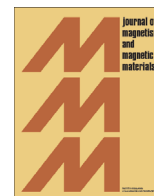




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## Heisenberg coupling constant predicted for molecular magnets with pairwise spin-contamination correction

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## ABSTRACT

New method to eliminate the spin-contamination in broken symmetry density functional theory (BS DFT) calculations is introduced. Unlike conventional spin-purification correction, this method is based on canonical Natural Orbitals (NO) for each high/low spin coupled electron pair. We derive an expression to extract the energy of the pure singlet state given in terms of energy of BS DFT solution, the occupation number of the bonding NO, and the energy of the higher spin state built on these bonding and antibonding NOs (not self-consistent Kohn–Sham orbitals of the high spin state). Compared to the other spin-contamination correction schemes, spin-correction is applied to each correlated electron pair individually. We investigate two binuclear Mn(IV) molecular magnets using this pairwise correction. While one of the molecules is described by magnetic orbitals strongly localized on the metal centers, and spin gap is accurately predicted by Noodleman and Yamaguchi schemes, for the other one the gap is predicted poorly by these schemes due to strong delocalization of the magnetic orbitals onto the ligands. We show our new correction to yield more accurate results in both cases.

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## 1. Introduction

Single molecule magnets (SMMs) are promising candidates for the implementation of quantum computing [1–3], data storage, and spintronics [4–10]. Numerous new SMMs have been reported with a wide variety of topologies and nuclearities, incorporating a variety of transition metal atoms. A majority of molecules demonstrating SMM behavior have been synthesized using manganese, iron or nickel. Examples include Mn<sub>12</sub> magnetic wheels like [Mn<sub>12</sub>O<sub>12</sub>(O<sub>2</sub>CCH<sub>2</sub>Bu<sup>t</sup>)<sub>16</sub>(H<sub>2</sub>O)<sub>4</sub>] with  $S=8$  [11] and [Mn<sub>12</sub>O<sub>12</sub>(O<sub>2</sub>CCHCl<sub>2</sub>)<sub>8</sub>(O<sub>2</sub>CCH<sub>2</sub>Bu<sup>t</sup>)<sub>8</sub>(H<sub>2</sub>O)<sub>3</sub>], with  $S=10$  [12] ground state. Another SMM complex with Jahn–Teller isomerism is [Mn<sub>12</sub>O<sub>12</sub>(O<sub>2</sub>CC<sub>6</sub>H<sub>4</sub>–2–CH<sub>3</sub>)<sub>16</sub>(H<sub>2</sub>O)<sub>4</sub>]·CH<sub>2</sub>Cl<sub>2</sub>·2H<sub>2</sub>O that was reported by Rumberger et al. [13]. Other topologies seen in SMMs include Mn<sub>4</sub> dicubane [14] and the Mn<sub>4</sub> cubane [15] complexes, and rod-shaped Mn<sub>6</sub> clusters. One-dimensional chains of weakly interacting SMMs are also known, such as the complex [Mn<sub>4</sub>(hmp)<sub>6</sub>Cl<sub>2</sub>]<sub>n</sub>(ClO<sub>4</sub>)<sub>2n</sub>, reported by Yoo et al. [16]. Smaller

molecular wheels include [Mn<sub>4</sub>(anca)<sub>4</sub>(Htea)<sub>2</sub>(dbm)<sub>2</sub>]·2.5Et<sub>2</sub>O [17], while larger wheels include Mn<sub>24</sub> one, which consists of eighteen Mn(III) ions and six Mn(IV) ions [18].

Due to the size of these systems, spin-polarized or unrestricted Kohn–Sham formalism, known as broken symmetry Density Functional Theory (BS DFT) is the only first-principle method capable to describe their electronic structure. DFT is widely used to make accurate prediction of structure and properties for the molecules and solids, including aggregation and crystallization, [19–22] and their emission fingerprints [23], reaction mechanisms and reaction rates [24–26], linear and non-linear optical properties [27–30]. However, conceptual disadvantage of BS DFT approach is that spin-polarized Slater determinant no longer is an eigenfunction of the spin operator. The average value of  $\langle \hat{S}^2 \rangle$  is not equal to the correct value of  $S_z(S_z + 1)$  (here  $S_z$  is  $\frac{1}{2}$  of the difference in total numbers of  $\alpha$  and  $\beta$  electrons) [31]. This situation is known as spin contamination, and  $\langle \hat{S}^2 \rangle$  is often used as its measure. The common rule [32] is to neglect spin contamination if  $\langle \hat{S}^2 \rangle$  differs from  $S_z(S_z + 1)$  by less than 10%. Due to of spin contamination, spin density becomes incorrect, electron energy deviates from that of the pure spin state, and molecular geometry may be distorted toward the diradical one. Some researchers argue that despite this incorrect spin-density, the total density and electron energy in BS DFT are

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predicted correctly [33]. Hence, the phenomenon of spin-contamination should be ignored. In fact, spin energy gap, predicted with BS DFT, can be found in a reasonable agreement with experimental values [34,35]. Other researchers, however, recognize spin contamination as a problem affecting the energy. Possible solutions to spin contamination problem include constrained DFT [36,37] and spin purification schemes [38,39], discussed below.

Heisenberg exchange coupling constant  $J$  is often used to describe the difference in energy between the low and the high spin state. Positive value of  $J$  corresponds to ferromagnetic, and negative value corresponds to anti-ferromagnetic coupling. Since BS DFT does not produce the energies of the pure spin states, the expression for  $J$  must account for spin contamination. The following expressions had been suggested for this purpose [40–44]:

$$J_1 = \frac{(E_{BS} - E_T)}{S_{\max}^2}, \quad (1)$$

$$J_2 = \frac{(E_{BS} - E_T)}{S_{\max}(S_{\max} + 1)} \quad (2)$$

$$J_3 = \frac{(E_{BS} - E_T)}{\langle S^2 \rangle_T - \langle S^2 \rangle_{BS}} \quad (3)$$

Of these three,  $J_3$  suggested by Yamaguchi [45,46] can be reduced to  $J_1$  and  $J_2$  in the weak and strong coupling limits, respectively. Here  $E_{BS}$  is the energy of the low-spin unrestricted Kohn–Sham (KS) determinant,  $E_T$  is the energy of the high-spin KS determinant,  $\langle S^2 \rangle_{BS}$  and  $\langle S^2 \rangle_T$  are average values of the respective operators, and  $S_{\max}$  is high-spin value for the operator  $S_z$ .

A more complicated expressions for variable spin-correction, including dependence of  $J$  on the overlap between corresponding spin polarized orbitals  $p$  and  $q$  were also derived recently [47,48]. Taking the orbital overlap into account resulted in more accurate  $J$  values for  $\text{Cu}^{2+}$  binuclear complexes [48,49]. However, this variable spin-correction approach had not been applied to systems with two or more correlated electron pairs. In this contribution we derive the new approach to spin contamination correction, and apply it to study two examples of binuclear molecular magnets.

## 2. Theoretical derivation

Here we propose an alternative approach to variable spin-correction, based on canonical Natural Orbitals (NO) [50]. First, let us consider a diatomic system AB with one correlated electron pair, such as stretched  $\text{H}_2$  molecule. We assume that restricted Kohn–Sham formalism yields higher energy for this system than unrestricted one, as the case of  $\text{H}_2$  molecule far from equilibrium. Unrestricted KS description produces the natural orbitals  $a, b$  as eigenvectors of the total density matrix with the orbital occupation numbers  $n_a, n_b$  as corresponding eigenvalues. We further assume that  $n_a < n_b$  which means that orbital  $a$  is antibonding, and orbital  $b$  is bonding NO. They are symmetry-adapted ( $a$  is  $\Sigma_u$  and  $b$  is  $\Sigma_g$  in case of  $\text{H}_2$  molecule). Corresponding spin-polarized broken symmetry orbitals  $p, q$  can be expressed [51] as a linear combination of  $a$  and  $b$  using polarization parameter  $\lambda$ :

$$p = \frac{1}{\sqrt{1 + \lambda^2}}(b + \lambda a); \quad q = \frac{1}{\sqrt{1 + \lambda^2}}(b - \lambda a) \quad (4)$$

This parameter is determined by the occupation numbers  $n_a$  and  $n_b$  as shown below. If alpha and beta electrons are localized on different parts of the molecule and do not overlap, the polarization parameter become unity and we arrive to Noodleman's weak interaction limit. In the general case of many-electron system the

orbitals of the alpha set, besides being orthogonal to each other, are also orthogonal to the orbitals of the beta set for a single excitation of the corresponding beta orbital. The spin polarized orbitals obtained with the most standard quantum chemistry codes do not possess this property, which is why one has to produce the corresponding spin-polarized orbitals from NOs. One can express the BS solution in terms of pure spin states S and T as flows. First, BS can be written as the Slater determinant in the basis of these corresponding orbitals and their spin components  $\alpha$  and  $\beta$  as:

$$BS = 1/\sqrt{2} \|p_\alpha q_\beta\| = \frac{1}{\sqrt{2}} \|p_{1\alpha} p_{2\alpha} q_{1\beta} q_{2\beta}\| \quad (5)$$

Substitution of the corresponding orbitals from Eq.(4) into Eq. (5) separates the pure singlet and triplet components:

$$BS = \frac{1}{\sqrt{2}} \|p_{1\alpha} p_{2\alpha} q_{1\beta} q_{2\beta}\| = \frac{1}{(1 + \lambda^2)} S + \frac{\lambda}{(1 + \lambda^2)} T \quad (6)$$

$$= \frac{1}{(1 + \lambda^2)} (b_1 b_2 - \lambda^2 a_1 a_2) \frac{\alpha_1 \beta_2 - \beta_1 \alpha_2}{\sqrt{2}} + \frac{\lambda}{(1 + \lambda^2)} (a_1 b_2 - b_1 a_2) \frac{\alpha_1 \beta_2 + \beta_1 \alpha_2}{\sqrt{2}}. \quad (7)$$

Here indexes 1 and 2 mark coordinates of the electrons. The first term in this expression contains the linear combination of the two closed-shell singlets, the lower closed shell singlet  $S_1$ :

$$S_1 = b_1 b_2 \frac{\alpha_1 \beta_2 - \beta_1 \alpha_2}{\sqrt{2}} \quad (8)$$

and the higher closed shell singlet  $S_2$ :

$$S_2 = a_1 a_2 \frac{\alpha_1 \beta_2 - \beta_1 \alpha_2}{\sqrt{2}} \quad (9)$$

while the second term is proportional to one of the possible triplet states:  $T = T_0 \sqrt{2}$ ,

$$T_0 = \frac{(a_1 b_2 - b_1 a_2) \alpha_1 \beta_2 + \beta_1 \alpha_2}{\sqrt{2}} \quad (10)$$

This triplet component of BS is the reason why BS DFT solution is spin contaminated. Therefore, we are looking to extract the energy of the singlet term from BS energy  $E_{BS}$  using the energy of the triplet. The expectation value of Kohn–Sham operator  $\hat{H}$  then becomes,

$$E_{BS} = \langle BS | \hat{H} | BS \rangle = \frac{1}{(1 + \lambda^2)^2} + \langle S | \hat{H} | S \rangle + \frac{\lambda^2}{(1 + \lambda^2)^2} \langle T | \hat{H} | T \rangle + \frac{\lambda}{(1 + \lambda^2)^2} (\langle S | \hat{H} | T \rangle + \langle T | \hat{H} | S \rangle) \quad (11)$$

The last two terms in Eq. (11) vanish out due to orthogonality of S and T states, introduced in Eq. (6). Using normalization condition and substituting the Eq. (12) into Eq. (6) one can obtain:

$$\langle S | S \rangle = \langle b_1 b_2 - \lambda^2 a_1 a_2 | b_1 b_2 - \lambda^2 a_1 a_2 \rangle = 1 + \lambda^4 \quad (12)$$

$$BS = \frac{\sqrt{1 + \lambda^4}}{1 + \lambda^2} S_0 + \frac{\lambda \sqrt{2}}{1 + \lambda^2} T_0 \quad (13)$$

where

$$S_0 = \frac{S}{\sqrt{1 + \lambda^4}} = \frac{1}{\sqrt{1 + \lambda^4}} (S_1 + \lambda^2 S_2) \quad (14)$$

Hence the BS DF energy can be written in terms of renormalized

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