

## A Few Comments on the Application of Density Functional Theory to the Calculation of the Magnetic Structure of Oligo-Nuclear Transition Metal Clusters

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**Abstract:** First principle calculations of the magnetic structure of high nuclearity clusters appears challenging in order to validate fits of magnetic experiments. Density Functional Theory (DFT)-Broken Symmetry approach pair became, in the past few years, the most widely applied computational tool to investigating the chemical-physical properties of complex systems, in particular magnetic molecular compounds. However, the application of the Broken Symmetry formalism requires the knowledge of the energies of  $2^N/2$  single Slater determinants, and this task can easily become difficult for large  $N$ . Three main approximations are therefore usually done in order to limit the computational efforts: the model dimer approach (MDA), the doped cluster approach (DCA), and the minimum cluster approach (MCA). The whole cluster approach (WCA) will be also applied as reference and in order to check the importance of spin Hamiltonian high order terms. A systematic comparison between these different approaches has been, therefore, performed. Since this study is aimed for being of help in choosing the best method of calculation, we check here the validity of the above approaches by computing the magnetic structure of some test systems: the tetrahedral system  $(\text{HeH})_4$  and linear  $[\text{Cu}(\text{II})]_3$  and  $[\text{Mn}(\text{II})]_4$  complexes.

### Introduction

Density Functional Theory (DFT) became, in the past few years, the most widely applied computational tool to investigating the chemical-physical properties of complex systems,<sup>1–4</sup> and particular attention was devoted to the understanding of the magnetic properties of molecular aggregates.<sup>5</sup> The “unusual” properties of these *molecular magnets*, as Olivier Kahn<sup>6</sup> called them in 1993, are related to the common nature of their ground and excited states, which always consist of a manifold of states of different spin multiplicities nearly degenerate with respect to the temperature quantum  $kT$  ( $\sim 200 \text{ cm}^{-1}$  at room temperature). A few paramagnetic molecules were discovered to show (at sufficiently low temperatures) hysteresis of the magnetization mimicking the bulk magnets behavior. These molecules appeared, therefore, possible precursors of building blocks for future molecular-sized storage devices.<sup>7</sup> These *Single Molecule Magnets* (SMM) are high nuclearity clusters, also

called *molecular nanomagnets*, like  $\text{Mn}_{12}(\mu_3\text{-O})_{12}(\text{CH}_3\text{COO})_6(\text{H}_2\text{O})_4$ ,<sup>8</sup> whose magnetic hysteresis is due to the *magnetization tunneling* between the quantum states of the ground spin manifold.<sup>9</sup> The complete description of the electronic structure of magnetic systems can be achieved only within a relativistic formalism. However, the complexity of  $n$ -electron relativistic approaches prevents its application even to fairly complex systems. Calculations are therefore usually performed using a simpler, nonrelativistic, Hamiltonian, eventually including scalar relativistic effects on the valence electrons. Coupling between spins and orbital angular momenta (*spin-orbit coupling* (SOC)), in the case of orbitally nondegenerate ground states, is included via perturbation theory.<sup>10</sup> Notwithstanding these simplifications, calculation of magnetic properties remains a formidable task. It requires a computational approach that is capable of handling systems of chemical complexity and includes both static and dynamic electron correlation required to describing the many-body problem. Indeed, the main difficulty which arises in these cases is the correct definition of the different

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spin states of the paramagnetic cluster. The highest spin state, in which all the majority spins, say  $\alpha$ , of the individual paramagnetic centers are aligned parallel, is usually called the *ferromagnetic state* of the cluster,  $|F\rangle$ . This state can be generally represented, in a molecular orbital framework, with a single Slater determinant formed by  $n_\beta$  doubly occupied molecular orbitals and  $(n_\alpha - n_\beta)$  singly occupied  $\alpha$  molecular orbitals ( $n_\alpha$  and  $n_\beta$  being the number of  $\alpha$  and  $\beta$  electrons, respectively), using either a spin unrestricted or a restricted open shell formalism. This state, neglecting the small spin contamination due to the unrestricted formalism, is an eigenstate of the total spin operator,  $\mathbf{S}^2$  ( $\mathbf{S} = \sum \mathbf{S}_i$ ), with eigenvalue  $S_{\max} = [n_\alpha(n_\alpha+1)]/4$ . Another state, the *antiferromagnetic state*,  $|AF\rangle$ , is, in general, written down with one single Slater determinant in which the spins of the individual centers are aligned antiparallel to each other and represents the state with the smallest spin multiplicity. This determinant, however, is not an eigenstate of the total spin operator, but only of its  $z$  component,  $S_z$ , with eigenvalue  $M_S = (n_\alpha - n_\beta)/2$ . In general, all the eigenstates of  $\mathbf{S}^2$  that correspond to states with spin multiplicity  $S_k < S_{\max}$  are linear combinations of eigenstates of  $S_z$  with eigenvalue  $s_k$ . To properly describe these states, therefore, multiconfiguration SCF (MC-SCF) (also called multireference (MR-SCF)) approaches must be applied. The method most widely used to define the multireference wave function is the complete active space method (CAS), also called full optimized reaction space (FORS). The correlation between the electrons introduced in this way is called *static* or *long-range* correlation. The correct energy of the eigenfunction is computed by adding the effect of all the other electrons in the molecule (*dynamic* or *short-range* correlation) through the use of *post*-HF configuration interaction (CI) on the multiconfigurational wave function either explicitly (MR-CI, DDCI,...) or perturbatively (CASPT2, MRPT, MRQDPT,...).<sup>11</sup> All of these approaches need big computational resources and can be applied only to rather small molecules.<sup>12</sup>

Molecular magnets can be experimentally studied by a number of techniques, the more common being magnetization measurements, electron magnetic resonances, and heat-capacity calorimetry. In all cases, the interpretation of their physical properties is performed using an effective Hamiltonian that, in the case of magnetic properties, acts on spin variables (*Spin Hamiltonian*, SH). The eigenvalues of the SH match exactly the low energy spectrum of the magnetic systems by incorporating proper parameters, whose values are derived from the experiments and from theoretical methods. Calculations of the magnetic properties are therefore devoted to calculating the SH parameters with quantum mechanical methods. For most molecular magnets, the magnetic properties arise from the collectivization of magnetic moments localized onto a given atom or ion or groups of atoms, called *magnetic centers*. When the orbital contribution to the individual magnetic moments is negligible, i.e. all the magnetic centers have orbitally nondegenerate ground states rather well isolated from excited states, they behave like Curie paramagnets. In these cases, it is possible to associate each center with a magnetic moment  $\mu_k^2 = g_k^2 \mu_B^2 S_k(S_k+1)$ , where  $S_k$  is the spin quantum number of center

$k$ ,  $g_k$  contains the SOC contribution to the magnetization, and  $\mu_B^2$  is the Bohr magneton. A convenient form of the SH to be used in these cases is<sup>13</sup>

$$H_{\text{Spin}} = \sum_{i < j} \mathbf{S}_i \cdot \mathbf{J}_{ij} \cdot \mathbf{S}_j + \sum_k H_{S_k} \quad (1)$$

The first term in the right-hand side in (1) is the quadratic coupling between the magnetic moments localized on the centers  $i$  and  $j$  bearing spins  $\mathbf{S}_i$  and  $\mathbf{S}_j$ , respectively. The coupling is parametrized by the *exchange coupling tensor*,  $\mathbf{J}_{ij}$ . This is a second-rank tensor that includes all the physics of the magnetic coupling. Higher order terms involving fourth-order powers of the spin operators are allowed by symmetry, and their form and calculation will be discussed later in the text.  $H_{S_k}$  represents the low lying energy levels of the magnetic center  $k$  and their interaction with the magnetic field. This Hamiltonian, neglecting any interaction with nuclear moments, can be expressed, in generalized form, as a sum of terms of the type  $B^l S_k^l$  ( $l_B$  and  $l_S$  non-negative integers;  $l_S \leq 2S_k$ ), where  $l_B + l_S$  is even to preserve time-reversal symmetry.<sup>14</sup> Although  $l_B$  is in principle unbounded, terms with  $l_B > 1$  are seldom included. The term with  $l_B = 1$ , linear with  $\mathbf{B}$ , and  $l_S = 1$  is the *linear Zeeman interaction* of the localized spins  $\mathbf{S}_k$  with the external magnetic field,  $\mathbf{B}$ . When  $S_k \geq 1$ , terms with  $l_B = 0$  and  $l_S = 2(4, \dots)$  must be considered that represent the *zero-field splitting* (ZFS) of the ground-state of the  $k$ -th magnetic center. A widely used form of  $H_{S_k}$ , including only quadratic terms with  $l_B = 0$  and  $l_S = 2$ , is

$$H_{S_k} = \mu_B \mathbf{B} \cdot \mathbf{g}_k \cdot \mathbf{S}_k + \mathbf{S}_k \cdot \mathbf{D}_k \cdot \mathbf{S}_k \quad (2)$$

The exchange coupling tensor can be conventionally decomposed as

$$\mathbf{J}_{ij} = J\mathbf{E} + \mathbf{S}_{ij} + \mathbf{A}_{ij} \quad (3)$$

where  $\mathbf{E}$  is the unit tensor,  $\mathbf{S}_{ij}$  is the symmetric traceless  $(\mathbf{J}_{ij} + \mathbf{J}_{ji})/2 - \text{Tr}(\mathbf{J}_{ij})/3$  tensor,  $\mathbf{A}_{ij}$  is the antisymmetric tensor  $(\mathbf{J}_{ij} - \mathbf{J}_{ji})/2$ , and  $J = \text{Tr}(\mathbf{J}_{ij})/3$  is referred to as the (isotropic) *exchange coupling constant*. A conventional form for (1) is

$$H_{\text{Spin}} = \sum_{i < j} [J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j + \mathbf{d}_{ij} \cdot \mathbf{S}_i \times \mathbf{S}_j + \mathbf{S}_i \cdot \mathbf{D}_{ij} \cdot \mathbf{S}_j] + \sum_k \mu_B \mathbf{B} \cdot \mathbf{g}_k \cdot \mathbf{S}_k + \mathbf{S}_k \cdot \mathbf{D}_k \cdot \mathbf{S}_k \quad (4)$$

The overall exchange interaction is decomposed into the isotropic or Heisenberg–Dirac–vanVleck (HDvV) interaction,<sup>15</sup> the anisotropic interaction, and the antisymmetric or Dzialozhinsky–Moryia interaction,<sup>16</sup> respectively. All of these interactions arise from two main mechanisms: direct *through-space* magnetic interactions and electron–electron (*through-bond*) correlation effects. The first mechanism is small, in transition-metal complexes, and it is often neglected in the calculation of the exchange parameters. It can be modeled as a classical dipolar (the simplest) interaction between localized magnetic moments and has the greatest effect on the anisotropic term. The second mechanism determines the isotropic exchange, which is often the leading term in the SH. Anisotropic and antisymmetric interactions are due to spin–orbit coupling mixing of excited states into

the ground state and are generally much smaller than the HDvV interaction. They influence the magnetic properties only at low temperatures, the antisymmetric interaction being responsible of the spin canting in antiferromagnets.<sup>6</sup> In Hamiltonian (4), the local zero-field splitting terms,  $\mathbf{S}_k \cdot \mathbf{D}_k \cdot \mathbf{S}_k$ , can have a relevant role. Similarly to the anisotropic magnetic interactions, they arise from spin–spin (dipolar) coupling and from spin–orbit coupling effects on each magnetic center and can significantly alter the pattern of the low lying energy levels. In transition-metal complexes the spin–spin interaction is usually much smaller than the spin–orbit coupling. Hamiltonian (2) was derived by the use of second order perturbation theory, higher order perturbations corresponding to term with  $l_S > 4$ .<sup>17</sup>

In many cases, the zero field splitting is smaller than the other terms. This is particularly true in paramagnetic centers with an odd number of electrons, where the time reversal symmetry imposes a Kramers doublet as the ground state (in the absence of external magnetic fields). In magnetic centers with even number of electrons, zero-field splitting effects can be large enough to be observable at high temperatures.<sup>18</sup> First principle calculation of single zero field splitting is a challenging field of research<sup>19</sup> that was up to now mainly confined to Ligand Field Theory.<sup>20</sup>

In a few cases a SH simpler than HDvV can be used to interpret the magnetic properties. This typically occurs in paramagnetic centers with odd electrons, when SOC is dominant in determining the low energy level spectrum of the magnetic centers. In this situation one isolated Kramers doublet can be the ground state. Strong magnetic anisotropy is then present, and the Lenz-Ising model Hamiltonian,<sup>21</sup>  $H_{LI} = \sum_{i < j} J_{ij} \mathbf{S}_{iz} \cdot \mathbf{S}_{jz}$ , can be applied provided that all the matrix elements of the spin–spin coupling operators between the two ground level states of each magnetic center vanish. Examples of *Ising-like* magnets can be typically found among the rare earths compounds<sup>22</sup> like dysprosium ethyl sulfate,  $\text{Dy}(\text{C}_2\text{H}_5\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$ , and in some high spin cobalt(II) linear chain compounds.<sup>23,24</sup>

The commonest way to experimentally determining the SH parameters of a molecular magnet is the fitting of the temperature (and/or magnetic field) dependence of its magnetization. The main computational difficulty is the diagonalization of the SH matrix to obtaining the eigenvectors,<sup>25</sup> since the matrix dimension rapidly grows with the number of magnetic centers of the clusters and their spins. Single ion ZFS and anisotropic or antisymmetric interactions cause smaller effects on the energy spectrum than the isotropic interaction. They produce effects that are measurable only at low temperatures when excited states start to depopulate. These effects are usually better observed with spectroscopies (EPR, Mössbauer) or calorimetric and low temperature magnetization techniques. In the high temperature range, the magnetic properties are therefore mainly influenced by the relative population of the spin multiplets of the cluster. A convenient working formula to compute the magnetic susceptibility of paramagnetic samples is

$$\chi = \frac{N_A g^2 \mu_B^2}{3kT} \frac{\sum_S S(S+1)(2S+1)e^{-E(S)/kT}}{\sum_S (2S+1)e^{-E(S)/kT}} \quad (5)$$

where  $E(S)$  are the eigenvalues of the HDvV SH that depend on the isotropic  $J_{ij}$ 's value. Equation 5 can be fitted to the measured values of  $\chi$ , and the exchange coupling constants can in principle be measured. It has to be mentioned that in deriving eq 5 a  $g$  value common to all the spin states was assumed. This approximation is generally done in order to reduce the number of parameters to fit, and it is generally not further verified. However, it can be argued that  $g$  and  $J$  values are correlated, and a different choice of  $g$  could produce different values of  $J_{ij}$ .

Magnetic anisotropy is anyway an important factor to be explored theoretically. In SMM, for example, high easy-axis anisotropy is required to “block” spontaneous reorientation of the magnetization of the magnetic units. Furthermore, feeble magnetic interactions between adjacent molecules are to be present as a prerequisite to recording magnetic bits independently in each molecule. The modeling of these last interactions and the calculation of SOC effects are challenging fields for the computational chemist.<sup>26</sup>

In the following part of this report we will discuss the mapping of the isotropic part of the HDvV spin Hamiltonian of eq 4 with DFT approaches. Binuclear transition-metal complexes received much attention because DFT allowed the reproduction of experimental data with *semiquantitative* accuracy at the computational cost of few SCF convergences on single Slater determinants. With the term *semiquantitative* we mean that the spin multiplicity of the ground states of the complexes was reproduced, and the energy of the next excited states was found in fair agreement (from a few percent to  $\pm 50\%$ ) with the experimental data. It is quite well established in the literature that the best agreement with the experimental data is reached using the Broken Symmetry (BS) approach, developed by L. Noodleman and J. G. Norman,<sup>27</sup> together with the B3LYP hybrid functional<sup>28</sup> and valence triple- $\zeta$  basis functions. Within the BS approach the energy of the low spin state (pure spin state) of the complex, that is the state mostly affected by static electron correlation effects, is approximately computed as a projection from a state of mixed spin and space symmetry (the BS state) obtained by an independent SCF calculation.<sup>29</sup> Within this formalism, it is, in principle, possible to handle clusters with nuclearity higher than 2. Using the HDvV Hamiltonian of eq 4, the number of independent coupling constants<sup>30</sup> can be  $N(N-1)/2$  unless symmetry is present to reduce this number. It is apparent that, when  $N > 2$ , the system becomes rapidly overparameterized making meaningless any fitting procedure. A magnetic symmetry is always imposed to reduce the number of parameters. It often happens that the data can be fit with different magnetic topologies, since a multiparameter function can have many equivalent minima. The *a priori* calculation of the magnetic structure of high nuclearity clusters appears therefore challenging in order to validate fits of experiments.<sup>31</sup> Application of the BS formalism requires the knowledge of the energies of  $2^N/2$  single Slater determinants, and this task can easily become difficult



for large  $N$ . Three main approximations are therefore usually done in order to limit the computational efforts:

**1. The Model Dimer Approach (MDA).** The magnetic exchange coupling constants are computed on simple binuclear model complexes build up to mimicking the various exchange pathways in the cluster.

**2. The Doped Cluster Approach (DCA).** BS calculations are performed on model clusters in which all the magnetic centers except two have been substituted with diamagnetic ions.

**3. The Minimum Cluster Approach (MCA).** The minimum number of BS determinants (equal to the number of independent magnetic coupling constants required by the symmetry) and the highest spin determinant are computed on the whole cluster.

To the best of our knowledge, no systematic comparison between these different approaches has been yet performed. Since this study is aimed for being of help in choosing the best method of calculation, we check here the validity of the above approaches by computing the magnetic structure of some test systems.

In the following we will first comment on the BS formalism, and later we will present and discuss the magnetic structure of the model tetrahedral system  $(\text{HeH})_4$  and of linear  $[\text{Cu}(\text{II})]_3$  and  $[\text{Mn}(\text{II})]_4$  complexes.

## The Broken Symmetry Formalism

**Binuclear Complexes.** For two interacting magnetic centers with localized spins  $\mathbf{S}_1$  and  $\mathbf{S}_2$ , the HDvV spin Hamiltonian of eq 4 takes the form

$$H_{\text{HDvV}} = J_{12} \mathbf{S}_1 \cdot \mathbf{S}_2 \quad (6)$$

and acts on the  $\{(2S_1+1)(2S_2+1)\}$  dimensional product space  $\{|S_1 m_1\rangle | S_2 m_2\rangle \equiv |S_1 m_1 S_2 m_2\rangle\}$  with  $-S_1 \leq m_1 \leq S_1$  and  $-S_2 \leq m_2 \leq S_2$ . Hamiltonian (6) commutes with  $\mathbf{S}^2$  and  $S_z$ ,  $\mathbf{S} = \mathbf{S}_1 + \mathbf{S}_2$ ; therefore, its eigenvectors can be labeled using the expectation values of  $\mathbf{S}^2$  and  $S_z$ . In order to compute the  $J_{12}$  parameter the energies of all the  $S$  spin multiplets,  $|S_1 - S_2| \leq S \leq S_1 + S_2$ , should be computed at the quantum mechanical level and compared with the eigenstates of (6). Assuming, however, the general validity of (6), only the energies of the highest spin state,  $S_{\text{max}} = S_1 + S_2$ , and of the lowest spin one,  $S_{\text{min}} = |S_1 - S_2|$ , are to be calculated. When the magnetic centers are in the highest spin states (*high spin complexes*), the state corresponding to  $S = S_{\text{max}}$  is usually well described by one single Slater determinant. The state corresponding to  $S = S_{\text{min}} = |S_1 - S_2|$  is, on the contrary, a linear combination of Slater determinants that are eigenstates of  $S_z$  with eigenvalue  $S_{\text{min}}$ . Without spin contamination from excited states the coefficients of this linear combination are the Wigner or Clebsch-Gordon coefficients appearing in the theory of the angular momentum.<sup>27b</sup> It is apparent that the energy of this state can be exactly computed only using multireference SCF approaches. The Difference Dedicated Configuration Interaction (DDCI), developed in the past few years by Malrieu et al.,<sup>32</sup> allowed accurate calculation of the exchange coupling constants in several binuclear transition-metal complexes.<sup>33</sup> Although the configuration space of DDCI is considerably reduced with respect to a full CI

calculation, the applications to clusters with  $N > 2$  are still rare.<sup>34</sup>

Using the DFT approach the calculation of the energy of the  $S = S_{\text{min}}$  state is not possible due to the single-determinant nature of the Kohn–Sham implementation. However, in the spin-polarized or unrestricted formalism, the energy of one single Slater determinant build up with open shell magnetic orbitals localized onto the two magnetic centers and bearing the magnetic electrons with opposite spins can be written as a weighted average of the energies of the pure spin multiplets.<sup>27,29</sup> This determinant, the Broken Symmetry (BS) determinant, is an eigenstate of  $S_z$  with eigenvalue  $M_s = S_1 - S_2$ , and the magnetic coupling constant can be obtained, neglecting the usually small spin contamination of the  $S = S_{\text{max}}$  state, by

$$J_{12} = \frac{E(S_{\text{max}}) - E(\text{BS})}{2S_1 S_2} \quad (7)$$

Equation 7 was originally derived using spin projection operators on the unrestricted BS determinant in the approximation that the  $\alpha$  magnetic orbitals on center 1 and the  $\beta$  magnetic orbitals on center 2 are orthogonal,  $S_{ij}^{\alpha\beta} = 0 \forall (i \in 1, j \in 2)$ , and can be a good approximation when  $(S_{ij}^{\alpha\beta})^2 \ll 1$ .<sup>27b</sup> Application of (7) to a number of transition-metal binuclear complexes, particularly copper(II) complexes, was found to give  $J_{12}$  values larger than the experimental ones, and an alternative formula was used<sup>35</sup> that read

$$J_{12}^{\text{un}} = \frac{E(S_{\text{max}}) - E(\text{BS})}{2S_1 S_2 + S_2} \forall (S_1 \geq S_2) \quad (8)$$

Equation 8 can be derived<sup>27a</sup> by spin projection from the unrestricted BS determinant under the condition  $(S_{ij}^{\alpha\beta})^2 = 1$ . In this case, the BS determinant is also an eigenfunction of  $\mathbf{S}^2$ , that for  $S_1 = S_2$ , corresponds to the singlet state of the complex. Using eq 8 one is assuming that the energy of the BS state computed with DFT is the energy of a pure spin state. We have here indicated the exchange coupling constant  $J_{12}^{\text{un}}$ , *un* meaning *un*-projected formula. This equation was successfully applied in the case of strong covalent bonding interaction between the magnetic centers.<sup>36</sup> It must be stressed that the BS determinant is strongly spin contaminated. For a single Slater determinant built with spatially orthogonal  $\alpha$  and  $\beta$  electrons the expectation value of  $\mathbf{S}^2$  is given by  $(n_\alpha \geq n_\beta)$ :<sup>37</sup>

$$\langle \mathbf{S}^2 \rangle_{\text{SD}} = \left( \frac{n_\alpha - n_\beta}{2} \right)^2 + \left( \frac{n_\alpha + n_\beta}{2} \right) = \langle S_z \rangle^2 + S_{\text{max}} \quad (9)$$

For the BS determinant of two  $S_1 = S_2 = 5/2$  spins this value is  $\langle \mathbf{S}^2 \rangle_{\text{SD}} = 5$ . Comparison with  $\langle \mathbf{S}^2 \rangle$  computed on the unrestricted BS determinant,  $\langle \mathbf{S}^2 \rangle_{\text{BS}}$ , with the value obtained by eq 9 gave an estimate of the deviation from the conditions under which eqs 7 and 8 were derived, i.e. of the overlap between the magnetic orbitals. Equations have been suggested correcting (7) to account for the overlap between the magnetic orbitals through the calculation of  $\langle \mathbf{S}^2 \rangle_{\text{BS}}$  and of  $\langle \mathbf{S}^2 \rangle$  in the high-spin state,  $\langle \mathbf{S}^2 \rangle_{\text{HS}}$ .<sup>38,39,29c</sup> In particular, in the Approximate Projection (AP) method<sup>39</sup> the working equation for the calculation of the exchange coupling constants is

$$J_{12}^{AP} = 2 \frac{E(S_{max}) - E(BS)}{\langle S^2 \rangle_{HS} - \langle S^2 \rangle_{BS}} \quad (10)$$

The use of eq 10 generally gives  $J$  values comprised between  $J_{12}^{un}$  and  $J_{12}$ , only in slight better agreement with experimental findings.

The theoretical foundations of eqs 7 and 8 were subject to some discussions,<sup>40,41</sup> and there is not in the literature a general agreement on their use.<sup>42</sup> In a number of cases a nice agreement with the experimental data was usually reached using eq 8 in conjunction with the B3LYP functional<sup>35</sup> (in some cases a mixing of HF exchange between 33% and 50% was found to give better results<sup>43</sup> than the 20% used by B3LYP), and we in general prefer to adopt the strategy of applying both of the formulas to obtain upper and lower limiting values for  $J_{12}$ .

A generalization<sup>44</sup> of the spin projection approach can be obtained considering that both the high-spin and the unrestricted BS wave functions are eigenstates of  $S_z$ , with eigenvalues  $M_S = S_{max}$  and  $|S_1 - S_2|$ , respectively. A one-to-one correspondence can thus be established between the diagonal elements of  $H_{HDvV}$  (6), on the product basis  $\{|S_1 s_1\rangle |S_2 \pm s_2\rangle \equiv |S_1 s_1 S_2 \pm s_2\rangle\}$ , and the energy of the BS states. The expectation values of (6) coincide with the eigenvalues of the Ising,  $H_{LI}$ , Hamiltonian, and the above procedure is often referred to as the mapping of the unrestricted-BS wave functions with  $H_{LI}$ ,<sup>45</sup> even if this Hamiltonian cannot be applied to describing the magnetic properties of the complex.

**Clusters.** The exchange interactions in a cluster with  $N$  magnetic centers is usually phenomenologically interpreted using the HDvV Hamiltonian of eq 4 including interactions only between adjacent centers, except in the case of linear clusters in which coupling between the terminal atoms is generally included. In the general cases,  $N(N-1)/2$  exchange coupling constants need to be determined. Ovchinnikov and Labanowski<sup>46</sup> developed a spin projection technique to express the energies of the spins states of a cluster as a weighted average of the energy of the highest spin state and those of the unrestricted Slater determinants corresponding to  $M_S = S$  with  $|S_1 - S_2 - \dots - S_N| \leq S < (S_1 + S_2 + S_N)$ . Application of this technique to clusters with  $S_i > 1/2$  easily becomes rather cumbersome. A procedure easier to handle is obtained by mapping the diagonal elements of  $H_{HDvV}$  (or equivalently mapping the eigenvalues of the  $H_{LI}$  Hamiltonian),  $\langle \Pi_i S_i m_i | \sum_{i < j} J_{ij} S_i \cdot S_j | \Pi_j S_j m_j \rangle = \sum_{i < j} J_{ij} m_i m_j$  for  $m_i = \pm s_i$  and  $m_j = \pm s_j$ , to the energies of appropriate BS states, as already done for the binuclear case. At variance with the binuclear case, this mapping cannot now be one-to-one since one has to compute  $N(N-1)/2$  exchange coupling constant and has  $2^N/2$  independent determinants, hence  $2^N - 2/2$  energy differences. For a 4-nuclear cluster, for example, the number of exchange coupling constants is 6 to be obtained by 7 energy differences that become 28 and 127, respectively, for a 8-nuclear system.

The energy of the ket  $|s_{max}\rangle = \Pi_{i < j} |S_i s_i S_j s_j\rangle$  is easily computed as  $E(S_{max}) = \sum_{i < j} J_{ij} s_i s_j$  and the energy difference with a ket,  $|s\rangle$ , with spin projection  $s < s_{max}$  can be written in general form as

$$\Delta E(S_{max} - s) = \sum_{i < j} (2J_{ij} |s_i s_j|) \lambda_{ij} \quad (11)$$

where  $\lambda_{ij} = 0$  if  $s_i$  and  $s_j$  have the same sign in  $|s\rangle$  and 1 otherwise. Equating (11) to the energy differences between the high spin and the BS states with the appropriate value of  $s$  yields all the equations needed to compute the  $J_{ij}$  values, as it will be discussed later.

A number of more complex approaches based on the concept of local spins have been recently proposed to compute the exchange coupling constants in clusters.<sup>47</sup> The results of these procedures are close to those obtained by the above reviewed approaches, and we will not discuss these models any longer in the present paper.

As already found for dinuclear complexes, the application of (11) often results in exchange coupling constants larger than the experimental values. A modified equation in which (8) is used to express the SH energy difference on the left-hand side of (11) has been proposed:<sup>48</sup>

$$\Delta E(S_{max} - s) = \sum_{i < j} J_{ij} (2|s_i s_j| + s_j) \lambda_{ij} \quad (s_i \geq s_j) \quad (12)$$

While (8) can be justified if, for some reason, DFT energies of BS states match those of pure spin multiplets, eq 12 cannot receive this support. In the general case, in fact, the energies of the spin states of a cluster cannot be computed in analytical form since the HDvV SH is not diagonal in the intermediate spin coupling space. Furthermore to any  $s < s_{max}$  a number of different BS determinant can be written that cannot be uniquely assigned to the particular  $S$  state. It is therefore misleading referring to (12) as to the nonprojected formula for clusters,<sup>48</sup> and (12) should be used, if one likes, as some kind of working equation not theoretically justified.

## Benchmark Calculations of the Exchange Coupling Constants

**The H<sub>4</sub>He<sub>4</sub> cluster.** The H–He–H binuclear paramagnetic system has been widely used to test theoretical models of superexchange interaction between two  $S_i = S_j = 1/2$  paramagnetic centers.<sup>49</sup> We have performed calculations on the cubane-like cluster shown in Figure 1 at various H–He distances.

All the adjacent H–He bond distances were kept equal to each other, resulting in a tetrahedral arrangement of the H<sub>4</sub> and He<sub>4</sub> subunits. The spin Hamiltonian describing the magnetic structure of this cluster is

$$H_{Td} = J(S_1 \cdot S_2 + S_1 \cdot S_3 + S_1 \cdot S_4 + S_2 \cdot S_3 + S_2 \cdot S_4 + S_3 \cdot S_4) \quad (13)$$

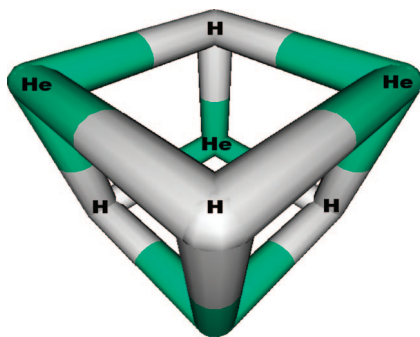
which can be written in the equivalent form

$$H_{Td} = \frac{J}{2}(S^2 - \sum_i S_i^2) \quad (14)$$

The eigenvalues of eq 6 depend only on the total spin  $S$ :

$$E_{Td}(S) = \frac{J}{2}S(S+1) - \frac{3J}{2} \quad (15)$$

Note that the constant term  $-3J/2$  is not important in this framework, since only the energy differences are important.



**Figure 1.** The  $\text{H}_4\text{He}_4$  model cluster.

Application of the BS approach requires the calculations of the unrestricted energies of the 8 Slater determinants shown in the following:<sup>50</sup>

$M_S$	determinant
2	$ HS\rangle =  ++++\rangle$
1	$ IS1\rangle =  -----\rangle$ $ IS2\rangle =  +-+-\rangle$ $ IS3\rangle =  ++--\rangle$ $ IS4\rangle =  +++-\rangle$
0	$ LS1\rangle =  -----\rangle$ $ LS2\rangle =  +-+-\rangle$ $ LS3\rangle =  ++--\rangle$

The intermediate spin,  $IS$ , determinants corresponding to  $M_S = 1$  are obtained from the high spin configuration by one-spin flip. Two-spin flips yielded the low spin determinants,  $LS$ , with  $M_S = 0$ . Using eq 11 we get two equations defining  $J$

$$\Delta E(2-1) = \frac{3J}{2} \quad (16)$$

$$\Delta E(2-0) = 2J \quad (17)$$

that can be used to compute the exchange coupling constant. The results of the DFT calculations for several H–He distances are shown in Table 1. Only for H–He distances larger than 1.5 Å eqs 16 and 17 are simultaneously verified. At shorter distances the  $J$  values computed with these equations,  $J_{2-1}$  and  $J_{2-0}$  respectively, significantly differ from each other. This shows that deviations from the spin ladder required by Hamiltonian (13) can be found. Since at any distance the degeneracy among each of the  $M_S = 1$  and  $M_S = 0$  states, which is expected because the  $T_d$  symmetry of the cluster, is preserved, these deviations cannot be ascribed to inaccuracy of the SCF convergences. It is apparent that the MCA scheme, in which only one of eqs 16 or 17 is used to compute  $J$ , cannot be safely applied in the whole range of bond distances.

**Table 1.** Distance Dependence of the  $J$  Value<sup>a</sup> ( $\text{cm}^{-1}$ ) Computed for the  $\text{H}_4\text{He}_4$  Cluster

$d_{\text{H-He}}$	$J_{2-1}$	$J_{2-0}$	$J_{2-1}J_{2-0}$
5.000	0.10	0.10	0.00
4.000	2.61	2.61	0.00
3.000	36.92	36.89	0.03
2.000	78.09	78.19	−0.01
1.750	43.93	43.94	−0.01
1.625	202.40	201.70	0.71
1.500	854.70	829.60	25.10
1.375	2800.73	2564.65	236.05

<sup>a</sup>  $J_{2-1}$ : value computed through eq 16;  $J_{2-0}$ : value computed through eq 17.

**Table 2.** Distance Dependence of the  $J_{1234}$  Value Computed for the  $\text{H}_4\text{He}_4$  Cluster<sup>a</sup>

$d_{\text{H-He}}$	$J$	$J_{1234}$	$ J_{1234}/J $
5.000	0.10	0.00	0.00
4.000	2.61	0.00	0.00
3.000	36.92	−0.16	0.00
2.000	78.09	0.54	0.01
1.750	43.93	0.06	0.00
1.624	202.40	−3.50	0.02
1.500	854.70	−134.01	0.16
1.375	2800.73	−1259.11	0.45

<sup>a</sup> Since the  $J$  computed with eqs 16 and 17 are fairly consistent up to  $d_{\text{H-He}} = 1.625$  Å (see Table 1), we chose to report the  $J$  computed with only eq 16.  $J_{1234}$  is computed from eq 18.

**Table 3.** Computed Exchange Coupling Constants for  $\text{H}_2\text{He}_2$  (MDA) and  $\text{H}_2\text{He}_6$  (DCA) Model Systems at Several H–He Bond Distances and Comparison with Full Cluster Calculations

	$\text{H}_2\text{He}_2$	$\text{H}_2\text{He}_6$	$\text{H}_4\text{He}_4$
$d_{\text{H-He}}$	$J_{12}^a$	$J_{12}^a$	$J^b$
5.000	0.04	0.09	0.10
4.000	1.29	2.56	2.61
3.000	18.94	37.03	36.92
2.000	42.92	75.94	78.09
1.750	19.69	50.93	43.93
1.625	117.81	249.17	202.40
1.500	557.21	1091.90	854.70
1.375	1935.80	3726.80	2800.73

<sup>a</sup> Computed with eq 7.  $J_{12}^b$  from eq 8 is half of this value.  
<sup>b</sup> Values from Table 2.

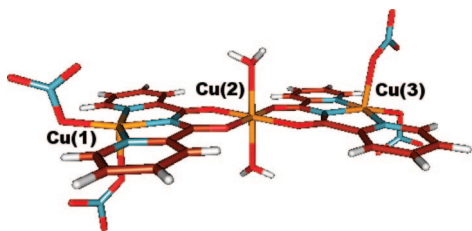
Additional terms that are commonly neglected can be added to the Hamiltonian (13), namely the biquadratic interactions. This can be done with the four-spin biquadratic interaction Hamiltonian<sup>51,52</sup>  $\sum_{ijkl} J_{ijkl}[(\mathbf{S}_i \cdot \mathbf{S}_j)(\mathbf{S}_k \cdot \mathbf{S}_l) + (\mathbf{S}_i \cdot \mathbf{S}_l)(\mathbf{S}_j \cdot \mathbf{S}_k) + (\mathbf{S}_i \cdot \mathbf{S}_k)(\mathbf{S}_j \cdot \mathbf{S}_l)]$ , where the summation runs on the three nuclear configurations invariant in the  $T_d$  symmetry group: the three coupling constants being equal,  $J_{ijkl} = J_{1234} = J_{1423} = J_{1324}$ . Adding this term to eq 13, modifies eq 16 that becomes

$$\Delta(2-1) = \frac{3}{2}J + \frac{3}{8}J_{1234} \quad (18)$$

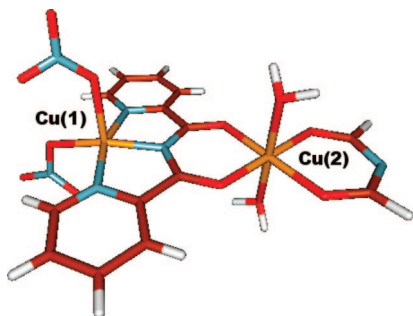
This spin ladder can be matched exactly with the parameters shown in Table 2. The exchange interaction is antiferromagnetic in the whole range of distances, and  $J$  increases on decreasing the H–He distance. The four-spin biquadratic exchange increases upon shortening the bond and can be as large as 45% of  $J$ .

In order to look at the performances of the model dimer, MDA, and doped cluster, DCA, approaches, we performed DFT calculations on the binuclear model system  $\text{H}_2\text{He}_2$  (MDA) and on the model cluster  $\text{H}_2\text{He}_6$  (DCA). The results of the calculations are summarized in Table 3. The computed exchange coupling constants are all positive (antiferromagnetic interaction) independently on the approximation in use, but it appears that DCA is closer to the full cluster calculation. For H–He distances shorter than 1.65 Å also the DCA results significantly deviates from the full clusters results. This can be attributed to the increasing importance of the four-center biquadratic exchange interaction and/or





**Figure 2.** Molecular structure of the  $[\text{Cu}(\text{bpca})_2(\text{H}_2\text{O})_2\{\text{Cu}(\text{NO}_3)_2\}_2]$  cluster (bpca = bis(2-pyridylcarbonyl)amine).



**Figure 3.** Dinuclear model of  $[\text{Cu}(\text{bpca})_2(\text{H}_2\text{O})_2\{\text{Cu}(\text{NO}_3)_2\}_2]$  used in the MDA calculations.

some polarization effects not accounted in the DCA. The computed values of  $\langle S^2 \rangle$  for the high spin state in the MDA and DCA is  $\langle S^2 \rangle_1 = 2.00$  independent of the H–He distance, showing that no appreciable spin contamination due to the unrestricted nature of the wave function is present, a result commonly found in DFT. The corresponding values for the BS state deviate from the value 1 expected from eq 9 below  $d_{\text{H-He}} = 1.75$  Å. The corresponding values for  $d_{\text{H-He}} = 1.625$ , 1.50, and 1.375 Å are  $\langle S^2 \rangle_0 = 0.99$ , 0.97, 0.89, respectively. Application of eq 10 does not significantly ameliorate the agreement between the DCA results and the full cluster calculations.

**Linear Three Spins: The  $[\text{Cu}(\text{bpca})_2(\text{H}_2\text{O})_2\{\text{Cu}(\text{NO}_3)_2\}_2]$  Complex (bpca = bis(2-pyridylcarbonyl)amine).** The magnetic properties of the trinuclear  $[\text{Cu}(\text{bpca})_2(\text{H}_2\text{O})_2\{\text{Cu}(\text{NO}_3)_2\}_2]$  complex<sup>53</sup> were satisfactorily interpreted using the spin Hamiltonian

$$H_{123} = J_{12}(\mathbf{S}_1 \cdot \mathbf{S}_2 + \mathbf{S}_2 \cdot \mathbf{S}_3) + J_{13}(\mathbf{S}_1 \cdot \mathbf{S}_3) \quad (19)$$

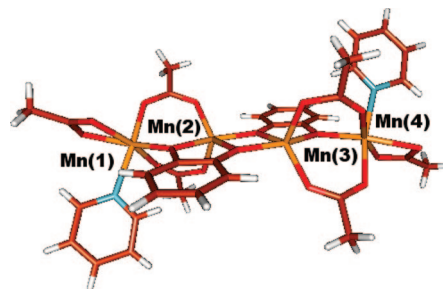
that takes into account the crystallographic  $C_i$  symmetry of the molecule ( $J_{12} = J_{23}$ ), following the atom numbering indicated in Figure 2. Calculation of the exchange coupling constants was performed in the model dimer approach (MDA) using the model dimer shown in Figure 3, in which one bpca ligand was substituted by one N-formylimidoformate molecule.

The doped cluster approach (DCA) was applied by substituting one  $\text{Cu}^{\text{II}}$  ion with one  $\text{Zn}^{\text{II}}$  ion in turn in the structure of Figure 2. Two symmetry independent doped clusters models were obtained indicated as  $\text{Cu}(1)\text{Cu}(2)\text{Zn}$  and  $\text{Cu}(1)\text{ZnCu}(3)$ . Due to the crystallographic  $C_i$  symmetry, only two BS determinant with  $M_S = 1/2$ , namely  $|BSI\rangle = |+-+ \rangle$  and  $|BSI\rangle = |++- \rangle$ ,<sup>50</sup> are required to compute the  $J_{ij}$  values of the whole cluster. In this case, therefore, the whole cluster approach (WCA) and the minimum cluster approach (MCA)

**Table 4.** Computed  $J_{12}$  and  $J_{13}$  Values ( $\text{cm}^{-1}$ ) with Different Approaches

	$J_{12}$	$J_{13}$
MDA <sup>a</sup>	−25.0 (−12.5; −25.0)	—
DCA <sup>a</sup>	−29.0 (−14.5; −29.0)	−5.71 (−2.85; −5.66)
WCA	−50.7	7.68
exp.	−14.1	5.7

<sup>a</sup> Computed with eq 7. The values reported in parentheses were computed with eq 8 for  $J_{12}^{\text{M}}$  and eq 10 for  $J_{12}^{\text{AP}}$ , respectively.



**Figure 4.** Molecular structure of the  $[\text{Mn}_4(\text{OAc})_6(\text{py})_2(\text{cat})_2]^{2-}$  cluster anion.

are identical. The relevant equations to be used in this approach follow from eq 11 as

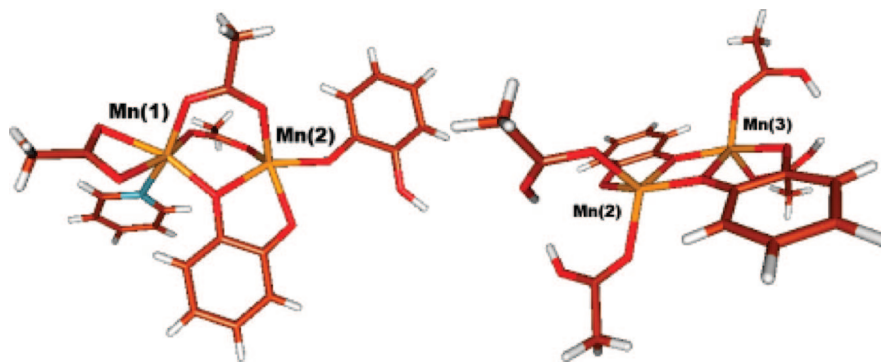
$$\Delta E\left(\frac{3}{2} - BS_1\right) = J_{12}; \Delta E\left(\frac{3}{2} - BS_2\right) = \frac{J_{12} + J_{13}}{2} \quad (20)$$

The  $J_{ij}$  values computed with the different approaches are reported in Table 4 and compared to the experimental findings. The close match between  $J_{12}$  and  $J_{12}^{\text{AP}}$  is due to the fact that  $\langle S^2 \rangle_{\text{BS}}$  and  $\langle S^2 \rangle_{\text{HS}}$  were computed very close to the theoretical values of 1.0 and 2.0, respectively. This shows that the BS state is a equal mixture of the singlet and triplet state, as expected in the weak covalent limit, and that the spin contamination of the triplet state is negligible.

$J_{12}^{\text{M}}$  in MDA and DCA closely match the experimental  $J_{12}$  value, as already often found for other  $\text{Cu}(\text{II})$  complexes, but the value of  $J_{13}$  is uncorrectly reproduced by DCA. The WCA calculations reproduced the alternation in sign of the  $J$ 's value, but  $|J_{12}|$  is quite far from the experiment.

**Linear Four Spins: The  $[\text{Mn}_4(\text{OAc})_6(\text{py})_2(\text{cat})_2]^{2-}$  (OAc = acetate, py = pyridine, cat = catecholate dianion) Complex.** This cluster is one of the few linear clusters containing high-spin  $\text{Mn}(\text{II})$  ions. This system seemed therefore particularly useful to test the consistency of different computational approaches since high spin  $\text{Mn}(\text{II})$  has an orbitally nondegenerate ground state,  ${}^6A_1$ , that is also the only possible sextet state. This fact minimizes the effects of spin–orbit coupling and assures that the ground-state can be described with one Slater determinant. The linear geometry renders the various coupling constants different from each other, and large relative deviations are expected. The magnetic properties of this compound have not yet been measured; therefore, comparison with experiment will not be possible.

The molecular structure of the cluster<sup>54</sup> is schematically shown in Figure 4 together with the numbering scheme of



**Figure 5.** Dinuclear models of  $[\text{Mn}_4(\text{OAc})_6(\text{py})_2(\text{cat})_2]^{2-}$  used in the MDA calculations.

the Mn(II) atoms. Since the molecule is centrosymmetric, the appropriate spin Hamiltonian is

$$H_{1234} = J_{12}(\mathbf{S}_1 \cdot \mathbf{S}_2 + \mathbf{S}_3 \cdot \mathbf{S}_4) + J_{23}(\mathbf{S}_2 \cdot \mathbf{S}_3) + J_{13}(\mathbf{S}_1 \cdot \mathbf{S}_3 + \mathbf{S}_2 \cdot \mathbf{S}_4) + J_{14}(\mathbf{S}_1 \cdot \mathbf{S}_4) \quad (21)$$

The 8 possible Slater determinants take the form shown in the following:<sup>50</sup>

$M_S$	determinant
10	$ HS\rangle =  ++++\rangle$
5	$ IS1\rangle =  +-++\rangle$ $ IS2\rangle =  -+++\rangle$ $ IS3\rangle =  ++-+\rangle$ $ IS4\rangle =  +++-\rangle$
0	$ LS1\rangle =  --++\rangle$ $ LS2\rangle =  -+-+\rangle$ $ LS3\rangle =  +-+--\rangle$

The energies of the intermediate spin states were found to be degenerate in couples according to the  $C_i$  symmetry of the complexes; therefore,  $E(IS1) = E(IS4)$  and  $E(IS2) = E(IS3)$ , leaving 5 independent energy differences to compute the 4 spin Hamiltonian parameters. The relevant equations, obtained by application of eq 11, are shown in Table 5 together with the computed DFT energy differences.

In the MDA, the dimers shown in Figure 5 were used. The exchange between Mn(1) and Mn(2) (equal to that between Mn(3) and Mn(4)) is propagated by two  $\mu_2\text{-OAc}^-$  ions and one  $\mu_1\text{-Cat}^{2-}$  ion (Figure 5 left); the model dimer for this interaction being  $[\text{Mn}_2(\text{OAc})_3(\text{py})(\text{Cat})(\text{CatH})]^{2-}$ . The second exchange pathway, between Mn(3) and Mn(4), is due to two bridging  $\mu_1\text{-Cat}^{2-}$  ions (Figure 5 right) and is modeled by the  $[\text{Mn}_2(\text{HOAc})_4(\text{Cat})_2]$  dimer.

In the DCA, four model dinuclear species were obtained by substituting two Mn(II) centers with diamagnetic Sn(II): MnMnSnSn, SnMnMnSn, MnSnMnSn, and MnSnSnMn. They permit the DCA calculation of  $J_{12}$ ,  $J_{23}$ ,  $J_{13}$ , and  $J_{14}$ , respectively.

WCA and MCA calculations were performed on the structure shown in Figure 4. In the Minimum Cluster Approach we need to choose 4 equations among the 5 possibilities shown in Table 5. This leads to 5 sets of equations that can be solved separately yielding 5 sets of possible  $J_{ij}$  values. If the system were exact, the five sets of solutions would be identical and equal to the WCA calculation. The results of the calculations are collected in Table 6.

WCA calculations are customarily performed assuming *a priori* the magnetic spin topology in order to reduce the number of exchange coupling constants, and, hence, the number of BS states, to be computed. In the general

**Table 5.** Energy Differences Used To Compute the Exchange Coupling Constants for  $[\text{Mn}_4(\text{OAc})_6(\text{py})_2(\text{cat})_2]^{2-}$

$E(\text{HS})-E(\text{X})$	$J_{12}$	$J_{23}$	$J_{13}$	$J_{14}$	$\Delta E$ ( $\text{cm}^{-1}$ )
IS1	25/2		25/2	25/2	603.8
IS2	25/2	25/2	25/2		530.0
LS1	25		25		1191.7
LS2	25	25/2		25/2	1123.7
LS3		25/2	25	25/2	-65.6

**Table 6.**  $J_{ij}$  Values ( $\text{cm}^{-1}$ ) of  $[\text{Mn}_4(\text{OAc})_6(\text{py})_2(\text{cat})_2]^{2-}$  Computed with MCA<sup>a</sup> Using Different Sets of BS States<sup>a</sup>

set	1	2	3	4	5
$J_{12}$	47.26	48.0	48.0	47.62	47.68
$J_{23}$	-5.27	-5.27	-5.98	-5.98	-5.27
$J_{13}$	0.40	-0.31	0.40	0.05	0.05
$J_{14}$	0.64	0.64	-0.08	0.64	-0.08

<sup>a</sup> The different MCA sets were obtained with the equations  $E(\text{HS})-E(\text{X})$  (see Table 6) with X: set 1 =  $\{IS1, IS2, LS1, LS2\}$ ; set 2 =  $\{IS1, IS2, LS1, LS3\}$ ; set 3 =  $\{IS1, IS2, LS2, LS3\}$ ; set 4 =  $\{IS1, LS1, LS2, LS3\}$ ; set 5 =  $\{IS2, LS1, LS2, LS3\}$ .

cases, it is impossible to determine the cluster's spin topology from experiments, due to overparameterization problems, and theoretical tools are mandatory to meaningfully solve the problem. This can be achieved, within DFT, by applying a procedure previously described<sup>55</sup> that consists in computing all the  $m$  energy differences between the high spin states and the possible BS determinants,  $\Delta E^{\text{DFT}}(S_{\text{max}}-s)$ ; building up a system of equations using (11); extracting the  $\{J_{ij}\}$  set that minimizes the test function  $f = \sum_s [\Delta E^{\text{DFT}}(S_{\text{max}}-s) - \Delta E(S_{\text{max}}-s)]^2$ , being 0 in the case of a perfect match between the SH expectation values and the BS energies.<sup>56</sup> From this procedure one obtains the  $J_{ij}$  values that best fit the DFT energies, together with their standard deviations. It is computationally heavy to applying this formalism to large clusters and a simplified procedure, in which only one subset of all the possible BS energies is evaluated, was applied.<sup>57,58</sup>

For the linear  $\text{Mn}_4$  cluster the spin topology one can assume is obtained neglecting  $J_{13}$  and  $J_{14}$  in (21), and we can check here the quality of this approximation. We have therefore 5 energy differences that can be used to computing up to a maximum of 4 exchange coupling constants. The results of the calculations are reported in Table 7. As expected,  $J_{12}$  and  $J_{23}$  are larger than the other two coupling constants. The inclusion of  $J_{13}$  and  $J_{14}$  in turn into the fitting procedure causes  $f$  to decrease without significantly altering the  $J_{12}$  and  $J_{23}$  values that average to  $47.7 \text{ cm}^{-1}$  and  $-5.5$



**Table 7.**  $J_{ij}$  Values<sup>a</sup> (cm<sup>-1</sup>) of [Mn<sub>4</sub>(OAc)<sub>6</sub>(py)<sub>2</sub>(cat)<sub>2</sub>]<sup>2-</sup> Computed with WCA with the Different Spin Hamiltonian Topologies<sup>b</sup>

$J_{12}$	$J_{23}$	$J_{13}$	$J_{14}$	$f$
47.73(2)	-5.38(6)	—	—	62.3
47.68(3)	-5.45(9)	0.11(3)	—	51.2
47.65(3)	-5.6(1)	0.08(3)	0.3(1)	28.1

<sup>a</sup>  $f = \sum_s [\Delta E^{\text{DFT}}(S_{\text{max}} - s) - \Delta E(S_{\text{max}} - s)]^2$ , see text. Standard deviations are shown in parentheses. <sup>b</sup> i.e. number of different  $J$ s taken into consideration in the SH.

cm<sup>-1</sup> respectively. It has to be noted that even in the fit with all the four parameters  $f$  is still different from 0 (28.8 cm<sup>-1</sup>).

In Table 8 a comparison between the  $J$  values computed at the different level of approximation is presented. In all the calculations  $J_{12}$  is the leading antiferromagnetic interaction, except when the DCA is applied. In this latter case  $J_{14}$  is the greatest term of the SH. This result is, of course, wrong and shows that the diamagnetic metal ions can be noninnocent partners in transmitting the superexchange interactions. The MDA results do not reproduce the sign alternation between  $J_{12}$  and  $J_{23}$  computed with WCA. MCA calculations are dependent on the chosen BS set (Table 7); in any case  $J_{12}$  and  $J_{23}$  compare well with the values obtained with WCA, and differences are seen only on the  $J_{13}$  and  $J_{14}$  values. Test calculations on systems with larger  $J$  values than the present ones must be performed in order to check if this is a general trend. Other spin topologies than the linear one also have to be checked in order to be able to generalize these results.

In the WCA calculations the match between DFT and SH energies is not perfect even if SH is considered with all the parameters free. This fact can be due to an internal inconsistency of the BS approach or to the inadequacy of the SH in the form given in eq 21. As already done for the H<sub>4</sub>He<sub>4</sub> model system, higher order (biquadratic) terms can be added to (21). These terms can be two-centers or four-centers that in  $C_i$  symmetry become

$$H_{bq}^2 = j_{12}[(\mathbf{S}_1 \cdot \mathbf{S}_2)^2 + (\mathbf{S}_3 \cdot \mathbf{S}_4)^2] + j_{23}(\mathbf{S}_2 \cdot \mathbf{S}_3)^2 + j_{13}[(\mathbf{S}_1 \cdot \mathbf{S}_3)^2 + (\mathbf{S}_2 \cdot \mathbf{S}_4)^2] + j_{14}(\mathbf{S}_1 \cdot \mathbf{S}_4)^2 \quad (22)$$

and

$$H_{bq}^4 = J_{1234}(\mathbf{S}_1 \cdot \mathbf{S}_2)(\mathbf{S}_3 \cdot \mathbf{S}_4) \quad (23)$$

The effect of these terms on the energies of the cluster can cause deviations from the HDvV behavior. Within the BS formalism it would be impossible to handle with these effects since the number of parameters easily exceed the number of available BS energies. The calculation of the energies of the spin states, which requires MR-CI approaches, is needed for an evaluation of the importance of these interactions.<sup>59</sup> However it is important to note that eq 22 only adds a

constant term,  $j_{bq} = (625/16)[2j_{12} + j_{23} + 2j_{13} + j_{14}]$ , to the diagonal elements of the HDvV matrix and does not contribute to the energy differences of Table 5. Therefore the effect of  $H_{bq}^2$  cannot be extracted from BS calculations. The expectation value of  $H_{bq}^4$  is nonzero only for the  $|IS| >$  and  $|IS2 >$  states, whose relative energies in Table 5 must be modified adding  $25j_{1234}/8$ . Inserting this new parameter, the relative energies of Table 5 can be reproduced with  $J_{12} = 47.62$  cm<sup>-1</sup>,  $J_{23} = -6.6$  cm<sup>-1</sup>,  $J_{13} = 0.05$  cm<sup>-1</sup>,  $J_{14} = 0.3$  cm<sup>-1</sup>, and  $J_{1234} = 1.4$  cm<sup>-1</sup>.

## Computational Details

Calculations have been performed using the NWCHEM 5.0 program package, as developed and distributed by Pacific Northwest National Laboratory, P.O. Box 999, Richland, WA 99352 U.S.A., and funded by the U.S. Department of Energy.<sup>60</sup> 6-311G\*\* basis sets<sup>61</sup> were applied to H and He atoms for the calculations on the model (HeH)<sub>4</sub> cluster. LANL2DZ Gaussian basis set<sup>62</sup> with their correspondent LANL2 pseudopotential were used for calculations on [Cu(bpca)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>{Cu(NO<sub>3</sub>)<sub>2</sub>}]<sub>2</sub> except for H atoms to which a 31G basis was applied. All electron Ahlrichs TZV basis sets<sup>63</sup> were used for the Mn cluster calculations except for H atoms to which a 311G basis was applied. All the basis sets came with the NWCHEM package. The hybrid B3LYP functional,<sup>28</sup> as implemented in NWCHEM 5.0, was used in all cases. The grid parameter was set to xfine, and the energies converged to 10<sup>-8</sup> hartree.

## Concluding Remarks

We have shown that the BS formalism give an internally consistent set of equations that can be used to determine the topology of the magnetic interactions in paramagnetic transition-metal clusters. Solving the whole set of BS equations allows the calculation of the exchange coupling parameters avoiding the indetermination that can be caused by an *a priori* choice of one particular subset, and the uncertainties on the computed values can be estimated from the least-squares fitting procedure. At least for the cases we computed here, these uncertainties arise from higher order terms that are not included in the HDvV spin Hamiltonian. BS formalism cannot be used to compute the biquadratic two-centers terms since their diagonal contributions in the spin Hamiltonian matrix is a constant but can be used to estimating the three and four center contributions.

We have seen that application of the BS formalism requires independent SCF convergences on several Slater determinants corresponding to the possible distributions of spin densities on the magnetic center. These convergences are prone to instability, and some criteria should be followed to

**Table 8.** Comparison between  $J_{ij}$  Values (cm<sup>-1</sup>) Computed for [Mn<sub>4</sub>(OAc)<sub>6</sub>(py)<sub>2</sub>(cat)<sub>2</sub>]<sup>2-</sup> with MDA, DCA, MCA, and WCA

calculation model	$J_{12}$	$J_{23}$	$J_{13}$	$J_{14}$
MDA <sup>b</sup>	53.8(44.8;53.7)	19.2(16.0;19.2)	—	—
DCA <sup>b</sup>	33.1(27.6;33.1)	35.0(28.3;35.2)	14.1(11.7;14.0)	72.9(60.7;72.8)
MCA <sup>a</sup>	47.26	-5.3	0.4	0.6
WCA	47.65(3)	-5.6(1)	0.08(3)	0.3(1)

<sup>a</sup> Set 1 was chosen among the results shown in Table 6. <sup>b</sup> Computed with eq 7. The values reported in parentheses are  $J_{12}^P$  and  $J_{13}^P$ , respectively (see eqs 8 and 10).

being sure that the correct solution is found. Often a number of orbitals are close in energy in the SOMO-LUMO region. Visual inspection of the magnetic orbitals is possible only when their number is limited; this was not easily possible already for the  $\text{Mn}_4$  cluster. Here we choose the quality of a SCF convergence looking at the spin density (Mulliken and/or Löwdin) of the metals and at the value of  $\langle S^2 \rangle_{BS}$  and  $\langle S^2 \rangle_{HS}$ . The computed values of the spin densities and of the expectation values of  $S^2$  for  $[\text{Cu}(\text{bpca})_2(\text{H}_2\text{O})_2\{\text{Cu}(\text{NO}_3)_2\}_2]$  and  $[\text{Mn}_4(\text{OAc})_6(\text{py})_2(\text{cat})_2]^{2-}$  are reported in Tables S1–S4. For Cu(II) spin densities were found to vary between 0.60 au to 0.66 au to be compared with the fully localized value of 1; for the Mn(II) complex spin densities were found to vary between 4.58 au and 4.67 au against a fully localized value of 5. The use of the WCA permits also the judging about the correctness of the SCF convergence, since we have found that when an incorrect energy is introduced into the BS set of equations a large error (hundreds of wavenumbers) is usually computed in the least-squares procedure.

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**Supporting Information Available:** MDA copper spin densities (SD) and  $\langle S^2 \rangle$  values for  $[\text{Cu}(\text{bpca})_2(\text{H}_2\text{O})_2\{\text{Cu}(\text{NO}_3)_2\}_2]$  (Table S1); DCA copper/zinc atoms spin densities (SD) and  $\langle S^2 \rangle$  values for  $[\text{Cu}(\text{bpca})_2(\text{H}_2\text{O})_2\{\text{Cu}(\text{NO}_3)_2\}_2]$  (Table S2); MDA manganese/tin atoms spin densities (SD) and  $\langle S^2 \rangle$  value for  $[\text{Mn}_4(\text{OAc})_6(\text{py})_2(\text{cat})_2]^{2-}$  (Table S3); and DCA manganese/tin atoms spin densities (SD) and  $\langle S^2 \rangle$  values for  $[\text{Mn}_4(\text{OAc})_6(\text{py})_2(\text{cat})_2]^{2-}$  (Table S4). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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