

MODELING OF NANOSTRUCTURES

More on Optimal Locations of Boron Atoms in the Exohedral and Endohedral C₆₀ Fullerene

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Abstract—Our recent work on multiple locations of boron atoms in the exohedral and endohedral C₆₀ fullerene, [1], carried out within the Hartree-Fock method with the second order Møller-Plesset perturbation theory MP2 (HF-MP2), prompted recently a comment from Xu and Hou, [2], who have performed several density functional theory (DFT) calculations using DFT functionals of different complexity. In three out of five cases considered in our work, DFT calculations give the same ground state confirmations whereas in two cases optimal configurations have turned out to be different. However, depending on the choice of the exchange-correlation functional, the geometry optimization within DFT can also result in different ground state confirmations. The energy balance between nearest confirmations in these molecular complexes is subtle, and various methods can give different ground state structures. We therefore argue that the presented DFT calculations are not benchmark, and their results should be compared with ours (HF-MP2) on equal ground. We also present additional HF geometry optimizations with the 6-31G* basis set, which confirm the ground state confirmations obtained at the HF/6-31G level.

Keywords: quantum chemical calculations, chemical bonding, fullerenes, nanomaterials, boron-neutron capture therapy

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1. INTRODUCTION

In our recent work, [1], we have suggested to use a single boron atom or diatomic molecule B₂ inside the C₆₀ fullerene cage for the boron neutron capture therapy. Using a fullerene cage for one or several boron atoms can be an option for the development of new radio-pharmaceuticals. Correspondingly, we have performed a set of ab initio calculations of these molecular complexes within the Hartree-Fock method with the second order Møller-Plesset perturbation theory, HF-MP2. We have also considered optimal configurations with one or two boron atoms located outside the C₆₀ fullerene. Our main goal in [1] was to obtain the binding energy of various configurations of boron atoms inside and outside the C₆₀ fullerene and to calculate the corresponding shifts of the energy E_{1s} of the 1s boron orbital, which then can be used in experiments (with the photon or electron impact spectroscopy) for the identification of the found configurations.

In [2], Xu and Hou claim that we use the method which is not “sufficiently reliable” and put forward their density functional theory (DFT) calculations. In the present paper we discuss the fact that in these

molecular complexes different methods give different ground state confirmations, analyse in detail equilibrium geometries found in our study [1] and [2] and investigate the role of the 6-31G* basis set. For that, using the GAMESS package [3] we have carried out additional HF-calculations at distinct equilibrium geometries of B₂@C₆₀ and B@C₆₀B obtained in [1] (HF-MP2) and in [2] (DFT).

2. RESULTS AND DISCUSSION

It is worth noting, that although the DFT approach is a powerful tool in modern quantum chemistry and can give very good results, a perfect comparison with experimental data and other ab initio methods is not guaranteed a priori. The Kohn-Sham (KS) foundation of DFT is well established, and the “method is capable, in principle, of yielding exact results, but because the equations of the Kohn-Sham (KS) method contain an unknown functional that must be approximated, the KS formulation of DFT yields approximate results” (p. 555 of [4]). “Various approximate functionals $E_{xc}[\rho]$ are used in molecular DFT calculations. To study the accuracy of an approximate $E_{xc}[\rho]$, one

Table 1. Comparison of the HF energies of the ground state of $B_2@C_{60}$ for two distinct equilibrium geometries found in [1] (E_1 , in a.u. with $S = 2$) and in [2] (E_2 , in a.u. with $S = 0$), $\Delta E = E_1(S = 2) - E_2(S = 0)$, in eV

Method/basis	$E_1(S = 2)$, a.u.	$E_2(S = 0)$, a.u.	ΔE , eV
HF/6-31G	−2320.06230	−2319.95969	−2.792
HF/6-31G*	−2320.92059	−2320.87520	−1.235
RIMP2/6-31G	−2325.51493	−2325.49605	−0.514

uses it in DFT calculations and compares calculated molecular properties with experimental ones. The lack of a systematic procedure for improving $E_{xc}[\rho]$ and hence improving calculated molecular properties is the main drawback of the DFT method” ([4], p. 559).

The HF method with the MP2 treatment, which we have used in our research, is a choice of ab initio approach, which takes into account dynamical correlation effects. It is not ideal, but in contrast to DFT it does not need the thorough validation. Since the geometry optimization of the low symmetry molecular complex of C_{60} with boron atoms within HF-MP2 is not conceivable, we have used plain Hartree-Fock method for that, calculating the full HF-MP2 energy only at the optimal configurations. Although in some cases HF-MP2 tends to overestimate correlation effects, it still remains one of the major tools used in modern quantum chemistry. In recent [5, 6] it is used for comparison with high level coupled cluster benchmark calculations of the benzene dimer.

In [2] for two configurations with two boron atoms the authors have found ground state geometries different from ours [1]. We will discuss this situation in full detail later. First, we would like to draw the attention to the fact that the authors of [2] instead of comparison their results with ours state that our results “could be incorrect”. Meanwhile, as can be seen from Table 1 of [2], the situation is ambiguous even within the DFT method, where various DFT exchange-correlation parts result in different ground state geometries of C_{60} with a single boron atom. While some single point calculations of total energy in [2] have been performed with 3- ζ and 4- ζ basis sets, the highest level of the geometry optimization is realized in ω B97XD/6-31G* (denoted in the following as DFT-I) and BPW91/6-31G* (denoted as DFT-II) with the 6-31G* (2- ζ) basis set. For a single boron atom with C_{60} , Table 1 of [2], we immediately see contradictory results for the ground state confirmations. For the endohedral case, i.e. $B@C_{60}$, the configuration Iso1 lies at 0.25 eV *lower* than the configuration Iso2 in DFT-I, whereas the same configuration lies at 0.84 eV *higher* than Iso2 in DFT-II. The same ambiguity applies to the exohedral BC_{60} : with DFT-I the configuration Iso1 ($\eta^{2(6-6)}$) lies at 0.22 eV *lower* than Iso2 ($\eta^{2(5-6)}$), while with DFT-II

Iso1 ($\eta^{2(6-6)}$) lies at 0.02 eV *higher* than Iso2 ($\eta^{2(5-6)}$). This ambiguity in DFT results, not discussed and explained properly in [2], is most likely related to the fact that the DFT-I variant include dispersion correction whereas DFT-II does not. The procedure when on top of these optimized geometries one calculates full energies using a better quality basis set and a more advanced DFT-functional cannot be considered as truly benchmark. It is clear that the optimal geometry for that case is slightly shifted aside which implies that the high level calculation is not performed exactly at the energy minimum point. If two confirmations are well separated in energy this does not matter, but in our case when two energies are almost equal, this procedure can introduce an uncontrolled error. Therefore, although the high level single point DFT calculations obtained at these geometries and listed in the last two lines in Table 1 of [2] are meaningful, they should not be considered as a benchmark of the calculations. Our opinion is that different ground state confirmations obtained with different DFT exchange-correlation functionals, indicate that the energy balance between two nearest confirmations is fragile, and it can be easily changed in various methods. There are other examples of such a situation in the literature, for example, the optimal position of the benzene dimer, which can be different in various methods [6]. This problem requires a careful study with high level methods, a priori one cannot say that some methods are “unreliable” and should be discarded. Therefore, we believe that the results of DFT should be compared with ours on equal ground.

We now discuss other results presented in [2]. Notice, that the final conclusions there largely support our calculations. For a single boron atom inside C_{60} and outside C_{60} the lowest conformations, Fig. 1 of [2] (upper left and middle panels), are in qualitative agreement with our findings (configurations (1,0) in Fig. 1 and (0,1) in Figs. 5a, 5b, 5c) of [1]). The same holds for the B_2 molecule outside the fullerene, B_2C_{60} , the configuration 0.2 mol in Figs. 7a, 7b of [1] and Iso1 in the upper right panel of Fig. 1 of [2]. *Thus, in three out of five cases written in our abstract and conclusions [1], the molecular ground state structures found in HF-MP2 and DFT are the same.* (The case of two carbon atoms in C_{60} substituted with two boron atoms (the right lower panel in Fig. 1 of [2]) has not been studied thoroughly in [1], only few comparative calculations have been done *without mentioning this case in our abstract and conclusions.*) Let us consider the two other cases where the results are different. These are two endohedral boron atoms in C_{60} , i.e. $B_2@C_{60}$, and the structure with one boron atom inside C_{60} and the other boron atom outside it, i.e. $B@C_{60}B$. For $B_2@C_{60}$ the ground state is the structure 2.0(mol) shown in Figs. 4e, 4f of [1], and the configuration Iso1 in lower left panel of Fig. 1 of [2]. In Table 1 we list the results of additional HF/6-31G, HF/6-31G* and

HF-RIMP2/6-31G calculations at two different geometries: the first [2.0 mol] is taken from our study, [1], while the second (Iso1)—from the supplement coordinate data-file of [2]. (Here RIMP2 stands for the resolution of identity (RI) version of MP2.) We see that at the level of HF/6-31G and HF/6-31G* the minima found in our study have *lower* energies, which once again confirms the correctness of our geometry optimization results within the HF method. The same applies to the B@C₆₀B case, Table 2. In our study the ground state is the configuration (1,1) in Fig. 6 of [1], in [2] – Iso1 in the lower middle panel of Fig. 1 of [2]. For B₂@C₆₀ our minimum remains the lowest in RIMP2, while RIMP2 for B@C₆₀B indicates that the Iso1 is the lowest.

In our work [1] we deal with the 6-31G basis set, which in comparison with 6-31G*, used in [2] for geometry optimization, lacks the polarization *d*-functions. Here it is worth mentioning that we have chosen this relatively poor basis only to be able to handle and complete the MP2 calculations. As well known, for open electron shells the HF-MP2 method requiring much memory and the CPU time, is laborious and time consuming. In [2] it has been pointed out that this basis set could lead to qualitative errors. Although in principle this is conceivable, this argument can be equally applied to the DFT study in that the results with a double- ζ basis set for searching the optimal geometry can be incorrect in respect to the geometry optimization obtained within a more representative triple- ζ basis set. For example, in going from double- ζ basis sets to triple- ζ basis sets for CCSD(T) applied to the T-shaped and parallel displaced (PD) benzene dimer configurations, Table 3 of [6], the ground state changes from the T-shaped to the PD configuration. However, in the present case such a situation is not expected by us. The boron being the left neighbor of carbon in the same row of periodic table, experiences a strong covalent bonding with it mainly through the valence atomic *2s*- and *2p*-functions, which are already included in the 6-31G basis set. The polarization *d*-functions in this binding play only a secondary role. This viewpoint is supported by our calculations presented in Tables 1 and 2. The optimal geometries found with HF/6-31G in [1] remain the lowest also in HF/6-31G*. Additional structural optimization at the HF/6-31G* level yields tiny changes in the geometry and total energy of the ground state: -2320.92123 a.u. for B₂C₆₀ and -2320.88924 a.u. for BC₆₀B, compare with E_1 in Tables 1 and 2.

It is worth mentioning that the numerical data quoted in [2], hinder a detailed comparison with our results [1]. The effective atomic charges for C and B atoms computed from molecular orbitals, are known to be ambiguous characteristics, and in our work we have used uniquely defined Bader charges [7]. It is regrettable that in [2] there is also no discussion of non-zero spin properties for solutions with two boron

Table 2. Comparison of the HF energies of the ground state of B@C₆₀B for two distinct equilibrium geometries found in [1] (E_1 , in a.u.) and in [2] (E_2 , in a.u.), $\Delta E = E_1 - E_2$, in eV. Spin quantum number $S = 0$

Method/basis	E_1 , a.u.	E_2 , a.u.	ΔE , eV
HF/6-31G	-2320.01492	-2319.97483	-1.091
HF/6-31G*	-2320.88715	-2320.86574	-0.583
RIMP2/6-31G	-2325.49143	-2325.51117	$+0.537$

atoms. Meanwhile, as has been pointed out in [1], the B₂ molecule has the spin quintet ($S = 2$) ground state [8, 9], which often leads to non-zero spin ground states for such complexes [1].

3. CONCLUSIONS

In summary, the results of DFT calculations in [2] should be compared with ours on equal ground, as done e.g. in the case of benzene dimer [5, 6]. In view of the fact that different variants of DFT result in different ground state geometries, without a proper discussion and explanation of this fact we cannot accept the results of [2] as benchmark calculations. Answering the question on the role of the polarization *d*-functions raised in [2], we have presented here the results of calculations using the DFT equilibrium geometries for B₂@C₆₀, Table 1, and B@C₆₀B, Table 2. (These are two cases where the DFT and HF geometry optimizations predict different ground state confirmations.) From Tables 1 and 2 it follows that in HF-method DFT-confirmations have higher energies. Therefore, in [1] there is no mistake in finding structures with lowest energies within the chosen method (HF). The conclusion holds for both 6-31G and 6-31G* basis sets, which shows that the polarization functions do not change the order of energy minima.

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CONFLICT OF INTEREST

The authors of this work declare that they have no conflicts of interest.

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