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Basis set effects on relative energies and HOMO–LUMO energy gaps of fullerene C₃₆

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Abstract Fifteen C₃₆ isomers were examined to determine the influence that the quality of basis sets has on the geometry parameters, the relative stability and HOMO–LUMO energy gaps of fullerene isomers calculated with density functional theory. It is worthwhile to note that the geometry parameters of all C₃₆ isomers are insensitive to basis sets. On the other hand, one set of *d*-type polarization functions plays an important role in evaluating relative stability and HOMO–LUMO energy gaps, while diffuse functions are not effective. To obtain reliable energies, at least a double-zeta plus polarization basis set is required, and a triple-zeta plus polarization basis set is suggested to lead to accurate energies at a reasonable computational cost.

Keywords Fullerene · Basis set · Relative energy · HOMO–LUMO energy gap · C₃₆

Introduction

Fullerenes are usually considered as even-numbered cages built only from pentagons and hexagons and based entirely on *sp*²-hybridized carbons (conventional fullerene). Since the discovery [1] and synthesis [2] of fullerenes, their chemistry has developed very rapidly. The stable and the most abundant fullerene is the I_h-symmetrical buckminsterfullerene, C₆₀. The next stable homologue is C₇₀, followed by higher fullerenes such as C₇₆, C₇₈, C₈₀, C₈₂, C₈₄, etc. [3–8]. Some fullerenes smaller than C₆₀, such as C₂₀ and C₂₈, were found to be stable in gas phase cluster-beam experiments [9]. The fullerene C₃₆, was produced by the electric DC arc-discharge method by Zettl and co-workers [10], and purified C₃₆ materials found to exist as a cluster-assembled materials in the solid state, not as a molecular form like C₆₀ [11].

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A number of isomers of fullerenes were investigated and characterized [12–24], and the structures and relative stabilities of fullerenes were calculated by theoretical methods [15–24]. Since it is not practical to calculate fullerene isomers using high-level ab initio correlation methods, density functional theory (DFT)-based approaches were usually employed along with Pople-type basis sets ranging from STO-3G to 6-31G(d) in such calculations, but it is not clear what influence the size of the basis set with a given functional would have.

In the present work, we report the results of calculations on C₃₆ fullerene (Fig. 1), in which the effects of basis sets on relative energies and energy gaps between the highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO) are explored. The HOMO–LUMO energy separation was used as an index of kinetic stability for fullerenes [25, 26]. It is well known that a small HOMO–LUMO energy gap implies low kinetic stability, because it is energetically favorable to add electrons to a low-lying LUMO and to receive electrons from a high-lying HOMO [25, 27, 28].

To the best of our knowledge, there was no systematic study for basis set convergence on relative energies and HOMO–LUMO energy gaps of fullerene isomers. In the present study, thirteen basis sets up to cc-pVQZ were employed, and the effects of polarization functions and diffuse functions were determined. The results of this work may be useful for other workers in choosing the most appropriate basis set for fullerenes when performing DFT calculations.

Computational details

The calculations were based on DFT at the generalized gradient approximation (GGA) level (Becke's 1988 functional for exchange and Perdew-Wang's 1991 functional for correlation: BPW91 [29, 30]), and an ULTRAFINE grid was employed to calculate the integrals for all calculations. Fifteen C₃₆ fullerene isomers were optimized using 3-21G,

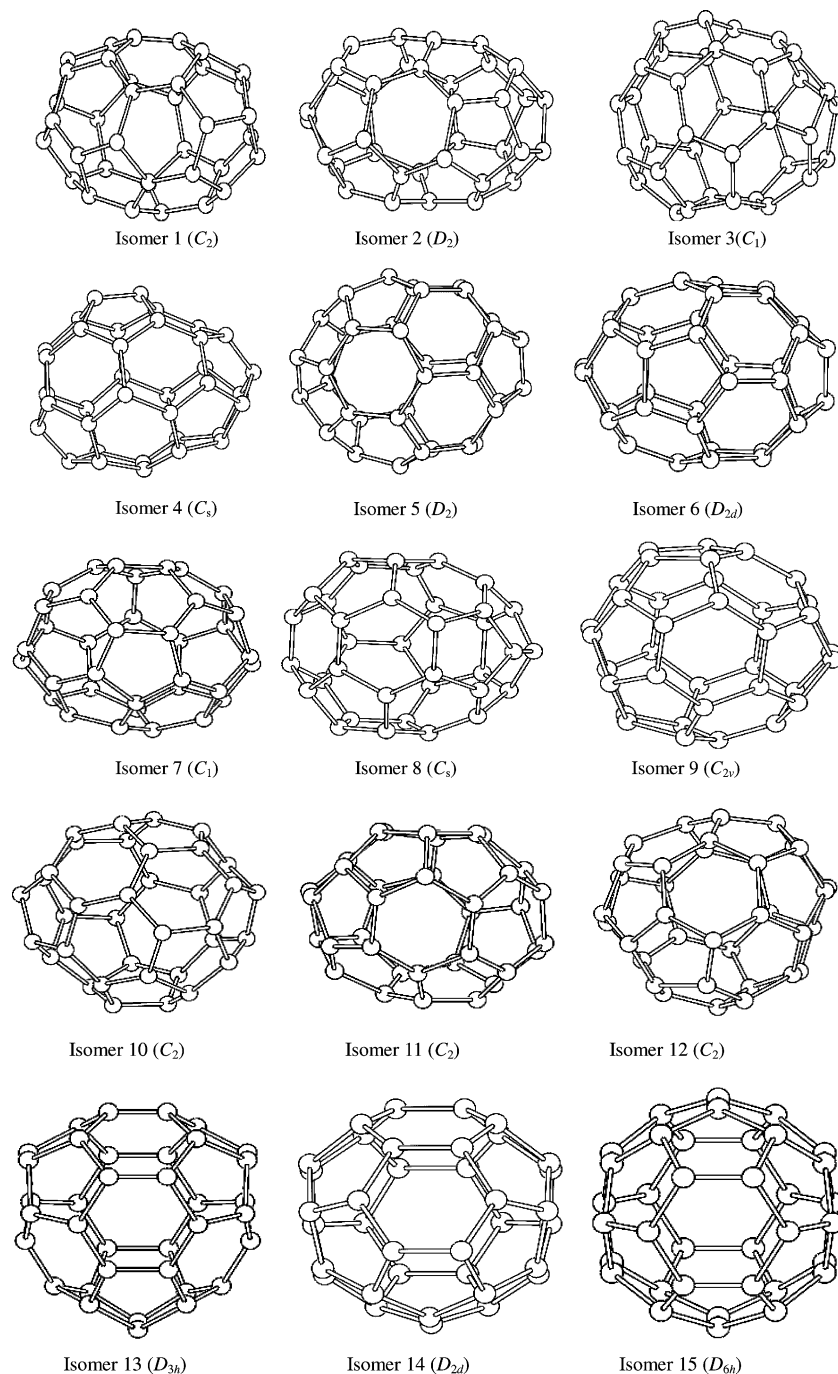


Fig. 1 Structures of 15 C_{36} fullerene isomers

4-31G, 6-31G, 6-31G(d), 6-31G(2d), 6-31+G(d), 6-311G(d), 6-311+G(d) [31], cc-pVDZ, aug-cc-pVDZ, cc-pVTZ, aug-cc-pVTZ, and cc-pVQZ [32]. The cc-pVQZ basis set, which includes three 'd', two 'f', and one 'g' functions on a carbon atom, has 1980 basis functions for C_{36} . The geometry optimizations were performed within the symmetry constraints. Vibrational frequency calculations were performed to verify the local minima of isomers for all basis sets except for aug-cc-pVTZ and cc-pVQZ. The density functional

calculations were performed with the Gaussian98 program package [33].

Results and discussion

Fifteen C_{36} isomers were optimized with thirteen basis sets up to cc-pVQZ and their optimized structures are shown in Fig. 1. The root mean square (RMS) deviation and maximum

Table 1 Root mean square (RMS) deviations and maximum deviation (MaxD) of bond lengths and angles of C₃₆ isomers, comparing with those of cc-pVQZ. (unit : bond length – Å, angle – degree)

Basis set	Bond length		Angle		Number of basis sets
	RMS	Max	RMS	Max	
3-21G	0.0127	0.0351	0.36	1.61	324
4-31G	0.0101	0.0288	0.22	1.44	324
6-31G	0.0132	0.0310	0.21	1.45	324
6-31G(d)	0.0053	0.0081	0.07	0.33	504
6-31+G(d)	0.0049	0.0078	0.07	0.35	648
6-311G(d)	0.0060	0.0088	0.06	0.33	648
6-31G(2d)	0.0028	0.0042	0.04	0.12	684
6-311+G(d)	0.0030	0.0044	0.03	0.13	936
cc-pVDZ	0.0072	0.0101	0.04	0.28	504
aug-cc-pVDZ	0.0069	0.0093	0.04	0.15	828
cc-pVTZ	0.0001	0.0005	0.01	0.09	1080
aug-cc-pVTZ	0.0001	0.0004	0.01	0.05	1656
cc-pVQZ	0.0000	0.0000	0.00	0.00	1980

Table 2 Relative energies and HOMO–LUMO gaps calculated with BPW91/cc-pVQZ (unit: kcal/mol)

Isomer	Symmetry	Relative energy	HOMO–LUMO gap
1	C ₂	82.622	4.562
2	D ₂	103.577	14.590
3	C ₁	56.841	7.624
4	C _s	75.720	8.785
5	D ₂	85.016	19.196
6	D _{2d}	34.809	14.326
7	C ₁	37.829	7.668
8	C _s	23.671	13.805
9	C _{2v}	9.217	10.216
10	C ₂	44.821	8.396
11	C ₂	12.917	12.218
12	C ₂	8.272	9.588
13	D _{3h}	34.177	10.285
14	D _{2d}	0.747	9.726
15	D _{6h}	0.000	11.025

deviation (MaxD) for bond lengths and angles with respect to the results using the largest basis set, cc-pVQZ, are listed in Table 1. It is noteworthy that the geometry parameters of fifteen C₃₆ isomers are insensitive to the basis sets. With the smallest basis set we employed, 3-21G, the RMS deviations (MaxD) for bond lengths and angles are only 0.013 Å (0.035 Å) and 0.36° (1.61°), respectively. In the following section, we have discussed basis-set convergence on relative energies and HOMO–LUMO energy gaps of fullerene isomers. The absolute values of relative energies and HOMO–LUMO gaps calculated at the BPW91/cc-pVQZ level were listed in Table 2.

Relative stability Table 3 summarizes RMS deviation and MaxD of relative energies of each isomer, with respect to the results using the largest basis set, cc-pVQZ. We could not calculate C₃₆ isomers with aug-cc-pVQZ for practical reasons, but the effects of diffuse functions on the relative energies (ΔE_{diff}) would be marginal for cc-pVQZ, because the ΔE_{diff} values are less than 0.4 kcal/mol with cc-pVDZ and cc-pVTZ, and the RMS deviations for ΔE_{diff} are 0.26 and 0.16 kcal/mol with cc-pVDZ and cc-pVTZ, respectively.

The lowest energy species is calculated to be isomer 15 (D_{6h}) for all basis sets except 3-21G, 4-31G, 6-31G,

and 6-31G(d), and isomer 14 (D_{2d}) is comparable in energy to isomer 15. With 3-21G, 4-31G, and 6-31G basis sets, the RMS deviations (MaxD) amount to 3.70 (8.01), 1.81 (3.03), and 2.02 (3.44) kcal/mol, respectively, but sharply decrease to 0.65 (0.89) kcal/mol with 6-31G(d), which shows that including a *d*-type polarization exponent is very important in evaluating the relative energies. The cc-pVDZ basis set also provides a similar deviation to that of 6-31G(d). The diffuse functions are not helpful in decreasing the deviation. A Pople-type triple-zeta basis set, 6-311G(d), reduces the deviation to 0.39 (0.67) kcal/mol. The relative energies with 6-31G(2d) show that the addition of another *d* polarization exponent to 6-31G(d) decreases the deviation to 0.30 (0.55) kcal/mol, which is comparable to the deviation with 6-311G(d). The cc-pVTZ basis set presents small deviations of 0.07 (0.14) kcal/mol, however, this basis set would be too expensive to calculate energies, particularly for higher fullerenes.

HOMO and LUMO energy gap The HOMO–LUMO energy separations were estimated using the thirteen basis sets, and their values range from 4.5 kcal/mol (isomer 1) to 19.2 kcal/mol (isomer 5) using cc-pVQZ. Table 4 lists the RMS deviations and MaxD for HOMO–LUMO energy gaps, compared with those of cc-pVQZ. With the 3-21G, 4-31G,

Table 3 Root mean square (RMS) deviations and maximum deviation (MaxD) of relative stability of C₃₆ isomers, comparing with those of cc-pVQZ. (unit: kcal/mol)

Basis set	RMS	Max	Number of basis sets
3-21G	3.70	8.01	324
4-31G	1.81	3.03	324
6-31G	2.02	3.44	324
6-31G(d)	0.65	0.89	504
6-31+G(d)	0.77	1.51	648
6-311G(d)	0.39	0.67	648
6-31G(2d)	0.30	0.55	684
6-311+G(d)	0.52	1.17	936
cc-pVDZ	0.50	0.98	504
aug-cc-pVDZ	0.70	1.29	828
cc-pVTZ	0.07	0.14	1080
aug-cc-pVTZ	0.12	0.28	1656
cc-pVQZ	0.00	0.00	1980

Table 4 Root mean square (RMS) deviations and maximum deviation (MaxD) of the energy difference between HOMO and LUMO of C₃₆ isomers, comparing with those of cc-pVQZ. (unit : kcal/mol)

Basis set	RMS	Max	Number of basis sets
3-21G	1.49	2.32	324
4-31G	1.57	2.78	324
6-31G	1.62	2.98	324
6-31G(d)	0.32	0.97	504
6-31+G(d)	0.34	0.77	648
6-311G(d)	0.14	0.33	648
6-31G(2d)	0.22	0.48	684
6-311+G(d)	0.13	0.26	936
cc-pVDZ	0.36	0.60	504
aug-cc-pVDZ	0.29	0.46	828
cc-pVTZ	0.03	0.06	1080
Aug-cc-pVTZ	0.01	0.03	1656
cc-pVQZ	0.00	0.00	1980

and 6-31G basis sets, the deviations are 1.49 (2.32), 1.57 (2.78), and 1.62 (2.98) kcal/mol, respectively, but sharply decrease to 0.32 (0.97) kcal/mol with the 6-31G(d) basis set. These results show that inclusion of a *d* polarization exponent is also important in estimating the HOMO–LUMO energy gaps of C₃₆ isomers. Although the addition of diffuse functions generally decreases the deviations, their effects are marginal (<0.2 kcal/mol). Instead, 6-311G(d) provides good estimates of HOMO–LUMO energy gaps with a deviation of 0.14 (0.33) kcal/mol, and has a slightly better quality than 6-31G(2d).

Many researchers have employed combined methods [34–36], which use a low-level quality of basis set for geometry optimization and high-level quality of basis set for the energies at the optimized geometry. We calculated relative stabilities and HOMO–LUMO energy gaps with BPW91/6-311G(d) at the BPW91/3-21G and BPW91/6-31G geometries, and compared their results with those obtained with BPW91/6-311G(d). BPW91/6-311G(d)//BPW91/3-21G and BPW91/6-311G(d)//BPW91/6-31G predict the relative stabilities with deviations of 0.11 (0.19) and 0.09 (0.16) kcal/mol, respectively, and the HOMO–LUMO energy gaps with deviations of 0.47 (0.86) and 0.77 (1.33) kcal/mol, respectively. Overall, the combined methods provide accurate

relative energies and HOMO–LUMO energy gap with a good performance-to-cost ratio, supporting that the geometries obtained from the basis sets without any polarization function are quite reliable.

Conclusions

The current work presents a systematic theoretical study on fifteen C₃₆ isomers examining the role of the quality of basis sets in evaluating the geometry parameters, the relative energies and the HOMO–LUMO energy separations. It is worth noticing that the geometry parameters of fifteen C₃₆ isomers are insensitive to basis sets. While the diffuse functions are not helpful in improving the relative energies of C₃₆ isomers, the inclusion of one set of *d*-type polarization functions is found to be essential for both relative energies and the HOMO–LUMO energy gaps. At least a double-zeta plus polarization basis set should be used to obtain reliable energies within chemical accuracy (± 1.0 kcal/mol), and a triple-zeta plus polarization basis set is suggested to provide accurate energies of fullerenes at a reasonable computational cost. Our calculations show that the errors caused by basis set deficiency are not significant in DFT calculations for fullerenes,

provided that the Pople-type basis set having at least a 6-31G(d) quality is used.

References

1. Kroto HW, Heath JR, O'Brien SC, Curl RF, Smalley RE (1985) *Nature* 318:162
2. Krätschmer W, Lamb LD, Fostiropoulos K, Huffman DR (1990) *Nature* 347:354
3. Diederich F, Whetten RL, Thilgen C, Ettl R, Chao I, Alvarez MM (1991) *Science* 254:1768
4. Diederich F, Ettl R, Rubin Y, Whetten RL, Beck R, Alvarez M, Anz S, Sensharma D, Wudl F, Khemani KC, Koch A (1991) *Science* 252:548
5. Kikuchi K, Nakahara N, Wakabayashi T, Suzuki S, Shiromaru H, Miyake Y, Saito K, Ikemoto I, Kainosho M, Achiba Y (1992) *Nature* 357:142
6. Hennrich FH, Michel RH, Fischer A, Richard-Schneider S, Gilb S, Kappes MM, Fuchs D, Bürk M, Kobayashi K, Nasage S (1996) *Angew Chem Int Ed* 35:1732
7. Thilgen C, Herrmann A, Diederich F (1997) *Angew Chem Int Ed* 36:2268
8. Balch AL, Olmstead MM (1998) *Chem Rev* 98:2123
9. Guo T, Diener MD, Chai Y, Alford MJ, Haufler RE, McCluree SM, Ohno T, Weaver JH, Scuseria GE, Smalley RE (1992) *Science* 257:1661
10. Piskoti C, Yarger J, Zettl A (1998) *Nature* 393:771
11. Koshio A, Inakuma M, Sugai T, Shinohara H (2000) *J Am Chem Soc* 122:398
12. Sun G, Kertesz M (2000) *J Phys Chem A* 104:7398
13. Azamar-Barrios JA, John T, Dennis S, Sadhukan S, Shinohara H, Scuseria GE, Pénicaud A (2001) *J Phys Chem A* 105:4627
14. Burda C, Samia ACS, Hathcock DJ, Huang H, Yang S (2002) *J Am Chem Soc* 124:12400
15. Nishikawa T, Kinoshita T, Nanbu S, Aoyagi M (1999) *J Mol Struct(Theochem)* 461:453
16. Crassous J, Rivera J, Fender NS, Shu L, Echegoyen L, Thilgen C, Herrmann A, Diederich F (1999) *Angew Chem Int Ed* 38:1613
17. Heine T, Zerbetto F, Seifert G, Fowler PW (2000) *J Phys Chem A* 104:3865
18. Sun G, Kertesz M (2001) *J Phys Chem A* 105:5468
19. Slanina Z, Zhao X, Uhlík F, Lee S (2003) *J Mol Struct(Theochem)* 630:205
20. Sun G (2003) *Chem Phys Lett* 367:26
21. Fowler PW, Heine T, Zerbetto F (2000) *J Phys Chem A* 104:9625
22. Varganov SA, Avramov PV, Ovchinnikov SG, Gordon MS (2002) *Chem Phys Lett* 362:380
23. Slanina Z, Uhlík F, Zhao X, Ōsawa E (2000) *J Chem Phys* 113:4933
24. Slanina Z, Zhao X, Ōsawa E (1998) *Chem Phys Lett* 290:311
25. Diener MD, Alford JM (1998) *Nature* 393:668
26. Moran D, Stahl F, Bettinger HF, Schaefer III HF, Schleyer PvR (2003) *J Am Chem Soc* 125:6746
27. Yang SH, Pettiette CL, Conceicao J, Cheshnovsky O, Smalley RE (1987) *Chem Phys Lett* 139:233
28. Handschuh H, Ganteför G, Kessler B, Bechthold PS, Eberhardt W (1995) *Phys Rev Lett* 74:1095
29. Becke AD (1988) *Phys Rev A* 88:3098
30. Perdew JP, Wang Y (1992) *Phys Rev B* 45:13244
31. Hehre WJ, Randon L, Schleyer PvR, Pople JA (1986) *Ab initio molecular orbital theory*. Wiley, New York
32. Dunning Jr TH (1989) *J Chem Phys* 90:1007
33. Gaussian 98, Revision A.6, Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, Zakrzewski VG, Montgomery JA Jr, Stratmann RE, Burant JC, Dapprich S, Millam JM, Daniels AD, Kudin KN, Strain MC, Farkas O, Tomasi J, Barone V, Cossi M, Cammi R, Mennucci B, Pomelli C, Adamo C, Clifford S, Ochterski J, Petersson GA, Ayala PY, Cui Q, Morokuma K, Malick DK, Rabuck AD, Raghavachari K, Foresman JB, Cioslowski J, Ortiz JV, Stefanov BB, Liu G, Liashenko A, Piskorz P, Komaromi I, Gomperts R, Martin RL, Fox DJ, Keith T, Al-Laham MA, Peng CY, Nanayakkara A, Gonzalez C, Challacombe M, Gill PMW, Johnson B, Chen W, Wong MW, Andres JL, Gonzalez C, Head-Gordon M, Replogle ES, Pople JA (1998) *Gaussian, Inc., Pittsburgh*
34. Slanina Z, Zhao X, Lee S-L, Osawa E (2000) *Scripta Mater* 43:733
35. Zhao X, Slanina Z, Goto H (2004) *J Phys Chem A* 108:4479
36. Slanina Z, Ishimura K, Kobayashi K, Nagase S (2004) *Chem Phys Lett* 384:114