariant with respect to rotations of the active orbitals one can localise φ_i and φ_j and recover the picture of localised magnetic orbitals. In the localised picture the Anderson model may be viewed simply as a valence bond wave function constructed from orthogonal atomic orbitals and including the situations where there is one magnetic electron per centre, neutral forms, and those where the two magnetic electrons are located at the same centre, ionic forms. Once one realises that the Anderson model is equivalent to that included in a CASCI wave function, the generalisation to many unpaired electrons per centre is straightforward. The next point concerns the performance of the CASCI wave function in predicting values of J. In general terms, the Anderson model qualitatively predicts the sign of J and is able to distinguish between ferro- and antiferromagnetic systems; however, the predicted value of J is usually too small, about 30% of the experimental value. Without pretending to give an exhaustive list of all publications using a CAS approach to calculate J some representative examples may be found in Refs. [19–21, 27–32].

The failure of the Anderson model to quantitatively predict the magnitude of the magnetic coupling constant in systems with localised spins, i.e. biradicals, binuclear complexes or wide-gap insulators, is due to the lack of dynamical correlation effects. To include these important effects it is necessary to use a wave function that goes beyond the CASCI wave function. In principle, one can choose any explicit correlated wave function, such as multireference CI, the different methods based on the cluster ansatz [27, 28] or the nonorthogonal CI approach [33, 34]. These approaches attempt to include all the important electron correlation effects in the total energy of each electronic state. An alternative approach consists not in improving the total energy of the individual states but instead of improving the energy difference by including the relevant terms only. Based on a theorem proven by Malrieu [35], de Loth et al. [36] were able to provide a complete analysis of the mechanisms contributing up to second order to the energy differences relevant to magnetic coupling. These physical mechanisms can be written in terms of second-order diagrams and one can include dynamical correlation to the magnetic coupling constant just by adding the contribution of these second-order diagrams. The practical applications of this idea [36, 37] were not entirely satisfactory; the values of J calculated following this strategy largely improved those arising from the Anderson model but were still rather far from experimental values and, in some case, faced the typical problems of perturbation theory with absurd results due to small denominators.

A major step towards a quantitative description of the magnetic coupling was achieved by Miralles and coworkers [38, 39], who realised that the problems arising in perturbation theory can be overcome by a variational treatment of the second-order diagrams contributing to the energy differences. This variational treatment led to the difference dedicated CI (DDCI) method, that makes use of a CI expansion not aimed at improving the energy of the individual states but at improving their energy difference. In principle, in magnetic problems it would be enough to include in the DDCI wave function the determinants with at most two degrees of freedom [39], i.e one hole and a particle out of the active space, two holes out of the active space or two particles out of the active space, and the resulting method is referred to as DDCI2 (Fig. 3). The DDCI2 approach has been successfully applied to problems concerning biradicals [40–42], dinuclear complexes [43–45] and ionic solids [19–21, 30, 46–52]. In most cases the agreement with experiment is excellent, although results for the magnetic coupling in ionic solids are not completely satisfactory, the calculated J values are usually about 60–70% of experimental values. In these systems quantitative agreement can be achieved by using the DDCI3 formalism, which extends the DDCI2 list by adding to the DDCI2 one the configurations with at most two holes and one particle or two particles and one hole out of the active space (Fig. 3). The configurations added in the DDCI3 list include the single excitations of the ligand-to-metal charge-transfer excitations, already present in DDCI2 but with too high an excitation energy. The values of the magnetic coupling constant predicted with the extended list of DDCI3 configurations are within the experimental error bars [53]; therefore, one may conclude that DDCI provides an efficient

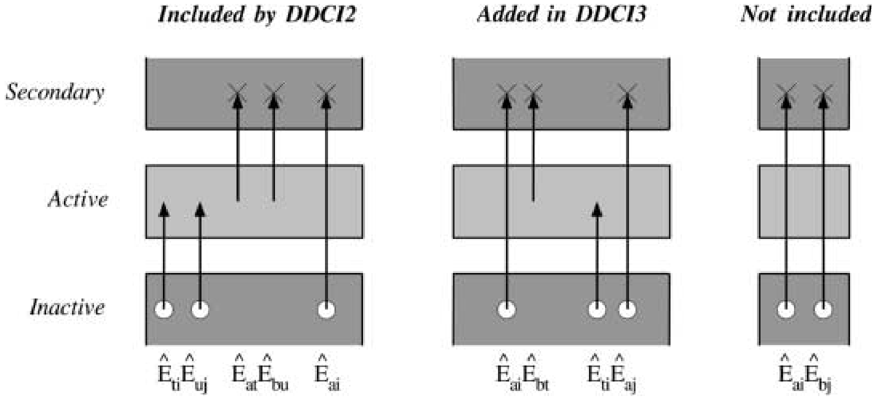

Fig. 3. Schematic representation of the different determinants included in the DDCI2 and DDCI3 methods and those explicitly excluded. *Circles* represent holes and *crosses* represent particles. Notice DDCI2 includes all single excitations plus all diexcitations resulting in determinants with at most two degrees of freedom out of the active space whereas DDCI3 includes those with three degrees of freedom as well

tool for the study of a very complex property. The only limitation of DDCI is perhaps the very large computational requirements needed when the magnetic centres have elevated spin moments ($S > 1$), for complexes with many magnetic centres or when voluminous ligands are present. In these cases DDCI cannot be carried out and one is forced to use a more approximate method such as those described in the next section.

4 The BS method and the DFT approach to magnetic coupling

The calculation of a magnetic coupling constant necessarily involves the computation of the energy of high-spin and low-spin states; therefore, the single determinant nature of the Kohn–Sham implementation of DFT poses some additional problems because it does not allow the use of pure spin eigenfunctions. The usual way in which DFT treats open shell systems is through the use of a spin-polarised, i.e. unrestricted, formalism in which α and β spin orbitals are allowed to have different spatial parts. The single determinant description of the high-spin state is not a problem, except for the small spin contamination inherent to the use of an unrestricted formalism. However, in the case of a pure low-spin state it is not possible to have a single Kohn–Sham determinant and one is forced to use a BS approach in which the open shell magnetic orbitals are localised in different centres and the magnetic electrons have opposite spin, so the final value of the z-component of total spin, S_z, takes the lowest possible value; for homonuclear dimers this leads to states with $S_z = 0$.

It is important to note that the BS approach can be used in any single determinant approach to magnetic coupling. This includes the unrestricted Hartree–Fock (UHF) and the primitive versions of DFT such as Xα scattered wave methods. The first attempt to compute singlet–triplet splittings through the Xα scattered wave method was reported about 30 years ago by Bagus and Bennett [54] and was extended by Ziegler et al. [55]. The BS approach to magnetic coupling was suggested by Noodleman and coworkers [56–58], initially also in the framework of Xα, and later Yamaguchi and coworkers [59–61] made significant contributions in the application of UHF to magnetic coupling. Since the BS approach does not lead to a pure singlet wave function (or to a density derived from a singlet wave function) it is necessary to relate the expectation value of the energy of the BS solution to that of the pure singlet. For a system with two magnetic centres with spins S_1 and S_2 it has been shown that the energy of the BS state is a weighted average of the energies of the pure spin multiplets [57, 62] and that J can be obtained through the equation

$$J = \frac{E(\mathrm{BS}) - E(S_1 + S_2)}{2S_1S_2} \ , \qquad (4)$$

which can be viewed as an effective recipe which allows the computation of J directly from the self-consistent-field (SCF) calculation of two single determinants. Interestingly enough Eq. (4) can also be derived by making use of projection operators on the UHF wave function. The BS solution is strongly spin contaminated, for the case of two unpaired electrons one has $\langle \hat{S}^2 \rangle \approx 1.0$ as one would expect for a 50% admixture of singlet and triplet; consequently the BS energy lies halfway between singlet and triplet. The same result can be obtained by realising that the UHF wave function is an eigenfunction of the z-component of the total spin operator and by using the mapping between exact and Ising Hamiltonians. These results are obtained by assuming that the α and β spin orbitals are orthonormal; however, explicit consideration of the overlap between α and β spin orbitals does not change this important conclusion [63]. Now, it is interesting to consider the case of four unpaired electrons in two magnetic sites, i.e. equivalent to the case of two particles with spin 1 discussed in Sect. 2, where, as expected, one usually gets $\langle \hat{S}^2 \rangle \approx 2.0$, which is precisely the value expected for a pure triplet state. This is not surprising because the triplet state and the antiferromagnetic state are degenerate for the Ising Hamiltonian. The mapping between exact and Ising models is in full agreement with the result predicted from Eq. (4) and with the expectation value for the total square spin operator.

The problems discussed so far involve either two radical centres or two magnetic transition-metal centres. Situations where unpaired electrons are simultaneously located at a transition metal and at a radical centre are possible. The BS approach has also been recently applied to these metal–radical systems and the results are usually very good [64]. However, it has been found that when the singlet state has an unusually large multireference character the magnetic orbitals obtained by the BS solution and by single-reference approaches are quite similar and significantly different from the correct multiconfigurational SCF ones. The role of the form of the magnetic orbitals has been somehow overlooked until now; this point is discussed at length in Ref. [64] together with the relationship between $\langle \hat{S}^2 \rangle$ and the overlap between α and β orbitals in unrestricted treatments. Finally we note that more general equations for the BS approach including mixed valence cases have been reported by Ovchinnikov and Labanowski [65].

The values of the magnetic coupling constants obtained from the BS approaches, either Xα or UHF, are qualitatively correct mainly because of the lack of electronic correlation. Not surprisingly the values obtained with the UHF BS approach are very close to those obtained from the CASCI approach [50–52]. In the framework of DFT electronic correlation effects can be included by means of the exchange–correlation functional. The performance of different exchange–correlation functionals in the computation of magnetic coupling in wide-gap insulators has been investigated recently by Martin and Illas [66, 67]. These authors found that the key point to improve the description of the magnetic coupling lies in the choice of the exchange functional and that the effect of the correlation functional was minor. At first sight one may think that this result is in contradiction with all the discussion in the previous section; however, one must realise that the meaning of exchange and electronic correlation terms is different in ab initio wave function and density functional formalisms [68]. In DFT, electronic correlation is better viewed in terms of Coulomb and Fermi holes and, therefore, it is not surprising that the exchange part of the functional carries an important part of the electronic correlation between parallel spins that in a wave function formalism is included through CI. Martin and Illas [66, 67] found that local exchange strongly overestimates the values of magnetic coupling, in agreement with the well-known failure of the local density approximation (LDA) to properly describe the electronic structure of strongly correlated systems. In fact, LDA band structure calculations, and even those going beyond LDA, such as the generalized gradient corrected approximation (GGA) usually result in metallic nonmagnetic ground-state solutions or exhibit extremely small insulating gaps [69]. Ad hoc corrections to the LDA [70, 71], such as the self-interaction corrections or the inclusion of on-site Coulomb repulsion [72–75], give more realistic results, but their use is rather scarce. Martin and Illas [66, 67] have shown that to reach almost quantitative agreement with experiment it is necessary to use a mixture of about 50% GGA and 50% Hartree–Fock exchange. Reasons have been given for using such hybrid approach but the precise amount of mixing remains largely semiempirical especially because results from the well-known hybrid B3LYP [76, 77] exchange–correlation functional that includes about 25% mixture of Hartree–Fock exchange leads to reasonable values for the magnetic coupling constant of organic biradicals and some dinuclear complexes [32, 78–82].

Before closing this section it is important to point out that, in the case of using a DFT formalism, not all authors agree on the interpretation of the BS solution given here. Since the Hohenberg and Kohn theorems do not make any reference to spin properties it is possible to claim that the lowest energy obtained for a Kohn–Sham determinant with zero total z-component of the total spin is a good approximation to the energy of the lowest singlet state. Additional support for this claim comes from Wang et al. [83], who state that spin contamination in DFT calculations is rather small [83]. On the basis of these arguments Ruiz and coworkers [84–87] suggested that accurate values of the magnetic coupling constant of dinuclear complexes can be obtained by using the B3LYP exchange–correlation functional and by considering that the energy of the BS solution is that of the lowest singlet. In spite of the impressive numerical results, there are many serious arguments against this point of view that suggest that one may have the right answer for the wrong reason. The first argument concerns the expectation value of the square of the total spin operator. For the cases with two unpaired electrons one invariably gets $\langle \hat{S}^2 \rangle \approx 1.0$, while for those with four unpaired electrons one gets $\langle \hat{S}^2 \rangle \approx 2.0$. The strong spin contamination values strongly suggest that the BS cannot adequately represent a singlet state. A second argument against this point of view comes from the fact that it will also violate the mapping procedure discussed in Sect. 2 and will lead to the absurd consequence that two equivalent BS approaches, such as UHF or DFT, will have to use two different ways to compute the magnetic coupling constant. By bringing this argument to the limit one will get the absurd conclusion that the antiferromagnetic state of a periodic system leads to the energy of the pure singlet state. A very strong argument against considering the BS as an effective singlet state comes from the analysis of the Ising model reported in Sect. 2 for the case of two particles with spin 1. In this case, the antiferromagnetic state is degenerate with the triplet state and, therefore, the energy difference between the quintet and the BS (or triplet) state is $2J$, while assuming that the BS has the energy of a singlet one gets $3J$. Notice that in this case the $|\mathrm{AFM}\rangle$ state behaves as pure triplet state, but will be considered as a singlet. Finally, we must note that even in the hypothetical case of accepting that the B3LYP values for the magnetic coupling of dinuclear complexes thus computed are accurate one would have quite inaccurate results for biradicals because it has been shown that the amount of Hartree–Fock exchange needed in these systems is quite different from that required for transition-metal complexes or solids [66, 67].

5 Concluding remarks

The various state-of-the-art computational approaches to magnetic coupling in biradicals, dinuclear complexes and wide-gap insulators have been critically reviewed. The magnetic coupling in these systems has been shown to be governed by the same physical mechanisms and, hence, the same ab initio methods can be applied not only to study the magnetic properties of these amazing systems but also to achieve a quantitative description.

The most rigorous wave-function-based methods provide an accurate description of magnetic coupling in all these systems, although such approaches may be inaccessible for medium-to-large systems. Density-functional-based methods within the BS approach provide an alternative, yet efficient, way; however, these methods have to be used with caution because of the impossibility (within the one determinant Kohn–Sham model system) of dealing with pure spin states. The use of mapping procedures provides a straightforward and consistent way to relate the BS solution to the appropriate spin state. The neglect of this procedure may lead to values in agreement with experiment, but at the cost of serious contradictions.

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