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Dipole Polarizability of C_{28} and its Counterparts Nb_4B_{18} and Ta_4B_{18} . Insights from a Density Functional Theory (DFT) Endeavour

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Abstract. We report on a preliminary investigation of the non linear optical (NLO) properties and in particular dipole polarizability. The target species are two perfect tetrahedral nanoclusters Nb_4B_{18} and Ta_4B_{18} , along with their nanofullerene counterpart that is C_{28} . Our study based on density functionals (DFs) that have gained popularity among the scientific community. In addition we performed Hartree-Fock calculations known for not including dynamic electron correlation. The DF obtained values are characterized by some dispersion, with maximal differences to be around 5 %, in all three cases. Given that the DFT introduces a fuzzy percentage of electron correlation sets the observed convergence of HF values to DFT ones is at least surprising. Furthermore, it should be said that though the values can be characterized as accurate their reliability should not be taken for granted. Last, we note the smooth convergence of LC-BLYP, LC-BP86, LC-BPW91 to LC- ω hPBE.

1. Introduction

The study of the field of nanoclusters emerged as a need to bridge the gap between molecules and matter. Species of this type are building blocks of larger architectures. As such Nb_4B_{18} and Ta_4B_{18} after self-assembling could form the respective face central crystals M_4B_{15} ($M=Nb, Ta$) [1].

On the other hand the importance of dipole polarizability ($\alpha_{\alpha\beta}$) has been elegantly described in the excellent book by Bonin and Kresin [2]. This list has been extended by studies relate it to hardness-softness [3], aromaticity [4], and other important natural phenomena such as electrostatic interactions that involve molecular polarization [5].

For these reason we have put some effort in calculating dipole polarizabilities of Nb_4B_{18} and Ta_4B_{18} in Density Functional Theory (DFT) levels of theory and for the shake of comparison at Hartree-Fock, as well. The DFT methods are still the only alternative as the size of the

architecture grows. Therefore, it seems mandatory to check their accuracy and reliability in such calculations.

2. Computational Details

We have calculated dipole polarizability ($\alpha_{\alpha\beta}/e^2\alpha_0^2E_h^{-1}$) via the Finite Field approach. To ensure the reliability of the method we have used carefully selected field strengths of 0.003 au.

Basis sets of TZVP quality have been used for B, C, Nb and Ta. For the latter two we have also implemented effective core potentials (ECPs) as to take into account the relativistic corrections related to the nature of the two heavy atoms. In particular, these two elements have been described by the def2-TZVP basis set obtained from *Basis Set Exchange* server [6]. All calculations have been performed with Gaussian 16 package [7].

The methods used in the present study are Hartree-Fock (HF) [9], B-[10] and B3-{LYP,P86,PW91} [11, 12, 13, 14], PBE1PBE [15] and HSEH1PBE [16], CAM-B3LYP [17], LC- ω PBE [18] as well as LC-{BLYP, BP86, BPW91}, M05 [19] and M052x [20], M06 and M062x [21], M08 [22], ω B97xD [23] and BMK [25] In the case of C_{28} (5A_2) all the above methods have been applied at the restricted open (RO) formulation.

In Fig. 1 we have drawn the structure of the three nanoclusters under study. We further add a picture of the HOMO and LUMO orbitals of them as to gain information on the shape of the frontier orbitals.

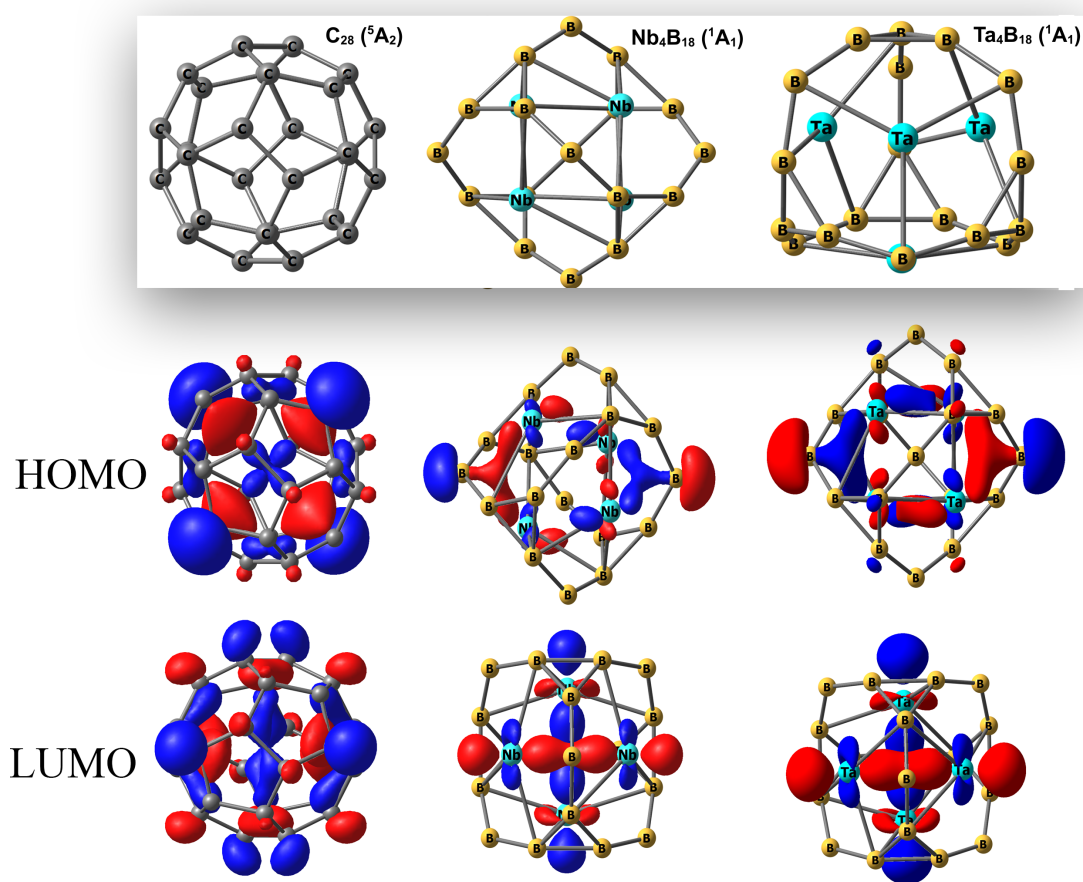


Figure 1. Structure and HOMO LUMO orbitals of and C_{28} Nb_4B_{18} and Ta_4B_{18} .

3. Results and Discussion

In the case of C_{28} the majority of DFT methods produce dipole polarizability values that are greater than the respective RO-HF ones. However, there are the LC-BLYP, LC-BP86, LC-BPW91 and LC- ω hPBE methods that diverge from the trend of the rest of DFT ones. That is the LC correction strongly affects the predictive capability of DF methods. Surprisingly enough the values of the LC methods are closer to ROHF ones, as it can be seen in Fig. 2. In particular the ROHF value is 246.4 when the LC- $\{BLYP, BP86, BPW91, \text{ and } \omega hPBE\}$ are 246.9, 247.7, 245.5 and 246.2, respectively. The others are lying in the vicinity of 255 as it can be also seen in Table 1. The same trend had been observed in a study by Sekino et al [26] on dipole (hyper)polarizabilities of polydiacetylene and polybutatriene.

Table 1. Dipole polarizability values of C_{28} , Nb_4B_{18} , and Ta_4B_{18} at HF and DFT levels of theory (*restricted open (RO) shell calculations have been performed in the case of C_{28}*).

	C_{28}	Nb_4B_{18}	Ta_4B_{18}
HF	246.4	362.82	362.09
BLYP	263.9	364.56	364.95
BP86	264.5	361.15	361.98
BPW91	262.0	357.07	357.95
LC-BLYP	246.9	352.24	351.92
LC-BP86	247.7	349.32	349.49
LC-BPW91	245.5	345.74	345.99
B3LYP	260.0	361.49	361.91
B3P86	259.7	356.96	357.87
B3PW91	258.6	355.89	356.69
CAM-B3LYP	254.2	358.40	358.47
PBE1PBE	257.3	355.56	356.12
LC- ω hPBE	246.2	347.57	347.79
HSEH1PBE	258.3	356.84	357.45
ω B97xD	255.5	361.95	362.98
BMK	259.8	367.39	369.41
M05	252.1	353.38	352.77
M052x	256.5	356.75	357.81
M06	261.4	360.19	361.46
M062x	257.5	355.74	356.81
M08	255.1	354.97	355.86

Quite opposite is the behaviour of the methods in the case of M_4B_{18} ($M=Nb, Ta$) nanoclusters.

When $M=Nb$ the BLYP(364.56), BP86(361.15), B3LYP(361.49) and ω B97xD(361.95) values are quite close to the HF(362.82). We note that in contrast to the rest of the methods BLYP(364.56) and BMK(367.39) values are larger than the HF ones. The LC correction affected the most the obtained values. This can be seen as a sharp lowering of the obtained values. In particular LC- $\{BLYP, BP86, BPW91 \text{ and } \omega hPBE\}$ values are 352.24, 349.32, 345.74 and 347.57, respectively. The M05 method produces a value of 353.38, that is the one being close to the LC family. The other functionals produce values that are in between 355 and 360 au.

For M being Ta , the BP86(361.98), B3LYP(361.91), M06(361.46) and ω B97xD(362.98) are the ones that are noticeable proximal to HF(362.09) one. A smooth convergence of LC-BLYP,

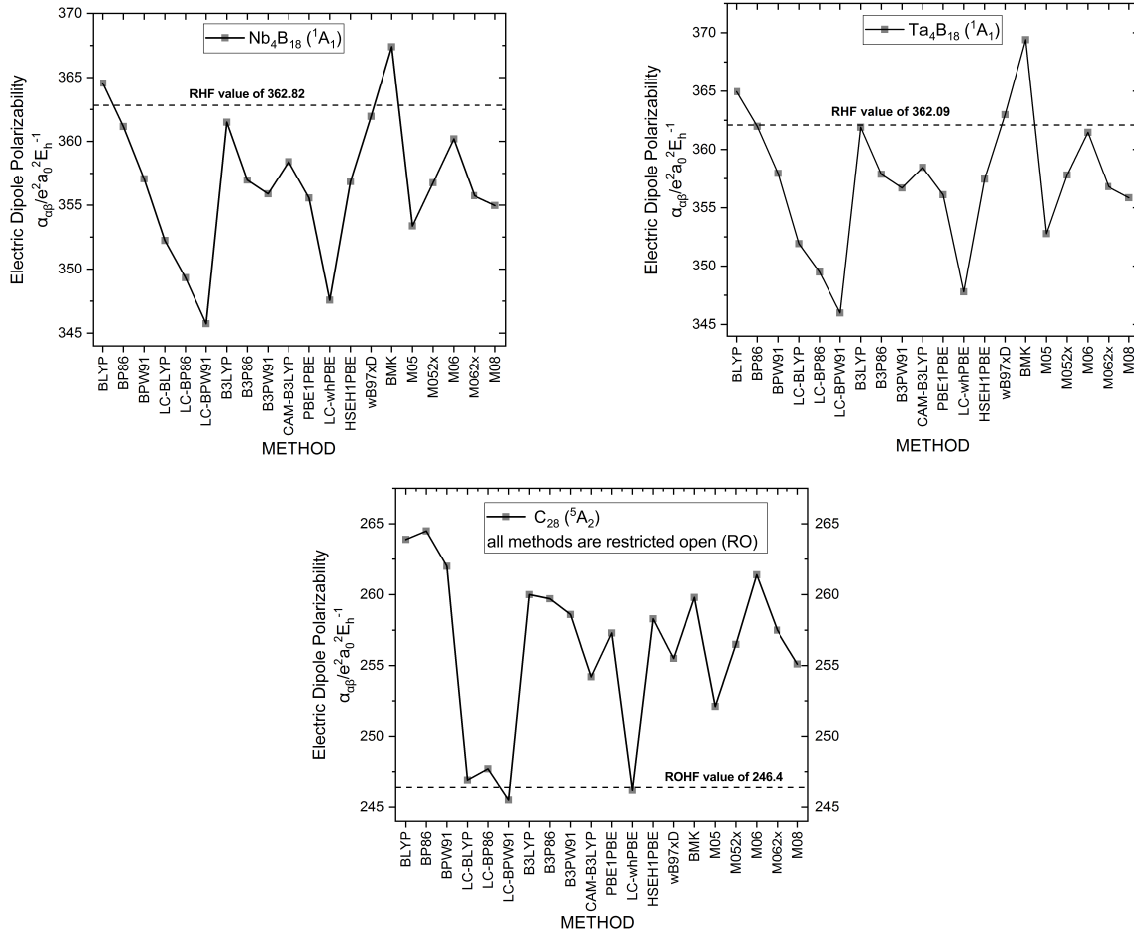


Figure 2. Dipole polarizabilities of Nb_4B_{18} , Ta_4B_{18} and C_{28} .

LC-BP86, LC-BPW91 values (351.92, 349.49, 345.99) to LC- ω PBE (347.79) has been also observed. Once again M05 (352.77) resembles the LC family results.

What we have seen from the above made analysis is that in all three cases DFs methods caused a positive (enhancement) or negative (lowering) of the respective HF dipole polarizability values. Furthermore, it is known that DFs methods introducing a (fuzzy) percentage of dynamic electron correlation. That is the reason of gaining their popularity (along with the fact that they need moderate computational resources). In the present study the DFs produced results differ by the most of 5 % from the HF ones. Moreover, it is the nature of them that does not allow for naming one of them as method of preference. That, probably, justifies the question of whether there is a need of a calculation of DFT type when a HF one produces similar results, without the accompanying uncertainty of the DFT methods.

Last but not least, we note the remarkably similarity of dipole polarizability of both M_4B_{18} ($M=Nb, Ta$). Thus, it is fair to assume that the nature of the heavy atom has a negligible effect on this interesting property.

4. Conclusion

Having performed restricted open shell calculations on the C_{28} (5A_1) fullerene we found that most of the functionals enhance the value of dipole polarizability. In striking difference is the LC-({BLYP, BP86, BPW91, ω PBE}) family of functionals that produces results quite similar

to ROHF ones. The inverse has been observed in M_4B_{18} ($M=Nb, Ta$) nanoclusters. In particular DF methods lower the value of Hartree-Fock polarizability. This is most intense in the case of LC family. However, in all cases the DFT values are around 5 % lower or greater than the HF ones. This could raise the question whether there is a need of calculation of DF type instead of a pure HF one, that it is known for its limitations. Last, we note that both heavy metal including moieties are characterized by almost identical dipole polarizability values. Therefore, it is fair to assume that there is a negligible effect of the nature of heavy atom on the value of dipole polarizability.

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