Fundamental Gaps in Cr₈, Cr₇Ni and Cr₇Cd Molecules

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In this paper we investigate fundamental gaps of three octametallic Cr-based molecular rings $Cr_8F_8(Piv)_{16}$, $Cr_7NiF_8(Piv)_{16}$ and $Cr_7CdF_8(Piv)_{16}$ using the SIESTA package. We find that for the ground-state antiferromagnetic configurations, the gap of the homometallic ring is significantly higher than those of the heterometallic rings. In addition, the HOMO and LUMO orbitals are plotted and discussed.

1. Introduction

Magnetic molecules have been an object of study ever since they were discovered [1]. One of the properties that are investigated are excitation gaps. One can distinguish two different types of those gaps. The fist one is electronic gap (fundamental gap) and the second one is optical gap [2, 3].

The electronic gap is defined as the difference between the first ionization energy and the first electron affinity or in other words it is the minimal energy required to create unbounded electron-hole pair.

Both types of band gaps can be determined for specific materials through experimental methods, however theoretical description of the gaps is still problematic. In theory the electronic gap cannot be viewed simply as the difference between energies of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). In practice these energies are obtained from DFT calculations, considering a modified system with an extra electron [2-3].

In this paper we focus on the determination of the fundamental gaps in the chromium-based ring molecules [4-6] which have not been estimated before. We consider homonuclear molecular ring $Cr_8F_8(O_2CH)_{16}$ (in short Cr_8) and its heteronuclear derivatives in which one of the Cr ions have been substituted with different metal ion - specifically Ni (Cr_7Ni) and Cd (Cr_7Cd). For these molecules we consider the parallel and anti-parallel orientations of the spins carried by the consecutive magnetic ions. Within our work we refer to these configurations as ferro- and antiferro-magnetic respectively.

2. Results and discussion

In the DFT calculations the energies of the HOMO and LUMO typically do not correspond to the ionization potential and electron affinity, respectively [2, 7–9]. Reliable estimates of the band gap can be obtained by performing two calculations [2, 7–9] of the Kohn-Sham HOMO energy, one for the N particle system and another for the $N + 1$ particle system with 1 extra electron. In this method the HOMO energies are related to the fundamental band gap as

$$E_g = E_H^{N+1} - E_H^N, \tag{1}$$

where E_H^{N+1} (E_H^N) stands for HOMO energy of the $N + 1$ (N) particle system.

In our Siesta [10] calculations the exchange and correlation effects are accounted for by the generalized gradient approximation (GGA) with PBE exchange-correlation potential [11]. One extra electron is simulated through calculations for charged molecule using Siesta 'NetCharge' option.

The HOMO-LUMO gap for N-particle system ($E_H^N - E_L^N$) and the HOMO energies for $N + 1$ (E_H^{N+1}) and N (E_H^N) particle systems, as well as fundamental gap determined according to Eq. (1) for Cr_8, Cr_7Cd and Cr_7Ni molecules in the ground antiferromagnetic (AFM) and ferromagnetic (FM) states are listed in Table.

TABLE

Fundamental gaps and HOMO energies for N and $N+1$ particle system for C_8, Cr_7Ni and Cr_7Cd molecules in the AFM and FM states.

	Cr₈		Cr₇Ni		Cr₇Cd	
	AFM	FM	AFM	FM	AFM	FM
$E_H^N - E_L^N$ [eV]	2.38	2.01	0.15	0.11	0.18	0.13
E_H^{N+1} [eV]	-2.40	-4.43	-1.91	-2.16	-1.90	-2.15
E_H^N [eV]	-5.54	-5.31	-3.16	-3.25	-3.23	-3.31
$E_H^{N+1} - E_H^N$ [eV]	3.14	0.88	1.25	1.09	1.33	1.16

For the Cr_8 molecule the HOMO-LUMO gap for N particle system in the AFM state is smaller than fundamental gap obtained from difference of HOMO levels of $N + 1$ and N particle systems. On contrary in the FM state the predicted fundamental gap is the smaller one. For Cr_7Ni and Cr_7Cd molecules in both magnetic configurations the estimation of fundamental gap leads to greater values than difference of HOMO and LUMO levels.

We do not find any evidence of the experimental data on this topic, but our outcomes seem to be consistent with other theoretical results. To be more specific –

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the HOMO-LUMO gap for N particle system for Cr8 molecule in the AFM state in Ref. [12] is reported as 2.36 eV and is consistent with our estimate, while with help of Hubbard U term it raises to 3.85 eV. In Ref. [13] the HOMO-LUMO gaps, calculated by the B3LYB functional for Cr_8 and Cr_7Ni, are presented with the following values, 4.0 eV and 4.2 eV, respectively. The last inconsistency should be verified by other theoretical studies and may be related to the estimates of magnetic couplings.

Additionally we present in Fig. 1 the plots of HOMO and LUMO levels in energy range [HOMO-0.1 eV:HOMO] and [LUMO:LUMO+0.1 eV] for the N and $N + 1$ particle systems, respectively, for all considered molecules in the AFM state.
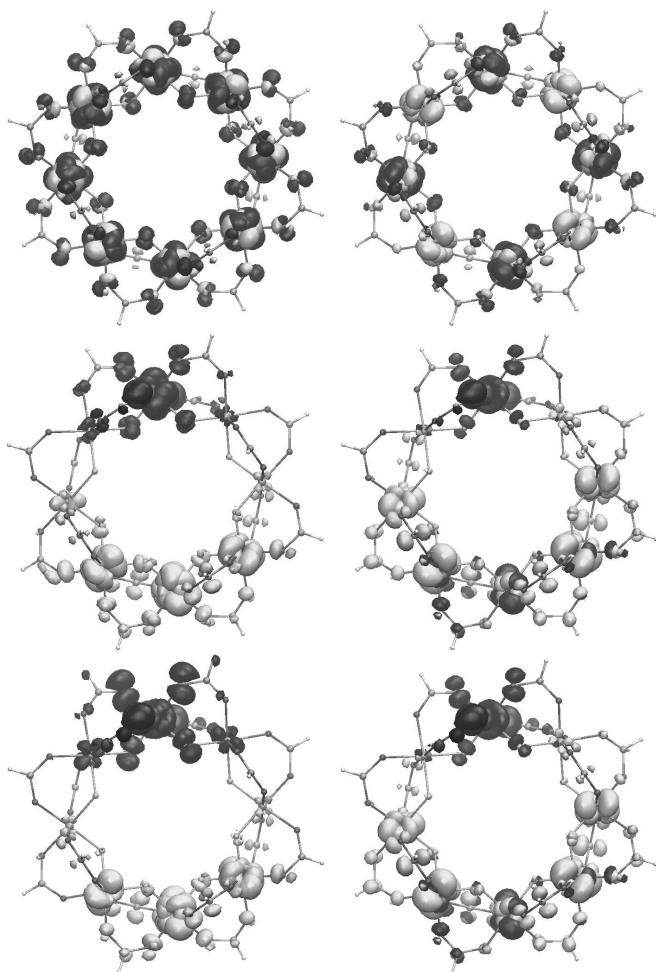

Fig. 1. Isosurface plots of the HOMO (dark) and LUMO (light) levels for N-particle system (left) and $N + 1$-particle system (right) in Cr_8 (top), Cr_7Ni (middle) and Cr_7Cd (bottom) molecule in the AFM state for isovalues of ± 0.05 a.u. Orbitals with energy that fall in the [HOMO-0.1 eV: HOMO] and [LUMO: LUMO+0.1 eV] energy windows are plotted.

For Cr_8 molecule the N particle system plot suggest that LUMO states are spread over all Cr ions, while $N+1$ system plot shows that in this molecule LUMO states can be restricted to the one spin channel i.e. to every other Cr ion. For heteronuclear rings the plots for N particle systems shows that LUMO states are mainly delocalized over a large portion of the ring as shown in Ref. [13] for Cr_7Ni. Furthermore, the picture for $N + 1$ system leads to the important conclusion that the LUMO orbital of the Cr ion located oppositely to the doping ion will be occupied first.

3. Conclusions

In this paper we show that for family of Cr_8 molecules the fundamental energy gaps are greater than those gained from Kohn-Sham HOMO and LUMO levels for N particle system. For Cr_8 molecule the fundamental gaps are significantly higher than those of heteronuclear molecules.

Acknowledgments

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