



Accurate calculations of the noncovalent systems with flat potential energy surfaces: Naphthalene dimer and azulene dimer



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ARTICLE INFO

Article history:

Received 22 March 2017

Received in revised form 27 April 2017

Accepted 28 April 2017

Available online 29 April 2017

Keywords:

CCSD(T)/CBS

Potential energy surface

DFT-D3

Naphthalene dimer

Azulene dimer

ABSTRACT

It is very challenging to construct the potential energy surfaces for the medium and large noncovalent systems employing the coupled clusters with singles, doubles, and perturbative triples, CCSD(T), at the complete basis set (CBS) limit. The main obstacle lies in the time-consuming and expensive CCSD(T) optimizations of the geometries. One method to overcome the obstacle is to use the cheap density functional theory with the D3 dispersion correction (DFT-D3) instead of the CCSD(T) method to optimize the geometries of the noncovalent systems. In the present study, the potential energy surfaces of the naphthalene dimer and azulene dimer were investigated using a combined DFT-D3 optimization and single-point CCSD(T)/CBS energy calculation scheme. The results clearly show that this scheme can give highly accurate CCSD(T)/CBS potential energy surfaces for the naphthalene dimer and the azulene dimer.

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1. Introduction

A potential energy surface plays an important role in structure study of molecule (or a collection of molecules) and analysis of reaction dynamics. Information about the potential energy surface of the noncovalent systems has improved enormously in recent years. However, it is still a challenging task to construct the highly accurate potential energy surfaces for the medium and large noncovalent systems, either from the analysis of experimental data or from the quantum chemistry calculations. The study of the benzene dimer is an obvious example. Although the potential energy surface for the benzene dimer has been extensively studied by theoretical methods [1–10], full geometry optimization and frequency calculation at the CCSD(T) level is still too expensive to be used to characterize the nature of the stationary points on the potential energy surface of the benzene dimer. Let us add here that the CCSD(T) method represents the current “gold standard” of electronic structure theory. Almost all the CCSD(T)/CBS potential energy surfaces of the benzene dimer were constructed by freezing the monomer geometry. That is to say, the CCSD(T) energies are not based on the corresponding CCSD(T) geometries. Fortunately, the effect of freezing the monomer geometry is very small on both the equilibrium geometry and binding energy of the benzene

dimer [3,4]. For the other noncovalent systems in which the effect of freezing the monomer geometry cannot be neglected, such a method may be infeasible for the construction of the CCSD(T)/CBS potential energy surface. Evidently, the core of the problem is to obtain very accurate geometries of the noncovalent systems studied. Many benchmarks with CCSD(T)/CBS values have validated the excellent performance of the DFT-D3 method for noncovalent interactions [9,11]. Considering that the DFT-D3 optimizations are very cheap and the results of DFT-D3 are very accurate, an alternative method to construct the CCSD(T)/CBS potential energy surface is to use the DFT-D3 optimizations to take the place of the CCSD(T) optimizations. In this work, employing the naphthalene dimer and azulene dimer as models, we investigated the reliability of the combined DFT-D3 optimization and single-point CCSD(T)/CBS energy calculation scheme.

The nonpolar naphthalene and polar azulene are the smallest members of the polycyclic aromatic hydrocarbons family. Naphthalene dimer and azulene dimer have been the subject of some earlier studies [12–24]. For the naphthalene dimer, the experimental results are in violent disagreement with the theoretical predictions [12,13]. It is very possible that the experimental measurements for the naphthalene dimer are incorrect, so we will not discuss the experimental results in this study [14–23]. It is well known now that the second-order Møller–Plesset perturbation (MP2) method considerably overestimates the interaction energies. Hence, the MP2 potential energy surfaces for the naphthalene dimer are unreliable [14–16]. The first CCSD(T)/CBS potential

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energy surface for the naphthalene dimer was reported by Tsuzuki et al. [18]. Also by freezing the monomer geometries, Janowski and Pulay performed more accurate CCSD(T)/CBS calculations for four stacked configurations of the naphthalene dimer [23]. Another CCSD(T)/CBS study on the naphthalene dimer are only restricted to two configurations with high symmetry [22]. The other reliable theoretical calculations for the naphthalene dimer include LC-DFT+ALL calculations [19], SAPT-DFT calculations [20] and DFT/CCSD(T) calculations [21]. The different calculation methods give significantly different results. The differences of these results are in part caused by the use of different geometries. Especially for the “gold-standard” CCSD(T)/CBS energies, the selection of the geometries of the naphthalene dimer are more important because we have no corresponding CCSD(T)/CBS geometries. We believe that the quality of the CCSD(T)/CBS potential energy surface for the naphthalene dimer will be greatly improved if we use more accurate geometries. Comparatively, the study of the azulene dimer was less specifically focused [24].

In the present study, the potential energy surfaces of the naphthalene dimer and azulene dimer were investigated by using high-level quantum chemical calculations. The naphthalene dimer was used as a representative of the dimer formed between two nonpolar aromatic hydrocarbons and the azulene dimer was used as a representative of the dimer formed between two polar aromatic hydrocarbons. On the one hand, we explored the reliability of the combined DFT-D3 optimization and single-point CCSD(T)/CBS energy calculation scheme in constructing the highly accurate potential energy surface. On the other hand, we presented high-quality reference data for the interaction energies and their energy components of the naphthalene dimer and the azulene dimer.

2. Theoretical methods

The CCSD(T)/CBS energy was estimated by using the following formula [25]:

$$E^{\text{CCSD(T)/CBS}} = E^{\text{MP2/CBS}} + \Delta\text{CCSD(T)/aVDZ}$$

where $E^{\text{MP2/CBS}}$ denotes the estimated MP2 value at the basis set limit and $\Delta\text{CCSD(T)/aVDZ}$ denotes the CCSD(T) correction term [$\Delta\text{CCSD(T)/aVDZ} = E^{\text{CCSD(T)/aVDZ}} - E^{\text{MP2/aVDZ}}$] calculated using the Dunning's augmented correlation consistent basis set aug-cc-pVDZ (aVDZ) [26]. MP2 calculations are also performed with the Dunning's augmented correlation consistent basis set aug-cc-pVTZ (aVTZ) [26], and extrapolated to the CBS limit using Helgaker's two-point scheme [27].

Employing the CCSD(T)/CBS values as a benchmark database, we evaluated the performance of some popular DFT-D3 methods including B3LYP-D3 [11,28,29], B3PW91-D3 [11,28,30], B97-D3 [11,31], BLYP-D3 [11,29,32], BMK-D3 [11,33], BP86-D3 [11,32,34], BPBE-D3 [11,32,35], CAM-B3LYP-D3 [11,36], LC- ω PBE-D3 [11,37], PBE-D3 [11,38], TPSS-D3 [11,39] and PBE0-D3 [11,38]. The basis set def2-TZVPP and the Becke-Johnson damping scheme were used with these DFT-D3 methods [40,41]. An “ultrafine” integration grid (99 radial, 590 angular points) was utilized for all the DFT-D3 calculations to minimize the integration grid errors.

DFT-D3 calculations were performed using the GAUSSIAN 09 electronic structure program package [42]. MP2 and CCSD(T) calculations were carried out with the MOLPRO suite of ab initio programs [43]. The basis set superposition errors for all the interaction energies were eliminated with the function counterpoise technique of Boys and Bernardi [44].

To further understand the nature of the noncovalent interactions between two naphthalene (or azulene) molecules, the total interaction energy decomposition analysis was carried out at the

SAPT2+(CCD)/aVDZ level of theory [45]. The SAPT2+(CCD) calculations were performed with the PSI4 program [46]. Density fitting approximations have been employed to enhance the efficiency of the SAPT2+(CCD) calculations.

3. Results and discussion

3.1. The CCSD(T)/CBS potential energy surface of the naphthalene dimer

In the combined DFT-D3 optimization and single-point CCSD(T)/CBS energy calculation scheme, a selection of the reliable DFT-D3 method is the most important thing. In order to reduce the computational costs, only three configurations with high symmetry for the naphthalene dimer are selected to evaluate the performance of twelve DFT-D3 methods (see Fig. 1).

In this study, the CCSD(T)/CBS energy is estimated by adding to MP2/CBS(aVDZ,aVTZ) a coupled cluster correction $\Delta\text{CCSD(T)/aVDZ}$. Here, MP2/CBS(aVDZ,aVTZ) denotes the estimated MP2 value at the complete basis set obtained with an aVDZ and aVTZ two-point Helgaker extrapolation. A natural question is whether the basis set aVDZ that is used for MP2/CBS(aVDZ,aVTZ) and $\Delta\text{CCSD(T)/aVDZ}$ calculations is too small to lead to accurate CCSD(T)/CBS energies [47,48]. In order to prove the reliability of the CCSD(T)/CBS(aVDZ,aVTZ) energies for the naphthalene dimer, the CCSD(T)/CBS(aVTZ,aVQZ) energies have also been calculated as a sum of the two-point (aVTZ and aVQZ) Helgaker CBS extrapolation of the MP2 energy and a coupled cluster correction with a larger basis set aVTZ ($\Delta\text{CCSD(T)/aVTZ}$). The basis set aVQZ is an abbreviation of the Dunning's augmented correlation consistent basis set

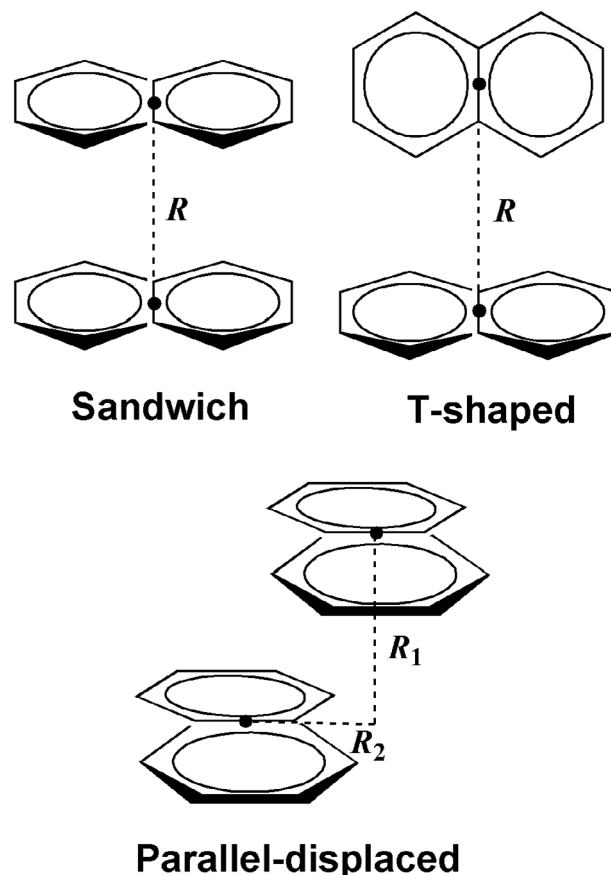


Fig. 1. Selected sandwich, T-shaped, and parallel-displaced configurations of the naphthalene dimer.

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