A comparative study of DFT/LDA with higher levels of theory on π-π interactions:

A typical case for the benzene dimer

A. Yaya[1], E. K. Tiburu[2], B. Onwona-Agyeman[3], D. Dodoo-Arhin[4] and J.K. Efavi[5]

Abstract

The description of the interactions involving species that have π-π configuration presents a real challenge in utilizing theoretical calculations. The problem arises from the kind of theoretical approaches employed to describe the nature of these non-covalent interactions. Various workers have described the interactions purely as Van der Waals, whilst others consider it as a competition between many other

[1] Department of Materials Science & Engineering, University of Ghana, Ghana, P.O Box LG 77 Legon. E-mail: ayaya@ug.edu.gh
[2] Department of Biomedical Engineering, University of Ghana, Ghana, P.O Box LG 77 Legon. E-mail: etiburu@ug.edu.gh
[3] Department of Materials Science & Engineering, University of Ghana, Ghana, P.O Box LG 77 Legon. E-mail: boagyeman@ug.edu.gh
[4] Department of Materials Science & Engineering, University of Ghana, Ghana, P.O Box LG 77 Legon. E-mail: ddodoo-arhin@ug.edu.gh
[5] Department of Materials Science & Engineering, University of Ghana, Ghana, P.O Box LG 77 Legon. E-mail: jkefavi@ug.edu.gh

forces. Present approaches describing these interaction effects are computationally expensive. We report a pseudopotential base density functional theory (DFT) calculations within the local density approximation (LDA) and compared our results with other higher theories describing the π-π stacking interactions. By using benzene dimer as a prototype species, we find that, DFT/LDA compares favourably well with other descriptions as a reliable alternative method.

Keywords: AIMPRO; CCSDT;MP; DFT/LDA and Pi-Pi interactions

1   Introduction

The benzene dimer has been widely studied as a prototype for understanding non-covalent bonding of π-π interactions, both theoretically and experimentally [1-4].

Theoretical and experimental studies suggest two minima on the potential energy surface for the benzene dimer: (i) parallel-displaced (PD), (ii) T-shaped (T) configurations, which are usually observed in crystal structures of simple aromatic compounds, with the T-shaped being the most dominant and the highest energy transitional structure, (iii) parallel-stacked (PS) (see Figure 1) [5, 6].

Although the benzene dimer can adopt a wider range of different relative configurations, only the three prototype structures mentioned above are critical in the understanding of π-π interactions.

The first theoretical studies on the benzene dimer using high levels of electronic structure theory such as couple-cluster theory CCSD(T) with corrections for basis set effects used for giving insights on prototype systems were done by Sinnokrot el al.[3] and Tsuzuki with co-workers [1]. This study was very instrumental in revealing mistakes made earlier by wrongly assuming that the (T-) shaped dimer was more stable energetically than the (PD) orientation. Rather, the

two configurations were found to be nearly isoenergetic.

The small binding energy for the benzene gas-phase dimer (~2-3 kcal mol-1) and the depth of its potential energy surface makes it highly challenging both experimentally and theoretically. The dimer is stable at low temperature and low pressure and is prepared in supersonic jet expansions into a vacuum. Due to the sizes and shapes of the various clusters produced, it is relevant to use detection techniques that are very sensitive to their masses. This makes it difficult to describe them in experiment. Also, the diverse experimental methods employed have often resulted in controversies in results and only matches if there are at least two separate low-energy potential minima or if the system is highly continuous with low barriers [2]. Work on beam electric resonance studies by Klemperer et al [14, 20], on the gas-phase dimer gave evidence for a T-shaped configuration with C_{2v} symmetry. Studies by Arunan and Gustowsky [21] on gas-phase benzene dimer using microwave spectroscopy reported the separation distance for the T-shape configuration as 4.96 Å. Also, an extensive study on benzene dimer and isotopomers by applying mass selective, ionization-detected simulated Raman spectroscopy (IDSRS) was done by Henson el al [22]. Their results showed that the T-shape geometry for the benzene dimer was dominant.

The existence of other configurations such as the parallel displaced and parallel-stacked was not ruled out since the methods used were only sensitive to dipole moments of molecules and these two configurations have no dipole moments. In fact, hole-burning spectroscopy suggests the existence of more than one isomers of the benzene dimer [23]. Further studies on the intermolecular vibrations of the benzene dimer by Felker and co-workers [24, 25] were consistent with a dimer which is composed of a monomer and not related by a symmetry element as is the case with the T-shaped geometry. The existence of parallel-displaced with C_{2h} symmetry was supported by optical absorption spectroscopy measurements by Bernstein et al. [26]. Using the experimental dissociation energy of the ions and the ionization potentials of the benzene dimer

and monomer, Grover et al., [27] and Krause et al., [28] gave the values of 2.4 ±
0.4 and 1.6 ± 0.2 kcal mol^{-1} respectively as the binding energies of the dimer.
Consequently, quantum mechanical studies has become pre-eminent in the study
of interactions involving π-π bonding. Higher order wave function methods such
as couple-cluster theory through the use of perturbative triples, CCSD (T), with
large basis sets [1, 29, 30], are known to reach a good level of accuracy. However,
the computational cost is too demanding: time scales to about O(N ^{7}), where N is
the number of atoms in the system. Less expensive methods such as
Møller-Plesset perturbation (MP2) can also become expensive when a large basis
function is taken into consideration. Also, they lead to overestimation of the
electron correlation effects that are inherent in pure π-π interactions [31]. These
then also leave problems for the theoretical understanding of larger systems
containing π-π stacking interactions, which are still not fully understood [29, 32].
Nonetheless, current theoretical chemistry literature suggests that, the high level of
electronic structure theory used by Sinnokrot et al [2] and Tsuzuki et al [1] gives
an accurate model of π-stacking interactions. However, the computational cost
means it cannot be applied to many of the larger systems such as
polymer-nanotube and polymer-graphene interactions. Therefore a simpler and
computationally less demanding approach is needed. One of the theoretical means
for understanding larger π-π systems is through the use of a density functional
technique which scales much less critically with basis set size than the advanced
wave functional methods.

In this paper, we explore non-covalent interactions such as π-π stacking by
the use of DFT/LDA methods for which the Benzene dimer is employed as a
prototype for π-π interactions. For the purpose, we examine to what extent a
simpler exchange-correlation functional such the LDA can successfully reproduce
the effects of the π-π interactions.

2   Methods

In our present calculations we use the Ab initio modeling package (AIMPRO) which is based on density functional approximation. Localized Gaussian basis sets with 38 functions per carbon and 16 per hydrogen were used, with Hartwigsen, Geodecker and Hütter relativistic pseudopotentials [33]. A Fermi temperature smearing for the electron population of kT=0.04eV was incorporated to improve the convergence. Two carbon basis sets were used – either 22 or 38 independent Gaussian basis functions.

Benzene was fully geometrically optimized. Single point energies were obtained for the benzene dimer in three different configurations (T-shaped, parallel-displaced and parallel-stacked) by initially optimizing the equilibrium geometry of a single benzene molecule and then systematically varying the distance between the center of mass of the two benzene monomers (denoted by R_1 in Figure 1), while the monomer geometries were kept rigid.

3   Results and Discussions

Accurate ab initio calculations of the benzene dimer necessitate both the use of an extensive basis set with diffuse functions and high levels of dynamic correlation in order to predict binding energies on the potential energy curves which are comparable to the CCSD (T) level of theory, which can then be used for calibrating other methods and for modeling π-π systems.

As shown in Figure 1, there are three stacking arrangements of the benzene dimer. Figure 1(i) represents the parallel stack, Figure 1(ii) displays the T-shaped and finally Figure 1(iii) represents the parallel-displaced stack. When the benzene dimer is parallel AA-stacked (R=0) (i), there is repulsive interaction due to the shorter distance between the benzene rings and as a result the main contribution to the total energy becomes positive exchange repulsion as shown in Figure 2. The

repulsive energy is primarily offset by the dispersion interaction, giving net total attraction energy of around -2.1 kcal/mol (see Figure 2). The electrostatic effects and inductive effects are relatively small and constant with lateral displacement of the two benzene rings. As the top benzene is laterally displaced away from the "AA" structure to the equilibrium "AB" structure (R ≈3.2 Bohr), the exchange repulsion drops significantly thereby reducing the binding dispersion.

According to Grimme [34], the dispersion component term is made up of two main components; an orbital-dependent part responsible for the π-stacking effects (PSE) which dominates at short intermolecular distances and a non-orbital dependent part which actually weakly counters the PSE and mainly dominates at larger intermolecular distances.

In this work, local density approximation techniques were used to validate results. In Figure 3, our calculated single point energies for the three different configurations shown in Figure 1, were compared with Lennard-Jones (LJ) best fit potential energy curve [35]. Figure 3(a) represents the parallel stack configurations. In the parallel stack (PS), there is no visible dipole correlation between the LJ curve (green) and LDA curve (red), and resulted in poor correlation to the LJ curve in the region around the minimum as well as the long-range dispersion interactions. It can be seen from (Figure 3b) that for the T-shape dimer, the LJ fit (green) passes through the minimum of the LDA (red) curve. This is due to the presence of dipole moments in this dimer, whose interaction our method is able to describe very well. As one moves away from the minimum, the long-range effects such as dispersion forces dominate which we were unable to capture. Finally, in Figure 3(c), (i.e., PD), we were able to identify very weak dipole interaction around the equilibrium distance, however as already discussed for the other dimer configurations, our method could not capture the long-range dispersive forces that characterizes these dimers.

For systems involving π-π interactions, the electrostatic interaction controls the geometry systems and orbital-dependent dispersion. The π-π interactions does

not, however, include classical (atom pairwise) dispersion and Van der Waal (vdW) forces. Although the addition of the vdW interactions is important, its contribution to the net interaction energy is very small [20, 36]. This approximation will not affect the structural integrity of the dimer but can influence the overall energy. The later caveat justifies DFT/LDA approach to quantify the vdW. Tables (1 & 2) give the binding energies for our single point analysis for the benzene dimer and the minimum lattice separations in comparison to other highly correlated methods. Our method compares favourably well with other methods such as MP2 and DF-LMP2, which are known to best describe non-covalent interactions [2, 37].

Although our binding energy estimations for the different dimer configurations are slightly overestimated (which is intrinsic in DFT/LDA) in comparison to the most highly efficient dispersion method to date, CCSD (T), it is still within reasonable margin of error. Though dispersion corrected function was not included in our calculation, our interlayer separations are in good agreement with the other methods.

In order to compare our dispersion estimates with other methods, we undertook to measure the binding energies and interlayer separations of our dimer in different stacking arrangements. In Figure 4(a, c), it can be seen that, our approach does better than the other dispersion corrected wave function methods such as MP2 and DF-LMP2. This is because the method is able to describe the minimum interactions energy and the distance of separation for PS and PD configuration by taking the CCSD(T) value as the standard reference method. Similarly, for the T-shaped dimer as shown in Figure 4(b), our method gave rather higher binding energy (indicated in black) as compared to the other methods near the equilibrium distance and this is attributed to the overestimation of binding energies by LDA. Figure 4(d) shows energy profile and interlayer separation for GGA in comparison to CCSD(T), vdW-DF and MP2. Clearly the GGA approach is not good for treating systems of this nature since it does not predict any binding.

Therefore the addition of vdW to the GGA should improve the binding considerably. In contrary, our LDA approach gives attractive binding for the different benzene dimer configurations and supports the results obtained from other correlated methods such as CCSD (T), MP2 and DF-LMP2. In addition, the LDA is also known to perform much better in interactions with systems involving sp^2-like materials, such as graphite [39, 40]. Theoretical studies by Tournus et al. [41], showed that, LDA is able to describe the interactions between benzene and carbon nanotube better than GGA, which is also governed by non-covalent π-π stacking interactions.

4   Labels of figures and tables

Table 1: Interaction energies (kcal mol^{-1}) for different configuration of benzene

dimer for this work compared with other methods taken from Ref [37].

Method	T-shaped	Parallel displaced	Parallel stacked
Our work	-4.250	-3.371	-2.501
CCSD(T)	-2.492	-2.513	-1.564
DF-LMP2	-3.503	-4.427	-3.147
DF-SCF-LMP2	-2.436	-2.604	-1.833
MP2	-3.516	-4.324	-3.222

Table 2: Interatomic distance, R_1 (Å) (see Figure 1))

for this work compared with other methods taken from Refs [2, 37].

Method	T-shaped	Parallel displaced	Parallel stacked
Our work	4.89	3.52	3.71

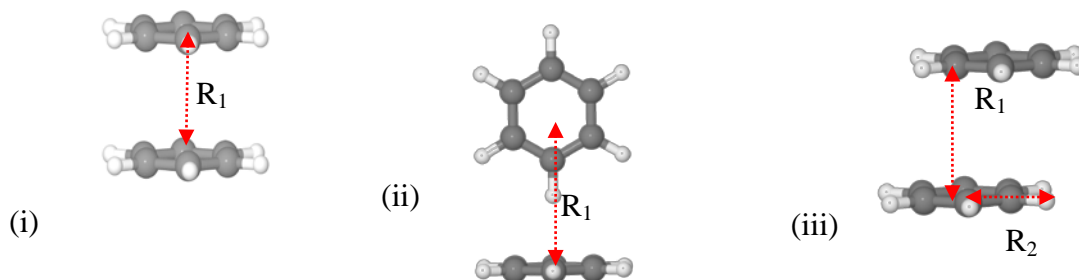| CCSD(T) [36]	5.00	3.60	3.90
DF-LMP2 [37]	4.89	3.70	3.72
DF-SCF-LMP2 [37]	5.04	3.54	3.89
MP2 [36]	4.90	3.40	3.70

Figure 1:   Our calculated benzene dimer in various geometries for

(i)   parallel-stacked (PS), (ii) T-shaped (T) and (iii) parallel-displaced (PD). Here R_1 is the distance of separation (center-center) and R_2 is the displacement from the center. Dashed-red vertical arrows indicate center-center separation and horizontal red-arrow is the displacement from the center position.
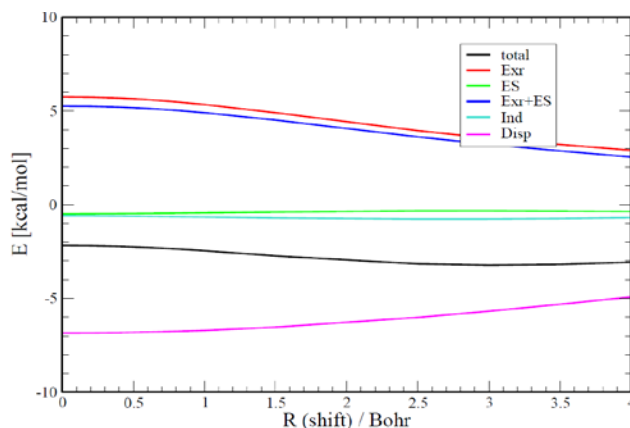
Figure 2:   Energy decomposition analysis (EDA) for benzene dimer indicating the lateral displacement of the top benzene ring, so R= 0, corresponds to "AA" parallel structure (Courtesy of Prof. Dr. Stefan Grimme [Private Communication, 2011]).
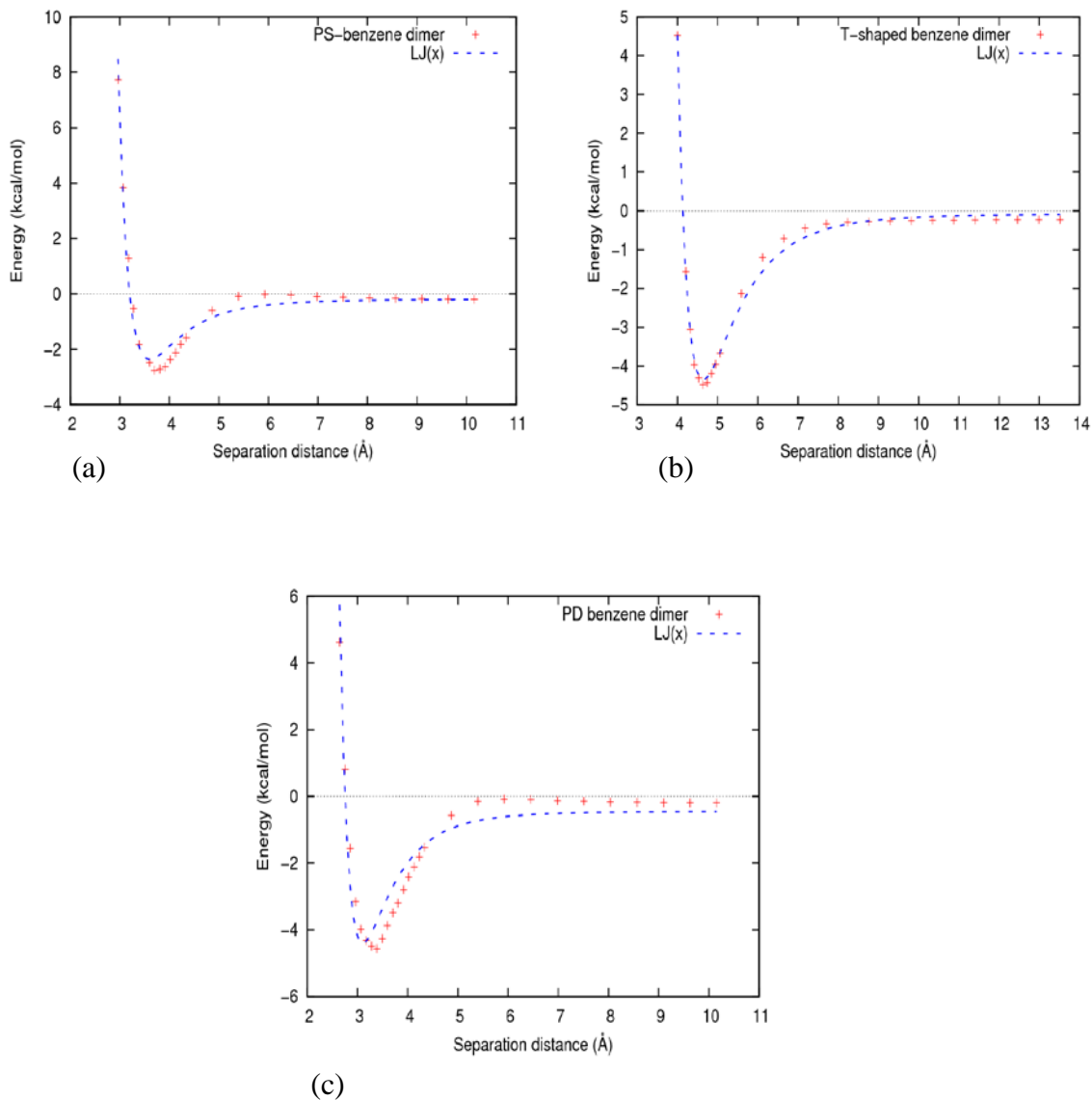
(a)

(b)

(c)

Figure 3:   Potential energy curves for (a) edge-on face (T-shaped), (b) parallel displaced (PD) and (c) parallel-stacked (PS) with Lennard-Jones (LJ) potential fit. Dashed blue lines are (LJ) and red crosses are data points from our DFT/LDA system for the single point energy calculated.
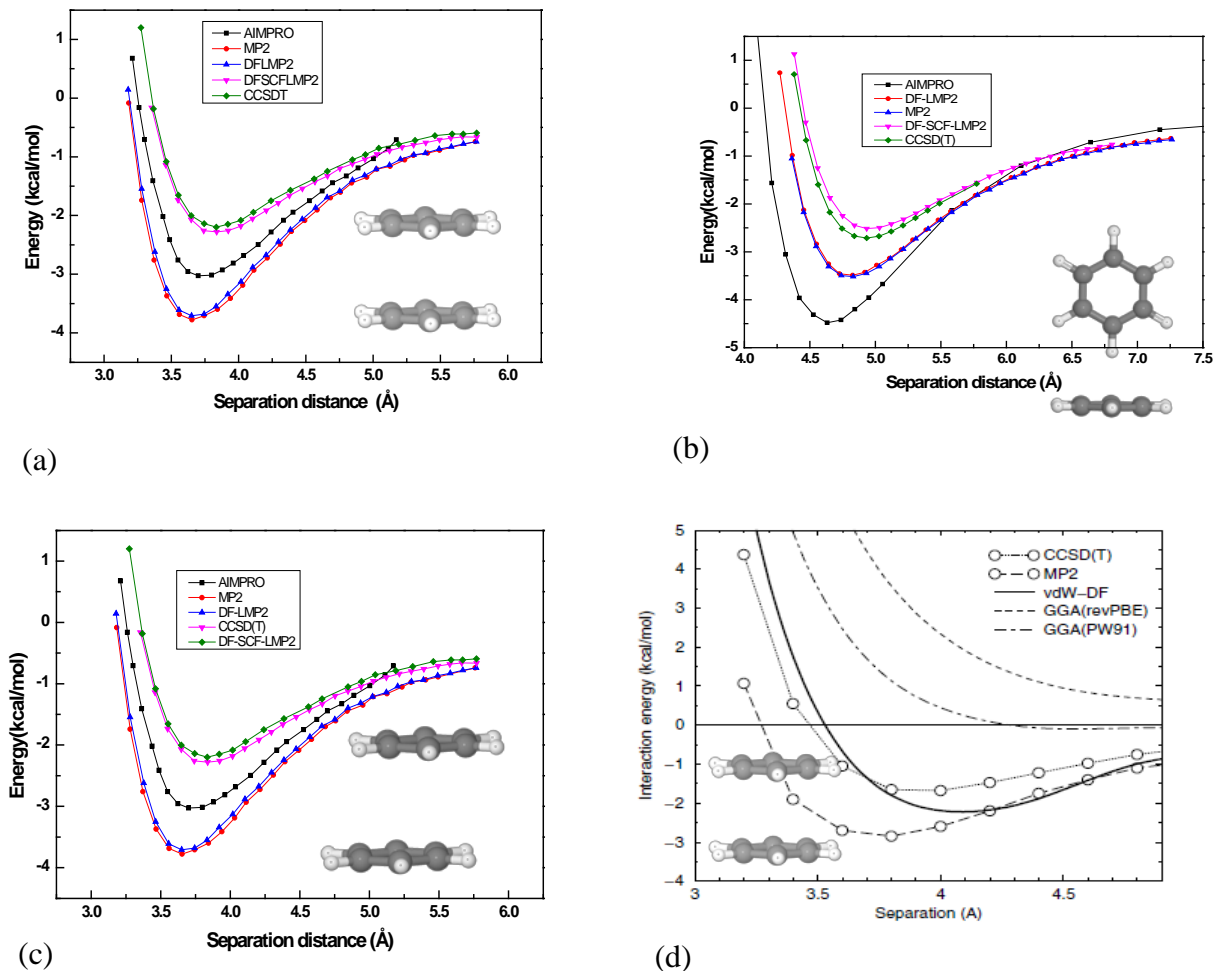
Figure 4: Comparison of the potential energy curves for (a) parallel-stacked, (b) T-shaped, (c) parallel-displaced benzene dimers between this work (AIMPRO) and that of CCSD(T), MP2, DF-LMP2, DF-SCF-LMP2 results of Grant et al [35] and (d) compares the results of CCSD(T), MP2, vdW-DF with that of GGAs (with revPDE and PW91) taken from the work of Dion et al. [38].

5   Conclusion

In conclusion, we have demonstrated in this work that although the dispersion interaction is lacking in DFT/LDA, the method is nonetheless able to predict with reasonable precision the interlayer interactions of benzene dimer as well as the relative stability of the isomers. It however slightly overestimates the binding interactions as compared to the CCSD (T) which is used as a standard for the benzene dimers calculations. Based on the good correlation between the potential energy curves for benzene dimers using AIMPRO/LDA and other correlated methods, this approach could be used for future characterization of other systems involving π-π stacking.

References

[1]   S. Tsuzuki, K. Honda, T. Uchimaru, M. Mikami, and K. Tanabe, Origin of Attraction and Directionality of the π-π Interaction: Model Chemistry Calculations of Benzene Dimer Interaction, *J. Am. Chem. Soc.*, **124**, (2002), 104 - 112.

[2]   M. O. Sinnokrot, E. F. Valeev, and C. D. Sherrill, Estimates of the Ab Initio Limit for π−π Interactions: The Benzene Dimer, *J. Am. Chem. Soc*. **124**, (2002), 10887-10893.

[3]   C. D. Sherrill, T. Takatani, E. G. Hohenstein, *J. Phys. Chem. A*., **113**, (2009), 10146-10159.

[4]   C. A. Hunter, Aromatic interactions in proteins, DNA and synthetic receptors, *J. Chem. Phys.*, **99**, (1993), 748-751.

[5]   J. Grant Hill, J. A. Platts, and H-J. Werner, Calculation of intermolecular interactions in the benzene dimer using coupled-cluster and local electron correlation methods, *Phys. Chem. Chem. Phys*., **8**, (2006), 40-72.

[6]   M. Gordon, L. Slipchenko, H. Li, and J. Jensen, Ann., The Effective Fragment Potential: A General Method for Predicting Intermolecular Interactions, *Rep. Comp. Chem*., **3**, (2007), 177-193.

[7]   A. L. Ringer, and C. D. Sherrill, The Effect of Multiple Substituents On Sandwich and T-Shaped π-π Interactions*, Chem. A Eur. J*., **14**, (2008), 2542-2547.

[8]   M. O. Sinnokrot, and C.D. Sherrill, High-Accuracy Quantum Mechanical Studies of π-π Interactions in Benzene Dimers, *J. Phys. Chem. A*, **110**, (2006), 10656-10668.

[9]   M. O. Sinnokrot, and C. D. Sherrill, Highly Accurate Coupled Cluster Potential Energy Curves For Benzene Dimer: The Sandwich, T-Shaped, and Parallel-Displaced Configurations, *J. Phys. Chem. A,* **108**, (2004), 10200-10207.

[10] T. Tran-Duc, N. Thamwattana, B. J. Cox, and J. M. Hill, Modelling the interaction in a benzene dimer, *Phil. Mag*., **90**, (2010), 1771.

[11] J. K. M. Sanders, and C. A. Hunter, The Nature of Pi-Pi Interactions, *J. Am. Chem. Soc.*, **112**, (2005), 5525-5534.

[12] W. Kim, M. W. Schaeffer, S. Lee, J. S. Chung, and P. M. Felker, Intermolecular vibrations of naphthalene trimer by ionization-detected stimulated Raman spectroscopy, *J. Chem. Phys*, **110**, (1999), 11264.

[13] G. Fischer, Molecular beam infrared spectroscopy of benzene dimers, *Chem. Phy. Lett*., **139**, (1987), 316-320.

[14] J. M. Steed, T. A. Dixon, and W. Klemperer, Molecular beam studies of benzene dimer, hexafluorobenzene dimer, and benzene–hexafluorobenzene, *J. Chem. Phys*., **70**, (1979), 4940.

[15] P. M. Maxton, M. W. Schaeffer, and P. M. Felker, Nonlinear Raman spectroscopy of intermolecular vibrations in benzene-(water)$_n$ clusters, *Chem. Phy. Lett.,* **241**, (1995), 603-610.

[16] M. W. Schaeffer, W. Kim, P. M. Maxton, J. Romascan, and P. M. Felker, Raman spectroscopy of naphthalene clusters: Evidence for a symmetrical trimer and an unsymmetrical tetramer, *Chem. Phy. Lett*., **242**, (1995), 632-638.

[17] K. Brendel, H. Mäder, Y. Xu, and W. Jäger, The rotational spectra of the fluorobenzene···water and *p*-difluorobenzene···water dimers: Structure and internal dynamics, *J. Mol. Spectr*., **268,** (2011), 47-52.

[18] S. Burley and G. Petsko, Aromatic-Aromatic Interaction: A Mechanism of Protein Structure Stabilization, *Science,* **229**, (1985), 23-28.

[19] C. A. Hunter, J. Singh, and J. M. Thornton, A procedure for the isolation of deoxyribonucleic acid from micro-organisms, *J. Mol. Biol*., **218**, (1991), 837-846.

[20] K. C. Janda, J. C. Hemminger, J. S. Winn, S. E. Novick, S. J. Harris, and W. Klemperer, Benzene Dimer: A Polar Molecule, *J. Chem. Phys*., **63**, (1975), 1419.

[21] E. Arunan, and H. Gutowski, The rotational spectrum, structure and dynamics of a benzene dimer, *J. Chem. Phys*., **98**, (1993), 4294.

[22] B.F. Henson, G.V. Hartland, V.A. Venturo, and P. M. Felker, Time-resolved Raman spectroscopy of benzene dimer: Nanosecond-plus lifetime at 992, *J. Chem. Phys*., **97**, (1992), 2189.

[23] M. P. Waller, A. Robertazzi, J. A. Platts, D. E. Hibbs, and P. A. Williams, Hybrid density functional theory for pi-stacking interactions: application to benzenes, pyridines, and DNA bases, *J. Comp. Chem*., **27**, (2006), 491-504.

[24] P. Felker, P. Maxton, and M. Schaeffer, Nonlinear Raman studies of weakly bound complexes and clusters in molecular beams, *Chem. Rev*., **94**, (1994), 1787-1805.

[25] V. Venturo and P. Felker, Intermolecular Raman bands in the ground state of benzene dimer *J. Chem. Phys*., **99**, (1993), 748-751.

[26] K. S. Law, M. Schauer, and E. R. Bernstein, Dimers of Aromatic Molecules *J. Chem. Phys*., **81**, (1984), 4871.

[27] J. R. Grover, E. A. Walters, and E. T. Hui, Dissociation energies of the benzene dimer and dimer cation, *J. Phys. Chem*., **91**, (1987), 3233-3237.

[28] H. Krause, B. Ernstberger, and H. J. Neusser, Binding energies of small benzene clusters, *Chem. Phy. Lett*., **184**, (1991), 411-417.

[29] C. D. Sherrill, T. Takatani, and E. G. Hohenstein, An Assessment of Theoretical Methods for Nonbonded Interactions: Comparison to Complete Basis Set Limit Coupled-Cluster Potential Energy Curves for the Benzene Dimer, the Methane Dimer, Benzene-Methane, and Benzene-H_2S *J. Phys. Chem. A* **113**, (2009), 10146-10159.

[30] W. Langel, Metal clusters at surfaces: structure, quantum properties, physical chemistry (Springer Series in Cluster Physics), *J. Solid. State Electrochem*, **6**, (2001), 359-360.

[31] R. Peverati, and K. K. Baldridge, Implementation and performance of DFT-D with respect to basis set and functional for study of dispersion interactions in nanoscale aromatic hydrocarbons, *J. Chem. Theory Comput*., **4**, (2008), 2030-2048.

[32] J.W.G. Bloom and S.E. Wheeler, Taking the Aromaticity out of Aromatic Interactions, *Angew. Chem. Int. Ed.*, **50**, (2011), 7847-7849.

[33] C. Hartwigsen, S.Geodecker and J. Hutter, Relativistic separable dual-space Gaussian pseudopotentials from H to Rn, *Phys. Rev. B*, **58**(7), (1988), 3641-3662.

[34] S. Grimme, Do Special Noncovalent p–p Stacking Interactions Really Exist? *Angew. Chem. Int. Ed. Engl.*, **47**, (2008), 3430-3434.

[35] J.E. Lennard-Jones, On the Determination of Molecular Fields, *Proc. R. Soc. Lond. A*. **106** (738), 1924, 463–477.

[36] J. Grant Hill, J. A. Platts, and H-J. Werner, Calculation of intermolecular interactions in the benzene dimer using coupled-cluster and local electron correlation methods, *Phys. Chem. Chem. Phys,.*, **8**, (2006), 4072.

[37] A.L. Ringer, and C.D. Sherrill, First Principles Computation of Lattice Energies of Organic Solids: The Benzene Crystal, *Chem. Euro J*. **14**, (2008), 2542-2547.

[38] M. Dion, H. Rydberg, E. Schröder, D.C. Langreth and B.I. Lundqvist, Van der Waals Density Functional for General Geometries, *Phys. Rev. Lett.*, **92**, (2004), 246401.

[39] R. Telling and M. Heggie, Stacking fault and dislocation glide on the basal plane of graphite, *Phil. Mag. Lett.*, **83**, (2003), 411-421.

[40] Yaya, A., B. Agyei-Tuffour, D. Dodoo-Arhin, E. Nyankson, E. Annan, D. S. Konadu, E. Sinayobye, E.A. Baryeh, and C.P. Ewels, Layered Nanomaterials-A Review, *Global Journal of Engineering Design and Technology*, **2**, (2012), 32-41.

[41] F. Tournus and J-C. Charlier, Ab initio study of benzene adsorption on carbon nanotubes, *Phys. Rev. B.,* **71**, (2005), 165421.