DFT BASED STUDIES ON BIOACTIVE MOLECULES

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DFT Based Studies on Bioactive Molecules

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FOREWORD

Density functional theory (DFT) based methods use the description of the electronic density of an atom or molecule to calculate a host of important properties, many of which are not easily obtained via experimental methods. Some attributes that may be accessed in this manner include molecular geometry, vibrational frequencies, dipole moments and higher-order moments, thermochemical properties, and so forth.

It gives me great pleasure in writing the foreword of this book. It is an outcome of a rigorous amount of effort, which has been devoted to conceptualizing, planning, and finally writing the book. The book contains all the ingredients required to understand, practice, and perform the DFT based studies. The first chapter of the book introduces the concept of DFT and the second chapter deals with its application to explore molecular systems using the popular *Gaussian* program. The subsequent chapters of the book discuss the results obtained by DFT calculations of various biologically important molecules. The last chapter exclusively focuses on the quantum theory of atoms in molecules, used for the study of various inter- and intra-molecular interactions. The book is also complemented with a sample output of the *Gaussian* as an appendix, which can be used to extract and interpret the results of DFT based calculations.

Despite the availability of high-performance computing and the emergence of new theoretical approaches, understanding of structure↔function correlation in molecular and macromolecular systems remains an elusive goal. I am confident that this book shall be of immense value for students, young researchers, scientists, teachers, and all those interested in exploiting DFT methods for molecular systems, particularly biologically active compounds. This book will help to learn and master the technique of applying the DFT based methods and the *Gaussian* program for analyzing various properties of biologically active molecules.

With best wishes,

Sugriva Nath Tiwari
Dean, Faculty of Science, Professor and Former Head, Department of Physics
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& Former President, Indian Science Congress Association (Physical Sciences Section)

PREFACE

The very idea of writing a book on density functional theory (DFT) based studies on molecular systems arose from the volume of work carried out by us over a while. We have always felt the need for a concise literature on the theory and practice of DFT followed by a proper compilation of the research work using the well-known suite of programs, such as, the *Gaussian*. The sole perspective of initiating this project was to make available a good pool of literature, which can presumably be of immense help to the young researchers and experimentalists among others, who are planning to work or have been already working in this rapidly growing and exciting field of research.

The book has been organized into seven chapters and written from the beginners' perspective in such a way that anyone interested to work on molecular systems using the DFT based methods and the *Gaussian* program, can get an exhaustive and a very apropos idea of "how to employ the DFT on molecules" to explore the various properties of the systems under study. The chapters of the book have been methodically presented so that before starting to work on any molecular system, it is assumed that the reader gets well acquainted with the basics of DFT. After becoming friendly with the fundamentals of DFT, the reader is exposed to the applications of DFT on molecular systems with the focus on the *Gaussian* and its usage in a much applied way. Thereafter, many interesting themes have been covered in the form of the subsequent chapters of the book, namely, DFT studies on synthetic compounds, unusual amino acids, and natural products followed by a chapter on a comprehensive account on the way theory is used to complement the experiment. Considering the role of interactions in biologically active molecules, an exclusive chapter on the quantum theory of atoms in molecule (QTAIM) has been included. To supplement the second chapter and make the content more digestive, an appendix has also been added.

All in all, we tried every effort to present a concise and at the same time, complete picture of DFT and its role, action, and applications on some biologically active molecules. We believe that this book will serve its purpose and all the readers, irrespective of their field and level of experience would benefit in some way or the other.

We wish you a happy DFT.

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CHAPTER 1

The Essence of Density Functional Theory

Abstract: This chapter outlines the basic principles of the density functional theory (DFT). The introduction of electron density to develop the Kohn-Sham approach has been systematically presented. The various approximations such as LDA, GGA, and hybrid functional for the exchange-correlation energy have been discussed. A separate discussion on the basis sets has also been included. The advantages and shortcomings of DFT based techniques are also revealed. The formulation of time-dependent DFT has been presented in a concise manner. This chapter is intended to provide an overview of the theoretical background of the methods adopted in the succeeding chapters.

Keywords: Basis sets, DFT, Electron density, Exchange-correlation energy, Gaussian, Generalized-gradient approximation, Gradient-corrected functional, Hohenberg-Kohn theorem, Hybrid functional, Kohn-Sham approach, Local density approximation, TDDFT.

INTRODUCTION

The central idea behind the density functional theory (DFT) is a different variant of quantum mechanics, and like the wavefunction-based methods, some DFT methods do not use any empirical parameters and are derived from the first principles. In contrast to wavefunction-based methods, however, instead of using approximate molecular orbital wavefunctions, DFT uses the knowledge of the overall electron density to solve for the desired properties. Methods based on DFT have gained in popularity due to recent theoretical advancements that often allow it to achieve greater accuracy, at a lower or similar cost in computation time, than commonly used wavefunction-based methods such as the Hartree-Fock (HF) theory.

Since the book is intended for the application of density functional theory (DFT) and time-dependent DFT methods, it is very relevant to describe the formulation of the theory.

The Schrödinger Equation

DFT attempt to solve the non-relativistic Schrödinger wave equation:

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$$\hat{\mathrm{H}}\Psi = E\Psi \qquad \textbf{(1)}$$

Here Ψ is the wavefunction, $\hat{\mathrm{H}}$ is time-independent non-relativistic Hamiltonian, and E is the energy of the system.

$$\hat{\mathrm{H}} = \hat{\mathrm{T}} + \hat{V} \qquad \textbf{(2)}$$

The kinetic energy operator $\hat{\mathrm{T}}$ can be expanded into the following components:

$$\hat{\mathrm{T}} = -\sum_{i=1}^{N}\frac{1}{2}\nabla_i^2 - \sum_{A=1}^{M}\frac{1}{2M_A}\nabla_A^2 \qquad \textbf{(3)}$$

where the first term is the kinetic energy for the electrons and the second is that for the nuclei. Similarly, the potential energy operator ($\hat{V}$) is given by.

$$\hat{V} = -\sum_{A=1}^{M}\sum_{i=1}^{N}\frac{\mathrm{Z}_A}{r_{iA}} + \sum_{i=1}^{N}\sum_{j>i}^{N}\frac{1}{r_{ij}} + \sum_{A=1}^{M}\sum_{B>A}^{M}\frac{\mathrm{Z}_A\mathrm{Z}_B}{R_{AB}} \qquad \textbf{(4)}$$

Here the first, second, and third terms represent the electron-nucleus attraction, the electron-electron repulsion, and the nucleus-nucleus repulsion, respectively.

Needless to mention that the Schrödinger equation can’t be solved “exactly” for any system other than the simplest (single-electron) atomic system [1]. To solve this, therefore, we require certain approximations as discussed below.

Born-Oppenheimer Approximation

The complete non-relativistic Hamiltonian using eq. (2), (3) and (4) is given below,

$$\hat{\mathrm{H}} = -\sum_{i=1}^{\mathrm{N}}\frac{1}{2}\nabla_i^2 - \sum_{A=1}^{N}\frac{1}{2M_A}\nabla_A^2 - \sum_{A=1}^{M}\sum_{i=1}^{N}\frac{\mathrm{Z}_A}{r_{iA}} + \sum_{i=1}^{N}\sum_{j>1}^{N}\frac{1}{r_{ij}} + \sum_{A=1}^{M}\sum_{B>A}^{M}\frac{\mathrm{Z}_A\mathrm{Z}_B}{R_{AB}} \qquad \textbf{(5)}$$

One can write $\hat{\mathrm{H}}$ into two parts considering the nuclear and electronic motions separately,

$$\hat{\mathrm{H}}_{\mathrm{elec}} = -\sum_{i=1}^{N} \frac{1}{2}\nabla_i^2 - \sum_{A=1}^{M}\sum_{i=1}^{N} \frac{Z_A}{r_{iA}} + \sum_{i=1}^{N}\sum_{j>i}^{N} \frac{1}{r_{ij}} \quad \textbf{(6)}$$

$$\hat{\mathrm{H}}_{\mathrm{nucl}} = -\sum_{A=1}^{M} \frac{1}{2M}\nabla_A^2 + \sum_{A=1}^{M}\sum_{B>A}^{M} \frac{Z_A Z_B}{R_{AB}} \quad \textbf{(7)}$$

According to the Born-Oppenheimer approximation, the motion of the electrons in a molecule can be considered in a field of fixed nuclei. This is based on the fact the nuclei are much heavier than the electrons. This implies that the kinetic energy of the nuclei, the first term in eq. (7) can be neglected and the nuclear repulsion energy, the second term in eq. (7), becomes constant for a specific molecular geometry [2]. Therefore, one has to deal with the electronic Hamiltonian, eq. (6). The eq. (6) can be solved for the electronic energy (E_{elec}.) considering a fixed set of nuclear coordinates. The total energy is then simply a sum of E_{elec} and the constant nuclear repulsion energy.

Electron Density and Wavefunction

Note that the electronic wavefunction (ψ) obtained by solving eq. (6) is not measurable or observable. The experiments can measure several parameters of molecular systems, including electron density (ρ), which is measurable by X-ray diffraction or electron diffraction. It might be a great idea to use one-electron density instead of many-electron wavefunctions for calculating the molecular geometries, energies, *etc.* In Table **1**, we compare the properties of wavefunction and electron density.

Table 1. Comparison of electron density and wavefunction.

Electron density	**Wavefunction**
Observable	Not observable
Real	Complex
One electron	Many electrons
3 coordinates for *N*-electron systems	3*N* coordinates for *N*-electron systems

In the Born interpretation, the probability density at any point is nothing but the one-electron wavefunction (ψ) squared (having the same unit as that of the wavefunction at that point). For multi-electron wavefunction, the relation between ρ and ψ is more complicated. Nevertheless, the relation between ρ and ψ reads,

CHAPTER 2

Applications of DFT on Molecular Systems: How Gaussian Works

Abstract: This chapter focuses on the practical application of DFT in molecular systems. We discuss the process of "geometry optimization" and the idea behind it, which is the very first step of every DFT calculation. We introduce the *Gaussian*, a popular software program to perform such calculations. We continue to discuss the capability of this program with a brief theoretical background, wherever needed. We talk about several kinds of calculations to be performed by the *Gaussian* such as thermodynamics, population analysis, NMR, NLO, NBO, TDDFT calculations to name a few. More importantly, we discuss how to perform these calculations, extract, and interpret the results. Ideally, this chapter provides all the ingredients needed to grasp the results discussed in the forthcoming chapters.

Keywords: DFT, Frequency calculation, Gaussian, GaussView, Geometry optimization, MESP, Molecular orbital, NBO, NLO, NMR, Population analysis, TDDFT, Thermodynamics, UV-vis-NIR.

INTRODUCTION

Having chosen an appropriate DFT method, *i.e.*, the suitable combination of exchange-correlation functional and basis set, the primary task of any DFT calculation is to obtain the "correct" structure of a molecular system. This is what is known as the geometry optimization of a molecule. The initial configuration of the molecular system required for this task can be derived from crystallographic parameters or modelled hypothetically. The process of geometry optimization has to be followed by the vibrational frequency calculation. This is to ensure that the optimized configuration of a molecule is stable, *i.e.*, its energy is "truly" minimum. Therefore, we shall first discuss these two terms.

Further applications of DFT on the molecular systems depend on the nature and/or property of the systems under study. For instance, if the molecule contains an electron-donating or withdrawing group, one might be interested in the charge distribution. Likewise, if the molecule is asymmetric, one might be interested in its optical activity and so forth.

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GEOMETRY OPTIMIZATION AND FREQUENCY CALCULATIONS

The objective of geometry optimization is to find an atomic arrangement that makes the molecule most stable. Molecules are most stable when their energy attains the lowest possible value. This is achieved by creating a "potential energy surface" (PES). Before we discuss the PES, let's first have a look over the minimization of a potential energy function in one-dimension, $V(x)$.

A "stationary point" of $V(x)$ is characterized by:

$$\frac{dV(x)}{dx} = 0 \qquad \textbf{(1)}$$

The $V(x)$ is said to have a minimum if,

$$\frac{d^2V(x)}{dx^2} > 0 \qquad \textbf{(2)}$$

and it has a maximum if,

$$\frac{d^2V(x)}{dx^2} < 0 \qquad \textbf{(3)}$$

But it is neither maximum nor minimum for,

$$\frac{d^2V(x)}{dx^2} = 0 \qquad \textbf{(4)}$$

In Fig. (**1**), we have plotted the $V(x)$, which shows the minimum and maximum stationary points. The "global" minimum is the point that is the lowest among all local minima.

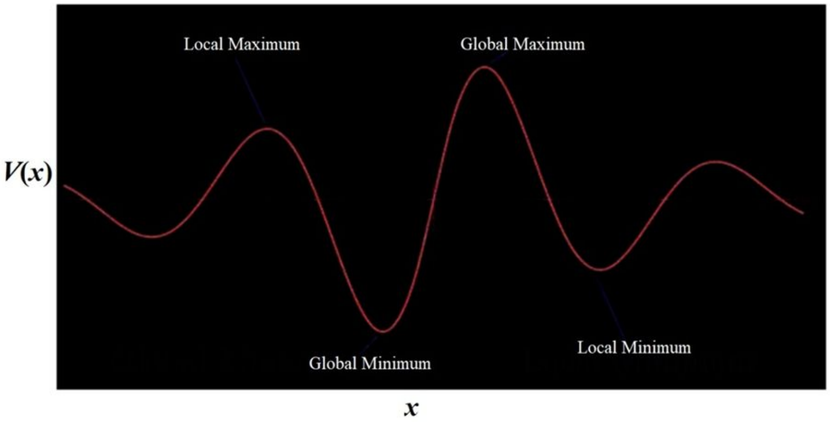

Fig. (1). Variation of *V(x)* with respect to the coordinate x. Various stationary points have also been shown.

The generalization of $V(x)$ to the three dimensions leads to the concept of a PES. Thus, the PES is a mathematical relationship between different molecular geometries and their corresponding energies. These values are usually displayed in a three-dimensional graph, representing the bond angle, bond distance and, energy values as shown in Fig. (**2**).

For a molecular system of N atoms, there are $3N$ coordinates (r). Therefore, eq. (1) can be written as follows:

$$|\nabla V(\vec{r}^{\,3N})| = 0 \tag{5}$$

The energy of a molecule system near its equilibrium structure (stationary points) becomes:

$$E = T + V = \frac{1}{2}\sum_{i=1}^{3\mathrm{N}} q_i^2 + V_{\mathrm{eq}} + \sum_{i=1}^{3\mathrm{N}}\sum_{j=1}^{3\mathrm{N}} \left(\frac{\partial^2 V}{\partial q_i \partial q_j}\right)_{\mathrm{eq}} q_i q_j \tag{6}$$

CHAPTER 3

DFT Study on Some Synthetic Compounds: (2,6), (2,4) and (3,4) Dichloro Substituted Phenyl-N-(1-3-thiazol-2-yl) Acetamides

Abstract: In this chapter, we present and discuss DFT study on three dichloro substituted (1, 3-thiazol-2-yl) acetamides; 26DTA, 24DTA and 34DTA using the B3LYP/6-31+G(d,p) method. We focus on the need of scaling the normal modes of vibrations and test two scaling schemes on 26DTA. We analyze their performance by comparing the scaled values against FTIR data. Subsequently, a detailed comparative study on the spectroscopic properties of 24DTA and 34DTA has been performed using a better scaling scheme. In addition, the NBO analysis is employed to explain the coordination ability of molecules and several electronic parameters are obtained to describe their chemical reactivity. This chapter is expected to provide the first flavor of the real application of DFT on biologically active molecules.

Keywords: Acetamide, B3LYP, Coordination ability, DFT, Electron parameters, FTIR, HOMO, LUMO, NBO, NPA, Scaling equation, Scaling factor, Vibrational spectra.

INTRODUCTION

Acetamide based heterocycles having nitrogen and sulphur atoms, form a distinct group of pharmacologically important compounds with an amide bond similar to that between amino acids in proteins (Chapter 4 will specifically address unusual amino acids). Several natural products and drug compounds contain such heterocyclic moieties [1, 2], including the derivatives of thiazole, which have several biological activities [3, 4]. For instance, the thiazoles have been used in the development of drugs for the cure of several diseases [5 - 12], fibrinogen receptor antagonists with antithrombotic activity [13] an inhibitor of bacterial DNA gyrase B [14]. It is, therefore, desirable to explore some novel compounds based on the thiazole ring. In this chapter, we present DFT based studies on three molecules, namely, 2-(2,6-Dichlorophenyl)-N-(1,3-thiazol-2-yl) acetamide [26DTA], 2-(2,4-Dichlorophenyl)-N-(1,3-thiazol-2-yl) acetamide [24DTA], and 2- (3,4-Dichlorophenyl)-N-(1,3-thiazol-2-yl) acetamide [34DTA]. The results [15 - 17] were obtained by the B3LYP functional and 6-31+G(d,p) basis set.

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MOLECULAR GEOMETRIES

The crystal structures obtained by X-Ray diffraction (XRD) of these compounds can be found in the literature [18 - 20], which were employed to generate the input structure of these molecules to be used for geometry optimization. The molecular structures, after optimization, of 26DTA, 24DTA, and 34DTA are displayed in Fig. (**1**) and some structural parameters can be found in Table **1**. The C–C bond lengths in the vicinity of Cl atoms become a bit longer than others. The bond angle C6-C1-C2 is decreased by 3-4^0 in molecules 26DTA and 24DTA having at least one substitution of Cl at *ortho* position. The positional change in the substitutions leads to the decrease in the dihedral C1-C2-C7-C8 continuously from molecule 24DTA to 34DTA. In the crystal phase [18 - 20], the existence of N$^{\cdots}$H–N hydrogen bonds modifies their structural parameters. These inter-molecular interactions can't be considered by performing calculations on an isolated molecule in the gas phase. These molecules also possess intra-molecular hydrogen bonds (see Chapter 7).

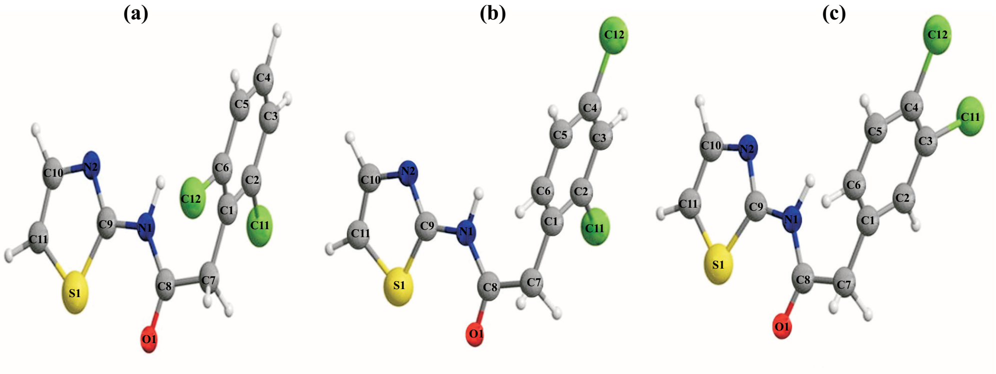

Fig. (1). Molecular structures of **(a)** 26DTA, **(b)** 24DTA, and **(c)** 34DTA at the B3LYP/6-31+G(d,p) level [17].

Table 1. Selected structural parameters at the B3LYP/6-31+G(d,p) level [17]. The corresponding experimental data are taken from Ref. [18-20].

Structural Parameters (Å, ^{0})	**26DTA**		**24DTA**		**34DTA**	
	Calc.	**Expt. [18]**	**Calc.**	**Expt. [19]**	**Calc.**	**Expt. [20]**
C1-C2	1.409	1.400	1.406	1.391	1.400	1.398
C2-C3	1.394	1.390	1.395	1.393	1.397	1.389
C3-C4	1.393	1.386	1.394	1.386	1.401	1.392
C4-C5	1.393	1.385	1.394	1.384	1.397	1.390
C1-C6	1.409	1.402	1.404	1.400	1.403	1.391
C1-C7	1.509	1.512	1.509	1.504	1.511	1.511

(Table 1) cont.....

C8-O1	1.224	1.226	1.224	1.227	1.225	1.225
C8-N1	1.371	1.363	1.372	1.368	1.371	1.365
C9-N2	1.306	1.311	1.305	1.315	1.305	1.315
C9-S1	1.752	1.730	1.752	1.727	1.752	1.720
C-Cl1	1.759	1.743	1.756	1.744	1.745	1.736
C-Cl2	1.759	1.738	1.752	1.741	1.744	1.728
C6-C1-C2	115.7	115.6	116.8	117.2	118.3	118.7
C5-C4-C3	120.2	120.3	121	122.2	119.3	119.3
C6-C1-C7	122.1	122.4	120.5	120.8	121	122.3
C1-C7-C8	118	110.3	117.7	113	117.9	111.9
C8-N1-C9	125.7	123.2	125.7	123.9	125.7	122.9
N1-C9-N2	120.4	121.1	120.4	120.6	120.4	120.8
C9-N2-C10	110.1	109.5	110.1	109.7	110.1	109.2
C9-S1-C11	87.7	88.8	87.7	88.7	87.7	88.7
C6-C1-C7-C8	90.4	91.89	100.3	112.4	86.8	110.9
C1-C7-C8-N1	0	125.3	14.8	172.5	3.7	-166.9

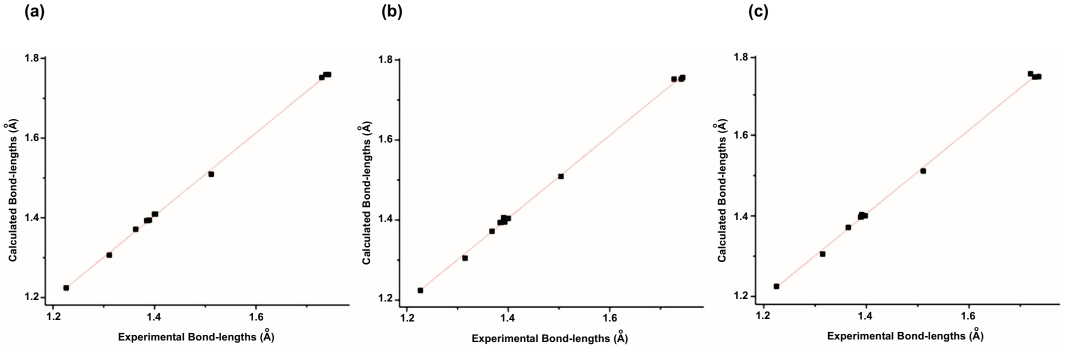

Fig. (2). Correlation between calculated and experimental bond lengths; **(a)** $d_{calc.} = 1.040\ d_{expt.} - 0.051$, $R^2 = 0.9991$ for 26DTA, **(b)** $d_{calc.} = 1.035\ d_{expt.} - 0.044$, $R^2 = 0.9986$ for 24DTA, and **(c)** $d_{calc.} = 1.039\ d_{expt.} - 0.050$, $R^2 = 0.9980$ for 34DTA.

In Table **1**, we have also listed the bond length obtained from XRD on these compounds for comparison. In Fig. (**2**), we have plotted correlation graphs between calculated and experimental bond-lengths, excluding the C-H bond-lengths. We obtain a nice linear correlation having a correlation coefficient (R^2) of 0.9980-0.9991, which verifies that the present computational method is quite appropriate to reproduce the experimental geometry.

CHAPTER 4

DFT Study on an Unnatural Amino Acid: 4-Hydroxyproline

Abstract: 4-hydroxy-*l*-proline is formed by hydroxylation of proline, an amino acid found in protein, whose inhibition results in hair problems in humans, causing scurvy disease. In this chapter, we discuss the DFT study on *cis* and *trans* conformers of 4-hydroxy-*l*-proline, *i.e.*, CHLP and THLP using the B3LYP/6-31+G(d,p)level. The equilibrium structures of both conformers are obtained to analyze their vibrational properties. We have also discussed the results of an in-depth study on *cis*-4-hydroxy-*d*-proline (CHDP). The scan of potential energy surface provides the global minimum structure of CHDP along with its possible conformers. HOMO, LUMO, and MESP surfaces as well as charge distribution, are used to explain the chemical reactivity. The equilibrium geometry of CHDP dimer has been obtained and intermolecular interactions are explored by the NBO analyses. Vibrational analysis has been carried out on CHLP, THLP, and CHDP (monomer and dimer). A complete assignment to vibrational modes has been presented based on their potential energy distribution. The calculated frequencies, after proper scaling, are compared with experimental FT-IR frequencies recorded by KBr disc and Nujol mull techniques. Several electronic as well as thermodynamic parameters have also been reported.

Keywords: B3LYP, Charge distribution, DFT, Dimer, Electronic parameter, FT-IR, H-bond, HOMO-LUMO, Hydroxyproline, Inter-molecular interaction, MESP, NBO, Proline, Thermodynamic parameter, Vibrational spectra.

INTRODUCTION

The protein structure and its functions have been the subject of investigation for a long time [1]. Proteins contain many amino acids of different types with complex structures. One of them is proline, which is unique due to the fact that the amine nitrogen is attached to two alkyl groups. Consequently leading it to a secondary amine. Proline possesses an enormous conformational rigidity due to the distinguishable cyclic form of its side-chain. This side-chain also changes the rate of the formation of peptide bonds among proline and other amino acids. The incorporation of unnatural amino acids leads to the exploration of protein structure and functions [2, 3]. Proline and related compounds are frequently employed in organic reactions as asymmetric catalysts. Furthermore, proteins with

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excess proline interact with polyphenols to form haze (turbidity) during brewing [4, 5].

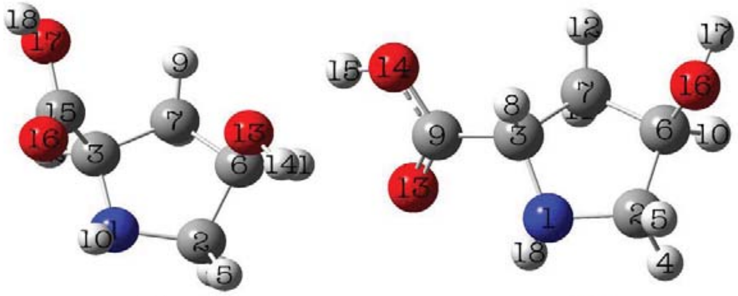
4-Hydroxyproline is derived from proline by substituting a hydroxyl (−OH) to the gamma carbon atom. Despite the fact that it is not directly found into proteins, it consists of almost 4% of all amino acids obtained in animal tissue, which exceeds several translationally incorporated amino acids [6]. Hydroxyproline becomes a main constituent of the protein collagen [7], playing an important role in collagen stability [8] by facilitating the sharp twisting of the collagen helix [9]. Therefore, it can be exploited as an indicator to estimate the amount of collagen and/or gelatin. The glycoproteins incorporating hydroxyproline have also been obtained in plant cell walls [10]. The hydroxylation of proline needs ascorbic acid, whose absence in humans results in the reduced stability of the collagen due to defect in the hydroxylation of proline residues of collagen, leading to scurvy disease. Nevertheless, the increased serum and urine levels of hydroxyproline are obtained in the case of Paget's disease [11]. 4-hydroxyproline is also found in the toxic cyclic peptides from Amanita mushrooms (*e.g.* alpha-amanitin and phalloidin) [12].

Many chemical and/or biological properties are closely associated with the molecular structures or geometries. The different conformations of the same molecule may lead to different chemical properties. The aim of the present study includes detailed structural and vibrational analyses of two potential conformers of 4-hydroxyproline, namely, *cis*-4-hydroxy-*l*-proline (CHLP) and *trans*-4-hydroxy-*l*-proline (THLP). In this chapter, we will first provide a comparative analysis of CHLP and THLP [13]. Subsequently, we will focus on the *cis*-4-hydroxy-*d*-proline (CHDP) and its dimer [14]. The CHLP and CHDP can be differentiated on the basis of the circular dichroism or optical rotatory dispersion, which will not be discussed here. All results described in this chapter are obtained at the B3LYP/6-31+G** or B3LYP/6-31+G(d,p) level using the *Gaussian 09* program.

CIS-4-HYDROXY-*L*-PROLINE AND *TRANS*-4-HYDROXY-*L*-PROLINE

Structural Properties

The optimized geometries of CHLP and THLP are shown in Fig. (**1**) and respective bond-lengths can be found in Table **1**. 4-hydroxyproline is composed of one hetero-pentagonal ring with one carbon replaced by nitrogen. This pentagonal ring deviates from planarity because of the repulsion due to non-bonding electrons of nitrogen. The covalent bond between the side-chain and nitrogen backbone has relevant structural consequences on the properties of both conformers. However, there is a strict dependence between the main- and side-chain proline conformations. This is reflected in the non-bonding distances between backbone atoms, R(1–4) which is 2.12 Å for CHLP and 2.118 Å for THLP and R(1–5), 2.128 Å (CHLP) and 2.12 Å (THLP) (not given in Table **1**).



(a) (b)

Fig. (1). Optimized geometries of **(a)** CHLP and **(b)** THLP [13].

In *cis* and *trans* conformers, the same groups (−OH and −COOH) are present at different angular positions of the hetero-pentagonal ring. This results in the change in ring geometries which have also been proven to be a sensitive indicator of the interaction between the substituent and the ring. Consequently, a re-adjustment takes place in the ring due to the presence of these groups in both *cis* and *trans* conformations. The average bond-length of C−C in the ring for CHLP (1.52 Å) takes a slightly lower value than in THLP (1.53 Å). However, C−N bond-length in *cis* (1.47 Å) becomes slightly higher than that in *trans* conformer, 1.46 Å (see Table **1**). In general, calculated bond-lengths are consistent with the observed values for 4-hydroxyproline [15] by X-ray and neutron diffraction. For instance, the C−C bond-lengths in 4-hydroxyproline are observed to be between 1.52 Å and 1.53 Å.

Table 1. Bond-lengths (R, in Å) of CHLP and THLP calculated at the B3LYP/6-31+G(d,p) level. Refer to (Fig. 1) for atomic labeling [13].

CHLP				**THLP**			
Parameter	**Value**	**Parameter**	**Value**	**Parameter**	**Value**	**Parameter**	**Value**
R(1-2)	1.475	R(6-7)	1.528	R(1-2)	1.475	R(6-7)	1.539
R(1-3)	1.469	R(6-11)	1.099	R(1-3)	1.462	R(6-10)	1.098
R(1-10)	1.016	R(6-13)	1.432	R(1-18)	1.017	R(6-16)	1.434
R(2-4)	1.099	R(7-8)	1.094	R(2-4)	1.094	R(7-11)	1.097
R(2-5)	1.096	R(7-9)	1.091	R(2-5)	1.095	R(7-12)	1.094
R(2-6)	1.537	R(13-14)	0.966	R(2-6)	1.553	R(9-13)	1.214

CHAPTER 5

DFT Study on Some Natural Products: Triclisine, Rufescine, and Imerubrine

Abstract: This chapter deals with three biologically active natural products, triclisine, rufescine, and imerubrine. The B3PW91/6-311+G(d,p) level of DFT is used to obtain the optimized structures of molecules under study. We carried out vibrational analyses of triclisine and rufescine at their optimized structures and provided detailed assignments of the prominent vibrational modes. The computed infrared frequencies are found to be in good agreement with the experimentally determined FT-IR spectra of both molecules. Similarly, their properties are also studied with the help of HOMO, LUMO, MESP surfaces, and several electronic as well as thermodynamic parameters. The vibrational spectrum of imerubrine is analyzed and the normal modes are accurately assigned based on the potential energy distribution. The nuclear magnetic resonance shifts of imerubrine are also obtained, analyzed, and compared with the corresponding experimental values. The chemical reactivity of imerubrine is also explained using HOMO, LUMO, and MESP surfaces as well as a number of reactivity descriptors.

Keywords: Azafluoranthenes, B3PW91, DFT, Electronic parameter, FT-IR, H-bond, HOMO, Imerubrine, LUMO, MESP, Natural product, NMR, Rufescine, Thermodynamic parameter, Triclisine, Vibrational spectra.

INTRODUCTION

Amazonian wines *Abuta rufescens* and *Triclisia gilletii* are employed to extract triclisine and rufescine, respectively, which are natural products belonging to the azafluoranthene group. The azafluoranthenes are present everywhere in nature, having their parent bases in the cigarette smoke, coal tar, street dust, rivers, and lake sediments [1, 2]. These compounds containing nitrogen-heterocycles have become one of the major contaminants in environment [3, 4]. Nevertheless, the natural products of the azafluoranthene group have been found to show potential-biological activities as antifungal, anti-HIV and cytotoxic agents [5 - 7]. For instance, the azafluoranthene eupolauridine exhibit the cytotoxic activity by targeting the DNA topoisomerase II [8]. Apart from the aforementioned biological activities, the molecules with the azafluoranthene core possess interesting spectral properties due to extensive conjugation. This makes them ideal for luminescent

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applications and electroluminescent devices [9 - 12]. The direct arylation [13] and electrocyclization [14] can be used to synthesize the azafluoranthene compounds and their derivatives. The comparative DFT study of triclisine and rufescine has been reported by us [15].

Likewise, *Abuta imene* is used to extract imerubrine, which belongs to the rare natural products from tropoloisoquinolines [16]. Biosynthetically, it is an analogue of alkaloids of azafluoranthene [17]. Boger and Takahashi [18] along with Lee and Cha [19] have reported the total syntheses of imerubrine and associated compounds using the cycloaddition reaction. The structure of imerubrine is derived from rufescine such that extra oxygen is attached to a phenyl ring, as studied by us [20]. Hence, it becomes obvious to perform a comparative analysis of imerubrine and rufescine. In this chapter, we present the results of triclisine, rufescine, and imerubrine at the B3PW91/6-311+G(d,p) level.

TRICLISINE AND RUFESCINE

Molecular Structures

The optimized structures of triclisine and rufescine molecules are shown in Fig. (**1**) with the labeling of atoms. The structural similarities in these compounds is due to the presence of four six-membered rings including a heterocyclic ring (R1) with the substitution of nitrogen and the functionalized ring (R4) having two $–OCH_3$ groups. In addition, there exist two more $–OCH_3$ groups, in rufescine, linked at the C2 and C16 sites of ring R4 and R3, respectively.

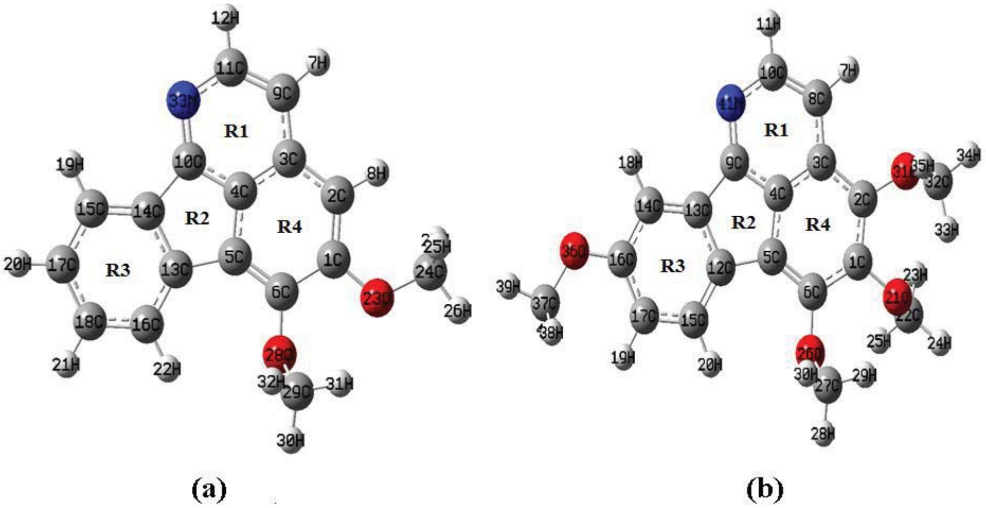

Fig. (1). Optimized molecular geometries of **(a)** triclisine and **(b)** rufescine (reproduced from [15] with the permission of Elsevier).

Infrared Spectroscopic Analysis

Infrared frequencies (wavenumbers) of both molecules are also calculated using the B3PW91/6-311+G(d,p) level. The calculated wavenumbers are scaled with the factor of 0.9648 as discussed in the previous chapters. The Perkin Elmer 1800 Spectrophotometer has been employed for recording the FT-IR spectra of these compounds in the region 4000-400 cm^{-1} using samples in CsI pellet as mentioned earlier [15]. The calculated spectra have been plotted in Fig. (**2**) along with corresponding FT-IR spectra for a quick comparison.

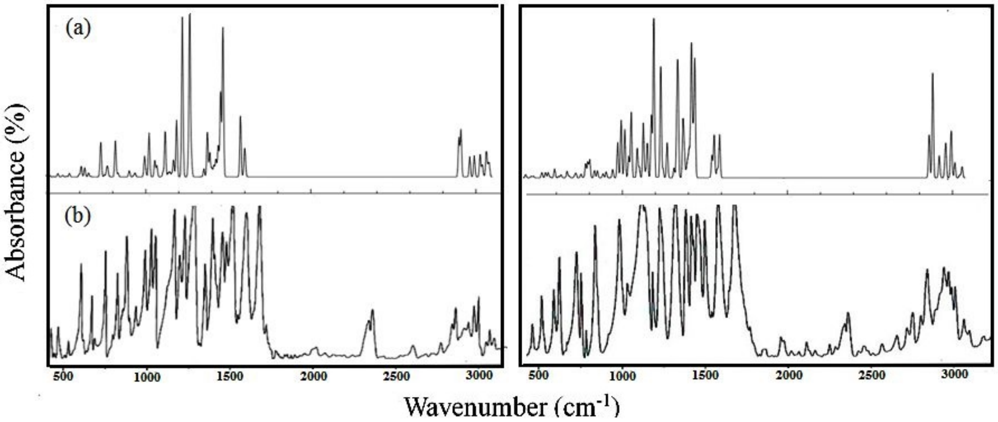

Fig. (2). **(a)** Simulated IR and **(b)** experimental FT-IR spectra of (left) triclisine and (left) rufescine (reproduced from [15] with the permission of Elsevier).

Tables **1** and **2** list the prominent vibrational modes for triclisine and rufescine, respectively. The detailed vibrational assignments of normal modes have been offered and respective FT-IR wavenumbers are also listed. To simplify the discussion, the vibrational spectrum has been divided into two parts, greater than 1500 cm^{-1} and less than 1500 cm^{-1}.

Table 1. Infrared spectral analysis of significant vibrations of triclisine (adopted from [15] with the permission of Elsevier).

Wavenumber (cm^{-1})		**FT-IR Value (cm^{-1})**	**IR Int. (a.u.)**	**Vibrational Assignments***
Calculated	**Scaled**			
3209	3094	3090	9.3	ν(CH)R3
3209	3093	-	6.6	ν(CH)R4
3201	3086	-	13.0	ν(CH)R3
3191	3076	3080	23.0	ν(CH)R1

CHAPTER 6

A Comprehensive DFT Study on a Thione Compound and its Tautomer

Abstract: In this chapter, we present an exhaustive study on a synthetic compound, 4-Amino-3-(4-hydroxybenzyl)-1H-1,2,4-triazole-5(4H)-thione (4AHT) and its tautomer employing both experimental and theoretical methods. 4AHT was synthesized by the reaction of 4-hydroxyphenylacetic acid and thiocarbohydrazide. The derivatives of 1,2,4-triazole are known to display antiviral, antidepressant, antimicrobial and anti-inflammatory activities. A DFT study on thione and thiol tautomers of 4AHT has been performed using the B3LYP/6-31+G(d,p) level. The calculated geometrical parameters are obtained to be in compliance with corresponding crystallographic values. The FT-IR spectrum of 4AHT obtained by the KBr disc technique has been explained by assigning the normal modes based on their potential energy distributions. The UV-visible spectrum of the title compound has been discussed by calculating the electronic transitions in several excited states using the TD-DFT method. The ^{1}H-NMR spectrum has also been studied by the GIAO method, which provides a good linear correlation between calculated and experimental chemical shifts. These spectroscopic results propose the dominance of the thione form of 4AHT in the solid-state and NH-SH tautomerism in the liquid form. This chapter is designed to provide a complete picture of the DFT based studies on molecular systems.

Keywords: B3LYP, DFT, Electronic parameter, Electronic transition, Experiment, FT-IR, HOMO, LUMO, MESP, NH-SH tautomerism, NMR, PES, Reaction, Synthesis, Tautomer, TD-DFT, Thermodynamics, Thiol, Thione, UV-visible.

INTRODUCTION

The well known heterocyclic triazoles have been recently in focus due to their adaptability for the synthesis of various heterocyclic systems. There exist two tautomers of triazoles, namely, the 1,2,3-triazole, symbolized as 1H and the 1,2,4-triazole, symbolized as 4H. The planar 4H rings are aromatic with 6π-electron-systems, which are very important in chemical science [1, 2]. The derivatives 1,2,4-triazole exhibit several biological activities, and hence, many 4H derivatives along with their N-bridged compounds were paid attention to in the past [3, 4]. The 1,2,4-triazole derivatives have been found to show anti-inflammatory [5],

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antiviral [6], antimicrobial [7], and antidepressant [8] activities. Therefore, the synthesis and extensive study of these heterocyclic systems are of immense importance.

Schiff bases [9, 10] and related heterocycles including triazoles [11 - 13] become potent corrosion inhibitors. Their chemisorption primarily takes place due to the −C=N− group interaction [10] and electronegative atoms such as N, O, S, *etc.* in the Schiff bases make them efficient corrosion inhibitors. Several compounds based on triazoles are reported to be good corrosion inhibitors for steel in acid media [14 - 17]. The synthesis of a few 1,2,4-triazole-5(4H)-thione compounds have been reported by Salgın-Gökşen *et al.* [18] along with their antimicrobial, analgesic, and anti-inflammatory activities. In this chapter, a comprehensive experimental and theoretical study of 4-Amino-3-(4-hydroxybenzyl)-1H-1,2,4-triazole-5(4H)-thione (4AHT) is presented, which was performed by us [19]. The 4AHT compound was synthesized by fusing a well-triturated mixture of 4-hydroxyphenylacetic acid ($C_8H_8O_3$) and thiocarbohydrazide (CH_6N_4S) in a round bottom flask for one hour on an oil bath at 413 K and subsequently cooling to room temperature [20]. The compound, thus obtained, was dried and recrystallized using methanol, yielding colourless block-like crystals, being triclinic with a P_1 symmetry group.

The reaction thermodynamics for the synthesis and spectroscopic analyses are performed using the density functional theory (DFT) based method. The chemical reactivity of 4AHT is studied with the help of molecular electrostatic potential (MESP) surface and several descriptors. The biological activities of 4AHT are also anticipated. We are of the firm view that these results will be useful in the future works on the 1,2,4-triazole-5(4H)-thione and related systems.

METHODS

Experimental

The sample has been estimated as 100% pure using the HPLC method. The Shimadzu 8400S spectrometer with the resolution of ±4 cm^{-1} was employed to record the FT-IR spectrum of sample in the wavenumber range 4000-400 cm^{-1} using the KBr pellet (see Chapter 4). The Bruker 400 MHz NMR spectrometer was used to record the ^{1}H-NMR spectrum of 4AHT with dimethyl sulfoxide (DMSO) solvent. The Shimadzu UV-2550 double-beam spectrophotometer having 1 cm matched quartz cell to measure the absorbance was utilized to record the UV-visible spectrum of 4AHT with ethyl alcohol (ethanol) solvent.

Computational

The optimization of the structure of 4AHT was performed with no constraints on symmetry in the potential energy surface (PES) with DFT at the B3LYP [21, 22] functional and a 6-31+G(d,p) basis set. The UV-visible spectrum was replicated by applying the time-dependent DFT (TD-DFT) approach using the equilibrium structure of 4AHT at the B3LYP level. The gauge independent atomic orbital (GIAO) method was used to calculate the ^{1}H-NMR chemical shifts at the same level. The polarizable continuum model devised by Tomasi *et al.* [23] has been exploited to incorporate the solvent effect during spectroscopic calculations. These computations were carried out by the *Gaussian 09* software [24].

RESULTS AND DISCUSSION

Synthesis and Thermodynamics

Fig. (**1**) displays the schematic of the reaction for the synthesis of 4AHT. The thermodynamics of this reaction can be analyzed by calculating various thermal parameters of reactants and products using room temperature. Table **1** lists the room temperature values of total electronic energy (*E*), thermal Enthalpy (*H*), Gibbs' free energy (*G*), and entropy (*S*) for these reactants ($C_8H_8O_3$, CH_6N_4S) and products ($C_9H_{10}N_4OS$, $2H_2O$).

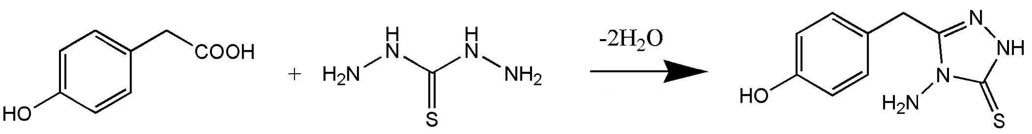

Fig. (1). Synthesis scheme of 4AHT [20].

One can see that the change in enthalpy change ($\Delta H_{\text{Reaction}}$), Gibbs free energy ($\Delta G_{\text{Reaction}}$), and entropy ($\Delta S_{\text{Reaction}}$) for this reaction are calculated to be -0.3010 a.u., -0.0415 a.u. and 24.8 cal/mol.K, respectively (1 a.u. = 627.5 kcal/mol). Thus, $\Delta H_{\text{Reaction}}$ and $\Delta G_{\text{Reaction}}$ possess negative values but the value of $\Delta S_{\text{Reaction}}$ is positive. This clearly reveals that the synthesis of 4AHT is favourable at room temperature due to the spontaneous and exothermic nature of the reaction.

Since both *H* and *S* favour the reaction path and so does *G* because $\Delta G = \Delta H - T\Delta S$. The equilibrium constant (K_{eq}) and $\Delta G_{\text{Reaction}}$ at temperature (*T*) are related as $K_{eq} = e^{-\Delta G/RT}$, which decides the nature (direction) of a chemical reaction. The K_{eq} value for the above mentioned reaction is found to be 1.285×10^{19} at $R = 1.987 \times 10^{-3}$ kcal/mol.K and $T = 298.15$ K. This further suggests that the reaction proceeds

CHAPTER 7

Inter- and Intra-Molecular Interactions by Quantum Theory of Atoms in Molecule

Abstract: In this exclusive chapter, we present a brief overview of the quantum theory of atoms in molecule (QTAIM) proposed by R. F. W. Bader. This theory is based on the topological analysis of the electron density and related parameters. One of the strengths of this theory is the accurate prediction, characterization, and quantification of various interactions, including H-bond and van der Waals interactions. Herein, we discuss the important aspects of QTAIM regarding the intra- and intermolecular interactions in biologically active molecules discussed in the preceding chapters. Within the framework of the QTAIM, I mention the criteria of H-bonds and characterize the various H-bonds on the basis of topological parameters, and continue to quantify the strength of the H-bond. I will also describe a very user-friendly software *AIMAll* to perform the QTAIM analysis and explain the obtained results. In order to provide the contents digestive, I will include examples of molecules from Chapters 3, 4, and 5. I believe that this chapter will guide the readers interested in various kinds of interactions in biologically active molecules.

Keywords: AIM, AIMAll, BCP, Bond strength, BSSE, Characterization, Complex, Counterpoise, Dimer, Electron density, H-bond, Intermolecular interaction, Intramolecular interaction, Laplacian, Molecular graph, QTAIM, RCP, Reactivity, Stabilization, Supermolecular approach, Topology.

INTRODUCTION

H-bonds play a key role in determining the shapes, properties, and functions of biomolecules and biologically active systems [1]. Despite the dominant role of H-bonding in nature, accurate data on the respective stabilization or interaction energies are quite rare. The situation with extended H-bonded complexes is, despite enormous progress in various experimental techniques, even less satisfactory and accurate data on stabilization energies of these complexes are almost unavailable. Reliable and consistent information on the stability of various types of inter-molecular H-bonded complexes, from the very weak to the strongest, comes from the high-level correlated quantum chemical wavefunction-based method or density functional theory (DFT) calculations, and these methods, thus, represent one of the most promising sources of relevant data. On the cont-

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rary, the intra-molecular H-bonds can not be directly quantified from a DFT calculation and this requires an alternative approach.

QUANTUM THEORY OF ATOMS IN MOLECULE (QTAIM)

The QTAIM [2] describes the interactions between atomic basins. It exploits some topological parameters *viz.* electron density (ρ) and its Laplacian $(\nabla^2\rho)$, kinetic energy density (G), potential energy density (V), and total electron energy density (H) at the bond critical point (BCP) of interaction atoms or fragments. The theory efficiently characterizes and quantifies various types of H-bonded and other interactions.

Existence of H-Bond

In QTAIM, the existence of H-bond follows Koch and Popelier criterion [3], which requires:

1. The existence of bond critical point (BCP) for the 'proton (H)···acceptor (A)' contact.
2. The value of electron density should lie in the range of 0.002–0.040 a.u.
3. The corresponding Laplacian ($\nabla^2\rho$) should be within the range of 0.024–0.139 a.u.

Characterization of H-Bond

The three types of H-bond are characterized on the basis of topological parameters. According to Rozas *et al.* [4], the characterization demands at BCP:

1. $\nabla^2\rho < 0$ and $H < 0$ for strong H-bond of covalent nature.
2. $\nabla^2\rho > 0$ and $H < 0$ for medium H-bond of partially covalent nature.
3. $\nabla^2\rho > 0$ and $H > 0$ for weak H-bond of electrostatic character.

Strength of H-Bond

According to Espinosa *et al.* [5], the interaction energy of A···B contact is defined as,

$$\Delta E = -\tfrac{1}{2}V \quad \textbf{(1)}$$

at BCP.

The *AIMAll* Program

There are various programs available to perform the QTAIM analysis, such as *AIMPAC* [6], *AIM2000* [7], *AIMAll* [8, 9], *etc.* In this chapter, we use the *AIMAll* program in order to explore intra-molecular and inter-molecular H-bond interactions such as hydrogen bonds (H-bonds). *AIMAll* is a user-friendly and efficient program. The graphical user interface of *AIMAll* is displayed in Fig. (**1**). It uses the formatted checkpoint (.fch or .fchk) file generated by the *Gaussian* program (see Chapter 2) as an input and automatically performs QTAIM analysis for the system under study. The basis set on reliability and stability in the values of QTAIM parameters have been studied and found that they are almost independent of the basis set in the case of used functional B3LYP in DFT [10].

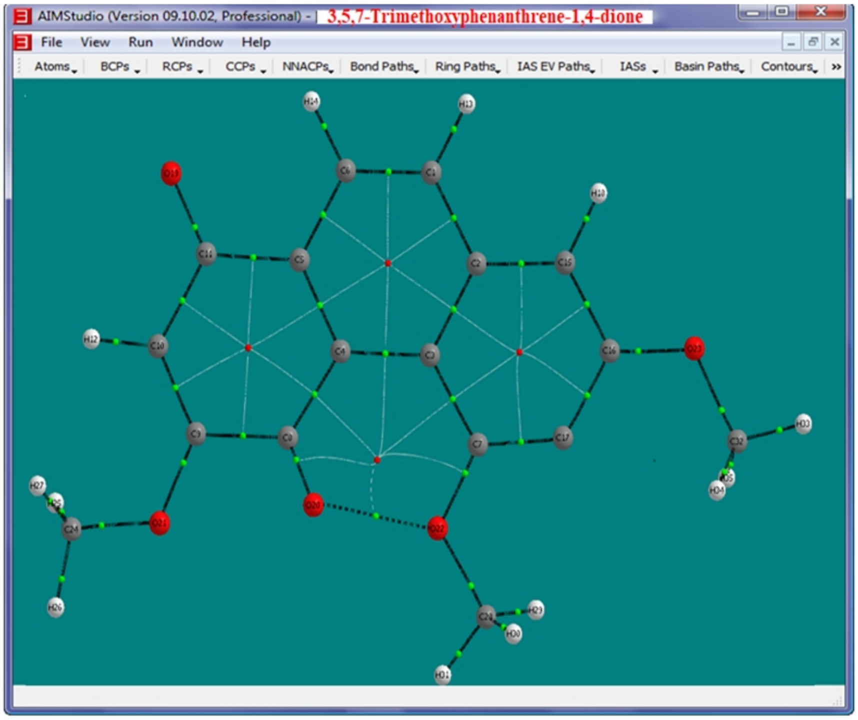

Fig. (1). The graphical user interface of *AIMAll* program displaying the molecular graph of 3,5,7-Trimethoxyphenanthrene-1,4-dione (TPD). The intra-molecular interaction is shown by a dotted line. Green and red points represent BCPs and RCPs, respectively.

The QTAIM calculations on TPD [11] reveal an intra-molecular O20···O22 interaction as depicted in the molecular graph shown in Fig. (**1**). The bond-distance O20···O22 calculated at B3LYP/6-31+G**method is 2.643 Å. The values of topological parameters at BCP of O22···O21 are as follows:

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APPENDIX

Gaussian Output File of Methane (CH_4)

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Copyright (c) 1988,1990,1992,1993,1995,1998,2003,2009,2010,
Gaussian, Inc. All Rights Reserved.
This is part of the Gaussian(R) 09 program. It is based on
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the Gaussian(R) 94 system (copyright 1995, Gaussian, Inc.),
the Gaussian 92(TM) system (copyright 1992, Gaussian, Inc.),
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Gaussian 09, Revision B.01,
M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria,
M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci,
G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian,
A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada,
M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima,
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Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr.,
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K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi,
M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross,
V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann,
O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski,
R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth,
P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels,
O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski,
and D. J. Fox, Gaussian, Inc., Wallingford CT, 2010.
*****************************************
Gaussian 09: IA32W-G09RevB.01 12-Aug-2010
29-Nov-2020
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2/9=110,12=2,17=6,18=5,40=1/2;
3/5=4,6=6,7=11,11=2,16=1,25=1,30=1,71=1,74=-5/1,2,3;
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5/5=2,38=5/2;
6/7=2,8=2,9=2,10=2,28=1/1;
7//1,2,3,16;
```

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2/9=110/2;
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4/5=5,16=3/1;
5/5=2,38=5/2;
7//1,2,3,16;
1/14=-1,18=20,19=15/3(-5);
2/9=110/2;
6/7=2,8=2,9=2,10=2,19=2,28=1/1;
99/9=1/99;
-------------------
Title Card Required
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Charge = 0 Multiplicity = 1
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H 2.12357 -0.4449 0.
H 2.12359 1.06831 0.87365
H 2.12359 1.06831 -0.87365
H 0.69692 0.56392 0.
GradGradGradGradGradGradGradGradGradGradGradGradGradGradGradGradGradGradGrad
Berny optimization.
Initialization pass.
----------------------------
```

```
! Initial Parameters !

! (Angstroms and Degrees) !

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! Name Definition Value Derivative Info. !

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! R2 R(1,3) 1.07 estimate D2E/DX2 !

! R3 R(1,4) 1.07 estimate D2E/DX2 !

! R4 R(1,5) 1.07 estimate D2E/DX2 !

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! A2 A(2,1,4) 109.4712 estimate D2E/DX2 !

! A3 A(2,1,5) 109.4712 estimate D2E/DX2 !

! A4 A(3,1,4) 109.4713 estimate D2E/DX2 !

! A5 A(3,1,5) 109.4712 estimate D2E/DX2 !

! A6 A(4,1,5) 109.4712 estimate D2E/DX2 !

! D1 D(2,1,4,3) -120.0 estimate D2E/DX2 !

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! D3 D(2,1,5,4) -120.0 estimate D2E/DX2 !

! D4 D(3,1,5,4) 120.0 estimate D2E/DX2 !

-----------------------------------------------------

Trust Radius=3.00D-01 FncErr=1.00D-07 GrdErr=1.00D-06

Number of steps in this run= 24 maximum allowed number of steps= 100.

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Input orientation:

-------------------------------------------------------------

Center Atomic Atomic Coordinates (Angstroms)
```

```
Number Number Type X Y Z
---------------------------------------------------------------------
1 6 0 1.766917 0.563910 0.000000
2 1 0 2.123572 -0.444900 0.000000
3 1 0 2.123590 1.068308 0.873652
4 1 0 2.123590 1.068308 -0.873652
5 1 0 0.696917 0.563923 0.000000
---------------------------------------------------------------------
Distance matrix (angstroms):
1 2 3 4 5
1 C 0.000000
2 H 1.070000 0.000000
3 H 1.070000 1.747302 0.000000
4 H 1.070000 1.747302 1.747303 0.000000
5 H 1.070000 1.747303 1.747303 1.747303 0.000000
Stoichiometry CH4
Framework group T[O(C),4C3(H)]
Deg. of freedom 1
Full point group T NOp 12
Largest Abelian subgroup D2 NOp 4
Largest concise Abelian subgroup D2 NOp 4
Standard orientation:
----------------------------------------------------------------------
Center Atomic Atomic Coordinates (Angstroms)
Number Number Type X Y Z
----------------------------------------------------------------------
```

```
1 6 0 0.000000 0.000000 0.000000
2 1 0 0.617765 0.617765 0.617765
3 1 0 -0.617765 -0.617765 0.617765
4 1 0 -0.617765 0.617765 -0.617765
5 1 0 0.617765 -0.617765 -0.617765
---------------------------------------------------------------------
Rotational constants (GHZ): 164.2463768 164.2463768 164.2463768
Standard basis: 6-311+G(d) (5D, 7F)
There are 10 symmetry adapted basis functions of A symmetry.
There are 8 symmetry adapted basis functions of B1 symmetry.
There are 8 symmetry adapted basis functions of B2 symmetry.
There are 8 symmetry adapted basis functions of B3 symmetry.
Integral buffers will be 262144 words long.
Raffenetti 2 integral format.
Two-electron integral symmetry is turned on.
34 basis functions, 56 primitive gaussians, 35 cartesian basis functions
5 alpha electrons 5 beta electrons
nuclear repulsion energy 13.6865184815 Hartrees.
NAtoms= 5 NActive= 5 NUniq= 2 SFac= 4.00D+00 NAtFMM= 50 NAOKFM=F Big=F
One-electron integrals computed using PRISM.
NBasis= 34 RedAO= T NBF= 10 8 8 8
NBsUse= 34 1.00D-06 NBFU= 10 8 8 8
Harris functional with IExCor= 402 diagonalized for initial guess.
ExpMin= 4.38D-02 ExpMax= 4.56D+03 ExpMxC= 6.82D+02 IAcc=2 IRadAn= 0 AccDes=
0.00D+00
HarFok: IExCor= 402 AccDes= 0.00D+00 IRadAn= 0 IDoV= 1
```

```
ScaDFX= 1.000000 1.000000 1.000000 1.000000
FoFCou: FMM=F IPFlag= 0 FMFlag= 100000 FMFlg1= 0
NFxFlg= 0 DoJE=T BraDBF=F KetDBF=T FulRan=T
Omega= 0.000000 0.000000 1.000000 0.000000 0.000000 ICntrl= 500 IOpCl= 0
NMat0= 1 NMatS0= 1 NMatT0= 0 NMatD0= 1 NMtDS0= 0 NMtDT0= 0
I1Cent= 4 NGrid= 0.
Petite list used in FoFCou.
Initial guess orbital symmetries:
Occupied (A) (A) (T) (T) (T)
Virtual (A) (T) (T) (T) (T) (T) (T) (A) (T) (T) (T) (T)
(T) (T) (A) (A) (E) (E) (T) (T) (T) (A) (T) (T)
(T) (T) (T) (T) (A)
The electronic state of the initial guess is 1-A.
Requested convergence on RMS density matrix=1.00D-08 within 128 cycles.
Requested convergence on MAX density matrix=1.00D-06.
Requested convergence on energy=1.00D-06.
No special actions if energy rises.
Keep R1 ints in memory in canonical form, NReq=1118393.
SCF Done: E(RB3LYP) = -40.5269656822 A.U. after 7 cycles
Convg = 0.1651D-08 -V/T = 2.0025
****************************************************************
Population analysis using the SCF density.
****************************************************************
Orbital symmetries:
Occupied (A) (A) (T) (T) (T)
Virtual (A) (T) (T) (T) (T) (T) (T) (A) (T) (T) (T) (T)
```

```
(T) (T) (A) (A) (E) (E) (T) (T) (T) (A) (T) (T)

(T) (T) (T) (T) (A)

The electronic state is 1-A.

Alpha occ. eigenvalues -- -10.14229 -0.70375 -0.39971 -0.39971 -0.39971

Alpha virt. eigenvalues -- 0.01085 0.05743 0.05743 0.05743 0.15177

Alpha virt. eigenvalues -- 0.15177 0.15177 0.21540 0.40328 0.40328

Alpha virt. eigenvalues -- 0.40328 0.60964 0.60964 0.60964 0.61552

Alpha virt. eigenvalues -- 0.87392 1.25394 1.25394 1.59531 1.59531

Alpha virt. eigenvalues -- 1.59531 2.34714 2.44084 2.44084 2.44084

Alpha virt. eigenvalues -- 3.13406 3.13406 3.13406 23.45834

Condensed to atoms (all electrons):

1 2 3 4 5

1 C 5.438146 0.375862 0.375862 0.375862 0.375862

2 H 0.375862 0.471076 -0.027446 -0.027446 -0.027446

3 H 0.375862 -0.027446 0.471076 -0.027446 -0.027446

4 H 0.375862 -0.027446 -0.027446 0.471076 -0.027446

5 H 0.375862 -0.027446 -0.027446 -0.027446 0.471076

Mulliken atomic charges:

1

1 C -0.941595

2 H 0.235399

3 H 0.235399

4 H 0.235399

5 H 0.235399

Sum of Mulliken atomic charges = 0.00000

Mulliken charges with hydrogens summed into heavy atoms:
```

```
1
1 C 0.000000
Sum of Mulliken charges with hydrogens summed into heavy atoms = 0.00000
Electronic spatial extent (au): <R**2>= 35.2014
Charge= 0.0000 electrons
Dipole moment (field-independent basis, Debye):
X= 0.0000 Y= 0.0000 Z= 0.0000 Tot= 0.0000
Quadrupole moment (field-independent basis, Debye-Ang):
XX= -8.4501 YY= -8.4501 ZZ= -8.4501
XY= 0.0000 XZ= 0.0000 YZ= 0.0000
Traceless Quadrupole moment (field-independent basis, Debye-Ang):
XX= 0.0000 YY= 0.0000 ZZ= 0.0000
XY= 0.0000 XZ= 0.0000 YZ= 0.0000
Octapole moment (field-independent basis, Debye-Ang**2):
XXX= 0.0000 YYY= 0.0000 ZZZ= 0.0000 XYY= 0.0000
XXY= 0.0000 XXZ= 0.0000 XZZ= 0.0000 YZZ= 0.0000
YYZ= 0.0000 XYZ= 0.7305
Hexadecapole moment (field-independent basis, Debye-Ang**3):
XXXX= -16.6677 YYYY= -16.6677 ZZZZ= -16.6677 XXXY= 0.0000
XXXZ= 0.0000 YYYX= 0.0000 YYYZ= 0.0000 ZZZX= 0.0000
ZZZY= 0.0000 XXYY= -5.0946 XXZZ= -5.0946 YYZZ= -5.0946
XXYZ= 0.0000 YYXZ= 0.0000 ZZXY= 0.0000
N-N= 1.368651848151D+01 E-N=-1.207227515305D+02 KE= 4.042785986351D+01
Symmetry A KE= 3.449759076308D+01
Symmetry B1 KE= 1.976756366809D+00
Symmetry B2 KE= 1.976756366809D+00
```

```
Symmetry B3 KE= 1.976756366809D+00

Calling FoFJK, ICntrl= 2127 FMM=F ISym2X=1 I1Cent= 0 IOpClX= 0 NMat=1 NMatS=1
NMatT=0.

***** Axes restored to original set *****

-------------------------------------------------------------------

Center Atomic Forces (Hartrees/Bohr)

Number Number X Y Z

-------------------------------------------------------------------

1 6 0.000000000 0.000000000 0.000000000

2 1 0.004838637 -0.013686260 -0.000000012

3 1 0.004838896 0.006843035 0.011852598

4 1 0.004838876 0.006843049 -0.011852598

5 1 -0.014516409 0.000000176 0.000000012

-------------------------------------------------------------------

Cartesian Forces: Max 0.014516409 RMS 0.007496241

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Berny optimization.

Internal Forces: Max 0.014516409 RMS 0.007759347

Search for a local minimum.

Step number 1 out of a maximum of 24

All quantities printed in internal units (Hartrees-Bohrs-Radians)

Mixed Optimization -- RFO/linear search

Second derivative matrix not updated -- first step.

The second derivative matrix:

R1 R2 R3 R4 A1

R1 0.37230
```

```
R2 0.00000 0.37230
R3 0.00000 0.00000 0.37230
R4 0.00000 0.00000 0.00000 0.37230
A1 0.00000 0.00000 0.00000 0.00000 0.16000
A2 0.00000 0.00000 0.00000 0.00000 0.00000
A3 0.00000 0.00000 0.00000 0.00000 0.00000
A4 0.00000 0.00000 0.00000 0.00000 0.00000
A5 0.00000 0.00000 0.00000 0.00000 0.00000
A6 0.00000 0.00000 0.00000 0.00000 0.00000
D1 0.00000 0.00000 0.00000 0.00000 0.00000
D2 0.00000 0.00000 0.00000 0.00000 0.00000
D3 0.00000 0.00000 0.00000 0.00000 0.00000
D4 0.00000 0.00000 0.00000 0.00000 0.00000
A2 A3 A4 A5 A6
A2 0.16000
A3 0.00000 0.16000
A4 0.00000 0.00000 0.16000
A5 0.00000 0.00000 0.00000 0.16000
A6 0.00000 0.00000 0.00000 0.00000 0.16000
D1 0.00000 0.00000 0.00000 0.00000 0.00000
D2 0.00000 0.00000 0.00000 0.00000 0.00000
D3 0.00000 0.00000 0.00000 0.00000 0.00000
D4 0.00000 0.00000 0.00000 0.00000 0.00000
D1 D2 D3 D4
D1 0.00499
D2 0.00000 0.00499
```

```
D3 0.00000 0.00000 0.00499

D4 0.00000 0.00000 0.00000 0.00499

ITU= 0

Eigenvalues --- 0.05269 0.05891 0.08766 0.16000 0.16000

Eigenvalues --- 0.37230 0.37230 0.37230 0.37230

RFO step: Lambda=-2.25043714D-03 EMin= 5.26881002D-02

Linear search not attempted -- first point.

Iteration 1 RMS(Cart)= 0.02071637 RMS(Int)= 0.00000000

Iteration 2 RMS(Cart)= 0.00000000 RMS(Int)= 0.00000000

ClnCor: largest displacement from symmetrization is 4.65D-14 for atom 3.

Variable Old X -DE/DX Delta X Delta X Delta X New X

(Linear) (Quad) (Total)

R1 2.02201 0.01452 0.00000 0.03876 0.03876 2.06076

R2 2.02201 0.01452 0.00000 0.03876 0.03876 2.06076

R3 2.02201 0.01452 0.00000 0.03876 0.03876 2.06076

R4 2.02201 0.01452 0.00000 0.03876 0.03876 2.06076

A1 1.91063 0.00000 0.00000 0.00000 0.00000 1.91063

A2 1.91063 0.00000 0.00000 0.00000 0.00000 1.91063

A3 1.91063 0.00000 0.00000 0.00000 0.00000 1.91063

A4 1.91063 0.00000 0.00000 0.00000 0.00000 1.91063

A5 1.91063 0.00000 0.00000 0.00000 0.00000 1.91063

A6 1.91063 0.00000 0.00000 0.00000 0.00000 1.91063

D1 -2.09440 0.00000 0.00000 0.00000 0.00000 -2.09440

D2 2.09440 0.00000 0.00000 0.00000 0.00000 2.09440

D3 -2.09440 0.00000 0.00000 0.00000 0.00000 -2.09440

D4 2.09440 0.00000 0.00000 0.00000 0.00000 2.09440
```

```
Item Value Threshold Converged?
Maximum Force 0.014516 0.000450 NO
RMS Force 0.007759 0.000300 NO
Maximum Displacement 0.038757 0.001800 NO
RMS Displacement 0.020716 0.001200 NO
Predicted change in Energy=-1.131979D-03
GradGradGradGradGradGradGradGradGradGradGradGradGradGradGradGradGradGrad
Input orientation:
---------------------------------------------------------------
Center Atomic Atomic Coordinates (Angstroms)
Number Number Type X Y Z
---------------------------------------------------------------
1 6 0 1.766917 0.563910 0.000000
2 1 0 2.130408 -0.464237 -0.000001
3 1 0 2.130427 1.077976 0.890397
4 1 0 2.130426 1.077977 -0.890397
5 1 0 0.676408 0.563923 0.000001
---------------------------------------------------------------
Distance matrix (angstroms):
1 2 3 4 5
1 C 0.000000
2 H 1.090509 0.000000
3 H 1.090509 1.780794 0.000000
4 H 1.090509 1.780794 1.780794 0.000000
5 H 1.090509 1.780794 1.780794 1.780794 0.000000
Stoichiometry CH4
```

```
Framework group TD[O(C),4C3(H)]
Deg. of freedom 1
Full point group TD NOp 24
Omega: Change in point group or standard orientation.

Old FWG=T [O(C1),4C3(H1)]
New FWG=TD [O(C1),4C3(H1)]
Largest Abelian subgroup D2 NOp 4
Largest concise Abelian subgroup D2 NOp 4
Standard orientation:
---------------------------------------------------------------
Center Atomic Atomic Coordinates (Angstroms)
Number Number Type X Y Z
---------------------------------------------------------------
1 6 0 0.000000 0.000000 0.000000
2 1 0 0.629606 0.629606 0.629606
3 1 0 -0.629606 -0.629606 0.629606
4 1 0 -0.629606 0.629606 -0.629606
5 1 0 0.629606 -0.629606 -0.629606
---------------------------------------------------------------
Rotational constants (GHZ): 158.1265094 158.1265094 158.1265094
Standard basis: 6-311+G(d) (5D, 7F)
There are 10 symmetry adapted basis functions of A symmetry.
There are 8 symmetry adapted basis functions of B1 symmetry.
There are 8 symmetry adapted basis functions of B2 symmetry.
There are 8 symmetry adapted basis functions of B3 symmetry.
```

```
Integral buffers will be 262144 words long.

Raffenetti 2 integral format.

Two-electron integral symmetry is turned on.

34 basis functions, 56 primitive gaussians, 35 cartesian basis functions

5 alpha electrons 5 beta electrons

nuclear repulsion energy 13.4291161863 Hartrees.

NAtoms= 5 NActive= 5 NUniq= 2 SFac= 4.00D+00 NAtFMM= 50 NAOKFM=F Big=F

One-electron integrals computed using PRISM.

NBasis= 34 RedAO= T NBF= 10 8 8 8

NBsUse= 34 1.00D-06 NBFU= 10 8 8 8

Initial guess read from the read-write file.

B after Tr= 0.000000 0.000000 0.000000

Rot= 1.000000 0.000000 0.000000 0.000000 Ang= 0.00 deg.

Initial guess orbital symmetries:

Occupied (A1) (A1) (T2) (T2) (T2)

Virtual (A1) (T2) (T2) (T2) (T2) (T2) (T2) (A1) (T2) (T2)

(T2) (T2) (T2) (T2) (A1) (A1) (E) (E) (T2) (T2)

(T2) (A1) (T2) (T2) (T2) (T2) (T2) (T2) (A1)

Harris functional with IExCor= 402 diagonalized for initial guess.

ExpMin= 4.38D-02 ExpMax= 4.56D+03 ExpMxC= 6.82D+02 IAcc=2 IRadAn= 0 AccDes= 0.00D+00

HarFok: IExCor= 402 AccDes= 0.00D+00 IRadAn= 0 IDoV= 1

ScaDFX= 1.000000 1.000000 1.000000 1.000000

FoFCou: FMM=F IPFlag= 0 FMFlag= 100000 FMFlg1= 0

NFxFlg= 0 DoJE=T BraDBF=F KetDBF=T FulRan=T

Omega= 0.000000 0.000000 1.000000 0.000000 0.000000 ICntrl= 500 IOpCl= 0
```

```
NMat0= 1 NMatS0= 1 NMatT0= 0 NMatD0= 1 NMtDS0= 0 NMtDT0= 0

I1Cent= 4 NGrid= 0.

Petite list used in FoFCou.

Requested convergence on RMS density matrix=1.00D-08 within 128 cycles.

Requested convergence on MAX density matrix=1.00D-06.

Requested convergence on energy=1.00D-06.

No special actions if energy rises.

Keep R1 ints in memory in canonical form, NReq=1119085.

SCF Done: E(RB3LYP) = -40.5280818642 A.U. after 6 cycles

Convg = 0.6849D-08 -V/T = 2.0052

Calling FoFJK, ICntrl= 2127 FMM=F ISym2X=1 I1Cent= 0 IOpClX= 0 NMat=1 NMatS=1
NMatT=0.

***** Axes restored to original set *****

-------------------------------------------------------------------

Center Atomic Forces (Hartrees/Bohr)

Number Number X Y Z

-------------------------------------------------------------------

1 6 0.000000000 0.000000000 0.000000000

2 1 0.000050603 -0.000143133 0.000000000

3 1 0.000050606 0.000071565 0.000123956

4 1 0.000050606 0.000071565 -0.000123956

5 1 -0.000151814 0.000000002 0.000000000

-------------------------------------------------------------------

Cartesian Forces: Max 0.000151814 RMS 0.000078397

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Berny optimization.
```

```
Using GEDIIS/GDIIS optimizer.
Internal Forces: Max 0.000151814 RMS 0.000081148
Search for a local minimum.
Step number 2 out of a maximum of 24
All quantities printed in internal units (Hartrees-Bohrs-Radians)
Mixed Optimization -- En-DIIS/RFO-DIIS
Update second derivatives using D2CorX and points 1 2
DE= -1.12D-03 DEPred=-1.13D-03 R= 9.86D-01
SS= 1.41D+00 RLast= 7.75D-02 DXNew= 5.0454D-01 2.3254D-01
Trust test= 9.86D-01 RLast= 7.75D-02 DXMaxT set to 3.00D-01
The second derivative matrix:
R1 R2 R3 R4 A1
R1 0.37188
R2 -0.00042 0.37188
R3 -0.00042 -0.00042 0.37188
R4 -0.00042 -0.00042 -0.00042 0.37188
A1 0.00000 0.00000 0.00000 0.00000 0.16000
A2 0.00000 0.00000 0.00000 0.00000 0.00000
A3 0.00000 0.00000 0.00000 0.00000 0.00000
A4 0.00000 0.00000 0.00000 0.00000 0.00000
A5 0.00000 0.00000 0.00000 0.00000 0.00000
A6 0.00000 0.00000 0.00000 0.00000 0.00000
D1 0.00000 0.00000 0.00000 0.00000 0.00000
D2 0.00000 0.00000 0.00000 0.00000 0.00000
D3 0.00000 0.00000 0.00000 0.00000 0.00000
D4 0.00000 0.00000 0.00000 0.00000 0.00000
```

```
A2 A3 A4 A5 A6
A2 0.16000
A3 0.00000 0.16000
A4 0.00000 0.00000 0.16000
A5 0.00000 0.00000 0.00000 0.16000
A6 0.00000 0.00000 0.00000 0.00000 0.16000
D1 0.00000 0.00000 0.00000 0.00000 0.00000
D2 0.00000 0.00000 0.00000 0.00000 0.00000
D3 0.00000 0.00000 0.00000 0.00000 0.00000
D4 0.00000 0.00000 0.00000 0.00000 0.00000
D1 D2 D3 D4
D1 0.00499
D2 0.00000 0.00499
D3 0.00000 0.00000 0.00499
D4 0.00000 0.00000 0.00000 0.00499
ITU= 1 0
Use linear search instead of GDIIS.
Eigenvalues --- 0.05269 0.05891 0.08766 0.16000 0.16000
Eigenvalues --- 0.37063 0.37230 0.37230 0.37230
RFO step: Lambda= 0.00000000D+00 EMin= 5.26881002D-02
Quartic linear search produced a step of 0.01120.
Iteration 1 RMS(Cart)= 0.00023197 RMS(Int)= 0.00000000
Iteration 2 RMS(Cart)= 0.00000000 RMS(Int)= 0.00000000
ClnCor: largest displacement from symmetrization is 1.12D-14 for atom 4.
Variable Old X -DE/DX Delta X Delta X Delta X New X
(Linear) (Quad) (Total)
```

```
R1 2.06076 0.00015 0.00043 0.00000 0.00043 2.06120
R2 2.06076 0.00015 0.00043 0.00000 0.00043 2.06120
R3 2.06076 0.00015 0.00043 0.00000 0.00043 2.06120
R4 2.06076 0.00015 0.00043 0.00000 0.00043 2.06120
A1 1.91063 0.00000 0.00000 0.00000 0.00000 1.91063
A2 1.91063 0.00000 0.00000 0.00000 0.00000 1.91063
A3 1.91063 0.00000 0.00000 0.00000 0.00000 1.91063
A4 1.91063 0.00000 0.00000 0.00000 0.00000 1.91063
A5 1.91063 0.00000 0.00000 0.00000 0.00000 1.91063
A6 1.91063 0.00000 0.00000 0.00000 0.00000 1.91063
D1 -2.09440 0.00000 0.00000 0.00000 0.00000 -2.09440
D2 2.09440 0.00000 0.00000 0.00000 0.00000 2.09440
D3 -2.09440 0.00000 0.00000 0.00000 0.00000 -2.09440
D4 2.09440 0.00000 0.00000 0.00000 0.00000 2.09440
Item Value Threshold Converged?
Maximum Force 0.000152 0.000450 YES
RMS Force 0.000081 0.000300 YES
Maximum Displacement 0.000434 0.001800 YES
RMS Displacement 0.000232 0.001200 YES
Predicted change in Energy=-1.239284D-07
Optimization completed.
-- Stationary point found.
----------------------------
! Optimized Parameters !
! (Angstroms and Degrees) !
------------------------- -------------------------
```

```
! Name Definition Value Derivative Info. !
---------------------------------------------------
! R1 R(1,2) 1.0905 -DE/DX = 0.0002 !
! R2 R(1,3) 1.0905 -DE/DX = 0.0002 !
! R3 R(1,4) 1.0905 -DE/DX = 0.0002 !
! R4 R(1,5) 1.0905 -DE/DX = 0.0002 !
! A1 A(2,1,3) 109.4712 -DE/DX = 0.0 !
! A2 A(2,1,4) 109.4712 -DE/DX = 0.0 !
! A3 A(2,1,5) 109.4712 -DE/DX = 0.0 !
! A4 A(3,1,4) 109.4712 -DE/DX = 0.0 !
! A5 A(3,1,5) 109.4712 -DE/DX = 0.0 !
! A6 A(4,1,5) 109.4712 -DE/DX = 0.0 !
! D1 D(2,1,4,3) -120.0 -DE/DX = 0.0 !
! D2 D(2,1,5,3) 120.0 -DE/DX = 0.0 !
! D3 D(2,1,5,4) -120.0 -DE/DX = 0.0 !
! D4 D(3,1,5,4) 120.0 -DE/DX = 0.0 !
---------------------------------------------------------------
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Input orientation:
--------------------------------------------------------------
Center Atomic Atomic Coordinates (Angstroms)
Number Number Type X Y Z
---------------------------------------------------------------
1 6 0 1.766917 0.563910 0.000000
2 1 0 2.130408 -0.464237 -0.000001
3 1 0 2.130427 1.077976 0.890397
```

```
4 1 0 2.130426 1.077977 -0.890397
5 1 0 0.676408 0.563923 0.000001
---------------------------------------------------------------
Distance matrix (angstroms):
1 2 3 4 5
1 C 0.000000
2 H 1.090509 0.000000
3 H 1.090509 1.780794 0.000000
4 H 1.090509 1.780794 1.780794 0.000000
5 H 1.090509 1.780794 1.780794 1.780794 0.000000
Stoichiometry CH4
Framework group TD[O(C),4C3(H)]
Deg. of freedom 1
Full point group TD NOp 24
Largest Abelian subgroup D2 NOp 4
Largest concise Abelian subgroup D2 NOp 4
Standard orientation:
---------------------------------------------------------------
Center Atomic Atomic Coordinates (Angstroms)
Number Number Type X Y Z
---------------------------------------------------------------
1 6 0 0.000000 0.000000 0.000000
2 1 0 0.629606 0.629606 0.629606
3 1 0 -0.629606 -0.629606 0.629606
4 1 0 -0.629606 0.629606 -0.629606
5 1 0 0.629606 -0.629606 -0.629606
```

```
---------------------------------------------------------------
Rotational constants (GHZ): 158.1265094 158.1265094 158.1265094
*************************************************************
Population analysis using the SCF density.
*************************************************************
Orbital symmetries:
Occupied (A1) (A1) (T2) (T2) (T2)
Virtual (A1) (T2) (T2) (T2) (T2) (T2) (T2) (A1) (T2) (T2)
(T2) (T2) (T2) (T2) (A1) (A1) (E) (E) (T2) (T2)
(T2) (A1) (T2) (T2) (T2) (T2) (T2) (T2) (A1)
The electronic state is 1-A1.
Alpha occ. eigenvalues -- -10.15133 -0.69745 -0.39634 -0.39634 -0.39634
Alpha virt. eigenvalues -- 0.00991 0.05736 0.05736 0.05736 0.14637
Alpha virt. eigenvalues -- 0.14637 0.14637 0.21072 0.40418 0.40418
Alpha virt. eigenvalues -- 0.40418 0.59906 0.59906 0.59906 0.60278
Alpha virt. eigenvalues -- 0.86494 1.25797 1.25797 1.59542 1.59542
Alpha virt. eigenvalues -- 1.59542 2.35038 2.42329 2.42329 2.42329
Alpha virt. eigenvalues -- 3.10057 3.10057 3.10057 23.43988
Condensed to atoms (all electrons):
1 2 3 4 5
1 C 5.441470 0.372433 0.372433 0.372433 0.372433
2 H 0.372433 0.475956 -0.027063 -0.027063 -0.027063
3 H 0.372433 -0.027063 0.475956 -0.027063 -0.027063
4 H 0.372433 -0.027063 -0.027063 0.475956 -0.027063
5 H 0.372433 -0.027063 -0.027063 -0.027063 0.475956
Mulliken atomic charges:
```

```
1
1 C -0.931204
2 H 0.232801
3 H 0.232801
4 H 0.232801
5 H 0.232801
Sum of Mulliken atomic charges = 0.00000
Mulliken charges with hydrogens summed into heavy atoms:
1
1 C 0.000000
Sum of Mulliken charges with hydrogens summed into heavy atoms = 0.00000
Electronic spatial extent (au): <R**2>= 35.9778
Charge= 0.0000 electrons
Dipole moment (field-independent basis, Debye):
X= 0.0000 Y= 0.0000 Z= 0.0000 Tot= 0.0000
Quadrupole moment (field-independent basis, Debye-Ang):
XX= -8.5144 YY= -8.5144 ZZ= -8.5144
XY= 0.0000 XZ= 0.0000 YZ= 0.0000
Traceless Quadrupole moment (field-independent basis, Debye-Ang):
XX= 0.0000 YY= 0.0000 ZZ= 0.0000
XY= 0.0000 XZ= 0.0000 YZ= 0.0000
Octapole moment (field-independent basis, Debye-Ang**2):
XXX= 0.0000 YYY= 0.0000 ZZZ= 0.0000 XYY= 0.0000
XXY= 0.0000 XXZ= 0.0000 XZZ= 0.0000 YZZ= 0.0000
YYZ= 0.0000 XYZ= 0.7811
Hexadecapole moment (field-independent basis, Debye-Ang**3):
```

```
XXXX= -17.2201 YYYY= -17.2201 ZZZZ= -17.2201 XXXY= 0.0000
XXXZ= 0.0000 YYYX= 0.0000 YYYZ= 0.0000 ZZZX= 0.0000
ZZZY= 0.0000 XXYY= -5.2429 XXZZ= -5.2429 YYZZ= -5.2429
XXYZ= 0.0000 YYXZ= 0.0000 ZZXY= 0.0000
N-N= 1.342911618634D+01 E-N=-1.201307897495D+02 KE= 4.031684346614D+01
Symmetry A KE= 3.447981936062D+01
Symmetry B1 KE= 1.945674701840D+00
Symmetry B2 KE= 1.945674701840D+00
Symmetry B3 KE= 1.945674701840D+00
1|1|UNPC-LAPTOP-VBAQNH7H|FOpt|RB3LYP|6-311+G(d)|C1H4|HP|29-Nov-2020|0|
|# opt freq b3lyp/6-311+g(d) geom=connectivity||Title Card Required||0
,1|C,1.76691739,0.563909725,0.|H,2.1304079871,-0.4642365757,-0.0000009
202|H,2.1304274232,1.077975738,0.8903970013|H,2.1304259205,1.077976800
6,-0.8903970013|H,0.6764082293,0.5639229371,0.0000009202||Version=IA32
W-G09RevB.01|State=1-A1|HF=-40.5280819|RMSD=6.849e-009|RMSF=7.840e-005
|Dipole=0.,0.,0.|Quadrupole=0.,0.,0.,0.,0.,0.|PG=TD [O(C1),4C3(H1)]||@

WERE I TO AWAIT PERFECTION, MY BOOK WOULD NEVER BE FINISHED.
-- HISTORY OF CHINESE WRITING

TAI T'UNG, 13TH CENTURY
Job cpu time: 0 days 0 hours 0 minutes 3.0 seconds.
File lengths (MBytes): RWF= 5 Int= 0 D2E= 0 Chk= 1 Scr= 1
Normal termination of Gaussian 09 at Sun Nov 29 23:31:54 2020.

Link1: Proceeding to internal job step number 2.
----------------------------------------------------------------
```

```
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RB3LYP/6-311+G(d) Freq

----------------------------------------------------------------

1/10=4,29=7,30=1,38=1,40=1/1,3;

2/12=2,40=1/2;

3/5=4,6=6,7=11,11=2,14=-4,16=1,25=1,30=1,70=2,71=2,74=-5,116=1/1,2,3;

4/5=101/1;

5/5=2,98=1/2;

8/6=4,10=90,11=11/1;

11/6=1,8=1,9=11,15=111,16=1/1,2,10;

10/6=1/2;

6/7=2,8=2,9=2,10=2,18=1,28=1/1;

7/8=1,10=1,25=1/1,2,3,16;

1/10=4,30=1/3;

99//99;

-------------------

Title Card Required

-------------------

Redundant internal coordinates taken from checkpoint file:

C:\Users\hp\Desktop\ch4.chk

Charge = 0 Multiplicity = 1

C,0,1.76691739,0.563909725,0.

H,0,2.1304079871,-0.4642365757,-0.0000009202

H,0,2.1304274232,1.077975738,0.8903970013

H,0,2.1304259205,1.0779768006,-0.8903970013

H,0,0.6764082293,0.5639229371,0.0000009202

Recover connectivity data from disk.
```

```
GradGradGradGradGradGradGradGradGradGradGradGradGradGradGradGradGradGrad
Berny optimization.
Initialization pass.
-----------------------------
! Initial Parameters !
! (Angstroms and Degrees) !
--------------------------- ---------------------------
! Name Definition Value Derivative Info. !
-------------------------------------------------------
! R1 R(1,2) 1.0905 calculate D2E/DX2 analytically !
! R2 R(1,3) 1.0905 calculate D2E/DX2 analytically !
! R3 R(1,4) 1.0905 calculate D2E/DX2 analytically !
! R4 R(1,5) 1.0905 calculate D2E/DX2 analytically !
! A1 A(2,1,3) 109.4712 calculate D2E/DX2 analytically !
! A2 A(2,1,4) 109.4712 calculate D2E/DX2 analytically !
! A3 A(2,1,5) 109.4712 calculate D2E/DX2 analytically !
! A4 A(3,1,4) 109.4712 calculate D2E/DX2 analytically !
! A5 A(3,1,5) 109.4712 calculate D2E/DX2 analytically !
! A6 A(4,1,5) 109.4712 calculate D2E/DX2 analytically !
! D1 D(2,1,4,3) -120.0 calculate D2E/DX2 analytically !
! D2 D(2,1,5,3) 120.0 calculate D2E/DX2 analytically !
! D3 D(2,1,5,4) -120.0 calculate D2E/DX2 analytically !
! D4 D(3,1,5,4) 120.0 calculate D2E/DX2 analytically !
--------------------------------------------------------------------
Trust Radius=3.00D-01 FncErr=1.00D-07 GrdErr=1.00D-07
Number of steps in this run= 2 maximum allowed number of steps= 2.
```

```
GradGradGradGradGradGradGradGradGradGradGradGradGradGradGradGradGradGrad
Input orientation:
---------------------------------------------------------------------
Center Atomic Atomic Coordinates (Angstroms)
Number Number Type X Y Z
---------------------------------------------------------------------
1 6 0 1.766917 0.563910 0.000000
2 1 0 2.130408 -0.464237 -0.000001
3 1 0 2.130427 1.077976 0.890397
4 1 0 2.130426 1.077977 -0.890397
5 1 0 0.676408 0.563923 0.000001
---------------------------------------------------------------------
Distance matrix (angstroms):
1 2 3 4 5
1 C 0.000000
2 H 1.090509 0.000000
3 H 1.090509 1.780794 0.000000
4 H 1.090509 1.780794 1.780794 0.000000
5 H 1.090509 1.780794 1.780794 1.780794 0.000000
Stoichiometry CH4
Framework group TD[O(C),4C3(H)]
Deg. of freedom 1
Full point group TD NOp 24
Largest Abelian subgroup D2 NOp 4
Largest concise Abelian subgroup D2 NOp 4
Standard orientation:
```

```
---------------------------------------------------------------
Center Atomic Atomic Coordinates (Angstroms)
Number Number Type X Y Z
---------------------------------------------------------------
1 6 0 0.000000 0.000000 0.000000
2 1 0 0.629606 0.629606 0.629606
3 1 0 -0.629606 -0.629606 0.629606
4 1 0 -0.629606 0.629606 -0.629606
5 1 0 0.629606 -0.629606 -0.629606
---------------------------------------------------------------
Rotational constants (GHZ): 158.1265094 158.1265094 158.1265094
Standard basis: 6-311+G(d) (5D, 7F)
There are 10 symmetry adapted basis functions of A symmetry.
There are 8 symmetry adapted basis functions of B1 symmetry.
There are 8 symmetry adapted basis functions of B2 symmetry.
There are 8 symmetry adapted basis functions of B3 symmetry.
Integral buffers will be 262144 words long.
Raffenetti 2 integral format.
Two-electron integral symmetry is turned on.
34 basis functions, 56 primitive gaussians, 35 cartesian basis functions
5 alpha electrons 5 beta electrons
nuclear repulsion energy 13.4291161863 Hartrees.
NAtoms= 5 NActive= 5 NUniq= 2 SFac= 4.00D+00 NAtFMM= 50 NAOKFM=F Big=F
One-electron integrals computed using PRISM.
NBasis= 34 RedAO= T NBF= 10 8 8 8
NBsUse= 34 1.00D-06 NBFU= 10 8 8 8
```

```
Initial guess read from the checkpoint file: C:\Users\hp\Desktop\ch4.chk

B after Tr= 0.000000 0.000000 0.000000

Rot= 1.000000 0.000000 0.000000 0.000000 Ang= 0.00 deg.

Initial guess orbital symmetries:

Occupied (A1) (A1) (T2) (T2) (T2)

Virtual (A1) (T2) (T2) (T2) (T2) (T2) (T2) (A1) (T2) (T2)

(T2) (T2) (T2) (T2) (A1) (A1) (E) (E) (T2) (T2)

(T2) (A1) (T2) (T2) (T2) (T2) (T2) (T2) (A1)

Requested convergence on RMS density matrix=1.00D-08 within 128 cycles.

Requested convergence on MAX density matrix=1.00D-06.

Requested convergence on energy=1.00D-06.

No special actions if energy rises.

Keep R1 ints in memory in canonical form, NReq=1119085.

SCF Done: E(RB3LYP) = -40.5280818642 A.U. after 1 cycles

Convg = 0.7046D-09 -V/T = 2.0052

Range of M.O.s used for correlation: 1 34

NBasis= 34 NAE= 5 NBE= 5 NFC= 0 NFV= 0

NROrb= 34 NOA= 5 NOB= 5 NVA= 29 NVB= 29

Symmetrizing basis deriv contribution to polar:

IMax=3 JMax=2 DiffMx= 0.00D+00

G2DrvN: will do 6 centers at a time, making 1 passes doing MaxLOS=2.

Calling FoFCou, ICntrl= 3107 FMM=F I1Cent= 0 AccDes= 0.00D+00.

FoFDir/FoFCou used for L=0 through L=2.

End of G2Drv Frequency-dependent properties file 721 does not exist.

End of G2Drv Frequency-dependent properties file 722 does not exist.

IDoAtm=11111
```

```
Differentiating once with respect to electric field.

with respect to dipole field.

Differentiating once with respect to nuclear coordinates.

Keep R1 ints in memory in canonical form, NReq=1020123.

There are 9 degrees of freedom in the 1st order CPHF. IDoFFX=4.

9 vectors produced by pass 0 Test12= 1.61D-15 1.11D-08 XBig12= 7.20D+00 1.49D+00.

AX will form 9 AO Fock derivatives at one time.

9 vectors produced by pass 1 Test12= 1.61D-15 1.11D-08 XBig12= 2.01D-01 2.19D-01.

9 vectors produced by pass 2 Test12= 1.61D-15 1.11D-08 XBig12= 6.03D-04 7.70D-03.

9 vectors produced by pass 3 Test12= 1.61D-15 1.11D-08 XBig12= 1.57D-06 4.26D-04.

9 vectors produced by pass 4 Test12= 1.61D-15 1.11D-08 XBig12= 5.58D-10 7.80D-06.

4 vectors produced by pass 5 Test12= 1.61D-15 1.11D-08 XBig12= 3.26D-13 2.44D-07.

Inverted reduced A of dimension 49 with in-core refinement.

Isotropic polarizability for W= 0.000000 13.81 Bohr**3.

End of Minotr Frequency-dependent properties file 721 does not exist.

End of Minotr Frequency-dependent properties file 722 does not exist.

***************************************************************

Population analysis using the SCF density.

***************************************************************

Orbital symmetries:

Occupied (A1) (A1) (T2) (T2) (T2)

Virtual (A1) (T2) (T2) (T2) (T2) (T2) (T2) (A1) (T2) (T2)

(T2) (T2) (T2) (T2) (A1) (A1) (E) (E) (T2) (T2)

(T2) (A1) (T2) (T2) (T2) (T2) (T2) (T2) (A1)

The electronic state is 1-A1.

Alpha occ. eigenvalues -- -10.15133 -0.69745 -0.39634 -0.39634 -0.39634
```

```
Alpha virt. eigenvalues -- 0.00991 0.05736 0.05736 0.05736 0.14637
Alpha virt. eigenvalues -- 0.14637 0.14637 0.21072 0.40418 0.40418
Alpha virt. eigenvalues -- 0.40418 0.59906 0.59906 0.59906 0.60278
Alpha virt. eigenvalues -- 0.86494 1.25797 1.25797 1.59542 1.59542
Alpha virt. eigenvalues -- 1.59542 2.35038 2.42329 2.42329 2.42329
Alpha virt. eigenvalues -- 3.10057 3.10057 3.10057 23.43988
Condensed to atoms (all electrons):
1 2 3 4 5
1 C 5.441470 0.372433 0.372433 0.372433 0.372433
2 H 0.372433 0.475956 -0.027063 -0.027063 -0.027063
3 H 0.372433 -0.027063 0.475956 -0.027063 -0.027063
4 H 0.372433 -0.027063 -0.027063 0.475956 -0.027063
5 H 0.372433 -0.027063 -0.027063 -0.027063 0.475956
Mulliken atomic charges:
1
1 C -0.931204
2 H 0.232801
3 H 0.232801
4 H 0.232801
5 H 0.232801
Sum of Mulliken atomic charges = 0.00000
Mulliken charges with hydrogens summed into heavy atoms:
1
1 C 0.000000
Sum of Mulliken charges with hydrogens summed into heavy atoms = 0.00000
APT atomic charges:
```

```
1
1 C -0.015942
2 H 0.003985
3 H 0.003985
4 H 0.003985
5 H 0.003985
Sum of APT charges= 0.00000
APT Atomic charges with hydrogens summed into heavy atoms:
1
1 C 0.000000
2 H 0.000000
3 H 0.000000
4 H 0.000000
5 H 0.000000
Sum of APT charges= 0.00000
Electronic spatial extent (au): <R**2>= 35.9778
Charge= 0.0000 electrons
Dipole moment (field-independent basis, Debye):
X= 0.0000 Y= 0.0000 Z= 0.0000 Tot= 0.0000
Quadrupole moment (field-independent basis, Debye-Ang):
XX= -8.5144 YY= -8.5144 ZZ= -8.5144
XY= 0.0000 XZ= 0.0000 YZ= 0.0000
Traceless Quadrupole moment (field-independent basis, Debye-Ang):
XX= 0.0000 YY= 0.0000 ZZ= 0.0000
XY= 0.0000 XZ= 0.0000 YZ= 0.0000
Octapole moment (field-independent basis, Debye-Ang**2):
```

```
XXX= 0.0000 YYY= 0.0000 ZZZ= 0.0000 XYY= 0.0000
XXY= 0.0000 XXZ= 0.0000 XZZ= 0.0000 YZZ= 0.0000
YYZ= 0.0000 XYZ= 0.7811
Hexadecapole moment (field-independent basis, Debye-Ang**3):
XXXX= -17.2201 YYYY= -17.2201 ZZZZ= -17.2201 XXXY= 0.0000
XXXZ= 0.0000 YYYX= 0.0000 YYYZ= 0.0000 ZZZX= 0.0000
ZZZY= 0.0000 XXYY= -5.2429 XXZZ= -5.2429 YYZZ= -5.2429
XXYZ= 0.0000 YYXZ= 0.0000 ZZXY= 0.0000
N-N= 1.342911618634D+01 E-N=-1.201307898411D+02 KE= 4.031684350874D+01
Symmetry A KE= 3.447981938511D+01
Symmetry B1 KE= 1.945674707876D+00
Symmetry B2 KE= 1.945674707876D+00
Symmetry B3 KE= 1.945674707876D+00
Exact polarizability: 13.812 0.000 13.812 0.000 0.000 13.812
Approx polarizability: 16.443 0.000 16.443 0.000 0.000 16.443
Calling FoFJK, ICntrl= 100127 FMM=F ISym2X=1 I1Cent= 0 IOpClX= 0 NMat=1
NMatS=1 NMatT=0.
Full mass-weighted force constant matrix:
Low frequencies --- -0.0012 -0.0011 -0.0003 46.1637 46.1637 46.1637
Low frequencies --- 1355.1285 1355.1285 1355.1285
Harmonic frequencies (cm**-1), IR intensities (KM/Mole), Raman scattering
activities (A**4/AMU), depolarization ratios for plane and unpolarized
incident light, reduced masses (AMU), force constants (mDyne/A),
and normal coordinates:
1 2 3
T2 T2 T2
```

```
Frequencies -- 1355.1285 1355.1285 1355.1285
Red. masses -- 1.1788 1.1788 1.1788
Frc consts -- 1.2754 1.2754 1.2754
IR Inten -- 20.7468 20.7468 20.7468
Atom AN X Y Z X Y Z X Y Z
1 6 -0.02 0.12 0.01 0.12 0.02 0.00 0.00 -0.01 0.12
2 1 0.31 -0.39 0.16 -0.32 0.17 0.26 0.22 0.26 -0.39
3 1 0.28 -0.42 -0.22 -0.33 0.16 -0.28 -0.24 -0.21 -0.35
4 1 -0.15 -0.34 -0.30 -0.40 -0.30 0.18 0.26 -0.20 -0.36
5 1 -0.18 -0.31 0.24 -0.41 -0.29 -0.20 -0.21 0.27 -0.38
4 5 6
E E A1
Frequencies -- 1582.6386 1582.6386 3030.2510
Red. masses -- 1.0078 1.0078 1.0078
Frc consts -- 1.4873 1.4873 5.4525
IR Inten -- 0.0000 0.0000 0.0000
Atom AN X Y Z X Y Z X Y Z
1 6 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00
2 1 -0.32 0.38 -0.07 -0.26 -0.14 0.40 -0.29 -0.29 -0.29
3 1 0.32 -0.38 -0.07 0.26 0.14 0.40 0.29 0.29 -0.29
4 1 0.32 0.38 0.07 0.26 -0.14 -0.40 0.29 -0.29 0.29
5 1 -0.32 -0.38 0.07 -0.26 0.14 -0.40 -0.29 0.29 0.29
7 8 9
T2 T2 T2
Frequencies -- 3135.0616 3135.0616 3135.0616
Red. masses -- 1.1018 1.1018 1.1018
```

```
Frc consts -- 6.3804 6.3804 6.3804

IR Inten -- 29.9080 29.9080 29.9080

Atom AN X Y Z X Y Z X Y Z

1 6 0.01 -0.09 0.00 -0.07 -0.01 0.06 -0.06 -0.01 -0.07

2 1 0.24 0.22 0.24 0.05 0.06 0.07 0.43 0.44 0.43

3 1 0.25 0.23 -0.25 0.43 0.44 -0.43 -0.01 -0.01 -0.01

4 1 -0.34 0.32 -0.34 -0.01 0.00 0.01 0.36 -0.38 0.36

5 1 -0.33 0.31 0.33 0.37 -0.38 -0.37 -0.08 0.07 0.06

-------------------

- Thermochemistry -

-------------------

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

Atom 1 has atomic number 6 and mass 12.00000

Atom 2 has atomic number 1 and mass 1.00783

Atom 3 has atomic number 1 and mass 1.00783

Atom 4 has atomic number 1 and mass 1.00783

Atom 5 has atomic number 1 and mass 1.00783

Molecular mass: 16.03130 amu.

Principal axes and moments of inertia in atomic units:

1 2 3

Eigenvalues -- 11.41327 11.41327 11.41327

X 0.04958 0.97439 -0.21932

Y -0.21486 0.22486 0.95041

Z 0.97539 0.00000 0.22050

This molecule is a spherical top.

Rotational symmetry number 12.
```

```
Rotational temperatures (Kelvin) 7.58887 7.58887 7.58887

Rotational constants (GHZ): 158.12651 158.12651 158.12651

Zero-point vibrational energy 117629.4 (Joules/Mol)

28.11410 (Kcal/Mol)

Vibrational temperatures: 1949.73 1949.73 1949.73 2277.06 2277.06

(Kelvin) 4359.85 4510.65 4510.65 4510.65

Zero-point correction= 0.044803 (Hartree/Particle)

Thermal correction to Energy= 0.047669

Thermal correction to Enthalpy= 0.048613

Thermal correction to Gibbs Free Energy= 0.027486

Sum of electronic and zero-point Energies= -40.483279

Sum of electronic and thermal Energies= -40.480413

Sum of electronic and thermal Enthalpies= -40.479469

Sum of electronic and thermal Free Energies= -40.500596

E (Thermal) CV S

KCal/Mol Cal/Mol-Kelvin Cal/Mol-Kelvin

Total 29.913 6.444 44.465

Electronic 0.000 0.000 0.000

Translational 0.889 2.981 34.261

Rotational 0.889 2.981 10.122

Vibrational 28.135 0.482 0.082

Q Log10(Q) Ln(Q)

Total Bot 0.227635D-12 -12.642760 -29.111032

Total V=0 0.922556D+08 7.964993 18.340074

Vib (Bot) 0.248057D-20 -20.605449 -47.445800

Vib (V=0) 0.100532D+01 0.002304 0.005305
```

```
Electronic 0.100000D+01 0.000000 0.000000

Translational 0.252295D+07 6.401908 14.740939

Rotational 0.363731D+02 1.560781 3.593830

***** Axes restored to original set *****

-------------------------------------------------------------------

Center Atomic Forces (Hartrees/Bohr)

Number Number X Y Z

-------------------------------------------------------------------

1 6 0.000000000 0.000000000 0.000000000

2 1 0.000050603 -0.000143132 0.000000000

3 1 0.000050606 0.000071565 0.000123956

4 1 0.000050605 0.000071565 -0.000123956

5 1 -0.000151814 0.000000002 0.000000000

--------------------------------------------------------------------

Cartesian Forces: Max 0.000151814 RMS 0.000078397

GradGradGradGradGradGradGradGradGradGradGradGradGradGradGradGradGradGrad

Berny optimization.

Internal Forces: Max 0.000151814 RMS 0.000081148

Search for a local minimum.

Step number 1 out of a maximum of 2

All quantities printed in internal units (Hartrees-Bohrs-Radians)

Second derivative matrix not updated -- analytic derivatives used.

The second derivative matrix:

R1 R2 R3 R4 A1

R1 0.34282

R2 0.00246 0.34282
```

```
R3 0.00246 0.00246 0.34282
R4 0.00246 0.00246 0.00246 0.34282
A1 0.00188 0.00188 -0.00118 -0.00257 0.02004
A2 0.00294 -0.00076 0.00327 -0.00545 -0.00893
A3 0.00574 -0.00461 -0.00510 0.00397 -0.01329
A4 -0.00076 0.00294 0.00327 -0.00545 -0.00893
A5 -0.00461 0.00574 -0.00510 0.00397 -0.01329
A6 -0.00519 -0.00519 0.00484 0.00554 0.02442
D1 -0.00363 -0.00363 -0.00256 0.00983 -0.01360
D2 0.00299 0.00299 -0.00769 0.00171 0.00826
D3 -0.00394 0.00693 -0.00385 0.00085 0.00413
D4 -0.00693 0.00394 0.00385 -0.00085 -0.00413
A2 A3 A4 A5 A6
A2 0.03773
A3 -0.02295 0.07372
A4 -0.00218 0.02535 0.03773
A5 0.02535 -0.03581 -0.02295 0.07372
A6 -0.02902 -0.02701 -0.02902 -0.02701 0.08763
D1 -0.01083 0.01481 -0.01083 0.01481 0.00564
D2 -0.00947 0.00693 -0.00947 0.00693 -0.00317
D3 -0.01438 -0.00049 0.00491 0.00742 -0.00159
D4 -0.00491 -0.00742 0.01438 0.00049 0.00159
D1 D2 D3 D4
D1 0.02992
D2 0.00149 0.01860
D3 0.00074 0.00930 0.01889
```

```
D4 -0.00074 -0.00930 0.00959 0.01889

ITU= 0

Eigenvalues --- 0.03818 0.04300 0.06530 0.13346 0.13403

Eigenvalues --- 0.34123 0.34124 0.34150 0.35021

Angle between quadratic step and forces= 0.00 degrees.

Linear search not attempted -- first point.

Iteration 1 RMS(Cart)= 0.00023171 RMS(Int)= 0.00000000

Iteration 2 RMS(Cart)= 0.00000000 RMS(Int)= 0.00000000

ClnCor: largest displacement from symmetrization is 1.11D-12 for atom 4.

Variable Old X -DE/DX Delta X Delta X Delta X New X

(Linear) (Quad) (Total)

R1 2.06076 0.00015 0.00000 0.00043 0.00043 2.06120

R2 2.06076 0.00015 0.00000 0.00043 0.00043 2.06120

R3 2.06076 0.00015 0.00000 0.00043 0.00043 2.06120

R4 2.06076 0.00015 0.00000 0.00043 0.00043 2.06120

A1 1.91063 0.00000 0.00000 0.00000 0.00000 1.91063

A2 1.91063 0.00000 0.00000 0.00000 0.00000 1.91063

A3 1.91063 0.00000 0.00000 0.00000 0.00000 1.91063

A4 1.91063 0.00000 0.00000 0.00000 0.00000 1.91063

A5 1.91063 0.00000 0.00000 0.00000 0.00000 1.91063

A6 1.91063 0.00000 0.00000 0.00000 0.00000 1.91063

D1 -2.09440 0.00000 0.00000 0.00000 0.00000 -2.09440

D2 2.09440 0.00000 0.00000 0.00000 0.00000 2.09440

D3 -2.09440 0.00000 0.00000 0.00000 0.00000 -2.09440

D4 2.09440 0.00000 0.00000 0.00000 0.00000 2.09440

Item Value Threshold Converged?
```

```
Maximum Force 0.000152 0.000450 YES
RMS Force 0.000081 0.000300 YES
Maximum Displacement 0.000433 0.001800 YES
RMS Displacement 0.000232 0.001200 YES
Predicted change in Energy=-1.316197D-07
Optimization completed.
-- Stationary point found.
--------------------------
! Optimized Parameters !
! (Angstroms and Degrees) !
------------------------ ------------------------
! Name Definition Value Derivative Info. !
-------------------------------------------------
! R1 R(1,2) 1.0905 -DE/DX = 0.0002 !
! R2 R(1,3) 1.0905 -DE/DX = 0.0002 !
! R3 R(1,4) 1.0905 -DE/DX = 0.0002 !
! R4 R(1,5) 1.0905 -DE/DX = 0.0002 !
! A1 A(2,1,3) 109.4712 -DE/DX = 0.0 !
! A2 A(2,1,4) 109.4712 -DE/DX = 0.0 !
! A3 A(2,1,5) 109.4712 -DE/DX = 0.0 !
! A4 A(3,1,4) 109.4712 -DE/DX = 0.0 !
! A5 A(3,1,5) 109.4712 -DE/DX = 0.0 !
! A6 A(4,1,5) 109.4712 -DE/DX = 0.0 !
! D1 D(2,1,4,3) -120.0 -DE/DX = 0.0 !
! D2 D(2,1,5,3) 120.0 -DE/DX = 0.0 !
! D3 D(2,1,5,4) -120.0 -DE/DX = 0.0 !
```

```
! D4 D(3,1,5,4) 120.0 -DE/DX = 0.0 !

----------------------------------------------------------------

GradGradGradGradGradGradGradGradGradGradGradGradGradGradGradGradGradGrad


1|1|UNPC-LAPTOP-VBAQNH7H|Freq|RB3LYP|6-311+G(d)|C1H4|HP|29-Nov-2020|0|

|#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RB3LYP/6-311+G(d) Freq||Title
Card Required||0,1|C,1.76691739,0.563909725,0.|H,2.1304079871,-0.4642365757-
-0.0000009202|H,2.1304274232,1.077975738,0.8903970013|H

,2.1304259205,1.0779768006,-
0.8903970013|H,0.6764082293,0.5639229371,0.0000009202||Version=IA32W-G09RevB.01|
State=1-A1|HF=-40.5280819|RMSD=7.046e-010|RMSF=7.8-
0e-005|ZeroPoint=0.0448027|Thermal=0.047669|Dipole=

0.,0.,0.|DipoleDeriv=-0.015942,0.,0.,0.,-0.015942,0.,0.,0.,-0.015942,0

.0578811,0.076215,0.,0.076215,-0.1307508,-0.0000002,0.,-0.0000002,0.08

48261,0.0578782,-0.038109,-0.0660074,-0.038109,0.0309334,-0.0933458,-0.066-
074,-0.0933458,-0.0768551,0.0578784,-0.0381089,0.0660071,-0.03810
89,0.0309332,0.093346,0.0660071,0.093346,-0.0768551,
0.1576958,0.0000029,0.0000002,0.0000029,0.0848261,0.,0.0000002,0.,0.0848261|Polar=13.
8120382,0.,13.8120382,0.,0.,13.8120382|PG=TD
[O(C1),4C3(H1)]|NImag=0||0.54767104,0.,0.54767104,0.,0.,0.54767104,-0.07688286,0.0848
9672,0.00000008,0.07885896,0.08489672,-0.28700193,-0.0000002-
,-0.09332226,0.30983122,0.00000008,-0.00000021,-0.046868-
9,-0.00000008,0.00000024,0.04586582,-0.0768860-
,-0.04245004,0.07352633,0.00331311,0.00442709,0.01113397

,0.07886248,-0.04245004,-0.10690019,-0.10397894,-0.01185643,-0.0127-
859,-0.02558442,0.04666298,0.11185534,-0.07352633,-0.10397894,-0.2269670
3,0.00173299,0.00100654,0.00147123,0.08082343,0.11429829,0.24383818,-
0.07688582,-0.04244995,0.07352603,0.00331309,0.00442711-
-0.01113397,0.00331337,0.00742900-
-0.00940146,0.07886221-
-0.04244995-
-
0.10690043,0.10397915,-0.01185639,-0.01271862,0.02558442,0.00742897,0.00856605,-0.01
329531,0.04666288,0.11185561,0.07352603,0.10397915,-0.22696703,-0.0017330-
,-0.00100656,0.00147128,0.00940143,0.01329533,-0.01981367,-0.080823

09,-0.11429853,0.24383818,-0.31701629,0.00000327,0.00000023,-0.0086023

0,-0.00042865,0.,-0.00860290,0.00021449,0.00037137,-0.00860286,0.00021
```

```
449,-0.00037136,0.34282435,0.00000327,-0.04686849,0.,0.03213837,0.0026
0791,-0.00000002,-0.01606900,-0.00080262,0.00196941,-0.01606904,-0.000
80262,-0.00196939,-0.00000360,0.04586582,0.00000023,0.,-0.04686849,0.0
0000002,0.,-0.00193985,-0.02783250,0.00196974,0.00147128,0.02783250,-0
.00196974,0.00147123,-0.00000025,0.,0.04586582||0.,0.,0.,-0.00005060,0
.00014313,0.,-0.00005061,-0.00007157,-0.00012396,-0.00005061,-0.000071
57,0.00012396,0.00015181,0.,0.|||@

... FOR AFTERWARDS A MAN FINDS PLEASURE IN HIS PAINS,
WHEN HE HAS SUFFERED LONG AND WANDERED FAR.

-- HOMER
Job cpu time: 0 days 0 hours 0 minutes 4.0 seconds.
File lengths (MBytes): RWF= 5 Int= 0 D2E= 0 Chk= 1 Scr= 1
Normal termination of Gaussian 09 at Sun Nov 29 23:31:58 2020.
```

SUBJECT INDEX

Ambrish Kumar Srivastava and Neeraj Misra

Ambrish Kumar Srivastava

Dr. Ambrish Kumar Srivastava is an Assistant Professor at the Department of Physics in Deen Dayal Upadhyaya Gorakhpur University, Gorakhpur, India. He obtained his Ph.D. from the University of Lucknow, India, and subsequently worked as a National Postdoctoral Fellow at D.D.U. Gorakhpur University. He teaches Biophysics and Advanced Quantum Physics to postgraduate students. His broad research areas include Computational Biophysics and Computational Materials Science. He has published over 110 research papers in various journals of international repute with an h-index of 20. Dr. Srivastava is the Guest Associate Editor of Frontiers in Chemistry and also serves the editorial board of many journals including Current Chinese Science from Bentham. He has reviewed more than 30 research articles for many journals. His works have been referenced in Wikipedia, the free encyclopedia. He has expertise in dealing with DFT calculations over a wide range of molecular systems. More details can be found at the website: https://cutt.ly/CMSLab

BOOK SUMMARY

This book is intended for young researchers and experimentalists among others, who wish to explore the DFT on molecular systems. The salient features of the book include concise and complete coverage of DFT on biologically active molecules. It begins with the basics of DFT for beginners followed by its application and usage using a powerful Gaussian program. Subsequently, discussions on synthetic compounds, amino acids, and natural products have been offered. The book also features an exclusive chapter on the quantum theory of atoms in molecule and supplemented by an appendix.