

# DFT Estimation of Exchange Coupling Constant of Cr<sub>8</sub> Molecular Ring using the Hybrid Functional B3LYP

M. WOJCIECHOWSKI<sup>a,\*</sup>, B. BRZOSTOWSKI<sup>a</sup> AND G. KAMIENIARZ<sup>b</sup>

<sup>a</sup>Institute of Physics, University of Zielona Góra, Prof. Szafrana 4a, 65-516 Zielona Góra, Poland

<sup>b</sup>Faculty of Physics, A. Mickiewicz University, Umultowska 85, 61-614 Poznań, Poland

A study of electronic and magnetic properties of an octametallic chromium-based homonuclear molecule Cr<sub>8</sub>F<sub>8</sub>(CO<sub>2</sub> – C(CH<sub>3</sub>)<sub>3</sub>)<sub>16</sub> is presented, using density functional theory (DFT) approach and linearized augmented plane wave (LAPW) method with Perdew, Burke and Ernzerhof (PBE) and Becke 3-term correlation (B3LYP) functionals. The exchange coupling parameters between transition metals ions are extracted, taking into account two different (ferro- and antiferromagnetic) spin configurations. The value  $J = 3.1$  meV found for the hybrid B3LYP functional improves significantly the one obtained for the PBE functional and gives an evidence for the superiority of the former in simulation of molecular nanomagnets. Moreover, the hybrid functional yields excellent spin density localisation, an enhancement of the HOMO-LUMO gaps and the value  $2.81\mu_B$  of magnetic moment at the chromium centre in good agreement with experiment.

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## 1. Introduction

Continued study of magnetic systems have been recently focused on single-molecule magnets [1]. They consist of paramagnetic core and organic ligand shell. Molecular rings are a subgroup of those materials that are ideal for investigating electric and magnetic properties of spin coupled systems. These properties depend mostly on transitional metals embedded in the molecule. These molecules exhibit many fascinating physical phenomena such as magnetic memory effect, resonant tunnelling of magnetization or hysteresis step curves of magnetization. They may also find application in next generation of high density data storage devices or in quantum computing.

The specific molecule, that was the object of our study, is the octametallic chromium ring [2], which is characterized by a antiferromagnetic exchange coupling between nearest neighbouring ions. The exact chemical formula of the ring is Cr<sub>8</sub>F<sub>8</sub>(Piv)<sub>16</sub>. The Piv group is pivalic acid — trimethyl acetic acid CO<sub>2</sub> – C(CH<sub>3</sub>)<sub>3</sub>. For short we refer to this molecule as Cr<sub>8</sub>. The Cr<sub>8</sub> molecule consists of 8 chromium  $s = 3/2$  ions arranged in a ring. They lay almost in a one plane, slightly alternating. Each pair of Cr atoms is connected with each other by a single fluorine bridge located inside a ring and two pivalic groups that span outside. The average distance between Cr atoms is 3.38 Å. The whole molecule consists of 272 atoms. In order to simplify this system and to reduce its computational complexity, each pivalic group is approximated by O<sub>2</sub>CH bridge [3, 4]. This procedure does not affect magnetic properties of the molecule [4], yet in case of Cr<sub>8</sub> allows to reduce the number of atoms from 272 to 80.

## 2. DFT approach

Within the DFT study of molecular magnets particular emphasis is given to the evaluation of the exchange interaction parameter  $J$  which has been significantly overestimated so far. This evaluation takes into account the energies of nonequivalent spin configurations. In the broken symmetry approach [5–7] the following spin Hamiltonian can be used for Cr<sub>8</sub> [4]:

$$H = J \sum_{i < j}^8 s_i s_j, \quad (1)$$

where  $s_i$  ( $s_j$ ) =  $\pm 3/2$  is the spin variable of the transitional metal ion. In case of Cr<sub>8</sub> the exchange interaction of interest is that for the nearest neighbours pair Cr-Cr. Quick and simple transformation of Eq. (1) allows us to obtain the expression for  $J$  in the form

$$J = (E_{\text{FM}} - E_{\text{AFM}})/36, \quad (2)$$

where  $E_{\text{FM}}$  and  $E_{\text{AFM}}$  are the energies of the ring in the ferromagnetic (FM) and antiferromagnetic (AFM) spin configuration.

It is worth mentioning that the exchange interaction between Cr ions is not direct. The actual exchange is carried through superexchange paths laid by the carboxylate and fluorine bridges. A series of Cr<sub>8</sub> rings have been synthesized that differ in the makeup of the bridges between Cr atoms [8]. The study of these rings shows, that the value of the exchange parameter is independent of the bridge makeup, as long as the valency of the bridge is the same as that in the original Cr<sub>8</sub> molecule.

In this paper we show the results of an all-electron density functional investigation of the Cr<sub>8</sub> antiferromagnetic molecular ring using the hybrid functional. We will particularly address the persisting problem of coupling constant significantly overestimated in previous calculations for Cr<sub>8</sub> ring [3, 4, 9–14] as well as for other chromium based molecules [5, 9, 15, 16].

\*corresponding author; e-mail: [mandalor85@gmail.com](mailto:mandalor85@gmail.com)

### 3. Computational details

In our present work we use the all electron linearized augmented plane wave technique (LAPW) [17, 18] implemented in WIEN2k computational package [19–21]. The LAPW method uses muffin-tin radii (RMT) approximation [22] to describe the atomic spheres. The values of the RMT parameters which have been chosen for different elements are the same as in [4], i.e. 2.40, 1.20, 1.24, 1.00 and 0.83 Bohrs for Cr, F, O, C and H, respectively. The parameters defining the basis set are  $RKMAX = 3.0$ ,  $GMAX = 20$  and the total number of basis functions per molecule unit is  $\approx 17000$ . We account for the exchange and correlation effects using two different potentials: both the PBE [23] and the hybrid Becke 3-term Lee-Yang-Parr (B3LYP) [24, 25] correlation functionals. In the case of B3LYP the onsite exact exchange is applied with a fraction  $\alpha = 0.2$ .

In our work we follow symmetrical structure approach, in which instead of encoding whole structure from unique atoms one uses smaller cells to reconstruct the molecule using symmetries. This approach substantially reduces the number of atoms as well as the computation time.

In our calculations we do not include spin-orbit coupling, as it was already shown that the differences in the results are negligible [4, 13] and the single-ion anisotropy for the Cr ions is known to be very small [2, 26, 27].

### 4. Results and discussion

The calculations were carried out for ferromagnetic and antiferromagnetic spin configurations with  $s = \pm 3/2$  for Cr ions. The ground state for the  $\text{Cr}_8$  molecule is an antiferromagnetic one with the total magnetic moment  $m = 0$ . Magnetic moments obtained for specific Cr ions are equal to  $-2.81\mu_B$  and  $+2.82\mu_B$  for the B3LYP functional and  $-2.68\mu_B$  and  $+2.67\mu_B$  for the PBE functional. The values of magnetic moments for the remaining atoms are close to 0. Strong localisation of magnetic moments on Cr ions is very well visible on the spin charge density plot shown on Fig. 1.

Magnetic moments obtained for the FM spin alignment are the following:  $+2.82\mu_B$  and  $+2.82\mu_B$  for the B3LYP functional and  $+2.73\mu_B$  and  $+2.72\mu_B$  for the PBE functional. These results compare very well with the theoretical values  $-2.71\mu_B$  and  $+2.72\mu_B$  for AFM configuration and  $+2.78\mu_B$  and  $+2.77\mu_B$  for FM configuration, obtained by the LAPW method for the PBE functional in [4] and with the experimental value  $2.97\mu_B$  [2, 26, 27].

Coupling constants were estimated using Eq. (2). The estimated coupling constant  $J$  for Cr ions has the value 6.3 meV for the PBE functional. This value compares very well with the earlier predictions found by the similar LAPW ( $J = 5.8$  meV) method [4] or the pseudopotential ( $J = 6.6$  meV) method [3]. From our calculations performed for the hybrid B3LYP functional, the exchange coupling amounts to  $J = 3.1$  meV, which is consistent

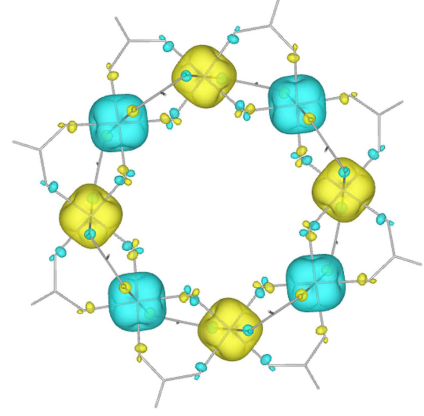


Fig. 1. Plot of the spin density for the AFM configuration. Yellow (blue) shades are positive (negative) isosurfaces for the value  $\pm 0.01$  e/Bohr<sup>3</sup>.

TABLE

The HOMO-LUMO (H-L) gaps calculated for minority (min.) and majority (maj.) channels are presented in Table. The previous B3LYP H-L majority gap [9] calculated for the AFM configuration amounts to 4.0 eV.

functional	H-L gap	AFM	FM
B3LYP	$E_{\text{min.}}$	3.67 eV	4.05 eV
	$E_{\text{maj.}}$	3.71 eV	3.40 eV
PBE	$E_{\text{min.}}$	2.35 eV	3.88 eV
	$E_{\text{maj.}}$	2.35 eV	2.31 eV
PBE [4]	$E_{\text{min.}}$	3.36 eV	4.08 eV
	$E_{\text{maj.}}$	2.36 eV	2.15 eV

with that found in literature ( $J = 3.2$  meV), using the Gaussian basis functions and the same B3LYP functional implemented in the NWChem package [9].

Even better estimates of  $J$  parameter [4, 13] were obtained with GGA+U or LDA+U methods. However, these results depend on  $U$  parameter which can be tuned to fit the experimental value. For the chain model of the  $\text{Cr}_8$  molecule, Fig. 7 in Ref. [13] presents the dependence of exchange interaction parameter  $J$  on the value of the Hubbard parameter  $U$  for GGA+U calculations. For  $U = 5$  eV the experimental value  $J = 1.5$  meV is reached. Because the chain model reproduces quite well properties of the  $\text{Cr}_8$  molecules [11, 12, 15], one can expect that the increase of the Hubbard parameter  $U$  in the calculations for the  $\text{Cr}_8$  molecule with unperturbed structure should improve the estimate of the exchange parameter  $J$ . On the other hand, Fig. 7 in Ref. [13] implies, that using the Hubbard parameter one can reproduce virtually any value of the exchange parameter  $J$ . Beyond the chain model [4], using the typical average value  $U = 2.7$  eV for the chromium oxide compounds, the coupling was estimated at  $J = 2.1$  meV. The Hubbard parameter  $U$  cannot be deduced in a unique way, there is no criteria on how it should be chosen (i.e. there is no minimum or plateau condition). This however is not the subject of

study in this work. Sufficient to say, that the family of  $+U$  approaches constitutes a whole class of methods and the results obtained with or without Hubbard parameter should not be compared directly.

Finally, we want to point out that so far we have compared estimates of  $J$  value obtained by standard broken symmetry approach proposed by Noodleman [6]. However, in the spirit of the unprojected broken symmetry (UBS) approach by Ruiz [7], which has been recently adopted [5, 28], our estimates of coupling constant lead to the values 4.7 meV and 2.3 meV for the PBE and B3LYP functionals, respectively. In the context of the UBS approach we have reached a significant improvement of the DFT estimate of  $J$ , which is surprisingly close to the experimental value  $J = 1.5$  meV [2, 26, 27].

## 5. Conclusions

We have shown that the LAPW method with the B3LYP hybrid functionals is an effective approach for estimation of the exchange coupling parameters between transition metals ions in the Cr<sub>8</sub> molecule. This approach does not affect the quality of the magnetic properties well reproduced in the previous calculations. It is important that our calculations, performed with different basis set with respect to that in Ref. [9] confirmed the earlier predictions found for the B3LYP functional so that it can be trusted more. Moreover, the B3LYP functional not only improves the coupling  $J$  systematically with respect to the PBE counterpart, but also enhances the HOMO-LUMO gaps, which suggests a relation between these two parameters.

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