

DFT study of L-alanine's Crystal, Molecule and Three Linear Molecules for Optoelectronic Behavior

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Abstract— L-alanine requires more insight in terms of the optoelectronic properties as the organic devices. For that an electronic structure of the L-alanine using the density of state (DOS) and band structure have been calculated by the density functional theory (DFT) using the plane wave method. The unit cell crystal, single molecule and hydrogen bonding approach were investigated first in this work using GGA-PAW. The molecular orbitals were also examined using BL3YP functional for the hydrogen bonding between the amine and the carboxylic groups and found the bandgap energy comparable to the GGA-PAW case. The indirect band gap was obtained in the band-structure calculation. The effect of three linear molecules in x, y and z direction in a crystal was investigated and the significant variations found in DOS in all three cases of L-alanine. The present study predicted the longer length wire or tube structures are most useful as the outcome to make the good organic optoelectronic material.

Keywords—L-alanine, Density of states, DFT, Energy bandgap, optoelectronics behavior

I. INTRODUCTION

An amino acid has special features like molecular chirality, absence of strongly conjugated bonds and Zwitter ionic nature to use to manufacture unique devices [1]. L-alanine ($\text{CH}_3\text{CHNH}_2\text{COOH}$) is a type amino acid occurred in orthorhombic crystal structure solid with space group $P2_12_12_1$ (19). The structure was originally derived by Bernal in 1931 [2]. It possesses high electro-optic parameters, good thermal and mechanical stability of the crystals [3] and reported the Nonlinear optical (NLO) property [4–6]. Such NLO materials have been attracting due to their chemical flexibility, high Non-linearity, high mechanical and thermal stability and good transmittance [7]. An experimental bandgap for the L-alanine was reported 4.74 eV for the lattice parameters a, b, c, α , β and γ are 6.028Å, 5.804Å, 12.317Å, 90°, 90°, and 90° respectively [8]. The same structure has been reported by Harry Simpson et.al. in 1966 [9]. The lattice parameters (6.036(3)Å, 12.342(5)Å, 5.788(3)Å, 90°, 90°, 90°) Neutron diffraction, [10] also agreed with XRD. In more condensed state lower to 23K, it has reported a reduction in cell parameters [6]. Single crystal at 293 K with different high pressure information is also available [11]. The theoretical work started with high pressure at standard temperature have been lacking in our literature survey. Recently, the works on the organic devices are booming and L-alanine also has great importance in various areas, especially in an optoelectronics devices and sensors which requires energy bandgap and related

properties. The main objective of this paper is the study of the three linear molecules in three different positions according to the placement in a crystal with optoelectronic behavioral concerned. The plane wave DFT method was performed with good PPs, best convergence criteria and proper cutoff which are explained in the methodology section. In the present study, the selection of the crystal system for relaxation has done first and then finding their optical energy band gap by analyzing density of state (DOS) have been done. This is given in the results and discussion section with the inspection of a unit cell structure, a single molecule and the connection of carboxyl and an amine group of two molecules in term of DOS.

II. METHODOLOGY

An MPI parallelization runs for four core processors with a single thread. The plain-wave method (PWSCF) was used for probing the system first for scf and then nscf. The Quantum espresso packages [12] was used as a main tool for the DFT calculation (with Davidson algorithm) for the ground state L-alanine in this work. The GGA-PBE exchange functional correlation pseudo-potentials (PP) was selected with Projector augmented-wave method [13] for the DFT calculation in UPF format. For this purpose, 2s,2p for C, 1s for H, 2s,2p for O and 2s for N outer orbitals were considered in PP and renormalized using gamma-point specific algorithms. The PP files were obtained as C.pbe-n-kjpaw_psl.1.0.0.UPF, H.pbe-kjpaw_psl.1.0.0.UPF, O.pbe-n-

kjpaw_psl.1.0.0.UPF, and N.pbe-n-kjpaw_psl.1.0.0.UPF pseudopotential. As a GUI, BURAI open source program (version 1.2) was used. The dense K-grids were selected according to different requirements of different jobs. For cross-checking, a hydrogen bonding in term of molecular orbitals, the BLY3P hybrid PP in a single point RHF calculation were done using ORCA codes [14]. The calculation utilized the def2-SVP [15] basis for an ab-initio Hamiltonian method of Hartree-Fock type (HFT) for SCF. The Avogadro software was used as a chemical analyzer and visualization [16] for the computation result obtained from the ORCA. The crystallographic data have been obtained from Crystallography Open Database (COD) data card_2104784 in cif form for the computation in this paper which was collected at 293 K with high pressure 1.5GPa for the L-alanine single crystal [11]. Its lattice parameters a , b , c , α , β and γ are 5.6999Å, 5.772 Å, 12.161Å, 90°, 90° and 90° respectively. This paper has reported there is no phase transition till 2.5Gpa on compression and decompression for the L-alanine crystal.

III. RESULTS AND DISCUSSION

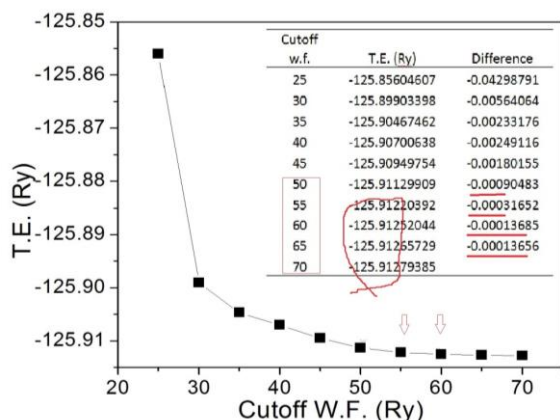


Figure 2: Finding cut-off from convergence of SCF for the DFT calculation

A. Selection Of Cut-off For System

For the DFT calculation of the single molecule, convergence of plane wave for cutoff for the scf calculation has been tested as illustrated in a Fig.2. The convergence started at 50Ry and consistent up to the three decimal places after 55 and up to five decimal places from 60 to onward. Therefore the 55 is better option and the 60 is best option for selecting the wave function cutoff, we select 50 Ry. All scf calculations have converged by nine cycles of iterations and takes approximately 120 minutes. The same way was done for the unit crystal (four formula units) of L-alanine 50Ry.

B. Density of States and Bandgap

Each unit cell contains four unit formula molecules. When the crystal dissolved in a good solvent, the molecules tend to separate from each other is considerable. In water, four zwitterions are formed per unit cell. At room temperature, L-alanine appeared in a colorless crystalline solid form. The DOS of its unit structure has shown in Fig.3. The band gap is found 4.8eV shown in Fig.3 plotted for DOS. It is just comparable to the band gap found in literature i.e. 4.74eV [8] and 4.99eV for pure crystal (if mixed with HCl, KCl or KDE then vary from 5.1 to 5.2 eV) [17].

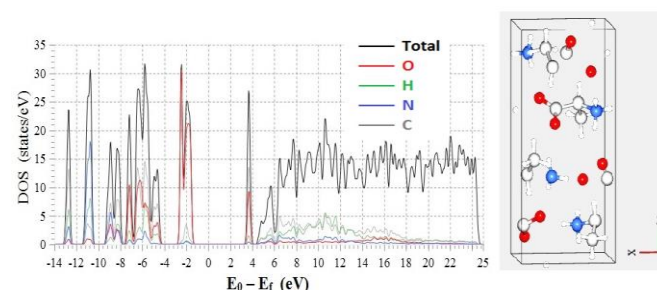


Figure 3: DOS of unit cell structure

The DFT of a pure single molecule of L-alanine in which carboxylic group and amine group form covalent bonding between C and C (This has also appeared in a second row of the crystal structure shown in Fig.1 and in a Fig.3) have calculated the band gap of 4.2eV from DOS (illustrated in Fig.4). The width of conduction band found smaller and a valence band is found broader around -2eV with compare to the unit cell case. The conduction bandwidth is comparable for Fig.4 and Fig.5, but the valence band and a band around -2eV seems dissimilar. In two molecules, two groups' interaction case i.e. in Fig.5, the band around -2eV is sorter in width and larger band gap exist with it in a valence band which is negligible in a single molecule case shown in Fig.4. The DFT of the two L-alanine molecules' different group's interaction lied in a same layer by varying the translational vector 'a'. Here the one of the 'O' of carboxyl and one of the 'H' of N forms hydrogen bond. The DOS is illustrated in Fig.5. This suggests 3.6eV band gap. First the scf and then the nscf calculations were performed. Some parameters are shown in Table1 which were obtained after convergence. In a crystal field, the force exerted on each atom is more and also the stress found over each atom. However, wherever the hydrogen bond connecting two groups in system, the total force seems reduced at 5th decimal in Ry/au unit. In the same fashion, fermi energy reduced at the 4th decimal.

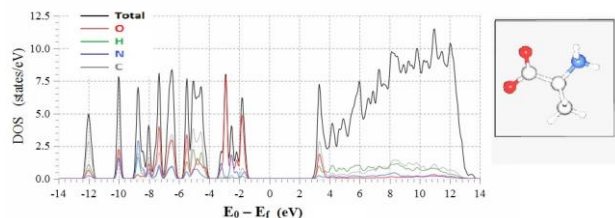


Figure 4: DOS of single molecule / unit formula structure

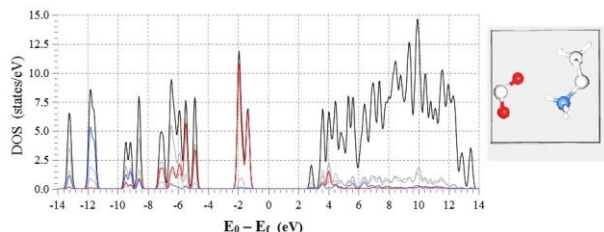


Figure 5: DOS of two group's connection of hydrogen bonding

Table 1: SCF calculation by PW

SCF calc.	Unit Crystal	Single molecule	Two group connection
Iterations	9	12	12
T.E. (Ry)	-503.59549927	-174.94460963	-174.94460584
Total Force (Ry/au)	1.833017	0.90252	0.902544
Stress (kbar)	218.45	68.88	68.88
E _g (eV)	4.8	4.2	3.6

From the above discussion, one should note down that if two molecules group interact more than the systems' (L-alanine) band gap should be gradually decreases. In a single molecule, the width of conduction band is smaller compared to the unit crystal. A single molecule interaction with other molecules in a crystal unit cell affects the band gap. In same system has shown in Fig.5 for the selection of grid points, we used (4 4 2) k-points and 54 bands out of 206 for the inspection of band structure using the path of the symmetry walk on the Brillion zone as shown in following Fig.6. A black line indicates an indirect transition from Gamma (Γ) to X points, which revealed the existence of indirect bandgap of 4.2 eV. This suggests the existence of phonon-photon interaction in a system. However, the direct bandgap do exist for the transition at Γ, which is slightly larger than the Γ→X transition case.

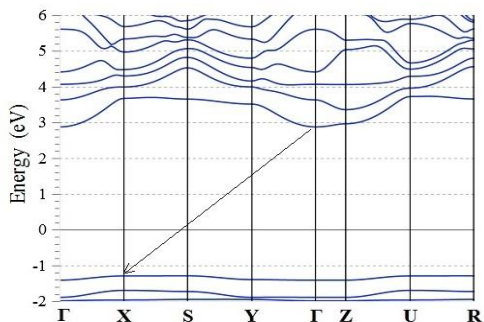


Figure 6: Band structure of the single L-Alanine molecule

C. Orbital Investigation

The single point RHF calculation (in ORCA) has converged on 11th iteration. After the Mulliken population analysis, Loewdin population analysis and Mayer population analysis, the HOMO LUMO energy states were obtained as illustrated in Fig.7 and given in following Table. From 19th to 28th orbitals (among 119 orbitals states started from 0 to 118) are obtained which form bonding and anti-bonding states (0th is 1st state and 118th is 119th state). The energy difference between LUMO-0 and HOMO-0 is found 4.28eV. This difference using single point (HFT) calculation is comparable to the band gap 4.2eV of a single molecules (however, greater than the hydrogen bond consideration of the two groups) calculated from the band structure by DFT calculation.

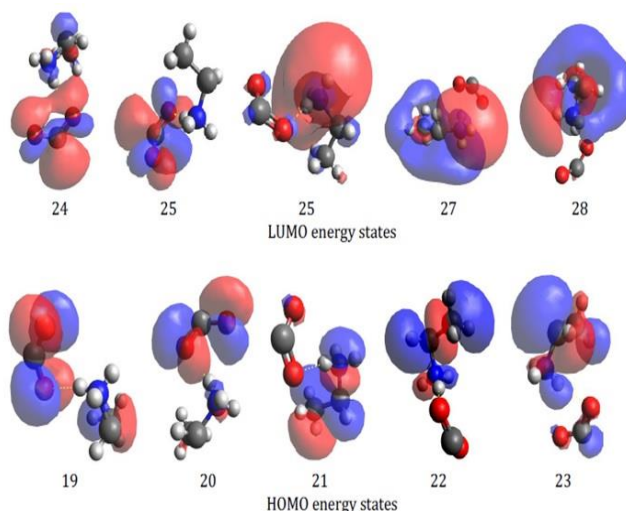


Figure 7: Molecular orbitals energy states

Table 2: Summary of Lowest Unoccupied and Highest Occupied Molecular orbital energy states

States	Orbital	Energy (eV)
28	LUMO +4	6.700
27	LUMO +3	6.130
26	LUMO +2	4.789
25	LUMO +1	2.853
24	LUMO 0	-1.615
23	HOMO 0	-5.892
22	HOMO -1	-12.371
21	HOMO -2	-14.208
20	HOMO -3	-14.400
19	HOMO -4	-14.865

D. Three Molecules in Different Directions

The three linear interaction of one L-alanine molecule with others are considered in this section. The following effect are found as a result if their combination chosen from the crystallographic position vector's directions (x, y and z axes) shown in Fig.8. The fermi level is being shifted toward

valence band from the conduction band as a position vector change in the direction of as x, y and z crystallographic axis. Possibility of existence of p-type in y- and z- direction due to the probability of holes for the conduction was expected in such cases, while in x axis n-type with less probability of electrons are expected. The molecular orientations for interactions are different in all directions. From the x to z direction, the space between molecules found increasing and also fermi energy is increasing (Table3). The E_g is geometrically dependent here, and variation in it is mentioned in a Table3. The E_g in y-direction found larger i.e. 3.69eV compare to other direction but not with very big difference.

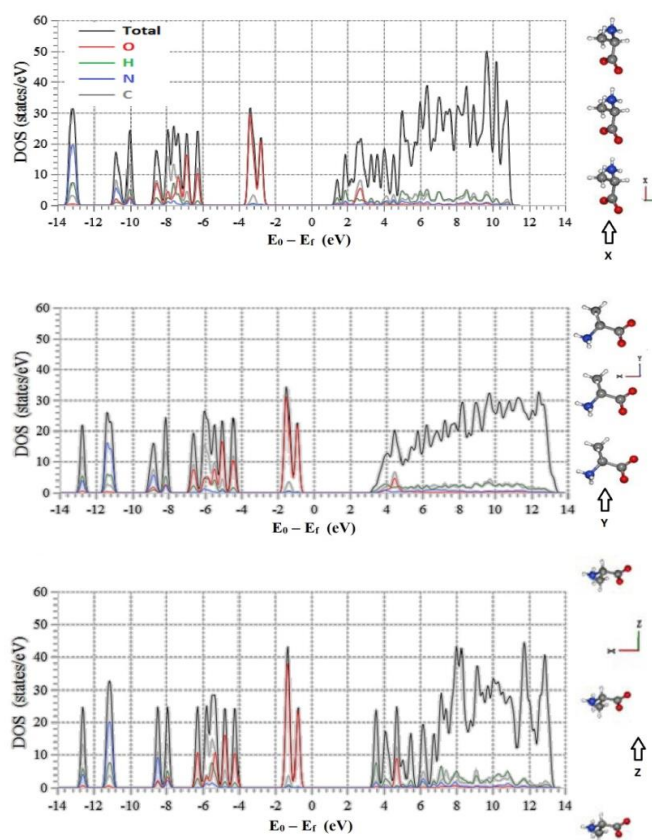


Figure 8: DOS for the effect of position vectors' direction

Table 3: Variation E_f and E_g for x, y and z direction of linear three molecules.

direction	x	y	z
E_f (ev)	-0.8859	-2.7477	-2.9683
E_g (ev)	3.61	3.69	3.64

E. Optoelectronic Indication

An experimental observation by L. Misoguti et al [5] was reported that the optical property of L-alanine crystal which shows UV absorption. The range of E_g is found in the same

region in our study. This UV absorption arises due to electronic transitions associated with the carboxylate anion ($-\text{COO}^-$) and the nitril cation ($-\text{NH}_3^+$) bonds. This has been shown in all DOS in a present worked. The UV region optoelectronics devices can be possible for all discussed L-alanine entities in this paper. The illustration in Fig.7 for an attempt of single hydrogen between two groups also reveals the same thing (in addition to the L-alanine molecules) in consecutive first HOMO and first LUMO states indicating the molecular orbitals 23rd and 24th respectively. The cut off wavelength found around 200 nm with a wide band gap of the grown crystal and the absence of absorption bands in the visible region were in a close agreement with our E_g data [18]. In other literature, a single crystal transparency window was found from 230 nm onwards, but with bandgap 3.9eV in DFT study using BYLP [19]. We have got the advantage of PAW and BL3YP's for approaching to more accurate computational result. Therefore, as an optical waveguide, all L-alanine entity has passed the necessary requirement for visible region also. It can render for the optical rectification and detection by an electro-optic field sensor [20].

IV. CONCLUSION AND FUTURE SCOPE

In the present study, the free (or an individual) molecules have different scenario for an electronic structure compare to the crystalline solid L-alanine. The energy band gaps are found different. The slight variations in parameters in the scf and nscf calculations have found in the connection of two groups by hydrogen bond comparable to the molecule with covalent. For the three linear molecules study in different directional position vectors indicate a significant change in Fermi energy and bandgap energy. A band gap was reduced in large amount in linear molecules in any particular directional compare to single molecule or crystal. So, the study reported that the making of devices elongated in any particular direction is more useful for the application in the optoelectronic area as an organic device. Therefore long length wire or tube structures are proposed on the basis of merely DOS study.

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