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Quantum Chemical Insights on Structural and Electronic properties of Anionic, Cationic and Neutral ZrO_2 nanostructures

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Abstract: The realistic structures of cubic and monoclinic phases of zirconia nanostructures are optimized and simulated successfully using B3LYP/ LanL2DZ basis set. The structural stability of zirconia nanostructures are described by calculated energy, chemical hardness and chemical potential. The point symmetry group and dipole moment of cubic and monoclinic zirconia nanostructures are also reported. Using HOMO – LUMO gap, electron affinity and ionization potential, the electronic properties of cubic and monoclinic zirconia are studied. The information provided in the work helps to improve structural stability and electronic properties of ZrO_2 nanostructures for anionic, neutral and cationic states which find its application in thermal barrier coating, ceramic biomaterial, nanoelectronic devices and catalysts.

Keywords: zirconia; electronic properties; HOMO; LUMO; chemical hardness; dipole moment.

Introduction

Zirconium oxide (ZrO_2) exhibit different properties from other metal oxides, its unique properties are basis sites sustentation, stability at high temperature and also heat insulation. Other properties of ZrO_2 include high dielectric constant, wide optical band gap, low optical loss and high transparency in visible and near infrared regions [1-6].These unique properties of ZrO_2 has wide applications in toughening ceramic materials, gas sensitive sensors, electrolytes in solid-oxide fuel cells, protective coating for optical filters and mirrors, thermal barrier coating, ceramic biomaterial, nanoelectronic devices, thermoluminescence UV dosimeter and as catalysts [7-13]. Zirconia exists in three polymorphs namely monoclinic at temperature below 1170^{o}C, tetragonal at temperature between 1170 to 2370^{o}C and cubic at temperature between 2370 to 2680^{o}C [14].

The nanostructure of ZrO_2 plays a significant role in preparing electrooptic, dielectric, piezoelectric and nanocomposites [15-17]. Mainly the performance of ZrO_2 depends on the crystal structure which influences the physical properties of ZrO_2. ZrO_2 can be synthesized by many methods such as electrospinning, direct electrochemical anodization method and hydrothermal route [18-20]. The controlled growth of ZrO_2 nanostructures with respect to morphology, superstructure and specific size leads to key aspects in the development of new functional materials in engineering field. With this as motive, the literature survey was conducted and most of the reported works are only in the synthesis and characterization of ZrO_2 thin films and nanostructures [21, 22]. From the survey it is inferred that not much work has been carried out in studying the structural and electronic properties of ZrO_2 using density functional theory (DFT). It is an important method to deliver good electronic properties and structural stability of zirconia [23-25]. In the present work, anionic, cationic and neutral state of monoclinic and cubic ZrO_2 nanostructures are studied and reported.

Computational Details

The realistic zirconia nanostructures are optimized and simulated successfully using DFT technique with the combination of B3LYP and LanL2DZ basis set. In DFT studies, exchange correlation functional consists of correlation of electron and exchange energy. The pseudo potential approximation mainly replaces the complex effects of valence electrons in an atom which transform the potential energy term in the Schrödinger equation. The optimization of ZrO_2 nanostructures are achieved by NWChem package [26-32]. In this work, the convergence of energy is obtained in the order 10^{-5} eV. LanL2DZ basis set is most suitable for H, Hf-Bi and Li-La elements. Moreover, it is suitable to optimize ZrO_2 nanostructures.

Results and Discussion

The existing work mainly focus on ionization potential (IP), electron affinity (EA), dipole moment (DP), chemical potential (CP), chemical hardness (CH), HOMO-LUMO gap and calculated energy of neutral, cationic and anionic state of ZrO_2 nanostructure in two phases namely cubic and monoclinic. Figure 1(a) and Figure 1 (b) represents cubic and monoclinic phases of ZrO_2 nanostructures. The cubic zirconia has eight Zr atoms and twelve O atoms to form cubic ball like structure. Monoclinic zirconia has eight Zr atoms and eleven O atoms in its nanostructure.

Figure.1(a) Structure of cubic zirconia nanostructure

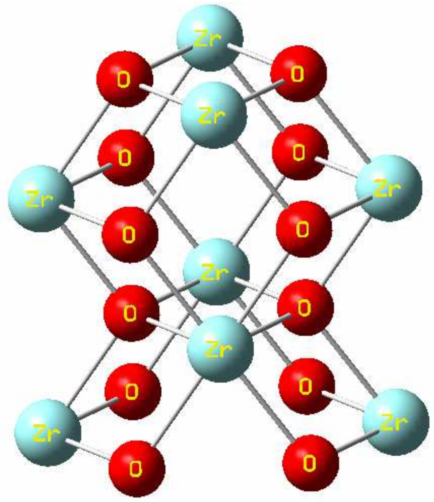


Figure.1(b) Structure of monoclinic zirconia nanostructure

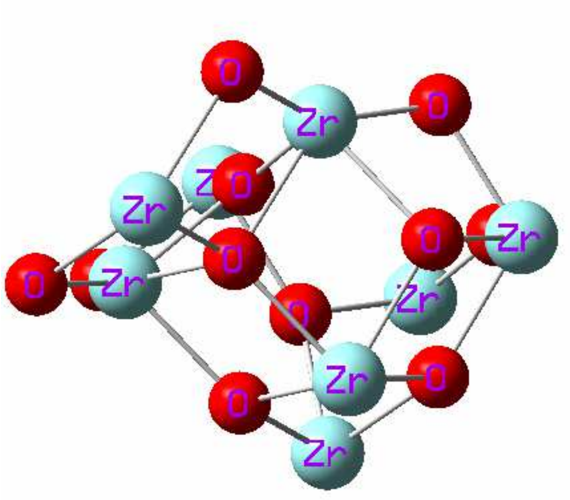


Table.1 Energy, point symmetry and dipole moment of zirconia nanostructures

Nanostructures	**Energy (Hartrees)**	**Dipole moment (Debye)**	**Point Group**
Cubic neutral zirconia	-1267.67	8.03	C_{2V}
Cubic cationic zirconia	-1267.54	18.73	C_{2V}
Cubic anionic zirconia	-1267.83	0.33	C_{2V}
Monoclinic neutral zirconia	-1192.7	10.4	C_1
Monoclinic cationic zirconia	-1192.63	11.17	C_1
Monoclinic anionic zirconia	-1193	8.28	C_1

The structural stability of zirconia can be analyzed by calculated energy. Table 1 contains calculated energy, point symmetry and dipole moment of zirconia nanostructure for neutral, cationic and anionic states. Cubic zirconia has the calculated energy of -1267 Hartrees and the calculated energy value for monoclinic zirconia is around -1192 Hartrees. The stability of cubic zirconia is slightly higher than the stability of monoclinic ZrO_2 nanostructure due to addition of one oxygen atom. Dipole moment gives insights to the distribution of charges across zirconia nanostructures. The charge distribution is not uniform in the case of cubic neutral and cubic cationic zirconia nanostructure. Since, high value of DP around 8.03 and 18.73 Debye is observed for neutral and cationic structures. In contrast the cubic anionic zirconia nanostructure has 0.33 Debye. It infers the uniform charge distribution inside the cubic anionic ZrO_2 nanostructure. DP of monoclinic zirconia nanostructures is in the range of 8.28 – 11.17 Debye. It shows the charges are not uniformly distributed in all the three states of monoclinic ZrO_2 nanostructures. Compared to monoclinic zirconia, atoms are uniformly arranged in cubic ZrO_2 nanostructures. The monoclinic ZrO_2 has point group of C_1 which has only one symmetry operation, identity operation E. Cubic ZrO_2 has the point symmetry of C_{2v} which has symmetry elements of E, C_n, and $n\sigma_v$.

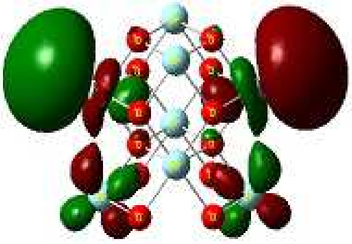
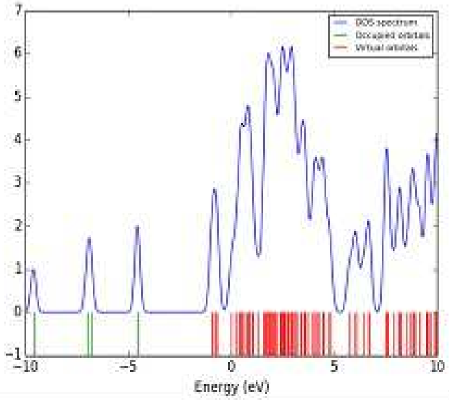
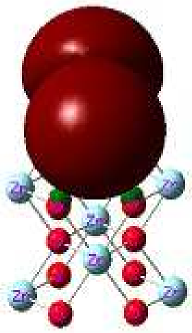
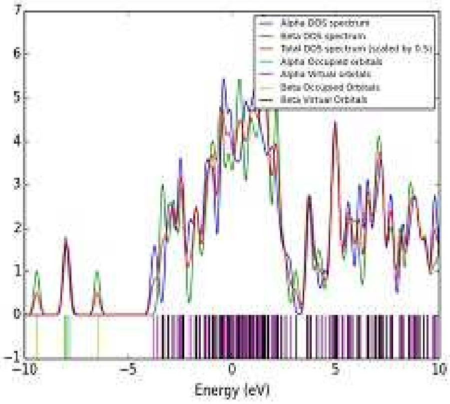
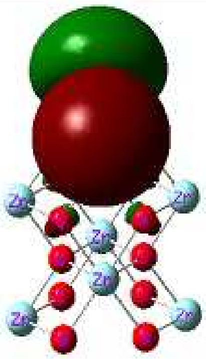
HOMO-LUMO gap of ZrO_2 nanostructures

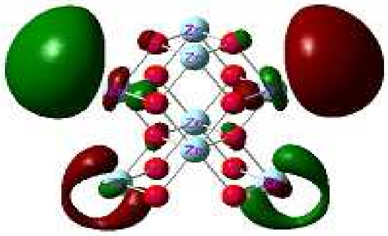
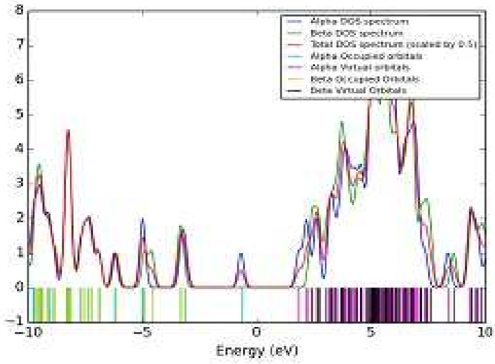
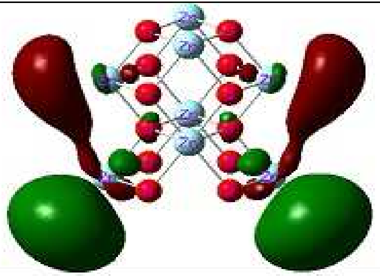
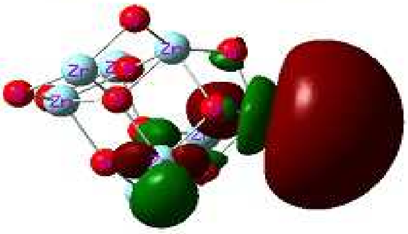
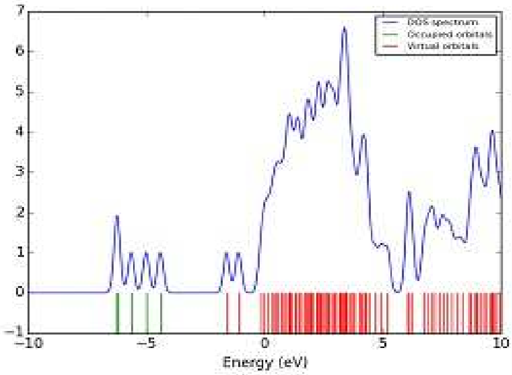
The electronic properties of cubic and monoclinic zirconia nanostructures are discussed by lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) [33, 34]. The HOMO – LUMO gap of ZrO_2 nanostructures shows both alpha gap and beta gap. The alpha gap arises due to spin up and beta gap arises due to spin down electron of ZrO_2 nanostructure. The alpha HOMO – LUMO gap of cubic neutral, cationic and anionic zirconia nanostructures are 3.59, 4.06 and 2.53 eV respectively and the corresponding alpha gap of monoclinic ZrO_2 nanostructures are found to be 2.8, 4.28 and 4.66 eV. It shows the zirconia has wide optical band gap and high dielectric constant. Moreover, the optical loss is very less and thermal stabilities are very high in zirconia nanostructures. This type of materials can be used in gas sensors, catalysis, ceramic and paint additives. Table 2 shows the HOMO –LUMO gap of ZrO_2 nanostructures. The localization of charges along zirconia nanostructures are discussed in terms of density of states (DOS). Moreover, in the virtual orbital the density of charges is found to be more which can be clearly seen by peak maximum. DOS spectrums of ZrO_2 nanostructures are displayed in Table 3.

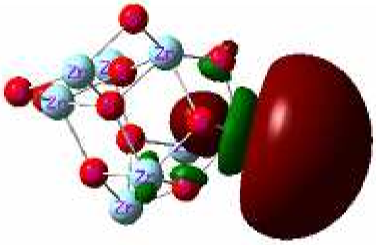
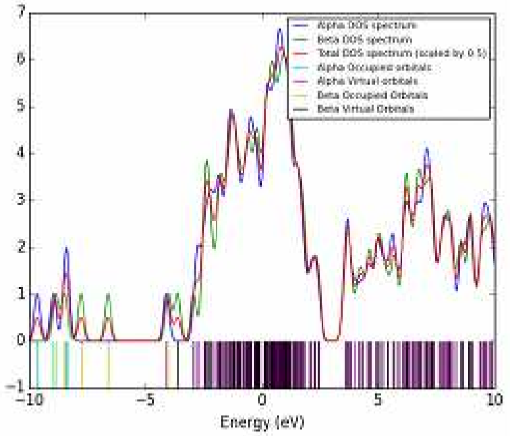
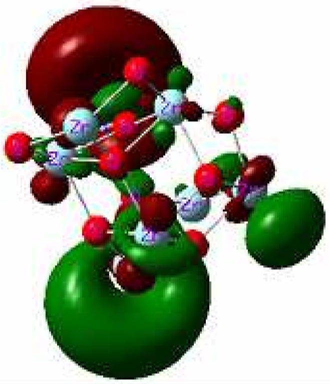
Table.2 HOMO, LUMO gap of ZrO_2 nanostructures

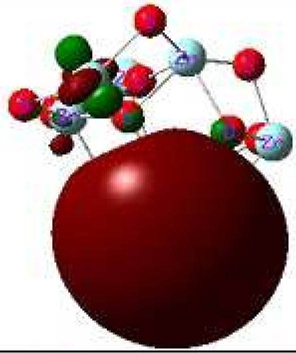
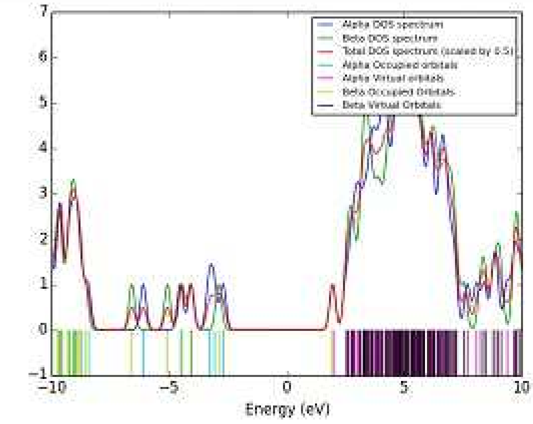
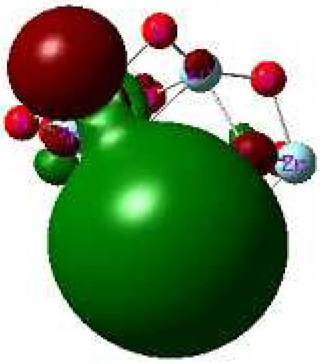
Nanostructures	HOMO	LUMO	E_g(eV) Alpha	HOMO	LUMO	E_g(eV) beta
Cubic neutral zirconia	-0.95	-4.54	3.59	-	-	-
Cubic cationic zirconia	-3.8	-7.86	4.06	-6.49	-7.94	1.45
Cubic anionic zirconia	1.86	-0.67	2.53	2.42	-3.25	5.67
Monoclinic neutral zirconia	-1.6	-4.4	2.8	-	-	-
Monoclinic cationic zirconia	-4.09	-8.37	4.28	-4	-6.61	2.61
Monoclinic anionic zirconia	1.97	-2.69	4.66	1.95	-2.88	4.83

Table.3 HOMO-LUMO gap and density of states of zirconia nanostructures

Nano structures	HOMO – LUMO Visualization 🟩 HOMO 🟥 LUMO	E_g (eV)	HOMO, LUMO and DOS Spectrum
Cubic neutral zirconia		3.59	
Cubic cationic zirconia (alpha)		4.06	
Cubic cationic zirconia (beta)		1.45	

Cubic anionic zirconia (alpha)		2.53	
Cubic anionic zirconia (beta)		5.67	
Monoclinic neutral zirconia		2.8	

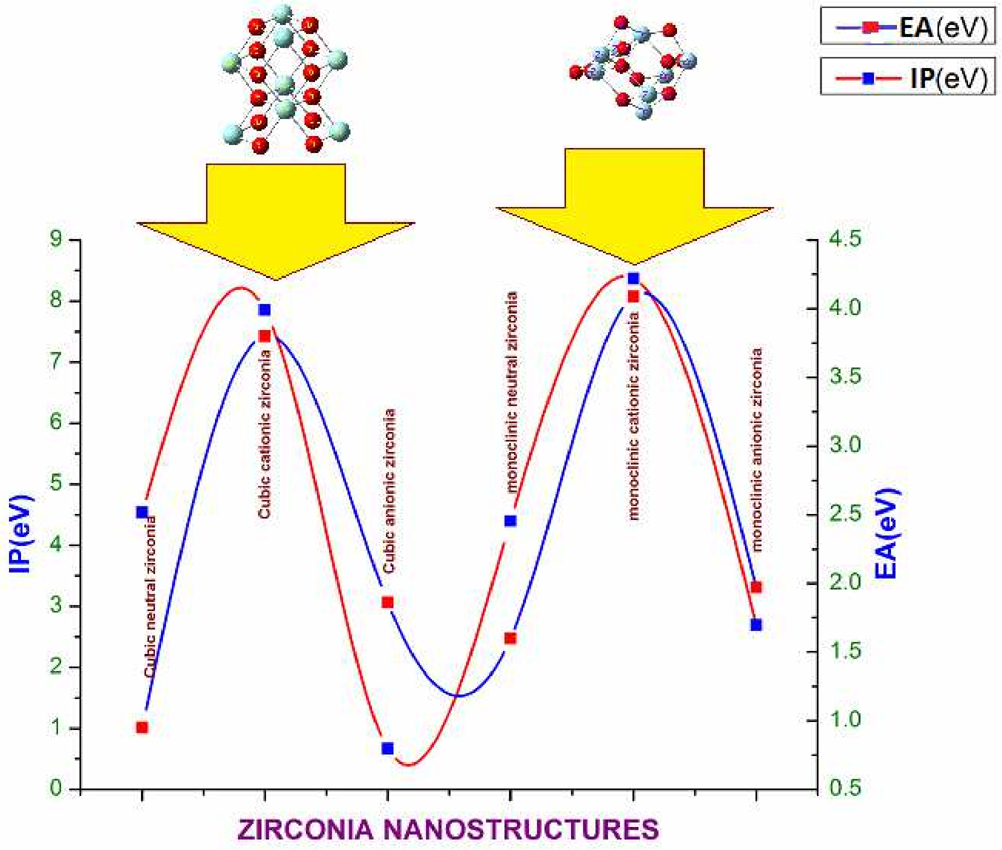
Monoclinic cationic zirconia (alpha)		4.28	
Monoclinic cationic zirconia (beta)		2.61	

Monoclinic anionic zirconia (alpha)		4.66	
Monoclinic anionic zirconia (beta)		4.83	

Ionization potential, Electron affinity, Chemical potential and Chemical hardness of ZrO_2 nanostructures

The electronic properties of zirconia can also be described by electron affinity (EA) and ionization potential (IP) [35]. The IP and EA of ZrO_2 nanostructures are graphically represented as shown in Figure 2.

Figure.2 IP and EA of zirconia nanostructures



The sufficient energy required to remove electron from ZrO_2 nanostructures are referred as IP. The energy change due to addition of electron in ZrO_2 nanostructures is referred as EA. Different trends are observed for both IP and EA of ZrO_2 nanostructures. IP values for cubic neutral, cationic and anionic zirconia are found to be 4.54, 7.86 and 0.67 eV respectively. The corresponding IP value for monoclinic neutral, cationic and anionic zirconia nanostructures are observed at 4.4, 8.37 and 2.69 eV. Therefore, more energy is required to remove electron from both phases of zirconia in cationic state. In contrast less energy is required to remove electron from anionic and neutral states of zirconia in both phases. Electron affinity plays a vital role in chemical sensors and plasma physics. The EA value of cubic neutral, cationic and anionic ZrO_2 nanostructures are 0.95, 3.8 and 1.86 eV respectively and the prominent EA value for monoclinic neutral, cationic and anionic ZrO_2 nanostructures are observed at 1.6, 4.09 and 1.97 eV. The cationic state of ZrO_2 has much change in EA which is more suitable for chemical sensor application. In contrast the energy change is not much noticed for neutral and anionic states for both phases of zirconia.

Chemical hardness and chemical potential are highly related to EA and IP. The structural stability zirconia can also be characterized by CH and CP [36]. The general formula for CH and CP is $\eta = (IP-EA)/2$ *and* $\mu = -(IP+EA)/2$ respectively.

Table.4 Chemical potential and chemical hardness of ZrO_2 nanostructures

Nanostructures	**Chemical potential (eV)**	**Chemical hardness (eV)**
Cubic neutral zirconia	-2.74	1.79
Cubic cationic zirconia	-5.83	2.03
Cubic anionic zirconia	-1.26	-0.59
Monoclinic neutral zirconia	-3.00	1.4
Monoclinic cationic zirconia	-6.23	2.14
Monoclinic anionic zirconia	-2.33	0.36

Chemical potential is nothing but the potential energy released or absorbed during the chemical reaction and it can also represented by electronegativity. Chemical potential and chemical hardness can be inferred by effective fragment potential method. CP and CH value have different trends as shown in Table 4. The prominent CP values of cubic neutral, cationic and anionic zirconia are -2.74, -5.83 and -1.26 eV and the corresponding CH values are 1.79, 2.03 and -0.59 eV respectively. The chemical potential value of monoclinic neutral, cationic and anionic ZrO_2 nanostructures are observed at -3.00, -6.23 and -2.33 eV respectively and the corresponding CH values are 1.4, 2.14 and 0.36 eV. More energy is absorbed or released only in the cationic state of zirconia nanostructures. For remaining states there is no significant energy is absorbed or released in ZrO_2 nanostructures.

Conclusion

Using DFT method, anionic, neutral and cationic states of cubic and monoclinic zirconia are optimized and simulated precisely with B3LYP/ LanL2DZ basis set. Electronic properties of zirconia are studied in terms of HOMO – LUMO gap, ionization potential and electron affinity. Structural stability of zirconia also discussed with the help of chemical hardness, calculated energy and chemical potential. Point symmetry and dipole moment for both monoclinic and cubic phases of zirconia has been reported. The information provided in the present will be useful to enhance the electronic properties and structural stability of cubic and monoclinic phases of zirconia nanostructures which are used in ceramic biomaterial, nanoelectronic devices and thermoluminescence material.

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