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Theoretical Study of Structural and Electronic Properties in $B_{12}N_{12}$: Exchange, correlation energy and NBO analysis

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ABSTRACT: In this paper, Exchange and Correlation energies of boron nitride with the formula of $B_{12}N_{12}$ are calculated by using the DFT methods with STO-3G, 6-31G AND 6-311G basis sets. The optimized structure and electronic properties calculations for the studied molecule have been performed using Gaussian 09 program. A mathematical equation of second grade was exploited for the correlation and exchange energy with the number of primitives. The Natural Bonding Orbital (NBO) analyses were performed on the $B_{12}N_{12}$ at the B3LYP/ 6-31G level of theory.

Keywords: *Boron-Nitride ($B_{12}N_{12}$), Correlation Energy, DFT Calculation, Exchange, NBO analyses, Primitive.*

INTRODUCTION

Theoretical investigations have considered the possible existence of small BN clusters [1-3]. Jensene and Toftlund performed ab initio calculations for $B_{12}N_{12}$ clusters in different geometries [1]. They concluded that $B_{12}N_{12}$ fullerenes. Contrary to C_{24} fullerenes, are more stable when formed from combinations of four- and six-membered rings due to the absence of wrong B-B or N-N bonds. In this paper, the structural properties of boron nitride with the formula of $B_{12}N_{12}$ are calculated by using the DFT methods with STO-3G, 6-31G and 6-311G basis sets. Then mathematical equations for correlation and exchange energies for this molecule have been calculated comparing to Primitive numbers. The band gap energy, total energy (E), chemical hardness (η),electronic chemical potential (μ), and Global electrophilicity index (ω), ionization potential (IP) and electron affinity (EA) for $B_{12}N_{12}$ have been calculated by using B3LYP/6-31g.

COMPUTATIONAL DETAILS

Methods

All computational on $B_{12}N_{12}$ are carried out using Gaussian 09 program at the restricted LSDA , B3LYP , PBEPBE , HF , MP2 levels in STO-3G , 6-31g and 6-311g basis sets. Exchange and Correlation energies in the above mentioned basis sets were calculated and the curve for correlation and exchange energies according to the number of primitives was drawn using Excell 2013 and the mathematical equation between them

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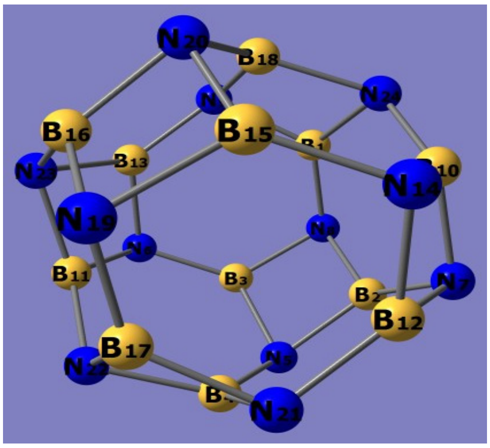

Fig. 1. The theoretical optimized possible geometric structure with numbering of $B_{12}N_{12}$.

was obtained. Energy minimum molecular geometries were located by minimizing energy. Natural bonding orbital (NBO) analysis were performed on the $B_{12}N_{12}$ at the B3LYP/6-31G level of theory.

RESULTS AND DISCUSSION

Molecular properties

The structure of $B_{12}N_{12}$ is shown in Fig. 1. All computational are carried out using Gaussian 09 program. Theoretical calculation of bond lengthes for the $B_{12}N_{12}$ was determined by optimizing the geometry (Table 1).

Exchange and Correlation Energy calculated:
The total optimized energy of $B_{12}N_{12}$ at the RHF and RMP2 levels in STO-3G , 6-31g and 6-311g basis sets are calculated using Gaussian 09. Correlation energy is calculated with equation 1. The results of these calculations are shown in Tables 2 and 3 [4-9].

Table 1. Calculated bond lengthes (A^0) for the $B_{12}N_{12}$.

BOND	bond lengths (A^0)	BOND	bond lengths (A^0)
B1-N8	1.438	B12-N2	1.438
B1-N9	1.486	B12-N7	1.486
B1-N24	1.487	B12-N14	1.486
B2-N5	1.486	B13-N6	1.486
B2-N7	1.438	B13-N9	1.438
B2-N8	1.487	B13-N23	1.486
B3-N5	1.486	B15-N14	1.438
B3-N6	1.438	B15-N19	1.486
B3-N8	1.486	B15-N20	1.486
B4-N5	1.438	B16-N19	1.487
B4-N21	1.486	B16-N20	1.486
B4-N22	1.486	B16-N23	1.438
B10-N7	1.487	B17-N19	1.438
B10-N14	1.487	B17-N21	1.486
B10-N24	1.438	B17-N22	1.487
B11-N6	1.487	B18-N9	1.438
B11-N22	1.438	B18-N20	1.486
B11-N23	1.487	B18-N24	1.487

Table 2. The correlation energy calculated for $B_{12}N_{12}$ at STO-3G , 6-31G and 6-311G basis sets.

Basis set	HF (au)	MP2 (au)	Ecorr. (au) = E (MP2) – E (HF)
STO-3G	-938.535	-0.940	937.595
6-31G	-950.561	-0.953	949.608
6-311G	-950.733	-0.954	949.779

Table 3. The primitive number and correlation energy calculated for $B_{12}N_{12}$.

Basis set	Primitive NO.	Ecorr. (au)
STO-3G	360	937.595
6-31G	672	949.608
6-311G	768	949.779

$$E_{correlation} = E_{RMP2} - E_{RHF} \quad (1)$$

To calculate the exchange energy, total optimized energy of $B_{12}N_{12}$ at the restricted LSDA , B3LYP, PBEPBE, HF, MP2 levels in STO-3G , 6-31g and 6-311g basis sets are calculated. The average of energy differences in different levels is equal to exchange energies in the mentioned levels. The results of the exchange energy are shown in Table 4.

The number of the primitives in STO-3G, 6-31G and 6-311G basis sets are 360 , 672 , 768 respectively. The correlation and exchange energies diagram in relation with the primitives' number is drawn using Excel 2013 and using fitting method mathematical equations are exploited. The results are shown in the Figs. 2 and 3.

NBO study on the structure of the $B_{12}N_{12}$:

NBO calculation are carried out using Gaussian 09 program at the B3LYP/6-31G level [8-10].

Frontier molecular orbital:

Both the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are the main orbital take part in chemical stability. The HOMO represents the ability to donate an electron; LUMO as an electron acceptor represents the ability to obtain an electron .The HOMO and LUMO energy were calculated by B3LYP/ 6-31G method. Energy difference between HOMO and LUMO orbital is called as energy gap that is an important stability for structures. The large LUMO-HOMO gap is often concerned as a molecule stability condition. The HOMO–LUMO energies and energy gap were also calculated at the B3LYP/6-31G and the values are listed in Table 5, respectively.

Chemical reactivity [4-6]:

The chemical reactivity descriptors calculated using DFT are ; total energy (E), chemical hardness (η), electronic chemical potential (μ), and Global electrophilicity index (ω).Chemical hardness is associated with the stability and reactivity of a chemical system. In a molecule it measures the resistance to change in the electron distribution or charge transfer. On the basis of frontier molecular orbitals, chemical hardness corresponds to the gap between the Highest Occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO). Chemical hardness is approximated using equation 2, where εLUMO and εHOMO are the LUMO and HOMO energies. The larger the LUMO– HOMO energy gap, the harder and more stable/less reactive the molecule. Table 6 contains the computed chemical hardness value for $B_{12}N_{12}$.

$$\eta = (\varepsilon LUMO - \varepsilon HOMO)/2 \quad (2)$$

Electronic chemical potential is defined as the nega-

Table 4. The exchange energy calculated for $B_{12}N_{12}$ at STO-3G ,6-31G and 6-311G basis sets.

	total energy (au)			energy difference (au)		
method	STO-3G	6-31G	6-311G	STO-3G	6-31G	6-311G
LSDA	-938.501	-950.694	-950.898	3.563	5.451	5.443
B3LYP	-934.938	-956.145	-956.341			
PBEPBE	-942.829	-954.969	-955.161	7.891	1.176	1.18
B3LYP	-934.938	-956.145	-956.341			
LSDA	-938.501	-950.694	-950.898	4.328	4.275	4.263
PBEPBE	-942.829	-954.969	-955.161			
average				5.260	3.634	3.629

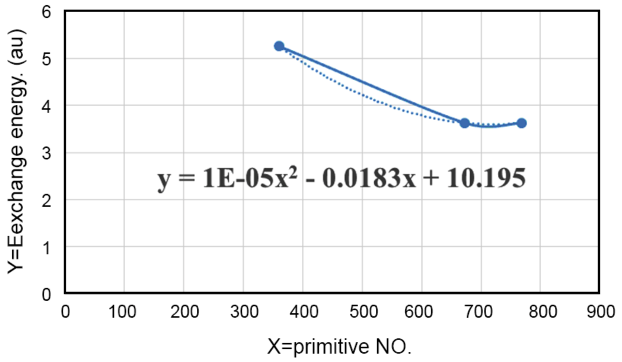

Fig. 2. The exchange energy of the $B_{12}N_{12}$ system as a primitive number at different levels of theory with STO-3G, 6-31G and 6-311G basis sets (▬ ▬ ▬ Calculated data, ▬ fitted).

tive of electronegativity of a molecule and determined using equation 3.

$$\mu = (\varepsilon HOMO + \varepsilon LUMO) / 2 \tag{3}$$

Physically, μ describes the escaping tendency of electrons from an equilibrium system. The values of μ for $B_{12}N_{12}$ are presented in table 6. The greater the electronic chemical potential, the less stable or more reactive is the molecule. Global electrophilicity index (ω), introduced by Parr is calculated using the electronic chemical potential and chemical hardness as shown in equation 4.

$$\omega = \mu 2 / 2\eta \tag{4}$$

Electrophilicity index measures the propensity or capacity of a species to accept electrons [9,4]. It is a measure of the stabilization in energy after a system accepts additional amount of electronic charge from the environment [7]. The electrophilicity value (Table 6) for $B_{12}N_{12}$ is 18.928 eV.

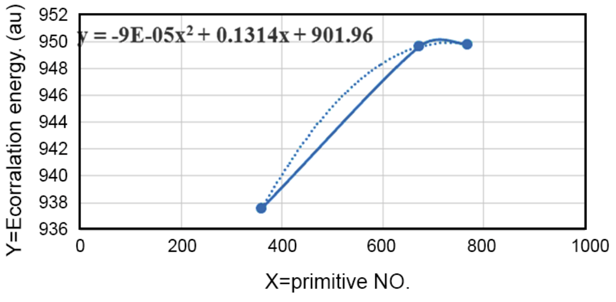

Fig. 3. The correlation energy of the $B_{12}N_{12}$ system as a primitive number at different levels of theory with STO-3G, 6-31G and 6-311G basis sets (▬ ▬ ▬ Calculated data, ▬ fitted).

Table 5. The HOMO–LUMO energies and energy gap for $B_{12}N_{12}$ at the level of B3LYP/6-31G theory.

E total / hartree	-956.145
E HOMO / ev	-7.709
E LUMO / ev	-0.867
E gap / ev	6.842

Table 6. Global chemical reactivity indices for $B_{12}N_{12}$ at the level of B3LYP/6-31G theory.

Global chemical reactivity indices at the level of B3LYP/6-31G theory	
μ / ev	-4.288
η / ev	3.421
ω / ev	2.687
EA / ev	0.867
IP / ev	7.708

The HOMO and LUMO orbital energies are related to gas phase ionization potential (IP) and electron affinity (EA) of $B_{12}N_{12}$ according to the Koopmans' theorem through equations 5 and 6. The ionization potential (IP) and electron affinity (A) values for $B_{12}N_{12}$ are presented in table 6.

$$EA = -\varepsilon LUMO \tag{5}$$

$$IP = -\varepsilon HOMO \tag{6}$$

CONCLUSIONS

DFT calculations are carried out using Gaussian 09 program. The structure of the molecule $B_{12}N_{12}$ is totally optimized. A mathematical equation of second grade was exploited for the correlation and exchange energy with the number of primitives. The electronic properties (IP, EA, μ, η, ω , Egap) are calculated by using B3LYP/6-31g and the values of these are 7.708 (ev), 0.867 (ev) , -4.288 (ev) ,3.421(ev), 2.687 (ev) and 6.841 (ev) respectively .Therefore $B_{12}N_{12}$ shows poor conductivity.

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