

UNIVERSITY OF OPORTO

DOCTORAL THESIS

Van Der Waals Interactions in Graphitic Systems

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- 1 The world is all that is the case.
- 2 What is the case - a fact - is the existence of states of affairs.
- ...
- 7 What we cannot speak about we must pass over in silence.

Ludwig Wittgenstein
Tractatus Logico-Philosophicus

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UNIVERSITY OF OPORTO

Abstract

Faculty of Sciences

Department of Chemistry and Biochemistry

Doctor of Philosophy

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by Karol STRUTYŃSKI

The treatment of the van der Waals interactions in graphitic materials is the main goal of this study. This is a difficult task, as the theoretical description of such interactions is troublesome. Only very computationally demanding methods can reproduce van der Waals interactions, but graphitic materials are too large to consider for these methods. At the other hand, most methods that are feasible do not account for the van der Waals interaction or fail to do it accurately.

The method intended for investigation of presented subject need to be feasible for graphitic materials and, at the same time, has to be able to reproduce the van der Waals interactions accurately. The Density Functional Method augmented with empirical dispersion, the so called DFT-D method, is chosen – it is feasible for large systems and the dispersion part can be adjusted to specific systems.

A short introduction to graphitic materials and van der Waals interactions is followed by a detailed presentation of the DFT-D method. The DFT-D method is then reparameterized to reproduce known features of the benzene dimer, a good model system of graphitic materials. The reparameterization is done using Relaxed Fitting, a new approach for fitting schemes. It ensures that the new method will produce well the geometries and their binding energies. The Relax Fitting approach is also used for two molecular mechanics' force fields. An extensive verification of the resulting methods supports the use of Relax Fitting - newly parameterized methods produce results that are substantially more accurate than other methods of similar use.

In the subsequent part several methods are used to study the energetical properties of the helicenes and phenacenes. The new DFT-D method is finally used to study the C_{60} complexes. The experimental observations suggest a small effect, namely that the C_{60} fullerene diameter changes slightly upon complexation. The studies using new DFT-D method confirm that and provide a theoretical support for that effect. All investigations show that the Relaxed Fitting methods produce results that are comparable with the most accurate methods at a fraction of their computational costs.

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Abbreviations

BD	B enzene D imer
BSSE	B asis S ets S uperposition E rror
CBS	C omplete B asis S et
DFT	D ensity F unctional T heory
FF	F orce F ield
HF	H artree F ock
MM	M olecular M echanics
MP2	M øller– P lesset theory of the second order
PES	P otential E nergy S urface
QM	Q uantum M echanics
RMS	R oot M ean S quare
RMSD	R oot M ean S quare D isplacement
SP	S ingle P oint
E_{int}	E nergy of I nteraction
BE	B inding E nergy
HOMO	H ighest O ccupied M olecular O rbital
LUMO	L owest U noccupied M olecular O rbital

Physical Constants

Ångström	Å	=	$1 \times 10^{-10} \text{ m}$
Joule	J	=	$1 \text{ kg m}^2/\text{s}^2$
Calorie	cal	=	4.184 J
Kilocalorie per mole	kcal/mol	=	$6.947 \times 10^{-21} \text{ J per molecule}$
Electronvolt	eV	=	$1.60218 \times 10^{-19} \text{ J}$
Hartree	E_{h}	=	$4.3597 \times 10^{-18} \text{ J}$
	E_{h}	=	27.211 eV
	E_{h}	=	627.509 kcal/mol

Chapter 1

Introduction

The studies presented here are concerned with the role that van der Waals interactions (vdW) play in graphitic materials. Effective ways of evaluating that role will be also discussed. A systematic study requires the proper description of the main parts of this problem. The dispersion forces play a very important part in their interactions and will be the primary focus. In order to adequately depict van der Waals interaction and their strength, the distinction between binding and interaction energy needs to be highlighted.

The dispersion plays important role in graphitic materials: often it is the driving force determining the most stable geometrical conformation, and it gives a major contribution to the strength of the interaction between the graphitic material and its surroundings.

The VdW interactions are challenging for theoretical investigations. They arise, partially, because of the electron correlation effects, which are intrinsically difficult to evaluate accurately. For that reason, approaches that give good van der Waals interaction energies are very computationally demanding. In practice, such methods are feasible only for very small systems. The methods that are less computationally demanding usually do not represent the dispersion accurately. Hence, they cannot be safely used for systems in which vdW forces are an important factor.

A method feasible for graphitic systems that could accurately reproduce van der Waals interactions will be a significant development, especially if full geometrical optimization is feasible. With such method, a comprehensive study of the conformational space or even the potential energy surface of graphitic system is possible.

A short introduction to graphitic materials and van der Waals interactions is followed by a detailed presentation of the DFT-D method - a possible solution for the problem considered here. The DFT-D method is then reparameterized to reproduce the known features of the benzene dimer, a good model system of graphitic materials. The reparameterization is done using Relaxed Fitting, a new fitting approach. It ensures that the new method will produce well the geometries and their binding energies. The Relax Fitting approach is also used for two molecular mechanics' force fields. An extensive verification of the resulting method supports the use of Relaxed Fitting - new methods produce results that are substantially more accurate

than other methods of similar use. In the subsequent part several methods are used to study the energetic properties of the helicenes and phenacenes. The new DFT-D method is finally used to study the C_{60} complexes. The experimental observations suggest a small effect, namely that the C_{60} fullerene diameter changes slightly upon complexation. The studies using new DFT-D method confirm that and provide the theoretical support for that effect. The Relaxed Fitting methods produce results that are comparable with the most accurate methods at a fraction of their computational costs.

The first, and necessary, step is to present the investigated systems and studied interactions. To fulfill that requirement brief introduction of graphitic materials is presented. It is followed by concise presentation of vdW interactions. This chapter ends with the highlighting the difference between the interaction and binding energy – that differentiation will be used in following chapters.

1.1 Graphitic systems

In this section, a detailed description of the structures of graphitic materials is presented. Particularly, an important classes of these systems, namely graphite, fullerenes and carbon nanotubes are included.

1.1.1 Graphite

The graphitic systems, as the name implies, are systems with a structure similar to that of graphite. Graphite is an allotrope of carbon known since the ancient times. It has a layered structure, where each layer is a honeycomb lattice of carbon atoms. The $C-C$ bond distance is about 1.42 Å. The a_z is the lattice constant of graphite, it describes twice the interlayer distance. The $a_z = 6.7$ Å, so the layers are 3.35 Å apart[1]. A single layer of graphite is called graphene. The most common stacking of graphite, the ABA stacking, is presented in Figure 1.1.

Generally each of carbon atom in a graphitic system is covalently bonded to three neighbours (carbon hybridization of sp^2). Usually such systems are locally flat, or with small curvature. The introduction of structural defects in the lattice of graphene, *e.g.* five- or seven-member rings, will produce significant curvature near the defect. In an extreme case the layer could fold on itself producing closed sphere, the fullerene.

1.1.2 Fullerenes

The fullerenes are hollow spheres composed of carbon atoms. They can also be ellipsoid or tube shaped. The first experimental observation of fullerenes was done in 1985 by Kroto et al. [2].

The prime example of fullerenes is the C_{60} , also called Buckminsterfullerene, it is the most commonly known fullerene. In general, all spherical fullerenes can be called Buckyballs, but I will use this name exclusively for C_{60} fullerene.

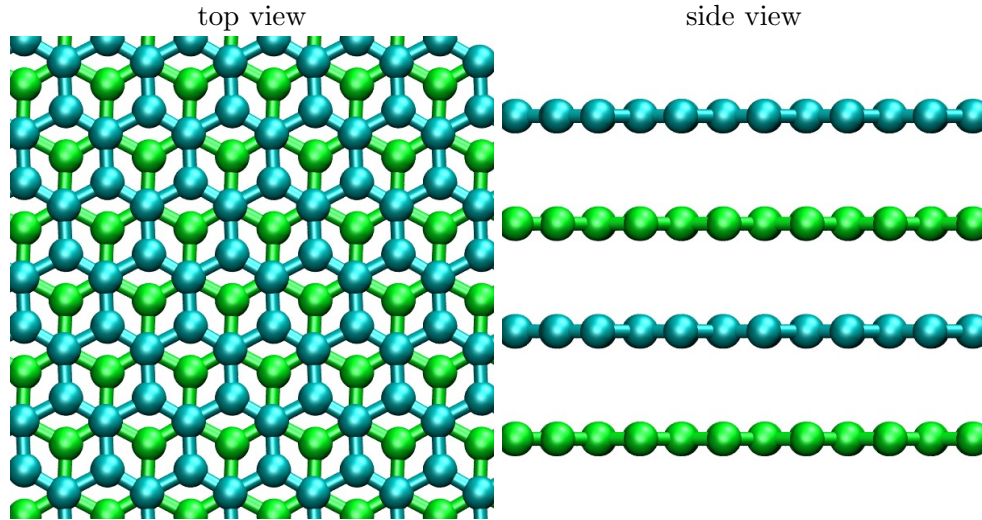


FIGURE 1.1: The structure of graphite in ABA stacking. Top (left) and side (right) view.

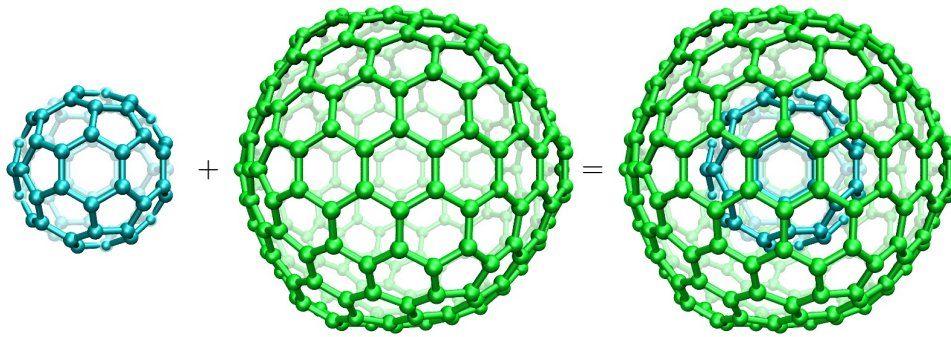


FIGURE 1.2: The example of fullerene onion $C_{60}@C_{240}$. The inner shell is Buckyball, C_{60} , the outer shell is C_{240} .

Smaller fullerenes can be encapsulated by larger ones, creating so called fullerene onions. An example of such fullerene onion is shown in Figure 1.2, it is $C_{60}@C_{240}$: C_{60} fullerene trapped inside the C_{240} .

As mentioned above, structural defects can produce fullerenes by folding parts of graphene sheet. That behaviour was observed experimentally[3]. Another possible folding of graphene sheet does not involve structural defects and produces carbon nanotubes.

1.1.3 Carbon Nanotubes

The carbon nanotubes (CNT's) are long cylindrical structures made out of carbon atoms. The CNT's have a long history, but it is unclear who should be considered their discoverer[4]. It seems that some papers (Iijima and Ichihashi [5], Bethune et al. [6]) from 1993 have precipitated the avalanche of new studies, but previous observations were made in Soviet Russia around 1950 and a first report of similar structures appeared in 1889.

It could be said that their structure is that of a graphene sheet that was rolled and glued at the ends. The internal structure of CNT's depends on the direction of that roll. Figure 1.3

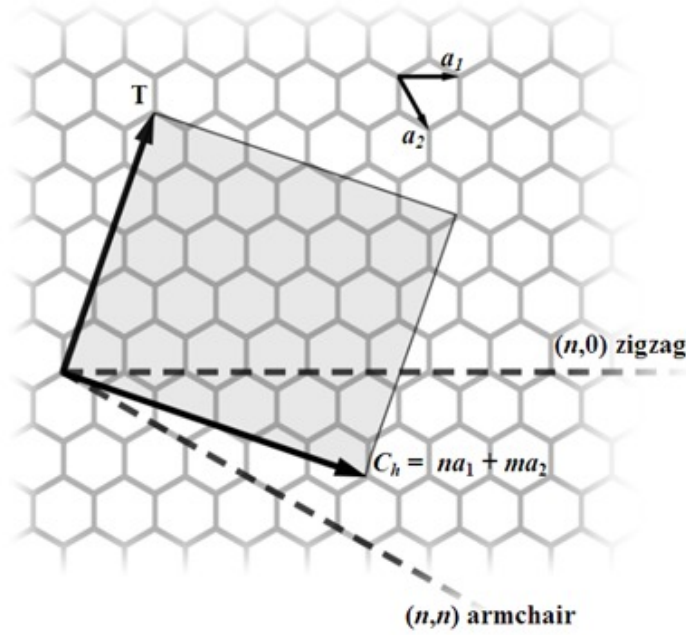


FIGURE 1.3: The naming scheme of carbon nanotubes.

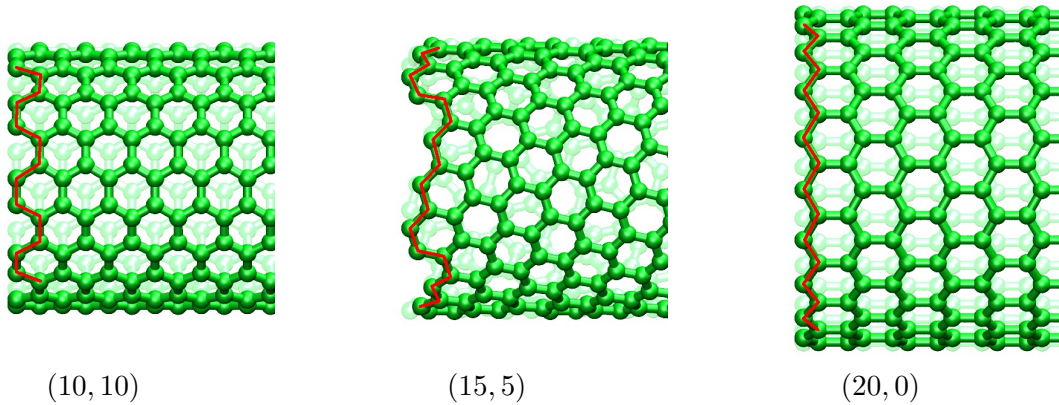


FIGURE 1.4: Various types of carbon nanotubes: armchair (10,10), chiral (15,5) and zigzag (20,0). The edges indicate the type of the tube.

(from [7]) presents simple scheme of naming carbon nanotubes. The vector C_h , constructed from basis vectors a_1 and a_2 , describes the direction of fictitious roll, the perpendicular vector T presents the axis of the created nanotube. For simplicity vector $C_h = na_1 + ma_2$ is represented as (n, m) .

The CNT's could be divided into zigzag, armchair and chiral ones. The armchair nanotubes are created from (n, n) vector, the zigzag ones have $C_h = (n, 0)$. The edge of the nanotube indicates the C_h vector describing it (compare Figures 1.3 and 1.4). Similar to fullerenes carbon nanotubes could form layered onion structures (see Figure 1.5).

The CNT's could be open- or close-ended. Figure 1.6 shows the different ending of CNT's, the closing of the tube could be similar to fullerene hemisphere. Closed nanotubes could be considered as a special case of fullerenes - the tube shaped fullerenes with high length to radius ratio.

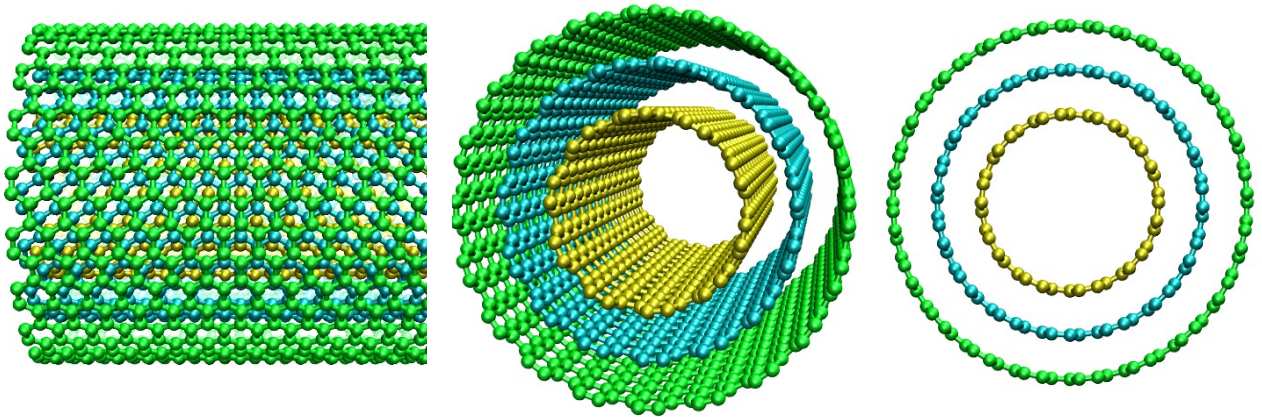


FIGURE 1.5: An example of multi-wall carbon nanotube, a view from different perspectives.

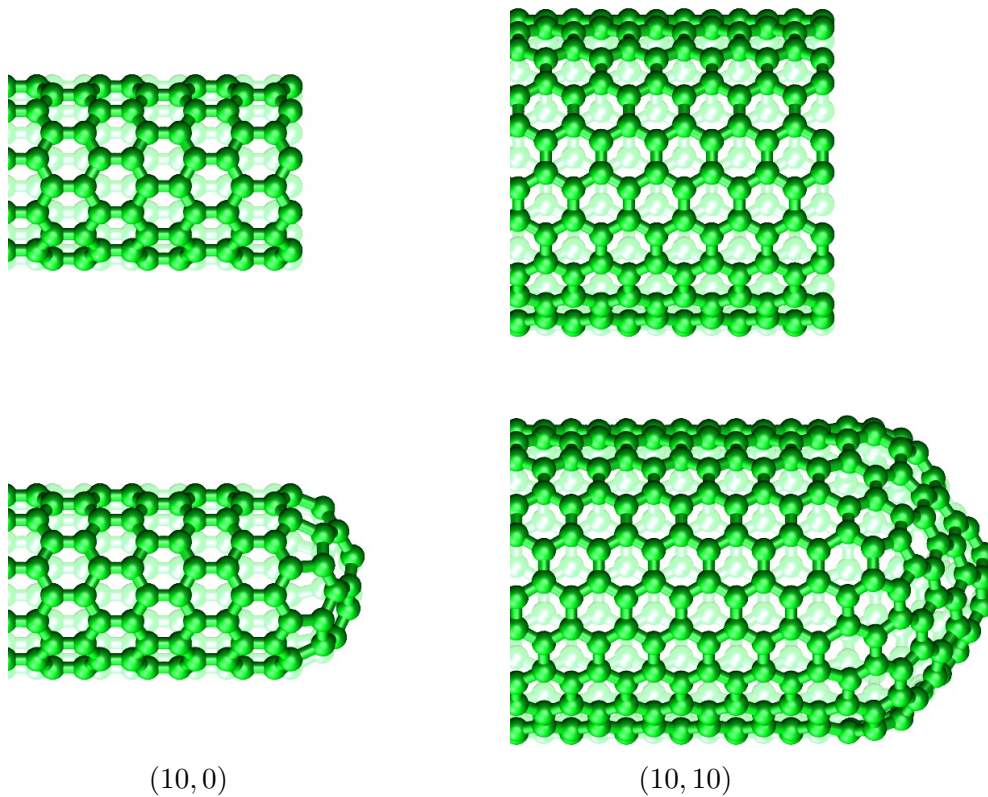


FIGURE 1.6: Different ends of carbon nanotubes. Some closed tubes (bottom) could be considered as open ones (top) terminated with parts of spherical fullerenes.

In normal open carbon nanotubes only six-membered rings are present, but the caps of the closed CNT's contains five member rings. When five- or seven-member rings are introduced into a carbon nanotube it will bend.

1.2 Van Der Waals Interactions

The interactions between closed-shell systems (atoms and molecules) are much weaker than those of typical bonds (usually of the order of few kcal/mol vs. hundreds kcal/mol).

According to International Union of Pure and Applied Chemistry (IUPAC), van der Waals (vdW) forces are defined as[8, 9]:

The attractive or repulsive forces between molecular entities (or between groups within the same molecular entity) other than those due to bond formation or to the electrostatic interaction of ions or of ionic groups with one another or with neutral molecules. The term includes: dipole-dipole, dipole-induced dipole and London (instantaneous induced dipole-induced dipole) forces. The term is sometimes used loosely for the totality of nonspecific attractive or repulsive intermolecular forces.

The interactions between a graphitic system and another molecule could arise from various sources, some of them not included in the definition above. For that reason, in this work the term will be used in the „loose” sense. Additionally, the term „dispersion” will be used interchangeably.

Despite their low strength vdW interactions are responsible for wide spectrum of chemical and physical phenomena: from solvation to self-assembly and protein folding.

1.3 Binding and interaction energy

In case of intermolecular interactions a good measure of their strength are the binding and interaction energy between the interacting moieties.

It is important to distinguish between both terms. Figure 1.7 shows the energetics of general dimerization process $A + B \rightarrow AB$. In principle, a monomer in the dimer will deform and its geometry in the dimer will be different from that of a separated moiety. The energy E_{rel} corresponds to the energy of that relaxation. The binding energy (BE) is the energy needed to separate the complex into two not interacting monomers (*i.e.* at infinite intermolecular distance):

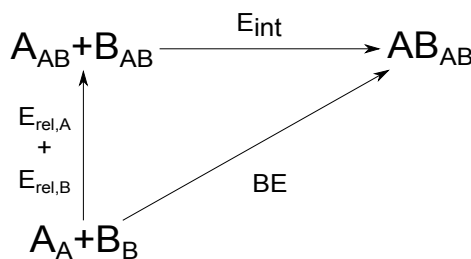


FIGURE 1.7: General dimerization process. Subscripts denotes the geometry of the moiety.

$$BE = E_{AB_{AB}} - E_{A_A} - E_{B_B}, \quad (1.1)$$

where the subscripts denote the geometry of the molecule: AB_{AB} denotes the whole complex and B_B is the free monomer B .

In theoretical studies, it is common to use yet a different measure: the interaction energy defined as the energy difference between the complex and the monomers without relaxation:

$$E_{int} = E_{AB_{AB}} - E_{A_{AB}} - E_{B_{AB}}. \quad (1.2)$$

This is a convenient definition, as one can use single point (SP) energies of the monomers, without optimizing their geometries. As monomers do not usually deform in a significant manner, relaxation energy is small and the E_{int} can be viewed as a first approximation of the more accurate binding energy.

Interaction energy could easily be generalized for more than two interacting moieties:

$$E_{int} = E_{ABC\dots ABC\dots} - \sum_{i=A,B,\dots} E_{i_{ABC\dots}}. \quad (1.3)$$

Analogous generalization is possible for binding energy. Most system studied here will be bundles of two interacting molecules. For that reason, Equations (1.1) and (1.2) will be usually utilized.

The definitions presented above follow the intuitive notion that negative values correspond to bonded systems. This is the reason, for not using the frequent convention, where both values are defined with a negative sign in Equations (1.1) and (1.2).

The difference between binding and interaction energies are especially important in situations when the monomers could deform in significant manners, or if the accurate geometry of the systems is not certain and little is known about various conformations. In the former case the E_{int} and BE would result in different values. If it is the latter case often one would confront SP interaction energies of various conformations without demanding geometry optimization to compare the conformations. That could lead to errors, since interaction energy is only an approximation to binding energy, which is closer to genuine chemical reality (*e.g.* reaction of complexation).

The terms interaction energy and binding energy are frequently used interchangeably in the literature. In most cases this does not present a problem when only one of the concepts is used. The production of accurate geometries is one of the aims of this study. For that reason, both term will be distinguished and used as defined above.

Chapter 2

Computational Methods

Van der Waals interactions are hard to model from theoretical point of view. In the case of graphitic materials this problem is more severe, as the method used needs to be feasible for large structures. In here, only quantum mechanical methods will be described. The density functional theory provides the methods that are viable for graphitic systems and are potentially augmented with accurate dispersion.

2.1 The Problem

In the IUPAC definition of van der Waals interactions (in Section 1.2) dipole-dipole, dipole-induced dipole and London interactions are included. All Quantum Mechanical (QM) methods include charge-charge interactions. If a given method can produce precise atomic charges then dipole-dipole interactions would be described accurately. The dipole-induced dipole (Debye) interactions also could be described accurately within most of QM methods. In contrast, London interactions, also called dispersion, are intrinsically hard to evaluate theoretically, as they arise from electron correlation.

The accurate description of electron correlation is computationally demanding. The „gold standard” of quantum mechanical methods is the CCSD(T) method[1–3]: the Coupled Cluster (CC) approach with single, double and perturbative triple excitations. It could describe dispersion accurately, but is feasible only for molecules much smaller than graphitic systems. For that reason, it could be applied only for the simplest model system – the benzene dimer.

Apart from model systems, the CCSD(T) approach is too computationally demanding for graphitic systems, even for single point (SP) calculations using small basis sets. The less accurate second order of Møller Plesset perturbation method[4] (MP2) is feasible for small graphitic systems. Such MP2 calculations are time consuming, but even geometry optimization is possible. Unfortunately MP2 is known to overestimate van der Waals forces[5–10].

The ideal method would be feasible for full geometry optimization with graphitic materials and will accurately describe van der Waals interactions. In practice, computational cost of most methods rises with higher accuracy. For that reason, some compromise between computational

cost and accuracy has to be made. To efficiently work with graphitic systems, the chosen method cannot be computationally demanding, but at the same time the method needs to include at least some dispersion interactions. Apart from mentioned CC and MPX approaches, there are many quantum methods that account for dispersion in some manner (*e.g.* SAPT: Symmetry Adapted Perturbation Theory method[11]). Unfortunately, for most of them, the computational cost is similar or slightly lower than that of MP2 method. For that reason, they are applicable only to small graphitic systems, or perhaps single point calculations for larger structures are possible.

The Density Functional Theory (DFT) method is an example of very efficient QM method: its computational cost is a fraction of that of CC or MP2 methods, and is comparable to that of Hartree-Fock (HF) method. The DFT is feasible for many graphitic systems, even geometry optimization for systems with hundreds of atoms is possible. As the name implies, it depends on the electron density of the system. In noncovalently bonded systems the electron density between the moieties is usually very small. For that reason, normal DFT method produces disappointing results for such systems[12, 13].

The problem with accurate theoretical description of van der Waals interactions was drafted above. The dispersion can be computed using very demanding methods and other methods, that are feasible to graphitic systems, are usually lacking or not accurate enough. There are many attempts to address this issue. The natural reaction is to augment feasible method with some estimation of the dispersion. The inclusion of dispersion in density functional methods is an active field of research. Several routes are being explored, including electron-density based approximations[14, 15], symmetry-adapted perturbation theory [16], reparameterization of existing functionals[17], use of effective core potentials[18] or instantaneous dipole moment of the exchange hole[19].

The most effective scheme to describe dispersion interactions is arguably that of adding a semi-empirical dispersion term, the so called DFT-D method[20, 21]. This method has many advantages: Any functional can be augmented with an additional dispersion term and it is easily incorporated into existing quantum mechanical programs, including the dispersion force gradients needed for geometry optimization. Furthermore, DFT-D allows for an easy interpretation of the results – the dispersion energy may be partitioned into individual parts of a molecule or different distance ranges.

2.2 DFT-D Method

The DFT-D method augments the conventional DFT energy (E_{DFT}) with a damped London-type dispersion energy (E_{disp}):

$$E_{DFT-D} = E_{DFT} + E_{disp}. \quad (2.1)$$

The general form of the additional dispersion for a system with N_{at} atoms can be expressed as:

$$E_{disp} = - \sum_n s_n \sum_{\substack{A,B \\ A \neq B}}^{N_{at}} \frac{C_{n,AB}}{R_{AB}^n} f_{dmp}(n, R_{AB}), \quad (2.2)$$

where $n = 6, 8, 10, \dots$ is the order of the expansion, $C_{n,AB}$ denotes the dispersion coefficient for an atom pair AB and s_n is a global scaling factor for the dispersion. To avoid near-singularities at small interatomic R_{AB} distances, the damping function f_{dmp} is introduced. Graphical representation of that approach is presented on Figure 2.1: pure DFT gives non bonding interaction energies, adding the attractive dispersion produce interaction energies similar to reference ones.

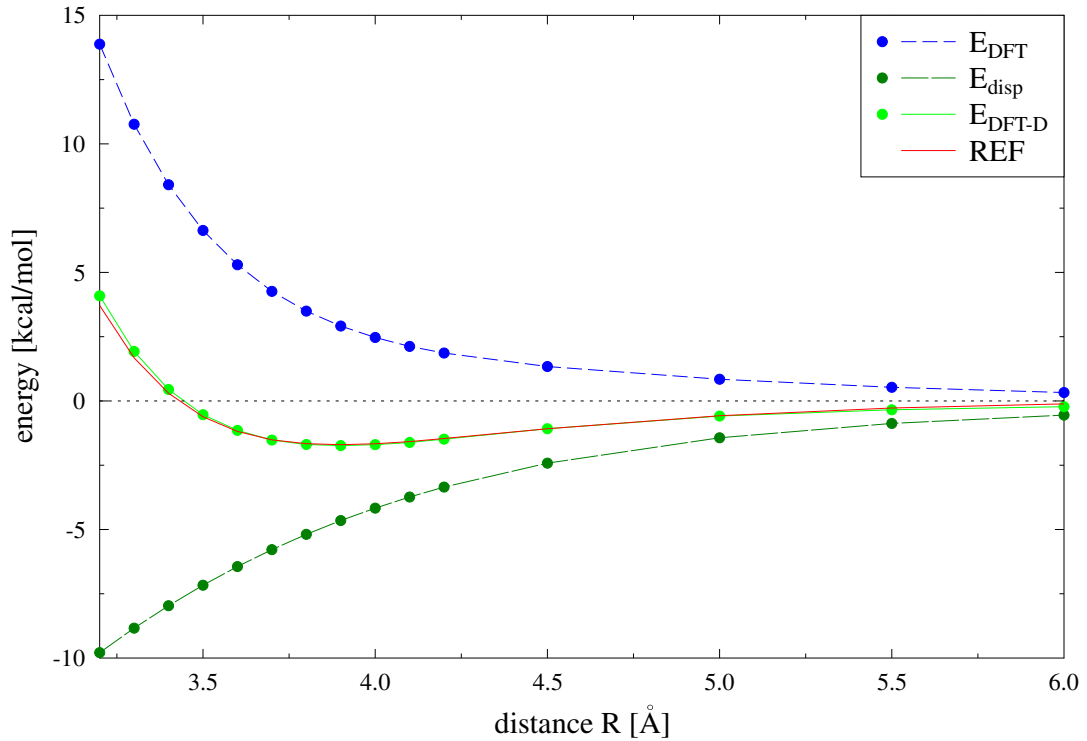


FIGURE 2.1: General idea of DFT-D approach. Additional dispersion E_{disp} augments lacking E_{DFT} producing more accurate E_{DFT-D} . Presented data is benzene dimer in sandwich conformation ($S_{D_{6h}}$), reference is CCSD(T) energy of interaction.

In principle this methodology of augmentation could be used to supplement other methods, *e.g.* HF, but only density functional methods will be considered here. The most relevant implementations of this methodology are Grimme's DFT-D1[22], DFT-D2[23] and DFT-D3[24]. The majority of the DFT-D methods truncate the Equation (2.2) at the first order, using only $n = 6$. Among presented methods, only the DFT-D3 uses a longer expansion.

The literature on the DFT-D method is extensive and notations vary widely. Furthermore there are multiple approaches to obtain values of $C_{6,AB}$ coefficients and to compute the damping function f_{dmp} . A concise review of the most commonly used variations within the DFT-D method is given to fix the notation.

2.2.1 Dispersion Coefficients

An important part of the dispersion correction are the dispersion coefficients $C_{n,AB}$. Along with the s_n scaling factor, they control the strength of the interaction. In DFT-D1 implementation, a mixed value in the form of a harmonic mean is used.

$$C_{6,AB} = 2 (C_{6,A} C_{6,B}) / (C_{6,A} + C_{6,B}), \quad (2.3)$$

where the atomic values are empirical parameters.

The subsequent DFT-D2 method uses the geometric mean:

$$C_{6,AB} = \sqrt{C_{6,A} C_{6,B}}, \quad (2.4)$$

with atomic values produced in a more *ab initio* manner: from the atoms' ionization potentials and their dipole polarizabilities: $C_{6,A} = 0.05 N I_{p,A} \alpha_A$.

Another mixing method often used is:

$$C_{6,AB} = 2 \frac{\left(C_{6,A}^2 N_{eff,A} C_{6,B}^2 N_{eff,B} \right)^{1/3}}{\left(C_{6,A} N_{eff,B}^2 \right)^{1/3} + \left(C_{6,B} N_{eff,A}^2 \right)^{1/3}}, \quad (2.5)$$

where $N_{eff,A}$ is the Slater-Kirkwood effective number of electrons[25–27].

2.2.2 Damping Function

It is important to note that the correction in the $1/R^6$ form is only valid at large distances and some medium-range correlation effects are already contained in the density functionals. At short distances standard functionals describe the systems rather well and some damping function must be used to seamlessly merge the short-range functional with the long-range correction.

The damping function used in DFT-D1 and DFT-D2 methods is:

$$f_{dmp}(R_{AB}) = \left\{ 1 + \exp \left[-\alpha \left(\frac{R_{AB}}{r_{scl} R_{AB}^0} - 1 \right) \right] \right\}^{-1}. \quad (2.6)$$

It uses the parameter α for controlling steepness and R_{AB}^0 to denote the cutoff distance. Usually R_{AB}^0 is a function of atomic van der Waals radii. The scaling factor, r_{scl} , is introduced to properly describe the medium-range behaviour of DFT-D method, so it depends on the functional being used. Figure 2.2 shows behaviour of this damping function for various values of α . When α is small the additional dispersion correction is „turn on” at close distances and slowly ascend to full strength. For large α values the dispersion is sharply introduced near the cutoff distance and quickly reaches full strength.

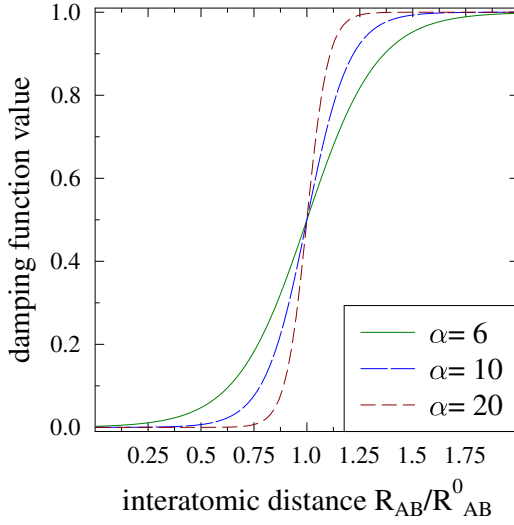


FIGURE 2.2: Comparison of various steepness parameter α values. For large α values damping function quickly switches the dispersion correction.

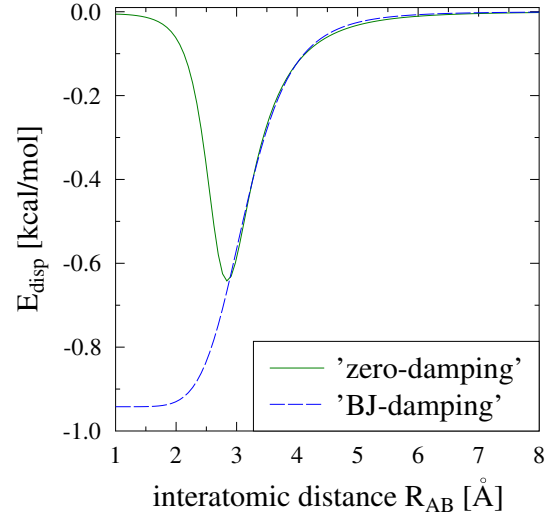


FIGURE 2.3: Comparison of two general types of damping function: zero-damping (green) and BJ-damping (blue). The BJ-damping produce some additional dispersion at small distances, zero-damping vanishes at those distances.

The newer DFT-D3 could be used with a different damping.

$$f_{dmp}(n, R_{AB}) = \left[1 + 6 \left(\frac{R_{AB}}{r_{scl,n} R_{AB}^0} \right)^{-\alpha_n} \right]^{-1}, \quad (2.7)$$

where the steepness parameters are $\alpha_6 = 14$, and $\alpha_{n+2} = \alpha_n + 2$. At short distances, this damping functions can introduce a repulsive force leading to longer interatomic distances. In order to avoid this another, so called Becke-Johnson (BJ), damping could be used in the DFT-D3. It changes the whole additional dispersion to:

$$E_{disp} = -\frac{1}{2} \sum_{n=6,8} \sum_{\substack{A,B \\ A \neq B}}^{N_{at}} \frac{C_{n,AB}}{R_{n,AB} + (a_1 R_{n,AB}^0 + a_2)^n}. \quad (2.8)$$

In order to distinguish usage Equation (2.7) from (2.8) as the damping function the former could be called zero-damping – it goes to zero for close distances. The BJ-damping uses two additional parameters a_1 and a_2 , but provides a constant and non vanishing E_{disp} for short interatomic distances. This ensures negligible force at those distances, which resolves the mentioned elongation of interatomic distances. Figure 2.3 shows the behaviour of both damping methods.

Various other damping methods were investigated[20, 28, 29] and an universal damping function was proposed[30]:

$$f_{dmp} = \left\{ 1 + a \exp \left[-b \left(\frac{R_{AB}}{r_{scl} R_{AB}^0} \right)^m \right] \right\}^n, \quad (2.9)$$

where by adjusting a , b , m and n parameters one can mimic other zero-damping types of f_{dmp} .

2.2.3 Cutoff Radii

All damping functions use a cutoff radius R_{AB}^0 .

Mixed values are usually the sum of the atomic ones

$$R_{AB}^0 = R_A^0 + R_B^0. \quad (2.10)$$

Another proposed mixing was [26]

$$R_{AB}^0 = \left(R_A^{0^3} + R_b^{0^3} \right) / \left(R_A^{0^2} + R_b^{0^2} \right). \quad (2.11)$$

The DFT-D1 and DFT-D2 methods use the sum of atomic radii for R_{AB}^0 . The atomic, R_A^0 radius, corresponds to the 0.01 au electron density contour in a ROHF/TZV calculation. The DFT-D1 uses the radii scaling value of $r_{scl} = 1.22$ and the DFT-D2 decreased it to $r_{scl} = 1.10$.

2.2.4 DFT-D3

The newest approach of Grimme's group, the DFT-D3 method, is significantly different from the general methods presented above. A longer expansion including the $n = 8$ term is used (with $s_8 = 1$), an additional three-body term could be used and most parameters are obtained in a more *ab initio* manner.

The three body term takes the form

$$E_{disp,DFT-D3}^{(3)} = \frac{C_{9,ABC} (\cos \theta_A \cos \theta_B \cos \theta_C)}{R_{AB} R_{BC} R_{CA}}, \quad (2.12)$$

where $C_{9,ABC} \sim -\sqrt{C_{6,AB} C_{6,BC} C_{6,AC}}$, and angles θ are internal angles of the triangle formed by atoms ABC . As of August, 2011 the three-body term is not recommended. Grimme stated[31, manual for DFTD3 program]: „Adding three-body corrections is currently not recommended, as very little is known about the three-body behaviour of common DFs in overlapping density regions.”

Dispersion coefficients are obtained in a more elaborate, less empirical, process. First the average dipole polarization of the hydrides ($\alpha_{X_n H_m}$) for all atoms are computed. $C_{6,AB}$ values are computed from $\alpha_{A_n H_m}$ and $\alpha_{B_l H_k}$:

$$C_{6,AB} = \frac{3}{\pi} \int_0^\infty \frac{1}{m} \left[\alpha_{A_m H_n}(i\omega) - \frac{n}{2} \alpha_{H_2}(i\omega) \right] \times \frac{1}{k} \left[\alpha_{B_k H_l}(i\omega) - \frac{l}{2} \alpha_{H_2}(i\omega) \right] d\omega. \quad (2.13)$$

For each atom several reference hydrides are used and the data containing the results and the corresponding coordination number are stored. Then, the values for $C_{6,AB}$ in the current

molecule are obtained from the 2D interpolation using stored values. The values for $C_{8,AB}$ are recursively obtained from $C_{6,AB}$.

The DFT-D3 method takes another approach to obtain cutoff radii: R_{AB}^0 is computed directly as the distance at which first-order AB interaction energy equals the cutoff energy. The cutoff energy was chosen to ensure the cutoff radii between carbon atoms to be the same as in the DFT-D2 method.

The DFT-D3 is an empirical method. The fact that most of the parameters are obtained in a systematic, *ab initio* fashion, does not change that, but rather it hinders the process of adjusting DFT-D3 for specific systems.

Chapter 3

Relaxed Fitting Method

3.1 Parameterization of DFT-D Method

Most of described DFT-D approaches depend on some parameters that are not obtained from first principles – the values of those parameters need to be given in advance. Usually the parameterization is made by optimizing the values of the parameters to reproduce some measurables known from experiment or more precise methods.

As the graphitic systems are the interest of this study, the very accurate theoretical data of a model system need to be used as a reference for the fitting. The benzene dimer (BD) is arguably the smallest molecular analogue of graphitic materials. Very accurate, coupled cluster method, calculations were made for many points on its potential energy surface[1, 2]. For that reason, the benzene dimer will be used as a training system for the parameterization of DFT-D method.

The parameterization scheme and its validation was published by Strutyński, Melle-Franco, and Gomes [3].

3.1.1 Benzene Dimer – the Reference

The study of aggregation of benzene molecules is difficult, both theoretically and experimentally, due to the weak binding. For that reason, experimental data on the BD are scarce: the interaction energy is about -2.4 kcal/mol[4]; The exact geometry of the BD is not known, but the experiments showed that the minima is most likely a T-shaped structure[5].

In contrast, the benzene dimer has been the object of many theoretical studies yielding two almost isoenergetic minima (PD_a and TT_b) and, at least, eight stationary points[6]. The binding energy of the BD was theoretically found to be less than -3.0 kcal/mol[1, 2, 7, 8].

The benzene dimer conformations presented in Figure 3.1 are used in this study, detailed XYZ structures are attached in Appendix A. Various types of structures are represented: parallel displaced (PD), sandwich type (S), T-shaped (T), tilted T-shaped (TT), V-shaped (V) and X-shaped (X). The subscript of the conformation indicates the symmetry of the molecule or

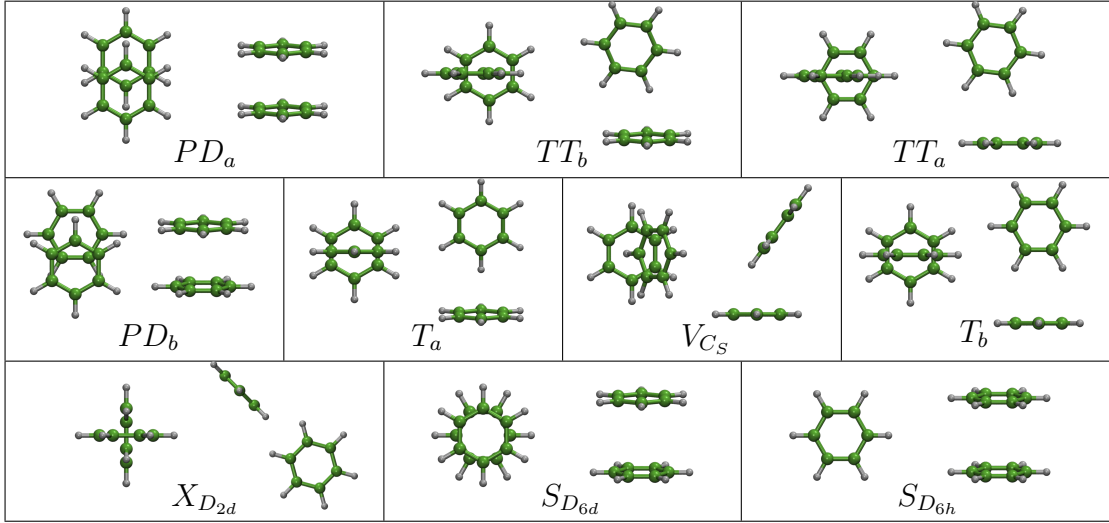


FIGURE 3.1: Benzene dimer conformations: including parallel displaced (PD), sandwich type (S), T-shaped (T), tilted T-shaped (TT), V-shaped (V) and X-shaped (X) configurations. The subscript of the configuration indicates the symmetry of the molecule or the position of one molecule with respect to the other (a - over atom, b - over bond). Conformations PD_a and TT_b are minima, the rest are stationary points.

the position of one molecule with respect to the other (a - over atom, b - over bond). Two of those conformations, namely the PD_a and the TT_b , are the minima, the rest are the stationary points. The interaction energies corresponding to that structures are shown in Table 3.1. They are extrapolated to Complete Basis Set (CBS):

$$E_{CBS}^{CCSD(T)} = E_{AVDZ}^{CCSD(T)} - E_{AVDZ}^{MP2} + E_{CBS}^{MP2} + E_{AV5Z*}^{HF}, \quad (3.1)$$

where the correlation part of the interaction energy was extrapolated from SCS-MP2/AVTZ and SCS-MP2/AVQZ data along with HF/AV5Z* results to get SCS-MP2/CBS limit. These, coupled cluster, energies were reported by Bludský et al. [1].

Usually, graphitic materials have small curvature and are locally flat. For that reason, one may expect that parallel conformations of benzene dimer are more relevant as a model system of graphitic materials. To check that assumption two set of references will be used: full set of ten conformations (PD_a , TT_b , TT_a , PD_b , T_a , V_{Cs} , T_b , $X_{D_{2d}}$, $S_{D_{6d}}$, $S_{D_{6h}}$) and four parallel conformations (PD_a , PD_b , $S_{D_{6h}}$, $S_{D_{6h}}$).

3.1.2 DFT-D for the Benzene Dimer

The benzene dimer was studied using DFT-D methods, and due to its small computational cost it was even used for molecular dynamics[9, 10].

The DFT-D method was already fitted for the benzene dimer[7, 10]. Namely, Pitoňák et al. [7] performed such parameterization using non-default mixing methods within DFT-D. Unfortunately, despite correspondence with the authors, reproduction of their E_{disp} values was

not achieved. Consequently, parameterization the DFT-D2 method for the benzene dimer with an optimization scheme suited to graphitic systems was undertaken.

The DFT-D2 method is already implemented in many QM programs. Furthermore, it is relatively easy to implement – it require small addition to original code and derivative are easy to compute. The implementations of the DFT-D3 method are less available. This may be caused by the fact that it is more complex and require relatively large database of reference values (in total several MiB of data); furthermore, BJ- and zero-damping require almost separate implementations. Grimme made the standalone DFT-D3 program freely available[11], program consist of current implementation of DFT-D3, newest database, and older DFT-D2 method.

Unfortunately, when geometry optimization is required, the use of standalone programs is cumbersome. At each step of QM calculation, energy and energy gradients have to be included from outside program. Unfortunately in most QM programs, if available, including external data could be problematic and may lead to errors. Moreover, customization of the DFT-D3 method for specific systems is less direct – the original database need to be augmented with polarization values of systems closer to desired one. In DFT-D2 method one need only to modify appropriate coefficients values.

TABLE 3.1: Interaction energies of benzene dimer conformations used as a reference. The values obtained from CCSD(T)/CBS method.

conformation	E_{int} [meV]	E_{int} [kcal/mol]
PD_a	-118.4	-2.73
TT_b	-122.3	-2.82
TT_a	-121.4	-2.80
PB_b	-118.0	-2.72
T_a	-117.1	-2.70
VC_S	-118.8	-2.74
T_b	-104.1	-2.40
$X_{D_{2d}}$	-77.6	-1.79
$S_{D_{6d}}$	-74.2	-1.71
$S_{D_{6h}}$	-74.2	-1.71

3.1.3 Comparison of the Results

To optimize values of the DFT-D parameters there is a need for some function that describes the accuracy of the results. The Root Mean Square difference of the binding energy was used:

$$RMS(\Delta BE) = \sqrt{\frac{1}{n_{sys}} \sum_{i=1}^{n_{sys}} (\Delta BE_i)^2}, \quad (3.2)$$

where ΔBE_i is the difference between reference and DFT-D binding energy of the i -th conformer,

$$\Delta BE_i = BE_{i,CCSD(T)} - BE_{i,DFT-D}. \quad (3.3)$$

The choice of that function was dictated by several factors: $RMS(\Delta BE)$ represents averaged value over all conformations, but it behaves correctly in presence of big errors¹, furthermore it is not affected by the sign of the error.

¹Value of $RMS(\Delta BE)$ is not extremely high or low relatively to other commonly used mean functions.

The structure of the molecule changes during geometry optimization. Those two structures could be compared using root mean square displacement of atoms (*RMSD*):

$$RMSD = \sqrt{\frac{1}{n_{sys}} \sum_{i=1}^{n_{sys}} \Delta r_i^2}, \quad (3.4)$$

where Δr_i is the distance of the i -th atom between two structures. This value is sensitive to relative position of the structures, because of that the reported value is always the minimum obtained after rotation and translation of the structures.

Interesting property of the *RMSD* is that root mean square of several *RMSD* values correspond to root mean square of the deviations of all atoms. For n_{sys} systems:

$$RMS(RMSD) = \sqrt{\frac{1}{n_{sys}} \sum_{i=1}^{n_{sys}} RMSD_i^2} = \sqrt{\frac{1}{n_{sys}} \sum_{i=1}^{n_{sys}} \frac{1}{n_{at,i}} \sum_{j=1}^{n_{at,i}} \Delta r_j^2}, \quad (3.5)$$

if each system has the same n_{at} number of atoms:

$$RMS(RMSD) = \sqrt{\frac{1}{n_{sys}n_{at}} \sum_{i=1}^{n_{sys}} \sum_{j=1}^{n_{at}} \Delta r_j^2}, \quad (3.6)$$

which is equivalent of *RMSD* of one $n_{sys}n_{at}$ atomic system. That means that if one have set of n_{sys} structures of n_{at} atoms, the root mean square of the *RMSD* values for each systems is equivalent to taking *RMSD* of one big system composed of all $n_{sys}n_{at}$ atoms. Hence, *RMSD* could be used as a indicator of geometrical accuracy for one or more systems.

This is very helpful, as all reference structures have the same number of atoms. For that reason, after geometry optimization the *RMS(RMSD)* could be used as a overall measure of the geometrical accuracy.

3.1.4 Parameterization Procedure

Various combinations of mixing schemes were tried at preliminary stage of the investigations. Changing them does not affect the results significantly. For that reason, the default DFT-D2 mixing schemes were used. Accordingly, unless stated otherwise, all presented E_{disp} will be computed using Equations (2.4), (2.6) and (2.10).

After preliminary testing, the BLYP[12, 13] functional was chosen, as the one of the fastest and more accurate functionals. Similarly, Jurečka et al. [14] found that BLYP behaves well, especially with small basis. The BLYP functional was previously used within DFT-D scheme for benzene dimer with reasonable results[7, 10].

Usually, the DFT-D parameters are obtained by fitting: A set of reference structures is established, with precise values of some properties already known; Then the parameters are fitted to reproduce those properties as well as possible. The DFT-D method was introduced as

a way to reintroduce van der Waals interaction into DFT methods. The interaction energy is a straightforward property that could be considered.

In most fitting schemes the geometry of the structures is not optimized – as the geometry optimization is more computationally and time demanding – it is not practical when there are many reference structures. Sometimes reference structures contain various distances of similar conformation to include some information about the Potential Energy Surface (PES).

This procedure is hazardous: after fitting, the single point interaction energies may correspond well to reference values, but when one tries to optimize these structures, the geometry obtained may be far from reference one. For example, during geometry optimization the distance between the moieties could shrink. If that happens, the resulting binding energy will, probably, be too large. In similar cases, the obtained method could be safely used only with limitations – to systems with known exact geometry.

To avoid that the binding energy could be used instead of the interaction energy – it requires full geometry optimization – one possible drawback is that in some cases during optimization conformation of the structure could change. In such cases one cannot compare binding energies with reference values, as they correspond to basically different structures. The reference set from Table 3.1 contains 10 conformations, which make it feasible to optimize all structures at each step of the fitting.

For systems composed mostly from carbon and hydrogen, the set of six parameters need to be considered $\{C_{6,C}, R_C^0, C_{6,H}, R_H^0, s_6, r_{scl}\}$, with possible addition of $C_{6,A}$ and R_A^0 for heteroatoms. It could be said that the strength of the interaction is more relevant and consequently, at least three parameters need to be adjusted, *i.e.* $\{C_{6,C}, C_{6,H}, r_{scl}\}$ set, to perform a reasonable fitting.

In the case of homoatomic interactions some DFT-D coefficients work in conjunction: an effective strength is given by the value of $s_6 C_{6,AA}$ product, similarly $R_{AA}^0 r_{scl}$ is the effective cutoff radius². For that reason, some set of parameters are more meaningful than others. More purposeful would be set containing only one of the correlated coefficients, *e.g.* $\{C_{6,AA}, R_{AA}^0\}$ or $\{C_{6,AA}, r_{scl}\}$, but not $\{C_{6,AA}, R_{AA}^0, r_{scl}\}$. Simultaneous optimization of conjoined parameters would be problematic, because there are highly correlated and different values could produce the same results. If one wants to optimize conjoined parameters, the safe solution is to optimize them separately: keep one of them frozen during first optimization, and reoptimize the second afterwards, while freezing the first one.

In the case of graphitic materials, carbon and hydrogen are the most abundant elements and usually hydrogen plays a small role in vdW interactions, with the consequence that the impact of non-carbon elements on dispersion energy is small. For example for the C_{60} -tetraphenylporphyrin complex all interactions with nitrogen are only 6% of E_{disp} , while C and H interactions account for 98 and 18% respectively. For that reason, it was decided to use global s_6 instead of

²In this case $2R_C^0 r_{scl}$, as the Equation (2.10) was chosen for radii mixing.

the separate $C_{6,A}$ coefficients, the fact that only one DFT functional was used facilitates that optimization scheme.

For simplicity, the values for $C_{6,C}$, $C_{6,H}$, $R_{6,C}$ and R_H^0 was fixed at their DFT-D2 values. Therefore, the values of s_6 and r_{scl} was optimized. Figure 3.2 presents used implementation of the relaxed fitting. In the initial step all geometries are optimized using the initial parameters ($s_6 = 1.05$, $r_{scl} = 1.22$). Then, these parameters are optimized using the Nelder-Mead method[15] to minimize the $RMS(\Delta BE)$ on the frozen geometries obtained in the last step. In order to avoid local minima, several fittings are performed from different starting points. In subsequent steps the geometry of all the molecules in the data set are progressively relaxed with new sets of parameters. The procedure is continued until convergence of the parameters or the $RMS(\Delta BE)$. Note that during geometry optimization some conformations may change.

In principle some geometrical score function

could be used to account for that, but for simplicity, the geometries were monitored and parameters that cause conformation switching were discarded. The optimization scheme presented here will be referred to as Relaxed Fitting (RF).

Usually, the optimization would require to evaluate the derivatives of the $RMS(\Delta BE)$ in respect to optimized variables. In presented case, the derivatives would have to be obtained numerically, which would produce numerical noise. For that reason, the Nelder-Mead methods was chosen for its simplicity, it does not involve any derivatives and could be used for functions with unknown form.

3.2 The Parameters of the RF Method

The described optimization scheme was applied with two sets of benzene dimer conformations as a reference (see Figure 3.1 and Table 3.1): the full set of ten conformations (PD_a , TT_b , TT_a , PD_b , T_a , VC_s , T_b , $X_{D_{2d}}$, $S_{D_{6d}}$, $S_{D_{6h}}$), and only parallel ones (PD_a , PD_b , $S_{D_{6h}}$, $S_{D_{6h}}$).

For all of the reference BD conformation, three different values of the steepness of the damping function were used, $\alpha = \{6, 15, 20\}$, producing what will be called RF-all- α sets of

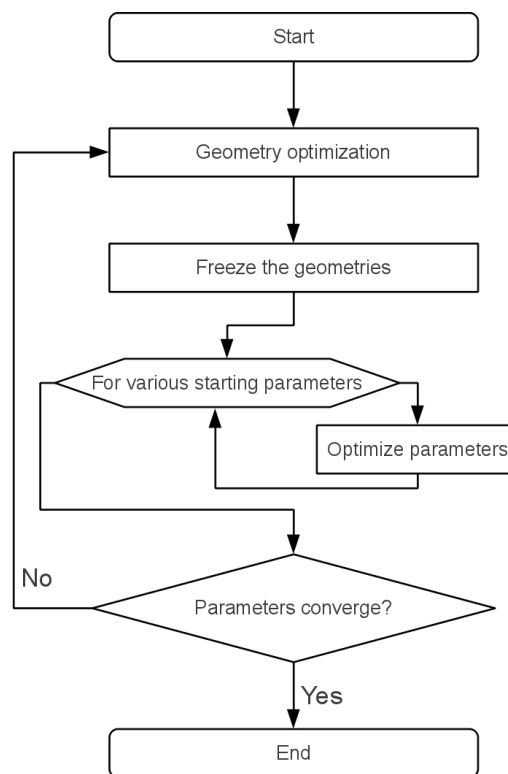


FIGURE 3.2: The relaxed fitting procedure flowchart.

parameters for various basis sets. Table 3.2 presents the parameters obtained during the optimization process. A damping function steepness of $\alpha = 15$ shows some of the intermediate behavior between $\alpha = 6$ and $\alpha = 20$. For that reason, the optimization with parallel structures, RF-par, was done only with $\alpha = \{6, 20\}$, producing the results shown in Table 3.3.

The set of parallel structures presents less variability in the types of BD structures. For that reason, it is easier to parameterize DFT-D for that set. The RF-par gives good agreement for four parallel-like structures, the RF-all method need to reproduce all 10 structures, hence $RMS(\Delta BE)$ and $RMSD$ values in Table 3.3 are smaller than in Table 3.2. The downside is that the produced RF-par method is less variable and could be safely used only for similar systems.

In case of the RF-par fitting, such parameterization model does not give a good representation of the other benzene dimer conformations. For example, with RF-par-6/6-31G the ΔBE for the $X_{D_{2d}}$ conformation was 1.2 kcal/mol, and for RF-par-6/6-311G with the T_b conformation $\Delta BE = 0.4$ kcal/mol. Moreover, this optimization process may lead to non physical parameter values in some cases³. For that reason, the RF-par method will not be used later.

As expected, the energetic and geometrical errors decrease with growing basis sets. The RF-all-6 method with the relatively large TZVP basis set produces the best results. In general, smaller $\alpha = 6$ produces slightly better results than $\alpha = 20$. For that reason, one may prefer to use the RF-all-6 method. The final aim here is to use the resulting parameters in studies of graphitic systems. However, for larger systems, the use of the TZVP basis set is expensive and may not be feasible. For this reason, the reasonable choice is the set of parameters that not only results in the required accuracy but also is affordable with the available computational resources. For very large systems, the RF-6/6-31G method appears as a reasonable compromise between accuracy and computational cost. The RF-6/6-311G is appropriate for smaller systems, or as an example of more robust method to validate less accurate methods.

TABLE 3.2: DFT-D parameter values for various basis sets, RF-all method. Scaling factor s_6 , radius scaling r_{scl} [Å], damping function steepness α , coefficients $C_{6,A}$ [Jnm⁶/mol], vdW radius R_A^0 [Å], root mean square geometrical displacements ($RMSD$ [Å]) and the root mean square of the binding energy error ($RMS(\Delta BE)$ [kcal/mol]) are presented.

Basis	s_6	r_{scl}	α	$C_{6,C}$	$C_{6,H}$	R_C^0	R_H^0	RMS_{GD}	$RMS_{\Delta BE}$
6-31g	1.619	1.489	6	1.75	0.14	1.32	0.91	0.0858	0.2149
6-31g*	1.519	1.458	6	1.75	0.14	1.32	0.91	0.0768	0.2084
6-31g**	1.450	1.430	6	1.75	0.14	1.32	0.91	0.0640	0.2059
6-311g	1.811	1.432	6	1.75	0.14	1.32	0.91	0.1245	0.1562
6-311g*	1.816	1.452	6	1.75	0.14	1.32	0.91	0.1150	0.1331
6-311g**	1.689	1.401	6	1.75	0.14	1.32	0.91	0.0841	0.1254

Continued on next page

³For example $r_{scl} < 0.5$

Table 3.2 – continued from previous page

Basis	s_6	r_{scl}	α	$C_{6,C}$	$C_{6,H}$	R_C^0	R_H^0	RMS_{GD}	$RMS_{\Delta BE}$
TZV	1.532	1.250	6	1.75	0.14	1.32	0.91	0.0367	0.1028
TZVP	1.513	1.219	6	1.75	0.14	1.32	0.91	0.0334	0.0896
6-31g	1.253	1.383	15	1.75	0.14	1.32	0.91	0.0982	0.2121
6-31g*	1.205	1.373	15	1.75	0.14	1.32	0.91	0.0905	0.2050
6-31g**	1.172	1.360	15	1.75	0.14	1.32	0.91	0.0814	0.2065
6-311g	1.504	1.377	15	1.75	0.14	1.32	0.91	0.1064	0.1480
6-311g*	1.479	1.380	15	1.75	0.14	1.32	0.91	0.1013	0.1276
6-311g**	1.382	1.341	15	1.75	0.14	1.32	0.91	0.0734	0.1272
6-31g	1.210	1.381	20	1.75	0.14	1.32	0.91	0.1022	0.2156
6-31g*	1.165	1.373	20	1.75	0.14	1.32	0.91	0.0938	0.2089
6-31g**	1.135	1.361	20	1.75	0.14	1.32	0.91	0.0853	0.2106
6-31+g*	1.427	1.356	20	1.75	0.14	1.32	0.91	0.0971	0.1518
6-31++g	1.441	1.390	20	1.75	0.14	1.32	0.91	0.1263	0.1899
6-311g	1.465	1.381	20	1.75	0.14	1.32	0.91	0.1073	0.1538
6-311g*	1.414	1.379	20	1.75	0.14	1.32	0.91	0.1022	0.1428
6-311g**	1.348	1.348	20	1.75	0.14	1.32	0.91	0.0765	0.1365
6-311+g*	1.507	1.370	20	1.75	0.14	1.32	0.91	0.0914	0.1110
TZV	1.375	1.306	20	1.75	0.14	1.32	0.91	0.0603	0.1221
TZVP	1.379	1.291	20	1.75	0.14	1.32	0.91	0.0511	0.1185
VTZP	1.448	1.313	20	1.75	0.14	1.32	0.91	0.0637	0.1282

TABLE 3.3: DFT-D parameter values for various basis sets, RF-par method. Scaling factor s_6 , radius scaling r_{scl} [Å], damping function steepness α , coefficients $C_{6,A}$ [Jnm⁶/mol], vdW radius R_A^0 [Å], root mean square geometrical displacements ($RMSD$ [Å]) and the root mean square of the binding energy error ($RMS(\Delta BE)$ [kcal/mol]) are presented.

Basis	s_6	r_{scl}	α	$C_{6,C}$	$C_{6,H}$	R_C^0	R_H^0	RMS_{GD}	$RMS_{\Delta BE}$
6-311g	1.488	1.211	6	1.75	0.14	1.32	0.91	0.03923	0.00605
6-311g*	1.540	1.281	6	1.75	0.14	1.32	0.91	0.05207	0.00701
6-311g**	1.394	1.198	6	1.75	0.14	1.32	0.91	0.04381	0.00775
6-31g	1.079	0.934	6	1.75	0.14	1.32	0.91	0.03116	0.00155
6-31g*	1.060	0.988	6	1.75	0.14	1.32	0.91	0.03080	0.00224
6-31g**	1.019	0.913	6	1.75	0.14	1.32	0.91	0.02551	0.00205
6-31g	1.099	1.202	20	1.75	0.14	1.32	0.91	0.03307	0.00317
6-31g*	1.065	1.218	20	1.75	0.14	1.32	0.91	0.03604	0.00356

Continued on next page

Table 3.3 – continued from previous page

Basis	s_6	r_{scl}	α	$C_{6,C}$	$C_{6,H}$	R_C^0	R_H^0	RMS_{GD}	$RMS_{\Delta BE}$
6-31g**	1.041	1.188	20	1.75	0.14	1.32	0.91	0.03896	0.00369
6-31+g*	1.357	1.264	20	1.75	0.14	1.32	0.91	0.04002	0.00683
6-31++g	1.336	1.256	20	1.75	0.14	1.32	0.91	0.07794	0.04347
6-311g	1.383	1.304	20	1.75	0.14	1.32	0.91	0.04040	0.00614
6-311g*	1.366	1.326	20	1.75	0.14	1.32	0.91	0.07241	0.01027
6-311g**	1.301	1.297	20	1.75	0.14	1.32	0.91	0.03170	0.00570
6-311+g*	1.489	1.354	20	1.75	0.14	1.32	0.91	0.04076	0.01162
VTZ	1.465	1.306	20	1.75	0.14	1.32	0.91	0.03644	0.00847
VTZP	1.430	1.292	20	1.75	0.14	1.32	0.91	0.02639	0.00509

Chapter 4

Verification of the RF Method

A necessary step in the development of new methods is the verification of the newly obtained approach. For example, one could try to apply the new method to systems not used in the fitting scheme. If the method depends on some parameters, like in the case of DFT-D method, one could explore the impact of these parameters on its performance. A good practice is to collate the new method with other methods that were designed to work with similar structures.

4.1 The Graphite Crystal

A short introduction to graphite was presented in Section 1.1 of Chapter 1. The geometrical structure of the graphite is well known experimentally. The interlayer distance in graphite is known experimentally to be 3.35 Å, the monolayer *C-C* bond distance is about 1.42 Å[1, 2]. In contrast its energetical features are not known precisely. One of the problem in the studies of graphite energetics is that there are many possible measurables that can be obtained. Table 4.1 present the concepts that are relevant to energetics of the graphite crystal.

TABLE 4.1: The possible measurables of the energetical aspects of the graphite crystal.

crystal binding energy	}	– energy required to separate all crystal layers
interlayer cohesion energy		
exfoliation energy		– energy needed to separate single layer from a crystal
cleavage energy		– energy required to separate a crystal into two smaller sub-crystals
graphene binding energy		– energy required to separate two graphene layers

It is not always clear to which concept the authors refer to and the values of the different concepts can differ extensively. The binding energy of the graphite crystal is about twice that of two graphene layers[3]. Usually, the binding energy of two graphene layers is the reported value¹.

The few experimental values available have been obtained indirectly with the fundamental aid of molecular mechanics simulations. The microscopy analysis of collapsed nanotubes by

¹It is inferred from the context, as often it is described just as binding energy.

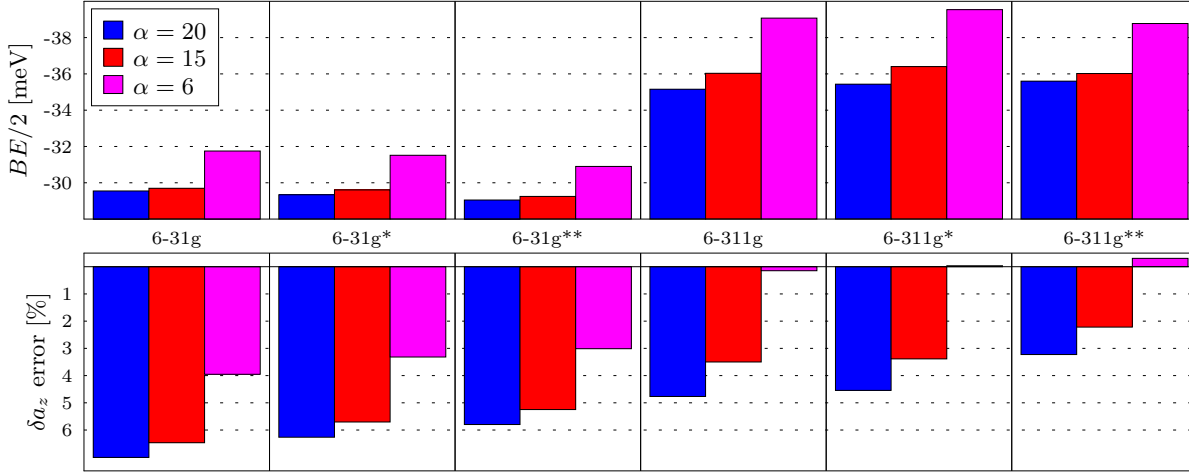


FIGURE 4.1: Results of RF methods for graphite crystal. Half of crystal binding energy ($BE/2$ [meV], top) and the error of interlayer lattice constant reproduction (δa_z [%], bottom).

Benedict et al. yielded a (-35 ± 15) meV/atom[4]. A higher value, (-52 ± 5) meV/atom, was obtained from the desorption of poly-aromatic hydrocarbons on graphite by Zacharia et al. [3].

The two most recent, and likely to be accurate, theoretical studies of graphite give more convergent results with binding energies of -56 meV/atom and -48 meV/atom for quantum Monte Carlo and RPA-DFT respectively [5, 6]. Dispersion corrected DFT (B97-D2) has already been applied to the interaction of poly-aromatic hydrocarbons of increasing sizes yielding the extrapolated binding energy of graphene of -66 meV/atom[7].

All graphite calculations concerning the RF methods were done using Crystal 09 program[8, 9] by Manuele Melle-Franco. They were done using periodic boundary conditions, hence correspond to crystal of infinite size. The calculations cannot be performed if the basis set contains highly diffused functions². Figure 4.1 presents halved binding energies and errors of the geometries³ obtained using the RF-all parameters for Pople’s double- and triple- ζ basis sets. The best interlayer distances and largest binding energies are systematically obtained using the RF-all-6 method. The halved BE value (comparable to the BE of graphene) converges to about -40 meV/atom, which is well within the range of the mentioned literature data.

4.1.1 Exploration of Parameter Space

A good practice is to check the robustness of optimization. In order to do that, the parameter space available for RF optimization was explored.

Considering the lack of concordance of the energetics of the graphite, only the known interlayer distance was compared. It is known experimentally and it is sensitive to van der Waals interactions. It is not the case with the intralayer $C-C$ bond distance – most of the QM methods can accurately reproduce it.

²Such functions can interact outside the periodic box which causes problems.

³that is $\delta a_z = (6.7 - a_z)/6.7 \cdot 100\%$.

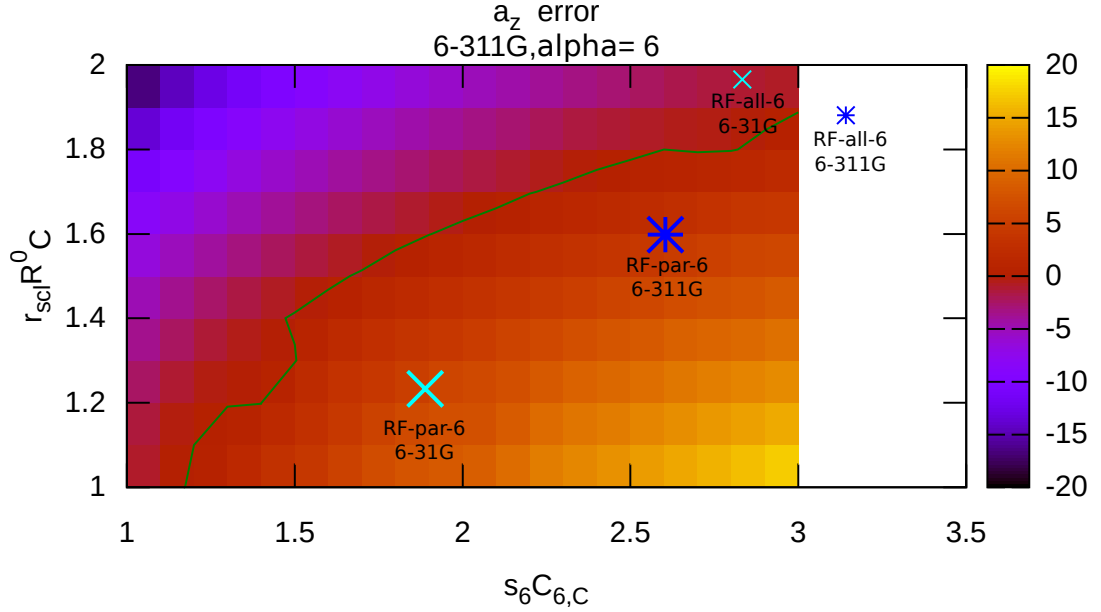


FIGURE 4.2: The error of graphite a_z reproduction with different DFT-D parameters. The location of parameters obtained after RF optimization are indicated. Graphite geometry optimization using RF-all-6/6-311G. The line on with geometry optimization reproduced experimental a_z is shown.

The geometry of graphite crystal for various values of $r_{scl}R_C^0$ and $s_6C_{6,C}$ was optimized (including the lattice constants). The error of obtained a_z lattice constant is shown on Figure 4.2, the crystal binding energies corresponding to obtained geometries are presented on Figure 4.3. Presented results are obtained using RF-all-6/6-311G parameters. The location of various RF optimizations are included for comparison, but the point corresponding to the method used is the most relevant. Unfortunately, the chosen range of the parameters was too narrow to include the values obtained from the relaxed fitting. Nevertheless, the point indicating the values of RF-all-6/6-311G parameters from relaxed fitting is very close to extrapolation of the line indicating no a_z error. For comparison, obtained BE are shown on Figure 4.3. In some cases the calculations with default conditions do not converge in the case of the single graphene sheet (necessary for obtaining the binding energy). For that reason, some of the points are missing or show unusual values.

4.2 Reproduction of the Minima

A necessary step in the development of new methods is the comparison with established methods. It is the simplest way of falsifying the new approach. If another method behaves better than the new one, then it is inadequate – the reference database or the methodology used needs to be changed. The RF method is based on the DFT method, hence it will be compared to another DFT functionals with similar basis sets, some of them with dispersion correction. The Slater exchange[10] with Perdew 81 correlation[11] functional was used as a simple LDA comparison. The M05 and M06 family of functionals[12, 13] were chosen, as they were tailored for

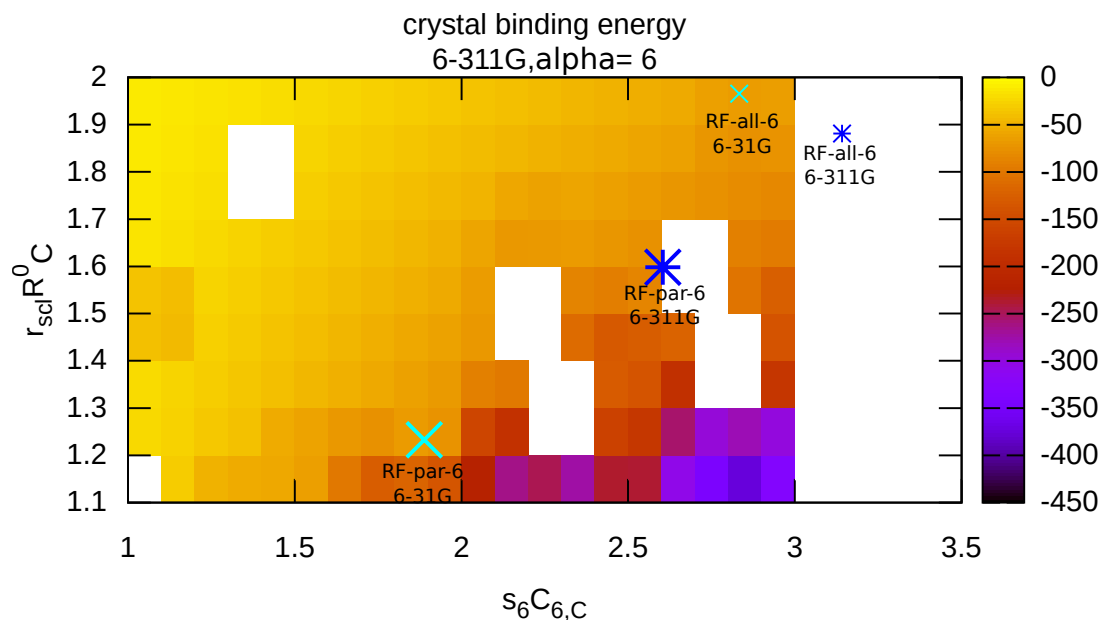


FIGURE 4.3: The BE of graphite crystal with different DFT-D parameters. The location of parameters obtained after RF optimization are indicated. Graphite geometry optimization using RF-all-6/6-311G method.

vdW interactions; because of their numerical instability with the default grid, bigger numerical grid was chosen⁴. Only successful functionals are presented. Some of the tested functionals failed to reproduce many of the BD geometries and produced wrong BE – for example, for the B3LYP[14–17] functional with DFT-D3 dispersion using the 6-31G basis set $S_{D_{6d}}$, TT_a , T_a and T_b conformations switched, and the good ones produce ΔBE of 0.7–1.2 kcal/mol.

The geometry optimization using different functionals and DFT-D methods lead to small relaxation of the benzene monomer (the *RMSD* of 0.001–0.021 Å) in comparison to reference geometry.

Figure 4.4 presents binding energies and geometrical errors of the investigated methods. Error bars show minimal and maximal discrepancies from the reference values among the BD conformations. It is important to note that RF methods provide precise results, this being confirmed by the very small gap between the best and worst binding energies. Asterisks indicate that at least one conformation was not conserved during geometry optimization. Geometrical optimization using the M05-2x-D3/TZV and the M05-2x-D3/TZVP methods changed the $S_{D_{6d}}$ conformation into the PD_b , but the M05-2x without dispersion could reproduce it: the M05-2x/6-311G and the M05-2x/TZVP have problems with V_{C_S} and PD_b conformations, respectively. The BLYP-D2 method causes switching of the V_{C_S} conformation into the T_A .

In Figure 4.4, it is hard to compare the overall performance of the different methods. More informing is the XY plot of the binding energies and geometrical errors as presented in Figure 4.5. The results for each functional with growing basis set are connected with arrows. The methods with a bigger basis set should produce smaller geometrical differences and binding energies closer

⁴NWChem keyword „grid euler lebedev 96 11”

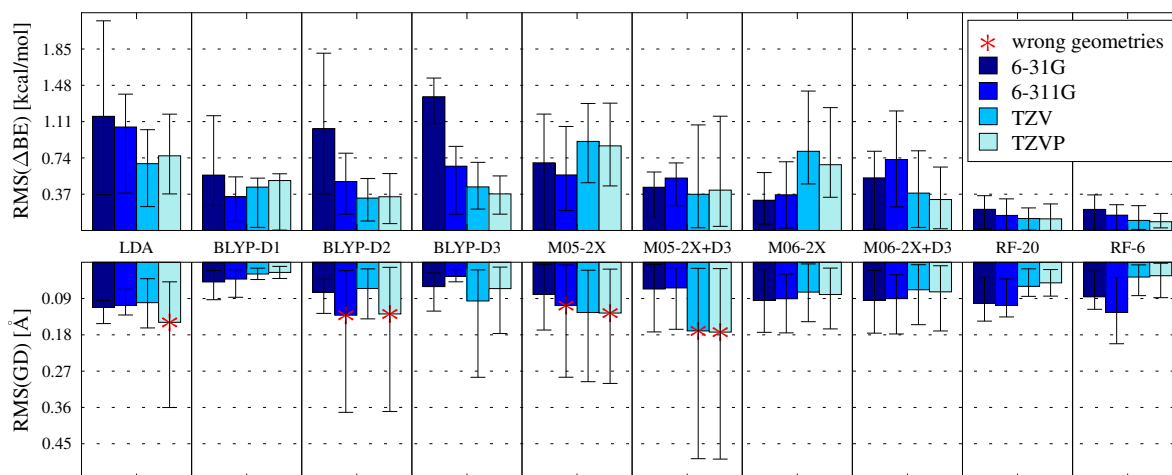


FIGURE 4.4: Binding energy errors (top) and geometrical differences (bottom) for the benzene dimer. Asterisks indicate that some conformations switch during geometry optimization. Error bars represent minimal and maximal $|\Delta BE|$ (top) or $RMSD$ (down) among the benzene dimer conformations.

to the reference, CCSD(T)/CBS, data. Hence, methods with growing basis sets should result in points closer to the origin of the plot. Only BLYP-D3 and RF methods behave as expected. However, the BLYP-D3 method produces very large errors with small basis sets and could not be used with relatively large, graphitic systems. Surprisingly, the first generation of the Grimme, the BLYP-D1 method, gives very accurate geometries, its binding energies are comparable to other investigated methods. From Figure 4.5, it is clear that relaxed fitting method performs very well. The RF geometrical errors are comparable to other methods, and the corresponding binding energies are superior.

To obtain the interaction energy, the previously known geometry of the complex is required or its geometry optimization must be performed. The E_{int} could be viewed as a first approximation of the true binding energy, which is more computationally demanding. Figure 4.6 shows the differences when one goes from E_{int} , at reference geometries, to BE, with complex and monomer relaxation.

Most methods considered here produce smaller errors without geometry optimization. This indicates that most methods were designed to reproduce single point interaction energies and not true binding energies. The problem with that methodology arises when the structure of the systems is not known and the optimization of the geometry is required: methods that could not reproduce all BD conformations may produce inaccurate geometries. The RF method and the M05-2X functional perform consistently better using binding energies, but only the RF method provides satisfactory performance with growing basis sets and can reproduce all BD conformations⁵.

The standard procedure in theoretical studies is to perform geometry optimization with a less accurate method as a first step, usually it is the same functional with a smaller basis set. A careful study of Figure 4.5 suggests that a good strategy for obtaining accurate binding energies

⁵Some of the ΔBE in M05-2X correspond to wrong geometry, so overall $RMS(\Delta BE)$ is not reliable.

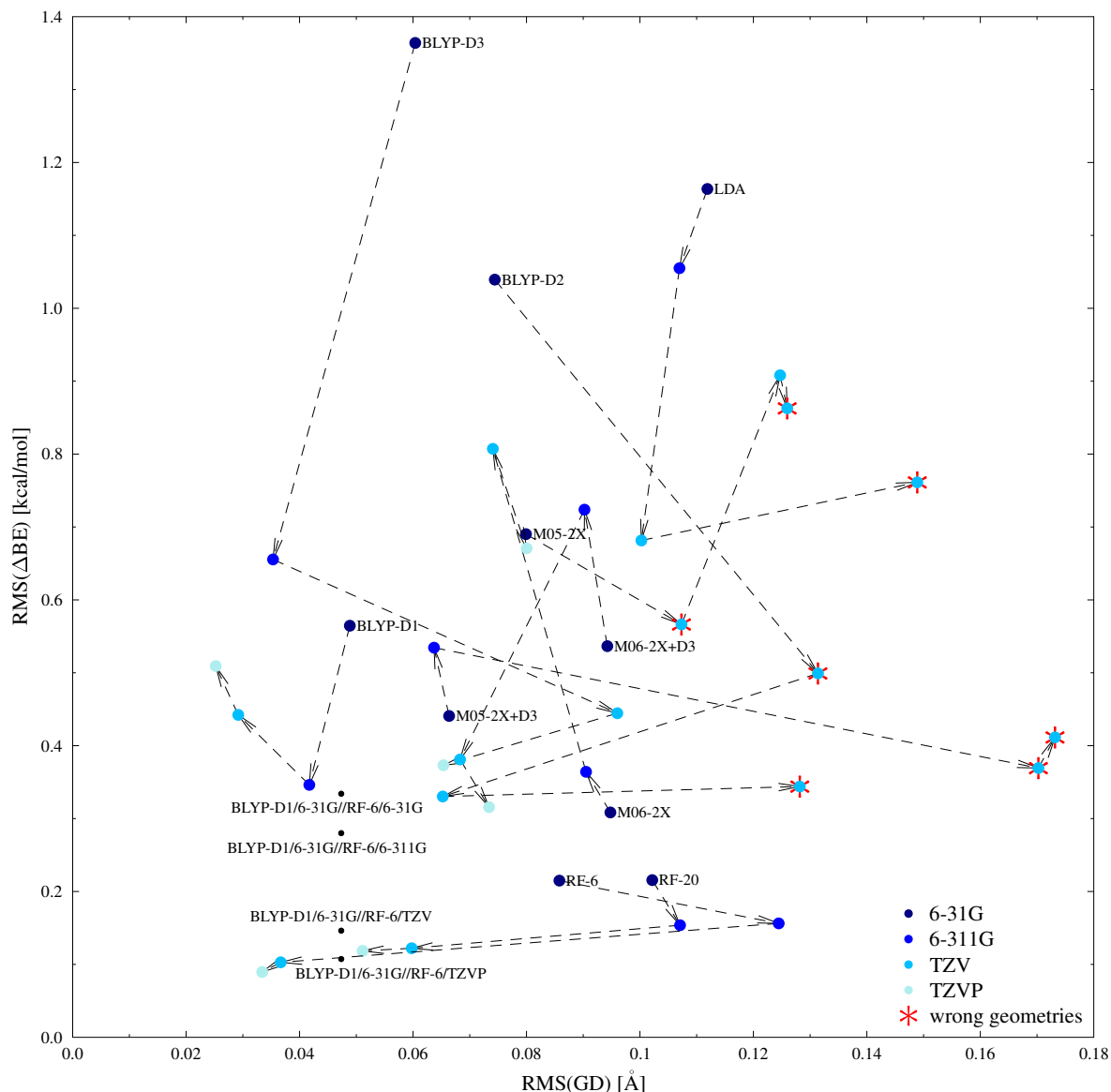


FIGURE 4.5: Binding energies and geometrical errors for the benzene dimer with different methods, XY plot. The RF methods provide very good results and ensure proper behavior with growing basis sets. The SP energy calculations using geometries obtained from the BLYP-D1/6-31G method are also shown as small black dots.

and geometries is to optimize the geometry of the system using BLYP-D1 with the 6-31G basis set and to get interaction energies from the RF method with a TZV or a TZVP basis set. The black points in Figure 4.5 represent results obtained using the RF-6 method on BLYP-D1/6-31G geometries. When one uses BLYP-D1/6-31G geometries for the SP calculation of the interaction energy with the RF-6/TZVP method, results are satisfactory: $RMS(\Delta BE) = 0.11$ kcal/mol with RMS for geometrical differences of 0.047 Å, at a fraction of the computational time for a TZVP geometry optimization (speedup of 5.6). For comparison, the results after geometry optimization at the RF-6/TZVP level are similar: $RMS(\Delta BE) = 0.09$ kcal/mol and $RMSD = 0.033$ Å. The approach works well when large TZV or TZVP basis set are to be used to obtain the final energies, otherwise full geometry optimization is preferable.

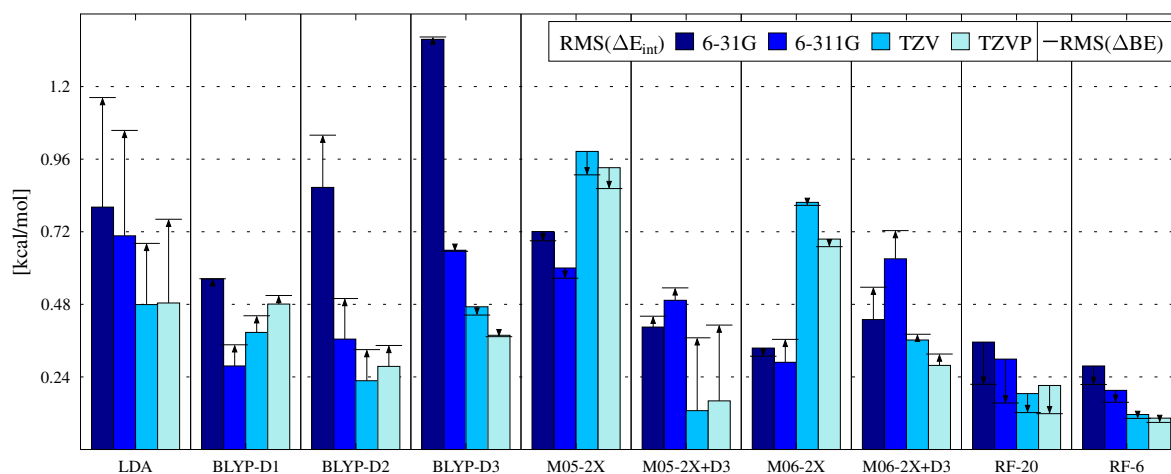


FIGURE 4.6: RMS differences between the calculated interaction and binding energies and the reference values. The arrows point from the interaction energies (colored bars) to the binding energies for various methods. For binding energies, the new RF method gives better results than any other method, and especially small basis sets appear to be acceptable.

4.3 Potential Energy Curves

The accurate representation of the geometry of the minima does not guarantee a good description of van der Waals interaction, especially when the geometry of the system is optimized. During geometry optimization some steps may lead to conformations far from the geometry of the minima. The state of affairs is even worse when the geometry of the system is not known, as is the case with some graphitic materials. The appropriate method should describe the whole potential energy surface (PES) as accurately as possible.

At small intermolecular distances, where the molecules repel each other, the DFT functionals can properly describe the system. At medium-range distances, near the optimal geometry, DFT has problems with the vdW complexes due to the inaccurate description of the electron correlation effects. However, most of the functionals investigated here behave properly in that range – they were especially tailored for such systems. When the distance is large the electron density is low in the region between the monomers, but some van der Waals interactions are still present. The pure DFT description of the system fails to account for that. With growing intermolecular distance the interaction energy goes asymptotically to zero, so the dimer energy is equal to the sum of the energies of the free monomers.

The potential energy scan can show the behavior of the given method at all of the mentioned intermolecular distances. The important part of the PES scan is between the minima and the long-range tail, because at those distances the pure DFT approach is lacking. This region is crucial for the description of the vdW bonded systems and shows

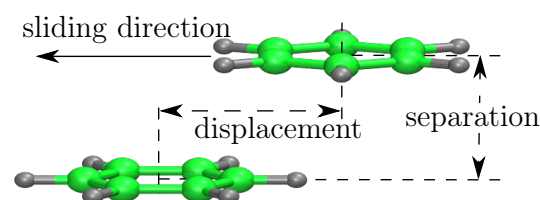


FIGURE 4.10: The attributes of the PD_b conformation. The sliding motion changes the displacement, while the separation is conserved.

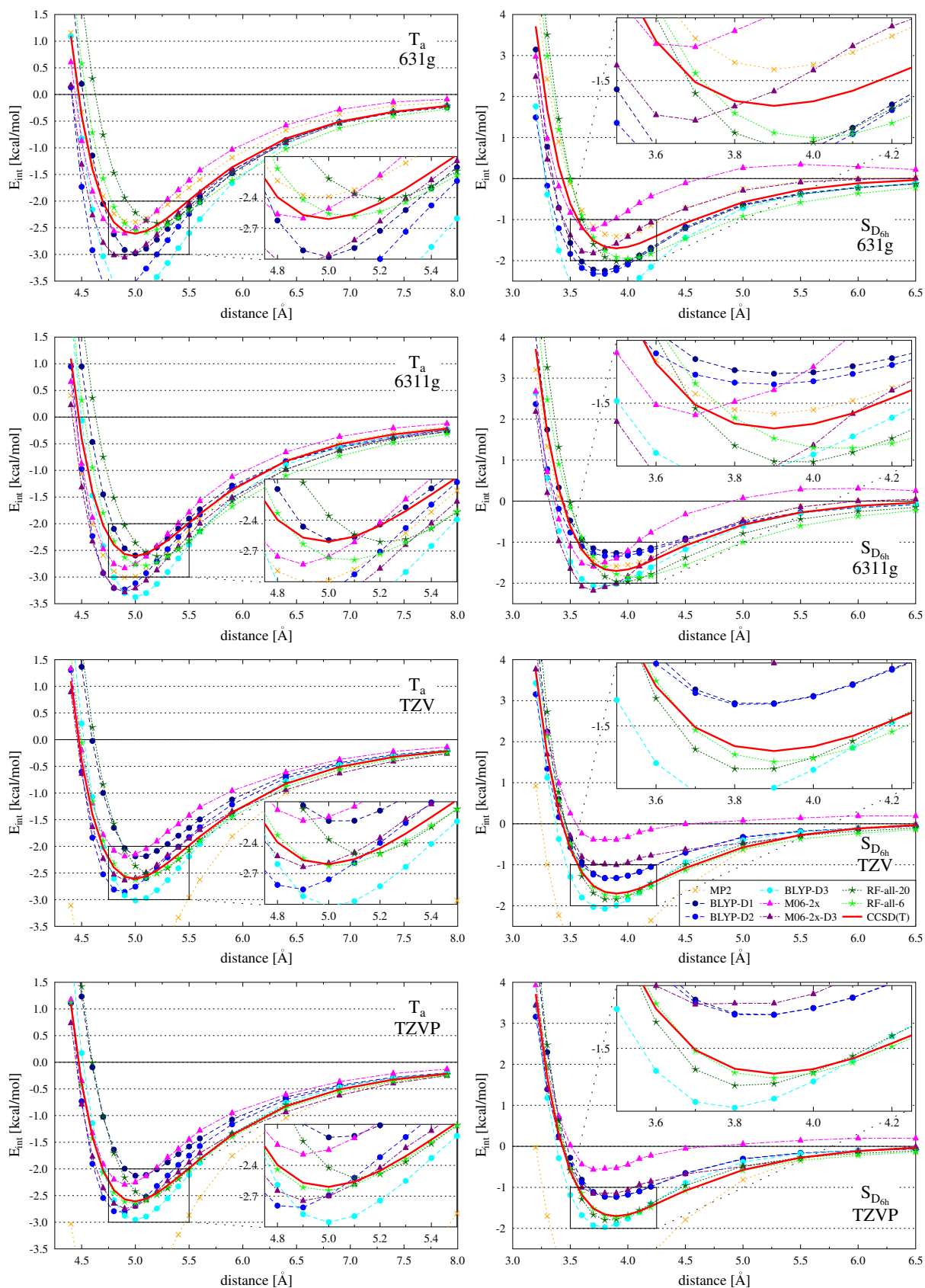


FIGURE 4.7: Potential energy curves for different functionals. The T_a (left) and $S_{D_{6h}}$ (right) benzene dimer conformations with various basis sets. Only the RF method behaves well with different basis set.

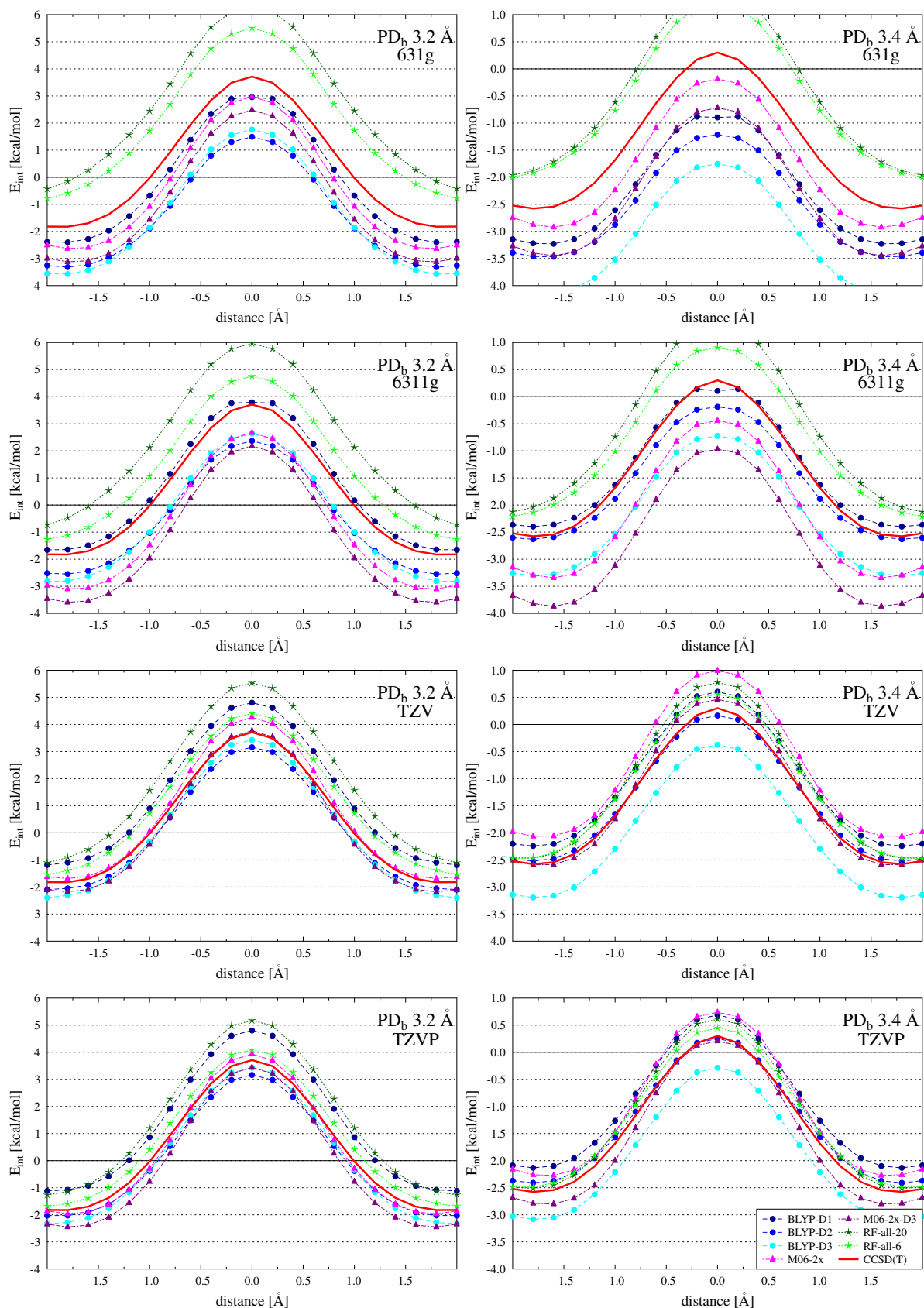


FIGURE 4.8: Potential energy curves for different functionals. Various displacements of monomers in PD_b conformations at 3.2 and 3.4 Å separation.

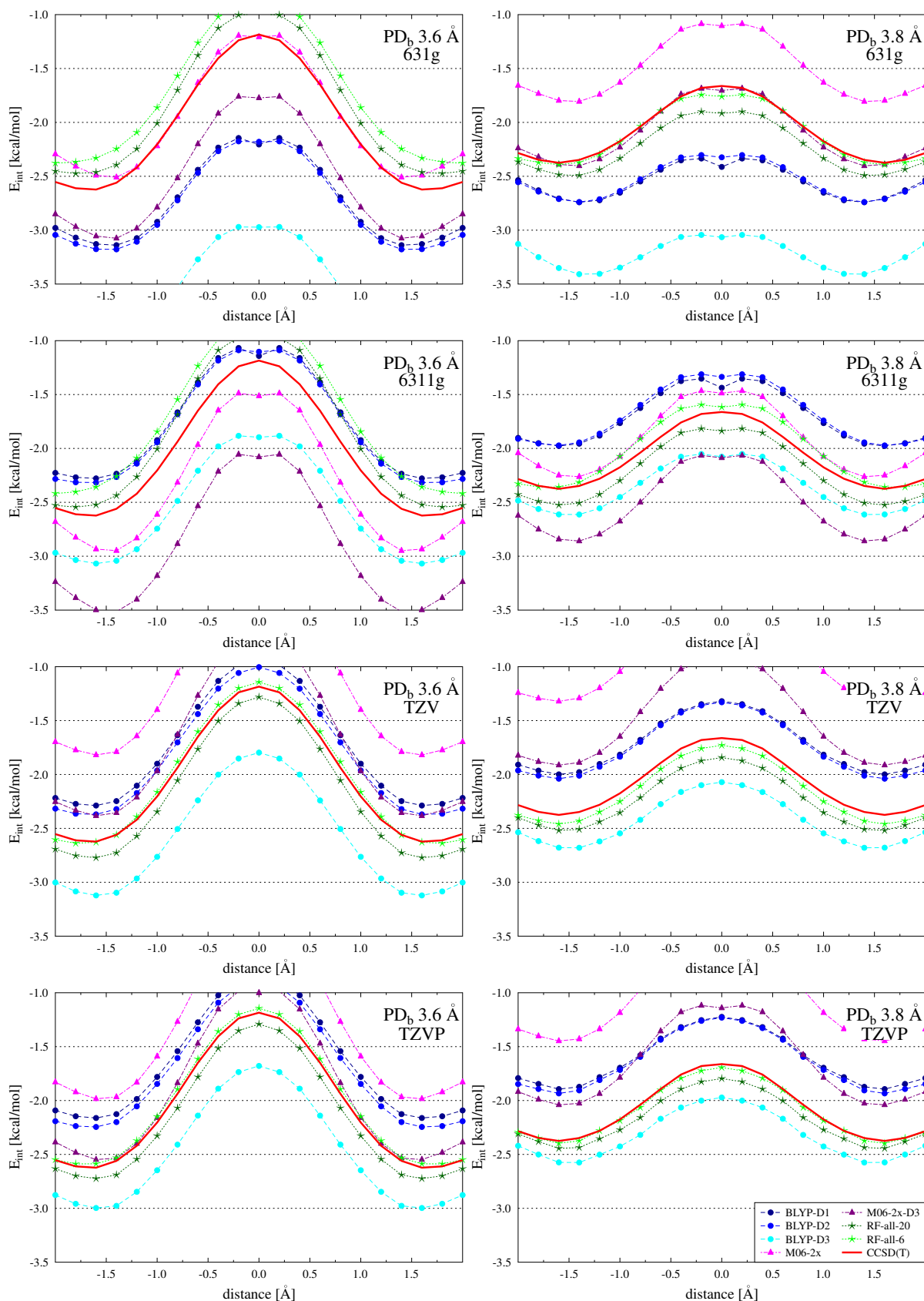


FIGURE 4.9: Potential energy curves for different functionals. Various displacements of monomers in PD_b conformations at 3.6 and 3.8 Å separation.

how the additional dispersion connects non interacting monomers, at large distances, with systems at short distances, that are well described by the DFT. The wrong description of this region of the PES could result in a shifted position of the minima and wrong interaction energies.

Figure 4.7 shows the evolution of the interaction energy with growing intermolecular distance for two conformations, $S_{D_{6h}}$ and T_a , with various basis sets. Figures 4.8 and 4.9 show the evolution of the E_{int} for the PD_b conformation "sliding" motion (see Figure 4.10). It corresponds to fixed separation between the benzene planes (at 3.2, 3.4, 3.6 and 3.8 Å) as the displacement between the monomers changes⁶.

The reference data for potential energy surface were taken after Sinnokrot and Sherrill [18] and correspond to CCSD(T)/aug-cc-pVQZ* level of theory.

As expected, the interaction energy for the M06-2X functional quickly declines as the intermolecular distance grows (see Figure 4.7). This shows how a simple reparameterization of the hybrid functional is insufficient to fully describe van der Waals interactions – commonly used DFT methods will always fail for large distances, where electron density is low. The MP2 method with higher basis set is overbinding. This is not surprising, as it is known that MP2 is not suited to such systems[19–24].

The general features of the PES are reproduced in all cases, but some important differences must be stressed. The position of the minimum, in Figure 4.7, depends markedly on the functional used, but is less sensitive to the basis set. The same cannot be said about the energy of this equilibrium point, which show important variations. The RF-all methods are the exception, as the position of the minimum is still almost unchanged, but the variations of the E_{int} are also small. Furthermore, the use of larger basis sets with the RF-all-6 and RF-all-20 methods improves the reproduction of the rigorous CCSD(T) curve.

As mentioned before, the method with small steepness of $\alpha = 6$ may be preferred. This assessment is confirmed by the fact that the minimum position of the T_a conformation is more accurate with the RF-all-6 than with the RF-all-20 method.

It is important to mention that these PES curves were not used as reference data during optimization. The fact that RF-all-6 method could reproduce so accurately PES curves vouches for its reliability.

4.4 The Transferability of the Obtained Parameters

It is important to check if the designed method is applicable to systems outside the fitting reference set. Part of it was done by presenting the results for graphite and various points on benzene dimer potential energy surface.

Another significant test is to try the new method for systems outside from the reference. It is possible that the new method could be applicable outside the scope of the target systems.

⁶Hence, with the displacement of 0 Å the system is a sandwich $S_{D_{6d}}$ conformation with given separation between monomers.

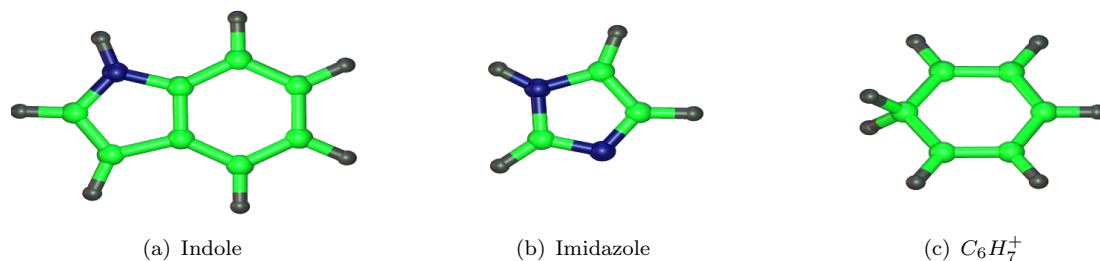


FIGURE 4.11: Various complexes with these molecules and benzene were used to test the transferability of obtained DFT-D parameters.

TABLE 4.2: Comparison of RF-6 and BLYP-D2 methods in the case of protonated benzene dimer. Differences between the reference CCSD(T) value and the BE are presented. All values are in kcal/mol. The RF-6-approach is more accurate, especially for the small 6-31G basis set.

BLYP-D2						RF-6					
system	631g	6311g	TZV	TZVP	REF	system	6-31G	6-311G	TZV	TZVP	REF
PD_a	4.96	3.40	2.69	2.77	-11.60	PD_a	1.64	1.53	1.86	0.55	-11.60
T_a	6.56	4.94	4.32	4.25	-10.90	T_a	3.74	3.24	3.42	3.59	-10.90
VC_S	3.49	2.04	1.27	1.51	-10.80	VC_S	0.48	0.20	0.17	0.44	-10.80
$RMS(\Delta BE)$						$RMS(\Delta BE)$					
	5.16	3.66	3.03	3.06	—		2.37	2.07	2.25	2.11	—

Several systems were tested, including protonated benzene dimer, complexes of benzene with indole and benzene with imidazole (see Figure 4.11). The conformation of these complexes are shown in Appendix B.

The protonated benzene dimer was studied using CCSD(T) method by Jaeger et al. [25]. The complexes with with indole and imidazole were investigated by Karthikeyan and Nagase [26] using CCSD(T) method.

Tables 4.2 and 4.3 present the results. The difference between the reference CCSD(T) interaction energy and binding energy obtained from RF-6 method is shown. For the protonated benzene dimer the calculations with BLYP-D2 method were also performed. For that reason, comparison of two methods is possible for systems different from the relaxed fitting references. Table 4.2 shows that the RF-6 method is more accurate than BLYP-D2 method, especially for the smaller basis set. Table 4.3 presents complexes of benzene with indole or imidazole. For one structure (BzImidaD-D) the E_{int} is not given in the literature, so the binding energy is presented. Similarly to the protonated benzene dimer case the BLYP-D2 method was significant less accurate⁷. For the BzIndoD-A complex geometry optimization did not succeed⁸.

Presented here systems differ significantly from the benzene dimer, but the der Waals interactions are important for their structure. Considering that, the errors indicated in Tables 4.2 and 4.3 are surprising small. Especially, taking into account performance of unmodified BLYP-D2 method.

⁷The $RMS(\Delta BE)$ obtained using BLYP-D2 and the 6-31G basis set was 2.79 kcal/mol for the Indol complexes and 2.24 kcal/mol for the Imidazole complexes. The analogue RF-6 values are 1.41 and 0.62 kcal/mol.

⁸The conformation changed and the maximum number of iteration was reached.

4.5 Conclusions

The RF method was developed to work with graphitic systems. The set of known stationary points of benzene dimer, a simple analogue, was used as a training set to develop it.

In order to assess the usability of the newly develop RF set of parameters for the DFT-D method several tests were performed. The new method was used for the graphite crystal. The RF method can successfully reproduce its interlayer distance, a feature that depends on the vdW interactions and is known from experiment. Graphite was also used to evaluate the parameter space available for the relaxed fitting scheme. The results show that the relaxed fitting procedure can find adequate parameters.

The RF method was compared with similar quantum mechanical methods. Several of the QM methods were tested, but only BLYP-D1, BLYP-D3, M06-2X, M06-2X-D3, and newly developed RF-20

and RF-6 methods could reproduce all of mentioned stationary points (see Figure 4.4). Among those the RF methods produce best results and behaved as expected with growing basis set size (see Figure 4.5).

A subsequent validation test was replication of the known features of the potential energy surface of the benzene dimer. Most of the QM investigated methods behaved well, but arguably the RF methods was the most accurate. In the case of benzene dimer, the RF approach can accurately reproduce all of known CCSD(T) results with reasonable accuracy.

To test the transferability of obtained DFT-D parameters few systems were investigated. These complexes differ from the benzene dimer, and they were not an example of the target systems for the RF method. Nevertheless, the RF method could reproduce the reference energies with reasonable accuracy.

TABLE 4.3: Results from the RF-6 method with various basis sets. Differences between the reference CCSD(T) value and the BE are presented. The RF method tends to produce to bonded systems. All values are in kcal/mol. The values in **bold** indicate some problem.

system	benzene with indole				REF
	6-31G	6-311G	TZV	TZVP	
BzIndoD-A	0.84	1.09	-7.45	1.28	-3.49
BzIndoD-B	0.44	0.44	0.40	0.36	-2.74
BzIndoD-C	0.18	0.20	0.00	0.11	-5.80
BzIndoD-D	0.34	0.35	0.34	0.33	-2.34
BzIndoD-E	0.39	0.44	0.33	0.33	-2.75
BzIndoD-F	1.07	1.30	2.02	2.12	-3.26
<i>RMS(ΔBE)</i>	0.63	0.76	3.16	1.04	—

system	benzene with imidazole				REF
	6-31G	6-311G	TZV	TZVP	
BzImidaD-B	1.27	1.22	0.68	0.36	-2.98
BzImidaD-C	0.90	0.31	0.36	0.22	-2.23
BzImidaD-D	-5.68	-5.65	-5.50	-5.48	—
BzImidaD-E	0.32	0.28	0.27	0.19	-5.37
BzImidaD-F	0.38	0.35	0.20	0.17	-5.30
BzImidaD-G	2.70	2.69	0.22	0.10	-2.90
<i>RMS(ΔBE)</i>	1.41	1.34	0.39	0.25	—

Chapter 5

Semiempirical Methods and Molecular Mechanics

The aim of the RF methods are graphitic materials, which are very large structures. An ideal method should be applicable to wide range of graphitic structures, it should produce reliable geometries and corresponding to them energies, additionally its computational cost should be small. In practice, computational cost of most methods rises with higher accuracy. In this section, I will investigate the accuracy of methods with a computational costs smaller than that of QM methods, namely semiempirical methods and molecular mechanics. The RF-6 with small 6-31G basis will be included in comparison. To the best of my knowledge, it is the fastest basis set for DFT-D calculations of such systems – it enables full geometry optimization of systems with hundreds of atoms.

The benzene dimer and C_{60} -benzene complexes will be presented. It was already noticed that the benzene dimer is an molecular analogue of larger graphitic systems. The complex of the Buckyball with the benzene is an bigger example of graphitic systems. It is bounded by van der Waals interactions. However, it is too large to evaluate their strength using coupled cluster approach, the „gold standard” of QM methods. Only methods with substantially lower computational cost are feasible, for example DFT approach, semiempirical methods and molecular mechanics. For that reason, the C_{60} -benzene complex will be a good system for comparison of these methods.

5.1 Benzene Dimer

5.1.1 Reproduction of the Minima

Benzene dimer, as most vdW complexes, is a weakly bonded system, and it is not limited by some steric effects. For that reason, BD is a flexible system – most of its stationary points are available with small energy difference. It is possible, that a given method cannot easily reproduce all

stationary points. Whenever that happens the appropriate values in related Tables 5.1 and 5.2 are in bold.

Table 5.1 presents the *RMSD* obtained after geometry optimization of known benzene dimer structures using various methods, corresponding binding energies are shown in Table 5.2.

TABLE 5.1: The root mean square deviations of optimized geometries (*RMSD* in Å). The root mean square of the values ($RMS(RMSD)$) is presented as overall performance of the method.

In the case of switched conformation, new conformation is indicated in **bold**.

conf.	CHARMM	OPLS	RF- OPLS	AMOEBA	MM3	RF- MM3	PM6-DH2	PM7	RF-6/ 6-31G
PD_a	0.40	0.41	0.07	0.05	0.01	0.05	0.16	S_{D_{6h}}	0.12
TT_b	0.12	0.09	0.05	0.19	0.15	0.07	0.23	0.15	0.11
TT_a	0.11	0.09	0.05	0.22	0.16	0.07	T_b	0.13	0.11
PD_b	V_{C_s}	V_{C_s}	0.07	0.06	0.01	0.05	0.19	S_{D_{6d}}	0.12
T_a	0.07	0.05	0.03	0.07	0.09	0.05	0.07	0.07	0.04
V_{C_s}	0.29	0.15	0.05	PD_b	PD_b	0.01	PD_b	S_{D_{6d}}	0.08
T_b	0.03	0.02	0.05	0.01	0.04	0.08	0.11	0.12	0.07
$X_{D_{2d}}$	0.06	0.05	0.02	0.12	0.19	0.04	0.02	0.02	0.02
$S_{D_{6d}}$	0.06	0.06	0.06	0.15	0.13	0.06	0.19	0.06	0.07
$S_{D_{6h}}$	0.06	0.06	0.06	0.14	0.12	0.06	0.19	0.06	0.07
$RMS(RMSD)$	0.29	0.29	0.05	0.28	0.24	0.06	0.31	0.37	0.09

TABLE 5.2: The binding energy errors produced by various methods. The reference CCSD(T) binding energies are included. The root mean square ($RMS(\Delta BE)$) indicate the overall accuracy. Values in **bold** inform that the conformations switched during geometry optimization.

All values are in kcal/mol.

conf.	CHARMM	OPLS	RF- OPLS	AMOEBA	MM3	RF- MM3	PM6-DH2	PM7	RF-6/ 6-31G	<i>BE</i> CCSD(T)
PD_a	-0.53	-0.62	-0.22	0.06	-0.22	-0.43	0.88	2.09	-0.33	-2.73
TT_b	-0.54	-0.51	-0.17	-0.21	-0.86	-0.46	0.02	0.53	-0.01	-2.82
TT_a	-0.54	-0.51	-0.16	-0.19	-0.85	-0.44	0.03	0.54	0.02	-2.80
PD_b	-0.43	-0.46	-0.22	0.04	-0.22	-0.42	0.88	2.11	-0.30	-2.72
T_a	-0.60	-0.55	-0.14	-0.55	-0.92	-0.41	-0.09	0.62	-0.08	-2.70
V_{C_s}	-0.45	-0.48	-0.15	0.02	-0.24	-0.43	0.86	2.09	-0.03	-2.74
T_b	-0.19	-0.16	0.20	0.19	-0.45	-0.04	0.44	0.93	0.36	-2.40
$X_{D_{2d}}$	-0.39	-0.38	-0.30	-0.73	-0.78	-0.38	-0.32	-0.04	0.29	-1.79
$S_{D_{6d}}$	0.09	-0.01	0.63	0.37	0.66	0.48	1.77	3.12	0.14	-1.71
$S_{D_{6h}}$	0.08	-0.02	0.62	0.33	0.64	0.48	1.75	3.11	0.15	-1.71
RMS (ΔBE)	0.43	0.43	0.33	0.35	0.64	0.42	0.94	1.86	0.22	

Semiempirical Methods. Most of the semiempirical methods follow Hartree-Fock formalism, but instead of solving it from first principles these methods uses many approximations to speed up the process. These approximations are based on empirical data and aim to reproduce most expensive part of HF formalism.

The MOPAC 2012 program[1–3] was used for the semiempirical methods. Among those, AM1[4], RM1[5], MNDO[6], PM6, PM6-DH2[7], PM6-DH+[8] and PM7 methods were tested. The PM6 and PM7 families of methods are the most recent and the most accurate approaches among them. The dispersion is crucial for benzene dimer. For that reason, methods without it behaved badly. Only three methods included the dispersion, namely PM6-DH2, PM6-DH+

and PM7. Henceforth they will be called SE-D methods. For the benzene dimer, the PM6-DH2 and PM6-DH+ methods are equivalent, because of that only the PM6-DH2 and PM7 will be presented. Tables with all tested semiempirical method are available in the Appendix C.

The SE-D methods have problems with reproduction of some conformations. The PM7 method clearly favours the sandwich type conformations, it was the only method presented that cannot reproduce the two known minima conformation. Both of the semiempirical methods produce rather large errors and tend to produce overbinding energies. In the case of sandwich conformation, the errors are around 100% and 180% for PM6-DH2 and PM7 respectively.

Molecular Mechanics. Molecular mechanics uses simple approximations to obtain the results from the simplest assumptions, usually depending only on the structural information. Different approximations, the so called force fields (FF), use different approaches to estimate how the molecule's energy depends on its geometry. These force fields, are usually the constructs of empirically parameterized functions of some geometrical property (as bond length or angles). For that reason, they are exceptionally fast – the overall energy is just the sum of the values of these functions.

It is important to note that, in various situations, some of the approximations used may cause problems. For example, electrostatic interactions could be accounted for in various approaches, like partially charged atoms, or treating bonds as dipoles. When a given force field uses explicit charges placed on atoms it cannot be used for extended structures built from similar atoms – as electrostatic repulsion will deform the structure. This is the case with most of the larger graphitic systems – these structures contain many of the carbon atoms that are of the same type. The only solution, in case of such system, is to explicitly set carbon and hydrogen charges to 0. Usage of the multipole expansion to account for electrostatic interactions presents another problem: it can cause trouble if the periodic conditions are utilized.

The Tinker[9–12] molecular modeling package was used for all MM calculations. The force fields with explicit benzene or aromatic carbon parameters from TINKER were explored. The TINKER package has many subroutines designed to perform geometrical optimization: *optimize*, *minimize* and *newton*. Additionally, it is possible to optimize the structure without monomer relaxation using the *optrigid* subroutine. All of them were investigated, and it was found that the *optimize* and the *minimize* gives comparable results, the *newton* subroutine cause conformation switching more often.

The MM2[13], MM3[14], AMOEBA09[15–17], CHARMM22[18–20], OPLS All-Atom[21] and MMFF[22] force fields were tested. Additionally, polarizable molecular model for benzene by Dang[23, 24] was included.

Among MM methods tested the MM3, AMOEBA09, CHARMM22 and OPLS force fields gave reasonable results and will be presented¹. Tables with all molecular mechanics approaches are available in the Appendix C. Force fields presented here can reproduce almost all of the

¹Henceforth they will be named MM3, AMOEBA, CHARMM and OPLS

TABLE 5.3: Parameters of the reoptimized force fields: atom type (i), the atom size (r_i^0 in Å), homoatomic well depth ε_{ii} [kcal/mol] and optional offset (R_{off}).

original					RF				
MM3									
at	<i>i</i>	r_i^0	ε_{ii}	R_{off}	at	<i>i</i>	r_i^0	ε_{ii}	R_{off}
C	2	1.9600	0.0560		C	2	2.0138	0.0659	
H	5	1.6200	0.0200	0.923	H	5	1.1958	0.0242	0.8461
OPLS									
at	<i>i</i>	r_i^0	ε_{ii}		at	<i>i</i>	r_i^0	ε_{ii}	
C	87	3.5500	0.0700		C	87	3.5124	0.1085	
H	88	2.4200	0.0300		H	88	2.3213	0.0086	

BD conformations, including both minima. The MM3 force field gives the best geometries. For some conformations, it produces geometries better than that of the RF-6/6-31G method.

5.1.2 Relaxed Fitted Force Fields

Additionally, for two force fields (MM3 and OPLS) van der Waals parameters were reoptimized using relaxed fitting scheme. These, modified force fields, will be called RF-MM3 and RF-OPLS respectively.

In the MM3 force field the vdW interactions are modeled by Buckingham potential:

$$E_{vdw} = \epsilon_{ij} \left(184000 \exp \left(-12.0 \frac{R_{ij}}{r_{ij}^0} \right) - 2.25 \left(\frac{r_{ij}^0}{R_{ij}} \right)^6 \right). \quad (5.1)$$

The OPLS uses Lennard-Jones potential:

$$E_{vdw} = \epsilon_{ij} \left(\left(\frac{r_{ij}^0}{R_{ij}} \right)^{12} - 2 \left(\frac{r_{ij}^0}{R_{ij}} \right)^6 \right). \quad (5.2)$$

The R_{ij} is current distance between atom pair ij , and r_{ij}^0 is the reference value from the input, the ε_{ij} is the depth of the potential well. The TINKER uses three vdW parameters: r_i^0 , ε_{ii} and R_{off} . The R_{off} is an optional parameter indicating the offsetting the center of the vdW interaction. The MM3 mixing used was arithmetic for radius and geometric for the ε_{ij} , the OPLS uses geometric mixing for the radii and the ε_{ij} .

The force fields were found to produce more variable geometries. For that reason, the scoring function for the relaxed fitting was $RMS(RMSD) \cdot RMS(\Delta BE)$. The parameter of the reoptimized force-fields are presented in Table 5.3. The values for MM3 and OPLS are different because of the different mixing used in those force fields.

From Tables 5.1 and 5.2 follows that the relaxed fitted force fields are clear improvement over their predecessors. Both methods can reproduce all conformations with similar accuracy, obtained geometries are slightly more accurate than that of RF-6/6-31G method. Conversely,

the binding energies of RF-MM3 and RF-OPLS methods are slightly less accurate than RF-6/6-31G method.

From Tables 5.1 and 5.2, it follows that most minima and stationary points of benzene dimer are achievable by the investigated molecular mechanical and semiempirical methods. The MM3 and AMOEBA force fields have problems only with V_{C_s} conformation. The BE produced by MM3 force field are distant from the reference ones, but the AMOEBA force field can reproduce relatively small errors in BE. One may surmise that those methods could be applied for the benzene dimer, and are likely to work on bigger graphitic systems.

5.1.3 Potential Energy Curves

The results for the dissociation of the T-shaped and the sandwich conformation, and sliding of the top benzene in the Parallel Displaced (PD) conformation are shown on Figure 5.1.

In general, all methods can reproduce well the general shape of the PES for T_a and $S_{D_{6h}}$ conformations. That is not surprising, as these curves correspond to a simple dissociation of the dimer, any method that includes approximate vdW interactions will generate a similar curve. The position of the minima on those curves determines the equilibrium distance between the monomers. For the $S_{D_{6h}}$ conformation the SE-D methods are overbinding.

Figure 4.10 shows the generalization of the sliding motion of parallel displaced conformation. In the stationary points, the separation is about 3.5 Å for the PD_b conformation (with the displacement of 1.70 Å), for the $S_{D_{6d}}$ conformation it is about 3.9 Å.

The RF-6/6-31G is the only method that reproduce reference for this sliding motion accurately. All other investigated methods produce very large errors. The SE-D results for PD_b 3.8 Å are not shown there, as they were highly overbinding (see the Figure 5.2). Some methods, like MM3, produce rather small variation of the interaction energy under the sliding motion. For these methods, the sandwich and the parallel displaced structures are almost iso-energetic. For that reason, they can reproduce accurate binding energies for only one of those structures (compare Figure 5.1 with Table 5.2).

It is known that a Lennard-Jones type of potential is much too smooth to describe variations in the relative alignment of adjacent graphene layers[25]. Such, isotropic, treatment of van der Waals interactions cannot accurately reproduce π orbitals interaction, which is anisotropic. Furthermore, simple adjustment of the vdW parameters cannot correct this, as is indicated by the behaviour of the RF force fields. Kolmogorov and Crespi have shown that to correct this problem additional, anisotropic, term is needed[25].

The semiempirical methods performance is surprising. They are overbinding and show inadequate variations for the PD_b sliding motion.

Only the RF-6/6-31G method and relax fitted force fields (RF-MM3 and RF-OPLS) reproduced known stationary points of benzene dimer with reasonable accuracy. Unfortunately, RF force fields underestimated variation of the energy due to sliding motion in parallel displaced

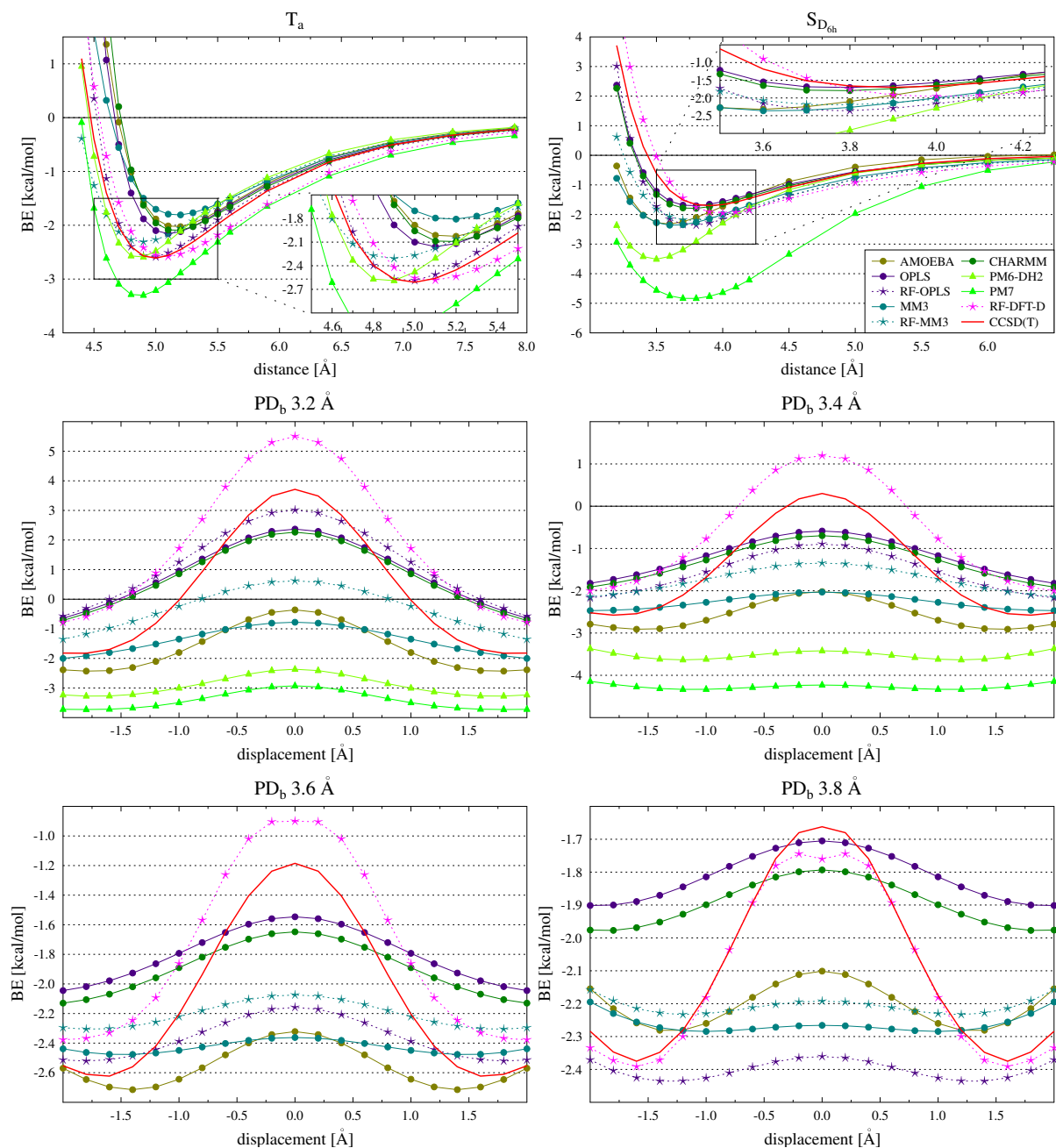


FIGURE 5.1: The binding energy (BE [kcal/mol]) of various benzene dimer scans. For the T_a and $S_{D_{6h}}$ conformations center of mass distance is used, for PD_b conformations it indicates the displacement of the benzenes. The RF method is clearly more accurate than any MM method. In case of PD_b conformations MM methods could not reproduce overall shape of the reference curves.

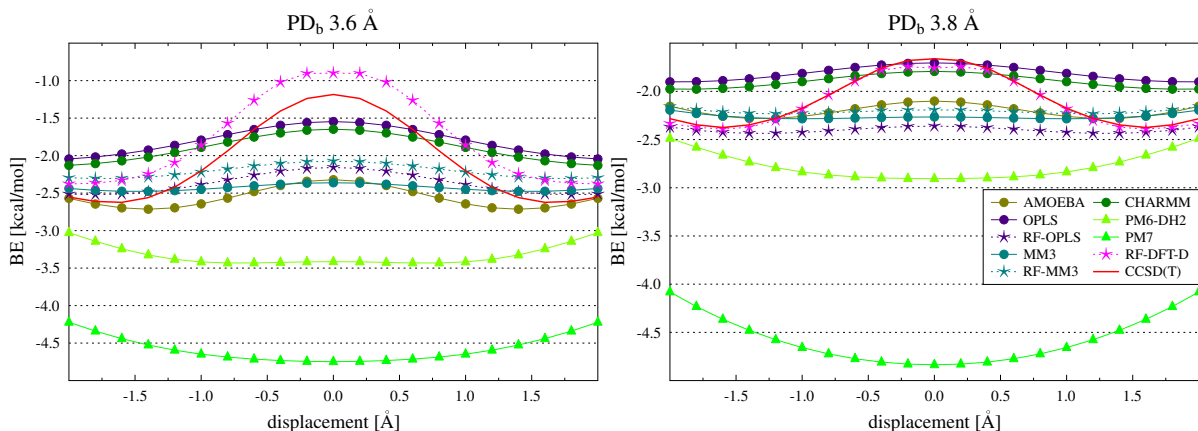


FIGURE 5.2: The SE-D methods are highly overbinding for some PD_b conformations sliding scans. Even the general shape of the curve is not reproduced.

conformation. It is not surprising, as that variation is caused by the anisotropic π orbitals interaction and, as such, cannot be reproduced by isotropic vdW interactions.

5.2 C_{60} -benzene complex PES

It is important to compare the behaviour of the RF-6/6-31G, the SE-D and the molecular mechanics methods for the larger system, closer to graphitic materials. The structure I have chosen is the C_{60} -benzene complex: it is relatively small and presents most of the features of a graphitic systems. The C_{60} fullerene with benzene was used as a simple example of vdW complexes of graphitic materials. The benzene could attach in different regions of the fullerene (atom, p or h bond, rings, etc.) producing different conformations. Apart from the location on the fullerene where benzene adheres two more general conformations could be considered: The benzene plane could be perpendicular or parallel to local Buckyball surface. I will call these respectively T and nT -shaped conformations. For the T conformation, the benzene CH bond could be placed perpendicular or parallel to nearby fullerene bonds (respectively, *per* and *par*). For the nT conformations a hydrogen or a CC bond from the benzene could be pointing toward the fullerene's CM (subscripts a for the hydrogen and b for the bond). For example the T - h -*par* conformation is when the benzene is located on top of fullerene's h bond (without rotation), the nT - $6r$ - a is conformation where hydrogen from the benzene is pointing towards the 6 membered ring of the fullerene (both conformations are presented in Figure D.1).

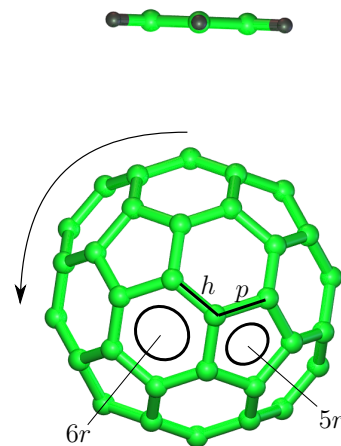


FIGURE 5.3: The initial point of the potential energy surface scan. The direction of the fullerene rotation is indicated. Additionally, naming convention of the fullerene structural features.

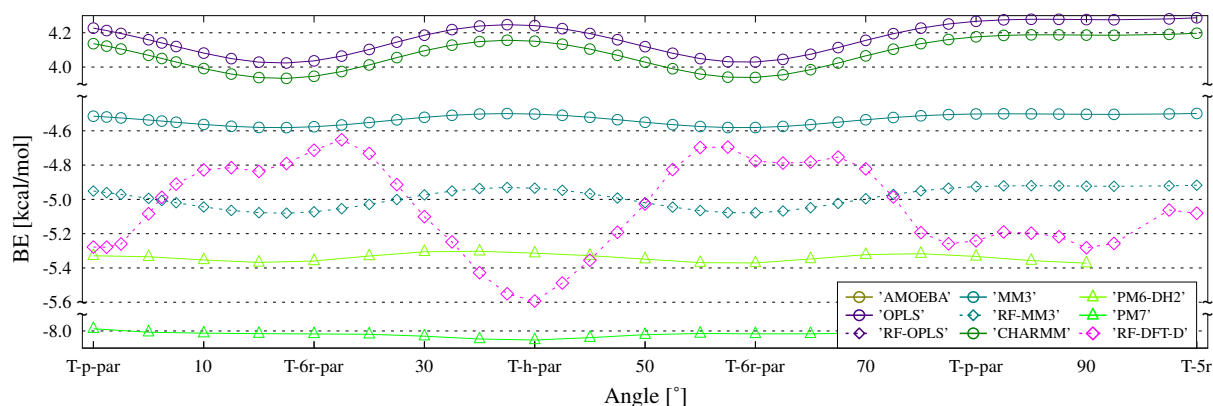


FIGURE 5.4: The binding energy (BE [kcal/mol]) of the C_{60} -benzene scan. The angle corresponds to rotation of the fullerene along C_2 axis, that the benzene faces both types of fullerene bonds and rings. The OPLS and CHARMM force fields produced interaction energies around +4 kcal/mol, for the RF-OPLS force field interaction energies are around +2.6 kcal/mol. The AMOEBA force fields is not shown because of convergence problems.

Appendix D contains detailed information of several complexes with C_{60} fullerene that are not presented here, including interesting $C_{60}@C_{240}$ complex.

For simplicity, only one potential energy surface scan will be presented: In the initial structure, the benzene is on top of fullerene's longer bond, then the fullerene is rotated perpendicular to that bond (see Figure 5.3): The detailed path is $T\text{-}p\text{-}par \rightarrow T\text{-}6r\text{-}par \rightarrow T\text{-}h\text{-}par \rightarrow T\text{-}6r\text{-}par \rightarrow T\text{-}p\text{-}par \rightarrow T\text{-}5r\text{-}par$.

The results are presented on Figure 5.4. The minimum of the RF-6/6-31G method corresponds to the conformations in which the benzene is on top of the fullerene's shorter bond. That conformation closely resembles the parallel displaced conformations in benzene dimer. The BD in that conformations shows BE that is about 1 kcal/mol lower than in sandwich type. Similar variation is presented on Figure 5.4.

Similar to the case of the benzene dimer, the SE-D methods show much smaller variation of interaction energy. The PM7 method produced low-lying interaction energies of about -8 kcal/mol, this behaviour is consistent with the fact that this method produced the lowest binding energies in the benzene dimer and interaction energies on its potential energy surface.

The AMOEBA force fields has problems with convergence of the induced dipoles. The variation of other force fields is smaller than that of the RF-6/6-31G. As in the case of the benzene dimer, the OPLS and CHARMM force fields produced similar results, but interaction energies generated by those methods indicate non bonded complex. Another scan, presented in Appendix D indicates that these methods prefer conformations in which the benzene is pointing toward the fullerene.

Only the RF-6/6-31G approach produced variation that was expected from studying simpler benzene dimer, additionally it pointed toward minimum with similar geometry. The RF-MM3 and PM6-DH2 methods produce interaction energies similar to that produced by the RF-6/6-31G method, but with much smaller variations. Both approaches could be used when only

interaction energies are important and detailed information on the structure of the PES are not necessary. The RF-MM3 force field behaved better than the PM6-DH2 method for the benzene dimer. Consequently, it is preferred, but only for studies in which sampling potential energy surface is not necessary.

5.3 Conclusions

In this chapter several semiempirical and molecular mechanics methods were applied to benzene dimer. Additionally, the C_{60} -benzene complex was investigated. It is an example of graphitic materials and due to its size it is usually studied by semiempirical and MM methods.

In the case of the benzene dimer, very accurate, CCSD(T) calculations exist, so that an objective evaluation on the accuracy of the investigated methods was possible. In contrast, accurate reference data for the C_{60} - C_6H_6 complex is lacking. Only a qualitative comparison of the results was possible for the bigger systems.

Benzene Dimer. Compared to the quantum mechanical approaches, the semiempirical methods tested were less successful with BD conformations. None of them could reproduce all of the conformations and the calculated binding energies were unsatisfactory. Molecular mechanics could reproduce almost all known BD conformations, but the estimated BE errors were rather large. The MM force fields after the relax fitting procedure behaved much better – they can reproduce all known conformations with relatively small energetical errors. This is not surprising, as a set of BD structures was used to train the RF methods.

C_{60} -benzene complex. A much larger C_{60} fullerene complex with benzene was used as an example of structures closer to graphitic materials. There are no accurate estimates of energetics and the structure of this complex is not known. For that reason, only a qualitative comparison was possible. The RF-DFT-D method was compared to methods usually used for similar systems – semiempirical methods and various force fields.

The results obtained from semiempirical methods for the fullerene complex were highly inconsistent – for the same structure some methods predicted bonded system and another methods indicated that it is non bonded. Furthermore, for the *T-6r-par* conformation almost all methods resulted in local minimum on the PES curves, while simple comparison with benzene dimer imply that it should be a maximum. Only the RF method produced expected behaviour.

Overall, the RF-6/6-31G method was superior to the other approaches investigated. The relax fitted force fields being a less computationally demanding, but at the same time, less accurate alternative. It is important to note that in this chapter only RF methods with a small 6-31G basis set was used. Previous studies already demonstrated that with larger basis set the RF method is substantially more accurate.

Chapter 6

Energetic properties of the Helicenes

Polycyclic Aromatic Hydrocarbons (PAH's) are compounds that consist mostly of fused aromatic rings. They can be *ortho*-fused or *ortho*- and *peri*-fused. In the *ortho*-fused configuration two rings are connected in such a way that exactly two atoms are in common¹. The *ortho*- and *peri*-fused systems are defined as[1, 2]:

Polycyclic compounds in which one ring contains two, and only two, atoms in common with each of two or more rings of a contiguous series of rings. Such compounds have n common faces and less than $2n$ common atoms.

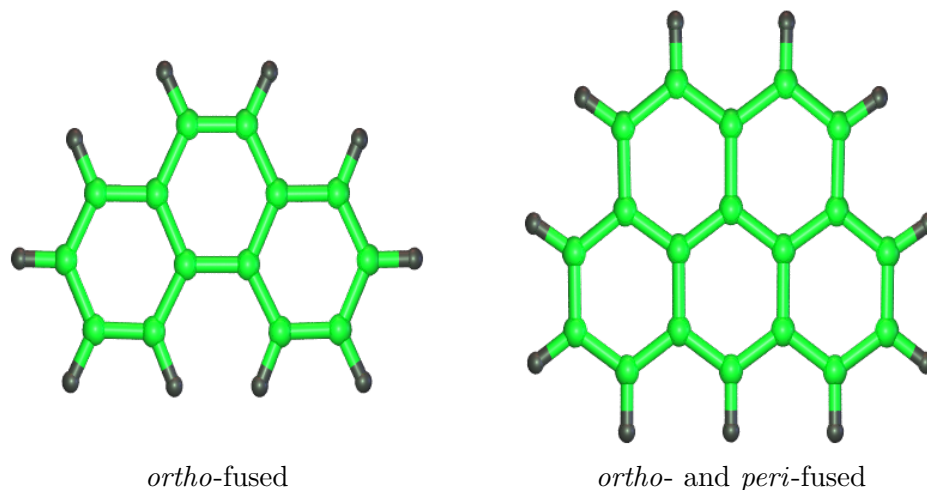


FIGURE 6.1: Different types of polycyclic aromatic hydrocarbons. The *ortho*-fused structures are string-like, while the *ortho*- and *peri*-fused moieties can create two dimensional slab of connected rings.

In simple terms the *ortho*-fused PAH's are continuous, string-like structures; the *ortho*- and *peri*-fused PAH's can create tiles of connected rings (see Figure 6.1).

¹They have always $2n$ common atoms for n common sides.

6.1 Structure of Polyacenes and Phenacenes

According to International Union of Pure and Applied Chemistry (IUPAC), polyacenes (or acenes) are defined as[2, 3]:

Polycyclic aromatic hydrocarbons consisting of fused benzene rings in a rectilinear arrangement.

In that configuration all rings are connected in such a way that they create a straight line (see Figure 6.2). The polyacenes can be named by indicating the number of the rings, *e.g.* the anthracene is the [3]acene and the pentacene is the [5]acene. The higher acenes are highly

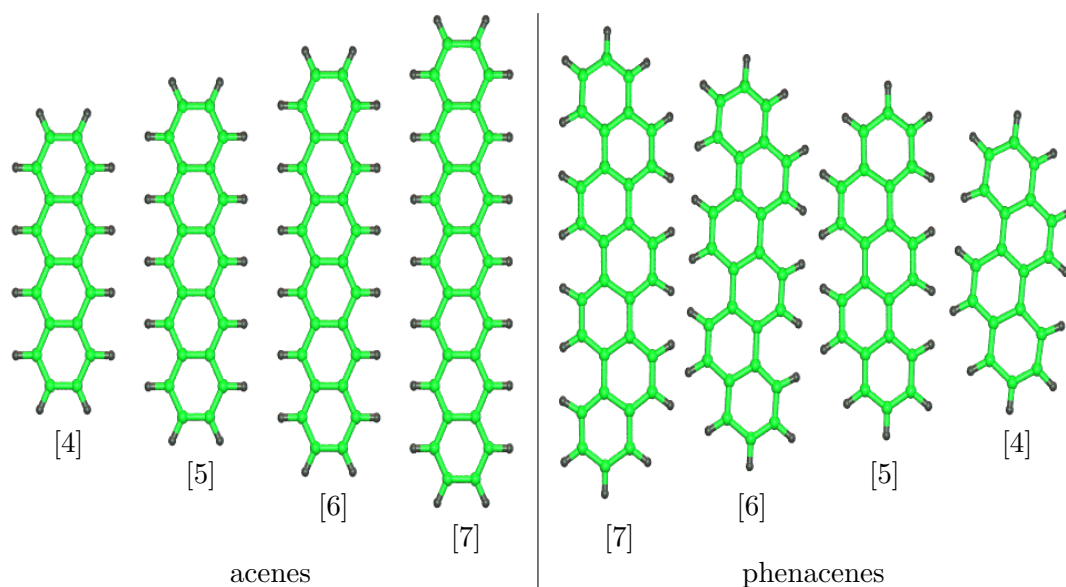


FIGURE 6.2: Examples of acenes (left) and phenacenes (right). The acenes are straight lines, while phenacenes structures resemble serpentine. The number indicate how many rings are in the structure.

unstable. The acenes with 5,6 or 7 rings have been reported to be unstable to air and light[4, after Portella et al. [5]]. Despite that, the [5]acene has been well characterized[6] and the [7]acene, [8]acene and [9]acene have been reported to be synthesized in literature[7, 8]. The instability of acenes is attributed to their multiradical character[9, 10].

The phenacenes are similar to polyacenes, but instead of straight line they are structured in anguine shape (see Figure 6.2). Unlike the acenes, the phenacenes are stable. Their derivatives have already been synthesized up to [11]phenacene, and the synthesis of [15]phenacene and [19]phenacene is undergoing[11–13].

6.2 Structure of Helicenes

Helicenes are polycyclic aromatic compounds. According to International Union of Pure and Applied Chemistry (IUPAC), helicenes are defined as[2, 14]:

ortho-Fused polycyclic aromatic or heteroaromatic compounds in which all rings (minimum five) are angularly arranged so as to give helically shaped molecules, which are thus chiral, e.g. hexahelicene.

According to the simplest naming convention they are named $[n]$ helicene, where n denotes the number of aromatic rings. The number could be exchanged with Greek prefix, hence pentahe-licene = $[5]$ helicene.

They are highly nonplanar, in a screw-like shape. This helical shape is the defining property of the helicenes. They can be composed of many fused rings, including 4-,5- and 6-membered rings. In this study only ones composed of fused six-membered, benzene like, rings will be examined. Figure 6.3 show structure of $[14]$ helicene, the C_2 symmetry axis is perpendicular to the helical axis. Figure 6.4 presents several helicenes. One of the most interesting features of the helicenes is that they are chiral even though they have no asymmetric carbon atoms and other chiral centers.

The left-handed helicenes are designated „minus” (– or **M**), the right-handed ones are „plus” (+ or **P**). Experimental measurements showed that **P**-helicenes are dextrorotatory, while **M**-helicenes are levorotatory[15, 16]. In the case of the helicenes composed from fusion of the benzene rings, to complete the first whole turn of 360° 6 rings are necessary. The whole turn would require more rings in the presence of five-membered rings, as the angle of neighbouring rings is larger in five-membered rings.

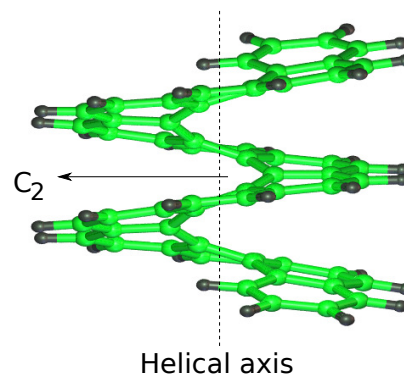


FIGURE 6.3: The structure of helicene, including helical and C_2 axes.

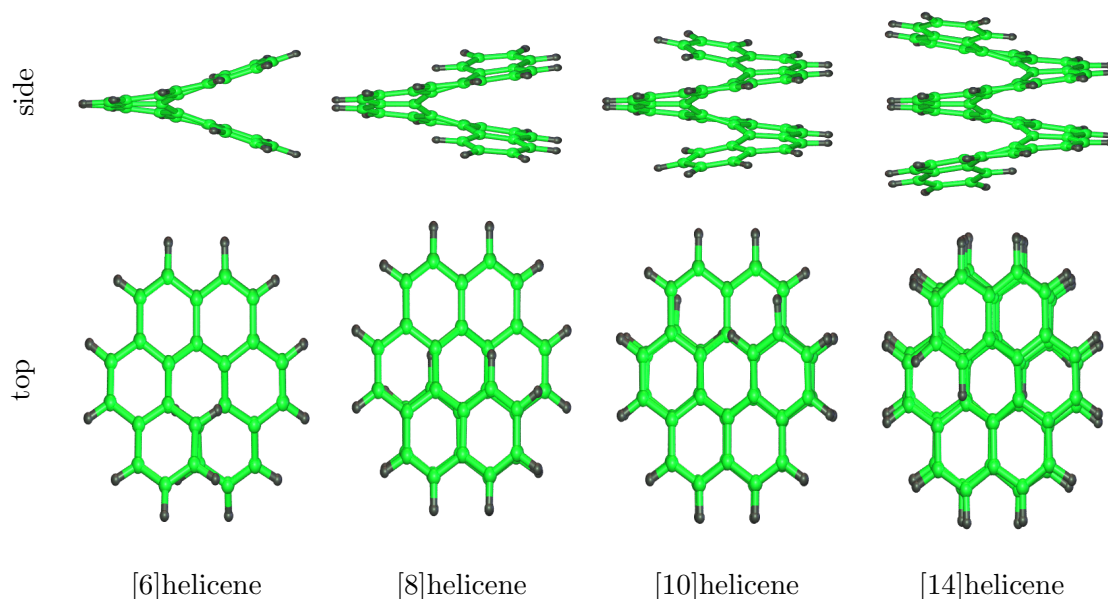


FIGURE 6.4: Examples of helicenes. Side and top views.

First helicenes were synthesized in 1903 by Meisenheimer and Witte [17]. Extensive review of helicenes chemistry were done, *e.g.* Shen and Chen [18] or Gingras [19]. The higher helicenes are stable. Helicenes at least up to [14]helicene were characterized and there are ways of relatively easy synthesis of higher ones[19, 20].

6.3 Reaction Energy

The following analysis will be concerned with the properties of the series with the growing number of rings. As mentioned above, the higher acenes are unstable due to their multiradical character. Using quantum mechanical methods, they require a methodology fundamentally different from that used otherwise. These calculations would demand more computational time. Additionally, to make the results comparable all structures would need to be computed that way. For these reasons, the acenes will be excluded from most of the following analysis.

The acenes, phenacenes and helicenes are aromatic[5, 21–23]. The theoretical investigation indicated that for the acene series the inner rings show more aromatic character, even though the outer rings are more reactive; in the case of phenacenes and helicenes the terminal rings are the most aromatic ones[5, 24]. As mentioned above, the higher acenes are very unstable. The phenacenes are the most stable among these series, that is among the $[n]$ acene, the $[n]$ phenacene and the $[n]$ helicene, the $[n]$ phenacene is the least reactive and has the lower energy[5, 21, 24]. The study of the literature indicates that the helicenes have lower HOMO-LUMO gap than phenacenes [25]. The same results was obtained in here, Figure 6.5 presents the HOMO-LUMO gaps obtained using RF method.

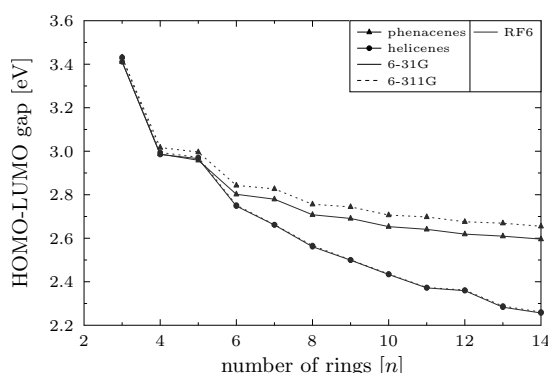


FIGURE 6.5: The HOMO-LUMO gap obtained from RF-6 calculations.

The $[n]$ acene, $[n]$ phenacene and $[n]$ helicene are isomers – even the number and the type of bonds are the same. Moreover, one may imagine a reaction that extends the $[n]$ th element of the given series into $[n + 1]$ th one: addition of naphthalene to $[n]$ th element would create element $[n + 1]$ th and the benzene (see Figure 6.6). Described reaction is homodesmotic[26–28], *i.e.* all of the formal bond and types of all atoms are conserved in the reactants and products. In order to assess the stability of growing series, one can define the reaction energy:

$$\Delta E_n = E_n + E_1 - E_{n-1} - E_2, \quad (6.1)$$

where E_n is the energy of the $[n]$ th item in the given series. The fact that the reaction is homodesmotic is helpful in theoretical calculations, as the errors associated with bond energies on both sides of the reaction will be greatly reduced, but it will not affect the trends in the

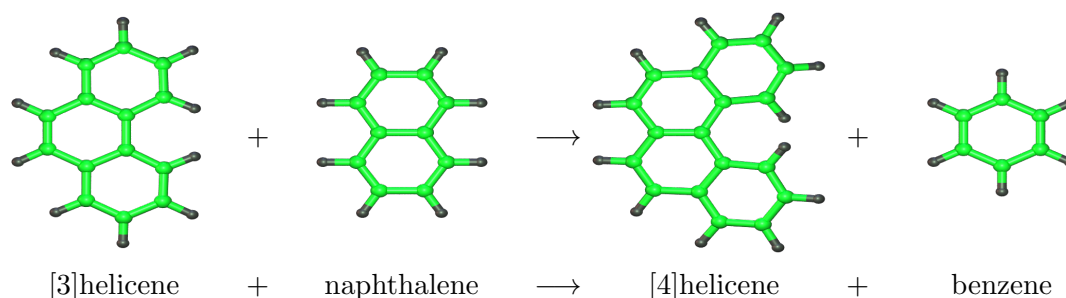


FIGURE 6.6: A homodesmotic reaction in which [3]helicene is extended to [4]helicene. There are analogous reactions for acenes and phenacenes.

series. For that reason, one may expect that the reaction energies will be accurate and it will be possible to assess the patterns with growing series of helicenes and phenacenes.

The negative value of the ΔE_n indicates that the $[n]$ th element is more stable than the $[n - 1]$ th one. For that reason, if all of the ΔE_n values in the given series are negative indicate that larger structures are more stable than the smaller ones (in that series). Conversely, the series of positive ΔE_n indicates that with the growing size the structures are less stable.

The ΔE_n of phenacenes is expected to converge to constant value rather quickly. Extending the chain

by constant unit will increase the energy by finite amount and the structure of phenacenes do not promote any additional energetical changes². The situation is different with the helicenes: only after finishing the first full turn the extending structure is similar to its predecessors. For that reason, one may expect the convergence of ΔE_n only after adding the 6th or 7th ring.

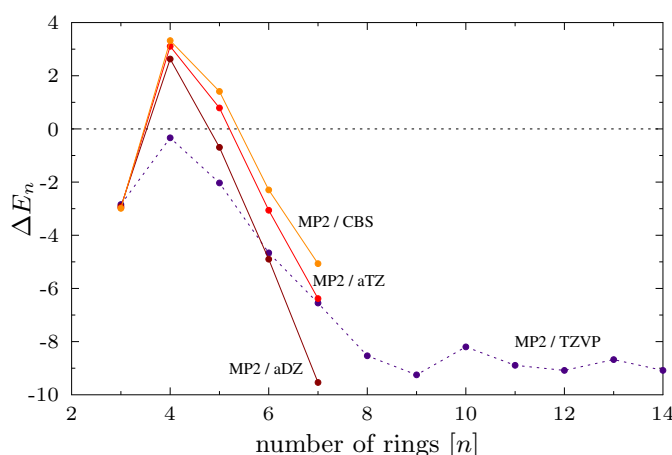


FIGURE 6.7: The reaction energy (ΔE_n) helicenes from MP2 method. The produced reaction energies are highly negative, which indicates that the MP2 is not suited for vdW interactions. Basis set aXZ denotes the aug-cc-PXZ from the correlation consistent basis sets series.

6.3.1 Quantum Mechanical Methods

Figure 6.7 shows the dependence of the ΔE_n on the growing size in the helicenes obtained from MP2 method, this data is from Valdés et al. [28]. Basis set aXZ denotes the aug-cc-PXZ from the correlation consistent basis sets series [29–31]. According to expectations, the ΔE_n seem to converge for higher helicenes. As mentioned before, the MP2 method tends to overestimated interaction energies of vdW bounded complexes. The helical structure of helicenes favours the vdW interactions, as many atoms are in optimal for them distances. On that account, it is reasonable to assume that in case of the helicenes, the MP2 method will overestimate the

²like steric effects or large scale interactions

binding between different parts of the molecule, and consequently lower its total energy. In higher helicenes this behaviour is stronger and consequently the MP2 method favours larger helicenes, producing negative ΔE_n . Using larger basis set helps to diminish the problem, but cannot correct it, as it is intrinsic to the MP2 method.

Figure 6.8 presents the ΔE_n obtained using various methods. Some values corresponding to larger basis sets are taken from literature[28, 32]. The results for the 6-31G and 6-311G basis sets were fully optimized, the results from the literature were usually optimized using smaller basis set. For the reasons elucidated above, the dispersion plays nontrivial role in the case of the helicenes. This may explain why, in the case of helicenes, the values of ΔE_n obtained from the functionals without additional dispersion and Hartree-Fock approach are significantly larger (see Figures 6.8(a), 6.8(c) and 6.8(d)). Moreover, for these methods only with the M06-2X functional the ΔE_n clearly converges – after addition of 9th ring the reaction energy stabilizes, for other approaches the ΔE_n continue to rise for larger structures. The more detailed comparison of the methods with dispersion is presented on Figure 6.9. For helicenes, only method with explicit dispersion are presented³, as methods without it do not show signs of convergence (see Figure 6.8).

As expected, inclusion of the van der Waals interactions resulted in lower ΔE_n . In the case of the phenacenes this effect is rather small (see Figure 6.9(b)). For the helicenes additional dispersion changes the trends in the reaction energy (see Figure 6.8) – additional dispersion stabilizes the growing helicene, thus resulting in smaller ΔE_n .

According to most methods the growing phenacene is more stable than its predecessor. This effect is small for the B3LYP functional and stronger in the case of M06-2X functionals. The situation is more complex in the case of the helicenes. The MP2 method predict that large helicenes are more stable – this is not surprising, as explained above the MP2 method is unsuited for such structures. The helicenes reaction energy obtained using M06-2X functional present large variation between the calculations and are lower than in other methods. Furthermore adding dispersion and using bigger basis set lower the ΔE_n . For the M06-2X+D3/6-311G it is slightly negative for large structures. This suggest, that the M06-2X method cannot be safely use for similar structures.

6.3.2 Semiempirical and Molecular Mechanics Methods

The helicenes and phenacene are one-molecule systems. Their framework is a series of *ortho*-fused carbon rings and are easily extensible by adding subsequent rings in appropriate positions. Such systems could be problematic for some force field within molecular mechanics approaches. For example, if a given force field⁴ uses explicitly charged atoms the resulting molecule will be unbalanced. With the default values, the extended carbon framework will be too highly charged to balance with remaining hydrogens. There are several possible solutions. One could re-balance

³The M06-2X functional was included. It was designed to mimic some dispersion and it shows converges in ΔE_n .

⁴Among force fields used, the CHARMM and OPLS used explicit charges.

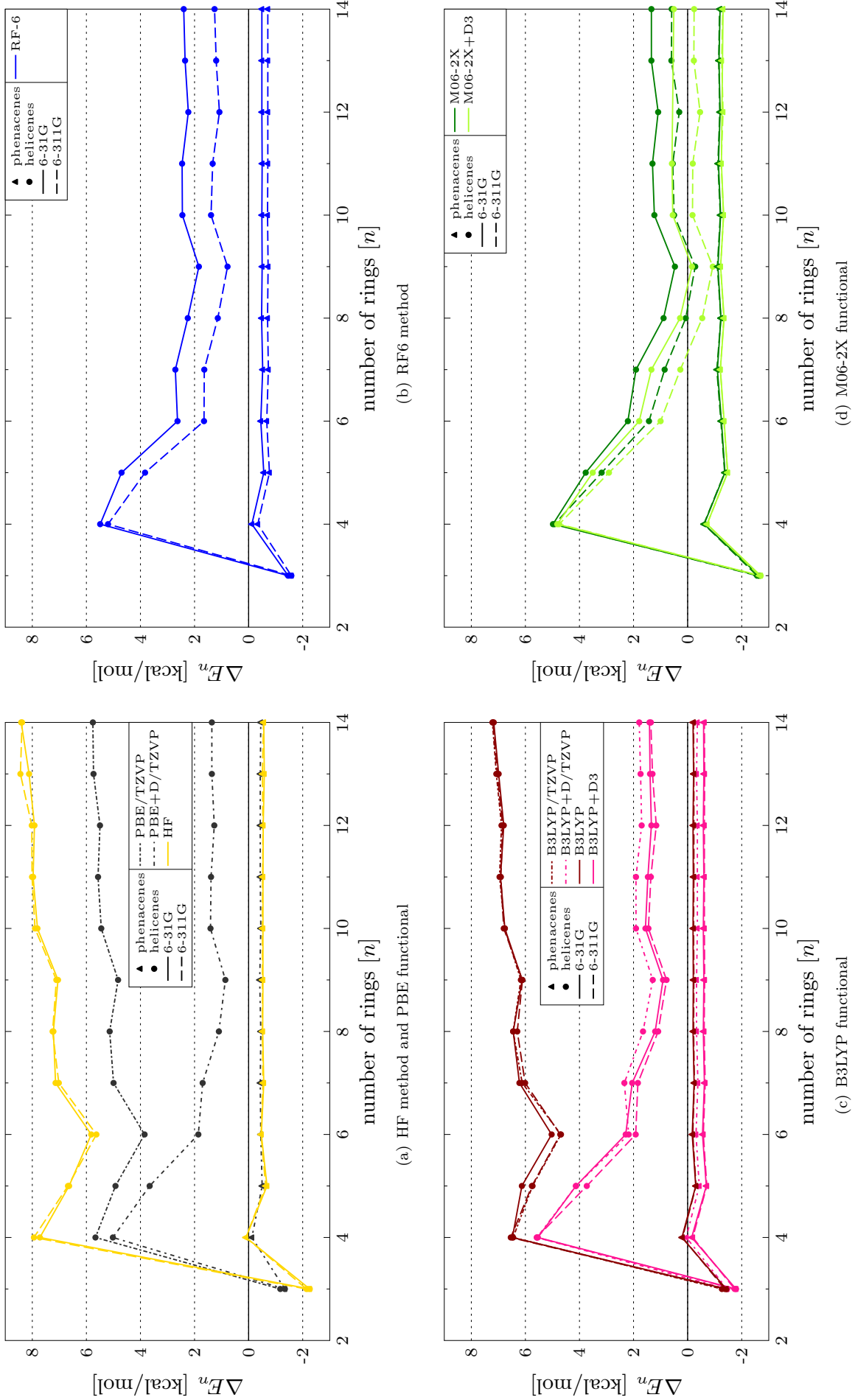


FIGURE 6.8: The reaction energy (ΔE_n) of helicenes and phenacenes as a function of the number of the rings. Various methods are presented. If not otherwise indicated the style of the line indicate the basis set.

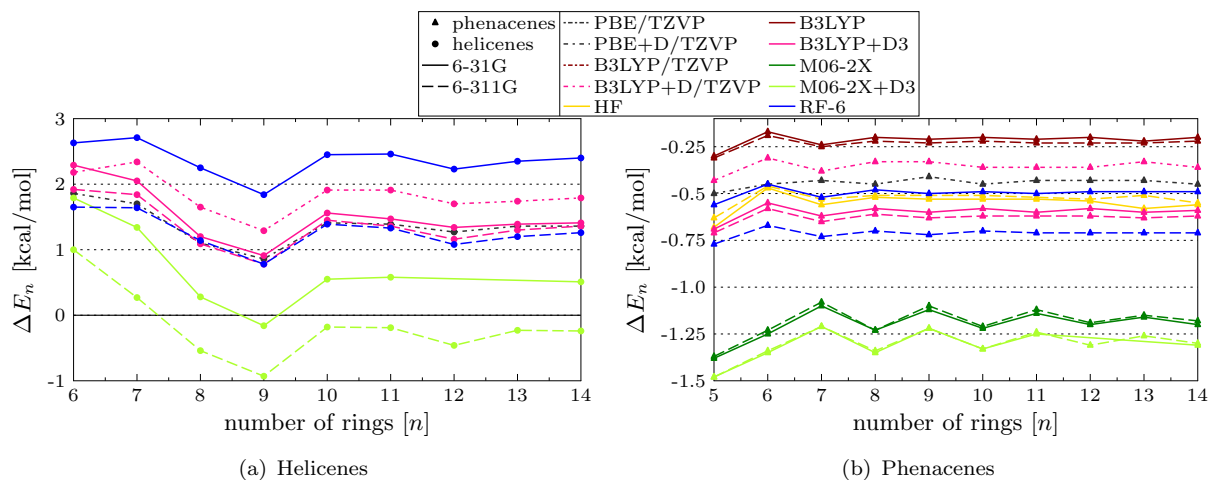


FIGURE 6.9: The reaction energy (ΔE_n) of as a function of the number of the rings. Only methods with dispersion are included for the helicenes (a). Only region near convergence is shown. If not otherwise indicated the style of the line indicate the basis set.

the partial charges for the atoms, but the carbon to hydrogen ratio is not conserved between the structures – each structure would require separate charge values. Generally, carbon atoms in infinitely extended graphitic materials, like graphite, are not charged. Hence, the other solution is not to use charges. Figure 6.10(a) shows the ΔE_n for force fields with and without charges. As expected, the default charges („ δ ” prefix in force field name) produce divergent result. Simple scaling of charges (carbon charge modified to balance total charge, „s δ ” prefix) and using no charges produced convergent ΔE_n , as expected. Using modified charges is problematic – there are many possible partitioning schemes to be used, moreover each structure would need different charges. For these reasons, in the following analysis, no charges will be used with OPLS, RF-OPLS and CHARMM force fields.

Additionally, for the MM2 and MM3 force fields it is possible to define π -system, and consequently perform the variable electronegativity self-consistent field calculations. These calculations are used to obtain bond orders, from which various stretching and torsional parameters are derived. The differences produced by the two approaches are shown on Figure 6.10(b). In the case of the helicenes, for the normal MM3 force field the ΔE_n converges to a high value of around 11 kcal/mol, while the MM3 with the π -system gives reaction energies much closer to ones obtained from QM methods. For that reason, the π -system will be used when possible.

Figure 6.11 shows the results obtained after using semiempirical and molecular mechanics approaches. In the case of the MM approaches, the most visible theme is that molecular mechanics do not predict any negative ΔE_n values – even for the phenacenes. All investigated quantum mechanical and semiempirical methods, apart from rudimentary MNDO approach, predict negative values of reaction energy for the phenacenes. All force fields presented on Figure 6.11(a) show stabilization of ΔE_n after first full turn in helicenes.

The reaction energies obtained from the use of semiempirical methods are shown on Figure 6.11(b). As already mentioned, the MNDO method produced positive ΔE_n values eve for

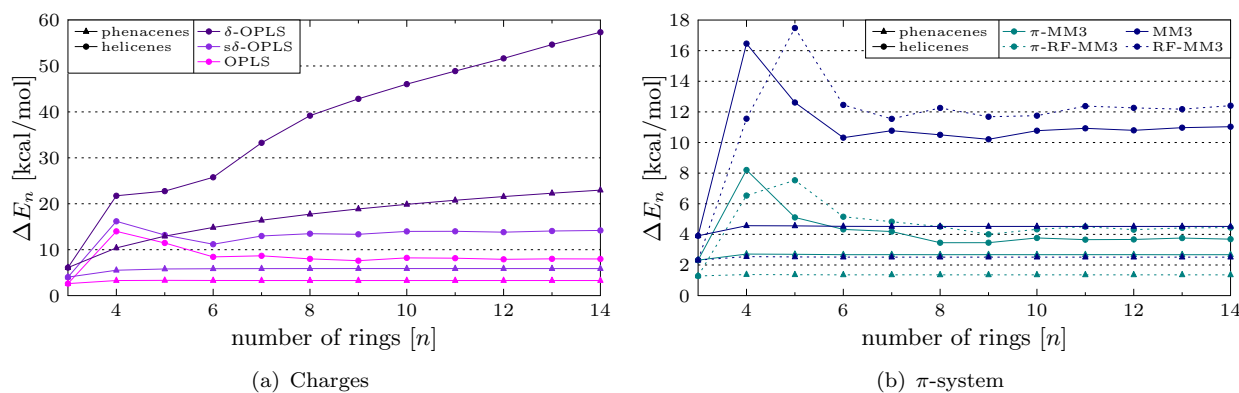


FIGURE 6.10: Influence of charges (a) and π atoms (b) on molecular mechanics. Force fields using the default charges („ δ ” prefix in the name of the force field) produce divergent results, scaled charges („ $s\delta$ ” prefix) and no charges are convergent. The explicit treatment of π -system („ π ” prefix in the name of the force field) lowers the ΔE_n .

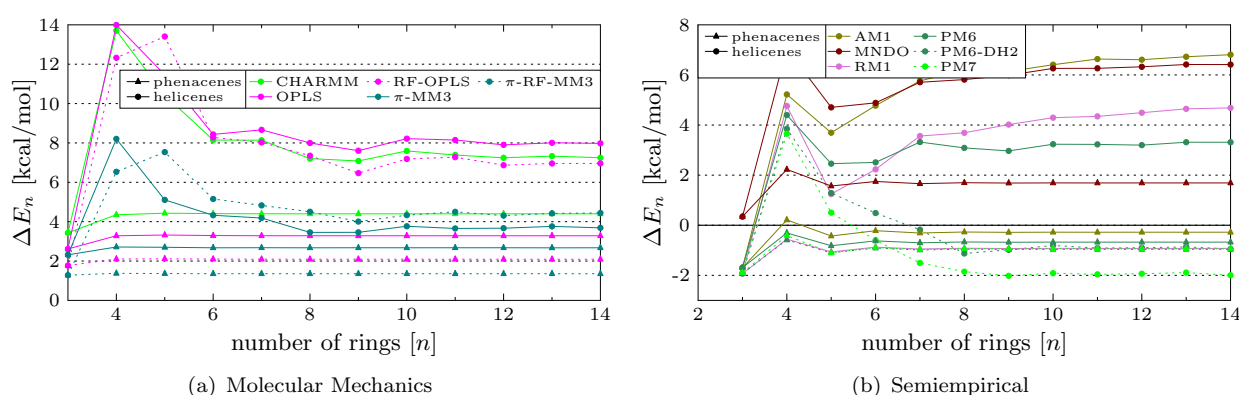


FIGURE 6.11: The reaction energy (ΔE_n) of as a function of the number of the rings. The results obtained from molecular mechanics (a) and semiempirical (b) methods.

the phenacenes. The MNDO is the simplest among semiempirical methods, hence it could generate unsound data. More interesting is the behaviour of the PM6-DH2 and PM7 approaches – for higher helicenes both methods produce highly negative ΔE_n , for the PM7 it was even lower than that for corresponding phenacene. The PM6-DH2 is a modification of PM6 method, its main advantage is inclusion of vdW interactions. The fact, that PM6 do not show negative reaction energies for helicenes, suggests that the additional dispersion is overestimated. The PM6-DH2 was trained on small molecules, mainly because high accuracy theoretical data is available for such structures. Unfortunately, it seems that in the case of semiempirical methods this approach was not suitable to produce method that is suited for larger structures, like helicenes.

6.4 Conclusions

The helicenes and phenacenes are an example of *ortho*-fused polycyclic aromatic hydrocarbons. They are isomers, but their spatial arrangement are very different – the phenacenes are planar,

serpentine shaped while the helicenes are helical three dimensional structures. Both kinds of compounds can be sorted into a series, in which the number of carbon rings determines the order. The study of the energetic properties of this series provides a good indicator of the reliability of a given method. The helicene and phenacene of the same order have the same number and order of bonds. This makes the comparison of their properties more robust – many possible errors, *e.g.* bond energy, will be eliminated. One of the main differences is that van der Waals interactions are more relevant in the case of the helicenes.

Several quantum mechanical, semiempirical and molecular mechanics methods were investigated. Expectedly, the MP2 method cannot be used for helicenes, as it highly overestimates the dispersion. In the case of helicenes, among QM approaches, methods with explicit dispersion provided the foreseen result – the ΔE_n was stabilized around 2 kcal/mol after the first full turn of the coil. Most QM methods predicted the convergence of the reaction energy of phenacenes in the region from -1 to 0 kcal/mol.

The semiempirical methods produced the expected stabilization of the ΔE_n , but helicenes result were widespread and much higher than the QM methods. The PM6 method gave the helicene ΔE_n of about 3 kcal/mol. Surprisingly, the semiempirical methods with dispersion, PM6-DH2 and PM7, produced highly negative ΔE_n for helicenes. The PM6 method, producing reaction energies near the QM values, has no dispersion and as such cannot be safely used for vdW bonded systems; The semiempirical methods with dispersion are unsuited to treat systems like helicenes.

Many force fields include explicit charge-charge interactions with charges that depend on the atom type. This is clearly not appropriate for structures, like helicenes. A simple correction is to neglect the charges. The molecular mechanics methods investigated produced reaction energies greater than zero even in the case of phenacenes. For the helicenes, among force fields tested, closest to that of QM methods were the MM3 and RF-MM3 force fields with the ΔE_n of about 4 kcal/mol.

Among the methods investigated only the quantum mechanical approaches with explicit dispersion can be safely used for structures similar to ones investigated here. They can reproduce the expected patterns of reaction energies and have no problems seen in semiempirical and molecular mechanics approaches. The inconvenience is that they are much more computationally demanding. The RF-6 is the recommended method, as it substantiated its excellency during another examinations.

Chapter 7

Shrinking of the Buckyball

7.1 Introduction

The structure of the C_{60} fullerene and its complexes is the main concern of this chapter. When isolated, C_{60} fullerene has a truncated icosahedron shape and the I_h point group symmetry[1, 2]. In that symmetry only two types of bonds determine the C_{60} structure: the longer, p bond, in the pentagons and the shorter, h bond, connecting separated pentagons (see Figure D.1). The p bond has a mostly single bond character, while h can be considered as closer to a double bond[3]. This work was published in Computational and Theoretical Chemistry by Strutyński and Gomes [4].

The fullerenes size will be described as the $R_{C_{60}}$, the distance between any of the carbon atoms and the center of mass (CM) of the molecule. If the I_h symmetry is broken, the average value of the distance between the CM and the carbon atom will be used for $R_{C_{60}}$.

Table 7.1 collects the C_{60} structural parameters from several experiments. These experimental results suggest that the fullerene is slightly smaller in solid phase. When another molecule is present in the crystal lattice the effect is stronger. It appears that the C_{60} fullerene shrinks slightly upon complexation.

The effect is rather small and, in some cases, it falls within the error bars of these measurements. One may dispute

TABLE 7.1: The experimental structural parameters of C_{60} molecule. Units are K for temperature and Å for length. The c-solid is the complex of C_{60} with another molecule present in the crystal lattice.

state	temp	p	h	$R_{C_{60}}$
gas ^a	1000	1.458(6)	1.401(10)	3.562(19)
gas ^b	1000	1.455(6)	1.398(10)	3.555(19)
solid ^c	295	1.455(1)	1.394(2)	3.552(3)
solid ^c	150	1.455(1)	1.396(2)	3.553(3)
solid ^c	4	1.460(2)	1.386(3)	3.552(5)
c-solid ^d	143	1.450(6)	1.387(6)	3.537(15)
c-solid ^e	104	1.446(5)	1.389(5)	3.532(13)
c-solid ^f	—	1.423(5)	1.388(9)	3.495(15)

^aelectron diffraction, C_{60} Hedberg et al. [5], thermal average

^belectron diffraction, C_{60} Hedberg et al. [5], scattering equation

^cneutron scattering, C_{60} Damay and Leclercq [6]

^dX-ray, $C_{60} \cdot 2(Fe(C_5H_5)_2)$ Crane et al. [7]

^eX-ray, $C_{60} \cdot 4C_6H_6$ Balch et al. [8]

^fX-ray, $C_{60}(OsO_4)(4\text{-tert-butylpyridine})_2$ Hawkins et al. [9]

its reality and origin, as the experiments were performed in different conditions and using various methods. I'll try to show that this shrinking effect is real, as the theoretical calculations find the same effect of complexation.

One of the experimental variables is the temperature of the measurements. It is well known that the crystal lattice expands with temperature, with a jump at phase transition[10]. The larger gas phase result in Table 7.1 corresponds to some thermal averaging, the smaller value is consistent with scattering equations. Usually the bonds are longer when averaged over thermal vibrations, indeed the thermal averaged values yield a larger Buckyball. Hence, one may expect that use of this $R_{C_{60}}$ will artificially amplify the shrinking. For that reason, $R_{C_{60}} = 3.555 \text{ \AA}$, the value consistent with the scattering equation, should be used for the gas phase. The thermal effect may explain the shrinking of the Buckyball as it goes from gas to solid but it cannot explain the further shrinking as it goes from solid to c-solid.

All DFT-D calculations were done using previously described RF-6 method (see Chapter 3). The NWChem 6.1.1[11] program was used for all the MP2, DFT and CCSD(T) calculation of isolated molecules. The periodic boundary condition calculations were performed using Crystal 09 program[12, 13]. The double- and triple- ζ basis set of Pople [14, 15] were used. It was determined that including polarization and diffusion functions did not change the result in significant manner for these basis sets, hence only the 6-31G and the 6-311G basis sets are presented as a representatives of the double- ζ and the triple- ζ basis sets respectively.

For obtaining and analyzing the fullerene structures the Fullerene 4.3[16–18] program was used.

The „gold standard” of Quantum Mechanical (QM) calculations is the CCSD(T)[19–21]: a coupled cluster method containing single, double and perturbative triple excitations.

The simplest model analogue of the complexes studied here is ethylene dimer. It was studied theoretically, but without full coupled cluster geometry optimization[22]. For that reason, the coupled cluster optimization for several conformations of ethylene dimer was performed. For the CCSD(T)/aug-cc-pVDZ CCSD(T) method, when another ethylene is stacked on top of the previous one the C-C bond distances is shortened by $0.00046 \text{ \AA}$, while in the X-shape conformation the bond is elongated by $0.00016 \text{ \AA}$. Apparently, the change in C-C bond length depends on the conformation: in the sandwich conformation the bond is shortened, in other conformations (*i.e.* X-shaped) it could be elongated.

The less accurate, mp2/aug-cc-pVDZ method gives qualitatively the same result. Even the RF-6 method provides analogous behaviour for ethylene dimer.

A bigger model system for the C_{60} complexes is benzene dimer. Both MP2 and RF methods produce average C-C bond lengths slightly shortened for parallel conformation of benzene dimer.

The investigated model systems suggest a behaviour similar to the one observed experimentally. In order to explore the presence of the shrinking effect with fullerene, various systems closer to the experimental ones were checked.

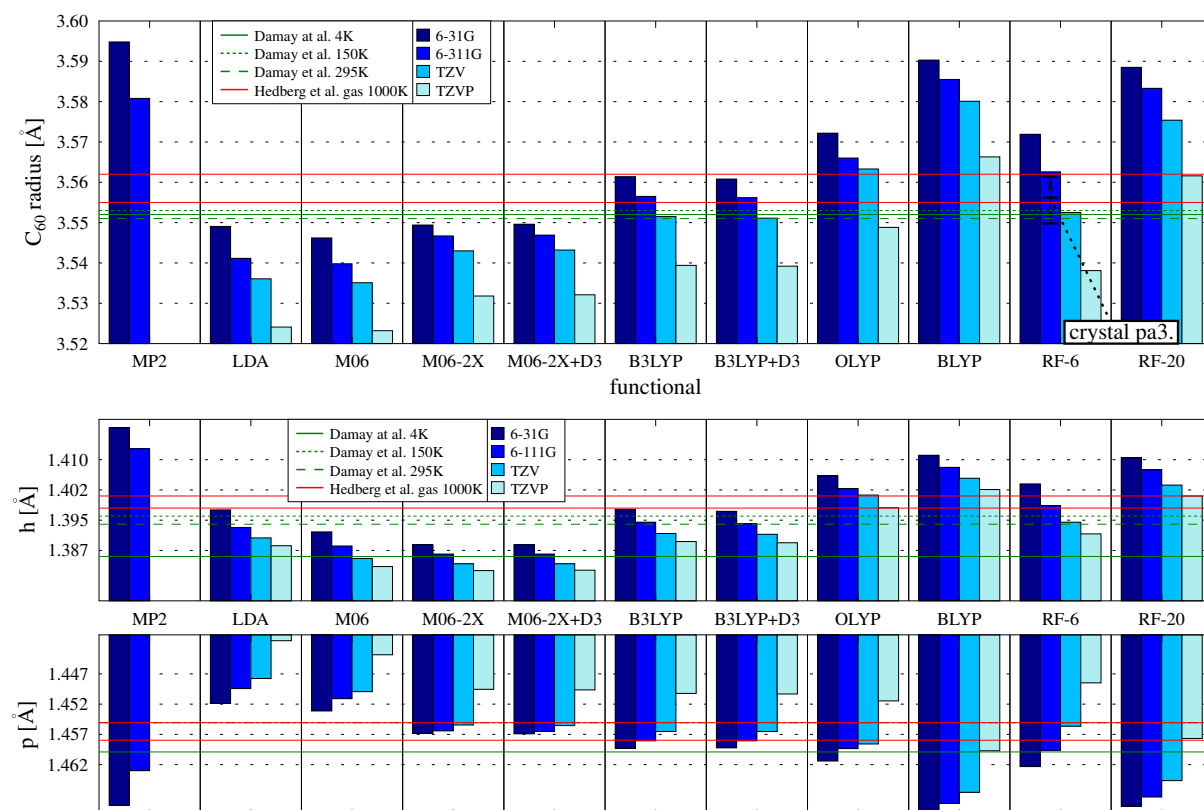


FIGURE 7.1: The radius (top) and the length of bonds (bottom) of the C_{60} fullerene obtained by various methods using different basis sets.

7.2 Isolated Buckyball

The standard quantum mechanical calculation corresponds to an ideally isolated molecule at 0K. Because of that one may expect that the experimental result from the gas phase[5] is the closest to theoretical investigations.

The optimization of the Buckyball was performed with several common quantum mechanical methods and various basis set sizes.

Figure 7.1 shows the results. Most functionals produced too short bond lengths. The OLYP and B3LYP functionals result in a good Buckyball size, but they do not include any dispersion, hence cannot be used for any C_{60} complexes. The BLYP tends to overestimate the length of the bonds. This make it a good choice – dispersion correction will probably shorten those bonds, hopefully resulting in good agreement. Indeed, the RF methods produce smaller $R_{C_{60}}$, closer to the reference one. Only the RF and the B3LYP+D3 methods include some dispersion interactions and are useful for vdW bounded systems. The B3LYP+D3 has problems with the reproduction of binding energies and geometries of the benzene dimer, a model system for graphitic systems. For that reason, among the methods investigated, only the RF method with 6-31G or 6-311G basis sets are applicable to vdW bonded complexes with fullerenes.

7.3 Solid Phase

There are several experimental measurements of the Buckyball structural features in the solid phase (see Table 7.1). In all cases molecular sizes seem to be slightly smaller than in the gas phase, especially when other molecules are present in the crystal lattice. The experimental data for solids are obtained assuming the I_h molecular symmetry, even if it is known that this symmetry is broken at low temperature. For that reason, the bond lengths are probably the result of some averaging over all bonds of the same type.

It is known that at room-temperatures C_{60} crystallizes in space group $Fm3m$, with disordered $Fm3$ packing. Upon cooling to $\sim 250K$, the phase transition to $Pa3$ space group with simple cubic packing begins.[10, 23–25]

The solid phase is not the main interest here. For that reason, only preliminary calculations were performed with periodic boundary conditions using RF-6/6-311G method. The resulting lattice constant was in good agreement with the experimental value (13.98 Å vs. 14.04 Å[10]). The $R_{C_{60}}$ obtained from calculations has an average of 3.5562 Å and ranges from 3.5498 to 3.5614 Å, while the appropriate value for the isolated molecule is 3.5624 Å. This shrinking is marginally larger than that observed experimentally – theoretical shrinking of about 0.006 Å, while it was 0.003 Å from experiment.

7.4 VdW Complexes

Naming convention used here was already discussed in Section 5.2.

Table 7.2 presents the results obtained for various C_{60} -benzene conformations. The BE is the binding energy; $R_{C_6H_6}$ is the distance between the CM of the fullerene and CM of the benzene (in case of multiple benzene molecules in the complex the average values were used); R_{min} , R_{max} and R_{avr} are respectively the minimal, maximal and average Buckyball radii.

In most cases when the benzene plane is parallel to the local fullerene surface (T conformations, see Figure Section 5.2) the shrinking effect was present, but for the nT conformations the averaged Buckyball diameter does not change when compared with the isolated fullerene. This indicates that the fullerene shrinking is not due to introducing another molecule into the system, but is specific to some type of interaction between the moieties. The main difference between those conformations is the π - π interactions present in T -shape conformation, which suggest that the contraction may be due to this type of interaction.

Additionally, as a test of veracity of the method several small molecules were encapsulated inside the C_{60} cage. The Buckyball radius did not change only in the case of the hydrogen molecule, the $H_2@C_{60}$. In all other cases, the fullerene expanded.

For the tested T conformations the $R_{C_{60}}$ was smaller than in the isolated molecule. Different conformations result in different C_{60} diameters, but the effect is smaller than that observed experimentally.

TABLE 7.2: The C_{60} radius for various conformations of C_{60} -benzene complex. All values are obtained using RF-6/6-31G method. All of the bounded complexes present smaller fullerene size than an isolated molecule. Complexation with more than one benzene results in smaller fullerene. The binding energies (BE) are in kcal/mol, the radii are in Å.

RF-6/6-31G						
conf.	BE	$R_{C_6H_6}$	R_{min}	R_{max}	R_{avr}	$R_{avr} - R_{C_{60}}$
C_{60}, I_h	—	—	3.5719	3.5719	3.5719	—
$nT-h-b-per$	-3.10	8.33	3.5685	3.5727	3.5719	0.0000
$nT-h-a-per$	-2.42	8.74	3.5695	3.5724	3.5719	0.0000
$nT-p-b-per$	-3.08	8.30	3.5692	3.5728	3.5719	0.0000
$nT-5r-b$	-3.24	8.34	3.5700	3.5728	3.5719	0.0000
$nT-6r-b-per$	-3.30	8.33	3.5705	3.5730	3.5719	0.0000
$T-h-per-ok$	-5.37	6.85	3.5679	3.5729	3.5714	-0.0005
$T-h-par$	60.75	6.91	3.5455	3.6328	3.5761	0.0042
$T-h-per$	60.76	6.91	3.5454	3.6328	3.5761	0.0042
$T-at$	-5.00	6.93	3.5633	3.5724	3.5714	-0.0005
$T-p-per$	-5.10	6.93	3.5681	3.5727	3.5718	-0.0001
$T-5r-par$	-4.96	6.97	3.5682	3.5726	3.5713	-0.0006
$T-p-par$	-5.11	6.92	3.5681	3.5727	3.5718	-0.0001
$T-2C_6H_6$	-10.19	0.31	3.5662	3.5722	3.5712	-0.0007
$T-4C_6H_6$	-21.05	0.08	3.5670	3.5731	3.5709	-0.0010
$T-6C_6H_6$	-30.34	0.01	3.5659	3.5731	3.5706	-0.0013
long	-0.44	10.00	3.5710	3.5720	3.5715	-0.0004
$H_2@C_{60}$	-3.557	—	3.5715	3.5725	3.5719	0.0000
$CH_4@C_{60}$	-3.555	—	3.5691	3.5786	3.5733	0.0014
$C_2H_4@C_{60}$	24.60	—	3.5502	3.6182	3.5800	0.0081
RF-6/6-311G						
conf.	BE	$R-C_6H_6$	R_{min}	R_{max}	R_{avr}	$R_{avr} - R_{C_{60}}$
C_{60}, I_h	—	—	3.5624	3.5624	3.5624	—
$T-h-par$	-6.32	6.75	3.5575	3.5643	3.5623	-0.0001
$T-h-per$	-6.32	6.73	3.5573	3.5641	3.5623	-0.0001
$T-p-par$	63.28	6.79	3.5236	3.6164	3.5664	0.004
$T-p-per$	63.16	6.78	3.5263	3.6158	3.5664	0.004
$T-5r$	-5.66	6.87	3.5576	3.5642	3.5622	-0.0002
$T-2C_6H_6$	-11.43	0.31	3.5562	3.5633	3.5620	-0.0004
MP2/6-31g						
C_{60}, I_h	—	—	3.5948	3.5948	3.5948	—
$T-h-per$	-7.86	6.53	3.5913	3.5968	3.5945	-0.0003

7.5 Verification

Attempts to falsify a hypothesis are a good practice in science. This step is essential if the initial hypothesis is tentative and it's not very clearly and directly supported by experimental data. The hypothesis presented here is that the C_{60} fullerene shrinks upon complexation. The experimental data suggest that, but are unequivocal. For that reason, it is necessary to attempt to falsify the shrinking hypothesis or explore other explanations for the observed theoretical and experimental data.

The shrinking effect is present in the results from the RF-6/6-31G method, but it is small and one might argue that numerical effects or artifacts of the QM methods used (like geometry optimization conditions) could be responsible. Moreover, the detected shrinking was smaller

than that observed experimentally. A possible source of that difference is that experiments were done in solid phase while an isolated molecule is considered in presented calculation.

7.5.1 Numerical Effects

Van der Waals complexes are weakly bonded systems, hence the benzene can easily change position without a significant change in energy. For this reason, the initial conditions in the geometry optimization may be relevant. To take that into account many optimizations were performed and various initial conformation were considered. Moreover, several conformations were reoptimized with tight convergence criteria¹. In all cases of tight optimization the results were analogous to normal optimization.

In all investigated structures the variance of $R_{C_{60}}$ due to optimization conditions was about 0.0001 Å, which shows that the calculations using RF method are numerically robust. The shrinking observed in theoretical calculations cannot be due to numerical instabilities of the RF method.

Several preliminary tests with the more accurate, but computationally more demanding, RF/6-311G method were performed and a similar shrinking effect was observed (see Table 7.2.

For the Single Point calculation of the h conformations with a 6-31G basis set the binding energies predicted an unstable complex (binding energies of more that +50 kcal/mol). After subsequent optimization, the Buckyball was slightly larger, a result opposite to that predicted by shrinking hypothesis. However, changing the symmetry of the calculation or forcing non-default initial orbitals solved this problem. Additionally, when another calculation leads to the h conformation during geometry optimization this effect was not present and the Buckyball shrunked as expected. These facts indicate that the positive binding energy is an artifact of the self consistent field (SCF) process falling into a local minimum. Interestingly, the same problem was found in the p conformation, when the RF-6/6-311G method was used. This further supports the idea that it is due to problems within SCF calculations.

7.5.2 Multiple molecules

A detailed study of the structures obtained after optimization suggests that the benzene influence is only local. In the T -shape conformations fullerene bonds closest to the benzene are smaller than the more distant ones, resulting in decreased average $R_{C_{60}}$; In the case of nT conformations, bonds close to the benzene were slightly longer than other bonds, but the average diameter remained unchanged.

The benzene molecule attached to a fullerene produces locally shortened fullerene bonds, hence the overall (averaged) Buckyball diameter is smaller. If that is the case, a second benzene attached to a different site on fullerene would produce shorter fullerene bonds near it and further

¹Using the NWChem keyword „tight” corresponding to thresholds of 1.5×10^{-5} for maximum gradient, 1×10^{-5} for RMS gradient, 6×10^{-5} for maximum Cartesian step and 4×10^{-5} for RMS Cartesian step. The default values are corresponding 4.5×10^{-4} , 3×10^{-4} , 1.8×10^{-3} and 1.2×10^{-3}

shrink the $R_{C_{60}}$. Hence, the effect should be cumulative when multiple benzenes are bonded to the fullerene.

The complexes of the Buckyball with 2, 4 and 6 benzene molecules were considered. The location of additional benzenes aim to simulate the environment of the C_{60} molecule in the solid state. When fullerene is surrounded by two or more benzene molecules there are more possible conformation and the calculations are more time consuming. For that reason, only preliminary runs were performed.

In the complex with two benzenes these were positioned on opposite sides of the fullerene, the benzenes being close to a *T-p-per* conformation. Then four benzenes were placed in square formation around the Buckyball. Two of them were close to *T-p-per* conformation, and the other two were close to *T-h-per* conformation. The complex with six benzenes was created by adding two benzene molecules above and below the C_{60} - $4C_6H_6$ complex, this being in the *T-6r-par* conformation.

All structures were fully minimized, the results are presented in Table 7.2. As expected, the Buckyball contracts further when it is surrounded with more molecules suggesting that the effect is really cumulative.

In the solid state there are additional interactions working at larger distances. To check the influence of more distant molecules another structure was optimized: The complex with the benzene molecule at about 3 Å further from fullerene than in normal complexes (conformation „long” in Table 7.2). The shrinking effect was still present, but to a lesser degree.

The distant molecules still have an effect on the Buckyball and that effect seems to be cumulative. For that reason, one may expect that in the crystal the overall shrinking of the fullerene will be larger when compared to the complexes presented here, especially if other molecules are also present in the lattice.

7.5.3 Basis Set Superposition Error

To make the calculations of large complexes feasible, the basis set used in the calculations was relatively small. For that reason, the effects of its incompleteness need to be examined. The binding energies obtained with the RF method do not need to be corrected for Basis Set Superposition Error (BSSE), as the method was parameterized to work without it. Nevertheless, the BSSE could affect the optimization of the geometry.

TABLE 7.3: The comparison of normal RF and counterpoise corrected RF optimization. The *BE* is the binding energy, the $R_{C_6H_6}$ is the distance between the fullerene and the benzene molecules, and the $R_{C_{60}}$ is the radius of the fullerene.

conf.	RF-6/6-31G				RF-6/6-311G			
	<i>T-p-per</i>		<i>T-5r</i>		<i>T-p-per</i>		<i>T-5r</i>	
		CP		CP		CP		CP
<i>BE</i>	-5.10	-3.37	-4.96	-3.04	-5.606	-4.50	-5.657	-4.35
$R_{C_6H_6}$	6.9257	7.1855	6.9712	6.9814	6.8264	6.9167	6.8676	6.9727
$R_{C_{60}}$	3.5718	3.5719	3.5713	3.5712	3.5623	3.5623	3.5622	3.5622

To ascertain this, a few optimizations were performed with the counterpoise correction (CP) method by Boys and Bernardi [26], an usual technique for including the BSSE in the quantum mechanical calculations. The results are summarized on Table 7.3. In all such optimizations, the shrinking effect was present with magnitude similar to that of normal RF calculations. The differences between CP and RF calculation were around 1×10^{-4} Å.

These tests suggest that the shrinking effect described here is not caused by the inaccuracies resulting from the basis set superposition error.

7.6 Conclusions

The experimental determination of the structural features of the C_{60} fullerene produce different diameters depending on the environment. The C_{60} fullerene appears to shrink in the presence of nearby, noncovalently bonded molecules. This effect is strongly suggested by the best experimental estimates collected here. This chapter gives strong support to the reality of this effect by quantum mechanical calculations at the best standard available today for this type of systems.

This investigation finds that fullerene shrinks after complexation, and this may be due to the presence of π - π interactions as only *T*-shape conformations of C_{60} -benzene are affected. This is the *ab initio* confirmation of the experimental observation.

Many tests were performed to confirm that the results are not simply a computational artifact. Any of these tests could falsify the shrinking hypothesis, but the effect was always retained. The shrinking was present in all tested *T*-shaped conformations. Trials that included multiple adjoined molecules suggest that the effect is cumulative and relatively long-range. The calculations with larger basis sets and counterpoise corrected optimization yielded a similar shrinking, showing that the shrinking is not an artifact of basis set incompleteness. The calculation of C_{60} crystal, the system closest to the experimental one, yielded marginally larger shrinking than that observed experimentally, which suggests that the differences in the magnitude of the observed shrinking between the experiment and presented calculations are mainly caused by the differences in the structures considered.

The shrinking found in singly complexed fullerene was smaller than that observed in experiments; including more benzenes reduced the difference. When full crystal calculations were done the shrinking was slightly larger. When the theoretical system approaches the experimental systems, the shrinking discrepancies (between theory and experiment) become smaller: the theory corroborates the experiment. This reaffirms that the shrinking effect is real, and that the RF-6 method is adequate to work with large graphitic systems.

Chapter 8

Conclusions

The main point of this work was the problem of accurate representation of van der Waals forces in the graphitic materials. The DFT-D2 approach was the method of choice. This augmentation of the density functional theory is easy to implement and modify. Compared to the DFT part of the calculations, the additional dispersion computational cost is negligible.

The benzene dimer was chosen as a simple molecular analogue of graphitic materials. Its structure is determined by the van der Waals forces, also crucial to the graphitic materials. Additionally, it has been the subject of many theoretical studies, hence reference data from very accurate *ab initio* calculations are available.

The new approach, the so called relaxed fitting, was used to obtain the DFT-D2 parameters. Its main feature was full geometry optimization of the reference structures at some steps of the process. The results for parameters obtained this way were compared with the ones obtained from similar *ab initio* methods, semi-empirical approaches and molecular mechanics. The RF method was found to be more suited. It could reproduce all known benzene dimer conformations as well as its potential energy surface accurately.

The RF method was also tried on larger graphitic systems, namely C_{60} -benzene complex and various PAHs series. In the case of the C_{60} fullerene complexes, only quantum methods were found to be appropriate. Additionally, an interesting effect was found - the C_{60} diameter shrinks slightly upon complexation. This effect seems to be confirmed by the experimental results, it was found to be robust and it was shown not to be the result of numerical errors or conditions of the calculations. The study of helicenes showed that, for these systems, semi-empirical and molecular mechanics methods were problematic. The RF method was able to show the expected features and reproduce the results of other higher-level calculations.

There are several ways in which the currently presented work could be continued or extended. The most straightforward is to apply the RF obtained DFT-D parameters to other systems. Various other systems were tested using RF method but were not included, mainly because these studies were not comprehensive enough to be safely presented. The results from the C_{60} -pyrene, C_{60} -Tetraphenylporphyrin and $C_{60}@C_{240}$ complexes are included in the Appendix D. These preliminary studies are encouraging. For example, all obtained binding energies are

similar to the ones found in the literature and the RF method correctly predicts the $C_{60}@C_{240}$ in the D_{5d} symmetry as the global minimum.

One may also extend the work presented here by obtaining other set of parameters for different systems, *e.g.* including explicit heteroatoms in the references or boron-nitrogen analogues of graphitic systems. The obvious difficulty in such a line of research is finding reliable and accurate reference data. Both geometrical structures and the corresponding energies of the reference are important in relaxed fitting. If the reference energies are inaccurate the RF method will produce erroneous results as well. Similarly, if there are nonphysical structures in the reference, the RF scheme could not reproduce them. In principle, if the references are reliable, the presented relax fitting method is applicable to a very wide range of systems.

A different continuation of this work may be applying this RF method as a reference for semi-empirical or molecular mechanics method. The accurate interaction energies for large structures are very hard to obtain. Hence, reliable reference data for such systems are scarce. Approaches that produce accurate vdW interactions usually are too computationally demanding and cannot be used for such large systems. The RF method is feasible for these structures and can produce accurate energies. This enables further development of semi-empirical and MM methods. For example, the RF method could provide sound data on the π orbitals interaction leading to precise reproduction of anisotropic aspects of van der Waals interactions in graphitic systems.

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Appendix A

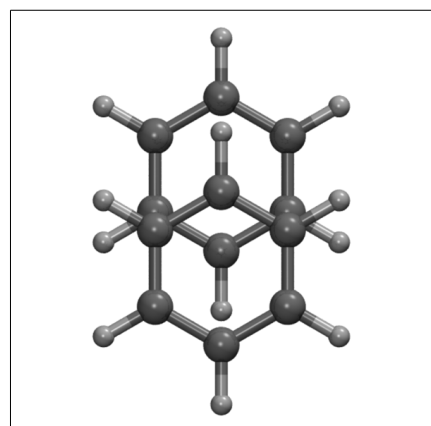
XYZ structres of Benzene dimer conformations

PD_a

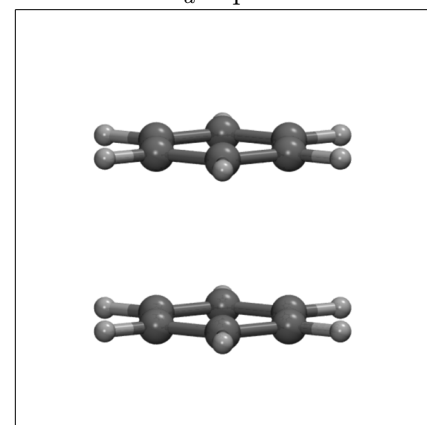
24

PD_{a}.nwo

C	1.205074	0.159427	-1.744191
C	0.000000	-0.536323	-1.744191
C	-1.205074	0.159427	-1.744191
C	-1.205074	1.550927	-1.744191
C	0.000000	2.246677	-1.744191
C	1.205074	1.550927	-1.744191
H	2.140382	-0.380573	-1.744191
H	0.000000	-1.616323	-1.744191
H	-2.140382	-0.380573	-1.744191
H	-2.140382	2.090927	-1.744191
H	0.000000	3.326677	-1.744191
H	2.140382	2.090927	-1.744191
C	-1.205074	-1.550927	1.744191
C	0.000000	-2.246677	1.744191
C	1.205074	-1.550927	1.744191
C	1.205074	-0.159427	1.744191
C	0.000000	0.536323	1.744191
C	-1.205074	-0.159427	1.744191
H	-2.140382	-2.090927	1.744191
H	0.000000	-3.326677	1.744191
H	2.140382	-2.090927	1.744191
H	2.140382	0.380573	1.744191
H	0.000000	1.616323	1.744191
H	-2.140382	0.380573	1.744191



PD_a top view



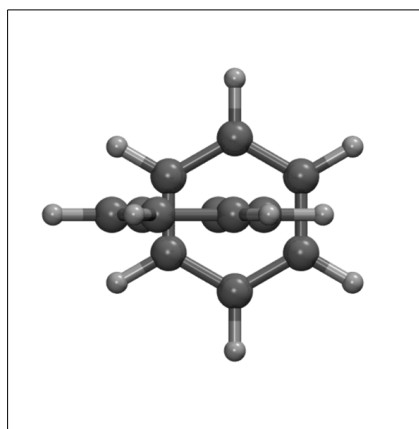
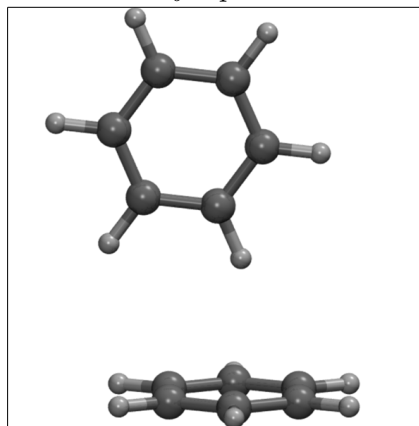
PD_a side view

TT_b

24

TT_{b}.nwo

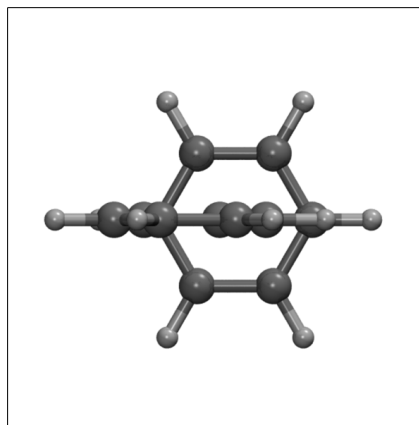
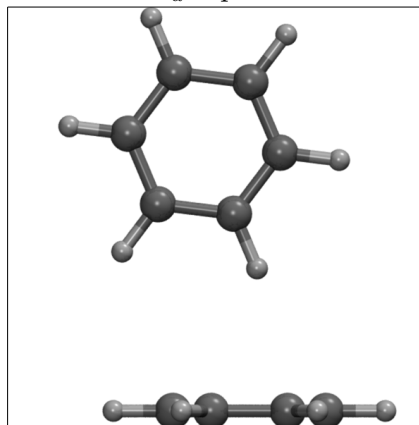
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C	0.425836	-1.391500	-2.425344
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C	-0.779238	0.695750	-2.425344
C	0.425836	1.391500	-2.425344
C	1.630910	0.695750	-2.425344
H	2.566218	-1.235750	-2.425344
H	0.425836	-2.471500	-2.425344
H	-1.714546	-1.235750	-2.425344
H	-1.714546	1.235750	-2.425344
H	0.425836	2.471500	-2.425344
H	2.566218	1.235750	-2.425344
C	0.127246	0.000000	1.148483
C	0.956499	0.000000	2.265896
C	0.403418	0.000000	3.542757
C	-0.978917	0.000000	3.702204
C	-1.808170	0.000000	2.584791
C	-1.255088	0.000000	1.307931
H	0.556515	0.000000	0.157459
H	2.029386	0.000000	2.142142
H	1.047035	0.000000	4.410027
H	-1.408186	0.000000	4.693228
H	-2.881056	0.000000	2.708545
H	-1.898705	0.000000	0.440661

*TT_b top view**TT_b side view***TT_a**

24

TT_{a}.nwo

C	0.000000	-1.802483	-2.433327
C	-1.205074	-1.106733	-2.433327
C	-1.205074	0.284767	-2.433327
C	0.000000	0.980517	-2.433327
C	1.205074	0.284767	-2.433327
C	1.205074	-1.106733	-2.433327
H	0.000000	-2.882483	-2.433327
H	-2.140382	-1.646733	-2.433327
H	-2.140382	0.824767	-2.433327
H	0.000000	2.060517	-2.433327
H	2.140382	0.824767	-2.433327
H	2.140382	-1.646733	-2.433327
C	0.000000	-0.130264	1.151404
C	0.000000	-0.969817	2.261099
C	0.000000	-0.428569	3.543021
C	0.000000	0.952231	3.715248
C	0.000000	1.791784	2.605553
C	0.000000	1.250537	1.323631
H	0.000000	-0.550348	0.156453
H	0.000000	-2.041513	2.127427
H	0.000000	-1.080181	4.404301
H	0.000000	1.372316	4.710200
H	0.000000	2.863480	2.739225
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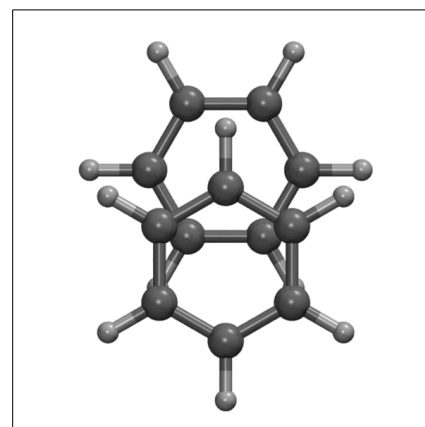
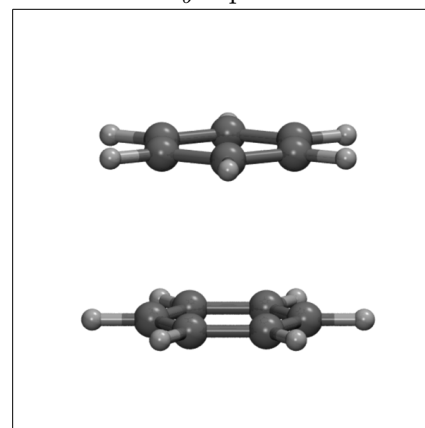
*TT_a top view**TT_a side view*

PD_b

24

PD_{b}.nwo

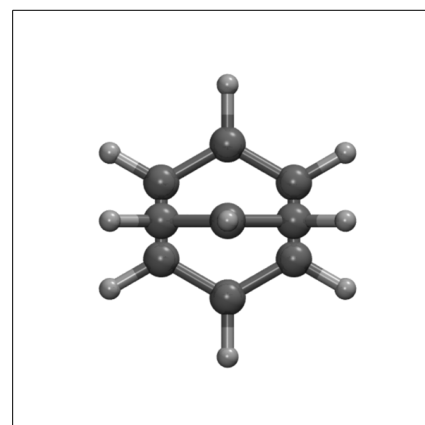
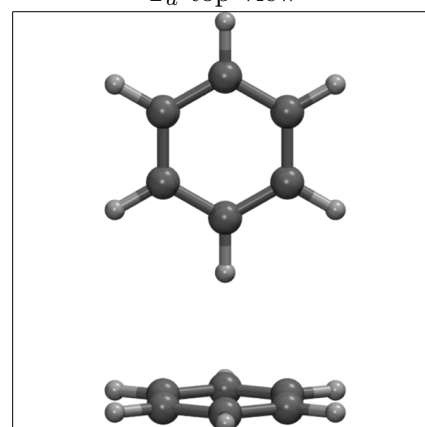
C	0.695750	-0.347278	-1.745551
C	-0.695750	-0.347278	-1.745551
C	1.391500	0.857796	-1.745551
C	-1.391500	0.857796	-1.745551
C	-0.695750	2.062870	-1.745551
C	0.695750	2.062870	-1.745551
H	1.235750	-1.282587	-1.745551
H	-1.235750	-1.282587	-1.745551
H	2.471500	0.857796	-1.745551
H	-2.471500	0.857796	-1.745551
H	-1.235750	2.998178	-1.745551
H	1.235750	2.998178	-1.745551
C	-1.205074	-1.553546	1.745669
C	0.000000	-2.249296	1.745786
C	1.205074	-1.553546	1.745669
C	1.205074	-0.162046	1.745434
C	0.000000	0.533705	1.745317
C	-1.205074	-0.162046	1.745434
H	-2.140382	-2.093545	1.745760
H	0.000000	-3.329296	1.745968
H	2.140382	-2.093545	1.745760
H	2.140382	0.377955	1.745343
H	0.000000	1.613705	1.745135
H	-2.140382	0.377955	1.745343

*PD_b* top view*PD_b* side view**T_a**

24

T_{a}.nwo

C	0.000000	-1.391500	-2.504600
C	0.000000	1.391500	-2.504600
C	-1.205074	-0.695750	-2.504600
C	1.205074	-0.695750	-2.504600
C	1.205074	0.695750	-2.504600
C	-1.205074	0.695750	-2.504600
H	0.000000	-2.471500	-2.504600
H	0.000000	2.471500	-2.504600
H	-2.140382	-1.235750	-2.504600
H	2.140382	-1.235750	-2.504600
H	2.140382	1.235750	-2.504600
H	-2.140382	1.235750	-2.504600
C	0.000000	0.000000	1.113100
C	1.205074	0.000000	1.808850
C	1.205074	0.000000	3.200350
C	0.000000	0.000000	3.896100
C	-1.205074	0.000000	3.200350
C	-1.205074	0.000000	1.808850
H	0.000000	0.000000	0.033100
H	2.140382	0.000000	1.268850
H	2.140382	0.000000	3.740350
H	0.000000	0.000000	4.976100
H	-2.140382	0.000000	3.740350
H	-2.140382	0.000000	1.268850

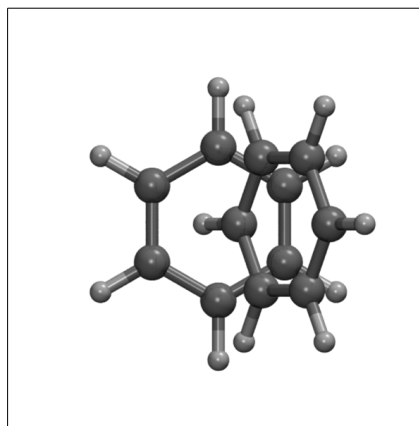
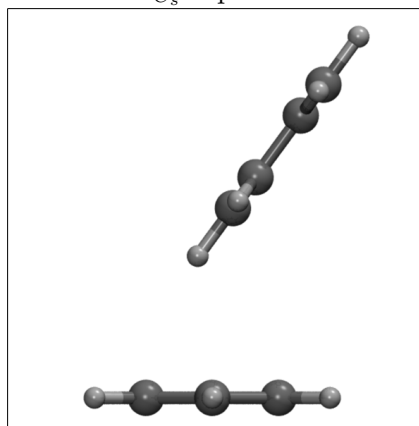
*T_a* top view*T_a* side view

V_{C_s}

24

 $V_{C_s}.nwo$

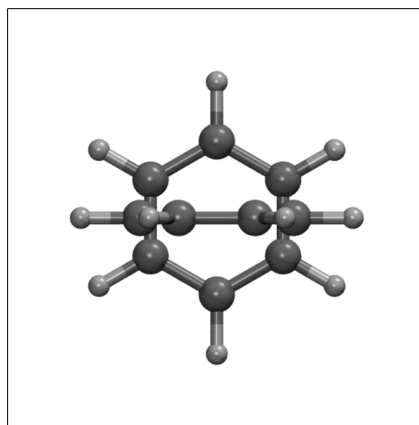
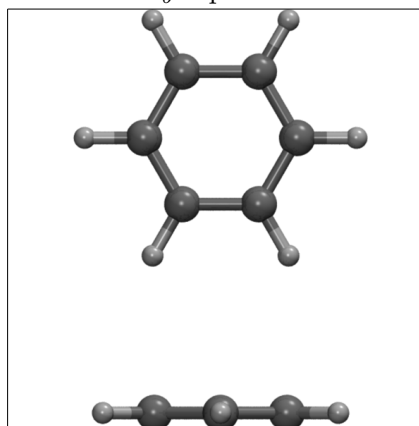
C	0.695750	-0.606319	-2.285238
C	-0.695750	-0.606319	-2.285238
C	1.391500	0.598755	-2.285238
C	-1.391500	0.598755	-2.285238
C	-0.695750	1.803829	-2.285238
C	0.695750	1.803829	-2.285238
H	1.235750	-1.541627	-2.285238
H	-1.235750	-1.541627	-2.285238
H	2.471500	0.598755	-2.285238
H	-2.471500	0.598755	-2.285238
H	-1.235750	2.739137	-2.285238
H	1.235750	2.739137	-2.285238
C	-1.205074	-1.010131	2.846342
C	0.000000	-1.421506	3.407447
C	1.205074	-1.010131	2.846342
C	1.205074	-0.187380	1.724133
C	0.000000	0.223995	1.163028
C	-1.205074	-0.187380	1.724133
H	-2.140382	-1.329416	3.281839
H	0.000000	-2.060076	4.278440
H	2.140382	-1.329416	3.281839
H	2.140382	0.131905	1.288637
H	0.000000	0.862566	0.292036
H	-2.140382	0.131905	1.288637

 V_{C_s} top view V_{C_s} side view T_b

24

 $T_{\{b\}}.nwo$

C	-2.499613	-1.391500	0.000000
C	-2.499613	-0.695750	-1.205074
C	-2.499613	0.695750	-1.205074
C	-2.499613	1.391500	0.000000
C	-2.499613	0.695750	1.205074
C	-2.499613	-0.695750	1.205074
H	-2.499613	-2.471500	0.000000
H	-2.499613	-1.235750	-2.140382
H	-2.499613	1.235750	-2.140382
H	-2.499613	2.471500	0.000000
H	-2.499613	1.235750	2.140382
H	-2.499613	-1.235750	2.140382
C	3.704687	0.000000	-0.695750
C	3.704687	0.000000	0.695750
C	2.499613	0.000000	1.391500
C	1.294539	0.000000	0.695750
C	1.294539	0.000000	-0.695750
C	2.499613	0.000000	-1.391500
H	4.639995	0.000000	-1.235750
H	4.639995	0.000000	1.235750
H	2.499613	0.000000	2.471500
H	0.359231	0.000000	1.235750
H	0.359231	0.000000	-1.235750
H	2.499613	0.000000	-2.471500

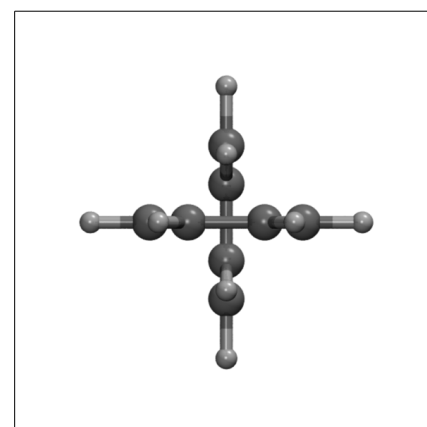
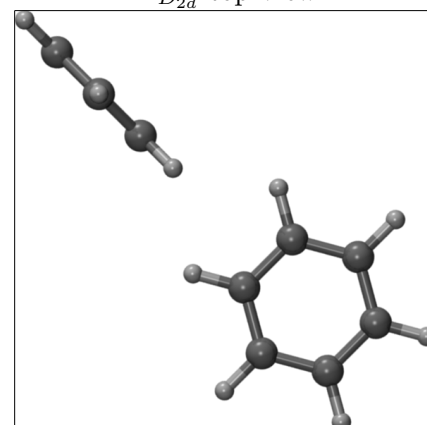
 T_b top view T_b side view

$X_{D_{2d}}$

24

 $X_{d2d.nwo}$

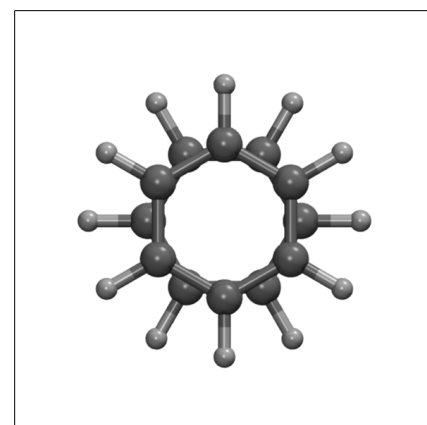
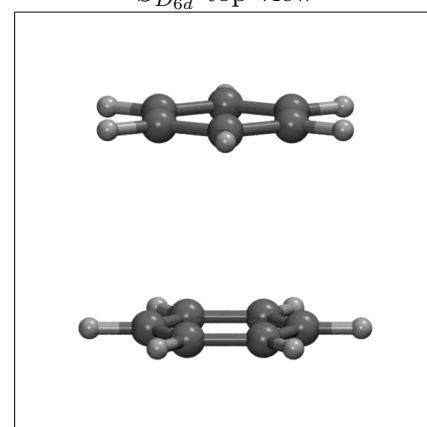
C	-4.251997	0.000000	0.695750
C	-4.251997	0.000000	-0.695750
C	-3.046923	0.000000	-1.391500
C	-1.841849	0.000000	-0.695750
C	-1.841849	0.000000	0.695750
C	-3.046923	0.000000	1.391500
H	-5.187305	0.000000	1.235750
H	-5.187305	0.000000	-1.235750
H	-3.046923	0.000000	-2.471500
H	-0.906541	0.000000	-1.235750
H	-0.906541	0.000000	1.235750
H	-3.046923	0.000000	2.471500
C	4.251998	-0.695750	0.000000
C	4.251998	0.695750	0.000000
C	3.046923	1.391500	0.000000
C	1.841849	0.695750	0.000000
C	1.841849	-0.695750	0.000000
C	3.046923	-1.391500	0.000000
H	5.187305	-1.235750	0.000000
H	5.187305	1.235750	0.000000
H	3.046923	2.471500	0.000000
H	0.906542	1.235750	0.000000
H	0.906542	-1.235750	0.000000
H	3.046923	-2.471500	0.000000

 $X_{D_{2d}}$ top view $X_{D_{2d}}$ side view $S_{D_{6d}}$

24

 $S_{d6d.nwo}$

C	1.391500	0.000000	-1.936483
C	0.695750	1.205074	-1.936483
C	-0.695750	1.205074	-1.936483
C	-1.391500	0.000000	-1.936483
C	-0.695750	-1.205074	-1.936483
C	0.695750	-1.205074	-1.936483
H	2.471500	0.000000	-1.936483
H	1.235750	2.140382	-1.936483
H	-1.235750	2.140382	-1.936483
H	-2.471500	0.000000	-1.936483
H	-1.235750	-2.140382	-1.936483
H	1.235750	-2.140382	-1.936483
C	1.205074	0.695750	1.936483
C	1.205074	-0.695750	1.936483
C	0.000000	-1.391500	1.936483
C	-1.205074	-0.695750	1.936483
C	-1.205074	0.695750	1.936483
C	0.000000	1.391500	1.936483
H	2.140382	1.235750	1.936483
H	2.140382	-1.235750	1.936483
H	0.000000	-2.471500	1.936483
H	-2.140382	-1.235750	1.936483
H	-2.140382	1.235750	1.936483
H	0.000000	2.471500	1.936483

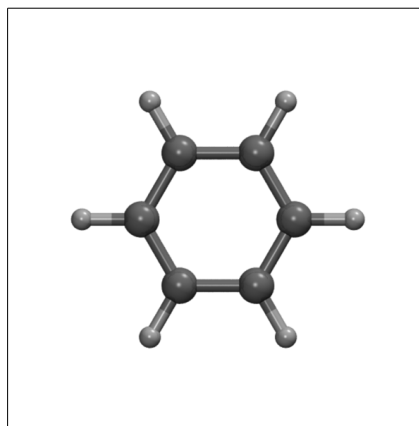
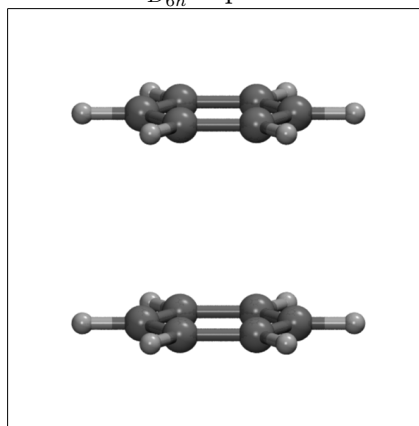
 $S_{D_{6d}}$ top view $S_{D_{6d}}$ side view

$S_{D_{6h}}$

24

S_d6h.nwo

C	1.391500	0.000000	-1.936672
C	0.695750	1.205074	-1.936672
C	-0.695750	1.205074	-1.936672
C	-1.391500	0.000000	-1.936672
C	-0.695750	-1.205074	-1.936672
C	0.695750	-1.205074	-1.936672
H	2.471500	0.000000	-1.936672
H	1.235750	2.140382	-1.936672
H	-1.235750	2.140382	-1.936672
H	-2.471500	0.000000	-1.936672
H	-1.235750	-2.140382	-1.936672
H	1.235750	-2.140382	-1.936672
C	1.391500	0.000000	1.936672
C	0.695750	-1.205074	1.936672
C	-0.695750	-1.205074	1.936672
C	-1.391500	0.000000	1.936672
C	-0.695750	1.205074	1.936672
C	0.695750	1.205074	1.936672
H	2.471500	0.000000	1.936672
H	1.235750	-2.140382	1.936672
H	-1.235750	-2.140382	1.936672
H	-2.471500	0.000000	1.936672
H	-1.235750	2.140382	1.936672
H	1.235750	2.140382	1.936672

 $S_{D_{6h}}$ top view $S_{D_{6h}}$ side view

Appendix B

Structures of other complexes with benzene

The structures of protonated benzene dimer conformations are shown on Figure B.1. The structures of benzene complexes with indole and imidazole are shown on Figure B.2.

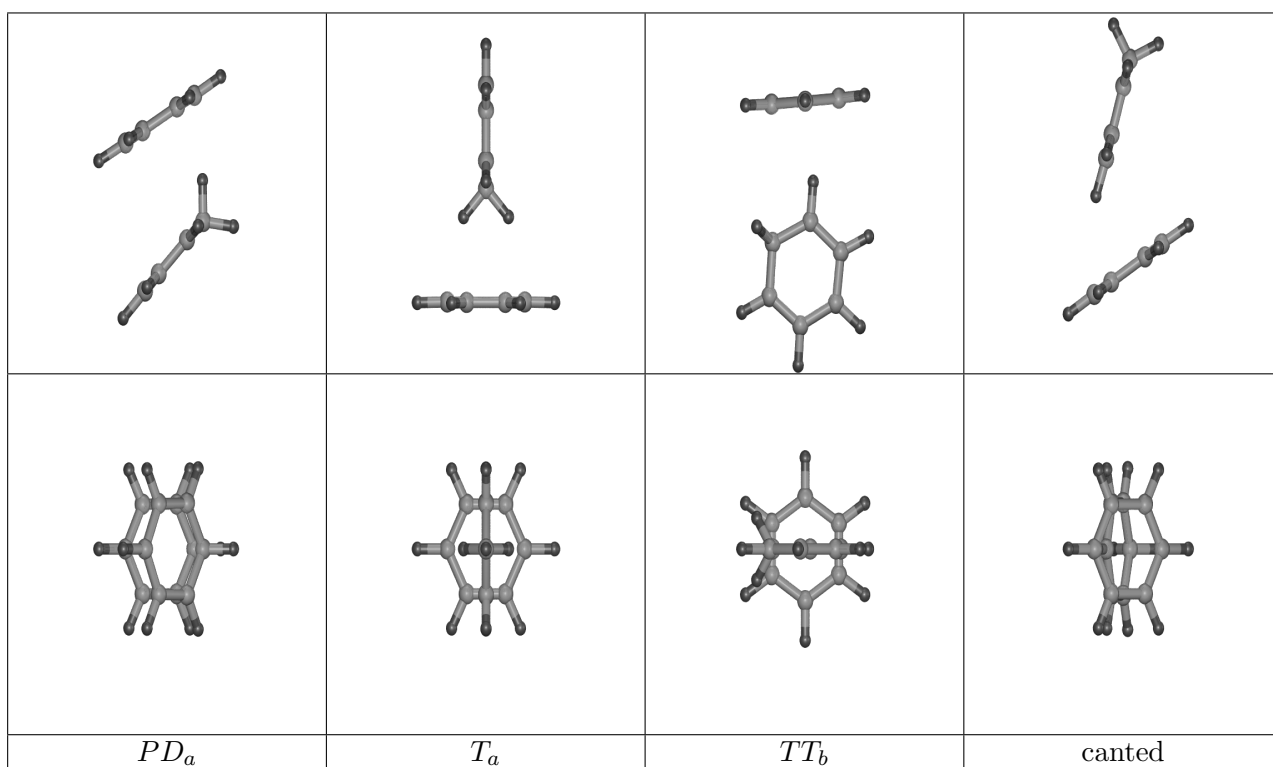


FIGURE B.1: The conformations of protonated benzene dimer complexes.

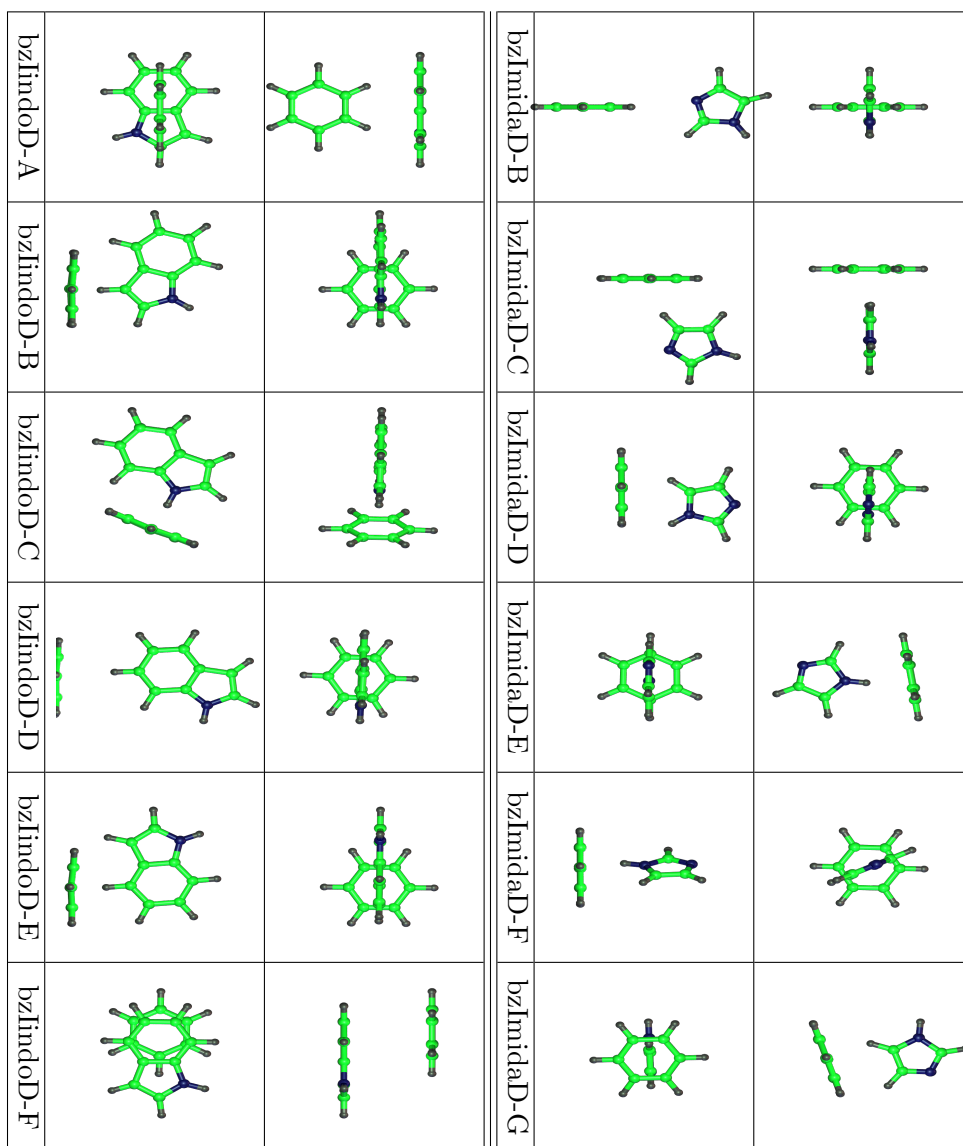


FIGURE B.2: The conformations of benzene complexes with imidazole and indol.

Appendix C

Semiempirical Methods and Molecular Mechanics methods

Tables C.1 and C.2 present the results obtained from all methods investigated. Figures C.1 and C.2 shows the result obtained for potential energy surfaces. Two measurements of accuracy are included: root mean square of correctly reproduced conformations (*RMS* ok) and all conformations (*RMS* all). In the case of the MM3 force field there is an option to mark atoms as part of a π -system. The Allinger MM force fields use this information to set up an MO calculation used to scale bond and torsion parameters involving π -system atoms. The RF-MM3 force field presented here was obtained using pisystem, but was tested with and without it.

TABLE C.1: The ΔBE and $RMSD$ of investigated molecular mechanics methods.

conf.	ΔBE										BE CCSD(T)
	CHARMM	OPLS	RF-OPLS	AMOEBA	MM3	π RF-MM3	RF-MM3	MM2	MMFF	DANG	
PD_a	-0.53	-0.62	-0.22	0.06	-0.22	-0.43	-0.37	1.04	22.53	-0.51	-2.73
TT_b	-0.54	-0.51	-0.17	-0.21	-0.86	-0.46	-0.39	-0.88	22.47	-0.35	-2.82
TT_a	-0.54	-0.51	-0.16	-0.19	-0.85	-0.44	-0.38	-0.88	22.48	-0.35	-2.80
PD_b	-0.43	-0.46	-0.22	0.04	-0.22	-0.42	-0.36	1.07	22.53	-0.50	-2.72
T_a	-0.60	-0.55	-0.14	-0.55	-0.92	-0.41	-0.36	-1.06	22.45	-0.36	-2.70
V_{C_s}	-0.45	-0.48	-0.15	0.02	-0.24	-0.43	-0.37	1.05	22.55	-0.34	-2.74
T_b	-0.19	-0.16	0.20	0.19	-0.45	-0.04	0.02	-0.48	22.86	-0.03	-2.40
$X_{D_{2d}}$	-0.39	-0.38	-0.30	-0.73	-0.78	-0.38	-0.34	-0.53	22.58	-0.47	-1.79
$S_{D_{6d}}$	0.09	-0.01	0.63	0.37	0.66	0.48	0.56	2.08	22.58	-0.83	-1.71
$S_{D_{6h}}$	0.08	-0.02	0.62	0.33	0.64	0.48	0.55	2.06	22.58	-0.84	-1.71
(ΔBE) all	0.43	0.43	0.33	0.35	0.64	0.42	0.40	1.23	22.56	0.51	
(ΔBE) ok	0.43	0.42	0.33	0.37	0.67	0.42	0.40	1.30	22.56	0.51	
conf.	$RMSD$										
	CHARMM	OPLS	RF-OPLS	AMOEBA	MM3	π RF-MM3	RF-MM3	MM2	MMFF	DANG	
PD_a	0.40	0.41	0.07	0.05	0.01	0.05	0.07	S_{D_{6h}}	0.76	0.71	
TT_b	0.12	0.09	0.05	0.19	0.15	0.07	0.17	0.13	0.24	0.08	
TT_a	0.11	0.09	0.05	0.22	0.16	0.07	0.18	0.16	0.24	0.07	
PD_b	V_{C_s}	v_{c_s}	0.07	0.06	0.01	0.05	0.07	S_{D_{6d}}	0.79	0.75	
T_a	0.07	0.05	0.03	0.07	0.09	0.05	0.08	0.08	0.22	0.07	
V_{C_s}	0.29	0.15	0.05	PD_b	PD_b	0.01	0.05	S_{D_{6d}}	0.39	0.14	
T_b	0.03	0.02	0.05	0.01	0.04	0.08	0.11	0.05	0.16	0.04	
$X_{D_{2d}}$	0.06	0.05	0.02	0.12	0.19	0.04	0.10	0.12	0.22	0.09	
$S_{D_{6d}}$	0.06	0.06	0.06	0.15	0.13	0.06	0.07	0.23	0.09	0.03	
$S_{D_{6h}}$	0.06	0.06	0.06	0.14	0.12	0.06	0.07	0.23	0.09	0.03	
$(RMSD)$ all	0.29	0.29	0.05	0.28	0.24	0.06	0.11	0.41	0.40	0.33	
$(RMSD)$ ok	0.18	0.16	0.05	0.13	0.12	0.06	0.11	0.16	0.40	0.33	

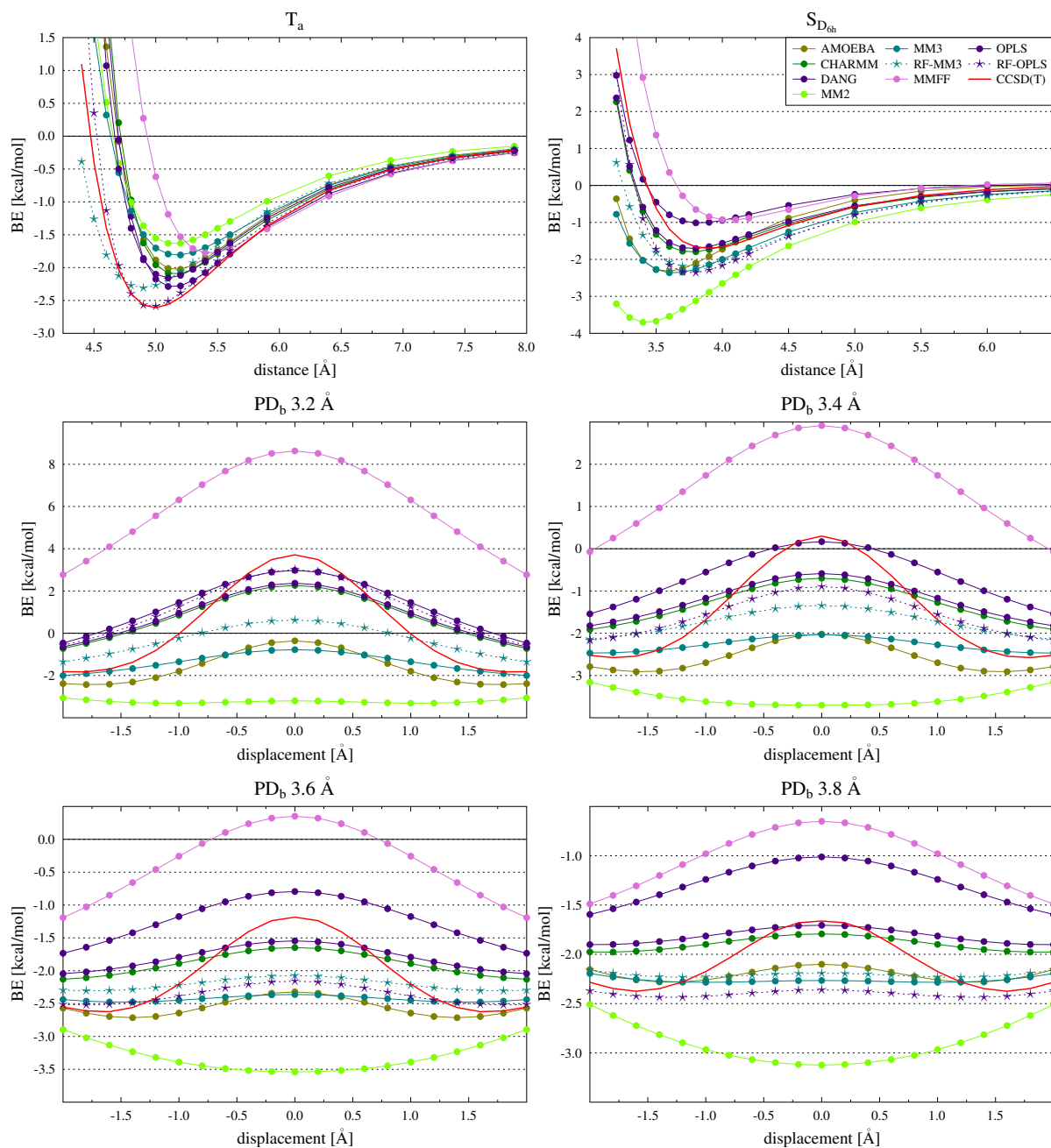


FIGURE C.1: The binding energy (BE [kcal/mol]) of various benzene dimer scans. For the T_a and $S_{D_{6h}}$ conformations center of mass distance is used, for PD_b conformations it indicates the displacement of the benzenes. The molecular mechanics methods.

TABLE C.2: The ΔBE and $RMSD$ of investigated semiempirical methods.

conf.	ΔBE							$BE_{CCSD(T)}$
	PM6	PM6-DH+	PM6-DH2	AM1	RM1	MNDO	PM7	
PD_a	-2.17	0.88	0.88	-2.82	-2.83	-2.75	2.09	-2.73
TT_b	-1.96	0.02	0.02	-2.76	-2.48	-2.81	0.53	-2.82
TT_a	-1.95	0.03	0.03	-2.73	-2.51	-2.79	0.54	-2.80
PD_b	-2.08	0.88	0.88	-2.86	-2.81	-2.73	2.11	-2.72
T_a	-1.90	-0.09	-0.09	-2.61	-2.41	-2.69	0.62	-2.70
V_{C_s}	-1.94	0.86	0.86	-2.65	-2.50	-2.74	2.09	-2.74
T_b	-1.57	0.44	0.44	-2.32	-2.19	-2.39	0.93	-2.40
$X_{D_{2d}}$	-1.33	-0.32	-0.32	-1.50	-1.55	-1.79	-0.04	-1.79
$S_{D_{6d}}$	-2.03	1.77	1.77	-1.84	-1.81	-1.73	3.12	-1.71
$S_{D_{6h}}$	-2.03	1.75	1.75	-1.81	-1.78	-1.73	3.11	-1.71
$RMS(\Delta BE)$ all	1.91	0.94	0.94	2.44	2.33	2.46	1.86	
$RMS(\Delta BE)$ ok	1.89	1.00	1.00	2.44	2.30	2.46	1.74	
conf.	$RMSD$							
	PM6	PM6-DH+	PM6-DH2	AM1	RM1	MNDO	PM7	
PD_a	0.84	0.16	0.16	1.27	0.84	1.28	S_{D_{6h}}	
TT_b	0.08	0.23	0.23	0.92	0.79	1.31	0.15	
TT_a	0.06	T_{b,par}	T_{b,par}	0.91	T_{a,par}	1.32	0.13	
PD_b	V	0.19	0.19	1.05	1.04	1.60	S_{D_{6d}}	
T_a	0.01	0.07	0.07	0.80	0.02	1.20	0.07	
V_{C_s}	T_{a,per}	PD_b	PD_b	1.02	0.49	1.07	S_{D_{6d}}	
T_b	0.07	0.11	0.11	0.78	0.02	1.19	0.12	
$X_{D_{2d}}$	0.02	0.02	0.02	0.02	0.09	1.40	0.02	
$S_{D_{6d}}$	0.14	0.19	0.19	1.06	0.86	1.07	0.06	
$S_{D_{6h}}$	0.15	0.19	0.19	1.27	1.16	1.30	0.06	
$RMS(RMSD)$ all	0.43	0.31	0.31	0.97	0.69	1.28	0.37	
$RMS(RMSD)$ ok	0.31	0.16	0.16	0.97	0.73	1.28	0.10	

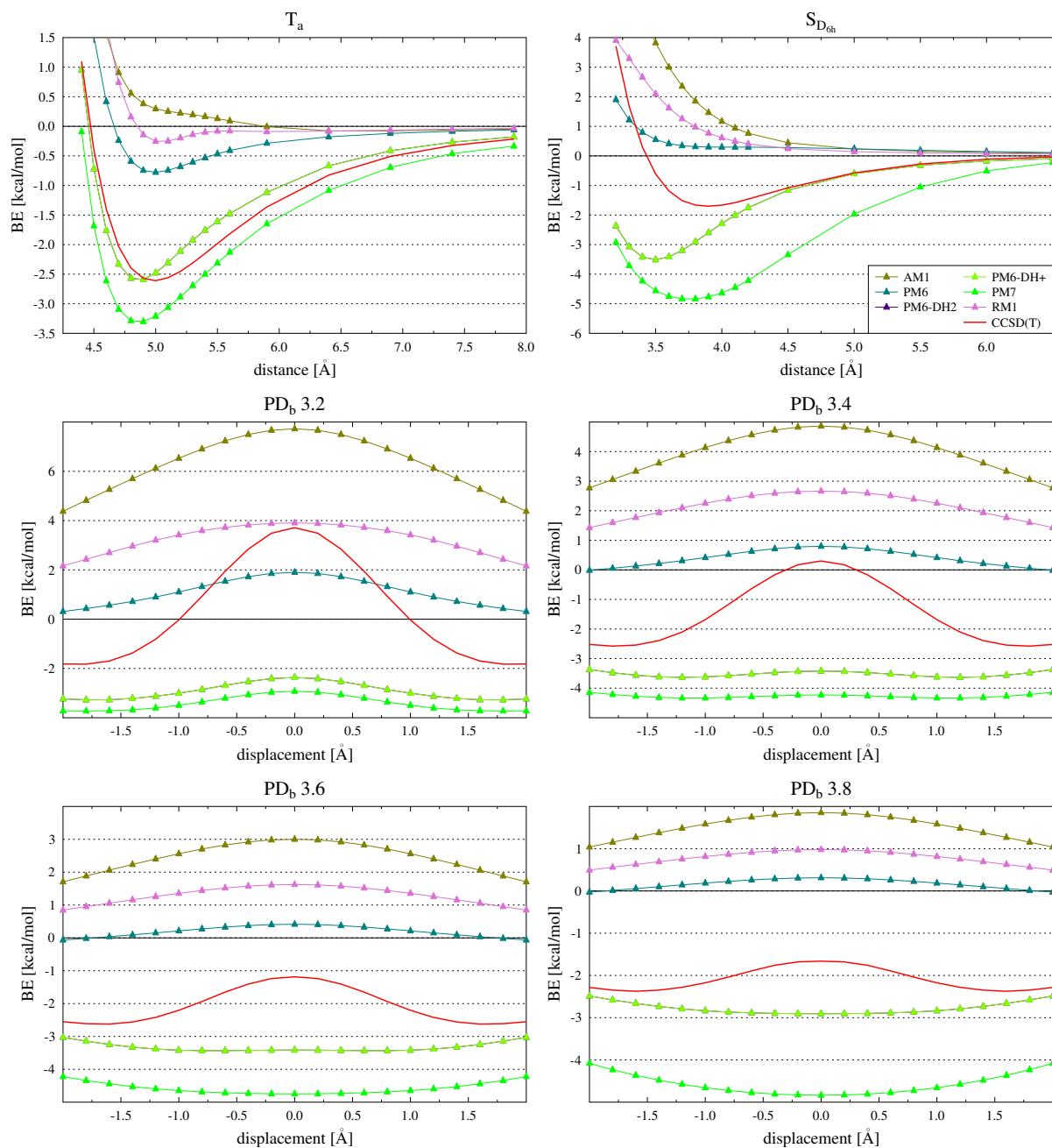


FIGURE C.2: The binding energy (BE [kcal/mol]) of various benzene dimer scans. For the T_a and $S_{D_{6h}}$ conformations center of mass distance is used, for PD_b conformations it indicates the displacement of the benzenes. The semiempirical methods.

Appendix D

Complexes with Fullerenes

D.1 Buckyball with Benzene

Figure D.2 presents the motion of scan from nT to T conformation. Figure D.3 shows the results of that scan. The AMOEBA, OPLS and RF-OPLS force fields are nonbonding for T

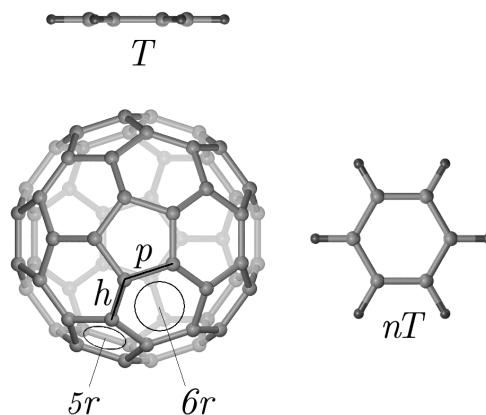


FIGURE D.1: The general structure of the C_{60} fullerene and its complexes: p and h are distinct fullerene bonds, the $5r$ and $6r$ are respectively the five and the six members rings; in the T conformation, benzene is parallel to local fullerene curvature and in nT it is perpendicular.

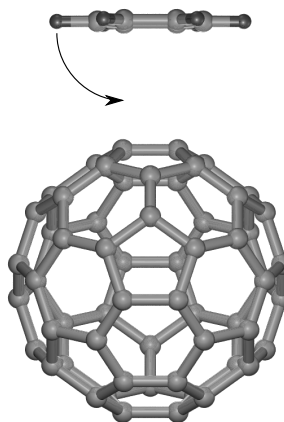


FIGURE D.2: The motion of $T - nT$ scan

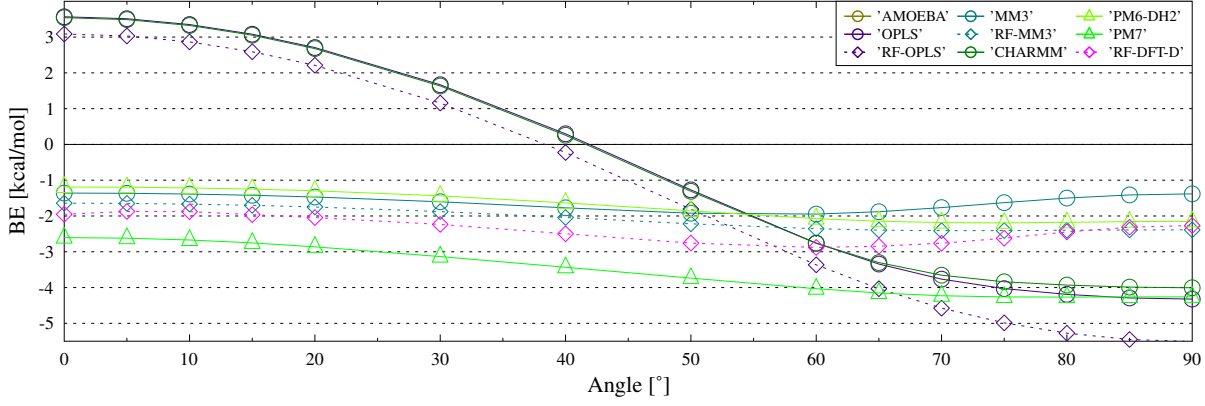


FIGURE D.3: The binding energy (BE [kcal/mol]) of the C_{60} -benzene scan. The angle corresponds to rotation of the benzene from T to nT conformation. The AMOEBA force fields is not shown because of convergence problems.

conformation, and bonded for the nT , with the difference of about 8 kcal/mol.

D.2 Buckyball with Pyrene

The binding energies of RF-6/6-31G methods are shown in Table D.1. I did not find any literature data for such complex. As may be expected the BE of the T conformation is larger in magnitude than that of nT ones. The variation between various T conformations is around 1 kcal/mol – similar to the case of C_{60} - C_6H_6 complex from the same method.

TABLE D.1: The RF-6/6-31G results of C_{60} -pyrene complexes at various conformations. All values are in kcal/mol.

conformation	E_{dft}	E_{disp}	BE
T -5r-par	2.961	-13.876	-10.915
T -6r-par	2.972	-14.084	-11.112
T -6r-per	3.088	-14.485	-11.397
T -at-ant-p	3.077	-14.476	-11.399
T -h-par	3.004	-13.968	-10.964
T -p-par	2.962	-13.895	-10.933
nT -5r-2-h	0.542	-4.483	-3.940
nT -5r-3-ant-h	0.651	-4.910	-4.259
nT -5r-ant-h	0.727	-4.693	-3.967
nT -6r-4-per	0.389	-4.712	-4.323
nT -at-3-ant-p	0.594	-4.790	-4.196
nT -h-1-per	0.071	-2.941	-2.870
nT -h-2-par	0.382	-4.245	-3.863
nT -h-3-par	0.403	-4.543	-4.140
nT -h-4-par	0.250	-4.452	-4.202
nT -h-per	0.676	-4.864	-4.188

D.3 Buckyball with Tetraphenylporphyrin

The binding energies of RF-6/6-31G methods are shown in Table D.2 (these conformations are shown on Figure D.4). The BE from the literature varies from -50 to 10 kcal/mol (*e.g.* Jung

and Head-Gordon [1]). As in the case of the C_{60} -benzene, in some conformations presented, obtained BE is highly positive.

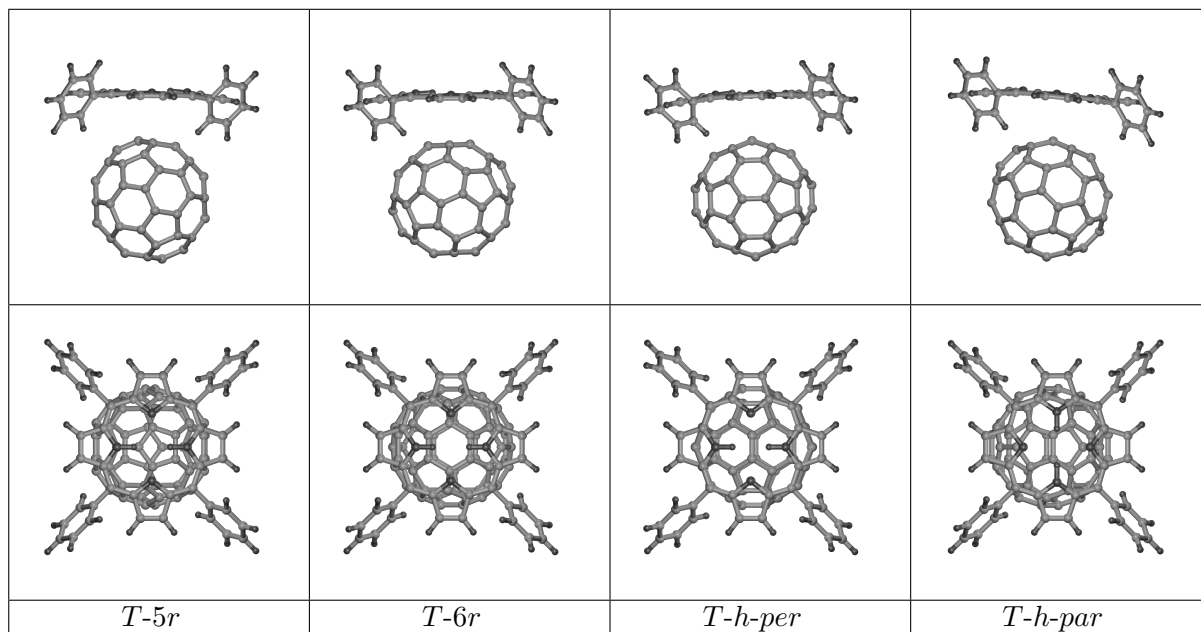


FIGURE D.4: Conformations of the C_{60} -TPP complexes.

TABLE D.2: The RF-6/6-31G results of C_{60} -Tetraphenylporphyrin complexes at various conformations. All values are in kcal/mol.

conformation	E_{dft}	E_{disp}	BE
<i>T-5r</i>	70.110	-28.210	41.900
<i>T-6r-per</i>	69.756	-30.086	39.671
<i>T-h-per</i>	5.692	-31.110	-25.417
<i>T-p-par</i>	5.437	-30.427	-24.990

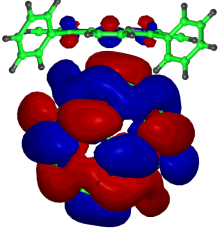
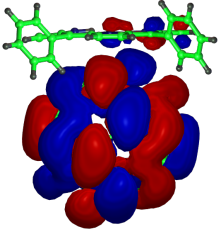
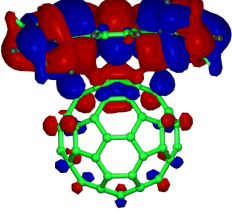
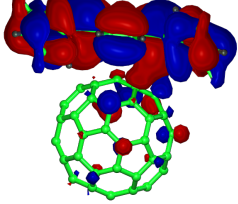
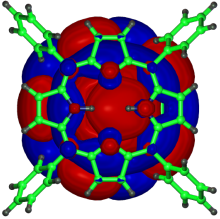
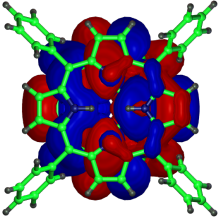
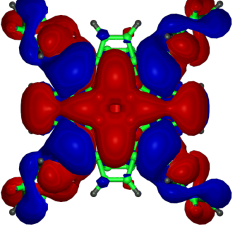
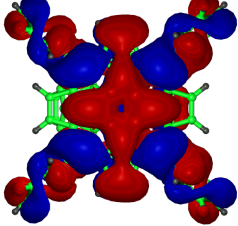
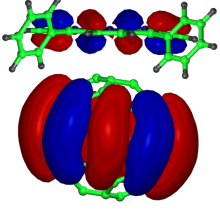
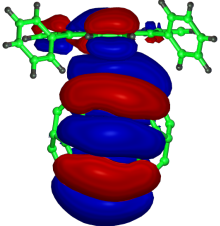
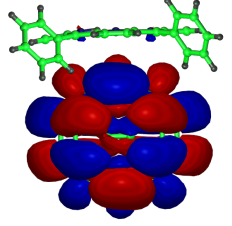
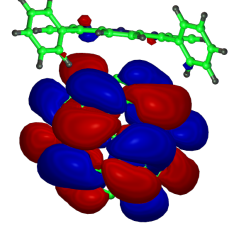
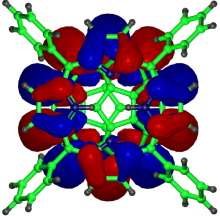
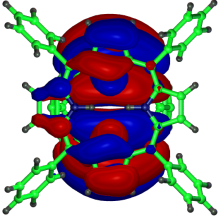
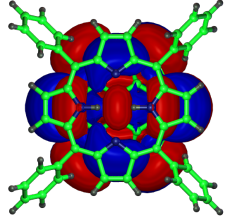
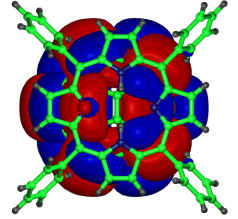
<i>T-5r</i>	<i>T-6r</i>	<i>T-h-per</i>	<i>T-h-par</i>
BE [kcal/mol]			
41.90	39.67	-25.42	-24.99
HOMO			
			
			
LUMO			
			
			

FIGURE D.5: HOMO and LUMO orbitals of the C_{60} -TPP complexes.

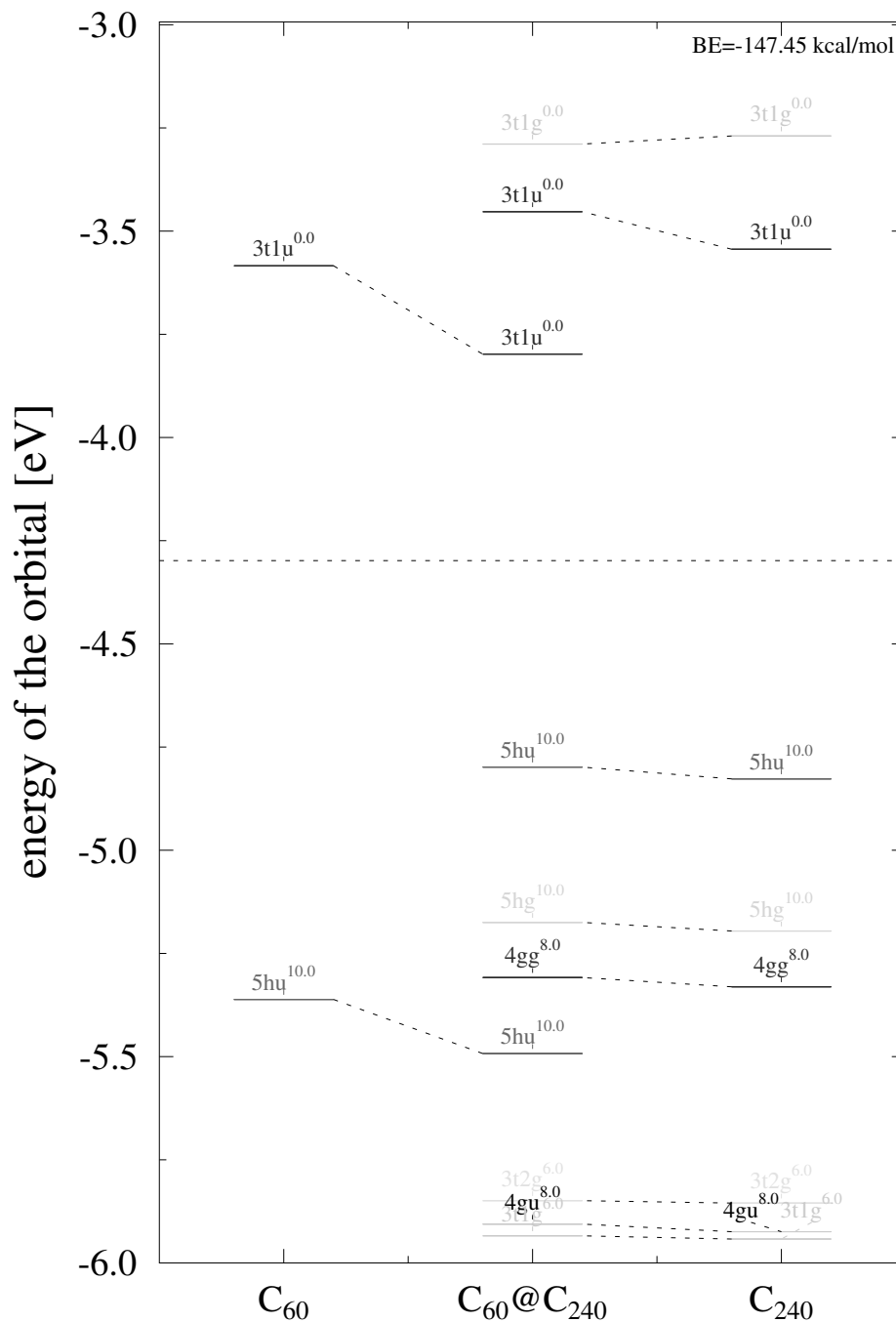
D.4 $C_{60}@C_{240}$

The RF-6/6-31G method was used for a complex in which the Buckminsterfullerene is encapsulated by the C_{240} . Grimme et al. [2] have shown that the complex with D_{5d} symmetry is the global minima and – the BE of the complex with the I_H symmetry is smaller. All molecular mechanics method investigated predicted the structure with the I_H symmetry as the minimum. The binding energies obtained from RF method confirmed that (see Table D.3), and are well within the range given by the literature (from -184 to 51 kcal/mol, see [2]).

Interestingly, the HOMO orbital is located on the outer shell and LUMO is on the inner shell (see Figures D.6 and D.7).

TABLE D.3: The energies of $C_{60}@C_{240}$ complex obtained from RF-6/6-31G method.

symmetry	E_{dft}	E_{disp}	BE
I_h	49.020	-196.470	-147.450
D_5	47.350	-196.030	-148.670

FIGURE D.6: The orbital diagram of $C_{60}@C_{240}$ complex with I_H symmetry. Data from RF-6/6-31G method. The first number indicate the degeneration of the orbital followed by its symmetry, the superscript indicate the occupation.

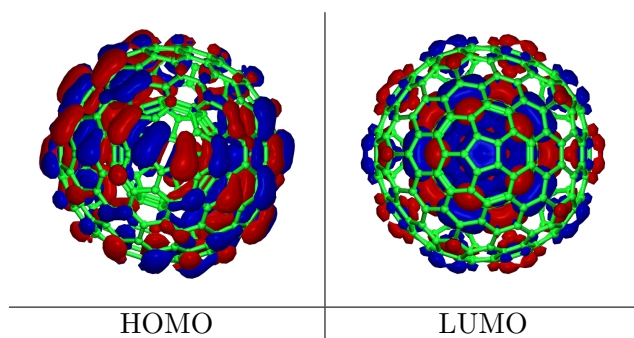


FIGURE D.7: An example of HOMO and LUMO orbitals of the $C_{60}@C_{240}$ complex.

Bibliography

- [1] Yousung Jung and Martin Head-Gordon. A fast correlated electronic structure method for computing interaction energies of large van der waals complexes applied to the fullerene–porphyrin dimer. *Phys. Chem. Chem. Phys.*, 8(24):2831–2840, May 2006. doi: 10.1039/B602438F. URL <http://pubs.rsc.org/en/Content/ArticleLanding/2006/CP/b602438f>.
- [2] Stefan Grimme, Christian Mück-Lichtenfeld, and Jens Antony. Noncovalent interactions between graphene sheets and in multishell (Hyper)Fullerenes. *The Journal of Physical Chemistry C*, 111(30):11199–11207, 2007. doi: 10.1021/jp0720791. URL <http://dx.doi.org/10.1021/jp0720791>.