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Structural dependence of magnetic exchange coupling parameters in transition-metal complexes

Juan I. Melo [a,*], Jordan J. Phillips [b], Juan E. Peralta [c,b]

[a] Departamento de Física, Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires, Argentina
[b] Science of Advanced Materials, Central Michigan University, MI, United States
[c] Department of Physics, Central Michigan University, MI, United States

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ABSTRACT

Magnetic exchange coupling parameters are routinely calculated within same structures for high- and low-spin states, neglecting structural relaxations and temperature effects present in measurements. To estimate these effects, we calculate magnetic couplings in a set of transition-metal complexes by relaxing the high-spin and broken-symmetry structures and taking into account the zero-point energies for both spin configurations. Structural relaxations slightly worsen results relative to experimental values, while zero-temperature ro-vibrational effects slightly improve calculated couplings. Because the complexes considered here are the gas-phase structures of the crystal units, our results can be regarded as an upper-bound for relaxation effects in the crystal-phase.

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1. Introduction

The magnetic behavior of polynuclear transition-metal (TM) complexes is commonly modeled using the Heisenberg-Dirac Hamiltonian [1,2], given by

$$\widehat{H} = -\sum_{i<j} J_{ij} \hat{\mathbf{S}}_i \cdot \hat{\mathbf{S}}_j, \tag{1}$$

where $\hat{\mathbf{S}}_i$ and $\hat{\mathbf{S}}_j$ are spin-operators associated with the spin-moments of the metal centers $\{\mathbf{S}_i, \mathbf{S}_j\}$, and J_{ij} is the magnetic exchange coupling parameter, which describes the isotropic interaction between $\mathbf{S}_i$ and $\mathbf{S}_j$. The theoretical determination of J_{ij} is usually done by differences in calculated total energies of reference spin-states. For example, for a system with two spin-centers, $\{S_A, S_B\}$, $S_A \leqslant S_B$, because the high-spin (HS) and low-spin (LS) states of total spin quantum numbers $S = S_A + S_B$ and $S = S_A - S_B$ coincide with the spin-states of Eq. (1), then using the relation $\widehat{S}^2 = \widehat{S}_A^2 + \widehat{S}_B^2 + 2\hat{\mathbf{S}}_A \cdot \hat{\mathbf{S}}_B$ one can show that J_{AB} is given by

$$J_{AB} = \frac{E_{LS} - E_{HS}}{2S_A S_B + S_B}. \tag{2}$$

A point of concern arises when using single Slater determinant approaches such as Density Functional Theory (KS-DFT) [3] to describe the electronic states. In this case the multireference low-spin eigenstate cannot be rigorously described and one must resort to broken-symmetry (BS) configurations, $|\uparrow\downarrow\rangle$, that are neither eigenfunctions of $\widehat{S}^2$ nor the Heisenberg Hamiltonian. In such cases the use of Eq. (2) is no longer theoretically valid and instead one must employ the spin-projection (SP) approach [4,5], where J_{AB} is given by

$$J_{AB} = \frac{E_{BS} - E_{HS}}{2S_A S_B}. \tag{3}$$

It should be noted that the use of Eq. (2) or Eq. (3) in KS-DFT is contentious: [6–8] While in this Letter the SP mapping is employed, we emphasize that our conclusions will be largely independent of whether Eq. (2) or Eq. (3) are used. We direct interested readers to several nice articles for more complete discussions on SP vs. NP mapping [9,10].

Implicit to the use of the model Hamiltonian in Eq. (1), and calculation of the coupling parameter by Eq. (2) or Eq. (3), is that the differences in the low-lying magnetic states can be reduced to a simplified description in terms of spin degrees of freedom only. In other words, in the theoretical determination of J_{AB} one uses the same molecular structure for the HS and BS configurations, and effects such as temperature and zero-point energy are usually neglected.

On the other hand the experimental determination of J_{AB} is usually done by measuring the temperature-dependent magnetic susceptibility of the material, typically provided in crystal phase. J_{AB} then appears as a free-parameter in the Bleaney–Bowers equation [11] to be determined by a best-fit with the experimental data [12,13]. Because the experimental determination of J_{AB} occurs across a domain of temperatures (up to a few hundred Kelvin), while the theoretical determination is done at zero Kelvin with a gas-phase molecular structure, a valid question to ask is to what extent structural relaxations and zero-point effects can impact

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* Corresponding author.
E-mail address: jmelo@df.uba.ar (J.I. Melo).

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the theoretically calculated coupling parameter [13]. Here it bears noting that relaxing structures when calculating magnetic couplings introduces subtleties deserving consideration. For example, Bovi and Guidoni [14] have found that if the same optimized structure is used for both the HS and BS configurations, then a bias will be created for the magnetic configuration in which the structure was relaxed. This means that using the BS optimized structure lowers E_{BS} relative to E_{HS}, thereby making the coupling more negative (more antiferromagnetic), while using the HS structure incurs the opposite energy penalty. If however one uses separate optimized structures for the HS and BS solutions, an additional concern raised by Neese [13] is that to the extent the two structures differ significantly then a Heisenberg-description may no longer be valid. With the above discussion in mind, in this Letter we estimate the magnitude of these effects in homo- and hetero-binuclear TM complexes by performing separate geometry relaxations on the HS and BS configurations and taking into account zero-point energy corrections.

2. Methodology and computational details

For the calculations in this Letter we have chosen a set of transition-metal (TM) complexes from the open-shell databases of Rudra [15] and Valero [16]. The complexes in these databases are well studied experimentally, both in terms of their crystallographic data and their magnetic properties. The following 14 systems are employed: four ferromagnetic complexes, given by YAFZOU, (6) Cu^{II}–Cu^{II}, (7) Cu^{II}–Cu^{II}, and (9) Mn^{III}–Cu^{II}; eight antiferromagnetic complexes, given by BISDOW, CAVXUS, $[Cu_2Cl_6]^{2-}$, CUAQAC02, PATFIA, (1) Cu^{II}–Cu^{II}, (2) Cu^{II}–Cu^{II}, and (4) V^{IV}–V^{IV}; and lastly, two ferrimagnetic complexes, given by (3) Mn^{II}–Cu^{II}, and (5) Mn^{III}–Mn^{IV}.

For the calculation of exchange couplings and geometry relaxations in this Letter we have used the same GAUSSIAN basis set: the 6-3111+G basis set plus an additional *f*-type function of exponent $0.5823a_0^{-2}$ for TM atoms, and the 6-31G* basis set for the rest of the elements. All magnetic exchange couplings were computed from the energy difference between HS and BS configurations. The BS solution was obtained from a standard SCF procedure using an initial guess constructed from the HS solution and ‘flipping’ the spin-density of one of the metal centers. In all cases, proper convergence to the BS solution was verified by analyzing atomic spin-densities. All calculations are performed with convergence criteria of 10^{-8} RMS variation in the density matrix, 10^{-6} maximum variation in any density matrix element, and 10^{-6} hartree ($\approx 0.2\ \mathrm{cm}^{-1}$) variation in energy (scf = tight keyword in GAUSSIAN) in the GAUSSIAN 09 suite of programs [17]. Also for all cases we used an atomic center numerical integration grid of 99 radial and 590 angular points (grid = ultrafine keyword in GAUSSIAN). All energies were obtained with the hybrid PBEh functional [18]. This hybrid functional supplies 25% of Hartree–Fock-like exchange and 75% of DFT exchange weighting, and has been shown to yield fairly accurate exchange couplings [16,19].

The optimized geometries for the calculation of exchange parameters were obtained as follows. Starting from the crystallographic structure, the geometry was optimized with the same basis set and density functional (PBEh) as for the calculation of *J* couplings. The crystallographic structure relaxed in the HS configuration was used as the initial structure for the relaxation of the BS configuration. Here we note that the accuracy of hybrid functionals for geometries of TM systems is well-established [20,21].

All magnetic couplings herein are calculated from the difference in total energies of the HS and BS configurations with the spin-projection [4,5] mapping of Eq. (3). In this Letter we calculate four different sets of *J* coupling parameters, which are defined as follows: J_{cryst}, being the coupling calculated using the crystallographic structure for the HS and BS configurations; J_{opt}, being the coupling calculated using optimized structures for both the HS and BS configurations; J_{ZPC}, being the coupling calculated using optimized structures for the HS and BS configurations, and including zero-point energy corrections (ZPC) in the energy difference $(E_{BS} - E_{HS})$;J_{ZPC}^{cryst}, being the coupling calculated using the crystallographic structure for the HS and BS configurations, but including the aforementioned ZPC in the energy difference as an approximation to the different zero-point energies of the HS and BS configurations in the crystal-phase. These four sets of couplings are then compared against experimental values, J_{exp}, by means of the relative mean error,

$$\delta_J = \frac{1}{N}\sum_i^N \left|\frac{J_{calc}^i - J_{exp}^i}{J_{exp}^i}\right|. \tag{4}$$

3. Results and discussion

It is expected that the more the relaxed structures differ from the crystallographic structures, then the more J_{opt} and J_{ZPC} will differ from J_{cryst}. As a way of characterizing structural changes upon relaxation, we show in Table 1 the distance between TM atoms, $d_{\mathrm{M-M}}$, for the crystallographic structure and the optimized HS and BS configurations. The data in Table 1 combined with a simple inspection of all the structures indicates that for most systems the bulk of the geometry relaxation was constituted by structural changes in the outer parts of the bulky ligands, but not in the ‘core’ ligand structure which bridges the metals. The largest changes in $d_{\mathrm{M-M}}$ correspond to YAFZOU and (1) Cu^{II}–Cu^{II}, followed by $[Cu_2Cl_6]^{2-}$, PATFIA, and CUAQAC02. For most of the systems the variations between the crystallographic $d_{\mathrm{M-M}}$ and the relaxed $d_{\mathrm{M-M}}$ are smaller than 0.1 Å, while the largest found is 0.33 Å for (1) Cu^{II}–Cu^{II}. On the other hand, the structural changes between the HS and BS relaxed structures are very small.

It is fair to ask wether one should or not relax the crystallographic structures to calculate exchange couplings. The general consensus is that since experiments are performed in crystal phase, pruned crystallographic structures should yield better calculated values. However, there are no estimates of how much calculated couplings on average depend on this. Our calculations show that relaxing the crystallographic structures indeed worsens calculated couplings. Nevertheless, despite any effects that may be contributed by structural relaxations, the error with respect to experiment contributed by such effects are appreciably smaller than those intrinsic to the approximate density functional used to calculate the coupling [16,19,22]. For example, the results of Valero and coworkers [16] with the M06-X [23] series of hybrid functionals

Table 1
Comparison of optimized and experimental intermetallic distances, $d_{\mathrm{M-M}}$ (in Å).

	$d_{\mathrm{M-M}}$		
	Cryst	Opt$_{hs}$	Opt$_{bs}$
(1) Cu^{II}–Cu^{II}	2.93	2.60	2.60
(2) Cu^{II}–Cu^{II}	5.41	5.34	5.32
(3) Mn^{II}–Cu^{II}	5.43	5.46	5.46
(4) V^{IV}–V^{IV}	3.08	3.08	3.06
(5) Mn^{III}–Mn^{IV}	2.55	2.59	2.56
(6) Cu^{II}–Cu^{II}	3.12	3.11	3.12
(7) Cu^{II}–Cu^{II}	2.88	2.87	2.87
(9) Mn^{III}–Cu^{II}	3.54	3.55	3.56
BISDOW	5.14	5.11	5.11
CAVXUS	5.46	5.51	5.51
$[Cu_2Cl_6]^{2-}$	3.39	3.59	3.60
CUAQAC02	2.62	2.53	2.53
PATFIA	3.24	3.39	3.40
YAFZOU	3.02	3.31	3.33

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