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# Consistent evaluation of magnetic exchange couplings in multicentre compounds in KS-DFT: the recomposition method

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**Abstract**

The use of broken symmetry calculations in Kohn-Sham density functional theory has offered an affordable route to study magnetic exchange couplings in transition metal-based compounds. However, computing this property in compounds exhibiting several couplings is still challenging and especially due to the difficulties to overcome the well-known problem of spin contamination. Here, we present a new and general method to compute magnetic exchange couplings in systems featuring several spin sites. To provide a consistent spin decontamination of $J$ values, our strategy exploits the decomposition method of the magnetic exchange coupling proposed by Coulaud *et al.* and generalises our previous work on diradical compounds where the overall magnetic exchange coupling is defined as the sum of its three main and properly extracted physical contributions (the direct exchange, the kinetic exchange and the spin polarisation). In this aim, the generalised extraction of all contributions is presented to systems with multiple spin sites bearing one unpaired electron. This is done by proposing

a new paradigm to treat the kinetic exchange contribution which proceeds through *mono*relaxations of the magnetic orbitals. This method, so-called the *recomposition* method, is applied to a compound featuring three Cu(II) ions with a linear arrangement and to a recently synthesised complex containing a $Cu_4O_4$ cubane unit presenting an unusual magnetic behaviour.

# 1 Introduction

Magnetic exchange coupling $J$ is one of the most fundamental magnetic interactions occurring in materials featuring locally unpaired electrons.[1] In the Heisenberg-Dirac-van Vleck (HDvV) Hamiltonian, $J_{IJ}$ expresses the magnitude of the coupling between two spin sites $I$ and $J$, defined by their local spin operators $\hat{\vec{S}}_I$ and $\hat{\vec{S}}_J$, respectively:

$$\hat{H}^{\mathrm{HDvV}} = \sum_{I,J} -2J_{IJ}\hat{\vec{S}}_I \cdot \hat{\vec{S}}_J \tag{1}$$

Whilst its origin comes from the quantum nature of electrons, this interaction induces the macroscopic phenomena called ferromagnetism, by favouring a parallel alignment of the unpaired electron spin momenta and anti-ferromagnetism, by favouring their anti-parallel alignment. At the molecular level, using the HDvV Hamiltonian of Eq. (1), ferromagnetism (respectively anti-ferromagnetism) translates to positive (respectively negative) $J$. Being able to control molecular properties for which $J$ is the key interaction is of strong interest, for instance for designing molecular-based magnets.[2] Therefore, its determination is essential for insights on the behaviour of magnetic compounds, either from the experimental[3–5] or theoretical point of view.[6–21] For the latter, the determination of $J$ mainly proceeds through energy differences between high and low spin states.

Wave-function-based methods are the reference approaches to compute magnetic properties due to their ability to properly take into account the multi-configurational character of the wave-function of low-spin states. Even though methods such as Difference Dedi-

cated Configuration Interaction (DDCI)[22] selects only the relevant electronic configurations to compute vertical energy differences between low and high spin states, in most cases its computational cost is prohibitive for real life applications. Despite this limitation, such models provide valuable knowledge in the physics of the magnetic exchange coupling, especially in the simplest case of two unpaired electrons in two magnetic centers, which has been deeply investigated either analytically by means of Quasi Degenerate Perturbation Theory (QDPT)[18,23–25] or numerically (see reference 18 for an extensive review). However, the increase in the number of unpaired electrons and/or magnetic centres makes the definition of the effective Hamiltonian a strenuous task.[18,26]

Density Functional Theory (DFT) in its Kohn-Sham (KS) formulation offers the possibility to compute magnetic exchange couplings by means of the Broken-Symmetry (BS) approach.[7,27–35] $J$ is calculated as the energy difference between the high spin state and a fictitious state in which the spin symmetry of the two unpaired electrons, rooted in their fermionic nature, is broken. Whilst some alternatives have been proposed such as the spin-flip time-dependent DFT (SF-TDDFT),[36–38] the use of non-collinear formalism,[39,40] constrained DFT,[41,42] SF-Constricted DFT,[43–45] the fractional occupation-based method restricted-ensemble KS (REKS)[46–49] or using multiconfigurational pair-DFT (MC-PDFT),[50] the BS approach has been widely used in the last three decades thanks to its ability to qualitatively or semi-quantitatively determine $J$ at a reasonable computational cost.[16,18,51] However, these successful applications shall not hide the potential issues of the BS-DFT $J$ determination. These include the strong dependence of the $J$ magnitude with the choice of the DFT exchange-correlation functional and its investigation has been widely reported in the literature.[52–59] Whilst hybrid-generalized gradient approximation (hGGA) appears as the preferred family of functionals,[59] the amount of Hartree-Fock exchange stays a key quantity.[60] Another important question regards the spin decontamination of $J$, since the BS determinant is not an eigenfunction of the $\hat{S}^2$ operator, i.e. a pure spin state. Accordingly, the energy difference in the $J$ expression must be *spin decontaminated*. Several spin decon-

tamination schemes have been proposed, the Yamaguchi formula, based on the determination of $\hat{S}^2$ expectation values for both the high-spin (HS) and the broken-symmetry states, being probably the most common one,

$$J = \frac{E_{\mathrm{BS}} - E_{\mathrm{HS}}}{\langle \hat{S}^2 \rangle_{\mathrm{HS}} - \langle \hat{S}^2 \rangle_{\mathrm{BS}}} \tag{2}$$

Despite its great interest, the use of the Yamaguchi formula cannot be considered as fully satisfying since it fails to correctly treat the spin polarisation effects, i.e the different polarisation of the core (non-magnetic) orbitals in the HS and BS determinants.[61] Indeed, this formula is based on the idea that the BS solution may be expressed as the linear combination of the singlet and the triplet states, illustrated by $\langle \hat{S}^2 \rangle$ between 0 and 1 depending on this mixture. However, the polarisation of the core orbitals introduces contaminations from higher spin states which may considerably increase $\langle \hat{S}^2 \rangle$ of the triplet state or on the BS determinant with for instance values greater than 1. Hence, $\langle \hat{S}^2 \rangle$ differences at the denominator can lead to an artificial over- or underestimation, having important consequences on the determination of $J$ or the singlet-triplet gaps as for instance in diradical organic molecules presenting strong polarisation of the core orbitals.[62,63]

Magnetic exchange couplings play a critical role on the magnetic properties of multicentre compounds such as polymetallic clusters, which are of great interest in molecular magnetism. However, dealing with more than two magnetic centres through the BS approach, where the Yamaguchi formula is no longer valid,[64] presents a challenging problem due to the difficult treatment of the spin contamination. The most common strategy resorts to neglecting the spin contamination and such an approach takes place in the Ising Hamiltonian. In computing the HS state and a set of properly chosen BS determinants, of which both correspond to Ising solutions, one may define a set of energy differences to map the different magnetic interactions of the system. However, in addition to neglecting the spin contamination which may be critical, it is worth noting that for systems featuring more than three magnetic

centres, it exists more BS solutions than couplings. Hence, it results in an overestimated set of equations where the coupling values may depend on the choice of the determinants.[42,65] From our knowledge, the main attempt to spin decontaminate BS calculations has been proposed by Shoji *et al.*[64] and more recently used in the context of the Extended-BS framework.[66] This strategy may be seen as a direct generalisation of the Yamaguchi formula in approximating $\langle \hat{S}^2 \rangle$ through its local operators. One may expect from this strategy to suffer from the same problem as for 2-centre systems, i.e. when compounds exhibiting strong spin contamination are considered. Furthermore, experimental determination of couplings in these compounds proceeds through a fitting over an unique magnetic susceptibility measurement of which several sets of couplings may be determined, leading to controversial values which often differ from the theoretical evaluation.[67–69] Hence, the possibility of proposing a method more affordable than WFT-based approaches while overcoming the current limitations of DFT in the computation of magnetic couplings in multicentre systems is particularly appealing.

Firstly defined in wave-function theory by means of QDPT,[23] the magnetic exchange coupling may be interpreted as the competition between three contributions, i) the ferromagnetic $J_0$ contribution, corresponding to the direct exchange between the magnetic centres $I$ and $J$, ii) the anti-ferromagnetic kinetic exchange contribution $\Delta J_{\mathrm{KE}}$ due to the relaxation of the HS magnetic orbitals in the BS determinant and iii) the previously presented spin polarisation contribution $\Delta J_{\mathrm{SP}}$, caused by the differential response of the non-magnetic orbitals to the different fields created by the unpaired electrons in the HS and BS states. The extraction of these contributions has been made accessible by the work of Coulaud *et al.*[70,71] in the case of systems with two magnetic centres bearing one unpaired electron through successive relaxations of the orbitals involved in the underlying mechanisms. This method provides a deep analysis of the magnetic exchange coupling values computed by the BS approach, being successfully used to rationalise magnetic interactions in dinuclear copper complexes,[72] to parametrise model Hamiltonians of a quantum spin liquid[73] or to analyse the symmetry breaking in disjoint diradical compounds.[74] More recently, some of the present

authors showed how this approach may be beneficial to compute $J$. Indeed, in evaluating $J$ as the summation of three properly spin decontaminated contributions, we proposed a more physical estimation of this quantity, preventing the over- or underestimation of the coupling due to the incorrect treatment of the spin polarisation through the Yamaguchi formula.[63]

The present paper proposes a new method for computing magnetic exchange couplings in multicentre complexes through a proper evaluation of their three main contributions. Whilst the direct exchange contribution does not require a special spin decontamination treatment, the kinetic exchange contribution is treated by considering the delocalisation between pairs of magnetic centres only, taking fully advantage of the selective relaxation of the orbitals. Its evaluation is done by extracting the $t$ and $U$ Hubbard Hamiltonian parameters, overcoming the problem of spin decontaminating an effective kinetic exchange contribution. The spin polarisation effects are treated by generalising the recent proposition of some of the present authors.[62] The couplings are defined as the sum of these three properly extracted contributions and may be used to dressed an effective CI matrix, generalising our previous works so-called *DFT-dressed CI*.[63,75] This paper is organised as follows. In section 2, we present the extension of the decomposition and the *recomposition* of magnetic exchange couplings in multicentre complexes featuring one unpaired electron per magnetic centre. For the sake of consistency, Appendix 1 recalls the basic features of the physics of the magnetic exchange coupling in the simplest case of a system with two electrons in two magnetic centres as well as the decomposition of this coupling in the BS approach. Section 3 presents the computational details and the systems studied in this work. This work focuses on complexes with Cu(II) metal ions and then presenting only one unpaired electron per magnetic centre, due to their $d^9$ configuration. Section 4 illustrates the recomposition method using to a simple linear 3-centre system. It is followed by the study of a recently synthesised cubane core tetranuclear Cu(II) complex exhibiting unusual magnetic properties.

# 2 Extraction of magnetic exchange couplings in multi-centre systems

Starting from the HDvV Hamiltonian presented in Equation (1), let us consider a multicentre magnetically coupled system featuring $n$ spin sites, labelled $A$, $B$, $C$, ..., $N$, all of them bearing one unpaired electron for a maximum number of $n(n-1)/2$ couplings $J_{IJ}$. Throughout this work, upper-case letters $A$, $B$, ... are used to refer to magnetic centres, of which are associated magnetic orbitals in lower-case letters $a$, $b$, ..., respectively. Furthermore, $i$, $j$,... correspond to core (non-magnetic) orbitals while $r$, $s$,... to virtual orbitals. Finally, the determinants are defined using the notation $\Phi_{ABC..N,\mathrm{RO}}$ where the first part of the subscript before the comma gives the spin distribution over the magnetic centres and the second the formalism used.

## 2.1 Direct Exchange

The starting point of the method is the computation of the HS state in the Restricted Open-shell (RO) formalism with a spin multiplicity equals to $(n+1)$ (for the $n$ sites with one unpaired electron). This determinant defines a set of $n$ Singly Occupied Molecular Orbitals (SOMOs) as well as a set of $N_c$ unpolarised core (non-magnetic) orbitals $i$. Localising the $n$ SOMOs, the HS,RO determinant is expressed as,

$$\Phi_{\mathrm{HS,RO}} = \Phi_{ABC...N,\mathrm{RO}} = |\prod_{i}^{N_c} i\bar{i}abc\ldots n| \tag{3}$$

where $a, b, c, \ldots, n$ correspond to the localised orbitals on the sites $A, B, C, \ldots N$, respectively. In order to determine the direct exchange contribution to the $n(n-1)/2$ couplings, $n(n-1)/2$ BS determinants need to be constructed by flipping the spin of some electrons in order to make the required $n(n-1)/2$ energy differences with the HS state. This may be done in different ways and may be adapted regarding the symmetry and the topology of the system.

For instance, flipping the electron spin of one site allows one to generate $n$ BS determinants with a multiplicity of $(n-1)$, such as,

$$\Phi_{\bar{A}BC\ldots N,\mathrm{NO}} = |\prod_{i}^{N_c} i\bar{i}\bar{a}bc\ldots n| \tag{4}$$

$$\Phi_{A\bar{B}C\ldots N,\mathrm{NO}} = |\prod_{i}^{N_c} i\bar{i}a\bar{b}c\ldots n| \tag{5}$$

$$\Phi_{AB\bar{C}\ldots N,\mathrm{NO}} = |\prod_{i}^{N_c} i\bar{i}ab\bar{c}\ldots n| \tag{6}$$

$$\vdots$$

and to generate $n$ energy differences between these determinants and the HS,RO,

$$E[\Phi_{\bar{A}BC\ldots N,\mathrm{NO}}] - E[\Phi_{ABC\ldots N,\mathrm{RO}}] = \sum_{K=1,K\neq A}^{n} J_0^{AK} \tag{7}$$

$$E[\Phi_{A\bar{B}C\ldots N,\mathrm{NO}}] - E[\Phi_{ABC\ldots N,\mathrm{RO}}] = \sum_{K=1,K\neq B}^{n} J_0^{BK} \tag{8}$$

$$E[\Phi_{AB\bar{C}\ldots N,\mathrm{NO}}] - E[\Phi_{ABC\ldots N,\mathrm{RO}}] = \sum_{K=1,K\neq C}^{n} J_0^{CK} \tag{9}$$

$$\vdots$$

There are now $n(n-3)/2$ BS determinants left to generate and this may be done by flipping the electron spin of two centres to create the determinants of ($n$-3) spin multiplicity,

$$|\Phi_{\bar{A}\bar{B}C\ldots N,\mathrm{NO}}| = |\prod_{i}^{N_c} i\bar{i}\bar{a}\bar{b}c\ldots n| \tag{10}$$

$$|\Phi_{\bar{A}B\bar{C}\ldots N,\mathrm{NO}}| = |\prod_{i}^{N_c} i\bar{i}\bar{a}b\bar{c}\ldots n| \tag{11}$$

$$|\Phi_{A\bar{B}\bar{C}\ldots N,\mathrm{NO}}| = |\prod_{i}^{N_c} i\bar{i}a\bar{b}\bar{c}\ldots n| \tag{12}$$

$$\vdots$$

providing the following energy differences,

$$E[\Phi_{\bar{A}\bar{B}C\ldots N,\mathrm{NO}}] - E[\Phi_{ABC\ldots N,\mathrm{RO}}] = \sum_{K=1,K\neq A,B}^{n} J_0^{AK} + J_0^{BK} \tag{13}$$

$$E[\Phi_{\bar{A}B\bar{C}\ldots N,\mathrm{NO}}] - E[\Phi_{ABC\ldots N,\mathrm{RO}}] = \sum_{K=1,K\neq A,C}^{n} J_0^{AK} + J_0^{CK} \tag{14}$$

$$E[\Phi_{A\bar{B}\bar{C}\ldots N,\mathrm{NO}}] - E[\Phi_{ABC\ldots N,\mathrm{RO}}] = \sum_{K=1,K\neq B,C}^{n} J_0^{BK} + J_0^{CK} \tag{15}$$

$$\vdots$$

This strategy provides a system of linear equations to solve for extracting all direct exchange contributions. It is worth noting that the direct exchange contribution corresponds to the exchange integral between two magnetic orbitals and then the extraction should not depend on the determinants chosen to define the system of linear equations.

## 2.2 Kinetic Exchange

The kinetic exchange contribution is the main challenge when multicentre systems are considered. Indeed, this contribution may be seen as the entry of ionic forms in the wave-function and results in complicated spin contamination; the reader may refer to the Appendix for further discussions. Whilst the Yamaguchi formula is a valuable tool for systems with two magnetic centres, its use is no longer possible with several sites.[64] Indeed, this formula is based on the fact that with two sites the HDvV Hamiltonian reduces to,

$$2SJ = E(S-1) - E(S) \tag{16}$$

where $S$ is the spin quantum number of the HS state. Except for very highly symmetric situations, this is no longer valid with more than two sites and the energy difference between two spin states would correspond to a sum of several couplings. Then, a rigorous extraction of an effective kinetic exchange contributions appears a tedious task. To overcome this problem,

one may rely on the use of the $t$ and $U$ Hubbard Hamiltonian parameters, corresponding to the hopping integral and the on-site repulsion energy, respectively. They provide a thinner description of the kinetic exchange contribution, of which a discussion may be found in the Appendix. However, except for highly symmetric situations, two sets of $U$ and $t$ parameters must be extracted since, even in the case of two electrons in two magnetic centres,

$$E_{a\bar{a}} - E_{a\bar{b}} \neq E_{b\bar{b}} - E_{a\bar{b}} \tag{17}$$

and,

$$\langle a\bar{a}|\hat{H}|a\bar{b}\rangle \neq \langle b\bar{b}|\hat{H}|a\bar{b}\rangle \tag{18}$$

and then at least four parameters should be extracted for each pair. In this aim, one may use the possibility of decomposition offered by the selective relaxation of orbitals a step further by relaxing a single magnetic orbital $a$, allowing it to mix with a corresponding virtual magnetic orbital $b$ such as Eq. 84, whilst the occupied orbital $b$ remains frozen. This allows one to define a BS determinant as,

$$|\Phi_{A'\bar{B}C\ldots N,\mathrm{FC}}| = |\prod_{i}^{N_c} i\bar{i}a'\bar{b}c\ldots n| \tag{19}$$

$$= |\prod_{i}^{N_c} i\bar{i}a\bar{b}c\ldots n|\cos\theta + |\prod_{i}^{N_c} i\bar{i}b\bar{b}c\ldots n|\sin\theta \tag{20}$$

of which the energy may be expressed as,

$$E[\Phi_{A'\bar{B}C\ldots N,\mathrm{FC}}] = E[\Phi_{A\bar{B}C\ldots N,\mathrm{NO}}]\cos^2\theta + E[\Phi_{B\bar{B}C\ldots N,\mathrm{NO}}]\sin^2\theta + 2\langle\Phi_{A\bar{B}C\ldots N,\mathrm{NO}}|\hat{H}|\Phi_{B\bar{B}C\ldots N,\mathrm{NO}}\rangle\cos\theta\sin\theta \tag{21}$$

$$= E[\Phi_{A\bar{B}C\ldots N,\mathrm{NO}}] + \big(E[\Phi_{B\bar{B}C\ldots N,\mathrm{NO}}] - E[\Phi_{A\bar{B}C\ldots N,\mathrm{NO}}]\big)\sin^2\theta \tag{22}$$

$$+ 2\langle\Phi_{A\bar{B}C\ldots N,\mathrm{NO}}|\hat{H}|\Phi_{B\bar{B}C\ldots N,\mathrm{NO}}\rangle\cos\theta\sin\theta$$

The second term of Eq. 22 is homogenous to the $U$ Hubbard Hamiltonian parameter whilst the last term to the $t$ hopping integral. Using the energies and $\langle \hat{S}^2 \rangle$ of the FC and NO BS determinants, both parameters may be extracted as,

$$E[\Phi_{B\bar{B}C\ldots N,\mathrm{NO}}] - E[\Phi_{A\bar{B}C\ldots N,\mathrm{NO}}] = \left(E[\Phi_{A'\bar{B}C\ldots N,\mathrm{FC}}] - E[\Phi_{A\bar{B}C\ldots N,\mathrm{NO}}]\right) \frac{2\alpha - 1}{\alpha - 1} \tag{23}$$

$$\langle \Phi_{A\bar{B}C\ldots N,\mathrm{NO}} | \hat{H} | \Phi_{B\bar{B}C\ldots N,\mathrm{NO}} \rangle = \left(E[\Phi_{A'\bar{B}C\ldots N,\mathrm{FC}}] - E[\Phi_{A\bar{B}C\ldots N,\mathrm{NO}}]\right) \sqrt{\frac{\alpha}{1-\alpha}} \tag{24}$$

with

$$\alpha = \frac{\langle \hat{S}^2 \rangle_{A'\bar{B}C\ldots N,\mathrm{FC}} - \langle \hat{S}^2 \rangle_{B\bar{B}C\ldots N,\mathrm{NO}}}{\langle \hat{S}^2 \rangle_{A\bar{B}C\ldots N,\mathrm{NO}} - \langle \hat{S}^2 \rangle_{B\bar{B}C\ldots N,\mathrm{NO}}} \tag{25}$$

These extractions are valid as long as only the relaxation of one orbital is considered, and the three equations may be expressed in a more general form as,

$$U = \left(E[\Phi_{FC}] - E[\Phi_{NO}]\right) \frac{2\alpha - 1}{\alpha - 1} \tag{26}$$

$$t = \left(E[\Phi_{FC}] - E[\Phi_{NO}]\right) \sqrt{\frac{\alpha}{1-\alpha}} \tag{27}$$

with

$$\alpha = \frac{\langle \hat{S}^2 \rangle_{FC} - \langle \hat{S}^2 \rangle_{ion}}{\langle \hat{S}^2 \rangle_{NO} - \langle \hat{S}^2 \rangle_{ion}} \tag{28}$$

Despite their generality, few requirements must be mentioned. Two relaxations of a single orbital must be performed to collect the two sets of parameters. It raises the question of the choice of the determinants used since four situations may be imagined; e.g.

i) $\Phi_{A'\bar{B}C\ldots N,\mathrm{FC}}$ with $a' = a\cos\theta + b\sin\theta$,

ii) $\Phi_{A\bar{B}'C\ldots N,\mathrm{FC}}$ with $b' = b\cos\theta + a\sin\theta$,

iii) $\Phi_{\bar{A}'BC\ldots N,\mathrm{FC}}$ with $a' = a\cos\theta + b\sin\theta$ and

iv) $\Phi_{\bar{A}B'C\ldots N,\mathrm{FC}}$ with $b' = b\cos\theta + a\sin\theta$.

This question will be more discussed in section 4.1.2. Finally, an overall kinetic exchange contribution is defined by summing both energetic contribution $t^2/U$ and $t'^2/U'$ associated to a pair of orbitals,

$$\Delta J_{\mathrm{KE}} = -\frac{t^2}{U} - \frac{t'^2}{U'} \tag{29}$$

in the same way as for the two electrons in two centres case (see Eq. (90) in Appendix 1).

## 2.3 Spin polarisation

Corresponding to the different response of the non-magnetic orbitals to the field created by the unpaired electrons in the different spin states, the core polarisation effects are determined through the relaxation of the core orbitals keeping frozen the magnetic orbitals. Before entering in the extraction of this contribution, let us recall some basic features of the spin polarisation contribution in the present context. Starting from the HS,RO determinant,

$$|\Phi_{ABC\ldots N,\mathrm{RO}}| = |\prod_{i}^{N_c} i\bar{i}abc\ldots n| \tag{30}$$

the mean field Fock operator for the core electron is,

$$\hat{F} = \hat{h} + \sum_{i}^{N_c}(2\hat{J}_i - \hat{K}_i) + \hat{J}_a - \hat{K}_a/2 + \hat{J}_b - \hat{K}_b/2 + \hat{J}_c - \hat{K}_c/2 + \cdots + \hat{J}_n - \hat{K}_n/2 \tag{31}$$

where $\hat{h}$ is the mono-electronic operator and $\hat{J}$ and $\hat{K}$ the Coulomb and exchange operators, respectively. Due to the Brillouin's theorem, all elements of the Fock matrix between occupied and virtual orbitals are zero,

$$\langle i|\hat{F}|r\rangle = 0. \tag{32}$$

Let us now define a singly excited determinant obtained by promoting an $\alpha$ electron from the core to the virtual orbital,

$$\hat{a}_r^\dagger \hat{a}_i |\Phi_{ABC\ldots N,\mathrm{RO}}\rangle = |\prod_j^{N_c-1} j\bar{j}r\bar{i}abc\ldots n\rangle \tag{33}$$

or $\beta$ one,

$$\hat{a}_{\bar{r}}^\dagger \hat{a}_{\bar{i}} |\Phi_{ABC\ldots N,\mathrm{RO}}\rangle = |\prod_j^{N_c-1} j\bar{j}i\bar{r}abc\ldots n\rangle \tag{34}$$

with $\hat{a}_\sigma^\dagger$ and $\hat{a}_\sigma$ the creation and annihilation operators, respectively. The interaction between these determinants and the reference wave-function is given by,

$$\langle\Phi_{ABC\ldots N,\mathrm{RO}}|\hat{H}\hat{a}_r^\dagger \hat{a}_i|\Phi_{ABC\ldots N,\mathrm{RO}}\rangle = \langle i| - \hat{K}_a/2 - \hat{K}_b/2 - \hat{K}_c/2 + \cdots - \hat{K}_n/2|r\rangle \tag{35}$$

$$\langle\Phi_{ABC\ldots N,\mathrm{RO}}|\hat{H}\hat{a}_{\bar{r}}^\dagger \hat{a}_{\bar{i}}|\Phi_{ABC\ldots N,\mathrm{RO}}\rangle = \langle i|\hat{K}_a/2 + \hat{K}_b/2 + \hat{K}_c/2 + \cdots + \hat{K}_n/2|r\rangle \tag{36}$$

These interactions result from the fact that, for the $\alpha$ excitation, the exchange operator is $\hat{K}_a + \hat{K}_b + \hat{K}_c + \cdots + \hat{K}_n$ instead of the average field imposed by the RO Fock operator. Similarly, the exchange operator for the $\beta$ excitation becomes zero, making both interactions of the same magnitude but with opposite signs.

These interactions result in an energy stabilisation contained in the spin polarisation of the HS such as,

$${}^{\mathrm{HS}}E_{\mathrm{SP}} = 2\sum_{i,r} \frac{\langle i|\hat{K}_a/2 + \hat{K}_b/2 + \hat{K}_c/2 + \cdots + \hat{K}_n/2|r\rangle^2}{F_{ii} - F_{rr}} \tag{37}$$

with the denominator defined by the Moller-Plesset perturbation theory. This spin polarisation is introduced by the relaxation of core orbitals through the interaction between the HS,RO determinant and the singly excited configurations. In the mean-field approximation, such an effect may be accounted by allowing the relaxation of the core MOs only, i.e. keeping

the magnetic orbitals frozen. Feeling a different exchange field due to the unpaired electrons, $\alpha$ and $\beta$ electrons are described by different spatial parts as allowed by the unrestricted formalism,

$$|\Phi_{ABC\ldots N,\mathrm{FM}}| = |\prod_{i}^{N_c} i'\bar{i}''abc\ldots n| \tag{38}$$

In the basis of the MOs defined by the HS,RO, the new core orbitals may be approximately expressed,

$$i' = i - \sum_{i,r} \frac{\langle i|\hat{K}_a/2 + \hat{K}_b/2 + \hat{K}_c/2 + \cdots + \hat{K}_n/2|r\rangle}{F_{ii} - F_{rr}} r \tag{39}$$

$$i'' = i + \sum_{i,r} \frac{\langle i|\hat{K}_a/2 + \hat{K}_b/2 + \hat{K}_c/2 + \cdots + \hat{K}_n/2|r\rangle}{F_{ii} - F_{rr}} r \tag{40}$$

Therefore, the stabilisation energy due to the relaxation of the core orbitals may be interpreted such as,

$$E[\Phi_{ABC\ldots N,\mathrm{FM}}] - E[\Phi_{ABC\ldots N,\mathrm{RO}}] = 2\sum_{i,r} \frac{\langle i|\hat{K}_a/2 + \hat{K}_b/2 + \hat{K}_c/2 + \cdots + \hat{K}_n/2|r\rangle^2}{F_{ii} - F_{rr}} \tag{41}$$

Let us now define a BS determinant where the electron spin of one site is flipped,

$$|\Phi_{\bar{A}BC\ldots N,\mathrm{NO}}| = |\prod_{i}^{N_c} i\bar{i}\bar{a}bc\ldots n| \tag{42}$$

this determinant being constructed from the orbitals defined by the RO solution, the Fock operator defined in Eqs (31) and (32) is still satisfied. As in the case of the HS, the $\alpha$ and $\beta$ core electrons do not feel the same exchange field due to the unpaired electrons. Therefore, the relaxation of the core orbitals,

$$|\Phi_{\bar{A}BC\ldots N,\mathrm{FM}}| = |\prod_{i}^{N_c} i'\bar{i}''\bar{a}bc\ldots n| \tag{43}$$

leads to a different spatial part for the $\alpha$ and $\beta$ orbitals, which may be approximated as,

$$i' = i - \sum_{i,r} \frac{\langle i| - \hat{K}_a/2 + \hat{K}_b/2 + \hat{K}_c/2 + \cdots + \hat{K}_n/2|r\rangle}{F_{ii} - F_{rr}} r \tag{44}$$

$$i'' = i + \sum_{i,r} \frac{\langle i| - \hat{K}_a/2 + \hat{K}_b/2 + \hat{K}_c/2 + \cdots + \hat{K}_n/2|r\rangle}{F_{ii} - F_{rr}} r \tag{45}$$

Therefore, the stabilisation energy due to the relaxation of the core orbitals may be expressed as,

$$E[\Phi_{\bar{A}BC\ldots N,\mathrm{FM}}] - E[\Phi_{\mathrm{BS,NO}}] = 2\sum_{i,r} \frac{\langle i| - \hat{K}_a/2 + \hat{K}_b/2 + \hat{K}_c/2 + \cdots + \hat{K}_n/2|r\rangle^2}{F_{ii} - F_{rr}} \tag{46}$$

Making the difference between the stabilisation energy in the HS and in the BS allows one to extract the polarisation of all couplings involving $A$,

$$E[\Phi_{\bar{A}BC\ldots N,\mathrm{FM}}] - E[\Phi_{\mathrm{BS,NO}}] - (E[\Phi_{ABC\ldots N,\mathrm{FM}}] - E[\Phi_{ABC\ldots N,\mathrm{RO}}]) \tag{47}$$

$$= \sum_{i,r} \frac{\langle i|\hat{K}_a|r\rangle\langle r|\hat{K}_b + \hat{K}_c + \cdots + \hat{K}_n|i\rangle}{F_{ii} - F_{rr}} \tag{48}$$

$$= \sum_{i,r} \frac{\langle i|\hat{K}_a|r\rangle\langle r|\hat{K}_b|i\rangle}{F_{ii} - F_{rr}} + \sum_{i,r} \frac{\langle i|\hat{K}_a|r\rangle\langle r|\hat{K}_c|i\rangle}{F_{ii} - F_{rr}} + \cdots + \sum_{i,r} \frac{\langle i|\hat{K}_a|r\rangle\langle r|\hat{K}_n|i\rangle}{F_{ii} - F_{rr}} \tag{49}$$

$$= \Delta J_{\mathrm{SP}}^{AB} + \Delta J_{\mathrm{SP}}^{AC} + \cdots + \Delta J_{\mathrm{SP}}^{AN} \tag{50}$$

For finding the $n(n+1)/2$ core polarisation contributions, a strategy similar to the direct exchange contribution may be employed. Therefore, in addition of the HS,FM determinant,

a set of $n$ BS determinants with one spin-flipped magnetic centre may be computed,

$$|\Phi_{\bar{A}BC\ldots N,\mathrm{FM}}| = |\prod_{i}^{N_c} i'\bar{i}''\bar{a}bc\ldots n| \tag{51}$$

$$|\Phi_{A\bar{B}C\ldots N,\mathrm{FM}}| = |\prod_{i}^{N_c} i'\bar{i}''a\bar{b}c\ldots n| \tag{52}$$

$$|\Phi_{AB\bar{C}\ldots N,\mathrm{FM}}| = |\prod_{i}^{N_c} i'\bar{i}''ab\bar{c}\ldots n| \tag{53}$$

$$\vdots$$

allowing us to generate $n$ energy differences between these determinants and the HS,FM,

$$\big(E[\Phi_{\bar{A}BC\ldots N,\mathrm{FM}}] - E[\Phi_{\bar{A}BC\ldots N,\mathrm{NO}}]\big) - (E[\Phi_{ABC\ldots N,\mathrm{FM}}] - E[\Phi_{ABC\ldots N,\mathrm{RO}}]) = \sum_{K=1,K\neq A}^{n} \Delta J_{\mathrm{SP}}^{AK} \tag{54}$$

$$\big(E[\Phi_{A\bar{B}C\ldots N,\mathrm{FM}}] - E[\Phi_{A\bar{B}C\ldots N,\mathrm{NO}}]\big) - (E[\Phi_{ABC\ldots N,\mathrm{FM}}] - E[\Phi_{ABC\ldots N,\mathrm{RO}}]) = \sum_{K=1,K\neq B}^{n} \Delta J_{\mathrm{SP}}^{BK} \tag{55}$$

$$\big(E[\Phi_{AB\bar{C}\ldots N,\mathrm{FM}}] - E[\Phi_{AB\bar{C}\ldots N,\mathrm{NO}}]\big) - (E[\Phi_{ABC\ldots N,\mathrm{FM}}] - E[\Phi_{ABC\ldots N,\mathrm{RO}}]) = \sum_{K=1,K\neq C}^{n} \Delta J_{\mathrm{SP}}^{CK} \tag{56}$$

$$\vdots$$

As for the direct exchange, there are $n(n-3)/2$ BS determinants left to generate which may

be done by flipping the electron spin of two centres and relaxing their core orbitals,

$$|\Phi_{\bar{A}\bar{B}C\ldots N,\mathrm{FM}}| = |\prod_{i}^{N_c} i'\bar{i}''\bar{a}\bar{b}c\ldots n| \tag{57}$$

$$|\Phi_{\bar{A}B\bar{C}\ldots N,\mathrm{FM}}| = |\prod_{i}^{N_c} i'\bar{i}''\bar{a}b\bar{c}\ldots n| \tag{58}$$

$$|\Phi_{A\bar{B}\bar{C}\ldots N,\mathrm{FM}}| = |\prod_{i}^{N_c} i'\bar{i}''a\bar{b}\bar{c}\ldots n| \tag{59}$$

$$\vdots$$

providing the following energy differences,

$$\big(E[\Phi_{\bar{A}\bar{B}C\ldots N,\mathrm{FM}}] - E[\Phi_{\bar{A}\bar{B}C\ldots N,\mathrm{NO}}]\big) - (E[\Phi_{ABC\ldots N,\mathrm{FM}}] - E[\Phi_{ABC\ldots N,\mathrm{RO}}]) = \sum_{K=1,K\neq A,B}^{n} \Delta J_{\mathrm{SP}}^{AK} + \Delta J_{\mathrm{SP}}^{BK} \tag{60}$$

$$\big(E[\Phi_{\bar{A}B\bar{C}\ldots N,\mathrm{FM}}] - E[\Phi_{\bar{A}B\bar{C}\ldots N,\mathrm{NO}}]\big) - (E[\Phi_{ABC\ldots N,\mathrm{FM}}] - E[\Phi_{ABC\ldots N,\mathrm{RO}}]) = \sum_{K=1,K\neq A,C}^{n} \Delta J_{\mathrm{SP}}^{AK} + \Delta J_{\mathrm{SP}}^{CK} \tag{61}$$

$$\big(E[\Phi_{A\bar{B}\bar{C}\ldots N,\mathrm{FM}}] - E[\Phi_{A\bar{B}\bar{C}\ldots N,\mathrm{NO}}]\big) - (E[\Phi_{ABC\ldots N,\mathrm{FM}}] - E[\Phi_{ABC\ldots N,\mathrm{RO}}]) = \sum_{K=1,K\neq B,C}^{n} \Delta J_{\mathrm{SP}}^{BK} + \Delta J_{\mathrm{SP}}^{CK} \tag{62}$$

$$\vdots$$

It results in a similar linear set of equations to solve. Finally, the coupling between two centres $I$ and $J$ may be evaluated as,

$$J^{IJ} = J_0^{IJ} + \Delta J_{\mathrm{KE}}^{IJ} + \Delta J_{\mathrm{SP}}^{IJ} \tag{63}$$

The fictitious system with all magnetic centres interacting with each other is the most complicated situation which may be treated by the present method. Obviously, the number of

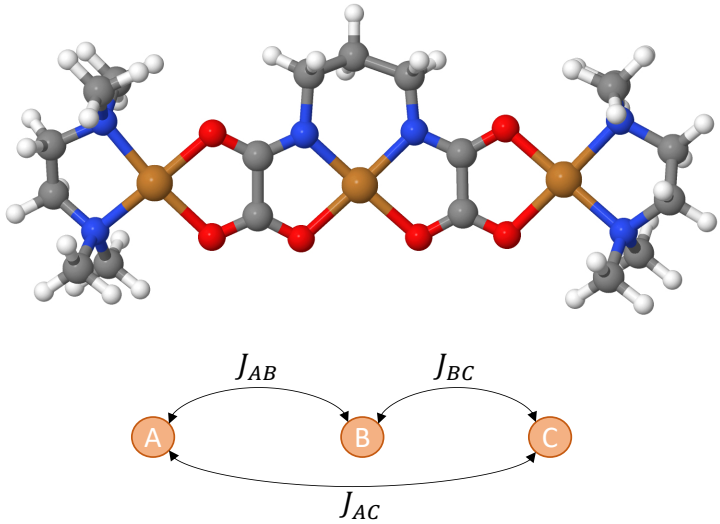


Figure 1: Molecular structure of HAKKEJ (top) and schematic representation of the three magnetic exchange couplings (bottom). Orange = copper, blue = nitrogen, red = oxygen, grey = carbon, white = hydrogen.

determinants to compute may be drastically reduced according to the physics of the system.

# 3 Computational Details

For the sake of simplicity, the present method is firstly described in the simplest multicentre case of 3-site systems. Previously studied by Reta *et al.* by means of the BS approach,[76,77] the compound, labelled HAKKEJ into the Cambridge Structural Database[78] (CSD) appears as a textbook case for our purpose. Presented in Fig. 4, it consists in a linear arrangement of three Cu(II) ions bridged by oxomato ligands and the chain ends with an $N, N, N', N'$-tetrametyletylenedimine at both ends.[79] Experimental magnetic exchange coupling has been determined from magnetic susceptibility measurements and a fit over the HDvV Hamiltonian, $\hat{H} = -2J(\hat{\vec{S}}_A \cdot \hat{\vec{S}}_B + \hat{\vec{S}}_B \cdot \hat{\vec{S}}_C)$, hence neglecting the long-distance $J_{AC}$ coupling, resulting in a coupling $J = -190$ cm$^{-1}$.

In addition to propose an overall estimation of couplings fully spin decontaminated, the recomposition method stays a powerful tool to get insights into the physics of these couplings, thanks to the straightforward extraction of its different contributions. Cu(II) cubane

complexes may exhibit very different magnetic properties due to their dependence on slight variations in the structure of the $Cu_4O_4$ unit. This leads to different classifications depending to the Cu-O bond lengths from Mergehenn and Haase[80] or the Cu-Cu distance from Ruiz *et al.*.[67,81] From the latter, three classes are defined, depending on the number of short + long bond lengths: 2+4, 4+2 and 6+0, of which a strength of coupling is associated. Recently, Mehrani *et al.* synthesised a new $[\{Cu(OH)(phen)\}_4]\cdot(ClO_4)_4$ exhibiting an exotic 1+1+4 magnetic pattern and presented Fig 2.[82] Labelled BUJRUW in CSD, magnetic couplings have been fitted over the experimental magnetic susceptibility measurement using the following model Hamiltonian,

$$\hat{H} = -2J_1\hat{\vec{S}}_A \cdot \hat{\vec{S}}_B - 2J_2\hat{\vec{S}}_C \cdot \hat{\vec{S}}_D - 2J_3\left(\hat{\vec{S}}_A \cdot \hat{\vec{S}}_C + \hat{\vec{S}}_A \cdot \hat{\vec{S}}_D + \hat{\vec{S}}_B \cdot \hat{\vec{S}}_C + \hat{\vec{S}}_B \cdot \hat{\vec{S}}_D\right) \tag{64}$$

The best fit results in two antiferromagnetic couplings $J_1 = -28$ cm$^{-1}$ and $J_3 = -15$ cm$^{-1}$, and a stronger ferromagnetic coupling $J_2 = 72$ cm$^{-1}$. However, this fit has been obtained using a Landé g-factor of 1.93, while expected greater than 2 for Cu(II).[82] In addition, whilst the magnetic properties of the compound may be understood through a structural analysis of the $Cu_4O_4$ unit, the crystallographic structure exhibits four counterions near the molecule. Indeed, an intriguing perchlorate ion exists on top of the magnetically-coupled $C$ and $D$ centres ($J_2$), with both distances between each copper and two oxygen atoms of the ion are at about 2.6 Å. In addition, three other $ClO_4^-$ stand at 2.1 Å of some of the hydroxo group of the $Cu_4O_4$ unit, of which the influence may be questioned too. These make BUJRUW an excellent candidate for a theoretical investigation requiring both, an accurate evaluation of the couplings as well as a deeper understanding of the physics governing them.

All calculations have been performed using the ORCA package.[83] The selective relaxation of the orbitals is done by means of the Local Self-Consistent Field method[84] available since ORCA version 4.2.0. Experimental crystallographic structures from the Cambridge Structural Database[78] has been used for all studied compounds. Regarding HAKKEJ,

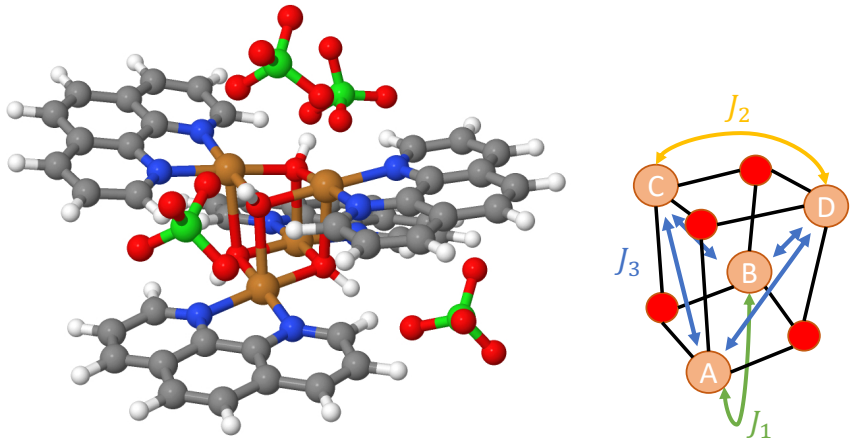


Figure 2: Molecular structure of BUJRUW (left) with the four perchlorate ions and schematic representation of the different couplings (right). Orange = copper, blue = nitrogen, red = oxygen, grey = carbon, white = hydrogen, green = chlorine.

counterions have been removed whilst for all structures, hydrogen atoms optimised at the B3LYP[85–88]/def2-SVP[89] level of theory using the RIJCOSX approximations.[16,90] The decomposition and computation of magnetic exchange couplings have been carried out using the B3LYP functional with the def2-SVP basis set for all atoms except the copper ones, of which the def2-QZVPP[89] basis set have been employed. Whilst the amount of HF exchange is a key quantity when transition metal-based compounds are studied and a balance of 35% has been several times advised,[55,56] such an amount was unable to reproduce the trends of couplings in BUJRUW. In this regard, the standard B3LYP has been kept throughout this work, even though an overestimation of the HAKKEJ couplings is expected. All molecular structures have been visualised using Jmol.[91] All structures are given in the Supporting Information (SI).

# 4 Results and Discussions

## 4.1 Proof of concept: 3-centre systems

In order to discuss the methodological aspect in the extraction of the different contributions and the evaluation of the overall magnetic couplings, we firstly consider the HAKKEJ 3-site

system. Here, no symmetry is considered, resulting in a general HDvV Hamiltonian defined as,

$$\hat{H} = -2\left(J_{AB}\hat{\vec{S}}_A \cdot \hat{\vec{S}}_B + J_{BC}\hat{\vec{S}}_B \cdot \hat{\vec{S}}_C + J_{AC}\hat{\vec{S}}_A \cdot \hat{\vec{S}}_C\right) \tag{65}$$

### 4.1.1 Direct Exchange

Table 1 presents the direct exchange contribution to the different couplings in HAKKEJ as well as the energy differences used to determine them, in the fifth and third columns, respectively. Following the topology and its almost symmetric structure, HAKKEJ presents two similar direct exchange contributions between the central copper atom and the two others, with $J_0^{AB} = 53$ cm$^{-1}$ and $J_0^{BC} = 52$ cm$^{-1}$. Furthermore, due to its linear structure, the two external copper atoms stand far away at about 10 Å with no direct interaction, resulting in a direct exchange coupling $J_0^{AC} = 0$. As mentioned in section 2, the direct exchange is insensitive to the choice of determinants. In Table S1 of SI we verify this property using the four-centres compound BUJRUW. It may be worth nothing that in the three-centres case, there are as many determinants as couplings and HAKKEJ cannot be used to stress out the consistency in the extraction of $J_0$.

Table 1: Energy differences and extraction of the direct exchange contribution for the three couplings in HAKKEJ in cm$^{-1}$.

| $\Delta E$ | $\sum J_0^{IJ}$ | | $J_0^{IJ}$ | |
|---|---|---|---|---|
| $E_{\bar{A}BC,\mathrm{NO}} - E_{ABC,\mathrm{RO}}$ | $J_0^{AB} + J_0^{AC}$ | 53 | $J_0^{AB}$ | 53 |
| $E_{A\bar{B}C,\mathrm{NO}} - E_{ABC,\mathrm{RO}}$ | $J_0^{AB} + J_0^{BC}$ | 104 | $J_0^{BC}$ | 52 |
| $E_{AB\bar{C},\mathrm{NO}} - E_{ABC,\mathrm{RO}}$ | $J_0^{AC} + J_0^{BC}$ | 52 | $J_0^{AC}$ | 0 |

### 4.1.2 Kinetic Exchange

Extracting the kinetic exchange contribution is the main challenge when multicentre systems are considered. Indeed, the relaxation of the magnetic orbitals, reflecting the entry of the ionic forms in the wave-function, brings the major part of the spin contamination. However, it may be the most important energetic contribution in transition metal-based compounds

and then a proper evaluation is a minimal requirement. Proceeding through the extraction of the $t$ and $U$ parameters offers this possibility, however, as previously mentioned, two different $t$ and $U$ for each pair must be determined since different relaxations may be considered. In the following, we illustrate the flexible-yet-consistent evaluation of the Hubbard parameters by considering all the possible relaxation paths.

Table 2: $t$ and $U$ Hubbard parameters coming from all possible single orbital relaxation and kinetic exchange contribution in cm$^{-1}$ in HAKKEJ.

| $J_{IJ}$ | relaxation | $t$ | $U$ | $-t^2/U$ |
|---|---|---|---|---|
| $AB$ | $(\bar{a}\cos\theta + \bar{b}\sin\theta)bc$ | -2534 | 39589 | -162 |
| | $(a\cos\theta + b\sin\theta)\bar{b}c$ | -2535 | 39532 | -163 |
| | $a(\bar{b}\cos\theta + \bar{a}\sin\theta)c$ | -2516 | 32105 | -197 |
| | $\bar{a}(b\cos\theta + a\sin\theta)c$ | -2518 | 32156 | -197 |
| $BC$ | $a(\bar{b}\cos\theta + \bar{c}\sin\theta)c$ | -2393 | 30624 | -187 |
| | $a(b\cos\theta + c\sin\theta)\bar{c}$ | -2394 | 30676 | -187 |
| | $ab(\bar{c}\cos\theta + \bar{b}\sin\theta)$ | -2425 | 39947 | -147 |
| | $a\bar{b}(c\cos\theta + b\sin\theta)$ | -2427 | 39906 | -148 |
| $AC$ | $(\bar{a}\cos\theta + \bar{c}\sin\theta)bc$ | -28 | 19753 | 0.0 |
| | $(a\cos\theta + c\sin\theta)b\bar{c}$ | -29 | 20850 | 0.0 |
| | $ab(\bar{c}\cos\theta + \bar{a}\sin\theta)$ | -31 | 21947 | 0.0 |
| | $\bar{a}b(c\cos\theta + a\sin\theta)$ | -31 | 21947 | 0.0 |

Table 2 presents the value of the different $t$ (third column) and $U$ (fourth column) parameters extracted through all possible relaxations as well as the resulting energetic contributions (fifth column). As mentioned, for one pair, 4 different relaxations may be considered whilst at least two sets of $t$ and $U$ parameters could be distinguished. For each pair of HAKKEJ, the different relaxations provide a consistent evaluation of $t$ with -2393, -2394, -2425 and -2427 cm$^{-1}$ for the $BC$ coupling and -2534, -2535, -2516 and -2518 cm$^{-1}$ for the pair $AB$. Two sets of $t$ parameters may be highlighted, for instance one reflecting the ability of an electron in $A$ to jump on $B$ at -2534 and -2535 cm$^{-1}$, and the other for $B$ to $A$ at -2516 and -2518 cm$^{-1}$. The extraction of the $U$ parameter provides results in the same vein as for $t$. Two distinct $U$ parameters must be extracted as expected for the $AB$ and $BC$ couplings with 39589/39532 and 32105/32156 cm$^{-1}$ and 30624/30676 and 39947/39906 cm$^{-1}$, respectively. Finally, for this contribution again, there is no interaction of this nature between the $A$ and

$C$ magnetic centres, reflected in very small values of $t$ at -28, -29 and -31 cm$^{-1}$, even though $U$ value is not. However, since there is almost no relaxation effects, the extraction of $t$ and $U$ implies tiny energy differences, at about 2.10$^{-7}$ $E_{\mathrm{h}}$, and no conclusions will be drawn with these values.

Whilst the analogy between the Hubbard parameters extracted through BS-DFT and HF gets some limits,[60] thinking the question of all these different numerical values in the WFT framework provides a conceptual explanation. Both hopping integrals associated to a pair of magnetic centres are analytically very slightly different in the WFT framework and they are numerically expected very close as confirmed in Table 2. For the $U$ parameter, four values could be defined for one pair of magnetic centres and this explain the four values extracted for the $AB$ pair, at 39589, 39532, 32105 and 32156 cm$^{-1}$. In WFT framework, these four $U$ values are associated to four energy differences between some ionic and neutral forms. In the present context, they may be highlighted by considering the different possible relaxations associated to a pair of centres, presented below in the case of the $AB$ coupling,

$$(\bar{a}\cos\theta + \bar{b}\sin\theta)bc \rightarrow U = E_{\bar{b}bc} - E_{\bar{a}bc} \tag{66}$$

$$(a\cos\theta + b\sin\theta)\bar{b}c \rightarrow U = E_{b\bar{b}c} - E_{a\bar{b}c} \tag{67}$$

$$a(\bar{b}\cos\theta + \bar{a}\sin\theta)c \rightarrow U = E_{a\bar{a}c} - E_{a\bar{b}c} \tag{68}$$

$$\bar{a}(b\cos\theta + a\sin\theta)c \rightarrow U = E_{\bar{a}ac} - E_{\bar{a}bc} \tag{69}$$

Except for systems featuring a centre of inversion, both $\bar{a}bc$ and $a\bar{b}c$ neutral forms would have different energies as well as for both $\bar{b}bc$ and $a\bar{a}c$ ionic ones. However, whilst the energy of both neutral forms should differ only from few 10$^{-6}$ $E_{\mathrm{h}}$, i.e. the order of magnitude of the direct exchange, one may expect from the energy of both ionic forms to be more different. Then, both relaxations of the orbital reflecting the inclusion of the same ionic component should provide very close $U$ values, e.g. 32105 and 32156 cm$^{-1}$, and these values would be significantly different of those from the opposite relaxation, e.g. 32105 and 32156 compared

to 39589 and 39532 cm$^{-1}$. Despite these small differences between $U$ values from relaxation of the same orbitals, in all couplings, two energetic contributions may be clearly distinguished, presented in the third column of Table 2. Whilst they differ from a few tens of cm$^{-1}$, both energetic contributions are of the same magnitude, according to the consistency in the evaluation of the $t$ and $U$ parameters. As mentioned in the section 2.2, an effective kinetic exchange contribution is defined by summing both energetic contributions, as presented in Table 3.

Table 3: Both energetic relaxations and the total kinetic exchange contribution for each coupling in HAKKEJ in cm$^{-1}$.

| $J_{IJ}$ | $-t^2/U$ | | $\Delta J^{IJ}_{\mathrm{KE}}$ |
|---|---|---|---|
| $\Delta J^{AB}_{\mathrm{KE}}$ | -163 | -197 | -360 |
| $\Delta J^{BC}_{\mathrm{KE}}$ | -187 | -148 | -335 |
| $\Delta J^{AC}_{\mathrm{KE}}$ | 0 | 0 | 0 |

### 4.1.3 Spin polarisation

Table 4: Energy differences and extraction of the spin polarisation contribution for the three couplings in HAKKEJ in cm$^{-1}$.

| $\Delta E$ | $\sum \Delta J^{IJ}_{\mathrm{SP}}$ | | $\Delta J^{IJ}_{\mathrm{SP}}$ | |
|---|---|---|---|---|
| $(E_{\bar{A}BC,\mathrm{FM}} - E_{\bar{A}BC,\mathrm{NO}}) - (E_{ABC\ldots N,\mathrm{FM}} - E_{ABC\ldots N,\mathrm{RO}})$ | $\Delta J^{AB}_{\mathrm{SP}} + \Delta J^{AC}_{\mathrm{SP}}$ | 1 | $\Delta J^{AB}_{\mathrm{SP}}$ | 1 |
| $(E_{A\bar{B}C,\mathrm{FM}} - E_{A\bar{B}C,\mathrm{NO}}) - (E_{ABC\ldots N,\mathrm{FM}} - E_{ABC\ldots N,\mathrm{RO}})$ | $\Delta J^{AB}_{\mathrm{SP}} + \Delta J^{BC}_{\mathrm{SP}}$ | 2 | $\Delta J^{BC}_{\mathrm{SP}}$ | 1 |
| $(E_{AB\bar{C},\mathrm{FM}} - E_{AB\bar{C},\mathrm{NO}}) - (E_{ABC\ldots N,\mathrm{FM}} - E_{ABC\ldots N,\mathrm{RO}})$ | $\Delta J^{AC}_{\mathrm{SP}} + \Delta J^{BC}_{\mathrm{SP}}$ | 1 | $\Delta J^{AC}_{\mathrm{SP}}$ | 0 |

Presented in Table 4, the last contribution extracted corresponds to the spin polarisation of the non-magnetic electrons due to the different field felt in the high and low spin states. As expected for transition metal-based compounds, this contribution is very small at 1, 1 and 0 cm$^{-1}$ for the $AB$, $BC$ and $AC$ couplings, respectively.

### 4.1.4 Total magnetic exchange couplings

Let us now focus on the impact on the total magnetic exchange couplings presented in Table 5 with the present method ($J_\Sigma$) in the fourth column, the usual BS approach evaluation

through a mapping over the Ising model ($J_{\text{Ising}}$) in the fifth column, reference DDCI calculation ($J_{\text{DDCI}}$) from Ref 76 in the sixth column and experimental evaluation ($J_{\text{exp}}$) by neglecting the $AC$ and considering the $AB$ and $AC$ couplings equivalent. DDCI calculations from Ref 76 have been performed in 6-311G for the Cu atom with an additional f function and the 6-31G(d,p) basis set for the H, C, N and O atoms.

Table 5: Decomposition (left) and magnetic exchange couplings (right) determined as the sum of the contributions ($J_\Sigma$), through the usual BS approach with a mapping over the Ising model ($J_{\text{Ising}}$), DDCI ($J_{\text{DDCI}}$) from Ref 76 and experimentally ($J_{\text{exp}}$) from Ref 79, for HAKKEJ in cm$^{-1}$.

| | $J_0^{IJ}$ | $\Delta J_{\text{KE}}^{IJ}$ | $\Delta J_{\text{SP}}^{IJ}$ | $J_\Sigma$ | $J_{\text{Ising}}$ | $J_{\text{DDCI}}$ | $J_{\text{exp}}$ |
|---|---|---|---|---|---|---|---|
| $J_{AB}$ | 53 | -360 | 1 | -306 | -331 | -112 | -190 |
| $J_{BC}$ | 52 | -335 | 1 | -282 | -305 | -100 | |
| $J_{AC}$ | 0 | 0 | 0 | 0 | -4 | -1 | / |

Evaluating the overall couplings as the sum of the three contributions ($J_\Sigma$) provides two strongly antiferromagnetic couplings for $AB$ and $BC$ at -306 and -282 cm$^{-1}$, respectively, and no coupling between the two distant copper atoms $A$ and $C$. These results are consistent with the couplings extracted through the usual BS approach since the $AB$ and $BC$ ones are at -331 and -305 cm$^{-1}$, respectively, even though the $AC$ coupling is here very weakly antiferromagnetic at -4 cm$^{-1}$. However, these results are slightly larger in magnitude than the couplings evaluated thanks to the recomposition method for $AB$ and $BC$. Regarding the large importance of kinetic exchange contributions in these couplings, the difference between both approaches may be attributed to the spin contamination which is neglected in the usual BS approach whilst it is an important concern for this contribution. It results in an overestimation of the coupling when this contribution is dominant due to the lack of a proper spin-decontamination. For such a system with a dominant kinetic exchange contribution, this trend may be readily thought by taking the example of two centres system. Indeed, in this context the $\langle \hat{S}^2 \rangle$ of the BS determinant would necessary be lower than 1 and using a decontamination scheme such as the Yamaguchi formula (Eq. 2) would lead to a denominator greater than 1. Hence, the spin contamination factor would squinch the energy

difference, resulting in a smaller value of the coupling compare to the non-spin decontaminated evaluation. Whilst this point has been pointed out by Shoji *et al.*,[64] it can only stand when the kinetic exchange contribution is dominating.

Finally, both DFT evaluations provide semi-quantitative pictures in agreement with the DDCI results for this compound with large antiferromagnetic $AB$ and $BC$ couplings at -112 and -100 cm$^{-1}$, respectively, even though they are overestimated. However, DDCI calculations seems to underestimate the couplings compare to the experimental value at -190 cm$^{-1}$. Finally, it may be worth noting that these reference values are presented here for a qualitative purpose and no comparison is drawn since DFT evaluations may be tweaked through the amount of HFX or the functional directly to reach quantitative agreement. Indeed, this quantity directly impacts the effects of the well-known self-interaction error, responsible of the overdelocalisation of the DFT orbitals and which plays a key role for an accurate prediction of magnetic exchange couplings.[72]

## 4.2 Applications to the 1+1+4 Cu(II) cubane complex

We now turn to the tetranuclear Cu(II) BUJRUW complex where six couplings may be considered. In order to fully take advantage of the present method, no assumption is made about the equivalence of some couplings and the full model Hamiltonian is considered,

$$\hat{H} = -2\left(J_{AB}\hat{\vec{S}}_A \cdot \hat{\vec{S}}_B + J_{BC}\hat{\vec{S}}_B \cdot \hat{\vec{S}}_C + J_{CD}\hat{\vec{S}}_C \cdot \hat{\vec{S}}_D + J_{AC}\hat{\vec{S}}_A \cdot \hat{\vec{S}}_C + J_{AD}\hat{\vec{S}}_A \cdot \hat{\vec{S}}_D + J_{BD}\hat{\vec{S}}_B \cdot \hat{\vec{S}}_D\right) \tag{70}$$

where $J_{AB}$ and $J_{CD}$ correspond to $J_1$ and $J_2$ in the model Hamiltonian used experimentally and presented in Eq. 64, respectively, and where $J_{AC}$, $J_{AD}$, $J_{BC}$ and $J_{BD}$ are considered equal and labelled $J_3$. As mentioned, this compound exhibits an unconventional 1+1+4 magnetic pattern, mainly explained through a structural analysis even though a perchlorate ion is present near the $C$ and $D$ centres implied in the $J_2$ coupling. Hence, in order to have a better understanding and to distinguish both aspects, the compound without the

perchlorate ion is firstly studied whilst these ions will be added afterwards. Finally, the different couplings using the whole crystallographic structure will be investigated to highlight the possible influence of the perchlorate ions near some of the hydrogen atoms of the $Cu_4O_4$ unit.

### 4.2.1 Reduced model compound

Table 6 presents the different contributions (third, fourth and fifth columns), the $J_\Sigma$ coupling from their recomposition (sixth column), the $J_{\text{Ising}}$ from the usual BS approach through a mapping over the Ising model, all considering the structure without the perchlorate counterions, and the experimental evaluation $J_{\text{exp}}$ (last column).

Table 6: Decomposition ($J_0$, $\Delta J_{\text{KE}}$ and $\Delta J_{\text{SP}}$) and magnetic exchange couplings determined as the sum of the three contributions ($J_\Sigma$), through the BS approach with a mapping over the Ising model ($J_{\text{Ising}}$) and experimentally ($J_{\text{Exp}}$), in BUJRUW in $\text{cm}^{-1}$.

| | | $J_0$ | $\Delta J_{\text{KE}}$ | $\Delta J_{\text{SP}}$ | $J_\Sigma$ | $J_{\text{Ising}}$ | $J_{\text{exp}}$ |
|---|---|---|---|---|---|---|---|
| $J_1$ | $J_{AB}$ | 102 | -138 | 28 | -8 | -17 | -28 |
| $J_2$ | $J_{CD}$ | 96 | -90 | 28 | 34 | 28 | 72 |
| $J_3$ | $J_{AC}$ | 5 | 0 | 0 | 5 | 4 | -15 |
| | $J_{AD}$ | 4 | 0 | -1 | 3 | 2 | |
| | $J_{BC}$ | 4 | 0 | -1 | 3 | 2 | |
| | $J_{BD}$ | 5 | 0 | 0 | 5 | 4 | |

Both DFT evaluations provide very close results for all couplings with a relatively weak antiferromagnetic $J_1$ (or $J_{AB}$) coupling at -8 and -17 $\text{cm}^{-1}$ for $J_\Sigma$ and $J_{\text{Ising}}$, respectively. In the same vein, both approaches evaluate $J_2$ as a stronger ferromagnetic coupling at 34 and 28 $\text{cm}^{-1}$ for $J_\Sigma$ and $J_{\text{Ising}}$, respectively. Interestingly, $J_\Sigma$ provides a weaker $J_1$, which is antiferromagnetic, and a larger $J_2$, which is ferromagnetic. Looking at the decomposition presented in the first columns, both couplings exhibit very large $\Delta J_{\text{KE}}$ contribution at -138 and -90 $\text{cm}^{-1}$ for $J_1$ and $J_2$, respectively. This remark is consistent with the previously mentioned effect of the spin decontamination, whose neglect tends to overestimate the antiferromagnetic kinetic exchange, resulting in the aforementioned differences. Finally, both methods evaluate $J_{AC}$, $J_{AD}$, $J_{BC}$ and $J_{BD}$ with homogeneous values at about 3 $\text{cm}^{-1}$. This

quantitatively confirms then the fair assumption of the experimental model Hamiltonian with a global $J_3$ coupling for these four pairs of magnetic centres. The decomposition comes to qualitatively support this trend since the four couplings are governed by the same physics, mainly the direct exchange contribution.

The DFT evaluations come to confirm the 1+1+4 pattern of the magnetic properties in BUJRUW. Indeed, theoretical and experimental determinations of $J_1$ and $J_2$ are in good qualitative agreements with a weak antiferromagnetic and larger ferromagnetic couplings, respectively. However, whilst $J_1$ exhibits a consistent value in each case with -8, -17 and -28 cm$^{-1}$ for $J_\Sigma$, $J_{\text{Ising}}$ and $J_{\text{exp}}$, respectively, the quantitative agreement is a bit worse for $J_2$. Indeed, the experimental value at 72 cm$^{-1}$ is about two times larger than the DFT ones. Despite this, the overall picture is quite well represented and the DFT calculations presented here tends to validate the structural rationalisation done by Mehrani *et al.*. The ferro- and antiferromagnetic characters of both $J_1$ and $J_2$ couplings have been justified regarding the Cu-O-Cu angles of both pairs of magnetic centres and the empirical relationship of Hatfield.[92–94] Indeed, it has been observed a dependence of the exchange coupling in binuclear Cu(II) complexes bridged by hydroxo groups on the Cu-O-Cu angles, which tends to be antiferromagnetic for an angle greater than 97.5° and ferromagnetic otherwise. Regarding the antiferromagnetic $J_1$ coupling, both concerned Cu-O-Cu angles are at about 99° whilst for the ferromagnetic $J_2$ couplings they are at about 97° (see Ref. 82 for further discussions). The present theoretical calculations numerically confirm the relevance of the structural analysis and specially since they have been performed on the compound only, no effect of the aforementioned perchlorate ion may occur. Furthermore, thanks to the decomposition, one may interpret this change in the sign of the coupling from a drastic change of $\Delta J_{\text{KE}}$ with the angle, with -138 and -90 cm$^{-1}$ for $J_1$ and $J_2$, respectively, whilst the other contributions are very slightly affected.

Despite this good qualitative and semi-quantitative agreements for the two first couplings, $J_3$ presents severe differences between the theoretical and experimental determina-

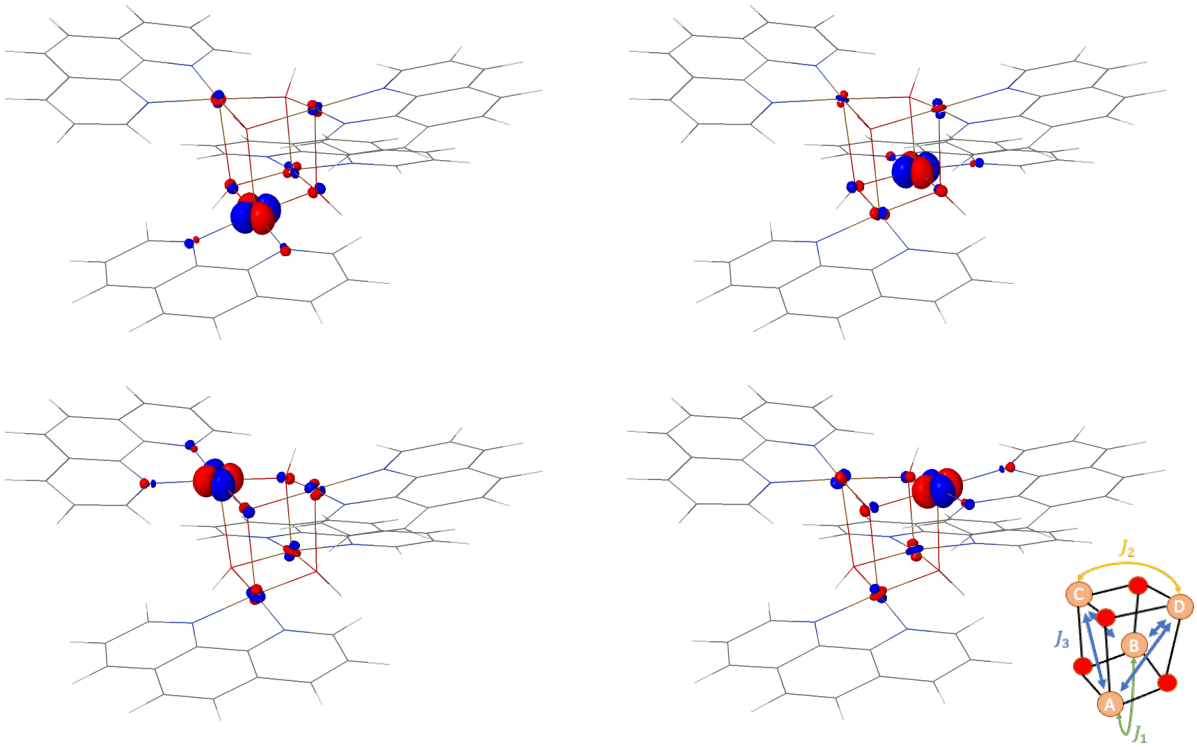


Figure 3: Isosurface of the four localised magnetic orbitals obtained from the HS,RO determinant and schematic representation of the different couplings (bottom right). Isovalue = 1.0 a.u..

tions. Indeed, the latter provides an antiferromagnetic coupling at -15 cm$^{-1}$ whilst both DFT evaluations agree on a very weak ferromagnetic value at about 3 cm$^{-1}$. In addition to this important qualitative discrepancy, the decomposition does not hint for any important antiferromagnetic contribution since there is a negligible spin polarisation and more importantly, no kinetic exchange contribution. This may be readily explained by looking at the magnetic orbitals obtained from the localisation of the HS,RO SOMOs and presented in Fig. 3. These four orbitals get a strong $d_{x^2-y^2}$ character spanning the plan implying $J_1$ and $J_2$. In such a spatial arrangement of the orbital lobes, a strong kinetic exchange mechanism may be expected for the latter couplings whilst it completely prevents such a contribution for the $J_3$ couplings, in agreement with Table 6. Finally, the literature tends to confirm a weak ferromagnetic coupling associated to the longest bond length in 2+4 cubanes and the present DFT results are perfectly consistent with the observations from Tercero *et al.*.[67]

### 4.2.2 Influence of the perchlorate ion on top of the $CD$ pair

Table 7 presents the different contributions (third, fourth and fifth columns), the $J_\Sigma$ coupling from their recomposition (sixth column), the $J_{\text{Ising}}$ from the usual BS approach through a mapping over the Ising model, all considering the molecular structure with the perchlorate counterion close to the $CD$ pair, and the experimental evaluation $J_{\text{exp}}$ (last column).

Table 7: Decomposition ($J_0$, $\Delta J_{\text{KE}}$ and $\Delta J_{\text{SP}}$) and magnetic exchange couplings determined as the sum of the three contributions ($J_\Sigma$), through the BS approach with a mapping over the Ising model ($J_{\text{Ising}}$) and experimentally ($J_{\text{Exp}}$) in BUJRUW with the perchlorate ion near the $CD$ pair and in parenthesis without (table 6) in cm$^{-1}$.

| | | $J_0$ | | $\Delta J_{\text{KE}}$ | | $\Delta J_{\text{SP}}$ | | $J_\Sigma$ | | $J_{\text{Ising}}$ | | $J_{\text{exp}}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $J_1$ | $J_{AB}$ | 105 | (102) | -135 | (-138) | 29 | (28) | -1 | (-8) | -9 | (-17) | -28 |
| $J_2$ | $J_{CD}$ | 94 | (96) | -53 | (-90) | 29 | (28) | 70 | (34) | 67 | (28) | 72 |
| $J_3$ | $J_{AC}$ | 4 | (5) | 0 | (0) | 0 | (0) | 4 | (5) | 4 | (4) | -15 |
| | $J_{AD}$ | 4 | (4) | 0 | (0) | -1 | (-1) | 3 | (3) | 3 | (2) | |
| | $J_{BC}$ | 4 | (4) | 0 | (0) | -1 | (-1) | 3 | (3) | 3 | (2) | |
| | $J_{BD}$ | 5 | (5) | 0 | (0) | -1 | (0) | 4 | (5) | 5 | (4) | |

With the presence of the perchlorate ion, both theoretical evaluations provide an overall picture of the magnetic properties of the system relatively different. Indeed, $J_1$ is still determined antiferromagnetic but with a weaker magnitude, with -1 instead of -8 cm$^{-1}$ without the perchlorate ion for $J_\Sigma$, and -9 instead of -17 cm$^{-1}$ for $J_{\text{Ising}}$. In the same vein, $J_2$ is evaluated as a stronger ferromagnetic coupling, at 70 instead of 34 cm$^{-1}$ without the perchlorate ion for $J_\Sigma$, and 67 instead of 28 cm$^{-1}$ for $J_{\text{Ising}}$. Finally, the values determined for the $J_3$ coupling at about 3 cm$^{-1}$ are consistent with the previous evaluation.

Let us now focus on the coupling that is the most concerned by the introduction of the perchlorate ion, $J_2$. This introduction strongly impacts the coupling and results in a more ferromagnetic value, going from 34 to 70 and from 28 to 67 cm$^{-1}$ for $J_\Sigma$ and $J_{\text{Ising}}$, respectively. Looking at the decomposition, $J_0$ and $\Delta J_{\text{SP}}$ are very slightly affected by the perchlorate ion, with contributions going from 96 to 94 and from 28 to 29 cm$^{-1}$, respectively. Hence, the strong difference of the $J_2$ coupling without and with the perchlorate ion comes from an import squinching of the antiferromagnetic $\Delta J_{KE}$ contribution, from -90 to -53

cm$^{-1}$. Being evaluated by means of the Hubbard Hamiltonian, the access to the $t$ and $U$ parameters, presented Table S2 of the SI, provides a thinner description of the kinetic exchange contribution. Hence, with the introduction of the perchlorate ion, $U$ appears slightly affected with a value going from 34202 and 34657 to 35109 and 3461 cm$^{-1}$ whilst the difference is proportionally more important for $t$ with an hopping integral going from about -1246 to about -966 cm$^{-1}$. $U$, $J_0$ and $\Delta J_{\mathrm{SP}}$ are intrinsic properties of the magnetic orbitals and since these quantities are almost unchanged, one may argue that the introduction of the perchlorate ion does not affect the definition of these orbitals. Hence, this ion mainly has the effect of preventing the relaxation of the magnetic orbitals towards the other sites, reflected by a quenched $t$ parameter, without intrinsically changing the magnetic orbitals.

Finally, it is interesting to focus on the $J_1$ coupling which, since associated to the $AB$ pair, should not be strongly affected by the introduction of the perchlorate ion near the $CD$ pair. Indeed, the overall couplings evaluated through $J_\Sigma$ and $J_{\mathrm{Ising}}$ are impacted, going from -8 to -1 cm$^{-1}$ and from -17 to -9 cm$-1$, respectively, with the introduction of the counterion. Regarding its position, these changes seem difficult to rationalise. This is confirmed with the decomposition which does not hint for any significant change in the different contributions, going from 102 to 105 cm$^{-1}$, -138 to -135 cm$^{-1}$ and 28 to 29 cm$^{-1}$, for $J_0$, $\Delta J_{\mathrm{KE}}$ and $\Delta J_{\mathrm{SP}}$, respectively. Despite small differences in each contribution, the overall coupling may appear as strongly impacted, specially regarding the small magnitude of the coupling. This shows how subtle magnetic exchange couplings are to evaluate, even theoretically due to the tiny energy differences implied.

### 4.2.3 Influence of the other pechlorate ions

Table 8 presents the different contributions (third, fourth and fifth columns), the $J_\Sigma$ coupling from their recomposition (sixth column), the $J_{\mathrm{Ising}}$ from the usual BS approach through a mapping over the Ising model, all considering the whole crystallographic structure, and the experimental evaluation $J_{\mathrm{exp}}$ (last column).

Table 8: Decomposition ($J_0$, $\Delta J_{\mathrm{KE}}$ and $\Delta J_{\mathrm{SP}}$) and magnetic exchange couplings determined as the sum of the three contributions ($J_\Sigma$), through the BS approach with a mapping over the Ising model ($J_{\mathrm{Ising}}$) and experimentally ($J_{\mathrm{Exp}}$) in the complete crystallographic structure of BUJRUW in cm$^{-1}$ and in parenthesis for BUJRUW with the perchlorate ion near the $CD$ pair (table 7).

| | | $J_0$ | | $\Delta J_{\mathrm{KE}}$ | | $\Delta J_{\mathrm{SP}}$ | | $J_\Sigma$ | | $J_{\mathrm{Ising}}$ | | $J_{\mathrm{exp}}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $J_1$ | $J_{AB}$ | 117 | (105) | -154 | (-135) | 35 | (29) | -2 | (-1) | -13 | (-9) | -28 |
| $J_2$ | $J_{CD}$ | 109 | (94) | -86 | (-53) | 35 | (29) | 58 | (70) | 51 | (67) | 72 |
| $J_3$ | $J_{AC}$ | 7 | (4) | 0 | (0) | -1 | (0) | 6 | (4) | 5 | (4) | -15 |
| | $J_{AD}$ | 5 | (4) | 0 | (0) | -2 | (-1) | 3 | (3) | 4 | (3) | |
| | $J_{BC}$ | 5 | (4) | 0 | (0) | -2 | (-1) | 3 | (3) | 4 | (3) | |
| | $J_{BD}$ | 6 | (5) | 0 | (0) | -1 | (-1) | 5 | (4) | 5 | (5) | |

Considering now all the counterions of the crystallographic structure, the $J_1$ coupling is mainly expected to be influenced by the presence of a perchlorate ion near one of the hydroxo group between the $AB$ pair, at a distance of 2 Å between the hydrogen atom and the closest oxygen atom of the perchlorate ion (Fig 2). Both DFT calculations indicate very slight variations of the total magnetic coupling since $J_\Sigma$ and $J_{\mathrm{Ising}}$ go from -1 to -2 and from -9 to -13 cm$^{-1}$, respectively, by considering this new system from the latter. Interestingly, the decomposition hints at more important effects since all contributions are larger, at 117 instead of 105 cm$^{-1}$ for $J_0$, -154 instead of -135 cm$^{-1}$ for $\Delta J_{\mathrm{KE}}$ and 35 instead of 29 cm$^{-1}$ for $\Delta J_{\mathrm{SP}}$. However, these changes in magnitude have no consequences on the overall coupling since the ratio between the different contributions is roughly equivalent.

The situation is different when considering the $CD$ pair where the $J_2$ coupling would be affected by two perchlorate ions, of which the closest oxygen stands at 2.1Å from the hydrogen atom of each hydroxo groups (Fig 2). Whilst $J_0$ and $\Delta J_{\mathrm{SP}}$ are impacted similarly as $J_2$, with the former going from 94 to 109 cm$^{-1}$ and the latter from 29 to 35 cm$^{-1}$, the kinetic exchange presents here a different behaviour. Indeed, $\Delta J_{\mathrm{KE}}$ goes from -53 to -86 cm$^{-1}$, indicating an enhanced contribution by both perchlorate ions. This results in a smaller ferromagnetic $J_2$ couplings, which goes from 70 to 58 and from 67 to 51 cm$^{-1}$ for $J_\Sigma$ and $J_{\mathrm{Ising}}$, respectively.

Finally, $J_3$ appears also slightly impacted by the introduction of the three left perchlo-

rate ions. Indeed, as for $J_1$ and $J_2$, $J_0$ and $\Delta J_{\mathrm{SP}}$ are slightly larger but this as a relative impact on the overall picture regarding the already small magnitude of this coupling and its contributions.

Tables 6, 7 and 8 highlighted the role of the perchlorate ions on the different couplings in BUJRUW. Whilst these couplings are relatively fairly estimated with the molecular structure only, the account of the counterions may be important for a thinner description, where they played a role not only qualitatively. However, even though both theoretical and experimental evaluations agree on a weak antiferromagnetic $J_1$ and a stronger ferromagnetic $J_2$, the DFT results are not in line with a significant antiferromagnetic $J_3$ coupling. Indeed, both $J_\Sigma$ and $J_{\mathrm{Ising}}$ plead for a very weak ferromagnetic coupling, whatever the system considered, and the decomposition presents no hints of a dominant antiferromagnetic contribution. In addition, either the orbitals analysis or the previous work from Tercero *et al.*,[67] they tend to agree on a very weak ferromagnetic coupling. The difficulty of fitting several parameters over one magnetic susceptibility curve may result in discrepancy with theoretical evaluations, which have been several times discussed.[68,69]

### 4.2.4 Remarks on the spin decontamination in BUJRUW

With three couplings exhibiting very different physics, BUJRUW appears as a perfect example to discuss the role that the spin contamination may play in multicentre compounds.

On the one hand, in $J_1$ the three contributions are important and the overall coupling results from the competition between the two ferromagnetic $J_0$ and $\Delta J_{\mathrm{SP}}$ and the dominating antiferromagnetic $\Delta J_{\mathrm{KE}}$. On the other hand, whilst in $J_2$ the three contributions are of similar signs and magnitudes as in $J_1$, $\Delta J_{\mathrm{KE}}$ is not the dominating contribution, resulting in a ferromagnetic coupling. As mentioned, $\Delta J_{\mathrm{KE}}$ is the main contribution to spin decontaminate and when such a treatment is absent, the contribution is overestimated. Let us take the example of $J_1$ and $J_2$ from Table 7. Since in $J_2$ the kinetic exchange is relatively weak at -53 cm$^{-1}$, the overestimation should consequently be moderate in $J_{\mathrm{Ising}}$, resulting in a small

difference between the recomposition method and the BS approach of 3 $cm^{-1}$ (70 and 67 $cm^{-1}$, respectively). On the contrary, the more important $\Delta J_{KE}$ at -153 $cm^{-1}$ in $J_1$ would lead to a more overestimated contribution in $J_{Ising}$. It results in a larger difference of 8 $cm^{-1}$ since $J_\Sigma$ and $J_{Ising}$ are determined at -1 and -9 $cm^{-1}$, respectively. More than the numerical difference of the couplings from both approaches, these differences may provide large discrepancies in the ratio between couplings. This ratio is an important point in DFT evaluations since, whilst the amount of HFX or the functional may be changed to tune and reach a numerical agreement, it should be constant as long as the electronic structure is properly represented.[76]

Finally, it may be interesting to end this discussion by focusing on the $J_3$ coupling. Indeed, in a sense it may be seen as an extreme case of the aforementioned situation since no kinetic exchange mechanism occurs. Then, since there is no contribution to spin decontaminate, $J_{Ising}$ should provide a fair determination, which is confirmed by the consistency with $J_\Sigma$ differing at the maximum of 1 $cm^1$ throughout this study of BUJRUW. Hence, one may imagine that the ratio from $J_{Ising}$ between such a coupling and a coupling exhibiting a strong $\Delta J_{KE}$ may be dramatically flawed, due to the inconsistency in both evaluations with the latter lacking for spin contamination.

# 5 Conclusion

In this article, we have presented a new and consistent method in KS-DFT to compute magnetic exchange couplings in multicentre compounds which provides fully spin decontaminated values. Based on our recent proposal to evaluate the $J$ coupling as the sum of its three main contributions,[63] this work proposes a completely general extraction of the direct exchange, the kinetic exchange and the spin polarisation contributions, whatever the number of magnetic centres considered. In line with our previous works, this extraction proceeds through the computation of several mean-field HS and BS solutions and exploits the selec-

tive relaxation of orbitals implied in the different physical mechanisms. However, here the kinetic exchange contribution is treated through the new idea of relaxing magnetic orbitals only one at a time, allowing the rigorous extraction of the different Hubbard Hamiltonian parameters. This has been done by means of the LSCF method[84] present in Orca since the version 4.2.0,[83] making this work available to any other users. All contributions being rigorously extracted, the so-called recomposition method provides overall couplings fully spin decontaminated.

Numerical applications on the HAKKUJ trinuclear copper compound have presented the implementation of the method on a simple and well-known system. In this part, we have detailed how the extraction of the different contributions is performed, with a special attention paid to discuss the possible evaluations of the kinetic exchange contribution. We finally compared the recomposition method with the usual BS evaluation, based on the Ising and which neglects the spin decontamination treatment.

Taking advantage of the rationalisation tool offered by the extraction of the different contributions, we investigated the more challenging BUJRUW tetranuclear copper compound. DFT calculations came to confirm the 1+1+4 pattern of this cubane system. However, whilst a good agreement has been found for two couplings, large discrepancies have been highlighted for the last one between the theoretical investigation and the experimental fit. In this work, we have also shown the non-negligible role of the perchlorate ions present in the cell.

Finally, the impact of the spin contamination has been discussed throughout this article. This work confirmed the overestimation of the couplings in the non-spin decontaminated approach already mentioned by Shoji *et al.*.[64] However, this work allows us to refine this statement since only the kinetic exchange contribution would be overestimated. It results in an overestimation of antiferromagnetic couplings and an underestimation of ferromagnetic ones compared to the recomposition method, at least when the spin polarisation is relatively moderate compared to the other contributions. Spin polarisation effects may have important

consequences on the evaluation when they are strong[61–63] and a future work will be dedicated to this aspect in systems such as organic polyradical compounds. Finally, the study of the BUJRUW compound highlighted the consequences of the lack of spin decontamination in systems exhibiting coupling with different physics. We shown how this aspect may lead to a flawed ratio between couplings.

For the sake of simplicity, this work has been restricted to Cu(II)-based complexes and future works will explore the computation of magnetic exchange couplings in systems featuring more unpaired electrons per centre.

## Acknowledgement

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## Supporting Information Available

Optimised coordinates for all compounds, energy and $\langle \hat{S}^2 \rangle$ of all determinants for the HAKKEJ compound, different ways of extracting the direct exchange for the reduced model of BUJRUW and the Hubbard model Hamiltonian parameters related to the study of the BUJRUW compound (Section 4.2).

# Appendix: Two unpaired electrons in two magnetic centres

The method proposed in the present work is deeply rooted in two theoretical frameworks developed for the simplest magnetic system, i.e. two electrons in two magnetic centres: i) the wavefunction-based quasi-degenerate perturbation theory and ii) the electron density-based decomposition of the magnetic exchange interaction. The main ingredients of these two approaches are recalled below.

## Quasi-degenerate perturbation theory analysis of $J$

Following the pioneering works of de Loth *et al.*[95] and Calzado *et al.*,[23–25] QDPT appears as a powerful conceptual tool to get insights into the physics of the magnetic exchange coupling. This section is strongly based on Ref. 23, of which the reader should refer for a deeper analysis. Let us consider a simple centro-symmetrical system featuring two magnetic centres $A$ and $B$, of which both bear one unpaired electron. Computing the triplet state in the Restricted Open-shell (RO) formalism generates a set of doubly occupied orbitals, referred as core orbitals, and two symmetry-adapted Singly Occupied Molecular Orbitals (SOMOs), $g$ and $u$. Both SOMOs may be readily localised through a unitary transformation, leading to two localised MOs $a$ and $b$ on each magnetic centre $A$ and $B$, respectively,

$$a = \frac{g+u}{\sqrt{2}} \text{ and } b = \frac{g-u}{\sqrt{2}} \tag{71}$$

This set of MOs allows us to define two $m_s = 0$ determinants $|a\bar{b}\rangle$ and $|b\bar{a}\rangle$, referred as *neutral* forms in the (orthogonal) valence bond language since both unpaired electrons are located on different spatial regions. These two determinants may be considered as a physically meaningful first order description of our situation and are used as a model space, being the

basis of the HDvV model Hamiltonian. It allows us to build a first CI matrix given by,

$$\begin{pmatrix} 0 & K_{ab} \\ K_{ab} & 0 \end{pmatrix} \tag{72}$$

where the diagonal terms have been shifted by the energy of the neutral form and with $K_{ab}$ the direct exchange integral equal to $\langle a\bar{b}|1/r_{12}|b\bar{a}\rangle$. To this CI matrix correspond two spin states, a triplet state and a singlet state, of which the former is the ground state with an energy splitting of $2K_{ab}$. It results in a magnetic coupling $J = K_{ab}$ and $J$ is always ferromagnetic in this primary description since $K_{ab}$ is positive.

We now can build an effective Hamiltonian $\hat{H}^{\text{eff}}$ upon this model space using the QDPT where the off-diagonal terms are defined as,

$$\langle \Phi_M|\hat{H}^{\text{eff}}|\Phi_N\rangle = \langle \Phi_M|\hat{H}|\Phi_N\rangle + \sum_{\alpha} \frac{\langle \Phi_M|\hat{H}|\alpha\rangle\langle\alpha|\hat{H}|\Phi_N\rangle}{E_{\Phi_M} - E_{\alpha}} \tag{73}$$

with $\Phi_M$ and $\Phi_N$ some configurations of the model space and $\alpha$ some single and double excited-configurations out of the model space, so-called outerspace.

The first important contribution to the magnetic exchange coupling coming from the outerspace is provided by the *ionic* forms $|a\bar{a}\rangle$ and $|b\bar{b}\rangle$,

$$\langle a\bar{b}|\hat{H}^{\text{eff}}|b\bar{a}\rangle = K_{ab} + \frac{\langle a\bar{b}|\hat{H}|a\bar{a}\rangle\langle a\bar{a}|\hat{H}|b\bar{a}\rangle}{E_{a\bar{a}} - E_{a\bar{b}}} + \frac{\langle a\bar{b}|\hat{H}|b\bar{b}\rangle\langle b\bar{b}|\hat{H}|b\bar{a}\rangle}{E_{b\bar{b}} - E_{a\bar{b}}} \tag{74}$$

$$= K_{ab} - 2\frac{{t_{ab}}^2}{U} \tag{75}$$

with $t_{ab}$ the hopping integral and $U$ the on-site repulsion energy from the Hubbard model Hamiltonian. The second term of Eq. (75) is the antiferromagnetic "kinetic exchange" contribution. It may be worth noting that Eq. (75) stands for centro-symmetrical systems where the hopping integral and the on-site repulsion energy resulting from the second and third terms of Eq. (74) are equal.

Finally the last important contribution corresponds to the differential response of the closed-shell electrons to the exchange field of the unpaired electrons in the triplet and the singlet states. This contribution comes from the interaction with the excited configurations of which an electron is promoted from the core ($i$) to the virtual ($r$) orbitals with a possible spin flip of the unpaired electrons and often labelled $1h1p$ (one hole-one particle). These interactions result in an energy stabilisation at second order expansion of,

$$^{3}E_{SP}^{(2)} = \sum_{i,r} \frac{1/2\langle i|\hat{K}_a - \hat{K}_b|r\rangle^2 + \langle i|\hat{K}_a + \hat{K}_b|r\rangle^2}{\Delta E_{i\to r}} \tag{76}$$

in the triplet state and,

$$^{1}E_{SP}^{(2)} = \frac{3}{2}\sum_{i,r} \frac{\langle i|\hat{K}_a - \hat{K}_b|r\rangle^2}{\Delta E_{i\to r}} \tag{77}$$

in the singlet state, with $\hat{K}_a$ and $\hat{K}_b$ the exchange operator of the $a$ and $b$ orbitals, respectively, and $\Delta E_{i\to r}$ a positive quantity representing the excitation energy of promoting an electron from an $i$ occupied orbital to a $r$ virtual one. The differential effect expresses the spin polarisation contribution and its pertubative expansion provides the following ferro- or antiferromagnetic contribution to the magnetic exchange coupling,

$$\frac{1}{2}\left(^{1}E_{SP}^{(2)} - {}^{3}E_{SP}^{(2)}\right) = 2\sum_{i,r} \frac{\langle i|\hat{K}_a|r\rangle\langle r|\hat{K}_b|i\rangle}{\Delta E_{i\to r}} \tag{78}$$

Whilst others may be distinguished, these three contributions are the most important for the magnetic exchange coupling, which may be fairly estimated as,

$$J = K_{ab} - 2\frac{{t_{ab}}^2}{U} + 2\sum_{i,r} \frac{\langle i|\hat{K}_a|r\rangle\langle r|\hat{K}_b|i\rangle}{\Delta E_{i\to r}} \tag{79}$$

## Decomposition in the BS approach

The first step of the procedure proceeds through the computation of the triplet state in the restricted open-shell (RO) formalism (T,RO). This calculation defines a set of $N_C$ core (i.e.

not magnetic) orbitals $i$ and two magnetic orbitals $a$ and $b$ located on the magnetic centres $A$ and $B$, respectively, obtained by the localisation of the singly occupied molecular orbitals (SOMOs),

$$\Phi_{\mathrm{T,RO}} = \Phi_{AB,\mathrm{RO}} = |\prod_{i}^{N_c} i\bar{i}ab| \tag{80}$$

It may be worth noting that, in practice, this first HS solution may also be computed using the quasi-RO (QRO) formalism[96] since the RO formalism may be difficult to converge. Then, one of the unpaired electrons is flipped to produce a first BS determinant, without optimising any orbital,

$$\Phi_{A\bar{B},\mathrm{NO}} = |\prod_{i}^{N_c} i\bar{i}a\bar{b}| \tag{81}$$

where NO means non-optimised and $A\bar{B}$ the flip of the electron of the $B$ magnetic centre generating the BS determinant. The energy difference between both determinants provides the first direct exchange contribution,

$$J_0^{AB} = E[\Phi_{A\bar{B},\mathrm{NO}}] - E[\Phi_{AB,\mathrm{RO}}] \tag{82}$$

The second contribution is obtained by relaxing the HS magnetic orbitals to adapt them to the BS determinant, in the field of the frozen core orbitals, leading to a new BS determinant,

$$\Phi_{A'\bar{B}',\mathrm{FC}} = |\prod_{i}^{N_c} i\bar{i}a'\bar{b}'| \tag{83}$$

where FC means frozen core orbitals and the prime symbolises the relaxation of the orbitals such as,[8]

$$a' = a\cos\theta + b\sin\theta \tag{84}$$

$$b' = b\cos\theta + a\sin\theta \tag{85}$$

This delocalisation of the magnetic orbitals from one centre to another may be interpreted

similarly as the entry of the ionic forms in the wave function and it results in the kinetic exchange contribution, calculated with the Yamaguchi formula,

$$\Delta J_{\mathrm{KE}}^{AB} = \frac{E[\Phi_{A'\bar{B}',\mathrm{FC}}] - E[\Phi_{AB,\mathrm{RO}}]}{\langle \hat{S}^2 \rangle_{AB,RO} - \langle \hat{S}^2 \rangle_{A'\bar{B}',\mathrm{FC}}} - J_0^{AB} \tag{86}$$

and where the relaxation of $a'$ and $\bar{b}'$ necessarily lowers the expectation value of $\hat{S}^2$ of $\Phi_{A'\bar{B}',\mathrm{FC}}$,

$$\langle \hat{S}^2 \rangle_{A'\bar{B}',\mathrm{FC}} < 1 \tag{87}$$

From this determinant, the effective $t_{ab}$ and $U$ Hubbard Hamiltonian parameters may also be extracted,

$$U = 2\frac{E[\Phi_{AB,\mathrm{RO}}] - E[\Phi_{A'\bar{B}',\mathrm{FC}}] + J_0^{AB}}{1 - \langle \hat{S}^2 \rangle_{A'\bar{B}',\mathrm{FC}}} - 2J_0^{AB} \tag{88}$$

$$|t_{ab}| = \frac{E[\Phi_{AB,\mathrm{RO}}] - E[\Phi_{A'\bar{B}',\mathrm{FC}}] + J_0^{AB}}{\sqrt{1 - \langle \hat{S}^2 \rangle_{A'\bar{B}',\mathrm{FC}}}} \tag{89}$$

These parameters are considered as effective since their physical meaning differs between DFT and WFT as previously discussed by some of the authors.[60] However, they lead to a thinner description of the kinetic exchange contribution which may be computed through the effective Hamiltonian defined previously,

$$\Delta J_{KE} = -2\frac{{t_{ab}}^2}{U} \tag{90}$$

or in a CASCI way,[23]

$$\Delta J_{KE} = \frac{U - \sqrt{U^2 + 16{t_{ab}}^2}}{4} \tag{91}$$

It may be noted that both formula are equivalent when $|t_{ab}| << U$, as expected for Heisenberg systems.

At last, keeping the magnetic orbitals frozen, the core orbitals are relaxed in the HS,RO,

$$|\Phi_{AB,\mathrm{FM}}| = |\prod_{i}^{N_c} i'\bar{i}''ab| \tag{92}$$

and $A\bar{B}$,NO determinant,

$$|\Phi_{A\bar{B},\mathrm{FM}}| = |\prod_{i}^{N_c} i'\bar{i}''a\bar{b}| \tag{93}$$

where FM means frozen magnetic orbitals. As shown by some of the authors,[62,63] these two determinants allow one to properly evaluate the contribution of the spin polarisation to the coupling,

$$\Delta J_{\mathrm{SP}}^{AB} = (E[\Phi_{A\bar{B},\mathrm{FM}}] - E[\Phi_{A\bar{B},\mathrm{NO}}]) - (E[\Phi_{AB,\mathrm{FM}}] - E[\Phi_{AB,\mathrm{RO}}]) \tag{94}$$

The total magnetic coupling may now be calculated as,

$$J^{AB} = J_0^{AB} + \Delta J_{\mathrm{KE}}^{AB} + \Delta J_{\mathrm{SP}}^{AB} \tag{95}$$

In addition to the decomposition allowing a deep analysis of the magnetic exchange coupling, this approach provides a consistent evaluation of $J$ since all the contributions are correctly extracted and prevents the potential issue of the use of the Yamaguchi formula when strong polarisation effects are present.[63] It is worth noting that the last term of Eq. (95) should formally be weighted by the importance of the delocalisation of the magnetic orbitals. However, in most cases for transition metal complexes, this weight is close to 1 and Eq. (95) remains valid.[63] Otherwise and as recently proposed,[75] this parameter may be used to dress an effective CI matrix.

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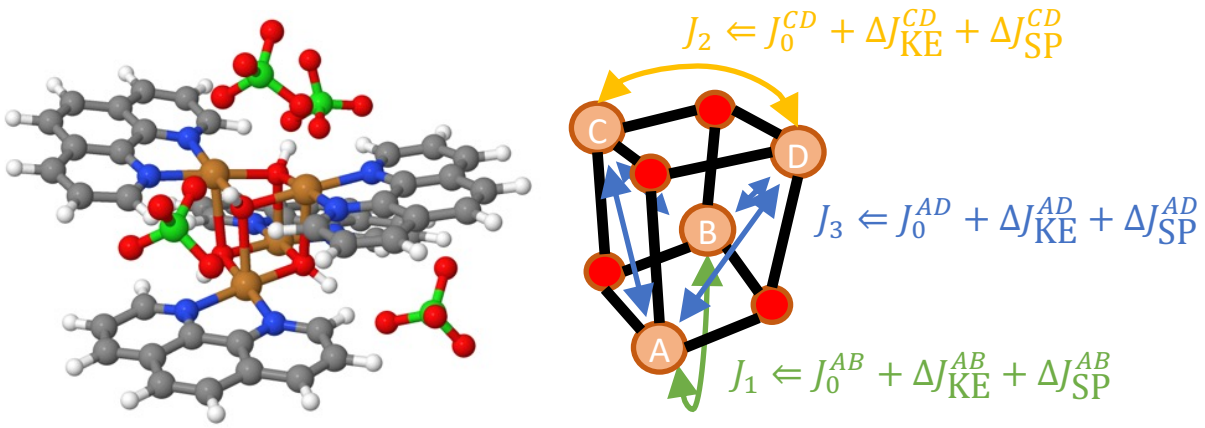


Figure 4: For Table of Contents Only