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Structural Relaxation of L-Alanine Molecule with Water Molecules and its Electrons Density of States by Dft

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ABSTRACT

Computer simulation methods currently have important predictive power and play a key role in understanding biological process including the model of protein, DNA and liquid water. The paper deals with the DOS and band gap of the L-Alanine calculated by DFT using plane wave method. The study conducted the ionic optimization for the relaxation in structure of L-Alanine in water to see its electron's density of state. As a relaxation progressed, how the variation in Eg, Ef and DOS occurred has been reported with supported explanation.

Keywords: DFT ground state calculation, Density of states, Energy band gap, L-Alanine, Protein

I. INTRODUCTION

L-alanine (CH_3CHNH_2COOH) is an amino acid. L-Isomer of alanine is the only natural form of alanine found in proteins. Its properties favors for possessing high electro-optic parameters and good thermal and mechanical stability of the crystals [1]. Its non-linear optical (NLO) property was reported [2]–[4]. Experimental band gap for the L-Alanine solid crystal was reported 4.74eV [5]. They found different solubility in different solvent [6]. Water soluble L-Alanine [7] starts the formation of zwitterions due to transfer of proton from carboxylic group (COOH) to amine group (NH_2) i.e. NH_2 becomes NH_3^+ and COOH becomes COO^-. Their molecules are free, so the structural relaxation can be done here. Therefore in present work, an optical energy band gap, bands, energy states for a L-Alanine single molecule aimed to uncover from the density of state using the DFT method. The work actually and essentially focused on to optimized the geometrical structure of L-Alanine single molecule (shown in Fig.1) in water (H_2O) environment for the relaxation which was initiated from the closely bounded water and L-Alanine molecules.

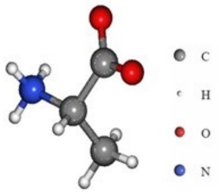

Figure 1. Shows L-Alanine single molecule

II. MATERIAL AND METHODS:

For the single molecule system with bounded water system formation in GUI, the essential data was obtained from the Crystallography Open Database (COD) data card 2104784 in cif form for computation in this paper [8], [9]. A MPI Parallelization runs for four core processors with single thread. The Quantum espresso packages [10] are used as a main tool for the DFT calculation for the ground state L-Alanine. The plain-wave method (PWSCF) is used for probing the system. The PBE exchange functional correlation was used with a projector augmented-wave (PAW) [11] pseudo potential [12] for the DFT calculation in UPF format. The BFGS (Broyden-Fletcher-Goldfarb-Shanno) ionic optimization method was selected for the structural relaxation. The ion's optimization threshold was kept 0.001 Ry/Bohr.

III. RESULT

The geometrical optimization has not converged till 100th iteration as per our criteria i.e for 5th decimal but it is converged for 4th decimal which is enough for present study. (shown in Fig.2). However, the variation of the density of state for the 1st 25th 50th and 100th clearly shows how the changes due to relaxation of the structure in water occurred which are illustrated in Fig.3 for the converged nscf calculations. The system at 100th relaxation of geometrical optimization converged to Hamiltonian -571.55133026 Ry which estimated the 0.030058 Ry/Bohr force per atom.

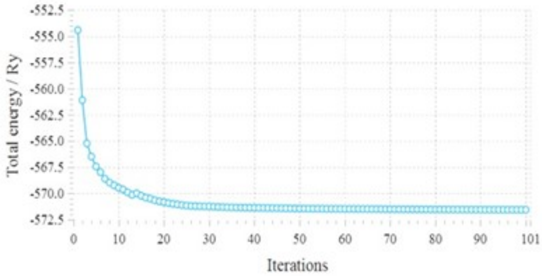

Figure 2. Convergence of relaxation in water

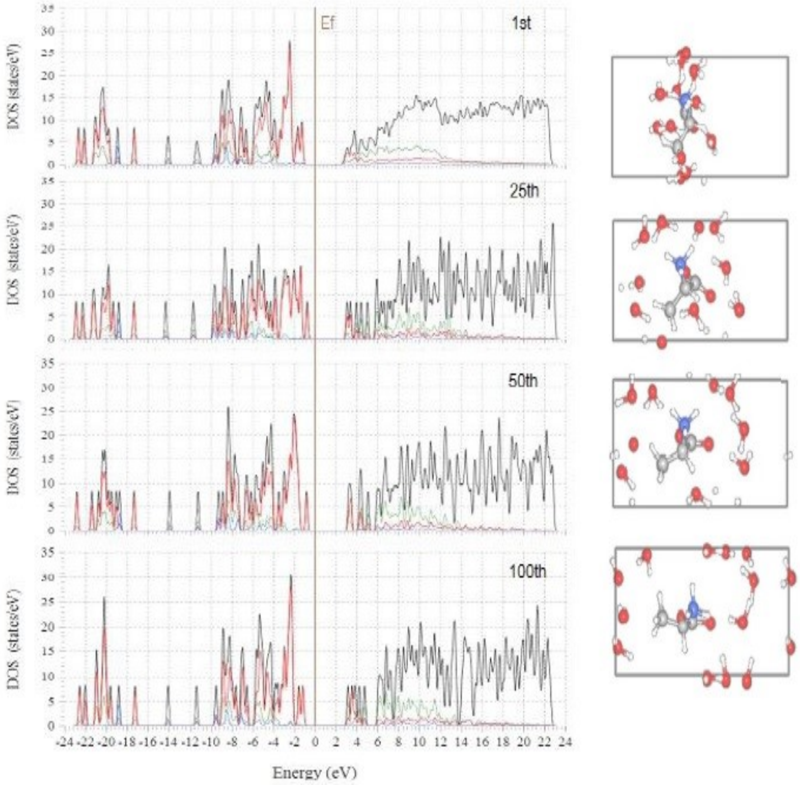

Figure 3. DOS of structural relaxation at 1st, 25th, 50th and 100th iteration for the convergence of Total Energy (Colour indication in a DOS diagram: Black-resultant/total, Orange-Oxygen, Green-Hydrogen, Gray-Carbon, Blue-Nitrogen)

DOS showed the existence of a band gap (E_g) between conduction band and the valance band for the electronic structure of the system. The occurrence of changes in both bands are observable, however, it is smaller in valence band and significantly great in conduction band. The overlapping of energy states in conduction bands were found becoming discrete in nature in the relaxation states with forming three mixed continuum. The shift in Fermi energy (E_f) was also observed. The E_f was increasing for 1st to near to 100th iteration and then showing fall. The variation in E_f (Fermi energy) and E_g (Band gap) are given in Table4.

Table 1. Variation In E_f And E_g With Structural Relaxation In Water

Iteration	**1**	**25**	**50**	**100**
E_f (ev)	-0.2684	-0.4988	-0.5526	-0.3776
E_g (ev)	3.45	3.22	3.41	3.72

IV. DISCUSSION

It is now well established that the effect of salvation has to be included in computer simulation to achieve physical meaningful results [13]. In this work, we were focused on dramatic effect of water on L-Alanine namely the behavior of stable zwitterions of L-Alanine in water environment. For the zwitterionic form of L-Alanine, we started with the most energetically favorable conformer. We performed the simulation of L-Alanine in the bulk water. L-Alanine is the smallest chiral α amino acid with non reactive methyl group (-CH3) as the side chain. It is one of the aliphatic amino acid that has the important property of not interacting favorably with water. This allows the hydrophobic effect to be studied. In this work, salvation shells are formed around L-Alanine molecule in two ways. The first hydration shell stabilizes the structure of a zwitterionic L-Alanine and the second fully covers the L-Alanine along with its first hydration. During second process the methyl group and hydrogen comes over the surface and a process of relaxation occurs. Such simulation methodology successfully been used in recent studies of biological relevance including the modeling of proteins, DNA and liquid water [14]–[17].

Moreover the existence of zwitterions determine the band gap [18] as per Split Charge Equilibrium (SQE) formalism, where at least two electronegative or two electropositive atoms at opposite end of molecule is required. The band gap support the fact that not only spatial arrangement of the L-Alanine molecules in the crystal, but also the type of lateral chain (zwitterionic state) is important to determine whether the energy gap of a L-Alanine crystal is direct or indirect [19]. The band gap of aqueous L-alanine gives semi conducting properties which can be used for making bioelectronics device. Other significance of band gap is the color of a material. The color of material is strongly dependent on the value of band gap as photons with energy lower than the band gap will be reflected, while photons with higher energy will be absorbed. Hence band gap can be used to rationalize the color properties of any organic system using zwitterions impurities [20].

V. CONCLUSION

From the present study, it is confirmed that the free individual L-Alanine molecules in structural relaxation have different DOS. The variations in parameters from nscf calculation are reported. Increase in relaxation in water of a single L-Alanine suggested that how an interaction of it with water molecule decreases and significant changes observed in Fermi and gap energies. The zwitterions are found explainable in connection with the energy band gap in DFT based calculations.

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