

Advantages of the DFT Augmented Symmetry Approach to Simulations of the Chromium-Based Ring Cr_8 within B3LYP Functional

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The DFT estimates of magnetic couplings in molecular nanomagnets are computationally demanding and their values have not achieved the satisfactory accuracy in spite of a lot of effort. We concentrate here on comprehensive tests for predictions of the recently proposed augmented symmetry approach aiming at reducing the computational complexity of the DFT calculations which is particularly important for the Wien2k code. Using the B3LYP functional, we demonstrate the numerical stability of magnetic couplings, magnetic moments and the HOMO-LUMO gaps, changing the fraction of exact exchange α . We reach the significant gain in the computing time without a loss in the accuracy of the final results with respect to those obtained by the standard PBE approach. We conclude that the value $\alpha = 0.25$ leads to best estimation of magnetic couplings for hybrid functionals within Wien2k.

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1. Introduction

Molecular nanomagnets are molecules or nanoparticles comprising clusters of magnetic metal ions coupled to each other by exchange interactions and exhibit many fascinating physical phenomena such as magnetic memory effect, resonant tunnelling of magnetization or hysteresis step curves of magnetization. Molecular chromium-based wheels [1–8] constitute a rich subgroup among magnetic molecules. These regular structures of various sizes which can comprise a large variety of paramagnetic ions are ideal investigation objects for better understanding electronic and magnetic properties of whole class of magnetic molecules, especially containing antiferromagnetically coupled spin systems. Despite a lot of effort [1–4, 9–13] the DFT estimates of the magnetic couplings in the molecular nanomagnets considered have not reached the level of the quantitative agreement with experiment [5–8].

In this paper we study electronic and magnetic properties of $\text{Cr}_8\text{F}_8(\text{Piv})_{16}$ molecular ring (in short Cr_8) using augmented symmetry (AS) approach [14, 15] and B3LYP hybrid functional implemented in Wien2k code exploiting non-Gaussian basis set [16].

The motivation for this work was to examine whether AS approach, which is computationally much more convenient to execute with respect to that based on the P1 symmetry of original Cr_8 molecule, can give reliable results for Cr_8 in conjunction with the B3LYP functional.

Another goal is to determine whether the change of the default value of mixing parameter α , defining a correction to the LDA exchange functional which takes into account the Hartree-Fock exact exchange [16], will get a better estimate of exchange couplings in Cr_8 .

2. Computational details

We carry out the Wien2k calculations using the same geometrical structures as those in [3, 17] and exploit PBE exchange-correlation potential as well as B3LYP. We took for the muffin-tin radii values of 2.40, 1.24, 1.20, 1.00, 0.83 a.u. for Cr, O, F, C and H respectively [17]. The energy cutoff for core electrons was chosen equal to -6 Ry and cutoff for plane waves $R_{MT}K_{\max} = 3.0$. Other parameters of calculation were selected as follows: the partial waves up to $l_{\max} = 10$ and the charge density was limited with $G_{\max} = 20$ Ry and a single k-point in the irreducible Brillouin zone. In order to decrease the number of atoms considered in the ring from 272 to 80, a process referred to as hydrogen saturation is employed [1, 3].

We consider only ferromagnetic (FM) and antiferromagnetic (AF) spin configurations of the Cr(III) ions in all cases. In the first step the PBE and B3LYP (with default $\alpha = 0.2$) calculation were carried out for Cr_8 in P1 symmetry with eight nonequivalent Cr ions and for AS model with five nonequivalent Cr ions. Next we perform calculation using AS approach for different values of α . A schematic representation of the position of the nonequivalent Cr ions in the Cr_8 molecule for both symmetries is shown in Fig. 1.

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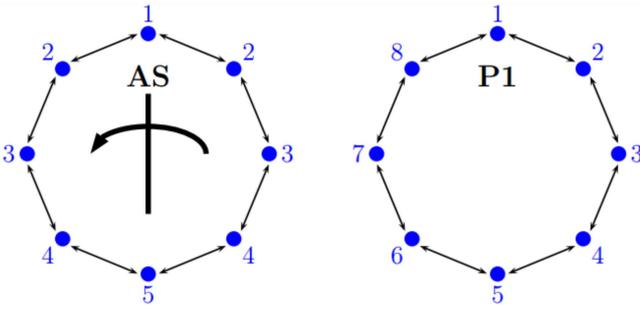


Fig. 1. Site numbering in AS and P1 symmetry.

3. Results and discussion

The ground state for Cr_8 molecule is a antiferromagnetic (AF) one with the total magnetic moment $M = 0\mu_B$. The ferromagnetic (FM) configuration corresponds to the highest total energy. Magnetic moments (M) obtained for specific Cr ions for both AF and FM state are in Table I. The values of magnetic moments for the remaining atoms are close to 0. The magnetic moments are strongly localized on Cr ions. Also values in the interstitial region are small enough since they lead at most to value of $0.01\mu_B$ per atom. For both symmetries result obtained with PBE functional are practically identical and coincide with other one obtained previously [3, 4, 17]. For B3LYP functional with default mixing parameter $\alpha = 0.2$ magnetic moments of Cr ions are very similar for AS and P1 symmetry. Let us notice that B3LYP improves estimation of magnetic moments and provides values which are close to experimental value of $2.94\mu_B$ [5]. Since we have shown that the AS approach leads to the results that are consistent with those obtained for whole molecule in P1 symmetry we calculated

TABLE I

Magnetic moments M in units μ_B for the whole ring, in the interstitial region and for specific magnetic ions obtained within augmented and P1 symmetry. For all cases two spin configurations are shown – antiferromagnetic (AF) and ferromagnetic (FM). Site numbering follows that in Fig. 1

M	AS				P1			
	PBE		B3LYB		PBE		B3LYB	
	AF	FM	AF	FM	AF	FM	AF	FM
tot	0.0	24.0	0.0	24.0	0.0	24.0	0.0	24.0
int	-0.01	1.42	-0.01	0.93	-0.01	1.42	-0.01	0.93
Cr1	2.73	2.78	2.88	2.89	2.73	2.78	2.88	2.90
Cr2	-2.73	2.77	-2.87	2.89	-2.72	2.77	-2.87	2.89
Cr3	2.73	2.78	2.88	2.90	2.73	2.78	2.88	2.90
Cr4	-2.72	2.77	-2.87	2.89	-2.72	2.77	-2.87	2.89
Cr5	2.73	2.78	2.88	2.90	2.73	2.78	2.88	2.90
Cr6	—	—	—	—	-2.72	2.77	-2.87	2.89
Cr7	—	—	—	—	2.73	2.78	2.88	2.90
Cr8	—	—	—	—	-2.72	2.77	-2.87	2.89

magnetic moment for Cr_8 molecule for different values of α using AS model which is computationally much less expensive. The results are presented in Table II. For $\alpha \geq 0.4$ magnetic moments of Cr ions have values greater than $3\mu_B$, which can not be accepted. But for $\alpha = 0.25$ and $\alpha = 0.30$ the values of magnetic moments of Cr ions are very close to experimental $2.94\mu_B$. For smaller values of α magnetic moment of Cr ions decreases (not shown).

TABLE II

Magnetic moments M in units μ_B for the whole ring, in the interstitial region and for specific magnetic ions obtained within augmented symmetry for different values of mixing parameter α .

M	α									
	AF					FM				
	0.20	0.25	0.30	0.40	0.5	0.20	0.25	0.30	0.40	0.5
tot	0.0	0.0	0.0	0.0	0.0	24.0	24.0	24.0	24.0	24.0
int	-0.01	-0.01	-0.01	-0.01	-0.01	0.93	0.82	0.71	0.47	0.21
Cr1	2.88	2.91	2.96	3.04	3.15	2.89	2.93	2.97	3.05	3.16
Cr2	-2.87	-2.91	-2.95	-3.04	-3.14	2.89	2.92	2.96	3.04	3.15
Cr3	2.88	2.92	2.96	3.05	3.15	2.90	2.93	2.97	3.05	3.16
Cr4	-2.87	-2.91	-2.95	-3.04	-3.14	2.89	2.92	2.96	3.04	3.15
Cr5	2.88	2.92	2.96	3.05	3.16	2.90	2.93	2.97	3.06	3.17

The next goal of our study was a more accurate estimation of exchange couplings. The magnetic coupling parameters J between transition metals in a ring are estimated within the standard projected broken symmetry approach [18], considering the following spin Hamiltonian:

$$H = \sum_{i=1}^8 JS_i S_{i+1}$$

where $S_i = \pm \frac{3}{2}$ is the spin projection of Cr ions, which is subject to the periodic boundary condition, i.e. $S_9 = S_1$ and J is the nearest-neighbor coupling between two Cr ions at positions i and $i + 1$.

The coupling parameters J and HOMO-LUMO gaps obtained with AS model for different values of fraction of exact exchange α in B3LYP functional are presented in Table III.

TABLE III

Coupling parameter J and HOMO-LUMO gaps in Cr_8 for different values of fraction of exact exchange α

α	0.10	0.15	0.20	0.25	0.30	0.40	0.50
J [meV]	4.58	3.46	2.59	2.12	1.33	0.58	2.59
E_{H-L}^{min}	3.03	3.44	3.47	3.54	3.51	3.30	3.04
E_{H-L}^{maj}	3.08	3.50	3.53	3.61	3.59	3.38	3.11

As the mixing parameter α increases, the value of exchange coupling J decreases and when it reaches the minimum for $\alpha = 0.4$ it starts to grow. For the α values 0.25 and 0.30 that gave the best estimate of magnetic moments, we have $J = 2.12$ meV and $J = 1.33$ meV, respectively. These estimates are better than those previously

obtained using DFT. These values are very close to the experimental value $J = 1.5$ meV [1]. We also note that for $\alpha = 0.25$ we get the greatest value of the HOMO-LUMO gap. This value seems to be consistent with other theoretical results [4, 19]. This means that for $\alpha > 0.25$ and $\alpha < 0.30$ one can obtain the best DFT estimates of the coupling parameter J and magnetic moments for Cr₈ molecule.

Finally, we want to point out that we compare estimates of J value obtained by standard broken symmetry approach proposed by Noodleman [18]. However, in the spirit of the unprojected broken symmetry (BS) approach by Ruiz [20], which has been recently adopted [9, 21], our estimates of coupling constant lead to values 1.6 and 1 meV for the $\alpha = 0.25$ and $\alpha = 0.30$, respectively. In the context of the BS approach, we have almost reached the experimental value of J for $\alpha = 0.25$, similar to those arising from the Hubbard model approach [22, 23].

4. Conclusions

We have demonstrated that the augmented symmetry approach can be combined with the B3LYP functional without a loss in the computational accuracy. The AS approach remains computationally stable and efficient so that the impact of the mixing parameter α on the physical characteristics can be analyzed. Our analysis shows that the values slightly higher than the default $\alpha = 0.20$ yield the estimates of the magnetic couplings and the local magnetic moments in agreement with experiment. The awaited increase of the HOMO-LUMO gaps has been achieved for the same range of the mixing parameter.

The AS model discussed in this paper mimics the eight-numbered molecules and is also suitable for investigating the properties of heterometallic Cr₇M molecules like Cr₇Cd, Cr₇Ni etc. An interesting question is whether the change in of value α in the B3LYP functional will also improve the results for these molecules. It is a great challenge to obtain better estimation of the ratio of exchange integrals J_{Cr-M}/J_{Cr-Cr} for the family of Cr₇M molecules. This ratio usually is overestimated [9] or even the relationship between the coupling parameters is reversed [4]. Due to the advantages demonstrated for the Cr₈ molecule, these aspects will be the subject of further research. Furthermore, after slight modifications AS model can be applied to a family of nine-numbered chromium ring molecules.

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