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Molecular magnetism in *closo*-azadodecaborane supericosahedrons

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ABSTRACT

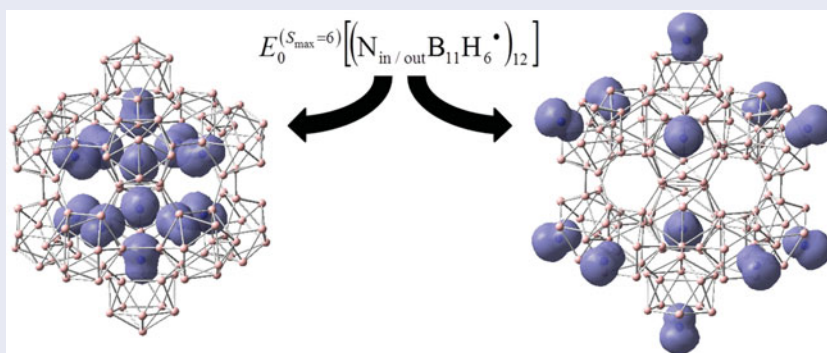
The connection of 12 $s = \frac{1}{2}$ *closo*-azadodecaborane radical units ($\text{NB}_{11}\text{H}_{11}^{\bullet}$), where a hydrogen atom is removed from the nitrogen atom, produces a supericosahedron $[(\text{NB}_{11}\text{H}_6^{\bullet})_{12}]^{(S)}$, S being the total spin of the system. This work describes the study of the low-lying energy spin-projected states of this supericosahedron with two different geometrical arrangements, each nitrogen atom pointing (1) inwards or (2) outwards with respect to radial axes. These spin-projected states are mapped into a Heisenberg spin Hamiltonian, thus allowing the determination of coupling constants between magnetic sites. The eigenvalues of this model Hamiltonian then predict the ground spin state and the corresponding combinations of spin orientations of the magnetic centres. We show that the energy minimum in the $[(\text{N}_{\text{in/out}}\text{B}_{11}\text{H}_6^{\bullet})_{12}]^{(S)}$ systems corresponds to a high-spin $S = 6$ state.

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KEYWORDS

Boron–nitrogen compounds; spin population; Heisenberg spin Hamiltonians; Heisenberg coupling constants



Geometrical arrangement of the supericosahedrons.

1. Introduction

In 1991, Paetzold and co-workers accomplished the synthesis and characterisation of *closo*-azadodecaborane $\text{NB}_{11}\text{H}_{12}$ [1,2] Figure 1(a), an unprecedented icosahedral heteroborane compound with a six-coordinated nitrogen atom whose structural evidence was confirmed by *ab initio* calculations [3]. Removal of the hydrogen atom bonded to nitrogen leads to the aza-*closo*-dodecaboran-1-yl radical $\text{NB}_{11}\text{H}_{11}^{\bullet}$ [Figure 1(b)] possessing an unpaired electron (with $s = \frac{1}{2}$ spin) around nitrogen. This radical can be considered as a suitable basic icosahedral block to build larger nano-structures, as was

proposed for the icosahedral borane and carborane units [4,5]. In fact, covalent bonding of 12 $\text{NB}_{11}\text{H}_6^{\bullet}$ units, linking 5 neighbouring radicals, leads to the construction of a supermolecule which could be a giant supericosahedron $(\text{NB}_{11}\text{H}_6^{\bullet})_{12}$ (Figure 2) composed of a simpler icosahedron on each vertex. Five B-H bonds in each unit would be replaced by five B-B bonds between neighbouring units, keeping the icosahedral symmetry (Figure 2). The large amount of magnetic sites displayed in this structure offers many possibilities of coupling for the magnetic moments, arousing interesting properties for this type of compounds. Likewise, the nitrogen atoms along

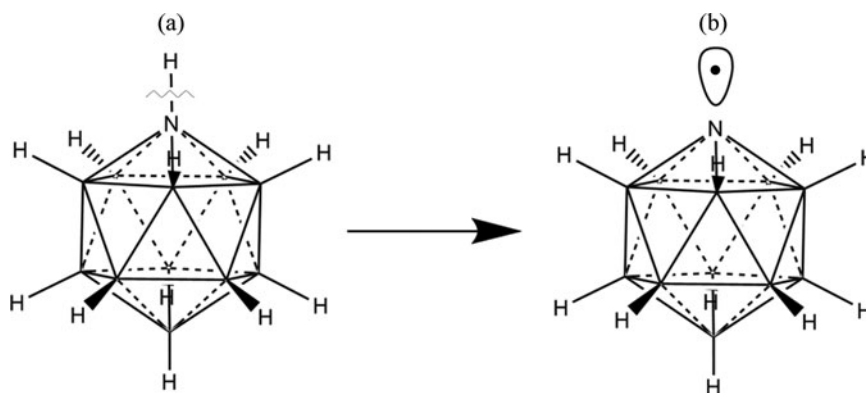


Figure 1. (a) Molecular structure of *closo*-azadodecaborane $\text{NB}_{11}\text{H}_{12}$. (b) Removal of the hydrogen atom bound to nitrogen in *closo*-azadodecaborane (zig-zag line) leads to the aza-*closo*-dodecaboran-1-yl radical $\text{NB}_{11}\text{H}_{11}^{\bullet}$. The lobe with the dot inside above the nitrogen atom represents an unpaired electron.

with the unpaired electrons can be placed in the icosahedron toward inside/outside with respect to the radial axes, providing multiple geometrical arrangements and consequently new and different coupling possibilities must be taken into account. The main aim of this work is to prove the construction of these supericosahedrons, studying the spin manifold of their lowest energy states in order to predict their magnetic features. For the sake of simplicity, we have limited this study to two cases in which the nitrogen atoms face all of them either the inside [Figure 2(a)] or the outside [Figure 2(b)] of the radial axes.

On the other hand, in previous works [6–8], we have proposed the mapping of results arising from spin population analyses onto a phenomenological Heisenberg spin Hamiltonian, describing low-lying excited states in polyhedral clusters as well as in simpler aggregates. The partitioning of the N-electron spin-squared expectation quantities $\langle \hat{S}^2 \rangle$ according to one- and two-centre

local spins (LSs) provides the determination of coupling constants between two magnetic sites. This quantitative evaluation has allowed the analysis of the nature of different magnetic interactions exhibited by polyhedral boranes and carboranes which have been studied as prototype of complex systems. Moreover, the introduction of these constants into the Heisenberg Hamiltonian model provides the construction of a Hamiltonian matrix whose diagonalisation shows the energy spectrum associated with that Hamiltonian model, identifying the ground state and the spin orientations of the magnetic units. Another purpose of this work is to test the suitability of this methodology to describe systems possessing multiple magnetic centres, such as those present in the supericosahedrons $(\text{NB}_{11}\text{H}_6^{\bullet})_{12}$, in which 12 unpaired electrons [9–11] are simultaneously interacting and, consequently, a high-spin multiplicity should be expected for their ground states.

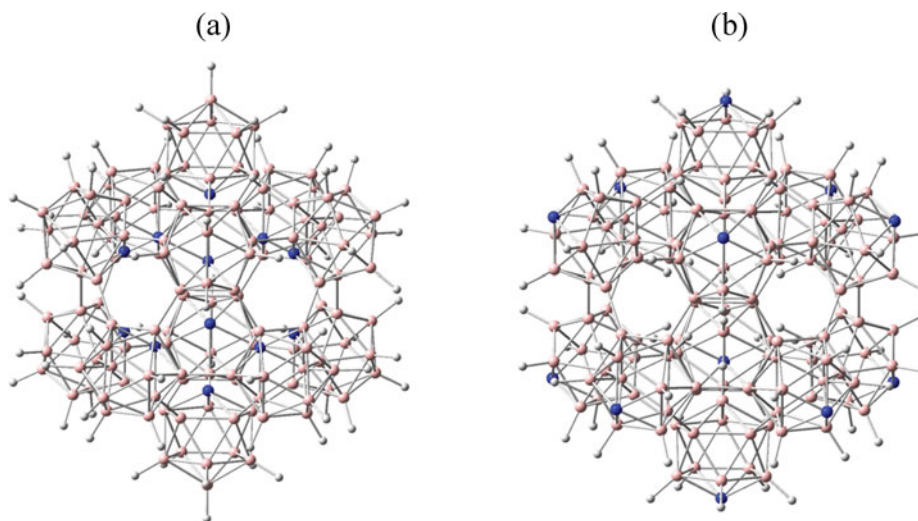


Figure 2. Geometrical arrangement (I_h) of the supericosahedron constituted by 12 radical $\text{NB}_{11}\text{H}_6^{\bullet}$ units. The nitrogen atoms are placed in the arrangement toward (a) inside or (b) outside with respect to the radial axes.

This work is organised as follows. In the next section, we summarise the notation and the theoretical framework used in this work. The computational details, the results found in the studied $(\text{NB}_{11}\text{H}_6^*)_{12}$ structures and the corresponding discussion are reported in Section 3. Finally, in the last section, we highlight the main conclusions of this work.

2. The theoretical models

In order to predict the energy of the different spin states in many-electron systems, we will use the phenomenological Heisenberg spin Hamiltonian which, assuming that the electron spin degrees of freedom are independent from the electron orbital degrees of freedom, can be expressed as

$$\hat{H} = E_0 + \sum_{i \neq j} J_{ij} \hat{S}_i \hat{S}_j. \quad (1)$$

In this equation, E_0 means the origin of the energy scale chosen, \hat{S}_i and \hat{S}_j represent the dimensionless spin operators corresponding to two sites i and j , and J_{ij} describes the strength of the interaction between these two sites.

The standard approach follows the Noodleman's scheme [12,13], where the evaluation of the J_{ij} parameters is based on the calculation of energy differences between a Slater determinant which describes the ferromagnetically coupled state, usually the highest pure spin multiplet (HS), and mixed spin-symmetry Slater determinants describing antiferromagnetically coupled states, broken-symmetry (BS) states. Hence, these energy differences are

$$E_{\text{HS}} - E_{\text{BS}} = \sum_{i \neq j} J_{ij} [\langle \hat{S}_i \hat{S}_j \rangle^{\text{HS}} - \langle \hat{S}_i \hat{S}_j \rangle^{\text{BS}}]. \quad (2)$$

The expectation values $\langle \hat{S}_i \hat{S}_j \rangle^{\text{HS}}$ and $\langle \hat{S}_i \hat{S}_j \rangle^{\text{BS}}$ in Equation (2) can be evaluated from the expectation value of the spin-squared operator [14,15],

$$\langle \hat{S}^2 \rangle = \sum_i \sum_j \langle \hat{S}_i \hat{S}_j \rangle. \quad (3)$$

In this equation, the one-centre LSs $\langle \hat{S}_i^2 \rangle$ account for the spin state of an atom or group of atoms in a molecule or cluster. The two-centre LS terms $\langle \hat{S}_i \hat{S}_j \rangle$ describe the spin correlation between the fragments i and j and hence provide the connection between experimental and theoretical results in terms of the Heisenberg spin Hamiltonian. We will consider the widely used approach [7,16–19] which identifies the terms $\langle \hat{S}_i^2 \rangle$ and $\langle \hat{S}_i \hat{S}_j \rangle$ (arising

from the spin atomic operator formulation) with those $\langle \hat{S}^2 \rangle_i$ and $\langle \hat{S}^2 \rangle_{ij}$ (arising from the direct partitioning of $\langle \hat{S}^2 \rangle$) [20]; the corresponding expressions reported in Ref. [19] will be used to this end. On the other hand, there are several possibilities to formulate the BS determinants, which represent all possible spin orientations of the individual centres. Hence, Equation (2) is a collection of linear equations in the variables J_{ij} [21], if the two-centre expectation values $\langle \hat{S}_i \hat{S}_j \rangle^{\text{HS}}$ and $\langle \hat{S}_i \hat{S}_j \rangle^{\text{BS}}$ have been evaluated.

In this framework, we will consider two models to describe spin interactions in the proposed clusters.

Model A: The J_{ij} parameter takes one single J value for any pair of magnetic sites,

$$J_{ij} = J \quad \forall i, j.$$

Model B: The J_{ij} parameter takes identical value J for first neighbours i, j sites and zero otherwise,

$$\begin{aligned} J_{ij} &= J & \forall j \in \text{first neighbour on site } i \\ J_{ij} &= 0 & \text{otherwise.} \end{aligned}$$

Hence, the LS quantities $\langle \hat{S}_i \hat{S}_j \rangle$ and the linear equation system (2) provide the evaluation of the J_{ij} parameters through LS-like treatments for both A and B models, LS-A and LS-B, respectively.

Alternatively, in the model A, the J constant can also be calculated using the Yamaguchi (YA) procedure [22,23],

$$J_{ij} (\text{YA}) = \frac{E_{\text{HS}} - E_{\text{BS}}}{\langle \hat{S}^2 \rangle^{\text{HS}} - \langle \hat{S}^2 \rangle^{\text{BS}}}. \quad (4)$$

In the next section, we report results arising from the application of this methodology to the above proposed $(\text{NB}_{11}\text{H}_6^*)_{12}$ structure models.

3. Results and discussion

The determinations of the spin density matrices, their corresponding spin densities, and the energies E_{HS} and E_{BS} required in the LS-A, LS-B, and YA treatments have been carried out at the unrestricted Hartree Fock (UHF) level of theory, with the STO-3 G basis sets. All the calculations were performed using the Gaussian 09 package [24]. The initial guess for the BS self-consistent field solution was generated by combining calculations on fragments, specifying the charge and spin for each fragment. In both systems, the supericosahedrons with the orientation of nitrogen atoms inside/outside, the geometries were optimised for the closed-shell ($S = 0$) states of the anion $[(\text{NB}_{11}\text{H}_6)^-]_{12}$ at UHF level with the STO-3 G basis

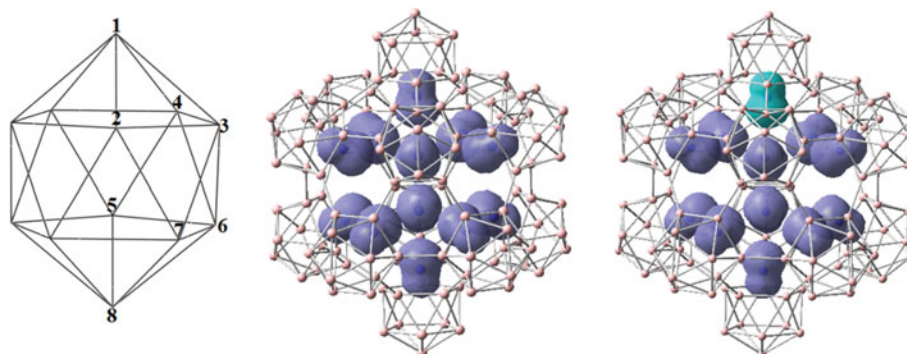


Figure 3. Geometrical arrangement and calculated spin densities of the supericosahedron constituted by 12 $\text{NB}_{11}\text{H}_6^*$ units. The orientation of nitrogen atoms is inside of the supericosahedron. Hydrogens are not shown. Colours in spin density represent the two (alpha/beta) spin-components. Spin density isovalue is ± 0.006 in the plots.

sets. Geometry optimisations were also performed at the UHF/STO-3 G level of theory and confirmed as minima by vibrational analysis. The evaluation of the one- and two-centre LSs, $\langle \hat{S}_i^2 \rangle$ and $\langle \hat{S}_i \hat{S}_j \rangle$, respectively, were performed in subsequent steps using our own codes. In our scheme, each $\text{NB}_{11}\text{H}_6^*$ cage, which possesses an unpaired electron, has been regarded as a magnetic site. Likewise, the solutions of the above mentioned linear equations providing the J_{ij} values have been obtained from Mathematica 9.0 [25]. For the studied systems, a $S_z = 6$ Slater determinant represents the HS state while we have chosen a $S_z = 5$ Slater determinant for the BS state. The results corresponding to the supericosahedrons with the orientation of nitrogen atoms pointing inside and nitrogens

pointing outside the supercage are shown in Figure 3 with Table 1, and Figure 4 with Table 2, respectively, where the numbers 1 to 8 stand for non-equivalent moieties. Two possible orientations of the cage spins are also depicted in Figures 3 and 4.

As can be observed from Table 1 and 2, the energy results show a ground state of HS type and a very close, almost degenerate, the BS state for both inside/outside facing nitrogen atom clusters (energy gap 0.380 and 0.068 mE_h , respectively). On the other hand, in order to describe the LSs in the supericosahedron, it is enough to show the values corresponding to four representative magnetic centres, whose plane contains the magnetic site having an opposite spin in the BS state (see schemes in

Table 1. Local spin populations, energies (E_h), $\langle S^2 \rangle$ expectation values and coupling constants (in cm^{-1}) for the supericosahedron constituted by 12 units $\text{NB}_{11}\text{H}_6^*$ with the orientation of nitrogen atoms inside studied in this work in the HS and BS states. In the BS state, the spin orientation on site 1 is opposite to rest of the magnetic sites.

Local spins								
HS state								
	1	2	3	4	5	6	7	8
1	0.7622	0.2500	0.2500	0.2500	0.2500	0.2500	0.2500	0.2500
2	0.2500	0.7622	0.2500	0.2500	0.2500	0.2500	0.2500	0.2500
5	0.2500	0.2500	0.2500	0.2500	0.7622	0.2500	0.2500	0.2500
8	0.2500	0.2500	0.2500	0.2500	0.2500	0.2500	0.2500	0.7622
BS state								
	1	2	3	4	5	6	7	8
1	0.7371	-0.2355	-0.2355	-0.2355	-0.2379	-0.2379	-0.2379	-0.2379
2	-0.2355	0.7572	0.2452	0.2452	0.2476	0.2476	0.2476	0.2476
5	-0.2379	0.2476	0.2476	0.2476	0.7623	0.2500	0.2500	0.2500
8	-0.2379	0.2476	0.2476	0.2476	0.2500	0.2500	0.2500	0.7622
	Energy	$\langle S^2 \rangle$	$J_{ij}(\text{YA})$	$J_{ij}(\text{LS-A})$	$J_{ij}(\text{LS-B})$			
HS state	-3905.636905	42.1469	-7.5900	-7.6225	-16.8671			
BS state	-3905.636525	31.1444						

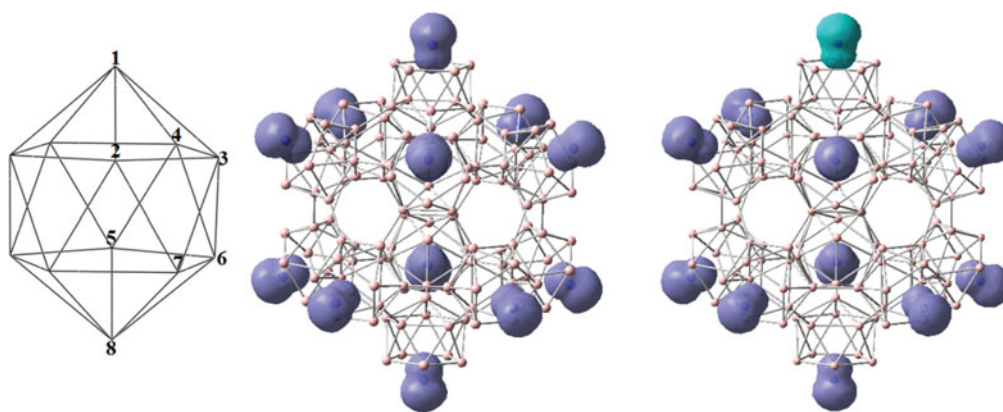


Figure 4. Geometrical arrangement and calculated spin densities of the supericosahedron constituted by 12 $\text{NB}_{11}\text{H}_6^+$ units. The orientation of nitrogen atoms is outside of the supericosahedron. Hydrogens are not shown. Colours in spin density represent the two (alpha/beta) spin-components. Spin density isovalue is ± 0.006 in the plots.

Figures 3 and 4, positions 1, 2, 5, and 8), and their non-redundant neighbour sites, which can be chosen on the right of that plane (positions 3, 4, 6, and 7). Consequently, in Table 1 and 2, only the values corresponding to these magnetic centres are shown. From a qualitative point of view, the LS results show that the electronic spin distribution is well-localised in each $\text{NB}_{11}\text{H}_6^+$ cage, for the nitrogen atom facing either outside or inside the supercluster, showing $\langle \hat{S}_i^2 \rangle$ quantities close to 0.75, mainly in their corresponding HS state, meaning that unpaired electrons are well localised in each cage [the canonical value is $1/2(1 + 1/2)$]. The sign of the two-centre LS components

$\langle \hat{S}_i \hat{S}_j \rangle$ is, in both clusters, positive for the HS state and positive/negative for the BS state, according to identical or opposite spin orientation of the i, j interacting sites (in BS states, we are considering the spin orientation on site 1 opposite to the rest of magnetic sites). Quantitatively, the orientation with nitrogen inside provides HS and BS states with lower energy and with higher energy gap than those corresponding to the nitrogen atom oriented outside. Consequently, the absolute values of the coupling constants $J_{ij}(\text{LS-A})$, $J_{ij}(\text{LS-B})$, and $J_{ij}(\text{YA})$ are higher in the inside orientation, reflecting stronger interaction between the magnetic centres in that situation.

Table 2. Local spin populations, energies (E_h), $\langle S^2 \rangle$ expectation values and coupling constants (in cm^{-1}) for the supericosahedron constituted by 12 units $\text{NB}_{11}\text{H}_6^+$ with the orientation of nitrogen atoms outside studied in this work in the HS and BS states. In the BS state, the spin orientation on site 1 is opposite to rest of the magnetic sites.

Local spins								
HS state								
	1	2	3	4	5	6	7	8
1	0.7615	0.2500	0.2500	0.2500	0.2500	0.2500	0.2500	0.2500
2	0.2500	0.7615	0.2500	0.2500	0.2500	0.2500	0.2500	0.2500
5	0.2500	0.2500	0.2500	0.2500	0.7615	0.2500	0.2500	0.2500
8	0.2500	0.2500	0.2500	0.2500	0.2500	0.2500	0.2500	0.7615
BS state								
	1	2	3	4	5	6	7	8
1	0.7467	-0.2411	-0.2411	-0.2411	-0.2425	-0.2425	-0.2425	-0.2425
2	-0.2411	0.7585	0.2470	0.2470	0.2485	0.2485	0.2485	0.2485
5	-0.2425	0.2485	0.2485	0.2485	0.7614	0.2500	0.2500	0.2500
8	-0.2425	0.2485	0.2485	0.2485	0.2500	0.2500	0.2500	0.7615
	Energy	$\langle S^2 \rangle$	$J_{ij}(\text{YA})$	$J_{ij}(\text{LS-A})$	$J_{ij}(\text{LS-B})$			
HS state	-3905.432479	42.1376	-1.3559	-1.3595	-3.0005			
BS state	-3905.432411	31.1374						

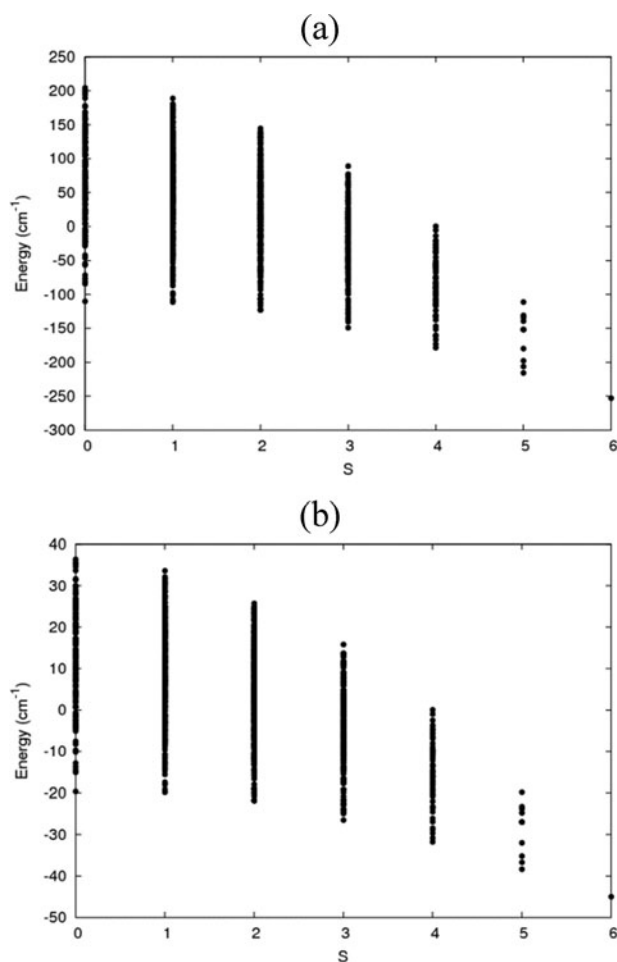


Figure 5. Heisenberg Hamiltonian spectrum of the supericosahedron constituted by 12 units $\text{NB}_{11}\text{H}_6^+$, (a) with the orientation of nitrogen atoms inside of the supericosahedron, (b) with the orientation of nitrogen atoms outside of the supericosahedron.

In both systems, $|J_{ij}(\text{LS-A})| < |J_{ij}(\text{LS-B})|$, as is obviously expected. Also in both systems, $J_{ij}(\text{LS-A})$ and $J_{ij}(\text{YA})$ values are close, which is in agreement with the high degree of unpaired electron localisation in these compounds.

In order to complement this study, we have computed the spectrum of the Heisenberg Hamiltonian [26] for both supericosahedrons using J_{ij} values obtained from the LS-B model, which could be considered more reliable than the LS-A one. We have used the FIT-MART software [27], which generates the matrix representation of Equation (1) using the basis wherein the individual spin operators \hat{S}_{iz} are diagonal, and provides the energy eigenvalues and eigenvectors by means of an exact diagonalisation. Figure 5 shows the resulting spin state distributions. As can be observed, an $S = 6$ ground state is predicted for each cluster. Moreover, for both clusters, the lowest energy value for each spin symmetry decreases with increasing spin, while the energy gap between the

lowest energy states for two consecutive spin values has the opposite behaviour.

4. Concluding remarks

In this work, we have analysed the electronic structure of two $[(\text{NB}_{11}\text{H}_6^+)_{12}]$ supericosahedrons, which could be obtained from covalent bonding of 12 $(\text{NB}_{11}\text{H}_6^+)$ icosahedral units. These studied clusters correspond to two different geometrical arrangements, according to their N atoms pointing inwards/outwards with respect to the radial axes. We have been able to describe the interactions between the magnetic centres in these clusters using two different models, within an LS evaluation scheme. Moreover, the calculated spin coupling constants that account for the magnetic interactions provide the corresponding spin state spectra, so that a ferromagnetic $S = 6$ ground state has been found for both compounds.

We are thus facing a challenging, original, and innovative research line towards the construction of molecular magnets based on non-metal elements, and containing heteroborane cages as the building unit, with the goal of obtaining an as large as possible maximum spin S_{max} . Of course, we are still far away from the achievements of molecular magnets based on molecules/ligands combined with metallic clusters, but we believe that the construction of molecular architectures based on heteroborane cages can lead to new and interesting results for nano-sciences and materials sciences.

We are planning to extend the applications of our LS-based methodology to the study of a high number of compounds with potentially interesting magnetic properties, such as in the next iteration of the supericosahedron construction presented in this work.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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References

- [1] J. Müller, P. Paetzold, and J. Runsink, *Angew. Chem. Int. Ed. Engl.* **30**, 175 (1991).
- [2] P. Paetzold, J. Müller, F. Meyer, H.-P. Hansen, and L. Schneider, *Pure Appl. Chem.* **66**, 255 (1994).
- [3] R. Zahradnik, V. Balaji, and J. Michl, *J. Comput. Chem.* **12**, 1147 (1991).
- [4] J. Müller, K. Base, and T.F. Magnera, *J. Am. Chem. Soc.* **114**, 9721 (1992).
- [5] D. Bhattacharya, D.J. Klein, J.M. Oliva, L.L. Griffin, D.R. Alcoba, and G.E. Massaccesi, *Chem. Phys. Lett.* **616–617**, 16 (2014).
- [6] J.M. Oliva, D.R. Alcoba, L. Lain, and A. Torre, *Theor. Chem. Acc.* **132**, 1329 (2013).
- [7] D.R. Alcoba, A. Torre, L. Lain, O.B. Oña, and J.M. Oliva, *Int. J. Quantum Chem.* **114**, 952 (2014).
- [8] J.M. Oliva, D.R. Alcoba, O.B. Oña, A. Torre, L. Lain, and J. Michl, *Theor. Chem. Acc.* **134**, 9 (2015).
- [9] A. Torre, D.R. Alcoba, L. Lain, and R.C. Bochicchio, *J. Phys. Chem. A* **109**, 6587 (2005).
- [10] D.R. Alcoba, R.C. Bochicchio, L. Lain, and A. Torre, *Chem. Phys. Lett.* **429**, 286 (2006).
- [11] P. Karafiloglou, *J. Chem. Phys.* **130**, 164103 (2009).
- [12] L. Noodleman, *J. Chem. Phys.* **74**, 5737 (1981).
- [13] L. Noodleman and E.R. Davidson, *Chem. Phys.* **109**, 131 (1986).
- [14] A. Clark and E.R. Davidson, *J. Chem. Phys.* **115**, 7382 (2001).
- [15] M. Podewitz, C. Hermann, A. Malassa, R. Westerhausen, and M. Reiher, *Chem. Phys. Lett.* **451**, 301 (2008).
- [16] D.R. Alcoba, L. Lain, A. Torre, and R.C. Bochicchio, *Chem. Phys. Lett.* **470**, 136 (2009).
- [17] A. Torre, D.R. Alcoba, L. Lain, and R.C. Bochicchio, *J. Phys. Chem. A* **114**, 2344 (2010).
- [18] D.R. Alcoba, A. Torre, L. Lain, and R.C. Bochicchio, *Chem. Phys. Lett.* **504**, 236 (2011).
- [19] D.R. Alcoba, A. Torre, L. Lain, and R.C. Bochicchio, *J. Chem. Theory Comput.* **7**, 3560 (2011).
- [20] C. Hermann, L. Yu, and M. Reiher, *J. Comput. Chem.* **27**, 1223 (2006).
- [21] I. Ciofini, C. Adamo, V. Barone, G. Berthier, and A. Rassat, *Chem. Phys.* **309**, 133 (2005).
- [22] K. Yamaguchi, Y. Takahara, and T. Fueno, in *Applied Quantum Chemistry*, edited by H. Smith, H.F. Schaefer, and K. Morokuma (D. Reidel, Boston, MA, 1986).
- [23] T. Soda, Y. Kitagawa, T. Onishi, Y. Takano, Y. Shigeta, H. Nagao, Y. Yoshioka, and K. Yamaguchi, *Chem. Phys. Lett.* **319**, 223 (2000).
- [24] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G.A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H.P. Hratchian, A.F. Izmaylov, J. Bloino, G. Zheng, J.L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J.A. Montgomery, Jr., J.E. Peralta, F. Ogliaro, M. Bearpark, J.J. Heyd, E. Brothers, K.N. Kudin, V.N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J.C. Burant, S.S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J.M. Millam, M. Klene, J.E. Knox, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, R.L. Martin, K. Morokuma, V.G. Zakrzewski, G.A. Voth, P. Salvador, J.J. Dannenberg, S. Dapprich, A.D. Daniels, Ö. Farkas, J.B. Foresman, J.V. Ortiz, J. Cioslowski, and D.J. Fox, *Gaussian 09, Revision D.01* (Gaussian, Inc., Wallingford, CT, 2009).
- [25] Wolfram Research, Inc., *Mathematica 9.0* (Wolfram Research, Inc., Champaign, IL, 2012).
- [26] E.R. Davidson and A.E. Clark, *J. Phys. Chem. A* **106**, 7456 (2002).
- [27] L. Engelhardt, S.C. Garland, C. Rainey, and R.A. Freeman, *Phys. Procedia* **53**, 39 (2014).