

Intermolecular Lennard-Jones (22-11) Potential Energy Surface in Dimer of N₈ Cubane Cluster

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Abstract. We have calculated the intermolecular potential energy surface (IPES) of the dimer of cubic N₈ cluster using *ab initio* and the density functional theory (DFT) calculations. The *ab initio* (HF/3-21G(d)) and DFT (B3LYP/6-31G(d) and aug-cc-pVDZ) calculations were performed for two relative orientations of N₈-N₈ system as a function of separation distance between the centers of cubic N₈ clusters. In this research, the IPES, $U(r)$, of the N₈-N₈ system is studied, where the edge of N₈ approaches to face or edge of the other considered N₈. Then, the Lennard-Jones (12-6) and (22-11) adjustable parameters are fitted to the computed interaction energies for edge-face and edge-edge orientations. In this research for the first time, the IPESs proportionated to the Lennard-Jones (22-11) potential are derived that are compatible with the computed IPES curves. Assuming a set of Lennard-Jones parameters, the second virial coefficients are obtained for the N₈-N₈ complex at a temperature range of 298 to 1000 K. Both the corrected and uncorrected basis set superposition error (BSSE) results are presented confirming the significance of including BSSE corrections.

Key words: Nitrogen cluster; IPES; Lennard-Jones (22-11) potential; second virial coefficient; BSSE; *ab initio*; DFT

Resumen. Se calculó la superficie de energía potencial intermolecular (SEPI) para el dímero del cúmulo N₈ cúbico usando cálculos *ab initio* y teoría de funcionales de la densidad (TFD). Los cálculos *ab initio* (HF/3-21G(d)) y TFD (B3LYP/6-31G(d) se realizaron para dos orientaciones relativas del sistema N₈-N₈ como función de la distancia de separación entre los centros de los cúmulos N₈ cúbicos. En esta investigación se estudió la SEPI, $U(r)$, del sistema N₈-N₈ donde la arista de un N₈ se aproxima a la cara o la arista del otro N₈ considerado. Entonces, los parámetros ajustables de Lennard-Jones (12-6) y (22-11) se ajustan a las energías de interacción calculadas para las orientaciones arista-cara y arista-arista. En este trabajo, por primera vez, las SEPIs proporcionadas para el potencial de Lennard-Jones (22-11) se derivan de manera que sean compatibles con las curvas SEPI calculadas. Asumiendo un conjunto de parámetros de Lennard-Jones, los segundos coeficientes del virial se obtienen para el complejo N₈-N₈ en el rango de temperaturas 298 a 1000 K. Se presentan resultados corregidos y sin corregir para error de superposición de bases (ESB), confirmando-se la relevancia de incluir correcciones ESB.

Palabras clave: cúmulos de nitrógeno, SEPI, potencial Lennard-Jones (22-11), segundos coeficientes del virial, ESB, *ab initio*; TFD

Introduction

A group of high energy density materials (HEDMs) are homo-polyatomic nitrogen clusters [1-2]. Although numerous nitrogen clusters are studied theoretically [3-14], only a few of them are known experimentally [15-22]. This stems from the fact that the triple bond of N₂ molecule has higher stability compared to single or double bond species in other polynitrogen compounds.

N₈ cubane is a hypothetical compound of interest for theoretical studies. However, there are speculations that it could be a moderately stable compound [10,23-26]. It is isoelectronic with the corresponding carbon cubane (C₈H₈) compound, which has been experimentally shown to be stable [27,28]. Whereas (C₈H₈) has been known experimentally for many years [29], cubic N₈ has never been observed experimentally. Besides, cubic N₈ is a candidate for HEDMs, with a high ratio of the energy release to the specific weight; since its energy content relative to the dissociation products (four N₂ molecules) is extremely high [10].

Intermolecular potential energy surface (IPES), or van der Waals interactions (intermolecular interaction potentials) has

an important role in determining the properties of HEDMs such as homo-polyatomic nitrogen clusters. These interactions are conclusive in determining the thermodynamic properties of molecular solids and liquids, while their magnitude are normally one or two orders of magnitude weaker than covalent bonds [30]. Quantum mechanical approaches have been widely employed to drive intermolecular interaction potential. Those approaches, which are sometimes practically difficult to implement, can be used to extract detailed information about the potential energy surface (PES). However, the quality of derived PES substantially depends on the applied computational level. In addition, the basis set superposition error (BSSE) should be corrected, because it has an important effect on the calculated interaction potential [31,32].

In this work, the IPES, $U(r)$, of the dimer of cubic N₈ cluster is investigated. The Lennard-Jones potential is used to determine the IPES components. The thermal decomposition and detonation of cubic N₈ has been simulated from 2030 to 4642 K by molecular dynamics [33]. Therefore in this research, the second virial coefficients for the dimer of cubic N₈ are estimated computationally from 298 to 1000 K before simulation of thermal decomposition.

Methods and Computations

The equilibrium geometry of a single cubic N_8 molecule was obtained at the HF/3-21G(d) level of theory. We modeled the cubic N_8 dimer first by fixing the nearest nitrogen-nitrogen, N-N, distance while the two monomers were left to rotate freely to obtain the most stable geometry. With several initial choices of reciprocal orientations and approaching the monomers from the far side, the edge-face and face-face orientations were found as the minimum-energy conformations (Fig. 1). Since the cubic N_8 molecule does not have a central atom, subsequently the nearest and farthest N-N distance were sampled in decreasing and increasing steps with a step size of 0.1 Å from minimum energy conformer to 2 and to 14 Å, respectively. During the scan, the individual N_8 molecular structures were allowed to entirely relax. We optimized all geometries at the framework of Hartree-Fock and DFT using the three-parameter Becke's exchange [34,35] and Lee-Yang-Parr's correlation non-local functional [36], usually known as B3LYP. We used the split valence type basis sets with polarized d function (3-21G(d) and 6-31G(d)) for electronic structure description of N_8 molecule and the interaction energy between N_8 dimer with HF and B3LYP methods, respectively. Also we used an augmented correlation consistent, polarized valence, double zeta basis set (aug-cc-pVDZ) [37] for electronic structure description of N_8 molecule and the interaction energy between N_8 dimer with B3LYP method. Subsequently, we examined all optimized geometries by re-optimizing them at the MP2 [38,39]/6-31G(d) [40-42] level in addition to re-computation of the second order derivatives of energy at the same level. Good agreement was found between both computational levels. To ensure the local minimum nature of all these species, all optimized geometries were undergone frequency analysis. All computations were performed using Spartan'10 suite of programs [43].

In cubic N_8 dimer, the calculated interaction energy is sensitive to the BSSE if a finite basis set is used. As the interacting nitrogen atoms of N_8 dimer approach each other, their basis functions start overlapping. Each monomer borrows basis functions from other species then the basis set is "effectively" increased and the calculated energy is improved. When the to-

tal energy as a function of the system geometry is minimized, an error appears due to differences between the long range energies from the unmixed basis sets and the short range energies resulting from the mixed basis sets. The BSSE was computed based on the Boys and Bernardi approach [31]. The IPES, $U(r)$, is analyzed for two interacting systems (i.e. A and B; monomers) forming a supermolecule (i.e. AB; dimer) [32,44]. In principle, we can simply give the interaction energy of two molecules A and B at a distance r , as

$$U(r) = E_{AB}(r) - E_A - E_B \quad (1)$$

The total energies of the two discrete molecules E_A and E_B and the total energy of the interacting system E_{AB} are taken from the solutions of Schrödinger's equation. The IPES, $U(r)$, is estimated by Roothaan's algebraic procedure as

$$U(AB) = E_{AB}^{\alpha\cup\beta}(AB) - E_A^\alpha(A) - E_B^\beta(B) \quad (2)$$

$E_X^\alpha(Y)$ is the total energy of the Y system at the X geometry as calculated with the s basis set, where α , β and $\alpha\cup\beta$ illustrate the basis sets applied to compute A, B, and AB systems, respectively.

In the counterpoise approach (CP), it is proposed to do the calculation of the energies of the separate components with the complete basis set of both monomers applied in the calculation of the supermolecule energy

$$U(AB)^{CP} = E_{AB}^{\alpha\cup\beta}(AB) - E_A^{\alpha\cup\beta}(A) - E_B^{\alpha\cup\beta}(B) \quad (3)$$

In this manner, the three terms on the right hand side of Eq. (3) are calculated using the same basis set. The BSSE is known as the difference between the IPESs computed by Eqs. (2) and (3)

$$\delta_{BSSE} = U(AB)^{CP} - U(AB) \quad (4)$$

$U(AB)^{CP}$ is a consistent method for correction of the IPES, U , with $\alpha\cup\beta$. For AB, A and B systems, $\alpha\cup\beta$ is a balanced basis set. The magnitude of these parameters are

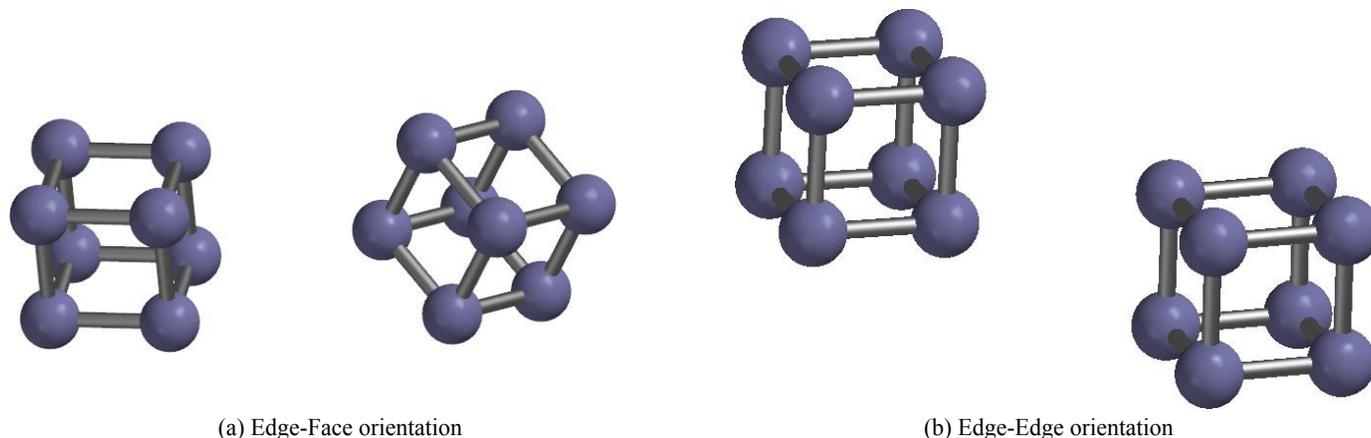


Fig. 1. Two different orientations of N_8 dimer.

determined by the second virial coefficient, B_2 , that calculated using the IPES, $U(r)$, (Equation (5)) [45],

$$B_2 = 2\pi N_A \int_0^\infty \left\{ 1 - \exp\left[-\frac{U(r)}{RT}\right] \right\} r^2 dr \quad (5)$$

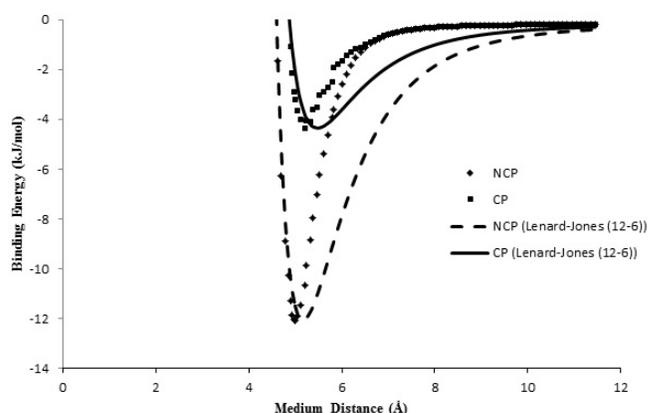
where r is the distance separation of two components, T is temperature and N_A is the Avogadro constant.

Results and Discussion

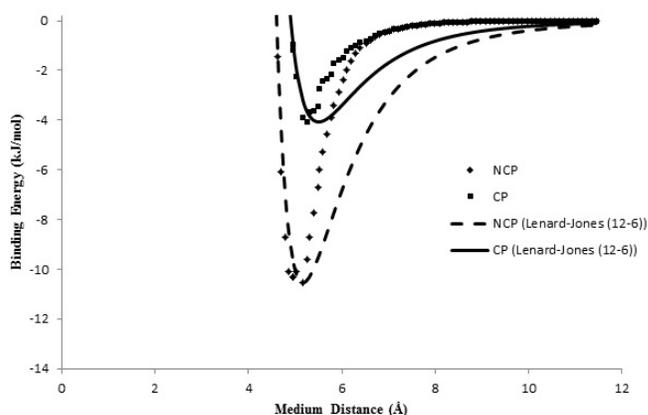
The *ab initio* and DFT methods are applied for exploring bond lengths, bond angles and dihedral angles (Table 1). A good agreement was found for the optimized geometrical parameters between B3LYP/6-31G(d) and B3LYP/aug-cc-pVDZ levels of theory.

For determining the IPES, $U(r)$, of the cubic N₈ dimer, the approaching of monomers from the far side based on the edge-face and face-face orientations were done. Two different orientations of N₈ dimer are shown in Fig. 1. Thermodynamic properties of N₈ and N₈ dimer clusters in two different face-face and edge-face orientations at the cited computational levels are listed in Table 2. The obtained thermodynamic properties for edge-face orientation show good agreement between the both 6-31G(d) and aug-cc-pVDZ basis sets with B3LYP method, but with aug-cc-pVDZ basis set the edge-edge orientation was not obtained.

Fig. 2 and Fig. 3 show the calculated IPES, $U(r)$, as a function of distance separation between the centers of N₈-N₈ system in the two different orientations using HF/3-21G and B3LYP/6-31G(d) levels, respectively. Fig. 4 shows the calculated IPES, $U(r)$, as a function of distance separation between



(a) Edge-Face orientation



(b) Edge-Edge orientation

Fig. 2. The BSSE corrected (CP) and uncorrected (NCP) potentials of N₈ dimer for (a) Edge-Face and (b) Edge-Edge orientations using RH-F/3-21G(d) level and comparison with Lenard-Jones (12-6) potential.

Table 1. The set of optimized geometry parameters of N₈ cluster.

Optimized geometry parameters	Values		
	HF/3-21G(d)	B3LYP/6-31G(d)	B3LYP/aug-cc-pVDZ
N-N bond length	1.561 Å	1.521 Å	1.522 Å
NNN bond angle	90.00°	90.00°	90.00°
NNNN dihedral angle	0.00°	0.00°	0.00°
	90.00°	90.00°	90.00°

Table 2. Thermodynamic properties of optimized N₈ and N₈ dimer clusters at 298.15 K and 1.00 atm.

Cluster	Level of theory	E ₀ (au)	ZPE (kJ/mol)	H _{th} (kJ/mol)	S _{th} (J/mol K)	C _v (J/mol.K)	H _{th} -TS _{th} (kJ/mol)
N ₈	HF/3-21G	-432.468727	102.7165	114.9938	278.1022	59.2031	32.0777
	B3LYP/6-31G(d)	-437.428470	90.5353	104.1746	283.7048	71.4168	19.5880
	B3LYP/aug-cc-pVDZ	-437.502149	91.0127	104.5836	283.4026	70.8652	20.0871
N ₈ dimer (Edge-Face)	HF/3-21G	-864.941938	207.7040	229.7346	378.6261	142.5478	116.8473
	B3LYP/6-31G(d)	-874.861102	182.4899	207.2814	390.5892	167.5787	90.8272
	B3LYP/aug-cc-pVDZ	-875.006390	183.2978	207.9857	390.4852	166.7697	91.5626
N ₈ dimer (Edge-Edge)	HF/3-21G	-864.941349	207.7070	229.7420	378.3436	142.5822	116.9389
	B3LYP/6-31G(d)	-874.861158	183.0752	207.8362	390.2179	167.2825	91.4928

the centers of the N_8-N_8 in the edge-face orientation using B3LYP/aug-cc-pVDZ. In Figures 2 to 4, the calculated IPES are compared with Lenard-Jones (12-6) potential with the BSSE corrected (CP) and uncorrected (NCP). The difference of Lenard-Jones (12-6) with computed data is very large. Therefore, this is a clear sign that Lenard-Jones (12-6) potential is “not” a proper function to fit the calculated data for N_8-N_8 supermolecule. The IPESs, $U(r)$, strongly depend on the BSSE corrections. The IPESs corrected for the BSSE are energetically much lower than the potential energy calculated without the BSSE correction. In particular, the BSSE correction is important for calculating the IPESs with small basis sets.

It is seen from comparison of edge-face and face-face orientations in Figures 2 and 3 that the orientations and separation distances between the centers of N_8-N_8 clusters are fairly effective on the position of minimum, depth and width of the calculated potential well of the IPES curves, especially at HF/3-21G(d) level (Fig. 2). Figures 2 and 3 show that the edge-face orientation has the IPES curve with the largest value of D_e ($D_e = -E_{int}(R_e) - E_{min}$), at the HF/3-21G(d) level of theory; whereas, at the B3LYP/6-31G(d) level of theory, both of orientations have relatively similar potential energy curves. Also based on the position of the minimum point (R_e) of the potential energy curves, the computed IPESs can be further compared. These quantities are very sensitive to the values of

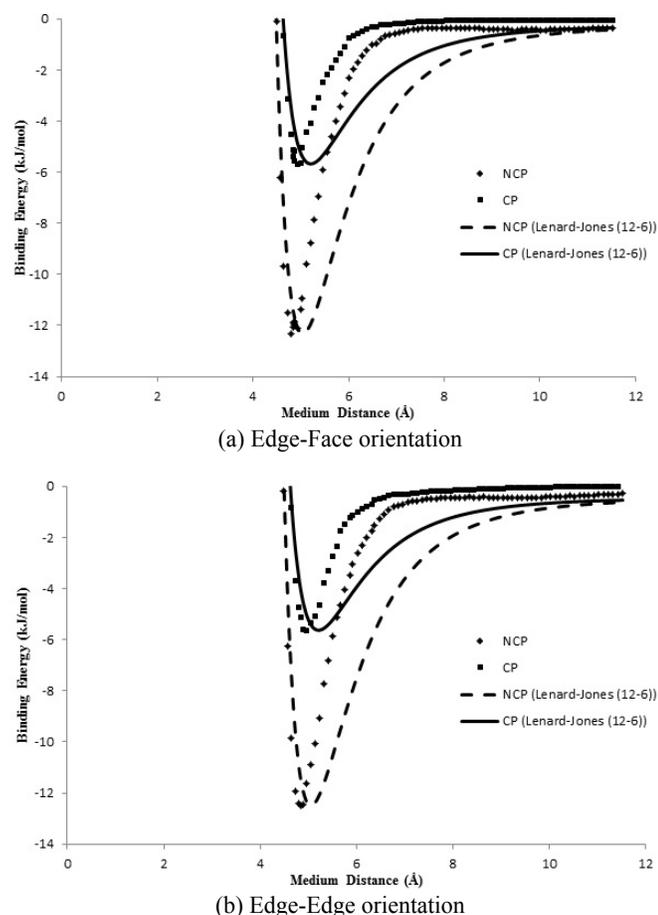


Fig. 3. The BSSE corrected (CP) and uncorrected (NCP) potentials of N_8 dimer (a) Edge-Face and (b) Edge-Edge orientations using B3LYP/6-31G(d) level and comparison with Lenard-Jones (12-6) potential.

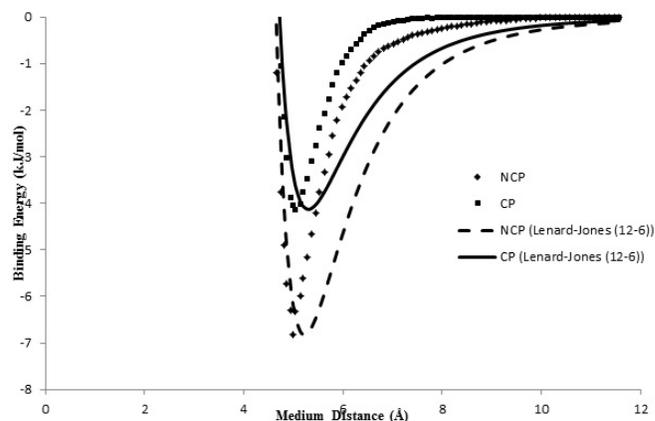


Fig. 4. The BSSE corrected (CP) and uncorrected (NCP) potentials of N_8 dimer with Edge-Face orientation using B3LYP/aug-cc-pVDZ level and comparison with Lenard-Jones (12-6) potential.

the separation distance of N_8-N_8 and different orientations of N_8 monomers to each other that is applied in the computational methods. In Table 3, the values of R_e and D_e are tabulated for the edge-face and edge-edge orientations. The potential well depths of the calculated IPESs, without the BSSE correction at RHF/3-21G(d) level are 2.5 to 3 times more than the BSSE corrected potential, while these ratios for B3LYP/6-31G(d) are 2 to 2.5 times more than the BSSE corrected potential and also for B3LYP/aug-cc-pVDZ level is less than 2 times more than the BSSE corrected potential.

In this work, the IPES, $U(r)$, for the cubic N_8 dimer system, was fitted to the Lennard-Jones (12-6) model (Equation (6)), which can be expressed as

$$U(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \quad (6)$$

where r is the separation distance between the centers of N_8-N_8 , s is the size parameter and e is the depth of Lennard-Jones function. We fitted the adjustable parameters s and e for two different orientations with the *ab initio* HF/3-21G(d) and B3LYP/6-31G(d) interaction energies, whereas these parameters are obtained for edge-face orientation at B3LYP/aug-cc-pVDZ level. In Table 3, the values of the adjustable IPES parameters are tabulated for various orientations. Also, the fitted curves of the calculated IPESs to the Lennard-Jones (12-6) potential with the BSSE corrected (CP) and uncorrected (NCP), are shown in Figures 2, 3 and 4. The fitted IPESs to the Lennard-Jones (12-6) potential are not completely compatible with the curves calculated ISEPs at HF/3-21G(d), B3LYP/6-31G(d) and B3LYP/aug-cc-pVDZ levels. In addition, in this research, we demonstrated that it is possible to obtain a IPES, $U(r)$, for the cubic N_8 dimer by quantum mechanical calculations fitted to the Lennard-Jones (22-11) potential, (Equation (7)), which can be expressed as

$$U(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{22} - \left(\frac{\sigma}{r} \right)^{11} \right] \quad (7)$$

where the adjustable parameters ϵ and s in Equation (7) are the same as the Lennard-Jones (12-6) model are tabulated in Table 3. The calculated IPES curves at HF/3-21G(d) and B3LYP/6-31G(d) levels are fitted to the Lennard-Jones (22-11) potential with the BSSE corrected (CP) and uncorrected (NCP) potential energy surfaces, as shown in Figures 5, 6 and 7. The IPESs fitted to the Lennard-Jones (22-11) potential are completely compatible with the curves of the calculated ISPs. Also, from the known $U(r)$ formula, the second virial coefficients, B_2 , are estimated for the cubic N₈ dimer system with the BSSE corrected (CP) and uncorrected (NCP) by quantum mechanical calculations. We calculated the second virial coefficients with the Lennard-Jones (12-6) and (22-11) potentials using Equation (5) and then tabulated the results for a range of temperatures from 298 to 1000 K in Table 4. However the equation (5) is valid if the systems is “spherical” (like an atom) but for this research we assumed N₈ molecule is almost spherical. In Figures 8 and 9, the computed values of the second virial coefficients for selected temperatures (Table 4) are plotted.

We considered the BSSE corrections to yield the following systematic results. The obtained second virial coefficients (B_2) with the Lennard-Jones (12-6) potential in the range of 298 to 1000 K with the BSSE corrected (CP) and uncorrected (NCP) potential energy surface are negatives, i.e. the attractive forces are dominated in the all range of 298 to 1000 K. Negative and positive second virial coefficients (B_2) imply dominance of attractive and repulsive forces, respectively between N₈ clusters. When we use the Lennard-Jones (22-11) potential, the obtained second virial coefficients in the range of 298 to 1000 K with the BSSE uncorrected (NCP) are negative, i.e. the attractive forces are dominated in the all range of 298 to 1000 K. While B_2 computed with the BSSE corrected (CP) potential energy surface are varied from negative (approximately for a range of temperatures from 298 to 600 K) to positive (approximately for a range of temperatures from 700 to 1000 K) values.

Conclusion

In this research the calculated IPESs were systematically studied for cubic N₈ dimer at the edge-face and edge-edge orientations applying both Hartree-Fock and DFT methods. The edge-face and edge-edge orientations were scanned at the HF/3-21G(d) and B3LYP/6-31G(d) levels but the edge-face is the only orientation that was obtained at B3LYP/aug-cc-pVDZ level. It

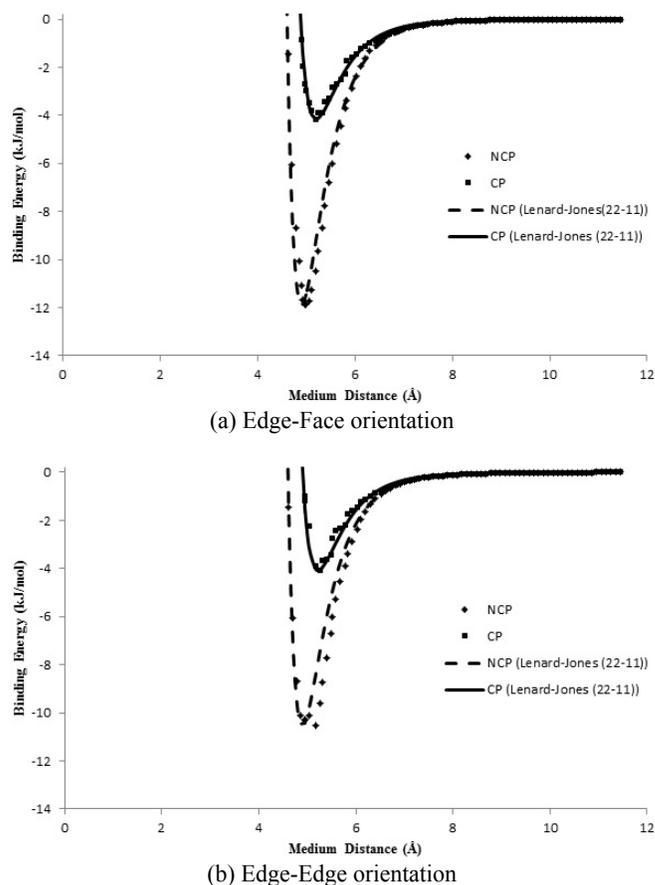


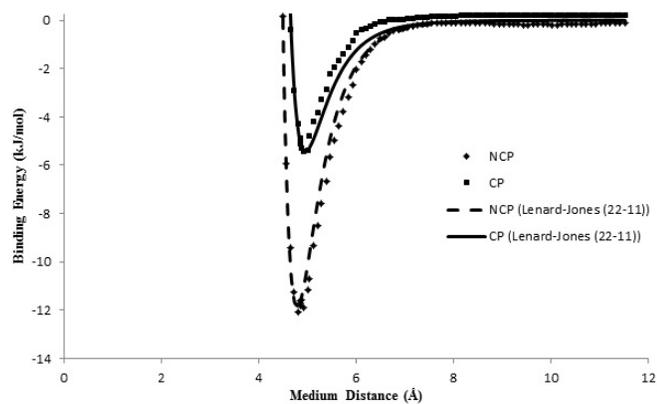
Fig. 5. The BSSE corrected (CP) and uncorrected (NCP) potentials of N₈ dimer for (a) Edge-Face and (b) Edge-Edge orientations using RH-F/3-21G(d) level and comparison with Lenard-Jones (22-11) potential.

was demonstrated that the BSSE corrections significantly affect the quality of calculated potentials. From this survey several significant conclusions about applying the current theoretical methods can be extracted to generate the IPESs.

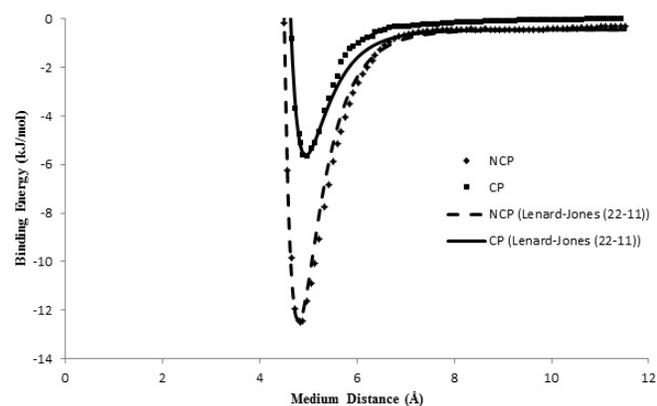
Although in this study, we do not apply the long-range intermolecular interactions by DFT methods with dispersion-corrected and meta-hybrid functional and also MP2 methods with correlation energy for weakly bound systems (in van der Waals interactions), the results yield attractive potentials for the cubic N₈ dimer system. The IPESs fitted to the Lennard-Jones (12-6) potential are not completely compatible with the curves of calculated IPESs at HF/3-21G(d), B3LYP/6-31G(d) and B3LYP/aug-cc-pVDZ levels, while the IPESs fitted to the Lennard-Jones

Table 3. Adjustable parameters ($\epsilon = D_e$ and σ) fitted to the Lenard-Jones potential and R_e for the two different orientations.

Different orientations	Adjustable parameters								
	RHF/3-21G			B3LYP/6-31G(d)			B3LYP/aug-cc-pVDZ		
	ϵ (kJ/mol)	σ (Å)	R_e (Å)	ϵ (kJ/mol)	σ (Å)	R_e (Å)	ϵ (kJ/mol)	σ (Å)	R_e (Å)
Edge-Face (NCP)	11.87	4.60	5.00	12.07	4.49	4.81	6.82	4.65	5.00
Edge-Face (CP)	4.15	4.88	5.20	5.42	4.65	4.93	4.13	4.72	5.05
Edge-Edge (NCP)	10.53	4.60	5.18	12.04	4.50	4.84	-	-	-
Edge-Edge (CP)	4.07	4.90	5.27	5.18	4.64	4.97	-	-	-



(a) Edge-Face orientation



(b) Edge-Edge orientation

Fig. 6. The BSSE corrected (CP) and uncorrected (NCP) potentials of N_8 dimer (a) Edge-Face and (b) Edge-Edge orientations using B3LYP/6-31G(d) level and comparison with Lenard-Jones (22-11) potential.

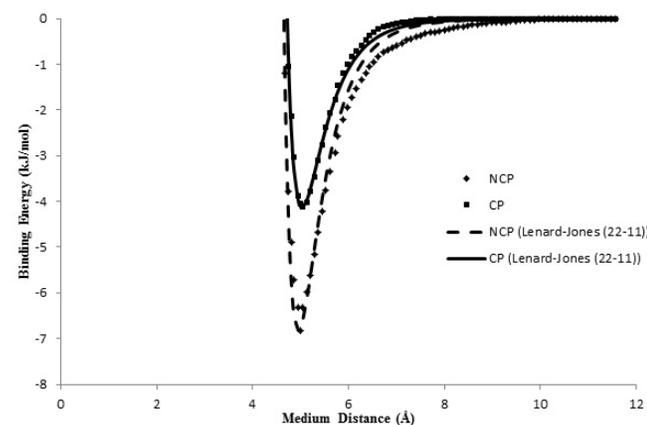
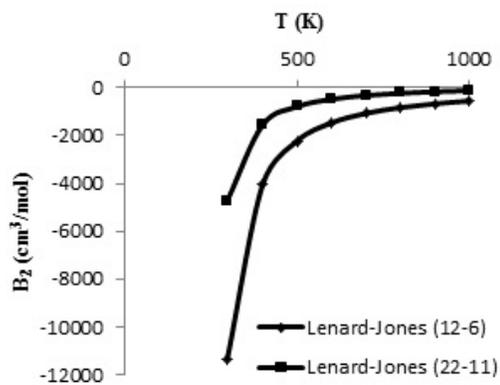
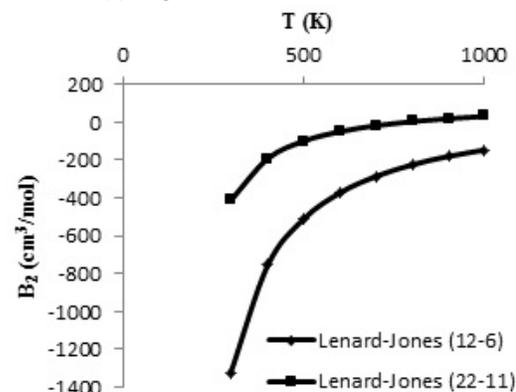


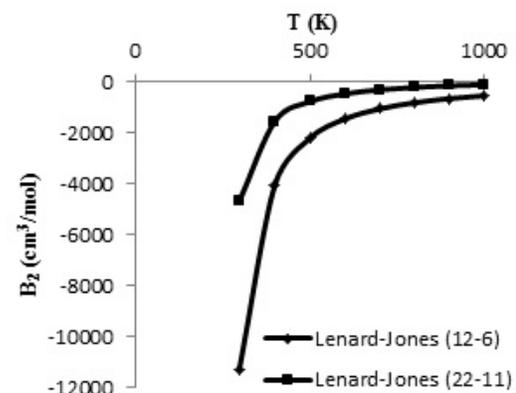
Fig. 7. The BSSE corrected (CP) and uncorrected (NCP) potentials of N_8 dimer with Edge-Face orientation using B3LYP/aug-cc-pVDZ level and comparison with Lenard-Jones (22-11) potential.



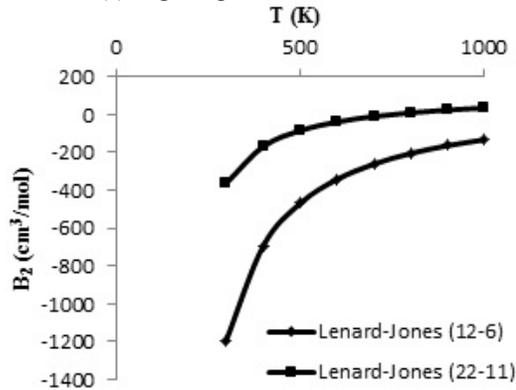
(a) Edge-Face orientation with NCP



(b) Edge-Face orientation with CP



(c) Edge-Edge orientation with NCP



(d) Edge-Edge orientation with CP

Fig. 8. Comparison between the computational data of the second virial coefficients for selected temperatures of N_8 dimer (Edge-Face orientation (a, b) and Edge-Edge orientation (c, d)) with BSSE corrected (CP) and uncorrected (NCP) potentials using B3LYP/6-31G(d) level.

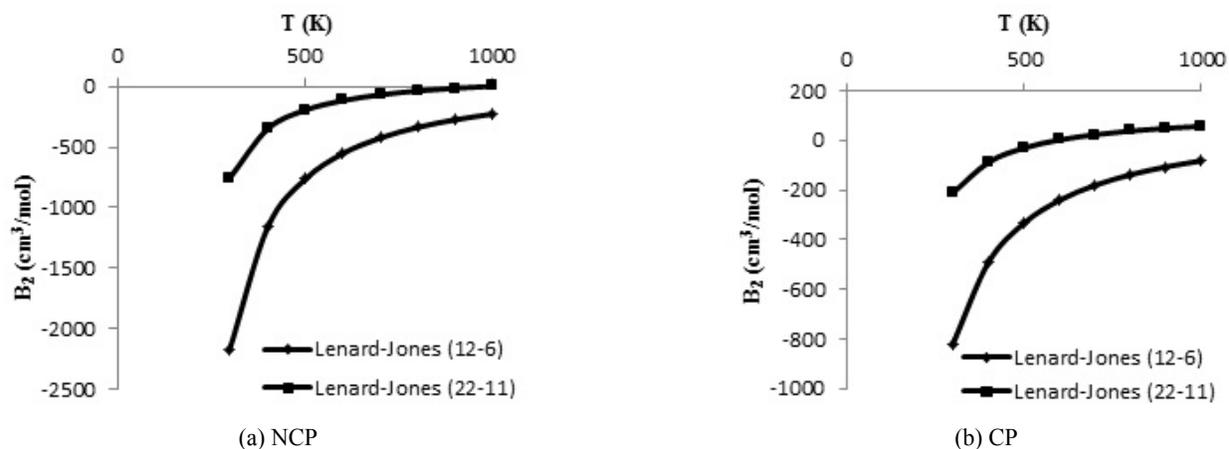


Fig. 9. Comparison between the computational data of the second virial coefficients for selected temperatures of N₈ dimer (Edge-Face orientation) with BSSE corrected (CP) and uncorrected (NCP) potentials using B3LYP/aug-cc-pVDZ level.

Table 4. Second virial coefficients from the theoretical potential for selected temperatures

T (K)	B ₂ (cm ³ /mol)							
	RHF/3-21G							
	Edge-Face				Edge-Edge			
	Lenard-Jones (12-6)		Lenard-Jones (22-11)		Lenard-Jones (12-6)		Lenard-Jones (22-11)	
	NCP	CP	NCP	CP	NCP	CP	NCP	CP
298	-11391.95	-916.78	-4722.26	-238.21	-7270.67	-895.93	-2928.11	-228.84
400	-4155.73	-545.76	-1591.67	-98.50	-2981.58	-534.23	-1096.84	-92.98
500	-2299.15	-370.93	-813.37	-34.79	-1743.82	-362.95	-586.11	-30.71
600	-1522.67	-268.29	-496.77	1.76	-1190.33	-262.12	-364.18	5.12
700	-1112.25	-201.01	-333.37	25.28	-884.94	-195.93	-244.61	28.21
800	-862.61	-153.64	-235.97	41.58	-693.60	-149.27	-171.17	44.24
900	-696.09	-118.56	-172.12	53.50	-563.22	-114.69	-121.96	55.96
1000	-577.63	-91.59	-127.36	62.54	-468.98	-88.09	-86.88	64.86
	B3LYP/6-31G(d)							
298	-11334.90	-1321.00	-4715.88	-412.43	-11295.59	-1198.62	-4696.98	-364.66
400	-4060.20	-754.80	-1563.24	-191.42	-4057.25	-691.45	-1560.89	-167.92
500	-2226.62	-509.40	-792.94	-98.99	-2227.96	-467.96	-792.64	-84.24
600	-1467.51	-371.75	-482.71	-48.46	-1469.47	-341.48	-482.77	-38.05
700	-1068.90	-284.08	-323.64	-16.90	-1070.78	-260.45	-323.72	-9.04
800	-827.52	-223.51	-229.24	4.55	-829.20	-204.26	-229.29	10.77
900	-667.04	-179.25	-167.57	20.02	-668.51	-163.08	-167.55	25.09
1000	-553.16	-145.54	-124.44	31.66	-554.44	-131.67	-124.36	35.88
	B3LYP/aug-cc-pVDZ							
298	-2176.77	-822.28	-758.66	-212.76				
400	-1161.29	-489.72	-349.23	-87.61				
500	-763.88	-332.81	-194.88	-30.46				
600	-553.17	-240.63	-115.28	2.34				
700	-423.61	-180.19	-67.37	23.46				
800	-336.23	-137.62	-35.61	38.11				
900	-273.44	-106.08	-13.11	48.81				
1000	-226.23	-81.84	3.59	56.94				

(22-11) potential are completely compatible with the curves of the calculated IPESs.

Our calculated Lennard-Jones (22-11) potential with the BSSE corrected (CP) from 298 ~ 600 K show that the attractive forces are dominated and from 700 ~ 1000 K relatively repulsive forces are dominated.

These conclusions can be useful for subsequent studies on thermal decomposition and detonation of the cubic N₈ as a high energy density material.

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References

- Hammerl, A.; Klapotke, T. M.; Schwerdtfeger, P. *Chem. Eur. J.* **2003**, *9*, 5511-5519.
- Christe, K. O. *Prop. Explos. Pyrotech.* **2007**, *32*, 194-204.
- Najafpour, J.; Foroutan-Nejad, C.; Shafiee, G. H.; Kordi-Peykani, M. *Computational and Theoretical Chemistry*. **2011**, *974*, 86-91.
- Dixon, D. A.; Feller, D.; Christe, K. O.; Wilson, W. W.; Vij, A.; Vij, V.; Jenkins, H. D. B.; Olson, R. M.; Gordon, M. S. *J. Am. Chem. Soc.* **2004**, *126*, 834-843.
- Fau, S.; Wilson, K. J.; Bartlett, R. J. *J. Phys. Chem. A* **2002**, *106*, 4639-4644.
- Ha, T. -K.; Suleimenov, O.; Nguyen, M. T. *Chem. Phys. Lett.* **1999**, *315*, 327-334.
- Nguyen, M. T. *Coord. Chem. Rev.* **2003**, *244*, 93-113.
- Cheng, L. P.; Li, S.; Li, Q. S. *Int. J. Quant. Chem.* **2004**, *97*, 933-943.
- Gu, J. -D.; Chen, K. -X.; Jiang, H. -L.; Chen, J. -Z.; Ji, R. -Y.; Ren, Y.; Tian, A. -M. *J. Mol. Struct. (THEOCHEM)*. **1998**, *428*, 183-188.
- Gagliardi, L.; Evangelisti, S.; Roos, B. O.; Widmark, P. -O. *J. Mol. Struct. (THEOCHEM)*. **1998**, *428*, 1-8.
- Zhou, H.; Zheng, W.; Wang, X.; Ren, Y.; Wong, N. -B.; Shu, Y.; Tian, A. *J. Mol. Struct. (THEOCHEM)*. **2005**, *732*, 139-148.
- Sharma, H.; Garg, I.; Dharamvir, K.; Jindal, V. K. *J. Phys. Chem. C* **2010**, *114*, 9153-9160.
- Chung, G.; Schmidt, M. W.; Gordon, M. S. *J. Phys. Chem. A* **2000**, *104*, 5647-5650.
- Hirshberg, B.; Gerber, R. B.; Krylov, A. I. *Nature Chemistry*. **2014**, *6*, 52-56.
- Christe, K. O.; Wilson, W. W.; Sheehy, J. A.; Boatz, J. A. *Angew. Chem. Int. Ed.* **1999**, *38*, 2004-2009.
- Vij, A.; Wilson, W. W.; Vij, V.; Tham, F. S.; Sheehy, J. A.; Christe, K. O. *J. Am. Chem. Soc.* **2001**, *123*, 6308-6313.
- Vij, A.; Pavlovich, J. G.; Wilson, W. W.; Vij, V.; Christe, K. O. *Angew. Chem. Int. Ed.* **2002**, *41*, 3051-3054.
- Ostmark, H.; Wallin, S.; Brinck, T.; Carlqvist, P.; Claridge, R.; Hedlund, E.; Yudina, L. *Chem. Phys. Lett.* **2003**, *379*, 539-546.
- Wilson, W. W.; Vij, A.; Vij, V.; Bernhardt, E.; Christe, K. O. *Chem. Eur. J.* **2003**, *9*, 2840-2844.
- Butler, R. N.; Stephens, J. C.; Burke, L. A. *Chem. Commun.* **2003**, *8*, 1016-1017.
- Schroer, T.; Haiges, R.; Schneider, S.; Christe, K. O. *Chem. Commun.* **2005**, *12*, 1607-1609.
- Butler, R. N.; Hanniffy, J. M.; Stephens, J. C.; Burke, L. *J. Org. Chem.* **2008**, *73*, 1354-1364.
- Engelke, R.; Stine, J. R. *J. Phys. Chem.* **1990**, *94*, 5689-5694.
- Lauderdale, W. J.; Stanton, J. F.; Bartlett, R. J. *J. Phys. Chem.* **1992**, *96*, 1173-1178.
- Leininger, M. L.; Sherrill, C. D.; Schaefer, III, H. *J. Phys. Chem.* **1995**, *99*, 2324-2328.
- Gagliardi, L.; Evangelisti, S.; Widmark, P. O.; Roos, B. O. *Theor. Chem. Acc.* **1997**, *97*, 136-142.
- Smith, L. R. *J. Chem. Ed.* **1978**, *55*, 569-570.
- March, J. *Advanced Organic Chemistry* New York, Wiley, **1985**.
- Eaton, P. E.; Cole, T. W. *J. Am. Chem. Soc.* **1964**, *86*, 3157-3158.
- Li, A. H. -T.; Chao, S. D. *J. Chem. Phys.* **2006**, *125*, 094312.
- Boys, S. F.; Bernardi, F. *Mol. Phys.* **1970**, *19*, 553-566.
- Monajjemi, M.; Khaleghian, M.; Mollaamin, F. *Molecular Simulation*. **2010**, *36*, 865-870.
- Shi, Y.; Brenner, D. W. *J. Chem. Phys.* **2007**, *127*, 134503.
- Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648-5652.
- Becke, A. D. *Phys. Rev. A* **1998**, *38*, 3098-3100.
- Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785-789.
- Woon, D. E.; Dunning Jr, T. H. *J. Chem. Phys.* **1993**, *98*, 1358-1371.
- Moller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618-622.
- Saebo, S.; Almlof, J. *Chem. Phys. Lett.* **1989**, *154*, 83-89.
- Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257-2261.
- Clark, T.; Chandrasekhar, J.; Spitznagel, G. W.; Schleyer, P. V. R. *J. Comp. Chem.* **1983**, *4*, 294-301.
- Hariharan, P. C. Pople, J. A. *Theor. Chim. Acta.* **1973**, *28*, 213-222.
- Spartan '10, Version 1.1.0, Deppmeier, B. J.; Driessen, A. J.; Hehre, T. S.; Hehre, W. J.; Johnson, J. A.; Klunzinger, P. E.; Leonard, J. M.; Pham, I. N.; Pietro, W. J.; Yu, Jianguo, Irvine, CA, Wavefunction, Inc., **2011**.
- Sordo, J. A. *J. Mol. Struct. (THEOCHEM)* **2001**, *537*, 245-251.
- Mierzecki, R. *Intermolecular Interactions* Warsaw, PWN, **1974**.