Ab Initio studies on electronic structure and charge density of chitosan

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ABSTRACT

Biopolymer Chitosan has physico-chemical properties that open up a wide span of applications in many sectors. In this paper we report a theoretical study of Chitosan. This is an ab initio study based on density functional theory implemented in computational program SIESTA with use of LDA and GGA scheme for an account of exchange co-relation effect to obtain density of states(DOS), projected density of states(PDOS), charge density, Mulliken, Hirshfeld, Voronoi population and crystal orbital overlap populations COOP analysis of Chitosan. In the first step structure of Chitosan is optimized for lowest energy value for LDA and GGA. On the basis of band plots and PDOS, it can be stated that for LDA the system under study is electronically semiconductor and for GGA it is insulator. The charge density analysis proves it as ionic conductors. The contributions to the top of valence band (HOMO) and bottom of conduction band (LUMO) come predominantly from O s/p, N s/p , C s/p and H s states, respectively. This is the first principles study to observe theoretically the effect of Chitosan before its further application as an electrolyte in various electro-chemical devices.

Key words: Charge Density; Density of states; Projected Density of States; Crystal Orbital Overlap and Hamilton populations.
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INTRODUCTION

Chitosan is a high-molecular copolymer with acetyloglucosamine and glucosamine radicals in its chain. After dissolution in diluted organic and inorganic acids, it forms viscid polyelectrolytes[1]. It consists of physicochemical properties such as Molecular weight, degree of polymerization, Degree of DeAcetylation, Viscosity, Solubility, Antimicrobial properties, Reactivity, Complexation ability[2]. Hence received great interest in many scientific research areas such as chemical sensor, electronic devices and optical devices. Chitosan is a natural carbohydrate biopolymer derived by deacetylation (DA) of chitin, a major component of the shells of crustacea such as crab, shrimp, and crawfish. After cellulose, Chitin is the second most abundant natural biopolymer found in nature[3]. Like cellulose, Chitosan is a fibre. However, unlike plant fibre, Chitosan possesses unique properties including the ability to form films, optical structural characteristics , binding capacity and much more. Chitosan also possesses a positive ionic charge, which gives it the ability to chemically bind with negatively charged fats, lipids and bile acids[4].

Chitosan is an attractive natural biopolymer with the presence of reactive amino and hydroxyl functional groups[5]. So many experimental work reported on this system [1,3,4,5] and theoretical analysis is almost missing. Chitosan has shown favourable biocompatibility characteristics. It is a non-toxic, biodegradable and biocompatible polymer[6]. Therefore, we thought it would be worthwhile to perform a comprehensive theoretical work based on density functional theory. In this work, we employ the first-principles density functional theory(DFT) to systematically investigate the electronic properties, density of states, band structure, projected DOS, charge density, Mulliken population, Hirshfeld population, Voronoi population and COOP analysis of Chitosan for LDA and GGA.

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MATERIALS AND METHODS

With the help of Avogadro software we sketched the molecular structures of Chitosan($C_6H_{11}NO_4$)n, n=1,[7] and further optimization process is performed in four steps i) optimization of mesh cut-off, ii) optimization of k-points iii) optimization of lattice constant/simulation box size and iv) final optimization. The LDA and GGA, exchange co-relational functions used for comparative analysis of structural ,charge density and electronic properties of this system. Density functional theory(DFT) calculations are performed using Siesta package, which employs norm-conserving psuedopotential and localized atomic orbitals as basis set[8,9]. The geometries are investigated by standard DFT using the local density approximation (LDA) of Caperley and Alder (CA) and the general gradient approximation (GGA) of Perdew, Burke and Emzerhof (PBE) used for all atoms in electronic structure calculations[9,10]. The main modelling parameters used Simulation Box size, Mesh-Cutoff, K grid along-with total energy after final optimization are listed in Table 1.

Table 1 Modelling Parameters of these systems Chitosan

System Used	Simulation Box size Å	Mesh-Cutoff	K Grid	Total Energy (eV)
Chitosan LDA	7x7x5	200	1x1x8	-3111.95
Chitosan GGA	7x7x6	350	1x1x8	-3124.69

RESULTS AND DISCUSSION

3.1 Structural Properties

The optimized structures of Chitosan are shown in Figures 1(a-b) for LDA and GGA respectively. Some important optimized bond lengths are shown in Table (2) for LDA and GGA both . By comparing an obvious structural change in the bond lengths can be observed in Chitosan. The optimized bond lengths N11-O9, N11-C1, N11-C4, O8-N11, N11-H16 obtained by LDA are slightly shorter than obtained bond lengths of GGA and bond lengths C6-C4, C8-C3, O8-O9, C3-H16, C5-H16 obtained by LDA are slightly larger than obtained bond lengths of GGA which are expected.

Table 2 Bond lengths of optimized Chitosan system

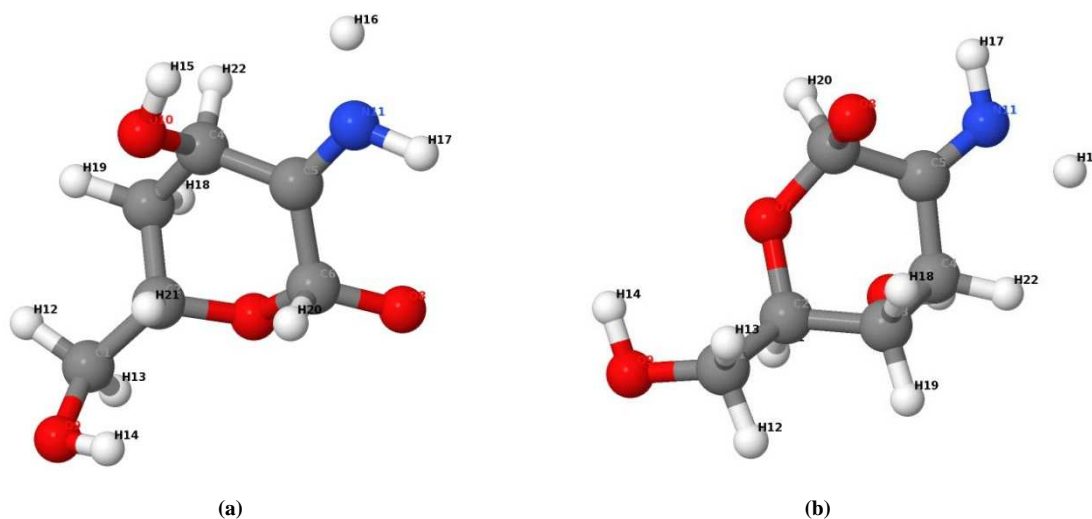| Bonds	Bond Length of Chitosan *(Å)*	
	LDA	GGA
N11-O9	6.32479	6.54598
N11-C1	5.61045	5.62692
N11-C4	2.40082	2.40827
C6-C4	2.57023	2.50320
C8-C3	4.07534	3.13926
O8-O9	5.32837	4.90416
O8-N11	2.94818	3.00552
N11-H16	1.40645	1.44451
C3-H16	4.06603	3.88789
C5-H16	2.27384	2.25700

(a)   **(b)**

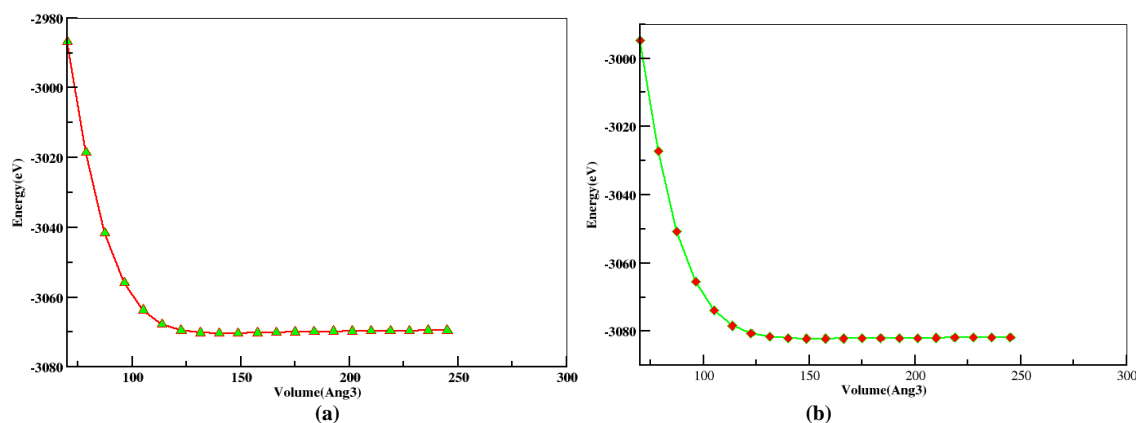**Figure 1: Molecular Structure of Chitosan (a) LDA (b) GGA**

Figure 2: Variation of total Energy with unit cell volume of Chitosan (a) LDA (b) GGA

The Figure-2 (a-b) shows the variation of energy with volume. The total energy of relaxed Chitosan LDA and GGA are -3111.95 eV and -3124.69 eV respectively. The calculated ground state energy reveals that the maximum energy is for LDA, which is more stable as compare to GGA.

3.2 Electronic Properties

The calculated energy band diagrams of Chitosan system are shown in Figures 3(a-b). It is clearly seen that the direct band gap of this system are 2.8eV and 3.8 eV for LDA, GGA respectively, which proves that this system is electronically semiconductor for LDA and insulator for GGA. DOS of a system describes the number of states per interval of energy at each energy level that are available to be occupied by electrons. A high DOS at a specific energy level means that there are many states available for occupation. A DOS of zero means that no states can be occupied at that energy level[11]. Figures 4(a-b) and Figures 5(a-b) show the DOS and PDOS plots of Chitosan for LDA and GGA. The highest occupied molecular orbital (HOMO) & lowest unoccupied molecular orbital (LUMO) gap in respective DOS plots are analogous to band gap measured in energy band plots of corresponding systems[12]. And from PDOS plots in Figures 5(a-b), it can be seen that the valence band is mainly composed of p orbitals of C, N and O, where O atom is showing maximum contribution. The comparative contribution of orbitals in conduction bands are also shown.

The energy difference between the HOMO and LUMO is termed as the HOMO‑LUMO gap (HLG). The charge transport properties[13] of the molecule mainly depends on HLG, hence, it is necessary to examine the variations in HLG and molecular orbital energy level.
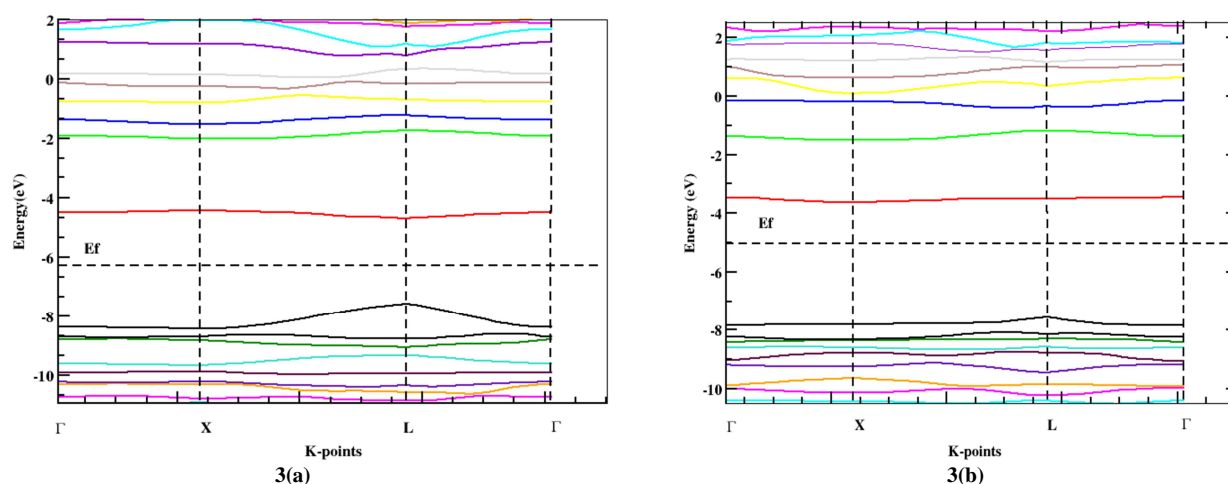

Figure 3: Band structure of Chitosan LDA and GGA shown2(a-b). The calculated HLG value of Chitosan LDA is 2.8eV and Chitosan GGA is 3.8eV

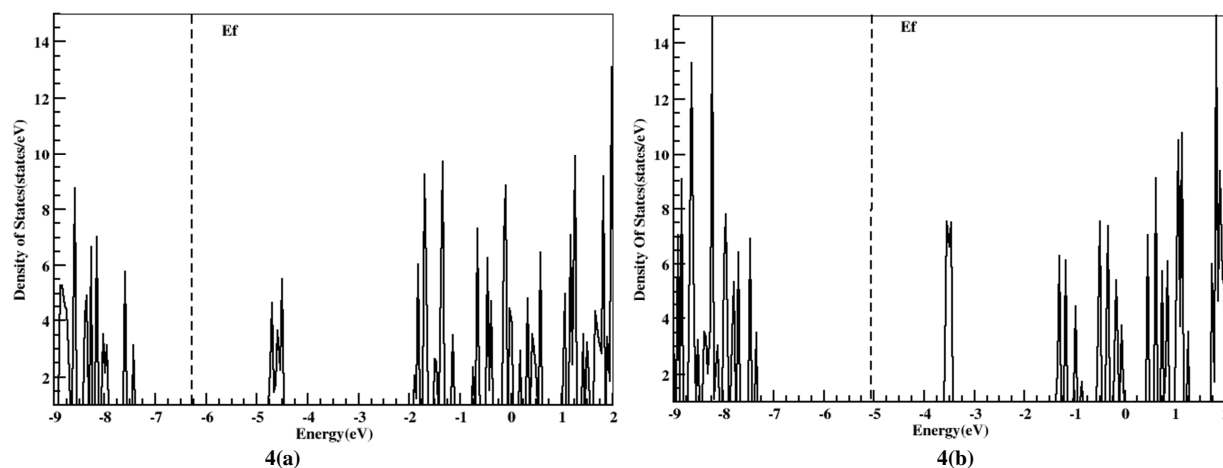_____

4(a)   **4(b)**

Figure 4: Density Of States of Chitosan 4(a) LDA and 4(b) GGA presented, the HOMO-LUMO gap of respective systems are obtained 2.8 eV and 3.8 eV which are analogous to band gap measured in energy band plots
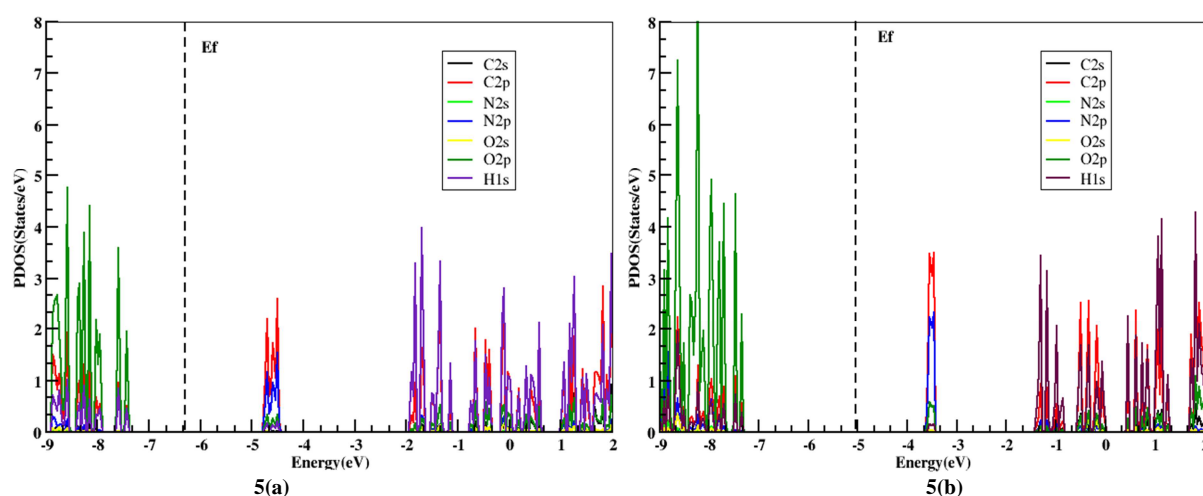

5(a)   **5(b)**

Figure 5: Projected Density Of states of Chitosan 5(a) LDA and 5(b) GGA. In the Figure 5(a)HOMO-LUMO gap value is 2.811eV and 5(b)HLG value is 3.821eV calculated which are closely analogous to band gap measured in energy band plots and density of states of these systems
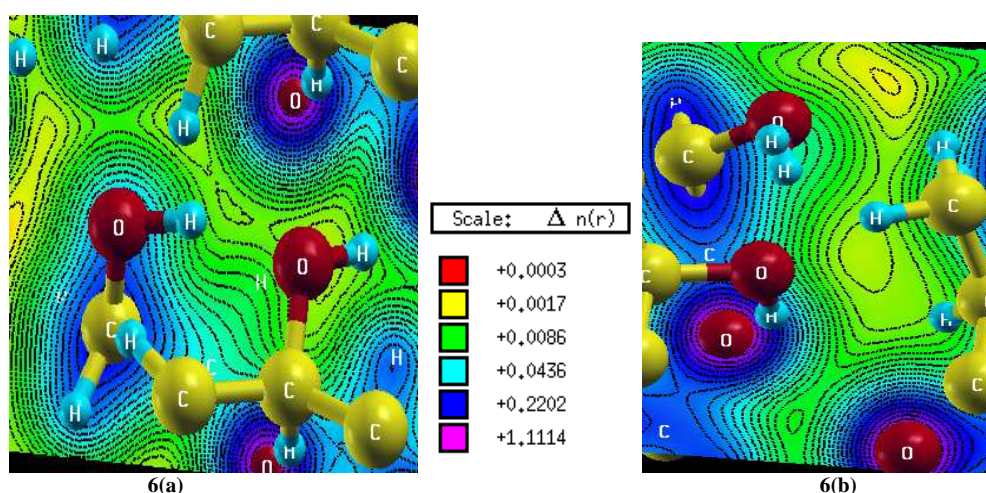

6(a)   **6(b)**

Figure 6 - Charged Distribution in 6(a-b) plots of Chitosan for LDA and GGA.) smaller overlap in wave-functions occurred around C, O atom consequently the bonding could be considered partly ionic and partly covalent

Electronic Charge Density

Figures 6(a-b) show charge distribution plots of Chitosan for LDA and GGA respectively. Carbon (C) is forming bonds with Oxygen (O), Hydrogen (H) and Nitrogen (N). C-O-N-H atoms are forming covalent bonds in their electronic wave-functions. The bonding shows a significant covalent character due to sharing of charge among these atoms. The highest charge density is observed around O atom by pink colour . It is clear that O atom shows

the ionic nature , the wave-functions around O atom are found spherical but some small overlaps are also showing with C and H atoms, which tells the partly ionic and partly covalent character of Chitosan for LDA, GGA both methods[11,14].The hump appears in the electronic charge density of O and C atoms, due to the high electro-negativity respectively.

3.4 Mulliken / Hirshfeld / Voronoi Population:

Mulliken charges obtain from the Mulliken population analysis and provide a means of estimating partial atomic charges from calculations carried out by the methods of computational chemistry. Specifically, these quantum chemical calculations mainly based on the linear combination of atomic orbital's molecular orbital method, and are routinely used as variables in linear regression [15] procedures. In the present work, the atomic charges have been estimated from Milliken population analysis (MPA) as well as Hirshfeld (HPA) and Voronoi population analysis (VPA) methods. Molecular orbitals are obtained from the combination of atomic orbitals, which predict the location of an electron in an atom. A molecular orbital is a mathematical function describing the wave-like behaviour of an electron in a molecule [15,16]. This function can be used to calculate the chemical and physical properties such as the probability of finding an electron in any specific region[17].

Table 3 Mulliken, Hirshfeld and Voronoi Populations of Chitosan

Atom Name	Atom No.	Mulliken		Hirshfeld		Voronoi	
		LDA	GGA	LDA	GGA	LDA	GGA
C	1	1.283	1.326	-0.024	-0.009	-0.002	0.013
C	2	1.169	1.224	0.022	0.031	0.014	0.026
C	3	1.242	1.281	-0.107	-0.082	-0.103	-0.078
C	4	1.148	1.258	-0.005	0.023	-0.008	0.021
C	5	0.955	0.998	0.097	0.093	0.081	0.077
C	6	1.077	1.118	0.085	0.089	0.082	0.099
O	7	0.932	0.869	-0.047	-0.054	-0.081	-0.097
O	8	0.929	0.929	-0.143	-0.175	-0.192	-0.212
O	9	0.967	0.936	-0.152	-0.178	-0.181	-0.196
O	10	0.968	0.913	-0.108	-0.119	-0.139	-0.145
N	11	0.362	0.359	-0.117	-0.106	-0.160	-0.134

The MPA charges of Chitosan of all C-atoms vary from 0.955 to 1.283e , all O-atoms 0.929 to 0.968e and N-atom is 0.362e for LDA. All C-atoms vary from 0.998 to 1.362e , all O-atoms 0.869 to 0.936e and N-atom is 0.359e for GGA. The HPA charges of Chitosan of all C-atoms vary from -0.005 to 0.097e , all O-atoms -0.047 to -0.152e and N-atom is -0.117e for LDA. All C-atoms vary from -0.009 to 0.093 , all O-atoms -0.054 to -0.178e and N-atom is -0.106e for GGA. The VPA charges of Chitosan of all C-atoms vary from -0.002 to 0.082e , all O-atoms -0.081 to -0.192e and N-atom is -0.160e for LDA. All C-atoms vary from -0.078 to 0.099e , all O-atoms -0.097 to -0.212e and N-atom is -0.134e for GGA.

3.5 COOP Analysis:

These curves are quite useful to analyse the electronic structure of all the systems to get insight about bonding characteristics[18,19]. In combination with the analysis of atom and orbital Projected density of states, the COOP technique is applied to analyze the chemical bonding in (C-C,C-H,C-O,C-N) Chitosan. COOP curves are energy resolved plots of Mulliken overlap population between two atoms or orbitals and provide a quantitative description of the bonding, nonbonding and anti-bonding interaction between two atoms. In all the plots positive, negative an zero COOP magnitudes indicates bonding, anti-bonding and non-anti-bonding respectively. C-C is showing bonding and C-O is showing anti-bonding interactions for all the systems. Whole range of valence band is of bonding character positive COOP and the anti-bonding negative COOP just below Ef which show larger intensity in the system.

In Molecular Orbital(MO) theory molecular orbitals form by the overlap of atomic orbitals. The atomic orbital energy correlates with electro-negativity as more electro-negative atoms hold their electrons more tightly, lowering their energies. MO modelling is only valid when the atomic orbitals have comparable energy when the energies differ greatly the mode of bonding becomes ionic.

In all the COOP curves maximum overlap of atomic orbitals is found below the Ef which indicates the higher energy and electro-negativity of atoms. These results are showing our systems have good ionic character.
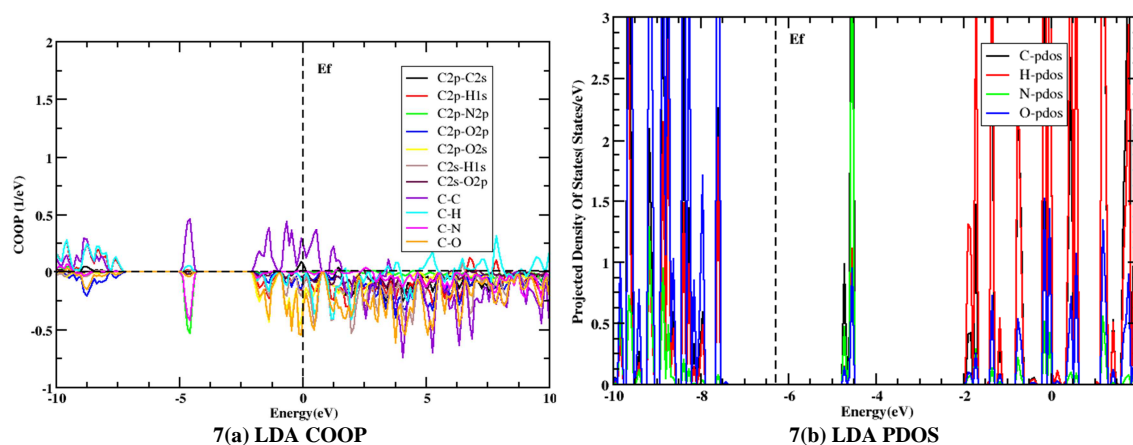
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7(a) LDA COOP

7(b) LDA PDOS

Figure 7- COOP Analysis of Chitosan presented in 7(a) in which black, red, green, blue, yellow, purple, maroon, violet, cyan, magenta and orange colour represent the association of C2p-C2s, C2p-H1s,C2p-N2p, C2p-O2p, C2p-O2s, C2s-H1s, C2s-O2p, C-C, C-H, C-N and C-O and 7(b) show the PDOS plots of Chitosan for LDA black, red, green and blue represent the PDOS associated with C, H, N and O. In the Figure 7(b) HOMO-LUMO gap value is calculated 2.8eV which are closely analogous to band gap measured in energy band plots and density of states of the systems
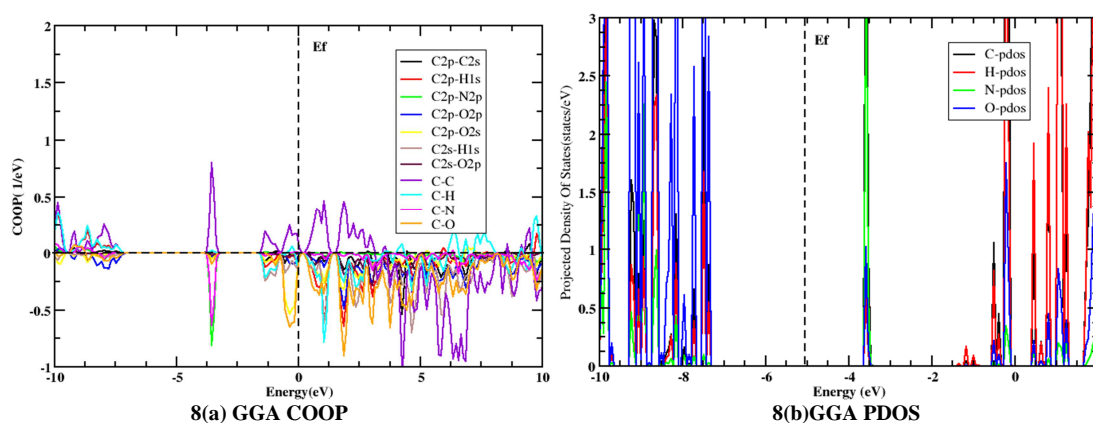

8(a) GGA COOP

8(b)GGA PDOS

Figure 8- COOP Analysis of Chitosan presented in 8(a) in which black, red, green, blue, yellow, purple, maroon, violet, cyan, magenta and orange colour represent the association of C2p-C2s, C2p-H1s, C2p-N2p, C2p-O2p, C2p-O2s, C2s-H1s, C2s-O2p, C-C, C-H, C-N and C-O and 8(b) show the PDOS plots of Chitosan for GGA black, red, green and blue represent the PDOS associated with C, H, N and O. In the Figure 8(b) HOMO-LUMO gap value is calculated 3.8eV which are closely analogous to band gap measured in energy band plots and density of states of the systems

CONCLUSION

The analysis of structural and electronic characteristics of the Chitosan for LDA and GGA have been reported. From its energy bands, DOS, PDOS, charge density, Mulliken Population, Hirshfeld Population, Voronoi Population analysis and COOP analysis computed using SIESTA software. It has been shown that this system is electronically semiconductor for LDA and insulator for GGA. The simple local density approximation (LDA) method still finds widespread use, reflecting the fact that this method frequently provides better results than fundamentally more accurate generalized gradient approximation (GGA) methods. The detail theoretical study is under progress in present lab. This is first principle study, which is preliminary only.

The details of complete Chitosan based electrolytes system using some alkali salts and plasticizer are under progress. This study may be a mile stone for such biomaterials as electrolyte in various electrochemical devices.

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