



## Note

# On the importance of the biquadratic terms in exchange coupled systems: A *post*-HF investigation

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## ABSTRACT

The importance of the many-body interactions was studied both at the experimental and theoretical level. However, no definitive proofs of their presence as high order terms in the Heisenberg–Dirac–Van Vleck (HDVV) Hamiltonian, as far as we know, were presented. The present work wants to reanalyze the HDVV Hamiltonian at the Full CI level on the two model systems  $N_2He$  and  $N_3He_3$ .

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## 1. Introduction

Generally the theories attempting to provide a microscopic explanation of the magnetic properties of materials start from the Heisenberg, Dirac, and Van Vleck (HDVV) Hamiltonian proposed by Heisenberg in the 1928 [1–3]:

$$H = \sum_{i < j} J_{ij} (\mathbf{S}_i \cdot \mathbf{S}_j) \quad (1)$$

where  $J_{ij}$  indicates the exchange coupling parameter.

This Hamiltonian is based on the approximation of pairwise interactions. This is of course a simplification of multi-body interactions, but it was justified at that time by the lack of experimental data that could account for the presence and importance of multi-body interactions. Only at the beginning of the 1960s, in order to explain the energy level spectrum of Mn pairs in MgO [4], the necessity to invoke the presence of a biquadratic interaction term took shape. Therefore, the HDVV Hamiltonian for a dimer turned into the following:

$$H = J(\mathbf{S}_1 \cdot \mathbf{S}_2) + j_{\text{bq}}(\mathbf{S}_1 \cdot \mathbf{S}_2)^2 \quad (2)$$

where  $J$  has the same meaning as in Eq. (1) and  $j_{\text{bq}}$  is the two-body biquadratic exchange.

The theoretical explanations of the origin of the biquadratic interaction were based on the theory of magnetoelastic effect by Kittel [5], and later by Anderson [6] and Huand and Orbach [7]

within the superexchange interaction theory. The importance of three-body forces in an interacting tree-nuclear system was provided through the inelastic-neutron-scattering experiment on  $CsMn_xMg_{1-x}Br_3$  [8]. The HDVV for a trimer turned into Eq. (3):

$$H = J(\mathbf{S}_1 \cdot \mathbf{S}_2) + j_{\text{bq}}(\mathbf{S}_1 \cdot \mathbf{S}_2)^2 + j_{\text{tr}}[(\mathbf{S}_1 \cdot \mathbf{S}_2)(\mathbf{S}_1 \cdot \mathbf{S}_3) + (\mathbf{S}_1 \cdot \mathbf{S}_2)(\mathbf{S}_2 \cdot \mathbf{S}_3) + (\mathbf{S}_1 \cdot \mathbf{S}_3)(\mathbf{S}_2 \cdot \mathbf{S}_3)] \quad (3)$$

where  $j_{\text{tr}}$  is the three-body biquadratic exchange.

Several theoretical and experimental papers appeared on the topic providing proofs on how much such HDVV higher order terms can affect the magnetic properties of both ferromagnets and anti-ferromagnets [9–18]. Recently, the microscopic origin of high order terms was studied for two-centers and three-centers embedded clusters as models of the  $La_2NiO_4$  perovskite [19]. The deviations from a strict Heisenberg behavior computed at the DDCI2 level of approximation for systems with more than two magnetic centers, was claimed to be due to atomic *non*-Hund states [19].

The importance of biquadratic terms in the magnetic properties of transition metal clusters, has not generally studied, yet. In fact, in experimental treatments of complex magnetic systems, like multi-center transition metal clusters, such terms are not included in order to avoid over-parametrization problems. The only way to have an insight into the importance of the two- three-body biquadratic terms is through *ab initio post*-HF calculations. Moved by this aim, the validity of the HDVV Hamiltonian will be here reanalyzed at the Full CI (FCI) level on two model systems:  $N_2He$  and  $N_3He_3$ . The basic concepts reported in Ref. [20] will be here developed. ORMAS approaches will be used with the aim of finding a

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computational economic and reliable tool to be applied to more complex systems in order to have an estimate of biquadratic terms. This would be of extreme importance, since these parameters cannot be computed at the DFT level.

## 2. Computational details

GAMESS US software package [21,22] was used throughout all the calculations. For both systems  $N_2He$  (**1**) and  $N_3He_3$  (**2**) we performed calculations for the following N–He distances: 1.5, 1.6, and 1.8 Å. The symmetry were  $D_{\infty h}$  and  $D_{3h}$ , respectively.  $C_1$  symmetry was used throughout the calculations.

The computed energies were fitted for **1** with the following SH :

$$SH1(1) : H = J\mathbf{S}_1 \cdot \mathbf{S}_2$$

$$SH2(1) : H = J\mathbf{S}_1 \cdot \mathbf{S}_2 + j_{bq}(\mathbf{S}_1 \cdot \mathbf{S}_2)^2$$

For system **2** we used the following SH :

$$SH1(2) : H = J(\mathbf{S}_1 \cdot \mathbf{S}_2 + \mathbf{S}_1 \cdot \mathbf{S}_3 + \mathbf{S}_2 \cdot \mathbf{S}_3)$$

$$SH2(2) : H = J\mathbf{S}_1 \cdot \mathbf{S}_2 + j_{bq}[(\mathbf{S}_1 \cdot \mathbf{S}_2)^2 + (\mathbf{S}_1 \cdot \mathbf{S}_3)^2 + (\mathbf{S}_2 \cdot \mathbf{S}_3)^2]$$

$$SH3(2) : H = J\mathbf{S}_1 \cdot \mathbf{S}_2 + j_{bq}[(\mathbf{S}_1 \cdot \mathbf{S}_2)^2 + (\mathbf{S}_1 \cdot \mathbf{S}_3)^2 + (\mathbf{S}_2 \cdot \mathbf{S}_3)^2] + j_{tr}[(\mathbf{S}_1 \cdot \mathbf{S}_2)(\mathbf{S}_1 \cdot \mathbf{S}_3) + (\mathbf{S}_1 \cdot \mathbf{S}_2)(\mathbf{S}_2 \cdot \mathbf{S}_3) + (\mathbf{S}_1 \cdot \mathbf{S}_3)(\mathbf{S}_2 \cdot \mathbf{S}_3)]$$

The symbols  $J$ ,  $j_{bq}$ , and  $j_{tr}$  have the same meaning as those presented in Eqs. (2) and (3).

Several levels of correlations were used to compute the energies spectra for both systems: ROHF–ORMAS $n$  (with  $n = 1–3$ ), and FCI. In these cases STO–3G basis sets were used. ORMAS calculations were done with three different correlation schemes. Reference orbitals were obtained by ROHF–Boys localized orbitals converged onto the high spin state. For  $N_2He$  [ $N_3He_3$ ], ORMAS scheme 1, ORMAS1, consists of two[three] active sets of orbitals containing the 2p orbitals belonging to a single N atom each. In this scheme, inside each set a Full CI was allowed (up to three excitations). No excitations from the core, the He orbital, and between the sets of active orbitals were allowed. In ORMAS2 scheme, we used the same two[three] sets as in ORMAS1 but we allowed a Full CI in and between the two[three] sets (up to six excitations). In ORMAS3 we added the He 1s atom as a new active orbital to the ORMAS2 scheme (the three He 1s for the  $N_3He_3$  system). Two electrons were allowed to be excited in both systems. In ORMAS3 we have, therefore, three[three] active sets of orbitals with 7[12] active electrons.

We chose such three ORMAS scheme in order to check the importance of the different contributions to the exchange interaction. In fact, with ORMAS1 we explicitly took into account only the direct exchange and the coulomb interactions. With ORMAS2 we included the kinetic exchange. Adding the He orbital(s) we added within the ORMAS3 scheme both the hole polarization and the charge transfer contributions between the “ligand(s)” and the paramagnetic centers.

Working in the STO–3G framework, the contributions coming from the charge transfer states  $N \rightarrow He$  were not possible to be taken into account.

In the case of the FCI calculation we had 11[18] active orbitals with 16[27] electrons.

In order to evaluate a possible basis set effect, two DDCI $_n$  calculations [23] were also performed on both systems, with a 4–31G basis set. The DDCI calculations differ by the inclusion,  $n = 1$ , or not,  $n = 2$ , of the core 1s–2s N orbitals in the active space. A FCI calculation was unfortunately impossible to perform due the large size of the configuration space, even within the  $D_{3h}$  symmetry.

A CI convergence of  $1.e-6$  was used for all the calculations.

The squares sum of the differences between *post*-HF and HDVV energies ( $e_{calc}$  and  $e_{fit}$ , respectively) falling below of  $0.04 \text{ cm}^{-1}$  were considered as a perfect agreement.

All the results for the system  $N_2He$  were reported in Table 1. The computed spin Hamiltonian parameters for SH1 and SH2 are shown at different N–He distances. For system  $N_3He_3$  all the computed spin Hamiltonian parameters for SH1, SH2 and SH3 are reported in Table 2.

## 3. Results

The validity of the HDVV Hamiltonian was tested using *post*-HF calculations on model systems like  $N_2He$  and  $N_3He_3$ . We can think at the N atoms as two quasi-localized interacting 3/2 spin centers for the  $N_2He$  model and three quasi-localized 3/2 spin centers for the  $N_3He_3$ . The He atoms mimic the role of closed shell ligand atoms. By choosing these two models we were able to investigate the importance of the higher order terms in the HDVV for the simple dimer interaction and for the more complex trimer interaction.

In order to do this we needed to get the “real” spectrum of energies for both the systems. This means that we needed to compute multiplet energies at the most accurate level as possible. Since it is

**Table 1**  
Results of the calculations on the model system  $N_2He$

	FCI	ORMAS1	ORMAS2	ORMAS3	DDCI_1	DDCI_2
$d_{NHe} = 1.5 \text{ Å}$						
$J_{SH1(1)}$	484(916)	–153(2)	423(621)	447(705)	570(2678)	610(3148)
$\Sigma(\Delta e_{calc} - \Delta e_{fit})_{SH1(1)}^2$	12822	27.92	17401	19749	75009	86065
$J_{SH2(1)}$	491(8)	–153.4	429.6	453.8	583(46)	624(55)
$J_{bq}$	–15(1)	–0.719	–12.67	–13.50	–26(6)	–28(7)
$\Sigma(\Delta e_{calc} - \Delta e_{fit})_{SH2(1)}^2$	110.5	<0.044	<0.044	<0.044	624.6	750.9
$d_{NHe} = 1.6 \text{ Å}$						
$J_{SH1(1)}$	217(40)	–76.4(1)	189(27)	200(31)	269(134)	298(225)
$\Sigma(\Delta e_{calc} - \Delta e_{fit})_{SH1(1)}^2$	1105	3.166	756.6	855.6	3766	6297
$J_{SH2(1)}$	218.8(2)	–76.29	190.7	202.1	272.6(6)	302(5)
$J_{bq}$	–3.19(2)	–0.171	–2.646	–2.813	–5.90(8)	–7.6(6)
$\Sigma(\Delta e_{calc} - \Delta e_{fit})_{SH2(1)}^2$	2.427	<0.044	<0.044	<0.044	8.200	6.574
$d_{NHe} = 1.8 \text{ Å}$						
$J_{SH1(1)}$	44.6(1)	–17.42	38.8(0.5)	41.2(0.5)	67(0.5)	75(1)
$\Sigma(\Delta e_{calc} - \Delta e_{fit})_{SH1(1)}^2$	2.062	<0.044	1.736	1.440	17.54	25.65
$J_{SH2(1)}$	44.67	–17.42	38.90	41.30	67.65	75.22
$J_{bq}$	–0.138	–8.56e–3	–0.1154	–0.1267	–0.4030	–0.4873
$\Sigma(\Delta e_{calc} - \Delta e_{fit})_{SH2(1)}^2$	<0.044	<0.044	<0.044	<0.044	<0.044	<0.044

Energy values are expressed in  $\text{cm}^{-1}$ . Errors are reported in parenthesis.

$\Delta e_{calc}$  and  $\Delta e_{fit}$  are defined as the following:  $e_{[3]} - e_{[5]}$ , with  $S_i = 2, 1, 0$ .

**Table 2**Results of the calculations on the model system  $N_3He_3$ 

	FCI	ORMAS1	ORMAS2	ORMAS3
$d_{NHe} = 1.6 \text{ \AA}$				
$J_{SH1(2)}$	197(1)	−129.4(4)	126.0(3)	179.1(5)
$\Sigma(\Delta e_{calc} - \Delta e_{fit})_{SH1(2)}^2$	697	3126	2201	4228
$J_{SH2(2)}$	196.0(4)	−129.4(4)	126.1(1)	179.3(2)
$J_{bq}$	2.3(6)	−0.5(7)	1.6(2)	2.4(3)
$\Sigma(\Delta e_{calc} - \Delta e_{fit})_{SH2(2)}^2$	120	2980	870.7	1299
$J_{SH3(2)}$	198.7(5)	−129.0(7)	126.6(1)	179.8(2)
$J_{bq}$	2.44(7)	−0.3(8)	1.9(2)	2.8(3)
$J_{tr}$	−1.02(7)	−0.3(2)	−0.39(5)	−0.48(9)
$\Sigma(\Delta e_{calc} - \Delta e_{fit})_{SH3(2)}^2$	13.9	2973.7	616.7	914.7
$d_{NHe} = 1.8 \text{ \AA}$				
$J_{SH1(2)}$	41.115(3)	−33.22(3)	22.4945(4)	35.9476(9)
$\Sigma(\Delta e_{calc} - \Delta e_{fit})_{SH1(2)}^2$	1.312	208.0	3.209	7.084
$J_{SH2(2)}$	41.0682(6)	−33.23(2)	22.4947(4)	35.9517(3)
$J_{bq}$	0.102(1)	−0.14(5)	0.0044(8)	0.1007(5)
$\Sigma(\Delta e_{calc} - \Delta e_{fit})_{SH2(2)}^2$	0.2057	197.8	3.199	2.021
$J_{SH3(2)}$	41.1783(8)	−33.04(4)	22.5305(4)	35.9744(4)
$J_{bq}$	0.1080(1)	−0.03(4)	0.0253(5)	0.1139(4)
$J_{tr}$	−0.0427(1)	−0.15(1)	−0.0296(1)	−0.0187(1)
$\Sigma(\Delta e_{calc} - \Delta e_{fit})_{SH3(2)}^2$	<0.044	159.1	1.749	1.440

Energy values are expressed in  $\text{cm}^{-1}$ . Errors are reported in parenthesis. $\Delta e_{calc}$  and  $\Delta e_{fit}$  are defined as the following:  $e_{[3/2]} - e_{[S_{12}S_1]}$ , with  $S_i = 7/2, 5/2, 3/2, 1/2$ .

known that, within a given basis set, FCI calculations allow one to account electron correlation at the maximum extent, our reference values for the multiplet energies were obtained from FCI calculations. Due to the impossibility to perform FCI calculations onto large basis sets, we used a minimal STO-3G basis sets. In principle, this choice did not impose a handicap on our approach since we are interested more in the microscopic origin of the observables (our spin Hamiltonian parameters) than in their absolute value.

DDCI calculations on the  $N_2He$  with a 4-31G basis set, were performed to support the previous statement. In fact, the DDCI approach is considered as one of the most accurate *post-HF* approach to reproduce spin Hamiltonian parameters [23].

### 3.1. $N_2He$

FCI results are reported in the second column of Table 1. The inaccuracy of the SH1(1) in reproducing the energy spectrum is evident at short distances. Only at N–He = 1.8 Å we have small, but still significant, deviation from the computed FCI energies. The agreements change significantly with the introduction of the biquadratic term,  $J_{bq}$ . In this case things get better already at N–He = 1.6 Å distance, where the agreement increased from 1105 (SH1) to 2.427  $\text{cm}^{-1}$  (SH2). A perfect agreement between the energies spectrum predicted by *non*-HDVV and the FCI energies is reached at N–He = 1.8 Å.

For all distances we computed a negative  $J_{bq}$ . A very strong dependence on the N–He distance is observed as well as for the  $J$  parameter. In fact, the  $J_{bq}$  value decreases exponentially passing from short distances to longer ones and its magnitude ranges in the expected values:  $10^{-1}$ – $10^{-3}$  J. To be stressed the computed error of 40  $\text{cm}^{-1}$  on the  $J$  value at N–He = 1.6 Å, when the SH1(1) was used.

In order to check the reliability of the FCI/STO-3G calculations we performed two DDCI calculations. The results are reported in the last two columns in Table 1. The computed  $J$  and  $J_{bq}$  values with DDCI3\_1 are larger than the ones computed at the FCI level. This is true for all the three N–He distances. The overall results are however in nice agreement with the FCI calculations. On the other hand, the reproduction of energy spectra deviates more than in FCI calculations, and only at N–He = 1.8 Å we have a perfect agreement with the *non*-HDVV. Therefore, we can say that the small size of the basis set seems to preserve the type of the interactions and

their physical content. In other words, the inclusion of the virtual orbitals seems to not play an important role if not on the magnitude of the single parameters. In fact, the dynamical correlation missing in the FCI/STO-3G calculation can be estimated on about 20% in the case of N–He = 1.6 Å and on about 30% for N–He = 1.8 Å.

The introduction of the N 1s and 2s into the active space (DDCI\_2) seems to not introduce a significant improvement in the computed  $J$  and  $J_{bq}$  values, as expected.

Once we have confirmed the reliability of the FCI calculations, we can assert the following about the question of the validity of the HDVV Hamiltonian. It comes out that the computed FCI energy spectra can only be perfectly reproduced using the SH2, that is with the inclusion of the biquadratic term, and only at *non*-bonding distances. At shorter distances, the importance of the  $J_{bq}$  is even bigger and it increase significantly the agreement with FCI calculations. This means that the full *non*-HDVV, when used in situations where the covalency (i.e. electronic delocalization) is not negligible, is not valid anymore at less of the introduction of an error that can be small, see for N–He = 1.6 Å, or huge, as in the case of N–He = 1.6 Å.

The results obtained at the ORMAS levels are reported in Table 1. For ORMAS1, since only the direct exchange and the coulomb interactions for the magnetic electrons are taken into account, we got ferromagnetic  $J$  values for all the distances. The perfect agreement can be explained by the fact that, in this case is like we were computing the exchange parameters of just two quasi-*non* interacting spins with no kinetic exchange or ligand effects. Even in this case the introduction of the biquadratic term significantly increase the agreements between the computed values with the HDVV ones. To notice the fact that ORMAS1  $J_{bq}$  are reduced of more than a factor of 10 with respect to the  $J_{bq}$  computed at the FCI level. The inclusion of the kinetic exchange, ORMAS2, shifted the  $J$  valued to an anti-ferromagnetic value in agreement with the FCI calculations. A constant error of  $\sim$ 13% is present for both SH1 and SH2. Ligand effects (i.e. superexchange) reduced the errors on the computed  $J$  to only the 8%. The agreement of ORMAS2–3 calculations with the SH2 energy spectrum has to be found into the ORMAS schemes and in the dimer system, in which the assumptions made for the validity of the HDVV are completely satisfied.

### 3.2. $N_3He_3$

The multiplets structure for system 2 was far too more complicated than for system 1. In this case the  $[S_{12}S]$  five spin states coming from the exchange coupling interaction were split to eight spin states by the introduction of the biquadratic two-centers interactions; the further introduction of the biquadratic three-centers term brought the total number of spin states to 12 (see Fig. 1). In this contest, we pushed forward the test of the validity of the HDVV.

As for system 1, we checked the validity of the SH1(2), SH2(2), and, in this case, also of the SH3(2). The FCI calculations confirmed what we found for system 1. The inclusion of  $J_{bq}$  plays a strong role on improving the agreement with the FCI energies, even if, in this case is not sufficient to get a perfect agreement. The perfect agreement was achieved only for N–He = 1.8 Å and when the full spin Hamiltonian, SH3, was used. Particularly interesting is the reproduction of the degeneracies and near degeneracies predicted by the full *non*-HDVV by the ORMAS3 and, better, by the FCI.

The computed  $J$  values for both distances are in very good agreement ( $\sim$ 9%) with the ones computed for system 1, suggesting a good portability of the single exchange interactions, in agreement with Ref. [24]. The computed  $J_{bq}$  were found, in this case, to be anti-ferromagnetic. They are, however, of the same magnitude as in system 1. Positive  $J_{bq}$  were found also in [19].  $J_{tr}$  were found negative and smaller than  $J_{bq}$  in magnitude. The origin of the signs

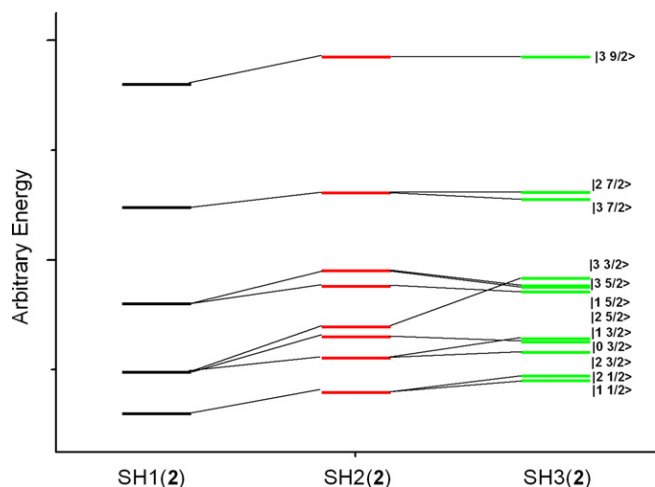


Fig. 1. Energy spectra for system 2 obtained for SH1, SH2, and SH3.

in these two parameters results quite hard to understand because of the complexity of system, where frustration effects cannot be negligible.

As expected, the  $J$  values computed at ORMAS1 level, are ferromagnetic for both distances and smaller of about the 20% than the correspondent parameters computed for system 1. In this case, ferromagnetic  $j_{bq}$  were found as in system 1, suggesting a competition between two-centers ferro- and anti-ferro contributions. At variance with system 1, the agreements are far from being good.

The  $J$  values computed at the ORMAS2 level are anti-ferromagnetic but they are lower of 36% and 45% than the ones computed at the FCI level at N–He = 1.6 and 1.8 Å distances, respectively.  $j_{bq}$  and  $j_{tr}$  are also very far from the correspondent FCI values. The inclusion of the kinetic energy did not significantly increase the agreement as in the dimer system 1.

At the ORMAS3 level things were much better. An error of about 10% on the computed  $J$ 's was found.  $j_{bq}$ 's were found really close to the values found at the FCI level (15–5%). Only  $j_{tr}$  values showed an error of about of 55%, even if related to really small numbers. Even in this case, ORMAS3 confirms to be a valid approximation to the FCI approach, encouraging us to test it on

more complex systems in virtue of its not resources demanding nature.

#### 4. Conclusions

We presented the validation of the HDVV spin Hamiltonian through the use of FCI and ORMAS approaches on the two model systems  $N_2He$  and  $N_3He_3$ . The results suggest that only using the full *non*-HDVV spin Hamiltonian we can have a perfect agreement between the computed and the spin Hamiltonian energies. The validity of the *non*-HDVV is therefore confirmed at longer distances, where covalency effects are negligible. Strong deviations from a strict HDVV behavior can be, therefore, addressed to delocalization effects. ORMAS3 approach seems to be a promising tool to investigate the role of the two-, three-centers term in more complex systems.

#### References

- [1] W. Heisenberg, Z. Phys. 49 (1928) 619.
- [2] P.A.M. Dirac, Proc. Roy. Soc. (Lond.) 123 (1929) 714.
- [3] J.H. Van Vleck, Phys. Rev. 45 (1934) 405.
- [4] E.A. Harris, J. Owen, Phys. Rev. Lett. 11 (1963) 9.
- [5] C. Kittel, Phys. Rev. 120 (1960) 335.
- [6] P.W. Anderson, Phys. Rev. (1959) 2.
- [7] N.L. Huang, R. Orbach, Phys. Rev. Lett. 12 (1964) 275.
- [8] U. Falk, A. Furrer, H.U. Güdel, J.K. Kjems, Phys. Rev. Lett. 56 (1986) 1956.
- [9] D.S. Rodbell, I.S. Jacobs, J. Owen, Phys. Rev. Lett. 11 (1963) 10.
- [10] H.A. Brown, Phys. Rev. B 14 (1975) 4725.
- [11] T. Iwashita, N. Uryū, Phys. Stat. Sol. (b) 137 (1986) 65.
- [12] T. Iwashita, N. Uryū, Phys. Stat. Sol. (b) 139 (1987) 597.
- [13] T. Iwashita, N. Uryū, Phys. Stat. Sol. (b) 152 (1989) 289.
- [14] T. Iwashita, N. Uryū, Phys. Stat. Sol. (b) 154 (1989) 747.
- [15] B.D. Gaulin, M.F. Collins, Phys. Rev. B 33 (1986) 6287.
- [16] S. Bhattacharjee, V.B. Shenoy, T. Senthil, Low Temp. Phys. 23 (2000) 273.
- [17] Y.A. Fridman, D.V. Spirin, Low Temp. Phys. 23 (2000) 273.
- [18] J. Lou, T. Xiang, Z. Su, Phys. Rev. Lett. 85 (2000) 2380.
- [19] R. Bastardis, N. Guihéry, C. de Graaf, Phys. Rev. B 76 (2007) 132412.
- [20] A. Bencini, F. Totti, Is still the Heisenberg Spin Hamiltonian reliable for multi-nuclear paramagnetic clusters? in: "Models and Theory for Molecular Magnetism", CECAM Workshop 2006.
- [21] M.W. Schmidt, K.K. Baldrige, J.A. Boatz, S.T. Elbert, M.S. Gordon, J.H. Jensen, S. Koseki, N. Matsunaga, K.A. Nguyen, S. Su, T.L. Windus, M. Dupuis, J.A. Montgomery, J. Comput. Chem. 14 (1993) 1347.
- [22] M.S. Gordon, M.W. Schmidt, in: C.E. Dykstra, G. Frenking, K.S. Kim, G.E. Scuseria (Eds.), Theory and Applications of Computational Chemistry: The First Forty Years, Elsevier, Amsterdam, 2005, p. 1167.
- [23] C.J. Calzado, J. Cabrero, J.P. Malrieu, R. Caballol, J. Chem. Phys. 116 (2002) 2728.
- [24] I. Ciofini, C. Adamo, V. Barone, G. Berthier, A. Rassat, Chem. Phys. 309 (2005) 133.