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Spin Decontamination of Broken-Symmetry Density Functional Theory calculations: deeper insight and new formulations

Authors : Nicolas Ferré[(a)], Nathalie Guihéry[(b)*] and Jean-Paul Malrieu[(b)]

Affiliations :

(a) Institut de Chimie Radicalaire UMR7273-CNRS Université d'Aix Marseille Case 521-Faculté de Saint-Jérôme Avenue Esc. Normandie Niemen 13397 Marseille cedex 20

(b) Laboratoire de Chimie et Physique Quantiques, Université de Toulouse 3, Paul Sabatier, 118 route de Narbonne, 31062 Toulouse, France

Abstract: This work re-examines the problem of the broken-symmetry Density-Functional Theory (DFT) solutions in diradical systems, in particular for the calculation of magnetic couplings. The Ms=0 solution is not an eigenfunction of the S^2 spin operator and the evaluation of the singlet state energy requires a spin-decontamination. A popular approximation is provided by the so-called Yamaguchi formula, which operates using the expectation values of S^2 relative to both Ms=1 and Ms=0 solutions. Referring to a previous decomposition of the magnetic coupling in terms of direct exchange, kinetic exchange and core polarization, it is shown that this expression will lead to unreliable values of the singlet-triplet energy gap when the spin polarization of the core orbitals becomes large. The here-proposed method of spin-decontamination is based on the Effective Hamiltonian Theory and uses the overlap between the two degenerate Ms=0 solutions. An approximate and convenient formula, which uses the expectation values of S^2 of the Ms=0 solutions before and after core polarization is proposed, which is free from the Yamaguchi's formula artefact, as illustrated on an organic diradical presenting a very high value of $<S^2>$ for the Ms=0 solution, the antiferromagnetic coupling being due to the spin polarization mechanism.

*nathalie.guihery@irsamc.ups-tlse.fr

I. Introduction

The correct treatment of magnetic systems is challenging for quantum chemists for several reasons. The states of low energy are intrinsically multireference and they are quasi-degenerate. Their calculation therefore requires the use of both non-dynamic and dynamic correlated methods. Detailed analyses[1,2,3,4,5,6] of the physical factors governing the energy spectrum have evidenced in particular the role of the direct exchange between the magnetic electrons, the kinetic exchange and the spin polarization. Among these various contributions, spin polarization effects are less intuitively understood. However, these effects have been widely studied and are known to play a crucial role in electron paramagnetic resonance,[7,8] and in molecular photochemistry, where they are for instance responsible for the singlet-triplet energy ordering in the twisted ethylene molecule.[9] They are also important in magnetic systems, in particular in poly-metallic complexes involving spin polarizable bridging ligands[10,11,12] and organic systems.[13,14]

In a zero-order description, diradicals may be seen as bearing two unpaired electrons, occupying remote magnetic orbitals, while all the other electrons populate doubly occupied Molecular Orbitals (MOs). The low energy states are a triplet and a singlet resulting from the coupling of the unpaired electrons spins S_1 and S_2, and their energy difference gives the magnitude and sign of the Heisenberg Hamiltonian magnetic coupling J. The Ms=1 component of the triplet is satisfactorily described at order zero by a single determinant, while a correct description of the singlet requires at least a two-determinant wave function. Of course wave-function based methods can handle the treatment of multireference states and specific treatments have been proposed, such as the very accurate Difference Dedicated Configuration Interaction (DDCI).[15,16] A general review of the WF-based treatments can be found in reference [1]. However such methods are computationally demanding and are therefore of limited use. Moreover they do not allow one to perform easily geometry optimizations. In contrast Kohn-Sham Unrestricted Density Functional Theory (UDFT) calculations[17,18] are inexpensive and make possible geometry-optimizations. They proceed to the energy minimization of i) the lowest broken symmetry (BS) Ms=1 solution essentially bearing two unpaired electrons with parallel spins in orbitals a and b respectively localized on the magnetic sites A and B. This solution is supposed to describe the Ms=1 component of the triplet state, and ii) the BS Ms=0 solution, with essentially two unpaired electrons of opposite spins. In practice the localized magnetic MOs of this solution are less localized than a and b and overlap. In both solutions, spin polarization distorts differentially the core orbitals of α and β spins.

Since the Ms=0 solution is essentially a mixture of a singlet and a triplet, its energy cannot be assimilated to that of the singlet state. Spin polarization of the core MOs introduces in the Ms=0 solution components on higher spin determinants involving excitations from the core orbitals to virtual ones. Several procedures have been proposed to estimate the energy difference between the singlet and triplet states from the energy difference between the Ms=0 and the Ms=1 UDFT solutions. The simplest one consists in a simple multiplication by a factor 2. This approximation assumes that the Ms=0 solution is a half and half mixture of the singlet and triplet states and becomes irrelevant when the Ms=0 solution tends to be closed-shell, i.e. for a covalent singlet state. An alternative solution[19] makes use of the overlap between the magnetic orbitals and has the advantage of being valid when the Ms=0 solution tends to be closed-shell. The most popular procedure has been proposed by Yamaguchi,[20,21,22] it exploits the expectation values of S^2 for both Ms=1 and Ms=0 solutions.

Section 2 recalls the elementary physics of both solutions. The Yamaguchi's formula is derived in section 3, where it is also be shown that the increase of $<S^2>$ in the Ms=0 solution, due to the spin-polarization of the core, cannot be attributed to an increased component of the low energy triplet state, and thus that the Yamaguchi's formula is not valid when the spin polarization of the core is important. Several examples of unreliable results obtained using this formula will be presented. Section 4 returns to the theoretical basis of the extraction of the Heisenberg Hamiltonian magnetic coupling in the context of BS calculations. Owing to the effective Hamiltonian theory, an accurate spin decontamination method is proposed. In its simplest and most rigorous acceptance, it only rests on the calculation of the overlap between the two degenerate BS Ms=0 solutions. A convenient approximation only uses the expectation values of $<S^2>$ and requires a preliminary calculation of the Ms=1 and Ms=0 solutions in which the core MOs are kept frozen while the magnetic MOs are relaxed. This convenient solution uses the same philosophy as a recent proposal[5,6] which aimed to differentiate and assess the direct exchange, kinetic exchange and core polarization contributions to the magnetic coupling. The superiority of the resulting formula over the Yamaguchi's one is illustrated in the problematic case of a cyclic diradical.

Finally the conclusion examines the possible use of this method for geometry optimization of spin-decontaminated singlet states and evokes further generalizations.

2 Physical content of Broken-Symmetry solutions in diradicals

For the sake of simplicity, the decomposition is introduced for the simpler case of a Hartree-Fock-Slater determinant. The transposition to DFT requires to consider the Kohn-Sham operator instead of the Fock one.

2.1 Description of the Ms=1 triplet state

2.1.1 Frozen core description

Let us consider a typical diradical with two equivalent magnetic sites A and B. The Ms=1 restricted solution is

$$\Phi_R^T = \left|\Pi_i i\bar{i}.ab\right| = \left|\Pi_i i\bar{i}.gu\right| \qquad (1)$$

where the core electrons populate doubly occupied MOs i. Let us call E_R^T the energy of this determinant:

$$E_T^R = \left\langle \Phi_R^T \middle| H \middle| \Phi_R^T \right\rangle. \qquad (2)$$

The magnetic MOs may be the symmetry-adapted g and u orbitals or the localized orthogonal orbitals a and b uniquely defined by the unitary transformation:

$$\begin{aligned} a &= (g+u)/\sqrt{2} \\ b &= (g-u)/\sqrt{2} \end{aligned} \qquad (3)$$

The energy minimization provides canonical doubly occupied MOs which are eigenvectors of the following Fock operator:

$$F = h + \sum_j 2J_j - K_j + J_a - K_a/2 + J_b - K_b/2 \qquad (4)$$

The calculation also gives virtual MOs, hereafter labelled j*, k*,…, orthogonal to all occupied MOs. The MOs satisfy the Brillouin’s theorem, namely

$$\left\langle \Phi_R^T \middle| H \middle| \left(a_{j*}^{+} a_i + a_{\bar{j}*}^{+} a_{\bar{i}} \right) \Phi_R^T \right\rangle = 2\langle i | F | j* \rangle = 0\,. \qquad (5)$$

2.1.2 Spin polarization of the core

The spin polarization introduced by the unrestricted description makes different the core MOs i’ and i” of the α and β spins. The BS solution writes:

$$\Phi_U^T = \left| \prod_i i'\bar{i}''.ab \right| \qquad (6)$$

where the magnetic orbitals a and b are practically unaffected by the spin polarization of the core MOs. Its energy is:

$$E_T^U = \left\langle \Phi_U^T \middle| H \middle| \Phi_U^T \right\rangle \qquad (7)$$

A perturbative expansion of Φ_U^T from Φ_R^T makes explicit the spin-dependent change of the occupied MOs. The exchange field felt by the α spin electrons, created by the magnetic orbitals, is $-(K_a + K_b)$ instead of the average field $-(K_a + K_b)/2$ appearing in the restricted Fock operator. Consequently, the restricted solution is mixed with the singly excited determinants $a_{j*}^{\perp} a_i \Phi_R^T$ through the interaction

$$\left\langle \Phi_R^T \middle| H \middle| a_{j*}^{+} a_i \Phi_R^T \right\rangle = \left\langle i \middle| F - \frac{K_a + K_b}{2} \middle| j* \right\rangle = -\left\langle i \middle| \frac{K_a + K_b}{2} \middle| j* \right\rangle \qquad (8)$$

Oppositely the β spin electrons of the core do not feel the exchange field of the magnetic electrons, so that Φ_R^T interacts with the singly excited determinant through:

$$\left\langle \Phi_R^T \middle| H \middle| a_{\bar{j}*}^{+} a_{\bar{i}} \Phi_R^T \right\rangle = \left\langle i \middle| F + \frac{K_a + K_b}{2} \middle| j* \right\rangle = \left\langle i \middle| \frac{K_a + K_b}{2} \middle| j* \right\rangle \qquad (9)$$

The configuration mixing between these determinants may be written as:

$$\Phi_U^T = \Phi_R^T + \sum_{i,j*} \frac{\langle i | K_a + K_b | j* \rangle}{2\Delta E_{ij*}} \left(a_{j*}^{+} a_i - a_{\bar{j}*}^{+} a_{\bar{i}} \right) \Phi_R^T + \vartheta(2)\,, \qquad (10)$$

where ΔE_{ij*} is the excitation energy of an electron from i to j*.

The orbital transformation leading to the unrestricted solution may be seen as a series of orbital rotations such as

$$\begin{aligned} i' &= i + \sum_{j^*} \lambda_{ij^*} j^* \\ \bar{i}'' &= \bar{i} + \sum_{j^*} \lambda_{ij^*} \bar{j}^* \end{aligned} \qquad (11)$$

where

$$\lambda_{ij^*} = \frac{\langle i | K_a + K_b | j^* \rangle}{2\Delta E_{ij^*}} \qquad (12)$$

Let us now evaluate the contribution of the spin polarization of the core to the expectation value of S^2 in the Ms=1 BS solution. The configuration $(a^+_{j^*}a_i - a^+_{\bar{j}^*}a_{\bar{i}})\Phi^T_R / \sqrt{2}$ is the product of an Ms=0 triplet component in the core by an Ms=1 triplet component in the magnetic orbitals. It is an equal combination of a triplet and a quintet, for which the expectation value of S^2 is equal to 4

$$\left\langle (a^+_{j^*}a_i - a^+_{\bar{j}^*}a_{\bar{i}})\Phi^T_R \middle| S^2 \middle| (a^+_{j^*}a_i - a^+_{\bar{j}^*}a_{\bar{i}})\Phi^T_R \right\rangle / 2 = 4 \qquad (13)$$

Hence

$$\left\langle \Phi^T_U \middle| S^2 \middle| \Phi^T_U \right\rangle = 2 + \sum_{i,j^*} 8\lambda^2_{ij^*} \qquad (14)$$

which is necessarily larger than 2.

2.2 Physical content of the Ms=0 solution

2.2.1 Frozen core description

As done in our previous papers,[5,6] we successively consider the relaxation of the magnetic MOs and that of the core MOs. Starting from the RDFT MOs of the triplet state, i.e. from

$$\Phi^0_{a\bar{b}} = \left| \Pi_i i\bar{i}.a\bar{b} \right|. \qquad (15)$$

in the frozen core description, the magnetic MOs are relaxed leading to the determinant:

$$\Phi^{fc}_{a\bar{b}} = \left| \Pi_i i\bar{i}.a'\bar{b}' \right|. \qquad (16)$$

The new magnetic MOs a’ and b’ are no longer orthogonal and have tails on the other site. They also differ from the MOs a and b due to the mixing with virtual orbitals. Nevertheless matrix elements with singly excited determinant involving virtual orbitals

$$\left\langle a^+_{j^*}a_a\Phi^{fc}_{a\bar{b}} \middle| H \middle| \Phi^{fc}_{a\bar{b}} \right\rangle = \left\langle j^* \middle| K_b \middle| a \right\rangle, \qquad (17)$$

are extremely small as they involve the vanishing electron distribution ab. Numerical computations confirm that this effect is negligible. The main change comes from the mixing between the MOs a and b, which may be described as

$$\begin{aligned} a' &= a\cos\varphi + b\sin\varphi \\ b' &= a\sin\varphi + b\cos\varphi \end{aligned} \qquad (18)$$

This rotation of the MOs implies a delocalization of the magnetic orbitals, which are no longer strongly localized. It introduces an ionic component in the wave function. Actually in the product

$$a'\bar{b}' = a\bar{b}(\cos\varphi)^2 + b\bar{a}(\sin\varphi)^2 + (a\bar{a} + b\bar{b})\sin\varphi\cos\varphi \qquad (19)$$

the two first components are neutral in the valence bond (VB) meaning, while the last ones are ionic. It may be rewritten as a combination of S^2 eigenfunctions:

$$a'\bar{b}' = (a\bar{b} + b\bar{a})/2 + (a\bar{b} - \overline{ba})(\cos 2\varphi)/2 + (a\bar{a} + b\bar{b})(\sin 2\varphi)/2 \qquad (20)$$

in which the first and last components are singlet functions while the intermediate one is a triplet. One may notice that

$$\left\langle S^2 \right\rangle_{Ms=0}^{fc} = (\cos 2\varphi)^2 < 1 \qquad (21)$$

At this stage, the expectation value of S^2 is necessarily smaller than (or equal to) 1.

Noticing that

$$\Phi'^{fc}_{a\bar{b}} = \lambda\Psi^{fc}_S + \mu\Psi^R_T \qquad (22)$$

where

$$\mu^2 = (\cos 2\varphi)^2/2 = \left\langle S^2 \right\rangle_{Ms=0}^{fc}/2, \qquad (23)$$

it is possible to express the energy of $\Phi'^{fc}_{a\bar{b}}$ as a function of the singlet and triplet energies

$$E^{fc}_{Ms=0} = \lambda^2 E^{fc}_S + \mu^2 E^R_T \qquad (24)$$

From which one may write

$$E^{fc}_{Ms=0} - E^R_T = \lambda^2(E^{fc}_S - E^R_T), \qquad (25)$$

and the energy difference between the singlet and triplet states writes

$$E^{fc}_S - E^R_T = \frac{E^{fc}_{ms=0} - E^R_T}{\lambda^2} = \frac{2}{2 - \left\langle S^2 \right\rangle_{ms=0}^{fc}}(E^{fc}_{ms=0} - E^R_T). \qquad (26)$$

At this stage the only approximation concerns the neglect of the mixing of the orbitals a and b with virtual orbitals in the optimization of a’ and b’. This expression is valid whatever the ratio of neutral versus ionic components is. It remains valid when the symmetry breaking vanishes, i.e. when the Ms=0 solution tends to become closed shell. In this case $\left\langle S^2 \right\rangle_{Ms=0}^{fc} = 0$, the denominator is equal to 2 and the decontamination factor is equal to 1 since the solutions are not spin contaminated. This expression is close to the well-known Yamaguchi's formula:

$$E_S - E_T = \frac{2}{\left\langle S^2 \right\rangle_T - \left\langle S^2 \right\rangle_{BS}} (E_{BS} - E_T) \qquad (27)$$

except that this formula is assumed to be correct after the spin polarization of the core MOs. It is perfectly valid for a frozen core solution but we shall demonstrate that this is no longer true after relaxation of the core MOs.

An alternative formulation[19] had been proposed at the same level of treatment in terms of overlap between the magnetic orbitals a' and b':

$$\left\langle a' \middle| b' \right\rangle = \sigma' = 2\cos\varphi \sin\varphi = \sin 2\varphi \qquad (28)$$

The overlap between the two equivalent Ms=0 solutions writes

$$\Sigma^{fc} = \left\langle \Phi^{fc}_{a'\bar{b}'}{}' \middle| \Phi^{fc}_{b'\bar{a}'} \right\rangle = \sigma'^2 = (\sin 2\varphi)^2 = 1 - \left\langle S^2 \right\rangle_{ms=0}^{fc} . \qquad (29)$$

And one may equivalently write

$$E_S^{fc} - E_T^R = \frac{2}{1+\Sigma^{fc}} (E^{fc}_{ms=0} - E_T^R) , \qquad (30)$$

The relevance of this formula will be discussed in section 4.

2.2.2 Relaxation of the core MOs

The full optimization of the MOs in the unrestricted scheme leads to the determinant:

$$\Phi'_{a'\bar{b}'} = \left| \Pi_i i''' \overline{i''''} . a' \bar{b}' \right| \qquad (31)$$

Previous analysis[5,6] have shown that the magnetic MOs are practically unaffected by the polarization of the core MOs and remain very close to a' and b'. Despite the change between the a' and b' orbitals, and as long as the ionic VB component of the |a'b'| determinant is small, one may consider that the relaxation of the core MOs is essentially due to the spin polarization. The α spin core electrons feel an exchange field $-K_a$, instead of the operator $-(K_a + K_b)/2$, which appears in the restricted DFT formalism. The β electrons feel an exchange field $-K_b$. Therefore the MOs are revised according to the following transformation:

$$\begin{aligned} i''' &= i + \sum_{j^*} \lambda'_{ij^*} j^* \\ i'''' &= i - \sum_{j^*} \lambda'_{ij^*} j^* \end{aligned} \qquad (32)$$

where

$$\lambda'_{ij*} \cong \frac{\left\langle i \middle| K_a - K_b \middle| j* \right\rangle}{2\Delta E_{ij*}} \qquad (33)$$

The rotations are opposite for α and β spins issued from the same closed-shell MO. The resulting energy

$$E^{u}_{ms=0} = \left\langle \Phi'_{a'\bar{b}'} \middle| H \middle| \Phi'_{a'\bar{b}'} \right\rangle \qquad (34)$$

now accounts for the spin-polarization effects.

3. Drawbacks of the traditional spin decontamination and alternative solution

3.1. Impact of the core polarization on the traditional decontamination factor

Let us now consider the impact of the core polarization on the $<S^2>$ value for the Ms=0 solution. This effect can be evaluated from the perturbative expansion:

$$\Phi'_{a'\bar{b}'} = \Phi^{0}_{a'\bar{b}'} + \sum_{ij*} \lambda'_{ij*} \left| (i\bar{j}* - j*\bar{i}).a'\bar{b}' \right| + \vartheta(2)\,. \qquad (35)$$

Each of these excited configurations is a product of the Ms=0 triplet component in the core orbitals multiplied by a half and half mixture of a singlet and a triplet in the magnetic ones, i.e. this function has components on singlet, triplet and quintet states. One may show that

$$\left\langle \frac{\left|(i\bar{j}* - j*\bar{i}).\,a\bar{b}\right|}{\sqrt{2}} \middle| S^2 \middle| \frac{\left|(i\bar{j}* - j*\bar{i}).\,a\bar{b}\right|}{\sqrt{2}} \right\rangle = 2 \qquad (36)$$

and thus

$$\left\langle \Phi'_{a\bar{b}} \middle| S^2 \middle| \Phi'_{a\bar{b}} \right\rangle = \left\langle S^2 \right\rangle^{fc}_{a'\bar{b}'} + 4\sum_{ij*} (\lambda'_{ij*})^2 \qquad (37)$$

The polarization of the core significantly increases the $\left\langle S^2 \right\rangle$ value of the Ms=0 solution. While the first term is necessarily less than one, the second term leads to values greater than 1. It is important to note that the configurations introduced by the core polarization in the wave function are not the low energy triplet configuration, they are orthogonal to it, and of much higher energies. The Yamaguchi's formula is based on the idea that the BS Ms=0 solution is a linear combination of the lowest singlet and triplet states and that the value of $\left\langle S^2 \right\rangle$ gives the mixture of these two states. This is clearly no longer the case after polarization of the core MOs.

As a consequence the difference $\left\langle S^2 \right\rangle_{Ms=1} - \left\langle S^2 \right\rangle_{Ms=0}$ appearing in the denominator of the Yamaguchi's expression may be significantly smaller than 1 and the corresponding spin decontamination factor may become significantly larger than 2, which is not correct.

Several examples of this failure can be found in the literature. The most striking is perhaps the evolution of the singlet-triplet gap in the series of polyacenes. Several studies[23,24,25] have noticed that polyacenes are subject to a spin-symmetry breaking as soon as the number of cycles is larger than six. This is not an artefact since the CASSCF treatments of the full π electron population in the set of valence bonding and antibonding MOs using powerful Density Matrix Renormalization Group (DMRG) techniques[26] have confirmed that the occupation numbers of the HOMO and LUMO tends to 1 when the size of the polyacene increases. The values of $\langle S^2 \rangle_{Ms=0}$ reported in reference [23] are 1.08 for octacene, 2.26 for nonacene, and 1.42 for decacene. For this last molecule the Yamaguchi's spin-decontamination factor is equal to 2/(2-1.42)=3.44, i.e. much larger than 2. It is not surprising then that the singlet-triplet gap follows a non-monotonic behavior, increasing for large polyacenes. The calculated values of these gaps are 5.8, 5.5 and 5.7 Kcal/mol for octacene, nonacene and decacene respectively. This increase of the energy difference is of course unphysical, it is an artefact due to the impact of $\langle S^2 \rangle_{Ms=0}$ on the Yamaguchi's spin-decontamination factor. This problem has also been faced recently by Trinquier *et al.*[27] in the treatment of other diradicals, constituted of polycyclic hydrocarbons substituted by two remote extracyclic CH_2 groups.

3.2 Alternative proposal

The core polarization energy correction of the BS solutions is

$$\Delta E_T^{SP} = E_T^U - E_T^R \qquad (38)$$

for the triplet and

$$\Delta E_{Ms=0}^{cp} = E_{Ms=0}^U - E_{Ms=0}^{fc} \qquad (39)$$

for the Ms=0 solution. Both quantities may be expressed at the second order of perturbation, leading to the following contribution of the core polarization effects to the energy difference between the Ms=0 the Ms=1 single determinantal energies

$$\Delta E_{Ms=0}^{cp} - \Delta E_{Ms=1}^{sp} = -2\sum_{i,j*} \frac{\langle i|K_a|j*\rangle\langle j*|K_b|i\rangle}{\Delta E_{ij*}} \qquad (40)$$

An analytic development[1,2] has shown that the core polarization effects brought by single excitations are only half of the total spin polarization correction, the double excitations giving the same contribution to the energy difference between the singlet and the triplet as the single excitations. Thus, the total contribution of the core polarization to the energy difference between the singlet and the triplet writes

$$\Delta E_{ST}^{cp} = 2(\Delta E_{ms=0}^{cp} - \Delta E_{ms=1}^{sp}) . \qquad (41)$$

The resulting energy difference between the singlet and the triplet becomes:

$$E_S - E_T = \frac{2}{2-\left\langle S^2 \right\rangle^{fc}_{ms=0}} (E^{fc}_{ms=0} - E^{R}_{T}) + 2(E^{U}_{ms=0} - E^{fc}_{ms=0} - E^{U}_{T} + E^{R}_{T}) \qquad (42)$$

$$E_S - E_T = 2(E^{U}_{ms=0} - E^{U}_{T}) + \left(\frac{2}{2-\left\langle S^2 \right\rangle^{fc}_{ms=0}} - 2 \right) (E^{fc}_{ms=0} - E^{R}_{T}) . \qquad (43)$$

As previously shown the signs of the first and second terms are opposite. As a consequence the excitation energy is bounded in absolute value by $2(E^{U}_{ms=0} - E^{U}_{T})$.

These alternative formulas behave properly when the Ms=0 BS solution tends to become closed shell. In such a case

$$\left\langle S^2 \right\rangle_{Ms=0} = 0 \qquad (44)$$

$$E^{fr}_{Ms=0} = E^{U}_{Ms=0} \qquad (45)$$

and, as expected,

$$E_S - E_T = E^{fr}_{Ms=0} - E^{U}_{T} \qquad (46)$$

This alternative solution avoids the drawbacks of Yamaguchi’s formula when the spin polarization becomes large and remains valid when the symmetry breaking disappears. It only requires to perform two additional frozen core calculations, namely the restricted Ms=1 calculation, and using the corresponding core orbitals, a constrained energy minimization for the Ms=0 solution. This procedure has been used in two recent papers’[6] for an analysis purpose. This procedure offers a practical solution to the divergent behavior of Yamaguchi’s formula in the situations where <S^2> for Ms=0 becomes larger than 1.

4. New spin decontamination method derived from the Effective Hamiltonian Theory

4.1 Theoretical basis of spin Hamiltonians

Spin Hamiltonians, and in particular the Heisenberg-Dirac-van Vleck Hamiltonian,[28,29,30] which describes the low energy spectrum of two interacting spins,

$$H_{HDvV} = J_{12} \vec{S}_1 . \vec{S}_2 \qquad (47)$$

are derived from the exact electronic Hamiltonian through the Effective Hamiltonian formalism. This formalism, as expressed by Bloch[31] or by des Cloizeaux,[32] projects the information relative to N lowest eigen-states and eigen-energies onto a model space of the same dimension. The model space is defined by its projector P_0, which one usually writes in terms of an orthogonal basis of N functions

$$P_O = \sum_{I=1,N} \left| I \right\rangle \left\langle I \right| . \qquad (48)$$

The eigenvectors of the exact Hamiltonian satisfy the equation:

$$H\left|\Psi_m\right\rangle = E_m\left|\Psi_m\right\rangle . \qquad (49)$$

The Bloch Effective Hamiltonian is entirely defined by the conditions

$$H^{eff}\,P_0\left|\Psi_m\right\rangle = E_m P_0\left|\Psi_m\right\rangle , \qquad (50)$$

its N eigenvalues are the eigenvalues of the exact Hamiltonian and its N eigenvectors are the projections of the corresponding eigenstates onto the model space. For spin systems the model space is spanned by the vectors of the same space configuration, bearing a single electron in the magnetic orbitals and differing by their spin distributions. In the simplest case of 2 electrons in two orthogonal orbitals a and b, the model space is defined by

$$\Phi^0_{a\bar{b}} = \left|\Pi_i i\bar{i}.a\bar{b}\right| \qquad (51)$$

and

$$\Phi^0_{b\bar{a}} = \left|\Pi_i i\bar{i}.b\bar{a}\right| . \qquad (52)$$

4.2 From a model space with a non-orthogonal basis to a spin decontaminated magnetic coupling

Let us define a model space spanned by the two BS non orthogonal Ms=0 degenerate solutions $\left(\Phi'_{a'\bar{b}'},\Phi'_{b'\bar{a}'}\right)$. The overlap matrix is

$$\begin{array}{ccc} & \Phi'_{a'\bar{b}'} & \Phi'_{b'\bar{a}'} \\ \Phi'_{a'\bar{b}'} & 1 & \Sigma \\ \Phi'_{b'\bar{a}'} & \Sigma & 1 \end{array} \qquad (53)$$

where

$$\Sigma = \left\langle \Phi'_{a'\bar{b}'} \middle| \Phi'_{b'\bar{a}'} \right\rangle \qquad (54)$$

The Effective Hamiltonian matrix writes

$$\begin{array}{ccc} & \Phi'_{a'\bar{b}'} & \Phi'_{b'\bar{a}'} \\ \Phi'_{a'\bar{b}'} & E_{Ms=0} & h \\ \Phi'_{b'\bar{a}'} & h & E_{Ms=0} \end{array} \qquad (55)$$

Since the two BS solutions are degenerate, the only unknown quantity is the off-diagonal element h. In order to calculate it, one may take benefit of the knowledge of the energy of the triplet state from the Ms=1 BS solution which is degenerate with the Ms=0 following function:

$$\Psi_T = (\Phi'_{a'\bar{b}'} - \Phi'_{b'\bar{a}'})/(\sqrt{2(1-\Sigma)}) \qquad (56)$$

One may note that while both vectors $\left(\Phi'_{a'\bar{b}'},\Phi'_{b'\bar{a}'}\right)$ contain ionic VB components, these components cancel in this antisymmetric combination. The energy is

$$E_T = (E_{Ms=0} - h)/(1-\Sigma) = E_{Ms=1}\,. \qquad (57)$$

Since we know the energy of the triplet, h is known. The energy of the singlet is given by

$$E_S = (E_{m_s=0} + h)/(1+\Sigma) \qquad (58)$$

and the energy difference between the singlet and the triplet is:

$$E_S - E_T = \frac{2(E_{Ms=0} - E_{Ms=1})}{1+\Sigma} \qquad (59)$$

While this equation is formally identical to equation (30) derived by Caballol *et al.*,[19] it now involves BS solutions in which the core orbitals have been relaxed.

As the overlap is smaller than 1, the following inequalities are always satisfied

$$1 < \frac{2}{1+\Sigma} < 2 \qquad (60)$$

which warrants that the spin decontamination factor is bounded.

4.3 Exploiting the expectation values of S^2

It is possible to evaluate the overlap between the two degenerate Ms=0 solutions from the knowledge of $<S^2>$ at the frozen core and core polarized levels. Actually one may return to the previously derived perturbative expansion of the core-polarized Ms=0 solution, and to calculate

$$\Sigma = \left\langle \Phi^0_{a'\bar{b}'} + \sum_{ij^*} \lambda'_{ij^*} \left|(i\bar{j}^* - j^*\bar{i}).a'\bar{b}'\right| \,\middle|\, \Phi^0_{b'\bar{a}'} - \sum_{ij^*} \lambda'_{ij^*} \left|(i\bar{j}^* - j^*\bar{i}).b'\bar{a}'\right| \right\rangle \qquad (61)$$

In the above expression we have taken into account the opposite rotations of the core MOs in the two degenerate Ms=0 solutions. The occupied MOs i and the virtual MOs j* are orthogonal to a' and b' since they are orthogonal to a and b. So that the overlap is the product of two overlaps, accounting for both the magnetic and core orbitals,

$$\Sigma = \Sigma^{fc}(1 - 2\sum_{ij^*} (\lambda'_{ij^*})^2) \qquad (62)$$

where Σ^{fc} is the overlap between the two degenerate solutions at the frozen core level, and already expressed in terms of $\left\langle S^2 \right\rangle^{fc}_{a'\bar{b}'}$,

$$\Sigma^{fc} = \left\langle a'\bar{b}' \middle| b'\bar{a}' \right\rangle = 1 - \left\langle S^2 \right\rangle^{fc}_{a'\bar{b}'}\,. \qquad (63)$$

Using the expression

$$\left\langle S^2 \right\rangle_{Ms=0} = \left\langle S^2 \right\rangle^{fc}_{Ms=0} + 4\sum_{ij^*} (\lambda'_{ij^*})^2\,, \qquad (64)$$

one gets the following relation

$$\Sigma = \Sigma^{fc}(1-(\langle S^2\rangle_{Ms=0} - \langle S^2\rangle^{fc}_{Ms=0})/2) < \Sigma^{fc}, \qquad (65)$$

and to a convenient approximation of the spin-decontaminated energy gap

$$E_S - E_T = \frac{2(E_{Ms=0} - E_{Ms=1})}{1+(1-\langle S^2\rangle^{fc}_{Ms=0})(1+(\langle S^2\rangle^{fc}_{Ms=0} - \langle S^2\rangle_{Ms=0})/2))} \qquad (66)$$

$$E_S - E_T = \frac{2}{2-(\langle S^2\rangle^{fc}_{Ms=0} + \langle S^2\rangle_{Ms=0})/2 + \langle S^2\rangle^{fc}_{Ms=0}(\langle S^2\rangle_{Ms=0} - \langle S^2\rangle^{fc}_{Ms=0})/2)}(E_{Ms=0} - E_{Ms=1}) \qquad (67)$$

This decontamination factor tends to 1 when the symmetry breaking vanishes, and is bounded by 2.

5. Numerical illustration

The para-dimethylene-di-hydro-anthracene, may be seen as a quinodimethane substituted by two allyl groups on the external carbons. It has been chosen as it presents a problematic value of the expectation value of S^2 for the Ms=0 BS solution. The allyl groups are compelled to remain in the plane of symmetry of the molecule by a cyclization through a saturated CH_2 group. The basis set is of 6-311G** quality, the exchange-correlation potential is the B3LYP one. The geometry has been optimized for the Ms=0 solution. The energies and expectation values of S^2 at the various steps of the calculation are reported in Table 1. They deserve the following comments:

- The direct exchange, given by the difference between the energies of the two restricted distributions with the same frozen core and the same magnetic orbitals, is very small, 0.000103 a.u.. This indicates that the overlap between the magnetic orbitals a and b is particularly small. This is consistent with the spatial extent of the localized magnetic orbitals, as pictured in Figure 1.
- The kinetic exchange, resulting from the delocalization between the orbitals a and b in the field of the frozen core is even smaller. This effect only stabilizes the Ms=0 solution by 0.000018 a.u.. For this solution $\langle S^2\rangle$= 0.999986, the deviation from 1 comes from an extremely small ionic VB component. At this level the magnetic coupling remains ferromagnetic, $E^{fc}_{Ms=0} - E^{R}_{T} = 0.000084$ a.u.. The spin decontamination reduces to a multiplication by a factor 2. The so-calculated value of E_S-E_T=-0.10 kcal/mol remains negative.
- The major effects are due to the core polarization. The Ms=1 solution is stabilized by 0.007632 a.u. and the value of $\langle S^2\rangle$ remains close to 2.0 (2.071), while the core polarization lowers the Ms=0 solution by 0.011112 a.u. and $\langle S^2\rangle$ for this solution reaches the particularly large value of 1.34.
- The here-proposed spin-decontamination procedures coincide in that case, and simply reduce to a multiplication by a factor 2 of the $E_{Ms=0} - E_{Ms=1}$ quantity. The value E_S-E_T

= 0.00679 a.u.= 4.25 kcal/mol obtained from our calculations is significantly lower than the one given by the Yamaguchi's formula (5.83 kcal/mol).

It is likely that our correction suppresses the pathological increase (see section 3.1) of the singlet-triplet energy gap in the acene series,[23] obtained from the Yamaguchi's spin decontamination factor.

	Energy			$\langle S^2 \rangle$		
	RDFT	UDFT Frozen core	UDFT	RDFT	UDFT Frozen core	UDFT
Ms=1	-.142970	-.150601	.150718	2.0	2.07082	2.07268
Ms=0	-.142867	-.142884	-.153997	1.0	0.99998	1.34215

Table 1: Energies in a.u. (the value -618 was subtracted from the values listed in the table) and $\langle S^2 \rangle$ values of the Ms=0 and Ms=1 broken symmetry solutions.

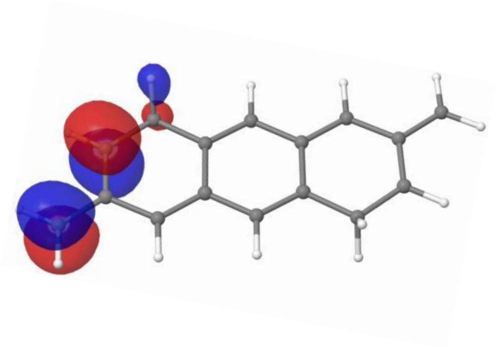

Figure 1: example of a localized magnetic orbital computed at the RDFT level on the studied compound.

6. Final discussion and conclusion

This work calls the attention on the problems encountered when using broken-symmetry solutions for the calculation of singlet triplet energy gaps in diradicals. This practice is of common use in the DFT community as it is cheap and convenient. Of course it suffers from the dependence of the results on the choice of the exchange-correlation functional, and this dependence may be dramatic. In hybrid DFT functionals the amount of exact Fock exchange is crucial. B3LYP may overestimate the value of the magnetic coupling and a higher percentage of Fock exchange (from 25 to 33%) has sometimes been recommended. However the main problem concerns the fact that the Ms=0 solutions of open-shell systems are not spin eigenfunctions and corrections are required to correctly assess the energy of the singlet state. The spin-decontamination formula proposed by Yamaguchi only exploits the expectation values of the S^2 operator and is extremely simple and popular. This work

i) shows that while the Yamaguchi decontamination factor is correct as long as the core remains closed shell, it becomes irrelevant for the treatment of the core polarization phenomenon. It can overestimate unduly the singlet triplet gap when the $\left\langle S^2 \right\rangle$ value relative to the Ms=0 solution becomes larger than 1, leading to a decontamination factor larger than 2.

ii) re-examines the physics of the BS solutions and proposes simple alternative decontamination treatments which are valid from the covalent to the diradical regimes. The decontamination factor is always bounded by 2.

The most rigorous version is based on the Effective Hamiltonian Theory, it is here formulated using a non-orthogonal basis set of the model space. It leads, for this elementary problem, to a very simple expression of the singlet triplet gap as a function of the Ms=1 and Ms=0 BS energies and the overlap between the two degenerate Ms=0 solutions. A direct evaluation of this overlap will be implemented shortly. We have derived an approximate expression as a function of the expectation values of S^2 at both the frozen-core and polarized-core levels.

Several prospects will be considered in the near future:

- The first one concerns geometry optimizations. Recent works have shown that the spin decontamination may strongly affect the geometry, the singlet state geometry being significantly different from that of the Ms=0 BS solution.[33,34] This geometry change has an impact on the singlet-triplet energy gap. The convenient procedure recently proposed in reference [33] can be combined with the revised spin decontamination factors.
- The second topic concerns the generalization to more than two ½ spins, and to the interaction between spins larger than ½.
- The non-orthogonal formulation of the Effective Hamiltonian can be applied to the recently proposed Projected Single Reference Configuration Interaction[35] which also suffers spin contamination problems.

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