

DFT and Falicov–Kimball Model Approach to Cr₉ Molecular Ring

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Based on density functional theory (DFT) calculations, we present electronic and magnetic properties of nanometallic homo-nuclear chromium-based molecular rings Cr₉F₉Cl₂(O₂C-C(CH₃)₃)₁₇ recently synthesized. The magnetic moments are calculated, the spin density maps are discussed and the exchange interaction parameter is extracted. The complementary studies are carried out using the Falicov-Kimball model which reproduces very well the energy levels determined by different magnetic broken symmetry configurations obtained by DFT.

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1. Introduction

Magnetic molecules have been an object of study ever since they were discovered [1]. A class of those molecules, molecular nanomagnets, have recently attracted much interest. They are small enough to exhibit quantum properties, yet at the same time they are too large for exact quantum calculations.

Molecular nanomagnets (MNMs) [1] exhibit many interesting quantum phenomena – hysteresis step curves of magnetization or quantum tunneling of magnetization are most recognizable among them. Furthermore they are widely studied in view of their various present and their possible future applications in engineering, e.g. in high density data storage or quantum information processing.

A class of MNMs which is intensively studied is that based on the Cr₈ molecule [2–4] and its analogues [5, 6]. It was shown [4] for the Cr₈ family that the Falicov–Kimball model (FKM) can describe energies extracted from DFT for all the non-equivalent spin configurations. In this paper we demonstrate that FKM can also describe the energy structure for the Cr₉F₉Cl₂(O₂C-C(CH₃)₃)₁₇ molecule (in short Cr₉) [6].

In our approach each pivalic group is substituted by a single H atom [3, 4]. The Cr atoms are connected to each other via two –O–C–O– bridges and –F– bridge and are almost in one plane. Only single pair of Cr atoms lacks one –O–C–O– bridge, but instead those two ions are connected to Cl atoms. This bonding defect leads to a weaker coupling between the corresponding Cr ions with respect to the remaining nearest neighbor couplings [5–7].

2. Results and discussion

We carry out the SIESTA [8] calculations for all non-equivalent spin configurations with $s = \pm 3/2$. In

Fig. 1. spin density for Cr₉ is plotted in the ground antiferromagnetic-like state with the total magnetic moment $m = 3\mu_B$ (both Cr ions connected with Cl have spin $s = +3/2$). A significant spin polarization of the charge density is found only close to the transition metal atoms, confirming a localized picture of the Cr magnetic moments [6]. For all Cr ions magnetic moments we find from Mulliken analysis the values $\pm(2.89-2.93)\mu_B$ whereas for the remaining atoms the values close to 0.

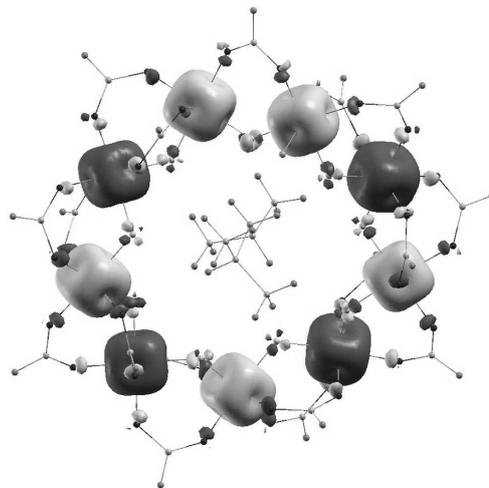


Fig. 1. Plot of the spin density. Light (dark) shades are positive (negative) isosurfaces for the value $\pm 0.01 e/\text{Bohr}^3$.

We also estimate coupling constants within the standard broken symmetry approach [4] for two different models of couplings between Cr ions presented in Fig. 2. For nearest neighbors (NN) we find $J = 4.6$ meV for 8 pairs of Cr ions and $J' = 1.1$ meV for distinctive pair of Cr ions. Considering NN and next NN couplings, we obtain $J = 4.6$ meV, $J' = 1.1$ meV and for the next NN $J'' = 0.1$ meV, respectively. The couplings J , J' and

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J'' are close to those found within DFT for the eight-numbered molecules [3, 4] but significantly overestimate the experimental values [6]. The ratio J'/J is underestimated by a factor of 2.

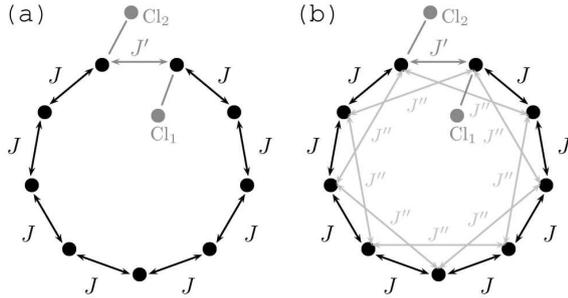


Fig. 2. Schematic representation of nearest neighbour exchange coupling between the Cr(III) ions (a) and for nearest and next nearest neighbors (b).

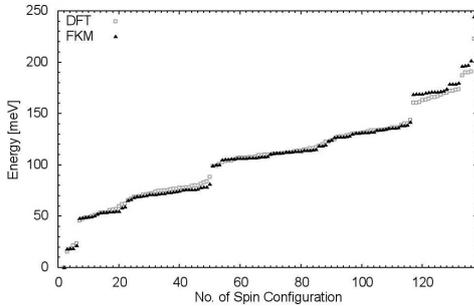


Fig. 3. Energies of Cr₉ ring for all the nonequivalent spin configurations of the ions, referred to the ground state, found within the DFT and FKM approach.

An alternative theoretical description of molecular magnetic rings is based on the Falicov–Kimball model (FKM) extended by Hund coupling between spins of electrons and ions [4]. The Hamiltonian of this model is

$$H = t_{mn} \sum_{\langle m,n \rangle} \sum_{\sigma=\uparrow,\downarrow} d_{m,\sigma} + d_{n,\sigma} + U \sum_m n_m^d n_m^f + J^H \sum_m s_m^z S_m^z,$$

where $\langle m, n \rangle$ denotes the nearest neighbor sites m and n of the ring, σ is a spin indice, $d_{m,\sigma}$ ($d_{m,\sigma}^\dagger$) is an annihilation (creation) operator of electron, n_m^d (n_m^f) is an occupation number of electron (ion), s_m^z (S_m^z) stands for a z -component of spin of electron (ion). The on-site interaction between electron and magnetic ion on the site is represented by two coupling constants: U which is Coulomb-type, and J^H which reflects the Hund's rule force. The electron hopping amplitude between two adjacent ions is t . Here the parameter U is irrelevant as all magnetic ions are the same.

For 9 itinerant electrons in the system and hopping amplitude $t \sim 96$ meV, setting $J^H = 2t$ and hopping amplitude between distinctive Cr ions $t' = t/2$ leads to proper representation of the total energies corresponding to different spin arrangements with respect to the anti-ferromagnetic ground state as shown in Fig. 3.

Let us notice that the chosen values for on-site Coulomb interaction parameter and for the hopping amplitudes coincide with those for Cr₈ molecule [4] and are comparable to the values provided in the literature for the Hubbard model [9].

3. Conclusions

We have carried out the systematic SIESTA-based DFT calculations for the Cr₉ molecule. We have shown that exchange couplings are in quantitative agreement with other DFT theoretical investigations for the Cr₈ family. Finally, we have shown that the approach as simple as Falicov–Kimball model is capable of providing accurate energy calculations for different spin configurations for molecular nanomagnets.

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