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Double-Hybrid Functionals and Tailored Basis Set: Fullerene (C₆₀) Dimer and Isomers as Test Cases

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Abstract

A computational protocol making use of Double Hybrid functionals in conjunction with a recently developed basis set tailored to reproduce non covalent interactions (hereafter named DH-SVPD) is here applied and tested for the evaluation of properties C₆₀ fullerenes namely intermolecular interactions in the weakly bound C₆₀ dimer and relative stabilities of C₆₀ isomers (as described by the C60ISO and iso-C60 datasets).

The obtained results suggest that the DH-SVPD performance is very close to that obtained with empirical corrections and larger quadruple- ζ basis for the C₆₀ dimer. In contrast, both approaches (tailored basis set and larger basis with empirical potential) do not reach the envisaged accuracy for the relative stabilities of C₆₀ isomers.

Nevertheless, this test well underlined how the DH-SVPD basis set is able to recover the performance obtained by coupling the DH functionals with empirical dispersion corrections and larger basis set, significantly reducing the computational effort for double hybrids and thus enabling to expand their application domain to larger molecular systems.

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1. Introduction

Double hybrid (DH) functionals¹, that are exchange-correlation functionals casting a fraction of correlation computed using a second order perturbative (PT2) approach², represent a further step forward with respect to the global hybrids (GH), introduced by Becke more than 20 years ago³. Indeed, modern DH schemes, firstly proposed by Truhlar⁴ and then popularized by Grimme⁵, provide enhanced performance for a number of properties, ranging from molecular structures to thermochemistry, reaction barriers, and even excited-state energies¹.

Contrarily to what can be expected from an error compensation between the (overbinding) PT2 and the (underbinding) DFT contributions, weak dispersion interactions are yet not very accurately reproduced by DHs⁶⁻⁹

An effective way to overcome this problem is to add an empirical correction based on pairwise classical potential^{10,11}. This simple and chemically sound approach meets a large success since in such a way interaction energies of non-covalently bonded or of weakly interacting systems can be reproduced with minimal computational extra cost and high accuracy¹². Such potentials depend, of course, both on the atom types involved in the interactions and on the exchange-correlation functional considered^{13,14}. Empirical corrections accounting for three-body interactions have been also developed, enabling to further increase the overall accuracy¹⁵.

When such empirical potentials are coupled to DHs, small errors are found on dispersion-ruled systems⁸, even if their contribution is lower than what found when these corrections are used in conjunction with more traditional functionals, such as GHs. Indeed, DHs provide a better estimation of the dispersion effects at intermediate intermolecular distances, which shows the delicate interplay between electronic effects at all ranges.¹⁶

In this paper we will focus on the behavior of two different double hybrids: the B2-PLYP⁵ and the PBE-QIDH¹⁷ functional. The first was developed in analogy to the parent B3LYP approach¹⁸, that is fitting the (few) coefficients contained its functional form on some reference dataset⁵. The second, instead, has been developed choosing a number of theoretical constraints among those that the universal functional should fulfill^{17,19-21}.

For the sake of clearness, hereafter we will denote as non-empirical all the exchange-correlation functionals whose internal coefficients are not determined by an error minimization procedure with respect to external reference datasets, but rather fixed using only theoretical arguments. The PBE-QIDH functional is thus ascribed to this category. By opposition, semi-empirical are those functionals whose coefficients are determined by a

parametrization procedure, albeit their functional form could respect some theoretical constraints²². The B2-PLYP is the most widely used DH for this category.

Potentials developed for weak interactions are, instead, empirical by their own definition, since both their form and coefficients are determined on the basis of the best agreement with respect to external reference values.

It then clearly appears how the present situation is vexing, since non-empirical DH functionals must be partnered with empirical potential in order to provide accurate results for dispersion interactions.

With this inconsistency in mind, we have recently developed a basis set, called DH-SVPD, which significantly improves the performances of DHs in reproducing interaction energies of noncovalent systems, without requiring further corrections and thus allowing to restore a full non-empirical DFT approach²³. This philosophy is even more stringent, since the DH-SVPD basis set is developed using a “self-consistent” approach where only energy contributions of the monomers and dimer computed at the same DH level of theory are considered, without need of any external reference values²⁴.

The first tests carried out on standard benchmarks, such as S22²⁵, S66²⁶ and L7²⁷ dataset, suggested that the PBE-QIDH/DH-SVPD model is well suited for noncovalent interactions, providing results close (or even better) than those obtained when the same DH is coupled to larger basis set and empirical dispersion corrections²³. They also showed the transferability of this basis set to other DHs.

Here we want firstly to verify the robustness of this approach extending our investigation to larger systems, namely the weakly bound dimer of C₆₀. This system represents indeed a challenging playground for any method rooted in Density Functional Theory (DFT) as pointed out by a recent work²⁸, due to the dispersion forces which dominate the intermolecular interaction. Next, two sets concerning the relative stabilities of C₆₀ isomers were considered^{29,30}. Albeit composed by the same molecule, the relative stabilities of the C₆₀ isomers seem not affected by dispersion, but their accurate evaluation at the DFT level is still troublesome, being related to an accurate description of the aromatic resonance structures. It is therefore interesting to verify the performance of our model on these two challenging sets in order to fully validate this approach beyond purely noncovalent interactions.

2. Computational details

Calculations were carried out with the non-empirical PBE0-DH³¹ and PBE-QIDH¹⁷ functionals and the semi-empirical B2-PLYP⁵ and DSD-PBEP86³² approaches. In some cases,

these functionals have been coupled to the empirical D3(BJ)³³ dispersion correction whose parameters are reported in Refs 34 and 35 for non-empirical DHs. Preliminary tests showed that, in contrast to our previous experience with smaller noncovalent systems (see comments in reference 21), the effect of three body-interactions, modelled by the Axilrod-Teller-Muto (ATM) potential¹⁵, were negligible for the C₆₀ dimer. Indeed, this contribution was computed to be 0.18 kcal/mol, that is about 1% of the PBE-QIDH interaction energy. Therefore, this contribution will be not considered in the following.

Note that the DH-SVPD basis set has been developed to be used in connection with any DH functional, by optimizing the diffuse functions of the small Def2-SVPD basis set³⁶. Since this basis set has been developed considering an error compensation between Basis Set Superposition Error (BSSE) and Basis Set Incompleteness Error (BSIE), the former will be not explicitly taken into account, if not explicitly mentioned. This approach is consistent with some recent works which do not recommended BSSE corrections for small or medium basis set^{37,38} due to an unbalanced behavior between BSSE and BSIE. Moreover, the so-called half-counterpoise approach, computed as the average of BSSE corrected and uncorrected energy, was recommended for MP2 calculations with small (lower than quadruple- ζ quality) instead of a full BSSE corrections³⁹.

For purposes of comparison with literature data, calculations were also carried out using the large Def2-TZVPP or nearly complete Def2-QZVP basis sets³⁶.

The structures of the C₆₀ dimer were taken from reference 28, while the structures of the C60ISO and iso-C60 datasets are those reported in reference 29 and computed at PBE-D3-Def2-TZVPP level of theory. For the sake of clarity, they are sketched in Figure 1.

All calculations were performed with the Gaussian code⁴⁰.

3. Results and discussion

3.1 C₆₀ dimer

The first system considered in this study is the weakly bound C₆₀ dimer for which accurate calculations have been recently reported²⁸. As mentioned by Clark and collaborators²⁸, the interaction between the two molecules in this dimer is largely dominated by dispersion interactions, but, in contrast with other systems, such as those collected in the L7²⁷ dataset, the many-body interactions are negligible. This dimer is, therefore, a perfect playground to verify the quality of the proposed PBE-QIDH/DH-SVP model where two-body interactions should be improved with respect to other density functionals by the presence of a PT2 contribution.

In Table 1 are reported the binding energies for the C_{60} dimer, computed at different DFT levels using the same reference structure²⁸, and completed with reference values obtained with wave-function correlated methods (all these latter values are taken from reference 28). These reference values are relatively homogeneous, ranging between -11.97 (CCSD(T)) and -12.94 (CEPA-1) kcal/mol²⁸. As expected, the interaction energy computed at the MP2 level is largely overestimated (-23.46 kcal/mol), whereas the SOS-MP2 result is in better agreement with the reference value (-14.17 kcal/mol). Concerning DFT approaches, it clearly appears from the data collected in Table 1, that all the methods missing an empirical potential significantly underestimate the interaction energy. The obtained values range between 6.14 kcal/mol at the B3LYP level, i.e. corresponding to an unbound dimer, to -3.95 kcal/mol for the B2-PLYP functional, where the negative value well underlines the role of the dynamical correlation contribution.

The empirical corrections have, as expected, a beneficial effect on the binding energies leading in all reported cases to a bound dimer, albeit the estimated energies are roughly one half of the reference values (all between -6 and -7 kcal/mol). The only exceptions are represented by M06-2X-D3(BJ) (-9.7 kcal/mol) and B2-PLYP-D3(BJ) (-11.07 kcal/mol), even if the discrepancy with respect to the reference values is still large. In all these cases (with and without dispersion corrections), these values have been obtained using the Def2-TZVP basis set.

In this context, the PBE-QIDH functional coupled with the Def2-TZVP and the D3(BJ) dispersion provides a better agreement with respect to the reference values, its estimation being -12.29 kcal/mol. A very close result, -12.27 kcal/mol, is then found using the non-empirical PBE-QIDH/DH-SVPD protocol. Noteworthy, this small basis leads also to significant improvements for two other DHs, namely B2-PLYP (-8.00 kcal/mol) and DSD-PBEP86 (-17.40 kcal/mol), thus further proving its transferability.

It should be also remarked that the Def2-QZVP basis has 3720 functions (6120 primitives) for the C_{60} dimer, while in the case of the smaller DH-SVPD basis only 1200 functions (1920 primitives) are present. Consequently, single point PBE-QIDH calculations with the latter basis set are roughly 4 times faster than those performed with the larger basis (for the C_{60} dimer at the equilibrium distance) if all other technical factors remain the same.

Beside the interaction energy at a fixed geometry, it is also interesting to analyze the full potential energy profile along the distance between the centers of mass of the two moieties constituting the C_{60} dimer. This test is even more stringent since the dispersion corrections could fail to reproduce the energy profile far from energy minima⁴¹, sometime giving spurious

discontinuities⁴². In our case, however, the validity of this test should be modulated, since the available reference values are calculated at the CEPA-1/cc-pVDZ level, while larger basis sets are normally used to reach energies at convergence with this level of theory (triple- or quadruple- ζ , see for instance reference 43 and 44). Indeed, the dissociation energy at the CEPA-1 level is -12.94 kcal/mol with the cc-pVTZ basis set, and -6.88 kcal/mol with the smaller cc-pVDZ basis set²⁸.

The profile computed at the PBE-QIDH/DH-SVPD level is reported in Figure 2 together with other results taken from reference 28. This profile provides the deepest well with respect to the other ones reported, the reference CEPA-1 being the shallowest one. However, the PBE-QIDH/DH-SVPD potential does not show any unphysical discontinuities, as it is also the case for the others approaches tested, and, more interesting, its minimum is shifted toward a shorter distance (9.75 Å) in slight better agreement with the CEPA-1 results than B3LYP-D3(BJ) or VV10-SCNL (9.95 and 9.85 Å, respectively). Equilibrium distances and binding energies are also reported in Table 2 for sake of clearness.

In order to give an estimate of the correlation between BSIE and BSSE, this latter was evaluated using different basis sets. Indeed, the BSSE for the DH-SVPD (5.9 kcal/mol) is, as expected, intermediate between that computed for the smaller Def2-SVPD (9.8 kcal/mol) and that for the larger Def2-TZVP basis set (1.7 kcal/mol). In other words, the optimized exponents in the DH-SVPD are the results of the balance between the underestimation of the interaction energy due to BSIE set and its overestimation coming from BSSE.

3.2 C60ISO and iso-C60 benchmarks

The second test concerns the relative stability of selected isomers of the C₆₀. Here two different sets have been considered. The first is the so-called C60ISO, composed by the five energetically lowest and by the five energetically highest isomers of C₆₀ selected among the 1812 ones identified by Grimme and co-workers²⁹. The second set, named iso-C60, contains 8 isomers chosen so that their relative energies cover a large interval (from 73.5 to 256.7 kcal/mol)³⁰. In the first case, reference energies are computed at CCSD(T)/CBS level, while in the second set reference values are given using a composite method, namely the G4(MP2) approach. In view of their accuracy and the high energy differences, the reference values obtained by these two methods can be considered of a comparable precision.

Results obtained for the C60ISO dataset are reported in Table 3. As it can be easily seen from the data obtained with the Def2-QZVP basis, results obtained adding the empirical dispersion correction (here D3(BJ)) are very similar to those not including it. In particular, a slight

deterioration of the MADs is observed for most of the functionals, including B3LYP (+0.22 kcal/mol), PBE0 (+0.19 kcal/mol) and PBE0-DH (+ 0.21 kcal/mol). An opposite behavior, but always with marginal variations, is found for B2-PLYP (-0.26 kcal/mol) while PBE-QIDH is practically constant (-0.01 kcal/mol). This trend, already commented in literature²⁷, indicates that dispersion interactions play a negligible role in such systems.

It is not therefore surprising that the results obtained with the DH-SVPD basis are also very close. Indeed, these results globally show the same trend observed when the empirical correction is added to the functionals using the larger Def2-QZVP basis. Some exceptions can however be noticed. For instance, the mPW2-PLYP functional is not affected by the D3(BJ) correction when the Def2-QZVP basis set is used (variations of -0.01 kcal/mol upon adding it), while the small basis set significantly increases the MAD with respect to the value obtained with the larger basis set (5.10 vs. 4.66 kcal/mol, i.e. + 0.44 kcal/mol).

More in general it should be remarked that, despite the apparent high deviations obtained for some functionals, all the functionals provide quite accurate results. Indeed, considering the percent error with respect to the sum of all the total energies, the deviations range between 0.2 % (B3LYP/Def2-QZVP) and 0.8 % (B2-PLYP/DH-SVPD). Therefore, the overall error is clearly less dramatic than that appears at a first sight.

The same behavior is observed for the other set, iso-C60. Here the MADs computed using the Def2-TZVPP basis set are significantly larger, as it could be expected in view of how the isomers have been selected. Indeed, they range between 3.3 (mPW2-PLYP) and 13.9 (PBE0) kcal/mol. A small decrease of the error is observed when the DH-SVPD basis set is considered, with the PBE-QIDH and mPW2-PLYP functionals providing the lowest MADs, of 3.8 kcal/mol and 1.5 kcal/mol, values which correspond to a deviation of less than 0.4% with respect to the sum of all the energies. Such a small deviation is close to those found for the C60ISO set and can be, in our opinion, considered as acceptable for any chemical applications involving this kind of challenging systems.

Despite the fact that the relative stabilities of the C60 isomers for both sets seem not to be ruled by dispersion interactions, these results show the interest in the developed computational protocol. Indeed, in both datasets, the results obtained with the DH-SVPD basis set are very close to (or better) than those obtained with the larger Def2-QZVP or Def2-TZVPP basis coupled to empirical corrections showing that this basis set does not deteriorate the description of covalent interactions. The DH-SVPD basis is therefore a valid and fast alternative to more time-consuming protocols.

It is also interesting to remark that there is not a systematic improvement in going from GGA to hybrids to double hybrids for the relative stabilities of the C60 isomers. Indeed, for the C60ISO set the PBE/Def2-QZVP deviation is 11.06 kcal/mol³⁰, a very low value is found for PBE0 (2.16 kcal/mol) and finally the PBE-QIDH functional gives a slightly high error (3.48 kcal/mol). A similar trend can be found for the BLYP family. However, the behavior is different for the two sets. Indeed, for the iso-C60 set the MAD increases in going from GGA to GH and then decreases back when DHs are considered (3.0, 13.9 and 5.5 kcal/mol for the PBE, PBE0 and PBE-QIDH functionals, respectively, with the Def2-TZVPP basis set). Again, a similar behavior is found with the corresponding functional casting the BLYP model (BLYP, B3LYP and B2-PLYP). At the best of our knowledge⁴⁵, these are one of the very few sets for which there is not a systematic improvement in going from GGA to GH to DH.

It has been argued for the iso-C60 set that the oscillating behavior for MAD is related to the quantity of HF (or exact) exchange introduced in the functional, more than 3%-5% deteriorating the results³⁰. This argument is, however, not fully applicable to the C60ISO set, where the introduction of a not negligible quantity of HF exchange ($\geq 20\%$) significantly improves the results. It is however true that a larger quantity of HF exchange significantly deteriorates the performance. Indeed, the MAD computed for the PBE-QIDH functional without taking into account the PT2 contribution (the so called PBE-QIH model) is 42.5 kcal/mol for the iso-C60 set and using the DH-SVPD basis set. This well illustrate the increasing in going from PBE0 (11.9 kcal/mol) to PBE-QIH (42.5 kcal/mol), which parallels their HF contribution, 25 and $\sim 70\%$, respectively. This trend is also found for the C60ISO, where the values obtained with the DH-SVPD basis set are 2.2 and 18.3 kcal/mol for PBE0 and PBE-QIH, respectively. However, in DHs the observed error results from a strong compensation between the large HF contribution and the PT2 counterpart. For instance, the MAD for the iso-C60 set is 42.5 kcal/mol for PBE-QIH and only 3.8 kcal/mol for PBE-QIDH (DH-SVPD basis set). A similar behavior can be found for the other DHs when the PT2 contribution is not considered (see Table 3 and 4). As a consequence, the different order found for the computed MADs, $GGA > GH < DH$ for the C60ISO or $GGA > GH > DH$ for iso-C60 depends on how large is the error at GGA level for the given set, an error that could not be efficiently compensated by the PT2 contribution in the final DH. .

4. Conclusions

Fullerene represents a challenging and interesting molecule to test new DFT-based approaches: in the tackled dimer, the intermolecular interaction is ruled by weak noncovalent

forces, which, instead, do not affect the relative stabilities of its isomers, for which an accurate description of the electronic structure is fundamental. On such difficult playground we have tested how double-hybrid functionals coupled to a small basis set tailored for weak interactions (the so-called DH-SVPD basis) may work. Beyond of a detailed comparison with reference values obtained with accurate wave-function methods, we have used as relevant feature the deviations obtained with respect to functionals incorporating empirical dispersion potentials, since these latter represent the most-common approach in the field. Indeed, the DH-SVPD basis set has been specifically developed to avoid their use with double hybrids, without loss in accuracy.

The obtained results confirm that the DH-SVPD values are always very close to those obtained with empirical corrections. Indeed, the PBE-QIDH/DH-SVPD model provides an accuracy for the interaction of the C_{60} dimer comparable to those obtained with the best functionals using empirical dispersion and larger quadruple- ζ basis. In contrast, both approaches (tailored basis set and larger basis with empirical potential) do not reach the same level of accuracy in the prediction of relative stabilities of C_{60} isomers. Nevertheless, this test well underlined how the DH-SVPD basis set can efficiently replace the use of dispersion potentials coupled with larger basis set, at a fraction of the computational cost, thus significantly reducing the computational effort for double hybrids and enabling the description of larger molecular systems.

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Supporting information

The Supporting Information is available free of charge on the ACS Publications website: raw data of Table 3 and 4 and Figure 1 obtained with the DH-SVPD basis set.

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Table 1. Binding energies (ΔE , kcal/mol) for the C_{60} dimer.

Method	Basis set	ΔE
DLPNO-CCSD ^a	CBS	-12.15
DLPNO-CCSD(T) ^a	CBS	-11.97
DLPNO-CEPA-1 ^a	CBS	-12.94
MP2 ^a	Def2-TZVP	-23.46
SOS-MP2 ^a	Def2-TZVP	-14.17
B2-PLYP ^a	Def2-TZVP	-3.95
B2-PLYP-D3(BJ) ^a	Def2-TZVP	-11.07
DSD-PBEP86-NL ^a	Def2-TZVP	-0.19
B3LYP ^a	Def2-TZVP	6.14
B3LYP-NL ^a	Def2-TZVP	-7.81
B3LYP-D3(BJ) ^a	Def2-TZVP	-7.09
ω B97X-D3 ^a	Def2-TZVP	-6.03
M06-2X ^a	Def2-TZVP	-2.64
M06-2X-D3(BJ) ^a	Def2-TZVP	-9.69
PBE-QIDH-D3(BJ)	Def2-TZVP	-12.29
B2-PLYP	DH-SVPD	-8.00
DSD-PBEP86	DH-SVPD	-17.40
PBE-QIDH	DH-SVPD	-12.27

a) From reference 28

Table 2. Equilibrium distances (R_e , Å) and binding energies (ΔE , kcal/mol) of the C_{60} dimer, extracted from the energy profiles reported in Figure 1.

Method	Basis set	R_e	ΔE
DLPNO-CEPA-1 ^a	cc-pVDZ	9.75	-6.88
B3LYP-D3(BJ) ^a	cc-pVDZ	9.85	-7.73
VV-SCNL ^a	cc-pVDZ	9.85	-9.27
BP86-D3(BJ) ^a	Def2-TZVP	9.75	-10.07
PBE-QIDH	DH-SVPD	9.75	-12.27

a) From reference 28

Table 3. Mean Absolute Deviations (kcal/mol) for the C60ISO set by Grimme. Reference values are computed at the DLPNO-CCSD(T)/CBS level²⁹. In parenthesis are reported the values obtained without inclusion of the PT2 contribution to the exchange-correlation energy.

	Def2-QZVP	Def2-QZVP+D3(BJ)	DH-SVPD
B3LYP	2.01	2.22	2.27
PBE0	2.16	2.35	2.21
PBE0-DH	2.91	3.12	2.84
B2-PLYP	7.02	6.76	7.49 (12.72)
mPW2-PLYP	4.66	4.65	5.10 (13.49)
DSD-PBEP86	7.86	7.56	7.47
PBE-QIDH	3.48	3.47	4.26 (18.32)

Table 4. Mean Absolute Deviations (kcal/mol) for the iso-C60 set by Karton et co-workers³⁰. Reference values are computed at the G4(MP2) level. In parenthesis are reported the values obtained without inclusion of the PT2 contribution to the exchange-correlation energy.

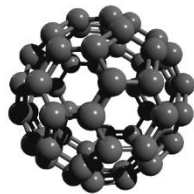
	Def2-TZVPP	Def2-TZVPP+D3(BJ)	DH-SVPD
B3LYP	11.06	11.16	9.35
PBE0	13.29	13.30	11.93
PBE0-DH	13.70	13.85	12.18
B2-PLYP	3.59	3.81	4.83 (32.68)
mPW2-PLYP	3.39	2.38	1.50 (34.11)
DSD-PBEP86	4.83	4.82	6.21
PBE-QIDH	5.54	5.58	3.82 (42.50)

Figure captions

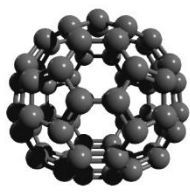
Figure 1. Structures of the fullerene isomers in the C₆₀ISO (top) and iso-C₆₀ (bottom) set. Reference energies (DLPNO-CCSD(T)/CBS for the former and G4(MP2) for the latter) and point group symmetries are also reported (in kcal/mol).

Figure 2. Potential energy profile of the fullerene dimer computed as function of the distance between the C₆₀ centers of mass. CEPA-1, B3LYP-D3(BJ), VV10-SCNL and BP86-D3(BJ) data are taken from reference 28.

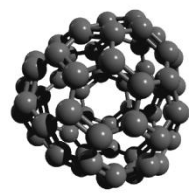
C60ISO



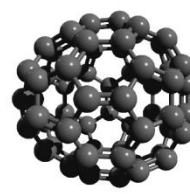
I_h (0.00)



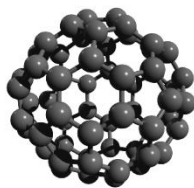
C_{2v} (37.40)



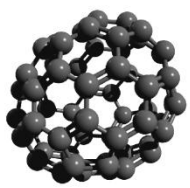
D_3 (56.87)



C_s (56.89)



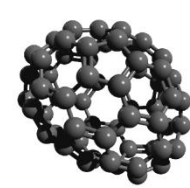
C_2 (69.89)



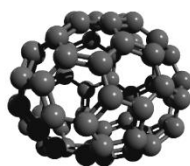
C_1 (100.48)



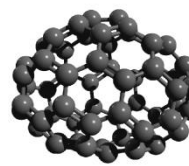
C_1 (111.72)



C_s (142.18)

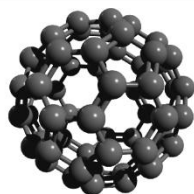


C_{2h} (143.96)



C_2 (164.88)

iso-C60



I_h (0.00)



D_{2d} (73.49)



D_{2d} (74.43)



C_{2h} (133.46)



C_{2v} (134.44)



C_{2v} (155.00)



C_{2v} (166.16)



D_{6h} (256.69)

Figure 1

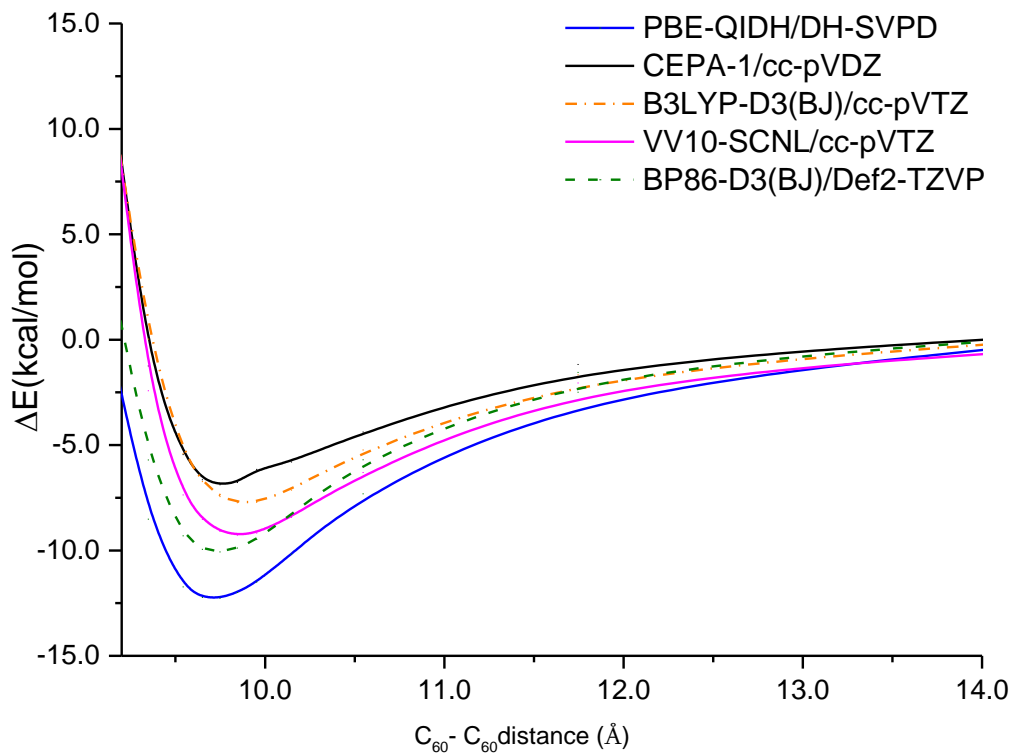


Figure 2

TOC Graphic

