DFT Calculation of interaction energies in model Alanine and Valine using different Basis sets

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ABSTRACT

Hartree energy of Alanine and Valine aminoacids using BVWN DFT method and different basis sets are calculated. Alanine (-248.3843246 Hartree) as well as Valine (-327.4475422) energies are found minimum for tzv(2p,d) basis set. Muliken population, Muliken charge, total valance, bond valance, dipole moment, and molecular energy levels of L- Alanine and L- valine aminoacids are calculated using BVWN DFT method and tzv(2p,d) basis set. For Alanine 19 energy levels (E_{19} = -0.2088a.u.) are occupied, while that for Valine 27 (E_{27} = -0.2031 a.u.) energy levels are filled and vacant above that.

1. INTRODUCTION

Aminoacids are the basic building blocks of the entire living organism. Sequencing of amino acids in particular manner determines type of proteins formed and slight change, replacement or modification in any amino acid will change the type of protein synthesized. Study of energy, charge, potential and dipole moment of amino acids are important in protein synthesis in laboratory are found recent interest in genetic engineering, DNA, RNA modeling and biosciences. Amino acids may be also important weapons for future construction of molecular, pollution free, biodegradable green devices. Density functional theory is a quantum mechanical theory used in physics and chemistry to investigate the electronic structure (principally the ground state) of many-body systems, in particular atoms, molecules and the condensed phases. DFT is among the most popular and versatile methods available in condensed matter physics, computational physics, and computational chemistry. Lee et al. have reported Dynamics of Conformational Isomerism in Alanine and Valine di-peptide [1]. DFT ab initio calculation of tri-peptides was reported by Paarthsarathi et al. [2]

The Kohn-Sham DFT equation is expressed as follows $[-\hbar^2/2m \nabla^2 + V_s(r)]\phi_i(r) = \varepsilon_i \phi_i(r)$, which yields the orbitals ϕ_i that reproduce the density $n(\vec{r})$ of the original many-body system $n(r) = n_s(r) = \sum_i^N \phi_i^2$ and The effective single-particle potential V_s can be written in more detail as [3,4];

$$V_s = V + \int \frac{e^2 n_s(r')}{|r - r'|} d^3 r' + V_{XC}[n_s(r)]$$

where the second term denotes the so-called Hartree term describing the electron-electron Coulomb repulsion, while the

Table 1: Energy of Alanine and Valine using BVWN DFT method with different basis set

Basis	Energy (Hatree) Alanine	Energy (Hatree) Valine
MINI	-246.6107897	-325.1559582
MIDI	-246.816987	-325.4007978
STO-2G	-237.8382149	-313.6760619
STO-3G	-245.0640027	-323.1676875
STO-4G	-246.8415167	-325.5085309
STO-5G	-247.3158145	-326.136828
STO-6G	-247.463542	-326.3329886
3-21G	-246.9094735	-325.5302502
6-21G	-247.9822279	-326.9510202
4-31G	-247.9473788	-326.8929404
5-31G	-248.1520914	-327.1615575
6-31G	-248.204757	-327.2306485
6-311G	-248.2746094	-327.3178057
DZV	-248.2442627	-327.2757183
DH	-248.2442627	-327.2757183
TZV	-248.2951938	-327.342114
MC	-248.2746094	-327.3178057
CCD	-248.2974112	-327.3419507
CCD(3p,2d)	-248.2974112	-327.3419507
TZV(P)	-248.3121754	-327.3693029
TZV(2P,d)	-248.3767801	-327.4475422
TZV(3p,2d)	-248.3824036	
TZV(3p,3d)	-248.3843246	

last term V_{XC} is called the exchange correlation potential, which includes all the many particle interactions.

Since the Hartree term and V_{XC} depend on n(r), which depends on the ϕ_i, which in turn depend on V_S, the problem of solving the Kohn-Sham equation has to be done in a self-consistent (i.e. iterative) way.

Selection of $V_{XC,}$ (i.e. selection of DFT type) and ϕ_I (Basis

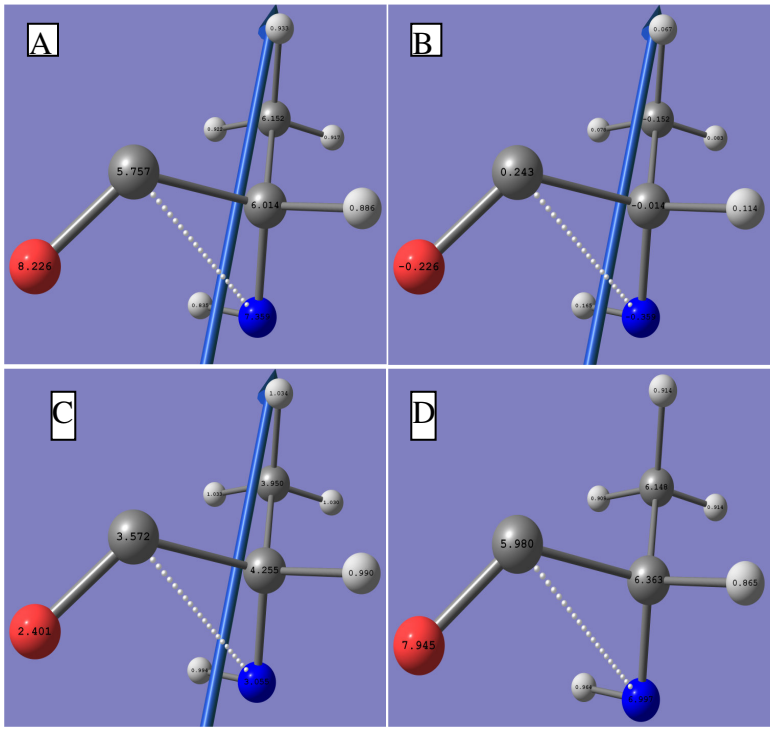

Fig.1: (A) Mulliken population (B) Mulliken charge (C) Total valance of atoms (D) Low population of Alanine

set) results different energy values ε_I for the ground satae of particular molecular system. Selection of basis set depends on the no. of atoms and their atomic arrangement as well as electronic distribution in different atomic orbital. A basis set in chemistry is a set of functions used to create the molecular orbital, which are expanded as a linear combination of such functions with the weights or coefficients to be determined. In this work we have used Becke Vosko-Wilk-Nusair (BVWN) correlation function with different simple as well as complex basis sets to calculate energy of Alanine and Valine amino acids. Recently we have calculated energies and other properties of alanine dipepetide and other basic aminoacids using different basis sets and DFT type [5].

2. COMPUTATIONAL DETAILS

WINGAMESS software package was used on XP operating system (Core 2-duo, 2.54 GHz & 2 GB RAM) for the complete computational calculations. GABEDIT computational software was used for the creation of input file for GAMESS, while CHEMCRAFT was used for graphical visualization of GAMESS output file. Potential energy, mulliken charges, dipole moments of these amino acids are calculated. We have made following inputs for the creation of input file of WINGAMESS through GABEDIT for Alanine

Runtype =Energy; SCFtype=RHF ; Maximum iteration=100
THE POINT GROUP OF THE MOLECULE IS C1
THE ORDER OF THE PRINCIPAL AXIS IS 0

3. Results and Discussion

Energy values for Alanine and Valine amino acids are calculated using BVWN DFT method and different basis sets, which are depicted in Table 1. Potential energy values for Alanine as well as Valine is found minimum for TZV (2p,d) basis set. It is -248.3121754 Hartree for Alanine, while that for -327.3693029 Hartree for Valine with above basis set.

We have calculated muliken population, muliken charge, total valance of atoms, low population and dipole moments of Alanine and Valine amino acids using TZV (2p,d) basis set and BVWN DFT method.

For Alanine Amino acids with TZV (2p,d) basis set and BVWN DFT method we found following results.

TOTAL NUMBER OF BASIS SET SHELLS = 85
NUMBER OF CARTESIAN GAUSSIAN BASIS FUNCTIONS = 220
NUMBER OF ELECTRONS = 38
CHARGE OF MOLECULE = 0
SPIN MULTIPLICITY = 1
NUMBER OF OCCUPIED ORBITALS (ALPHA) = 19
NUMBER OF OCCUPIED ORBITALS (BETA) = 19
TOTAL NUMBER OF ATOMS = 10
THE NUCLEAR REPULSION ENERGY= 160.0815656638

WAVEFUNCTION NORMALIZATION = 1.0000000000

ONE ELECTRON ENERGY = -651.6749733037
TWO ELECTRON ENERGY = 243.2090829999
NUCLEAR REPULSION ENERGY = 160.0815656638

TOTAL ENERGY = -248.3843246400

ELECTRON-ELECTRON POTENTIAL ENERGY = 243.2090829999
NUCLEUS-ELECTRON POTENTIAL ENERGY = -898.2426886018
NUCLEUS-NUCLEUS POTENTIAL ENERGY = 160.0815656638

TOTAL POTENTIAL ENERGY = -494.9520399380
TOTAL KINETIC ENERGY = 246.5677152980
VIRIAL RATIO (V/T) = 2.0073675880

SCF energy get converged upto 20 itterations.

Mulliken population, Mulliken charge, Total valance of atoms and Low population of Alanine, and direction of dipole

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moment (shown by arrow) is displayed in fig. 1. Energy of first molecular (Lowest energy level) orbital of Alanine is -18.8858 a.u. Energy corresponding to Highest Occupied Molecular Orbital (HOMO) for Alanine is -0.2088 a.u. , while that of for lowest unfilled Molecular Orbital (LUMO) of it is -0.1802 . Therefore 0.0286 a.u. energy is required for the transition of one electron valance band (HOMO) to conduction band (LUMO). Energy level diagram, having energies of different molecular orbital of Alanine is presented in figure 2.

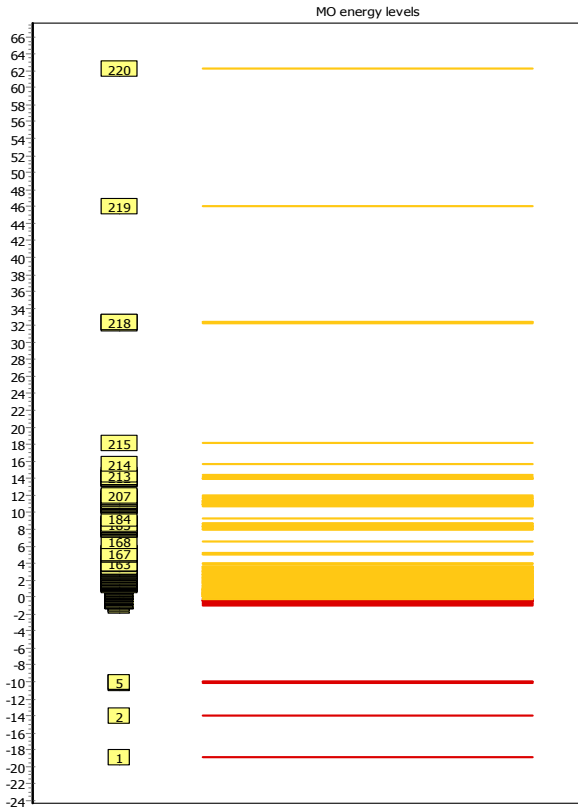

Fig. 2: Molecular energy level diagram of Alanine

For Valine Amino acids with TZV (2p,d) basis set and BVWN DFT method we found following results.

TOTAL NUMBER OF BASIS SET SHELLS	= 108
NUMBER OF CARTESIAN GAUSSIAN BASIS FUNCTIONS	= 221
NUMBER OF ELECTRONS	= 54
CHARGE OF MOLECULE	= 0
SPIN MULTIPLICITY	= 1
NUMBER OF OCCUPIED ORBITALS (ALPHA)	= 27
NUMBER OF OCCUPIED ORBITALS (BETA)	= 27
TOTAL NUMBER OF ATOMS	= 16
THE NUCLEAR REPULSION ENERGY	=302.4936699171

WAVEFUNCTION NORMALIZATION =	1.0000000000
ONE ELECTRON ENERGY =	-1040.0147253669
TWO ELECTRON ENERGY =	410.0735132168
NUCLEAR REPULSION ENERGY =	302.4936699171
TOTAL ENERGY =	-327.4475422330
ELECTRON-ELECTRON POTENTIAL ENERGY =	410.0735132168
NUCLEUS-ELECTRON POTENTIAL ENERGY =	-1365.1334425960
NUCLEUS-NUCLEUS POTENTIAL ENERGY =	302.4936699171
TOTAL POTENTIAL ENERGY =	-652.566259
TOTAL KINETIC ENERGY =	325.1187172291
VIRIAL RATIO (V/T) =	2.0071629989

SCF energy of Valine converged upto 26 itterations.

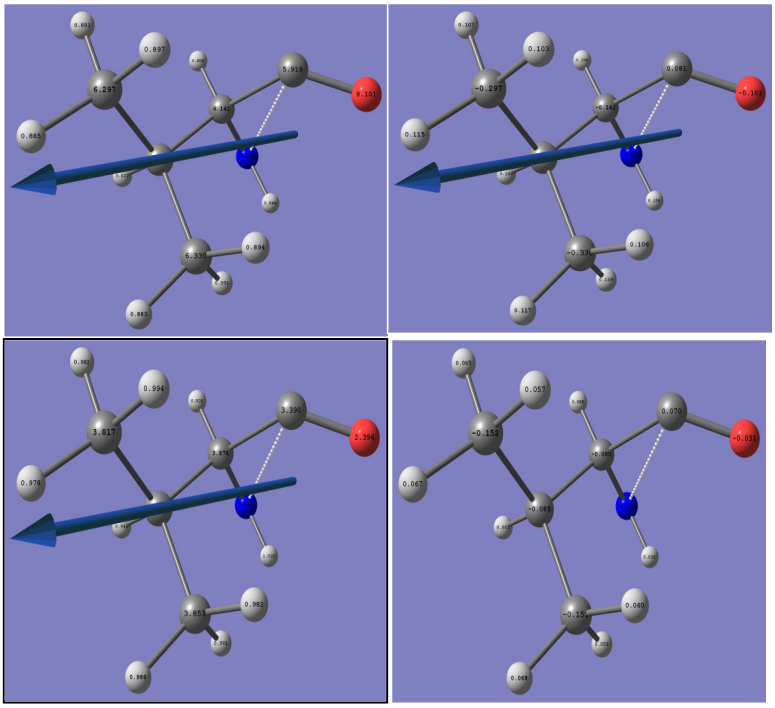

Fig.3: (A) Mulliken population (B) Mulliken charge (C) Total valance of atoms (D) Low population of Valine

Mulliken population, Mulliken charge, Total valance of atoms and Low population ofValine, and direction of dipole moment (shown by arrow) is displayed in fig. 3.

Energy of first molecular (Lowest energy level) orbital of Valine is -18.8816 a.u.. Energy corresponding to Highest Occupied Molecular Orbital (HOMO) for Alanine is -0.2031 a.u. , while that of for lowest unfilled Molecular Orbital (LUMO) of it is -0.175 . Therefore 0.0281 a.u. energy is required for the transition of one electron valance band (HOMO) to conduction band (LUMO). Band-gap energy of Valine is almost equal to that of Alanine. Energy level diagram of Valine having molecular orbital energy of Valine amino acids with most stable structure is shown in fig. 3: Fig. 2 shows dipole moment of Valine, which is shown by arrow.

4. CONCLUSIONS

TZV(2P,d) basis set yields least energy and hence most stable structure for both Alanine as well as Valine amino acids. Minimum energy for Alanine using TZV(2P,d) bais set is -248.3767801, while that of for Valine using same basis set is -

327.4475422 Hartree. There are 19 occupied α orbitals and 19 occupied β orbitals in alanine, while that of 27occupied α orbitals and 27 occupied β orbitals for Valine using BVWN exchange correlation potential and TZV(2P,d) basis set. The HOMO to LUMO transition energy for Alanine is 0.0286 a.u., while that for Valine is 0.0281 a.u.

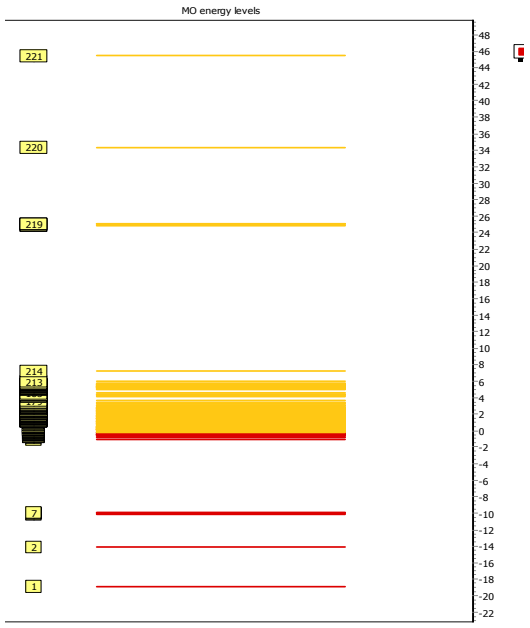

Fig. 2: Molecular energy level diagram of Valine

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