



Quantum Chemical Study Of Cdte Cluster By Using First Principal

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Abstract

In present communication geometry stability of $(\text{CdTe})_n$; $n=1-8$ cluster by using HF and DFT method with LANL2DZ basis set. In DFT with have applied two functional B3LYP and B3PW91 for same calculation. For this study all possible conformers are designed and after geometry optimization have been done by using HF/LANL2DZ. The minimum energy conformers of $(\text{CdTe})_n$; $n=1-8$ further optimised by using HF, DFT/B3LP/B3PW91 method along with LANL2MB basis set. The optimised geometry have no imaginary frequencies for $(\text{CdTe})_n$, $n=1-8$ clusters. The electronic properties and reactivity of $(\text{CdTe})_n$ cluster are computed with HOMO (highest occupied Molecular orbital) and LUMO (lowest unoccupied molecular orbitals). The reactivity parameters of $(\text{CdTe})_n$ described that reactivity of odd clusters are high as compared with even clusters. The polarisability of $(\text{CdTe})_n$ increases with increasing size of clusters however dipole moment does not shows any pattern. The computational data explained that HF method overestimate results and DFT method underestimate results. we hope our study play important role in designing new clusters in semiconductor field.

Key Word: HF, DFT, clusters, HOMO LUMO

Introduction

Semiconductor nanocrystals, frequently known as quantum dots [1], have been used widely for a varied range of applications in bio-imaging and bio-sensing. These quantum dots (QDs) are generally composed of atoms from groups II and VI or groups III and V of the periodic table. The diameters of QDs typically are between 1 and 10 nm, and each dot contains a relatively small number of atoms in a discrete cluster [2]. Cadmium telluride (CdTe) is a crystalline compound formed from cadmium and tellurium with a zinc blende (cubic) crystal structure. In the bulk crystalline form it is a direct band gap semiconductor. Recently Zhang Yun et. al. [3] have used cadmium telluride quantum dots as a proton flux sensor and have successfully used it to detect H9 avian influenza virus. Sander F. Wuister et. al. [4] have used efficiently luminescing colloidal CdTe quantum dots (QDs) for the preparation of mono-dispersed and mixed size QD solids. In recent years, quantum dots (QDs) have emerged as an attractive alternative to traditional fluorescent organic dyes for biological labeling owing to their unique, size-tunable spectral properties and excellent photostability[5,6]. One challenge in the application of QDs, however, is their stability and biocompatibility in biological systems. As an important kind of visible light emitting, CdTe QDs have been widely used in biological labeling, such as living-cell imaging [7,8] and cancer marker targeting [9,10]. Structurally, QDs also possess large surface areas for the attachment of multiple diagnostic and therapeutic agents [11,12]. Earlier a brief study of structure and energetics on CdTe cluster by ab initio theory has been carried out[13]. With the increasing interest in Cadmium Telluride nano crystals as non linear optical devices, quantum dots and nanosensors [3,4], the present chapter deals with the calculation of molecular geometry, dipole moment electric polarizability and DFT based reactivity descriptors such as molecular chemical potential, chemical hardness, global electrophilicity index, as well as homo lomo energies of Cadmium Telluride clusters $(\text{CdTe})_n$, $n=1-8$ in gas phase using HF and density functional theory based methods. It is necessary to explore the possible relationships of these reactivity descriptor with cluster size.

Theoretical Background

Parr et.al and Chhatraj et.al [14,15] have interpreted that chemical potential (μ) could be written as the partial derivative of the system's energy with respect to the number of electrons at a fixed external potential $v(r)$:

$$\mu = (\partial E / \partial N)_{v(r)} \quad \text{----(1)}$$

Iczkowski and Margrave [16] proposed to define electronegativity as

$$\zeta = - (\partial E / \partial N)_{v(r)} \quad \text{-----(2)}$$

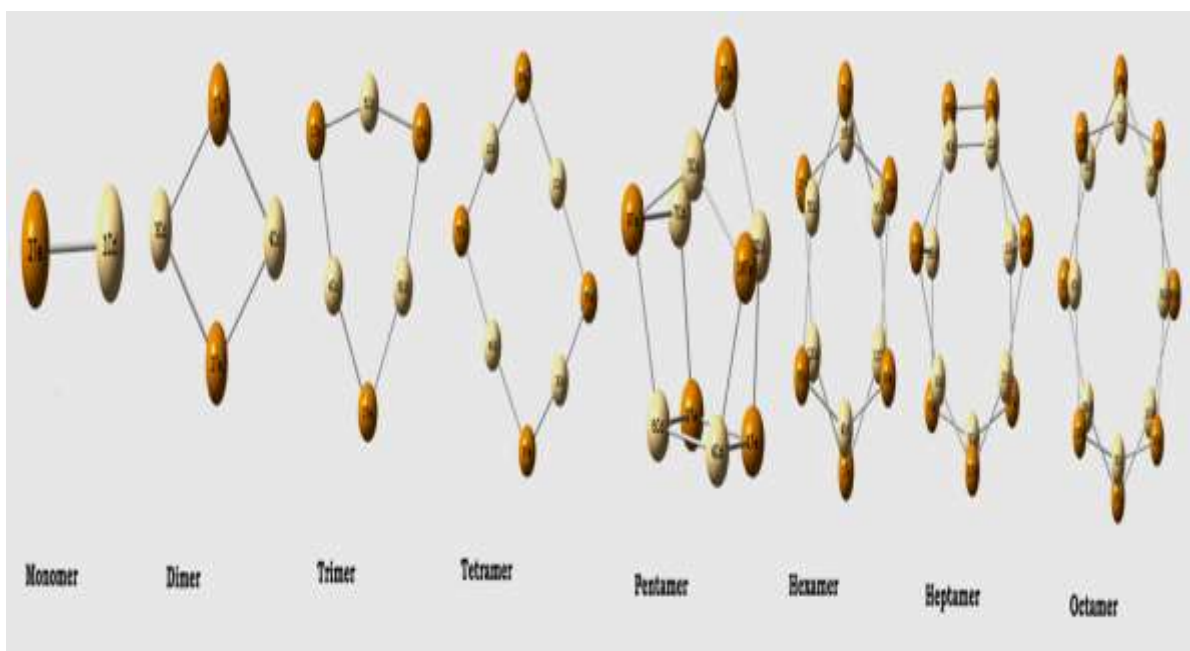


Fig .1 Molecular Geometries of $(\text{CdTe})_n$ cluster ($n= 1- 8$) at B3LYP/ LANL2DZ basis set.

for a fixed nuclear charge. $\mu \approx -(\varepsilon_{\text{HOMO}} + \varepsilon_{\text{LUMO}}) / 2$

The working formulas in DFT for calculating chemical potential (μ), electronegativity (ζ) and hardness (η) are as follows:

$$\mu \approx -(I+A)/2 ; \zeta \approx (I+A) / 2 ; \eta \approx (I-A) / 2 \quad \text{-----(3)}$$

The ionization potential and electron affinity can be replaced by the HOMO and LUMO energies, respectively, using Koopmans' theorem [17] within a Hartree-Fock scheme yielding

$$\zeta = - (\varepsilon_{\text{HOMO}} + \varepsilon_{\text{LUMO}}) / 2 \quad \text{-----(4)}$$

and so on. The ionization potential and electron affinity may be better expressed as:

$$I \approx E(N-1) - E(N) \quad \text{-----(5a)}$$

$$A \approx E(N) - E(N+1)$$

----- (5b)

Parr et al. [14] have introduced the global electrophilicity index (ω) as a measure of energy lowering due to maximal electron flow between a donor and an acceptor in terms of the chemical potential and the hardness as

$$\omega = \mu^2/2\eta$$

----- (6)

Binding energy of the cluster be also defined as given below:

$$\text{binding energy per atom } \{E_b\} = \{-E(\text{CdTe})_n + n(\text{Cd}) + n(\text{Te})\}/2n$$

Results and Discussion-

The calculated molecular geometries for the CdTe and its clusters are shown in Fig.1. These geometries lie on true minima. The HOMO and LUMO of $(\text{CdTe})_n$; $n=1,3,5,7$ and $(\text{CdTe})_n$; $n=2,4,6,8$ are shown in Fig.2 and Fig.3. The calculated values of dipole moment, homo and lumo energies, and chemical potential, chemical hardness mean, polarizability, global electrophilicity index and binding energy are listed in Table 1, Table 2, Table 3 and Table 4.

Binding energy and HOMO LUMO analysis:

The binding energy curve for CdTe cluster is shown in Fig. 5.4 for different basis set with cluster size. The binding energy per atom of the cluster is defined with respect to free atoms follow the mathematical equation:

$$E_b = -[E_{\text{cluster}} - n(E_{\text{Cd}}) - n(E_{\text{Te}})]/2n \quad \text{where } E_{\text{cluster}}, E_{\text{Cd}}, E_{\text{Te}} \text{ are optimized of cluster, free cadmium and free tellurium atom.}$$

The stability of the compound is usually measured in terms of binding energy, bond length, bond dissociation energy, frontier orbital energy and their gap. Frontier orbital energy band gap has been used to evaluate stability. It is found that binding energy per atom with cluster size monotonically increases and dimer, tetramer hexamer and octamer are more stable than monomer, trimer, pentamer and heptamer.

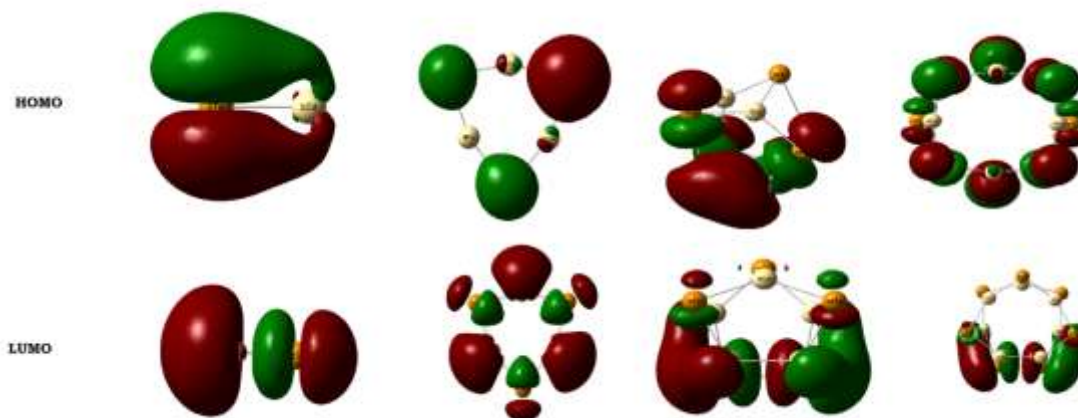


Fig .2 HOMO and LUMO of CdTe Clusters monomer, trimer, pentamer and heptamer.

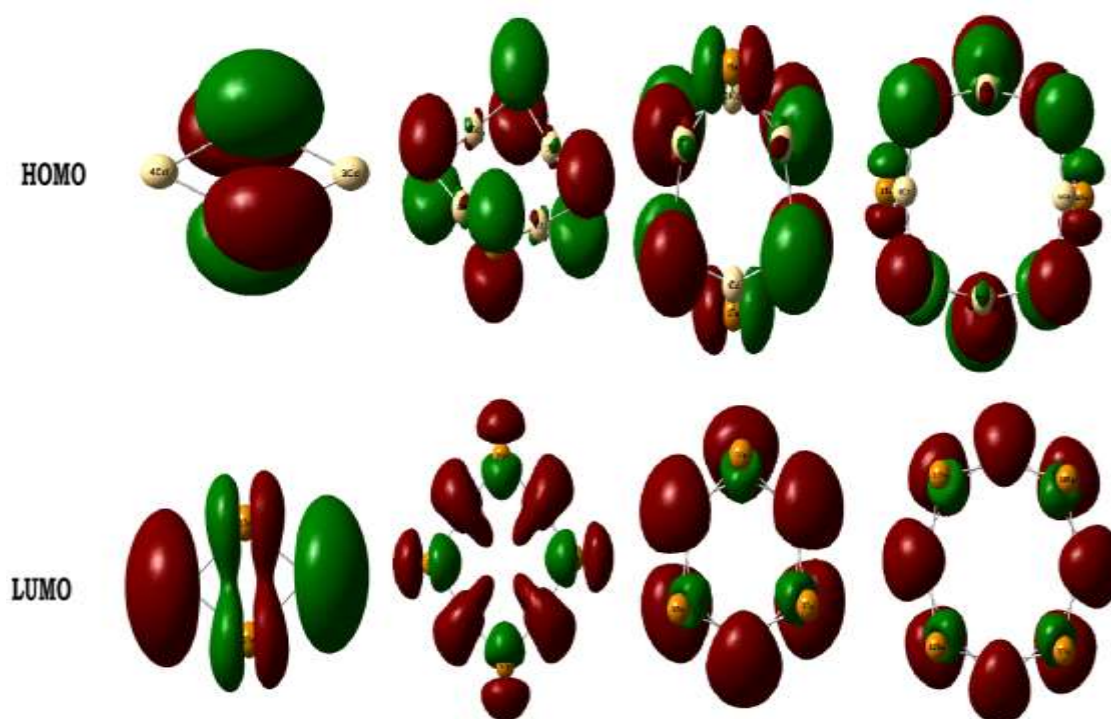


Fig .3 HOMO and LUMO of CdTe Clusters dimer, tetramer hexamer and octamer.

Table :1 Parameters for odd values of n (1,3,5,7) for (CdTe)_n with LANL2DZ basis set

Cluster	method	LANL2DZ							
		Dipole moment in Debye	Homo in eV	Lumo in eV	Chemical potential μ in e.v.	Hardness η in eV	Mean α in a. u.	ω in eV	Binding energy in eV
Monomer	HF	6.4892	-7.6192	-1.6055	-4.613	-3.006	87.99	-3.54	-0.545
	B3LY	5.3258	-5.4967	-4.2450	-4.87	-0.626	79.14	-15.559	-0.830
	B3PW	5.7277	-5.5512	-4.2178	-4.89	-0.667	89.27	-17.925	-0.955
Trimer	HF	0.0002	-8.2451	-0.3538	-4.300	-3.551	197.64	-2.603	-1.767
	B3LY	0.0052	-6.0410	-2.9116	-4.477	-1.564	227.21	-6.407	-1.875
	B3PW	0.0004	-6.1498	-2.7756	-4.463	-1.687	221.21	-5.903	-2.09
Pentamer	H	2.6318	-7.2927	-0.5442	-3.9185	-3.374	343.559	-2.2683	-3.768
	B3LY	3.5295	-5.4695	-3.2654	-4.3675	-1.102	386.816	-8.6540	-3.706
	B3PW	0.9033	-5.6056	-3.2110	-4.4083	-1.197	378.877	-8.1154	-4.192
Heptamer	HF	4.3212	-7.7009	-0.5986	-4.1498	-3.551	482.264	-2.4247	-4.026
	B3LY	4.2178	-5.7416	-3.5103	-4.6260	-1.115	551.931	-9.5903	-3.858
	B3PW	4.0563	-5.7961	-3.5375	-4.7620	-1.129	531.428	-10.0401	-4.344

Table:2 Parameters for even values of n (2,4,6,8) for (CdTe)_n with LANL2DZ basis set

Cluster	method	LANL2DZ							
		Dipole moment in Debye	Homo in eV	Lumo in eV	Chemical potential μ in eV	Hardness η in eV	Mean α in a. u.	ω in eV	Binding energy in eV
Dimer	HF	7.2138	-7.1839	-1.1429	-4.164	-3.020	161.40	-2.870	-1.01
	B3LY	0.0116	-5.0886	-3.5103	-4.300	-0.789	172.27	-11.717	-1.3775
	B3PW9	0.0035	-5.0341	-3.5919	-4.313	-0.721	169.53	-12.900	-1.5375
Tetramer	HF	0.0006	-8.1907	-0.2177	-4.2042	-3.9865	275.98	-2.2169	-4.215
	B3LY	0.7442	-6.0410	-2.8300	-4.4355	-1.6055	322.618	-6.1270	-3.850
	B3PW9	0.8332	-6.2042	-2.7484	-4.4763	-1.7280	312.639	-5.7978	-4.275
Hexamer	H	0.0002	-8.0274	-0.6259	-4.3266	-3.700	387.738	-2.5292	-4.172
	B3LY	1.9340	-6.1498	-3.1021	-4.6260	-1.524	444.209	-7.0219	-4.073
	B3PW9	1.8859	-6.2887	-2.9389	-4.5988	-1.659	431.137	-6.3706	-4.592
Octamer	H	0.0020	-8.0546	-0.5714	-4.3130	-3.7416	535.242	-2.4858	-4.283
	B3LY	2.5036	-6.1770	-3.1293	-4.6532	-1.5238	623.0997	-7.1047	-4.078
	B3PW91	2.4570	-6.3131	-2.9933	-4.6532	-1.6599	602.755	-6.5222	-4.584

Table:3 Parameters for odd values of n (1,3,5,7) for (CdTe)_n with LANL2MB basis set

Cluster	method	LANL2MB							
		Dipole moment in Debye	Homo in eV	Lumo in eV	Chemical potential μ in eV	Hardness η in eV	Mean α in a. u.	ω in eV	Binding energy in eV
Monomer	HF	5.0194	-7.7553	-1.5238	-4.64	-3.115	86.37	-3.456	-0.260
	B3LY	4.6491	-5.6327	-4.4899	-5.062	-0.571	70.72	-22.437	-0.525
	B3PW9	4.9917	-5.6872	-4.5171	-5.102	-0.585	71.34	-22.248	-0.620
Trimer	HF	0.0002	-8.2723	-0.8708	-4.572	-3.700	190.35	-2.824	-1.168
	B3LY	0.0008	-6.1770	-3.3742	-4.776	-1.401	214.20	-8.140	-1.406
	B3PW9	0.0005	-6.3131	-3.3198	-4.816	-1.496	207.99	-7.752	-1.59
Pentamer	H	2.6318	-7.2927	-0.5442	-3.9185	-3.3742	343.559	-2.2683	-3.768
	B3LY	3.2693	-5.8504	-3.5647	-4.7076	-1.1429	352.601	-9.6953	-2.976
	B3PW9	3.1819	-5.9321	-3.5103	-4.7212	-1.2109	340.423	-9.2038	-3.393
Heptamer	HF	4.3212	-7.7009	-0.5986	-4.1498	-3.5511	482.264	-2.4247	-4.026
	B3LY	3.7799	-6.0682	-3.7280	-4.8991	-1.1701	513.416	-10.2519	-3.086
	B3PW9	3.63132	-6.2042	-3.7824	-4.9933	-1.2109	493.366	-10.2953	-3.504

Table :4 Parameters for even values of n (2,4,6,8) for (CdTe)_n with LANL2MB basis set

Cluster	method	LANL2MB							
		Dipole moment in Debye	Homo in eV	Lumo in eV	Chemical potential μ in eV	Hardness η in eV	Mean α in a. u.	ω in eV	Binding energy in eV
Dimer	HF	7.0837	-7.2111	-1.7143	-4.463	-2.748	163.72	-3.624	-0.645
	B3LY	5.1197	-5.2246	-4.1634	-4.694	-0.530	166.91	-20.786	-1.09
	B3PW91	5.4977	-5.2791	-4.1089	-4.694	-0.612	164.05	-18.001	-1.225
Tetramer	H	0.0000	-8.2723	-0.5987	-4.4355	-3.8368	273.211	-2.5638	-3.024
	B3LY	0.5634	-6.2315	-3.0205	-4.6260	-1.6055	309.666	-6.6446	-2.958
	B3PW9	0.5646	-6.3675	-2.9933	-4.6804	-1.6871	300.006	-6.4922	-3.282
Hexamer	H	0.0002	-8.0274	-0.6259	-4.3266	-3.7007	387.738	-2.5292	-4.172
	B3LYP	1.6704	-6.4491	-3.5919	-5.0205	-1.4286	402.344	-8.8217	-3.252
	B3PW9	1.6206	-6.5852	-3.5103	-5.0478	-1.5374	387.507	-8.2868	-3.695
Octamer	HF	0.0020	-8.0546	-0.5714	-4.3130	-3.7416	535.242	-2.4858	-4.283
	B3LY	2.1644	-6.4764	-3.5647	-5.0205	-1.4558	582.369	-8.6569	-3.248
	B3PW9	2.1071	-6.6124	-3.4831	-5.0478	-1.5647	559.581	-8.1422	-3.681

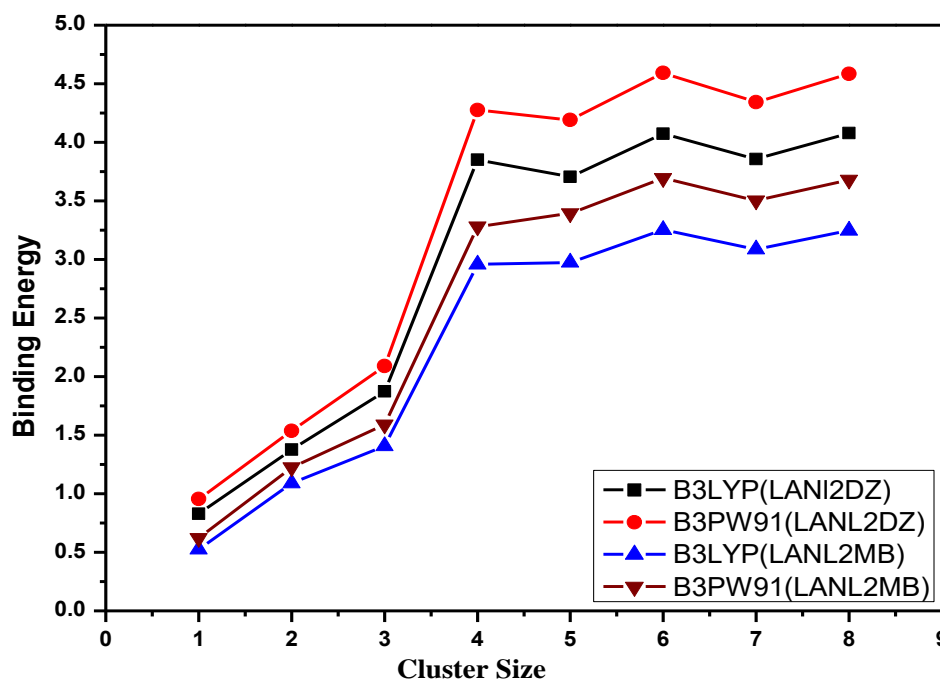


Fig .4 Variation of Binding Energy with cluster size n=1-8.

The E_b values are listed in Table1, Table 2, Table 3, Table4 and a graph between E_b and cluster size is given in Fig 4. The maximum binding energy is obtained as 4.584 eV per atom for $(\text{CdTe})_8$. Fukui et al. [18] described the eminent role played by HOMO and LUMO as a governing parameter of chemical reaction. Several studies show that band gap $E_{\text{homo-lumo}}$ is a very important stability index of molecules [19,20]. A large band gap implies high stability where as a small band gap implies lower stability. Variations of HOMO LUMO composition is also shown in Fig.(5.2,5.3). It decreases with cluster size from 6.0137 eV to 2.3846 eV for hartee fock theory (Fig.5) whereas it increases for DFT functional with cluster size from 1.2517 eV to 2.3946 eV.

Global Reactivity Descriptors:

Basic reactivity descriptors play a very important role in rationalizing molecular structure and chemical reaction . DFT has provided the basis for calculation of reactivity descriptors. The chemical potential (μ) characterizes the escaping tendency of electrons from equilibrium. The hardness (η) can be seen as resistance to charge transfer and softness (S) has been quantitatively related to polarizability of system. The value of these descriptors are listed in Table1, Table2, Table 3, Table 4 and their variation with respect to cluster size are

shown in Fig. 6, Fig. 7, Fig. 8. It has been found that tetramer, hexamer and octamer are more harder (more stable) than neighbouring cluster. In Fig. 7 plot of chemical hardness has been shown with the lowest value of 0.530 eV and 3.9865 eV as maximum value. A harder molecule means it is hard to react or more stable. As hardness and softness are important factors of the charge transfer resistance and inversely proportional to each other [14]. For small chemical systems the softness is readily related with polarizability. The polarizability (α) measures the distortion of the electron density of the molecules in the response of the molecule to the external electric field. As shown in Fig8 the mean polarisability monotonically increases with cluster size for both even and odd cluster size and have maximum value 623.0997 a.u. for octamer.

The chemical potential (μ) characterizes the tendency of electron to escape from the molecule in the equilibrium state. Koopman's theorem has been used to calculate μ of the molecules [17]. In present calculation the chemical potential varies with size but it increase for even n values of cluster (Fig 6), a reverse trend for odd n has been observed except for heptamer.

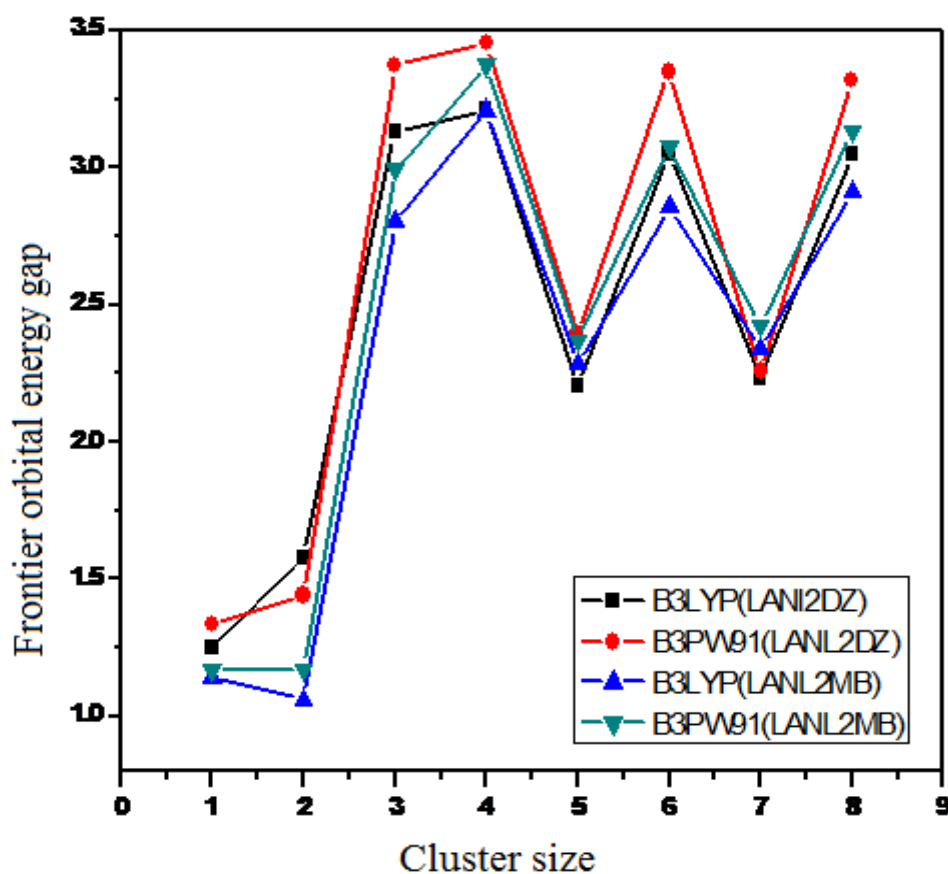


Fig 5 Variation of Frontier Orbital energy gap with cluster size n=1-8.

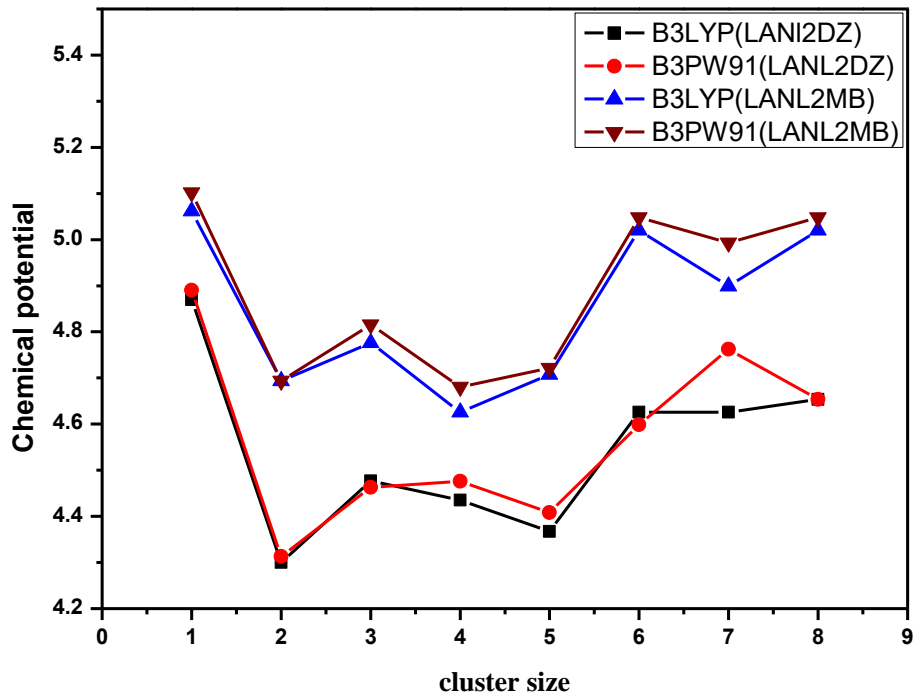


Fig6 Variation of Chemical Potential with cluster size n=1-8.

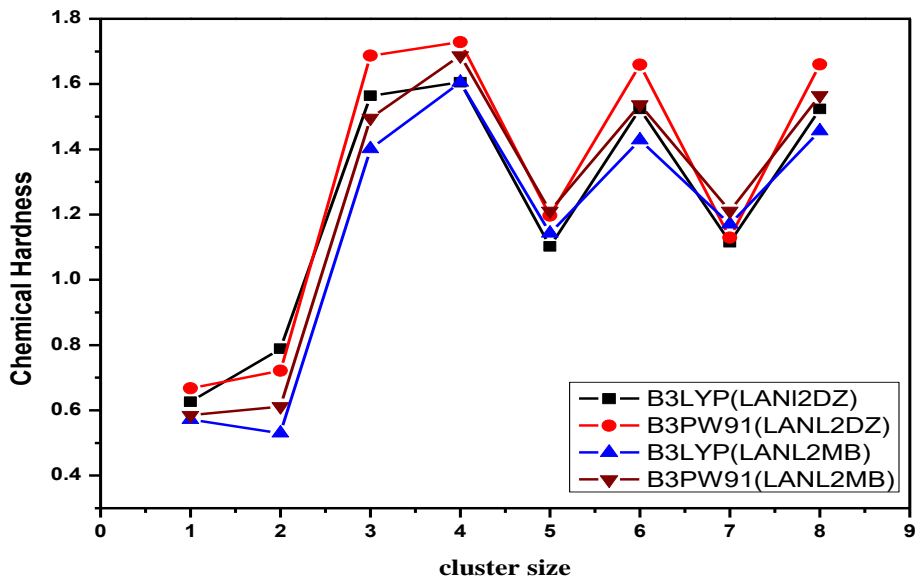


Fig 7 Variation of Chemical Hardness with cluster size n=1-8.

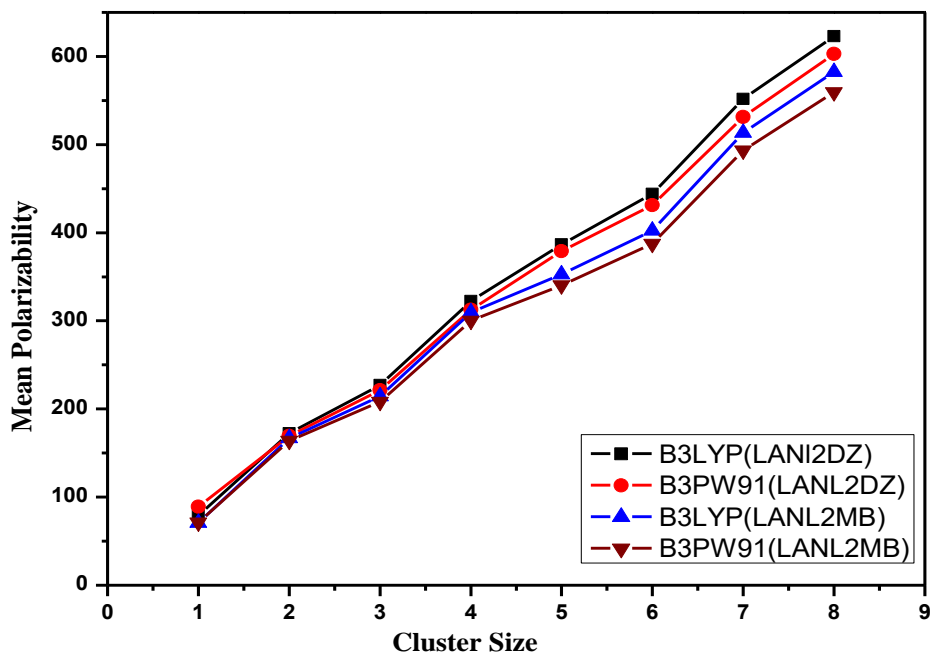


Fig.8 Variation of Mean Polarizability with cluster size n=1-8.

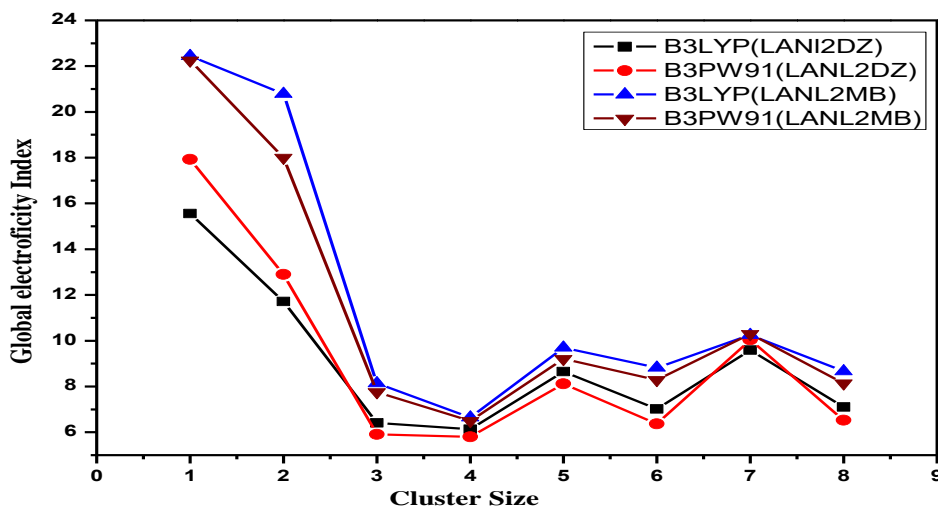


Fig.9 Variation of Global Electrophilicity Index with cluster size n=1-8.

Global electrophilicity index:

The generalized concept of philicity was proposed by Chattaraj et. al. [20].

The group concept of philicity is very useful in unraveling reactivity of various molecular system. The condense philicity summed over a group of relevant atoms is defined as the group philicity. It can be expressed as:

$$\omega = \mu^2/2\eta$$

In the present work it is seen that the global electrophilicity index first decreases with cluster size and is minimum for trimer and then rises slowly for both n even and odd values (Fig. 5.9).

Conclusions

According to the present calculations on CdTe clusters (n=1-8), we observed that with change in cluster size binding energy increases, the even n clusters i.e. dimer, tetramer, hexamer and octamer have more binding energy than preceding odd n clusters monomer, trimer, pentamer and heptamer. It has also been found that mean polarisability increases with cluster size, whereas dipole moment does not follow any trend. Calculation of chemical hardness and homo – lumo gap also confirms the greater reactivity of odd n, CdTe clusters. The present quantum chemical study may further play an important role in understanding in the use of CdTe clusters in various devices.

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