

# Magnetic Coupling Constants in Three Electrons Three Centres Problems from Effective Hamiltonian Theory and Validation of Broken Symmetry Based Approaches

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## Abstract.-

In the most general case of three electrons in three symmetry unrelated centres with  $\hat{S}_1 = \hat{S}_2 = \hat{S}_3 = 1/2$  localized magnetic moments, the low energy spectrum consists of one quartet ( $Q$ ) and two doublet ( $D_1, D_2$ ) pure spin states. The energy splitting between these spin states can be described with the well-known Heisenberg-Dirac-Van Vleck (HDVV) model spin Hamiltonian, and their corresponding energy expressions are expressed in terms of the three different two-body magnetic coupling constants  $J_{12}, J_{23}$  and  $J_{13}$ . However, the values of all three magnetic coupling constants cannot be extracted using the calculated energy of the three spin adapted states, since only two linearly independent energy differences between pure spin states exist. This problem has been recently investigated (JCTC **2015**, *11*, 3650), resulting in an alternative proposal to the original Noodleman's broken symmetry mapping approach. In the present work, this proposal is validated by means of ab initio effective Hamiltonian theory, which allows a direct extraction of all three  $J$  values from the one-to-one correspondence between the matrix elements of both effective and HDVV Hamiltonian. The effective Hamiltonian matrix representation has been constructed from configuration interaction wave functions for the three spin states obtained for two model systems showing a different degree of delocalization of the unpaired electrons. These encompass a trinuclear Cu(II) complex and a  $\pi$ -conjugated purely organic triradical.

## 1. Introduction.

Magnetic interactions among unpaired electrons in organometallic complexes have been extensively studied, both experimental<sup>1-4</sup> and theoretically.<sup>5-8</sup> This resulted in accurate magneto-structural relationships<sup>1,6</sup> and on the successful description of many complex phenomena such as single molecule magnetism<sup>9</sup> or spin-crossover.<sup>10</sup>

From a theoretical point of view, prior to the study of any magneto-structural relationship is the correct description of the low-lying energy spectrum of a given molecule. Provided that the interacting unpaired electrons can be assigned to localized magnetic centres, such description is granted by the use of the so-called Heisenberg-Dirac-Van Vleck<sup>11-13</sup> (HDVV) model spin Hamiltonian, which provides an appropriate formal description of the magnetic states since it commutes with the total spin  $\hat{S}^2$  operator and consequently, its eigenfunctions are spin-adapted. Thus, by appropriately writing the energy differences between the spin-adapted states, one can extract the magnetic coupling constants.

The mapping strategy described above is not the unique way to extract coupling constants in magnetic molecular systems<sup>14,15</sup> but often constitutes the method of choice.<sup>7,8</sup> Hence, mapping based approaches have been broadly applied to organic biradicals and to binuclear complexes for which crystal structures and magnetic data are available,<sup>4,8</sup> thus providing excellent test systems to benchmark the consistency of computational approaches for the description of magnetic interactions. However, most of the currently interesting magnetic systems become computationally intractable by means of explicitly correlated wave function based methods. Thus, one is constrained to the use of Density Functional Theory (DFT) based methods. However, except in the case of ensemble Kohn-Sham based formalisms,<sup>16</sup> the use of DFT methods necessarily implies describing the electron density by means of a single Slater determinant and, consequently, to make use of broken symmetry (BS) solutions to approach the low spin states which are necessary for extracting magnetic coupling constants. This is obviously not the best approach for magnetic states that are multi-reference in nature, and further considerations need to be addressed.<sup>5,7,8</sup> Nevertheless, with the appropriate spin projection,<sup>17-19</sup> the mapping approach, as originally proposed by Noodleman,<sup>20-22</sup> provides a way to use BS solutions to extract magnetic coupling constants that can be associated to the ones that one would obtain performing spin-adapted calculations. The mapping procedure allows one to establish a univocal relationship between the low

energy spectrum arising from calculations using the exact, non-relativistic time-independent electronic Hamiltonian and the eigenvalues of the HDVV model spin Hamiltonian.<sup>7,8</sup> In case of dealing with pure spin states, the one-to-one correspondence holds whereas when using BS solutions, as is the case in DFT calculation, appropriate spin projection is required. This approach is rather general and has proven to provide consistent results for rather complex systems.<sup>6,23</sup>

Instead of attempting to obtain the eigenvalues and eigenfunctions of the spin-adapted states from appropriate combination of BS solutions and then mapping them to the analytic expression of the energy of the pure spin states of the HDVV Hamiltonian, Moreira and Illas suggested to directly link the energy corresponding to DFT calculated BS solutions to the expectation energy of the HDVV Hamiltonian.<sup>7</sup> In both cases, the magnetic coupling constants of interest appear in the analytic expression of the eigenvalue or energy expectation value of the HDVV as shown in Section 2, with the advantage of not requiring the use of a spin projector, which cannot always be defined.<sup>24</sup>

Despite of the success of theoretical approaches in extracting magnetic coupling constants from appropriate mapping of the calculated energy of the spin adapted states of interest to the eigenvalues of the HDVV Hamiltonian, there are many situations where this mapping procedure cannot be used. This is the case when the number of spin-adapted states is equal or less than the number of relevant magnetic coupling constants. The case of three electrons in three magnetic centres problems provides a paradigmatic example. In the case of trinuclear Cu(II) complexes, envisaging also three electrons in three magnetic centres, a solution to recover the mapping approach was proposed which made use of the mapping between BS solutions obtained from DFT calculations and expectation values of the HDVV Hamiltonian for an equivalent type of BS solutions.<sup>25</sup> The problem here is the exceedingly large dependence of the calculated magnetic coupling constants with the choice of the exchange-correlation potential used in the DFT calculations. However, it was empirically found that an almost constant relationship between the two most relevant magnetic coupling constants exists independent of the density functional method used in the calculations. This relationship can be taken as an additional independent equation thus allowing extracting the three independent coupling constants defining the HDVV of this system from accurate calculations of the two linearly independent energy differences. While this procedure provided consistent results for a Cu(II) trinuclear compound, it is based on an empirical

finding and requires either the combined use of wave function based calculations for the states of interest and of DFT calculations to extract the above mentioned relationship or experimental input to assist in choosing the appropriate DFT method. In any case, one can properly claim that the obtained results might be biased by the imposed relationship between the coupling constants. Clearly, a more theoretically grounded procedure is required.

Here, by means of effective Hamiltonian theory, we first justify the correctness of this approach and then show its general validity by analyzing a more difficult three electrons in three centres problem. Based on the work by Rajca and co-workers,<sup>26</sup> we consider a simplified  $\pi$ -conjugated odd alternant hydrocarbon involving rather delocalized unpaired electrons.

## 2. Obtaining Spin Hamiltonians from *ab initio* effective Hamiltonian theory.

### 2.1. Matrix representation of the HDVV model spin Hamiltonian

The general form of the HDVV Hamiltonian is well-known.<sup>1,5</sup> However, in practice, it is necessary to consider its explicit form for each case under scrutiny. For a system with three  $S=1/2$  magnetic centres in a 1-2-3 asymmetrical topology, the low energy spectrum is well described by a HDVV Hamiltonian as in Eq. (1) below

$$\hat{H}^{HDVV} = - \sum_{\langle i,j \rangle} J_{ij} \cdot \hat{\mathbf{S}}_i \cdot \hat{\mathbf{S}}_j = - J_{12} \cdot \hat{\mathbf{S}}_1 \cdot \hat{\mathbf{S}}_2 - J_{23} \cdot \hat{\mathbf{S}}_2 \cdot \hat{\mathbf{S}}_3 - J_{13} \cdot \hat{\mathbf{S}}_1 \cdot \hat{\mathbf{S}}_3 \quad (1)$$

where  $J_{ij}$  is the exchange coupling constant between the  $\hat{\mathbf{S}}_i$  and  $\hat{\mathbf{S}}_j$  localized spin moments and the  $\langle i,j \rangle$  symbol indicates that the sum refers to nearest neighbour interactions only. According to the adopted definition in Eq. (1), a positive value of the exchange coupling constant  $J_{ij}$  corresponds to a ferromagnetic interaction between  $S_i$  and  $S_j$  magnetic moments. Conversely, a negative  $J_{ij}$  value describes an antiferromagnetic interaction (parallel and antiparallel spins alignments respectively). The number, sign and magnitude of the most relevant  $J_{ij}$  determine the low-energy spectrum of the problem and consequently the magnetic ordering of the system. It is worth noting that spin adapted wave functions are also eigenfunctions of the total squared spin operator  $\hat{\mathbf{S}}^2 = \hat{S}_x \cdot \hat{S}_x + \hat{S}_y \cdot \hat{S}_y + \hat{S}_z \cdot \hat{S}_z$ , given that  $[\hat{H}^{HDVV}, \hat{\mathbf{S}}^2] = 0$ . The matrix representation of this operator on the basis formed by the neutral determinants, those with one spin per enter only, is presented in Table 1.

Diagonalization of the low  $S_z = +1/2$  sub block, leads to the three spin-adapted  $|S, M_S\rangle$  states, one quartet and two doublets describing the low energy spectrum.<sup>27</sup>

$$|Q\rangle = |3/2, 1/2\rangle = 3^{-1/2}(|\alpha\alpha\beta\rangle + |\alpha\beta\alpha\rangle + |\beta\alpha\alpha\rangle) \quad (2)$$

$$|D_1\rangle = |1/2, 1/2\rangle = 2^{-1/2}(|\alpha\alpha\beta\rangle - |\alpha\beta\alpha\rangle) \quad (3)$$

$$|D_2\rangle = |1/2, 1/2\rangle = 6^{-1/2}(|\alpha\alpha\beta\rangle + |\alpha\beta\alpha\rangle - 2 \cdot |\beta\alpha\alpha\rangle) \quad (4)$$

and the corresponding eigenvalues are

$$E_Q = -1/4 \cdot (J_{12} + J_{13} + J_{23}) \quad (5)$$

$$E_{D_1} = 1/4 \cdot (J_{12} + J_{13} + J_{23}) - 1/2 \cdot X \quad (6)$$

$$E_{D_2} = 1/4 \cdot (J_{12} + J_{13} + J_{23}) + 1/2 \cdot X \quad (7)$$

$$X = (J_{12}^2 + J_{13}^2 + J_{23}^2 - J_{12} \cdot J_{13} - J_{12} \cdot J_{23} - J_{13} \cdot J_{23})^{1/2} \quad (8)$$

Here, the problem of the mapping approach using spin adapted functions becomes evident since there are three different magnetic coupling constants, but only two energy differences. To simplify the problem, one can either neglect one of the coupling constants—based on distances between the magnetic centres—or make use of the symmetry of the problem (if any) to establish relationships among the coupling constants. Scheme 1 exemplifies this problem with two simplified models: an equidistant linear and an equilateral triangle arrangement. In the equilateral case, all three coupling constants become equal, the two doublet states become degenerate, and the spectrum involves one energy difference only, which allows obtaining the magnetic coupling constant provided accurate energy values for the quartet and (degenerate) doublet states are available. In the linear case, assuming it is centre-symmetrical, the coupling constants between the two closest neighbours are equal and one can safely assume that the external one vanishes. In this case, there are two linearly independent equations as a function of the same parameter  $J$ , which permits checking the consistency of the spectrum, again provided that the energy differences have been calculated with enough accuracy. In case of relying on BS solutions it is enough to consider the diagonal terms of HDVV in Table 1. The problem here is, as stated above, that the energy of the BS solutions heavily depends on the choice of the exchange-correlation functional.<sup>7,16,17</sup> Nevertheless, the almost constant relationship between  $J_{23}/J_{12}$  found along a series of DFT-based calculations suggest that the underlying physics is correct.

## 2.2. Obtaining the *ab initio* effective spin Hamiltonian.

To obtain a more physically grounded argument supporting the almost constant relationship between  $J_{23}/J_{12}$  found in previous work<sup>25</sup> and to extend the approach to any general three electrons in three centres problem, we rely in effective Hamiltonian theory. Here, an appropriate matrix representation of the effective spin Hamiltonian is constructed from accurate configuration interaction wave function calculations. Next, a direct comparison between its matrix elements and those of HDVV Hamiltonian written in the same basis set permits an extraction of all magnetic coupling constants and allows checking the consistency of DFT-based values. Thus, effective Hamiltonian theory offers a rigorous mathematical scheme to reduce the electronic Hamiltonian to a spin Hamiltonian of the HDVV type by means of projection techniques. It is important to stress that the utility of the effective Hamiltonians relies in their interpretative power of a very complex problem (the full electronic problem) by means of a projection in a suitable reduced subspace that provides the essential interpretative valence bond (VB) forms. Additionally, the effective Hamiltonian theory also provides a tool to extract additional information from the wave function that is not directly accessible from the energy spectrum. However, the construction of the effective Hamiltonian is tedious and a specific code is needed for each case of interest.

There are two main ways of constructing an effective Hamiltonian; the one developed Bloch<sup>28</sup> which leads to a non-hermitian representation, and the one proposed by des Cloizeaux<sup>29</sup> that solves this problem and for our purposes is the most convenient one. A more detailed explanation of effective Hamiltonian theory has been provided by Durand and Malrieu<sup>30</sup> and for applications to magnetic problems we refer to previous works.<sup>8,31</sup> The procedure starts by targeting the spin space determining the low-lying energy spectrum, which is the model space. Basically, the construction of the effective Hamiltonian implies the projection of the approximate solutions of the exact non-relativistic electronic Hamiltonian onto a  $N$ -dimensional model space  $S$  containing the information of interest. This formalism ensures that there is a one-to-one correspondence between the eigenvalues of the exact Hamiltonian and those of the effective Hamiltonian, and that the eigenfunctions of the effective Hamiltonian coincide with the projection of the (as accurate as possible) approximate solutions of the exact Hamiltonian into the model space. The validity and robustness of this theory when applied to molecular magnetism and highly correlated materials has been recently

reviewed by Malrieu et al.<sup>32</sup> (see also Chapter 9 in Ref. 5). Let  $E_m$  and  $\varphi_m$  be the energy and the corresponding eigenfunction of state  $m$ . Then:

$$\hat{H}\varphi_m = E_m\varphi_m \quad (9)$$

We can then define a projector targeting the model space  $S$  as:

$$\hat{P}_S = \sum_{I \in S}^N |I\rangle\langle I| \quad (10)$$

where  $\{|I\rangle\}$  is an orthonormal basis of this model space. In our case, it is constituted by the determinants corresponding to the localized valence bond forms that span the Heisenberg Hamiltonian  $|\alpha\alpha\beta\rangle$ ,  $|\alpha\beta\alpha\rangle$  and  $|\beta\alpha\alpha\rangle$  as in Table 1. In practice, this requires a previous orbital localization step. Thus, an Effective Hamiltonian can be defined as in Eq. (11)

$$\hat{H}^{eff}|\varphi_{S,m}\rangle = E_m|\varphi_{S,m}\rangle \quad (11)$$

being:

$$|\varphi_{S,m}\rangle = \hat{P}_S|\varphi_m\rangle \quad (12)$$

The basis set in which  $\varphi_{S,m}$  is written is not necessarily orthonormal. To overcome this we make use of the orthonormalized projections proposed by des Cloizeaux:

$$|\bar{\varphi}_{S,m}\rangle = S_{m,q}^{-1/2}|\varphi_{S,m}\rangle \quad (13)$$

where  $S_{m,q}$  are the elements of the overlap matrix between the states as in Eq. (14)

$$S_{m,q} = \langle\varphi_{S,m}|\varphi_{S,q}\rangle \quad (14)$$

Then the effective Hamiltonian is simply obtained from its spectral decomposition and its matrix representation in the space of neutral determinants is an Eq. (15)

$$H_{I,J}^{eff} = \sum_{m=1}^N \langle I|\bar{\varphi}_{S,m}\rangle E_m \langle\bar{\varphi}_{S,m}|J\rangle \quad (15)$$

The  $H_{I,J}^{eff}$  elements can now be directly compared to the elements of the Heisenberg Hamiltonian; in the present case to the matrix elements in Table 1.

### 3. Systems under study.

Two different three electrons in three centres systems have been investigated in this work. The first one is HAKKEJ homotrimeric Cu(II) complex<sup>33</sup> which constitutes a very convenient choice because of the availability of experimental crystalline and magnetic data. Also because this is the system for which an almost constant relationship between dominant magnetic coupling constants was found, independent of the DFT method used.<sup>25</sup> The second molecule investigated is a natural extension of systems studied in previous work<sup>34,35</sup> concerning  $\pi$ -conjugated odd alternant hydrocarbons polyradicals interacting through-bond. These molecules are known as candidates to achieve ferromagnetism in purely organic compounds.<sup>36-38</sup>

It is worth pointing out the different nature of the unpaired electrons in both systems; the former consisting in localized  $d^9$  orbitals in the Cu(II) metal atom, whereas in the latter the unpaired electrons are hosted in carbon  $sp^2$ -type orbitals delocalized over a large  $\pi$ -conjugated system. For none of them there is a symmetry operation relating the magnetic centres, implying that the spectra cannot be simplified. Both systems and the corresponding magnetic coupling constants of interest are depicted in Figure 1.

### 4. Computational details

The effective Hamiltonian for the trinuclear Cu(II) complex has been obtained from the energies and wave functions for the three pure spin states as obtained from Difference Dedicated Configuration Interaction (DDCI)<sup>39</sup> calculations at the experimental structure and using the same basis sets as in previous work.<sup>25</sup> The DDCI calculations use a reference CASSCF<sup>40</sup> wave function containing three electrons in the three magnetic orbitals—CAS(3,3)—corresponding to the three partially occupied 3d orbitals localized in the Cu atoms,

Calculations for the triradical model system in Figure 1 have been carried out using a variety of wave function and DFT based methods. The wave function based calculations employ pure spin states. On the other hand, the DFT based calculations all spin unrestricted and, whenever needed, make use of broken symmetry solutions. Geometry optimization has carried out using the popular B3LYP<sup>41</sup> hybrid functional and the standard 6-311g(d,p)<sup>42,43</sup> and all minima were characterized by frequency calculations for the quartet state. At the located minima, single point calculations were



performed using also the M06-2X hybrid meta-GGA developed by Zhao and Truhlar<sup>44</sup> and the MN12SX<sup>45</sup> functionals. For the wave function based calculations, we used a variety of methods of increasing accuracy. First, in order to compare to DFT-based methods, we start with the single determinantal unrestricted formulation of Hartree-Fock formalism (UHF). Then as in the case of the trinuclear complex, a minimal CAS(3,3) is defined and used to obtain the CASSCF wave function which is subsequently used as a reference to second order perturbation, introduced either variationally, through multi-reference configuration interaction (MRCI) calculations using the DDCI method,<sup>39</sup> or perturbatively through Multi Reference Møller-Pleset (MRMP).<sup>46-49</sup> Note that MRMP is sometimes denoted as MCQDPT for Multiconfigurational Quasi Degenerate Perturbation theory.

The MRMP on top of CASSCF calculations were carried out using the GAMESS13 code<sup>50,51</sup> and DDCI calculations were carried out using the the CASDI<sup>52</sup> code interfaced to the MOLCAS7.8 package<sup>53</sup>. All DFT based calculations have been carried out by means of the Gaussian-09 suite of programs.<sup>54</sup> Finally, it is worth pointing out that the DDCI calculation, which was later used to construct the effective spin Hamiltonian, was performed only for one of the minima found for the triradical, given that there is not a significant change in the magnetic coupling interactions at different minima. Additionally, this calculation was performed on a set of  $2p_z$ -like molecular orbitals previously localized to ensure that the CAS space is written on neutral determinants. The CASSCF wave function is invariant with respect to the unitary transformations within the doubly occupied, active or virtual orbital subspaces. Here a unitary transformation among the active, single occupied, orbitals is used to obtain localized orbitals. This is a necessary step to build the effective Hamiltonian in the appropriate physically meaningful space and also allows for a physical interpretation in terms of valence bond forms. Nevertheless, one has to warn that even if the CASSCF wave function is invariant with respect to localization of the active orbitals, the resulting DDCI wave functions may depend on the method of localization used although one expects that, for well localized orbitals, the effect on the computed effective Hamiltonian will be minor. Note also that, in the case of the trinuclear Cu(II) complex this localization step is not necessary since the magnetic orbitals are naturally localized at each Cu site. In the next section we will show that the two compounds exhibit similar trends and, since no additional localization step is used in the case of the trinuclear

Cu(II) complex, one can safely claim that the influence of the localization method in the organic triradical will be almost negligible.

Due to the larger size of the systems under study, the DDCI calculations have been carried out considering a subset of orbitals either in the occupied and virtual subspaces. The size of the largest DDCI calculations involves ~100 million determinants.

## 5. Results and discussion.

In the case of the trinuclear Cu(II) complex, despite the well-known large dependence of the calculated  $J_{ij}$  values with respect to the density functional used,<sup>25</sup> BS calculations consistently provided a  $J_{23}/J_{12} \sim 0.9$  relationship. Table 2 collects the energy and wavefunction components of DDCI magnetic states projected on the neutral determinants of the CAS(3,3) in localised orbitals in the (1)-(2)-(3) topology. These projected wave functions and energies are then used to construct the effective spin Hamiltonian which is presented in Table 3. A direct comparison of the matrix elements with the expression of the representation of the Heisenberg Hamiltonian shown in Table 1 ( $S_z = 1/2$  sub block) provides all the  $J$  values for the (1)-(2)-(3) topology:  $J_{12} = -2 \cdot (H^{eff})_{2,3} = -196.217 \text{ cm}^{-1}$ ,  $J_{23} = -2 \cdot (H^{eff})_{1,2} = -226.409 \text{ cm}^{-1}$  and  $J_{13} = -2 \cdot (H^{eff})_{1,3} = -1.022 \text{ cm}^{-1}$ . These values are in line with the observed Cu-Cu distances in the molecule. More importantly, these ab initio estimates of the relevant magnetic coupling constants provide  $J_{12}/J_{23} = 0.867$ , which is in good agreement with the corresponding value of 0.90 obtained by means of DFT methods using different hybrid functionals.<sup>25</sup> The apparent discrepancy regarding which coupling constant is larger ( $J_{23}/J_{12} < 1$  in previous work<sup>25</sup> or  $J_{12}/J_{23} < 1$ ) here is simply a matter of notation of the magnetic centres. A word of caution should be raised here regarding the assumption of symmetry used to derive a single magnetic coupling constant from experiment fitting of the magnetic susceptibility vs. T curves which, in any case, correspond to an arbitrarily averaged  $J$  value. The rather large difference between  $J_{12}$  and  $J_{23}$  values predicted from the effective Hamiltonian would imply an unphysical  $J_{13}$  value if this is to be obtained from a more refined fitting including two coupling constants.

Finally, let us turn our attention to the case of the organic triradical. Compared to HAKKEJ, this system presents an additional feature, namely, its intrinsic structural flexibility. Geometry optimization of this molecule at the B3LYP level, provided six

different local minima, lying very close in energy ( $< 1 \text{ kcal/mol}$ ), in line with what was reported for similar diradical molecules.<sup>35</sup> Such conformational richness can be described with the two dihedral angles indicated in Figure 1b. For the different **1-6** local minima, the values for  $\theta_1$  are -18.7, -18.0, -18.2, 17.4, -164.6 and -165.0 and for  $\theta_2$  17.1, -16.4, -16.4, 165.5, -166.5 and 166.7. For each of these conformations, the magnetic coupling constant values were calculated by means of different DFT-based calculations by mapping the energy of the different BS solutions to the diagonal elements of the HDVV in Table 1 and the numerical results are presented in Table 4. Here, the UHF results are included just for completeness; the poor description of the magnetic couplings and their relationships is a clear indication of the need to account for electron correlation effects to reach a qualitatively correct description. Hence, the UHF results will not be further discussed. Regarding the results from DFT methods, it is worth to mention that in this case, the different functionals provide a less disperse set of values for the magnetic coupling constants than in the case of HAKKEJ. In fact, if one compares B3LYP with M06-2X results for HAKKEJ, the predicted  $J_{12}$  and  $J_{23}$  values are more than three times larger for the former functional, while for the triradical at a given geometry, there is no significant difference. Also, in line with previous results,<sup>35</sup> the ground state of this purely organic triradical is not affected by the conformation adopted and the magnetic coupling constants remain practically the same. This is an indication of the robustness of ferromagnetism in odd alternant hydrocarbons. Further inspection reveals an almost constant  $\sim 0.7$  relationship for  $J_{12}/J_{23}$  along the six different minima and the different functionals used, indicating a larger delocalization as compared to the HAKKEJ case. Moving to the results from wave function based methods, Table 5 presents the energy difference values between the spin-adapted states, where similar tendencies as for DFT-based methods can be observed along the different geometries. For the geometry denoted **1**, the effective Hamiltonian for the three lowest energy states has been obtained from the DDCI magnetic states projected on the neutral determinants of the CAS(3,3) constructed with localised  $2p_z$  orbitals on the radical centres in the (1)-(2)-(3) topology. Table 6 presents the resulting energies and wavefunction components, which are later used to construct the effective Hamiltonian. The matrix elements (in  $\text{cm}^{-1}$ ) of the effective Hamiltonian obtained using Eq (15) on this model VB space can therefore be found in Table 7 and comparing to Table 1 allows for a direct estimate of the different coupling constants. Thus, one obtains  $J_{12} = -2 \cdot$

$(H^{eff})_{2,3} = 1471.206 \text{ cm}^{-1}$  (182.41 meV),  $J_{23} = -2 \cdot (H^{eff})_{1,2} = 1758.130 \text{ cm}^{-1}$  (217.98 meV) and  $J_{13} = -2 \cdot (H^{eff})_{1,3} = -9.079 \text{ cm}^{-1}$  (-1.13 meV). Here the apparent inconsistency on which coupling constant is larger ( $J_{23}$  or  $J_{12}$ ) appears again when comparing the results coming from DFT and effective Hamiltonian. As in the case of the HAKKEH, this is assigned to mismatching of the notation used, meaning that centres 1 and 3 in a (1)-(2)-(3) topology were swapped. Otherwise, these values are in line, but approximately twice smaller than those extracted from the DFT calculations using the BS approach (Table 4). Note that, as mentioned above, the magnetic couplings of the organic triradical are less dependent on the exchange-correlation potential. Nevertheless, it is important to point out that these ab initio estimates of the relevant magnetic coupling constants provide a value  $J_{12}/J_{23} = 0.837$  that is somewhat larger than the corresponding value predicted by the hybrid DFT calculations which is of  $\sim 0.70$ . This is likely to be originated from a larger degree of delocalisation present in some BS solutions (the asymmetric  $|\alpha\alpha\beta\rangle$  solution). This effect has a larger effect on the value of  $J_{13}$  which, at the DFT level, is overestimated by almost one order of magnitude. The precise numerical relation between the different magnetic coupling constants in complex magnetic systems is important since the subtle interplay between the dominant and the less intense but more frequent (i.e.: larger number of pairs) couplings is responsible for the magnetic structure and properties of the system.

## 6. Conclusions.

Extracting all relevant two-body magnetic coupling constants in a general three electrons three centers problem cannot be accomplished from the energy spectrum involving spin adapted states. Effective Hamiltonian theory provides a general and elegant way to solve the problem<sup>8</sup> as shown in the present work for two representative systems. However, building ab initio effective Hamiltonians is far from being straightforward as the overall procedure faces some technical difficulties that limits its applicability. First, very accurate wave functions for the relevant states need to be obtained. Second, a proper basis of localized orbitals is required to build the neutral valence bond determinants where to project the information. Finally, a number of mathematical manipulations are required which are difficult to code in a general enough way.

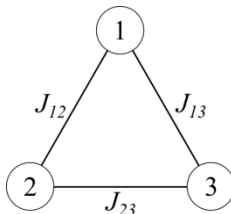
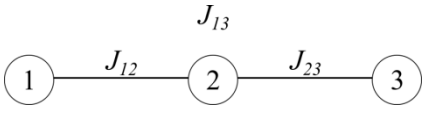
In the present work we also propose an alternative approach based on directly mapping the energy of the BS solutions to the expectation value of the HDDV Hamiltonian. The problem here is that the BS solutions involve necessarily the use of DFT methods with a concomitant dependence of the calculated energies on the exchange-correlation potential. This dependence may be severe as in the case of the HAKKEJ dinuclear complex or mild as for the organic triradical studied in the present work. As a result, assessing the accuracy of the magnetic coupling constants becomes cumbersome. However, the relationship between the dominant magnetic coupling constants appears to be less sensitive to the choice of the exchange-correlation functional, an empirical finding that here is validated from the ab initio effective Hamiltonian formalism. The latter is an important finding since validates this approach and provides compelling evidence that it does not arise from an artifact of the DFT methods. Nevertheless, for the presently examined cases the  $J_{23}/J_{12}$  relationship obtained from effective Hamiltonian and DFT approaches exhibit some variation. This is the case of the organic triradical and the reason is likely to reside on the difficulty of DFT methods to provide a proper and balanced description of spin delocalization in these largely delocalized systems. Yet, the case of radicals in  $\pi$ -conjugated systems provides surely the worst possible scenario.

To conclude, mapping the expectation value of the HDVV Hamiltonian to the energy of the equivalent BS solutions provides an alternative way to study magnetic coupling in organic and inorganic magnetic systems. Note, in passing by that, as previously suggested,<sup>7</sup> this unifies the logic behind the treatment of molecular systems and solids since in the latter, except for the closed shell and high-spin solutions, it is not possible to work with pure spin states and one needs to rely on BS solutions. Last but not least, the fact that the relationship between dominant coupling does not (excessively) depend on the choice of the DFT methods is a general trend validated from effective Hamiltonian theory. In practice one can safely add this relationship to energy differences between pure spin states obtained from post Hartree-Fock methods if the energy spectrum is not enough to determine all relevant magnetic couplings.

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**Scheme 1.** Equilateral and linear arrangement of three electrons in three centres and the resulting simplified energy expressions.

equilateral	linear
	
$J_{12} = J_{23} = J_{13} = J$	$J_{12} = J_{23} = J; J_{13} = 0$
$X = 0$	$X = J$
$E_Q = -\frac{3}{4} \cdot J$	$E_Q = -\frac{1}{2} \cdot J$
$E_{D_1} = E_{D_2} = E_D = \frac{3}{4} \cdot J$	$E_{D_1} = 0; E_{D_2} = J$
$E_Q - E_D = -\frac{3}{2} \cdot J$	$E_Q - E_{D_1} = -\frac{1}{2} \cdot J; E_Q - E_{D_2} = -\frac{3}{2} \cdot J$

**Table 1.** Matrix representation of the HDVV Hamiltonian in the basis set of neutral  $|\alpha\alpha\alpha\rangle$ ,  $|\alpha\alpha\beta\rangle$ ,  $|\alpha\beta\alpha\rangle$  and  $|\beta\alpha\alpha\rangle$  determinants where each spin  $\alpha$  or  $\beta$  is in a different center. The inner rectangle represents the sub block with all determinants having  $S_z = +1/2$ .

$\hat{H}^{HDVV}$	$ \alpha\alpha\alpha\rangle$	$ \alpha\alpha\beta\rangle$	$ \alpha\beta\alpha\rangle$	$ \beta\alpha\alpha\rangle$
$\langle\alpha\alpha\alpha $	$-\frac{1}{4}(J_{12} + J_{23} + J_{13})$	0	0	0
$\langle\alpha\alpha\beta $		$\frac{1}{4}(-J_{12} + J_{23} + J_{13})$	$-\frac{1}{2} \cdot J_{23}$	$-\frac{1}{2} \cdot J_{13}$
$\langle\alpha\beta\alpha $			$\frac{1}{4}(J_{12} + J_{23} - J_{13})$	$-\frac{1}{2} \cdot J_{12}$
$\langle\beta\alpha\alpha $				$\frac{1}{4}(J_{12} - J_{23} + J_{13})$



**Table 2.** Energy of the  $D_1$  and  $D_2$  states relative to that of the quartet state  $Q$  ( $\Delta E$ ) as predicted from the DDCI calculations for the HAKKEJ trinuclear complex, components from the projection of the DDCI wavefunction into the space spanned by the  $|\alpha\alpha\beta\rangle$ ,  $|\alpha\beta\alpha\rangle$  and  $|\beta\alpha\alpha\rangle$  neutral determinants and total contribution of these projections into the CAS ( $\sum_{I \in CAS} c_I^2$ ) and into the neutral components ( $\sum_{I \in N} c_I^2$ ) of the CAS wavefunction, respectively.

	$D_1$	$D_2$	$Q$
$\Delta E(cm^{-1})$	-317.8	-105.9	0.0
$ \alpha\alpha\beta\rangle$	-0.041316	0.811441	-0.574696
$ \alpha\beta\alpha\rangle$	-0.679604	-0.441623	-0.574696
$ \beta\alpha\alpha\rangle$	0.720920	-0.369817	-0.574696
$\sum_{I \in CAS} c_I^2$	0.86010	0.86248	0.86397
$\sum_{I \in N} c_I^2$	0.81888	0.84840	0.86397

**Table 3.** Matrix elements of the effective Hamiltonian of the HAKKEJ trinuclear complex in the  $|\alpha\alpha\beta\rangle$ ,  $|\alpha\beta\alpha\rangle$  and  $|\beta\alpha\alpha\rangle$  basis set as obtained from the spectral decomposition in Eq. (15) using the DDCI wave functions and energies in Table 3.

<i>a)</i>	$\hat{H}^{eff}$	$ \alpha\alpha\beta\rangle$	$ \alpha\beta\alpha\rangle$	$ \beta\alpha\alpha\rangle$
$\langle\alpha\alpha\beta $		-113.734	113.204	0.511
$\langle\alpha\beta\alpha $		113.204	-211.300	98.108
$\langle\beta\alpha\alpha $		0.511	98.108	-98.613

**Table 4.** Magnetic coupling constants of the triradical studied (in meV) as predicted from different DFT based methods at the different minima. The two rightmost columns report the average and standard deviation of the results for each method.

minima		1	2	3	4	5	6	$\mu \pm \sigma$	
								$J_{23}/J_{12}$	$J_{13}/J_{12}$
UHF	$J_{12}$	1782	1774	1768	1758	1758	1758	1.04	-0.05
	$J_{23}$	1860	1862	1854	1864	1868	1870		
	$J_{13}$	-92	-92	-88	-92	-92	-92		
B3LYP	$J_{12}$	428	426	422	418	422	422	0.70 $\pm$ 0.01	-0.025 $\pm$ 0.001
	$J_{23}$	298	296	294	302	298	294		
	$J_{13}$	-10.0	-10.0	-10.6	-10.8	-10.8	-10.8		
M062X	$J_{12}$	406	404	402	398	400	400	0.70 $\pm$ 0.01	-0.025 $\pm$ 0.001
	$J_{23}$	282	280	278	286	284	280		
	$J_{13}$	-9.2	-9.2	-10.2	-10.2	-10.4	-10.4		
MN12SX	$J_{12}$	372	370	366	364	368	366	0.69 $\pm$ 0.01	-0.021 $\pm$ 0.001
	$J_{23}$	258	254	252	260	254	250		
	$J_{13}$	-7.2	-7.0	-7.8	-7.8	-7.8	-8		

**Table 5.** Energy differences (meV) between the quartet ground state and excited doublet states ( $\Delta_{Q-D_1}$  and  $\Delta_{Q-D_2}$ ) calculated by different wave function based methods. Here, SS and SA stand for state specific and state average CASSCF calculations, respectively.

Method		minima						
(meV)	orbitals		<b>1</b>	<b>2</b>	<b>3</b>	<b>4</b>	<b>5</b>	<b>6</b>
CAS (3,3) SCF	SS	$\Delta_{Q-D_1}$	-93.0	-92.5	-92.0	-93.9	-93.1	-90.3
		$\Delta_{Q-D_2}$	-242	-242	-239	-242	-242	-238
	SA	$\Delta_{Q-D_1}$	-104	-104	-103	-104	-104	-102
		$\Delta_{Q-D_2}$	-250	-248	-246	-248	-248	-244
MC- QDPT	SS	$\Delta_{Q-D_1}$	-202	-201	-200	-205	-202	-196
		$\Delta_{Q-D_2}$	-549	-546	-539	-544	-544	-537
	SA	$\Delta_{Q-D_1}$	-337	-334	-333		-333	-327
		$\Delta_{Q-D_2}$	-462	-459	-454		-459	-454
CAS(3,3) CI	Orb quartet	$\Delta_{Q-D_1}$	-109					
		$\Delta_{Q-D_2}$	-341					
CAS(3,3) +DDCI	Orb quartet	$\Delta_{Q-D_1}$	-98					
		$\Delta_{Q-D_2}$	-301					

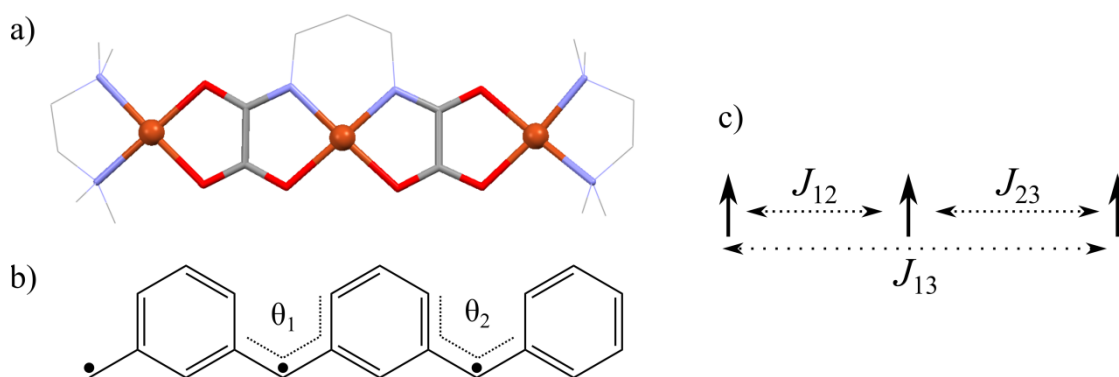
**Table 6.** Energy of the  $D_1$  and  $D_2$  states relative to that of the quartet state  $Q$  ( $\Delta E$ ) as predicted from the DDCI calculations for the minima **1** of the organic triradical in Figure 1b. Components from the projection of the DDCI wavefunction into the space spanned by the  $|\alpha\alpha\beta\rangle$ ,  $|\alpha\beta\alpha\rangle$  and  $|\beta\alpha\alpha\rangle$  neutral determinants and total contribution of these projections into the CAS ( $\sum_{I \in CAS} c_I^2$ ) and into the space spanning the neutral components ( $\sum_{I \in N} c_I^2$ ) of the CAS wavefunction, respectively, are also reported.

	$D_1$	$D_2$	$Q$
$\Delta E(cm^{-1})$	2431.5	788.8	0.0
$ \alpha\alpha\beta\rangle$	-0.6508127	-0.4457024	0.5580807
$ \alpha\beta\alpha\rangle$	0.0617992	-0.7876415	-0.558082
$ \beta\alpha\alpha\rangle$	0.7125919	-0.341919	0.5580924
$\sum_{I \in CAS} c_I^2$	0.93531	0.93638	0.93438
$\sum_{I \in N} c_I^2$	0.93516	0.93594	0.93437

**Table 7.** Matrix elements of the effective Hamiltonian of the HAKKEJ trinuclear complex in the  $|\alpha\alpha\beta\rangle$ ,  $|\alpha\beta\alpha\rangle$  and  $|\beta\alpha\alpha\rangle$  basis set as obtained from the spectral decomposition in Eq. (15) using the DDCI wave functions and energies in Table 3.

<i>a)</i>	$\hat{H}^{eff}$	$ \alpha\alpha\beta\rangle$	$ \alpha\beta\alpha\rangle$	$ \beta\alpha\alpha\rangle$
$\langle\alpha\alpha\beta $		874.528	-879.065	4.539
$\langle\alpha\beta\alpha $		-879.065	1614.680	-735.603
$\langle\beta\alpha\alpha $		4.539	-735.603	731.050

**Figure 1.** Schematic representation of the systems studied. Hydrogen atoms are not displayed. a) Trinuclear Cu(II) HAKKEJ. Blue, red and grey sticks stand for nitrogen, oxygen and carbon atoms respectively. Orange balls represent Cu(II) atoms. b) Organic triradical. The two dihedral angles  $\theta_1$  and  $\theta_2$  indicated are the structural parameters characterizing the different local minima found. c) Definition of the two body magnetic coupling constants relevant for the two systems.



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## Graphic for TOC

