Comment on "Multiple locations of boron atoms in the exohedral and endohedral C_{60} fullerene"

Jianzhi Xu and Gao-Lei Hou[*]

MOE Key Laboratory for Non-Equilibrium Synthesis and Modulation of Condensed Matter,
School of Physics, Xi'an Jiaotong University, Xi'an 710049, People's Republic of China

In a recent publication Bibikov *et al.* [Phys. Rev. A **105**, 022813 (2022)], theoretically investigated the structures of one or two boron atoms binding in endohedral or exohedral positions of C_{60}. We found their theoretical methods, i.e., HF/6-31G for structure optimization, may not be reliable, and therefore some of the structures identified as the most stable ones could be incorrect. Our more extensive and systematic calculations on these C_{60}/B complexes have corrected those deficiencies, and redetermined the most stable structures for those complexes with higher reliability.

In a recent study [1], Bibikov *et al.* investigated the bound structures of exohedral and endohedral C_{60} fullerene complexing with one or two boron atoms using an *ab initio* Hartree-Fock (HF) method [2] in combination with the 6-31G basis set [3,4]. They further calculated the single-point energies of the different isomers of those fullerene-boron complexes using the Second-order Møller-Plesset (MP2) theory [2]. Based on those calculations, they concluded that the most stable binding position of a single boron atom with the exohedral C_{60} is the double-bond midpoint between two hexagons and the center with the endohedral C_{60}; of two boron atoms in the exohedral cage is the B_2 molecule attaches vertically to the double-bond midpoint of two hexagons and the center in the endohedral C_{60}; of two boron atoms substituted for two carbon atoms in C_{60} is the opposite sides of the fullerene.

This study attracted our attention and interest as we have been interested in revealing the structures and properties of exohedral fullerene-metal complexes using a combined approach of infrared multiple photon dissociation (IRMPD) spectroscopy and theoretical calculations [5–8]. We realized that there might be non-ignorable errors with both the theoretical methods and conclusions in Ref. [1]. In this Comment, we aim to point out that several of the structures identified in Ref. [1] as the most stable ones are likely not correct due to the use of oversimplified computational methodology without proper validation.

First of all, omission of polarization functions in the basis set employed in Ref. [1] could result in quantitative, in certain cases even qualitative, error as documented previously [9–11]. Polarization functions describe the deformation of atomic orbitals in a molecular environment, of critical importance to reliably predicting the geometric and energetic properties of studied systems. Besides, the HF method ignores the Coulomb-correlation interaction, potentially leading to significant errors in the calculated energetic levels and stabilities.

Nowadays, it is well established that density functional theory (DFT) calculations can be both reliable and cost efficient in comparison with HF and MP2 calculations [12]. We have justified the performance of several of the most popular and common DFT methods, including PBE, BPW91, B3LYP, PBE0, M06-2X, and ωB97XD, and both the 2-ζ and 3-ζ quality basis sets (6-31G* and 6-311G*) were employed (Table I) (see the Appendix for computational details). For exohedral C_{60}B, we further calculated the single-point energies of its two low-lying isomers using a double-hybrid functional and the 4-ζ basis set, PWPB95-D3(BJ)/def2-QZVPP, which serves as a reference in the current work. Next, we will present in detail our rationalization and more convincing results regarding the structures and electronic properties of the reported C_{60}/B complexes in Ref. [1].

We first repeat the calculations in Ref. [1] using the same theoretical method HF/6-31G under both unrestricted (UHF) and restricted open-shell (ROHF) formalisms, which give overall similar results for endohedral C_{60}B as Ref. [1]. C_{60}B is an open-shell complex, and there might be spin contamination under UHF formalism, for which circumstances ROHF calculations would be desired. However, such issues seem not to exist for endohedral C_{60}B. The results in Table I show that polarization functions in the basis sets do change the relative stabilities by about 35%, emphasizing the importance of polarization functions.

When employing DFT methods in combination with the 6-31G* basis set, the relative stabilities of the two low-lying isomers seem to depend on the theoretical methods (Table I). However, the geometries obtained with BPW91 and ωB97XD functionals have only small deviations, as indicated by the calculated root-mean-square deviation (RMSD) values (Fig. 1). Single-point energies calculated at PWPB95-D3(BJ)/def2-QZVPP using geometries obtained with either ωB97XD or BPW91 show that the Iso2 is slightly more stable with almost the same extent, suggesting that both ωB97XD and BPW91 give reliable geometric structures. The accurate calculation of the electronic properties requires more advanced treatment on the electron correlation.

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[*]gaolei.hou@xjtu.edu.cn

TABLE I. Calculated relative stability (in eV) of the low-lying isomers of C_{60}/B (doublet) complex.

Theoretical levels	Endohedral $C_{60}B$ ($B@C_{60}$)		Exohedral $C_{60}B$		
	Iso1	Iso2	Iso1 ($\eta^{2(6-6)}$)	Iso2 ($\eta^{2(5-6)}$)	Iso3 (η^1)
UHF/6-31G	0.00	1.78	1.25	1.44	0.00
UHF/6-31G*	0.00	1.31	0.00	0.36	0.01[a]
ROHF/6-31G	0.00 (0.00)	1.93 (1.92)	0.00	0.23	1.03
ROHF/6-31G*	0.00	1.39	0.00	0.39	1.18
PBE/6-31G*	0.89[a]	0.00	0.02	0.00	1.10
BPW91/6-31G*	0.84[a]	0.00	0.02	0.00	1.09
B3LYP/6-31G*	0.18	0.00	0.00	0.00	1.07
PBE0/6-31G*	0.57	0.00	0.00	0.14	1.17
M06-2X/6-31G*	0.00	0.27[a]	0.00	0.18	1.20
ωB97XD/6-31G*	0.00	0.25	0.00	0.22	1.13
ωB97XD/6-311G*//ωB97XD/6-31G*	0.00	0.23	0.00	0.20	1.02
ωB97XD/6-31G*//BPW91/6-31G*	0.00	0.24	0.00	0.09	1.04
PWPB95-D3(BJ)/def2-QZVPP//ωB97XD/6-31G*	0.22	0.00	0.00	0.12	1.08
PWPB95-D3(BJ)/def2-QZVPP//BPW91/6-31G*	0.25	0.00	0.00	0.13	1.00

[a]Structures having imaginary frequency. Values in parentheses are from Ref. [1]

For exohedral $C_{60}B$, UHF calculations apparently do not give correct results as severe spin contamination in Iso3 of exohedral $C_{60}B$, for which ROHF calculations should be employed. All of our DFT calculations predict that the structures with B binding with the bridge sites, either those between two hexagonal rings or between one hexagonal and one pentagonal ring, are much more stable than η^1 $C_{60}B$ (B binds an atop site of C_{60}) with $\eta^{2(6-6)}$ $C_{60}B$ (a bridge site of two C_{60} hexagonal rings) being slightly more favorable at most of the adopted theoretical levels. The results suggest that the two bridge isomers are essentially degenerate in energy; they may convert to each other with low barriers, which deserves a more in-depth study.

In endohedral $C_{60}B$ (denoted as $B@C_{60}$), the calculated atomic charges of the B atom are -0.014 and $+0.426$ e in Iso1 and Iso2, respectively. In exohedral $C_{60}B$, the atomic charges of B in η^1, $\eta^{2(5-6)}$ (a bridge site between one hexagonal and one pentagonal ring), and $\eta^{2(6-6)}$ isomers are $+0.583$,

$+0.844$, and $+0.831$ e, respectively, suggesting appreciable charge transfer from the B atom to the C_{60} cage. This is in line with the high electron-accepting ability of C_{60} [13] and our recent finding in the C_{60}-metal complexes [6].

Our calculation on exohedral $C_{60}B_2$ in Fig. 2 predicts a similar most stable structure as in Ref. [1]. In this structure, the B_2 unit interacts perpendicularly to the C_{60} cage in a $\eta^{2(6-6)}$ fashion with the same B–B and C–B bond lengths of 1.56 Å. It is shown that the atomic charge of B closer to the C atom is -0.279 e, and the other B atom is $+0.640$ e, consistent with the high electron-accepting ability of the C_{60} cage.

For endohedral $C_{60}B_2$ ($B_2@C_{60}$), Ref. [1] concluded that two B atoms locate at the center of C_{60} along the line connecting two opposite pentagons (Iso3). Our calculation at the ωB97XD/6-31G* level predicts that the isomer with a B_2 (B–B: 1.77 Å) unit locating 1.19 Å below one pentagon (Iso1) has much higher stability than Iso3. The atomic charges of the

Endohedral $C_{60}B$

Iso1; 0.030 Å   Iso2; 0.086 Å

Exohedral $C_{60}B$

η^1 $C_{60}B$; 0.063 Å $\eta^{2(5-6)}$ $C_{60}B$; 0.030 Å $\eta^{2(6-6)}$ $C_{60}B$; 0.058 Å
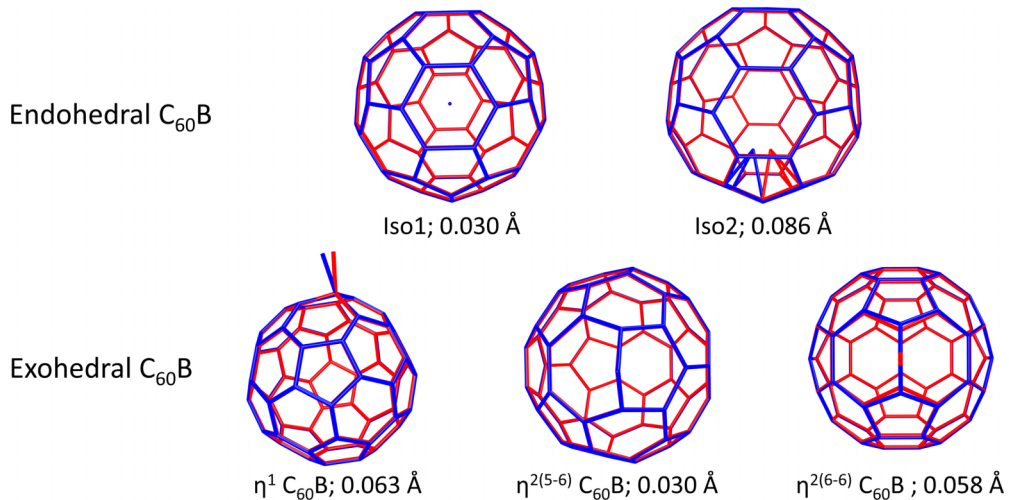
FIG. 1. Overlaid structures and RMSD values related to all atom positions for the isomers of both endohedral and exohedral C_{60}/B obtained at BPW91/6-31G* (blue) and ωB97XD/6-31G* (red).
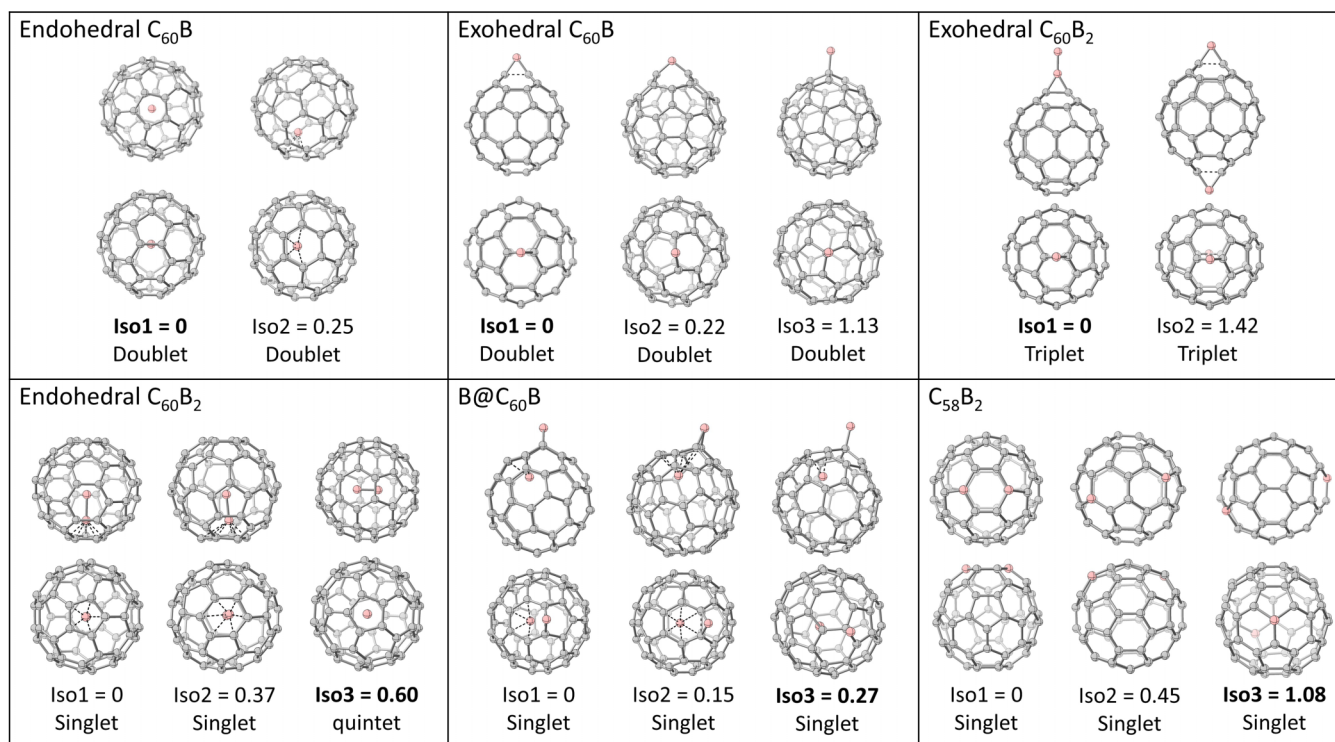
FIG. 2. Calculated typical low-lying isomers of C_{60}/B complexes at ωB97XD/6-31G*. Isomers in bold are the global minima determined in Ref. [1]. Relative stabilities (in eV) and multiplicities are indicated. Two different views are provided for better visualizing the structures.

two B atoms are calculated to be +0.253 and +0.329 e with the B atom closer to the C_{60} cage being less positive.

For $C_{60}B_2$ with one B inside the cage and one outside (denoted as B@C_{60}B), the isomer with the outer B atom in a $\eta^{2(5-6)}$ fashion with an equal C–B bond length of 1.53 Å and the inner B atom lying below an adjacent hexagon (Iso1) is predicted to be 0.27 eV lower in energy than the most stable one (Iso3) determined in Ref. [1]. It is interesting to note that encapsulating one B atom in C_{60} modulates the most stable binding position of the outer B atom from $\eta^{2(6-6)}$ in exohedral C_{60}B to $\eta^{2(5-6)}$ in B@C_{60}B. The atomic charges of the outer and inner B atoms are calculated to be +0.623 and +0.330 e, respectively.

For $C_{58}B_2$ with two B atoms substituting for two C atoms in C_{60}, the most stable structure in Ref. [1] was constructed by placing the two B atoms far away to avoid high Coulomb repulsion (Iso3). Indeed, this would be the first thought if only basing on chemical intuition; however, one could not ignore the attractive interactions induced by the B and C atoms. For example, previous studies [14,15] showed that the structure with the two B atoms replacing two C atoms at the diagonal positions of the same hexagon is most stable. Our calculations confirm this structure to be the most stable one (Iso1), over 1.0 eV more stable than the one reported in Ref. [1]. The atomic charges of the two B atoms are both calculated to be +0.831 e, and those of the neighboring C atoms are –0.302 e on average.

In conclusion, the HF method is not sufficiently reliable for the electronic structure calculations, while the well-developed density functional theory methods can achieve both good accuracy and low computational cost, becoming a more practical option even over the post-HF method, like MP2. Addition-
ally, polarization functions in the basis sets employed in DFT methods are essential for reliable calculations. Our work points out those defects in the calculations by Bibikov *et al.* [1] and reports more reliable results regarding the most stable structures and charge distributions of the C_{60}/B complexes. Furthermore, our work also hints at interesting structure conversion, charge transfer, and chemical bonding properties in those complexes, which will be reported in a more detailed study shortly.

The authors declare no competing financial interests

APPENDIX: COMPUTATIONAL METHODS

All the calculations are carried out by GAUSSIAN 09 [16] and ORCA [17] software. Several functionals, including GGA (PBE [18], BPW91 [19,20]), hybrid GGA (B3LYP [21,22], PBE0 [23], and ωB97XD [24,25]), and hybrid-meta GGA (M06-2X [26]) in combination with 6-31G* [3,4,27] are employed. Single-point energies of the two low-lying isomers of exohedral C_{60}B were evaluated using the double-hybrid functional and 4-ζ basis set, PWPB95-D3(BJ)/def2-QZVPP [28–31], which seems to support that the results from ωB97XD/6-31G* are more reliable. In calculating the open-shell systems, we used the default unrestricted

KS-DFT (UKS) method in GAUSSIAN [32]. We checked the performance of ROKS and UKS on Iso1 of the exohedral $C_{60}B$ as shown in Fig. 2 (see Supplemental Material [33]), and the calculated absolute total electronic energies (GAUSSIAN 09 E.01) are -2310.1873937 (UωB97XD) and -2310.1862366 a.u. (ROωB97XD), respectively. Their difference is 0.0011571 a.u. or 0.031 eV, small enough to be ignored.

However, considering the possible spin contamination in the UHF calculations in some cases, ROHF formalism might be employed. Harmonic frequency analysis is employed to ensure that all the geometries have no imaginary frequency. Atomic charges were calculated with natural population analysis implemented in the NBO 3.1 package [34].

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