REPUBLIC OF TURKEY
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GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES

THE INVESTIGATION OF CHEMICAL REACTIVITY, STABILITY AND ELECTRONIC PROPERTIES OF COMPLEX MOLECULES

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Master's Thesis

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THESIS APPROVAL

This thesis, which was prepared according to the thesis rules of the Graduate School of Natural and Applied Sciences, Firat University, was evaluated by committee members who have signed the following signatures and accepted unanimously as a result of the defense exam made open to the academic audience.

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DECLARATION

I hereby declare that I wrote this Master's Thesis titled “The Investigation of Chemical Reactivity, Stability and Electronic Properties of Complex Molecules” in consistent with the thesis writing guide of the Graduate School of Natural and Applied Sciences, Firat University. I also declare that all information in it is correct, that I acted according to scientific ethics in producing and presenting the findings, cited all the references I used, express all institutions or organizations or persons who supported the thesis financially. I have never used the data and information I provide here in order to get a degree in any way.

17/01/2020

Yousif Hussein AZEEZ

PREFACE

The study of Molecular Orbital Theory (MOT) is significant to forecast the chemical structure, the electronic properties of molecules, bond orders, and shapes of molecular orbitals. In theoretical chemistry, the frontier molecular orbital theory (FMOs) is a purpose of MOT that explaining the interaction between HOMO and LUMO energy orbitals. As well as, from the value of HOMO-LUMO energy quantum chemistry parameters can be calculated by using personal computer software with approximation method such as Density Functional Theory (DFT) and Hartree Fock Theory (HFT), which is important to expect the stability and reactivity of chemical compounds.

I would like to express my special thanks to my supervisor (Prof. Dr. Sinan Akpinar) together with the head of physics department (Prof. Dr. Niyazi Bulut) who helped me to make this work on the (Molecular Orbital Theory for complex molecules). This subject is more important to my future. I am grateful to them. Furthermore, I want to thank my friends and my parents for encouraging me to do this task.

Yousif Hussein AZEEZ

ELAZIĞ, 2019

TABLE OF CONTENTS

page

PREFACE…… iv

TABLE OF CONTENTS v

ABSTRACT…… vi

ÖZET…… vii

LIST OF FIGURES viii

LIST OF TABLES ix

LIST OF SYMBOLS x

LIST OF ABBREVIATIONS xi

1. INTRODUCTION 1

2. CHEMICAL PROPERTIES OF STUDIED MOLECULES 3

2.1. Cyclobutadiene (C_4H_4) 3

2.2. Propylbenzene (C_9H_{12}) 3

2.3. Phosgene (Carbonyl dichloride) ($COCl_2$) 4

2.4. 2-Chloro-5-(Trifluoromethyl) aniline ($C_7F_3NH_5Cl$) 4

3. THEORY…. 5

3.1. Linear Combination of Atomic Orbitals (LCAO) 5

3.2. Density Function Theory (DFT) 12

3.3. DFT from Hohenberg-Kohn Theory (HKT), and Kohn- Sham Theory 13

3.4. Hartree-Fock Method (HFT) 13

3.5. Molecular Orbital Energy 15

3.5.1. Bonding Molecular Orbital (HOMO) 15

3.5.2. Antibonding Molecular Orbital (LUMO) 16

3.6. Global Reactivity 17

4. RESULTS AND DISCUSSION 18

4.1. Cyclobutadiene (C_4H_4) 18

4.2. Propylbenzene (C_9H_{12}) 25

4.3. Phosgene (Carbonyl dichloride) ($COCl_2$) 31

4.4. 2-Chloro-5-(trifluoromethyl) aniline ($C_7F_3NH_5Cl$) 37

5. CONCLUSION 44

RECOMMENDATION 45

REFERENCE…… 46

CURICULUM VITAE

ABSTRACT

The Investigation of Chemical Reactivity, Stability and Electronic Properties of Complex Molecules

Yousif Hussein AZEEZ

Master's Thesis

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In this study, the optimized structure of (Cyclobutadiene (C_4H_4), Carbonyl chloride (Phosgene) ($COCl_2$), Propylbenzene (C_9H_{12}), 2-chloro-5-(trifluoromethyl) aniline ($C_7F_3NH_5Cl$) molecules were obtained in GAUSSIAN 09 program and the highest filled molecular orbital (HOMO) and lowest filled molecular orbital (LUMO) (boundary orbital) energy values were calculated with Hartree Fock Theory (HFT) and the Density Function Theory (DFT) using difference basis sets as (B3LYP/3-21G, 6-31+G (d, p), 6-31G, and 6-311G). Electronic properties as chemical potential (μ), dipole moment (D), electronegativity (χ), chemical hardness of molecules (η), chemical softness of molecules (S), and electrophilicity index (ω) were determined from these energies. As can be seen, experimental and theoretical results were in agreement.

Keywords: DFT**,** HOMO, LUMO, HFT, and FMOs.

ÖZET

Kompleks Moleküllerin Kimyasal Reaktivite, Stabilite ve Elektronik Özelliklerinin Araştırılması

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Bu çalışmada, Siklobutadien (C_4H_4), karbonildiklorür ($COCl_2$), Kümen (C_9H_{12}) 2-Chloro-5-(triflouromethyl) anilin ($C_7F_3NH_5Cl$). moleküllerinin optimize edilmiş yapıları GAUSSIAN 09 programında elde edilerek en yüksek dolu moleküler orbital (HOMO) ve en düşük dolu moleküler orbital (LUMO) (sınır orbital) enerji değerleri (B3LYP/3-21G, 6-31+G (d, p), 6-31G, ve 6-311G farklı baz setleri kullanılarak Hartree Fock (HFT) ve yoğunluk fonksiyon teorisiyle (DFT) hesaplandı. Elektronik özellikler (kimyasal potansiyel (μ), dipol moment (D), elektronegatiflik (χ), kimyasal sertlik (η), kimyasal yumuşaklık (S) ve, elektrofiliklik indeksi (ω) bu enerjilerden belirlendi. Deneysel ve teorik sonuçların uyum içerisinde olduğu görüldü.

Anahtar Sözcükler: DFT, HOMO, LUMO, HFT ve FMO.

LIST OF FIGURES

page

Figure 2.1. Cyclobutadiene structure (C_4H_4) 3
Figure 2.2. Propylbenzene structure (C_9H_{12}) (Cumene) 3
Figure 2.3. phosgene structure (Carbonyl dichloride) (COCl2)....4
Figure 2.4. 2-chloro-5-(trifluoromethyl) aniline ($C_7F_3NH_5Cl$) structure 4
Figure 3.1. Creation of molecular orbitals from two 1s orbitals of hydrogen atoms 5
Figure 3.2. Hydrogen ion....6
Figure 3.3 The interaction of two atoms of hydrogen by the molecular orbit diagram 16
Figure 4.1. Frontier Molecular Orbitals of cyclobutadiene with (3-21G) basis set by DFT and HFT methods....21
Figure 4.2. Frontier Molecular Orbitals of cyclobutadiene with (6-31G) basis set by DFT and HFT methods....22
Figure 4.3. Frontier Molecular Orbitals of cyclobutadiene with (6-31+G (d, p)) basis sets by DFT and HFT methods 23
Figure 4.4. Frontier Molecular Orbitals of cyclobutadiene with (6-311G) basis sets by DFT and HFT methods....24
Figure 4.5. Frontier Molecular Orbitals of Propylbenzene with (3-21G) basis sets by DFT and HFT methods....28
Figure 4.6. Frontier Molecular Orbitals of Propylbenzene with (6-31G) basis sets by DFT and HFT methods....29
Figure 4.7. Frontier Molecular Orbitals of Propylbenzene with (6-31+G (d, p)) basis sets by DFT and HFT methods. 30
Figure 4.8. Frontier Molecular Orbitals of Propylbenzene with (6-311G) basis sets by DFT and HFT methods....31
Figure 4.9. Frontier Molecular Orbitals of Phosgene with (6-31G) basis set by DFT and HFT methods… 34
Figure 4.10. Frontier Molecular Orbital energy of Phosgene with (6-31G) basis sets by DFT and HFT methods.....35
Figure 4.11. Frontier Molecular Orbital energy of Phosgene with (6-31+G (d, p)) basis sets by DFT and HFT methods. 36
Figure 4.12. Frontier Molecular Orbital energy of Phosgene with (6-311G) basis sets by DFT and HFT methods....37
Figure 4.13. Frontier Molecular Orbital energy of $C_7F_3NH_5Cl$ with (3-21G) basis set by DFT and HFT method 40
Figure 4.14. Frontier Molecular Orbital energy of $C_7F_3NH_5Cl$ with (6-31+G (d, p)) basis sets by DFT and HFT methods 41
Figure 4.15. Frontier Molecular Orbital energy of $C_7F_3NH_5Cl$ with (6-31G) basis sets by DFT and HFT methods....42
Figure 4.16. Frontier Molecular Orbital energy of $C_7F_3NH_5Cl$ with (6-311G) basis sets by DFT and HFT methods....43

LIST OF TABLES

Page

Table 4.1. Calculating quantum chemistry parameters for Cyclobutadiene (C_4H_4) by DFT and HFT with different basis sets.....20

Table 4.2. Calculating quantum chemistry parameters for Propylbenzene (C_9H_{12}) by DFT and HFT with different basis sets.....27

Table 4.3. Calculating quantum chemistry parameters for phosgene ($COCl_2$) by DFT and HFT with different basis set 33

Table 4.4.Calculating quantum chemistry parameters for ($C_7F_3NH_5Cl$) aniline by DFT and HFT with different basis sets.....39

LIST OF SYMBOLS

Symbols

σ	: Sigma (Bonding Molecular Orbital)
$1S_a^2$ And $1S_b^2$	: Atomic electron density
π	: Pi (Bonding Molecular Orbital)
σ*	: Sigma star (Antibonding Molecular Orbital)
π*	: Pi star (Antibonding Molecular Orbital)
H_e	: The Hamiltonian for the electronic motion
S, P, d, f	: Shapes of atomic orbital
Ψ	: Psi
c	: molecular orbital coefficients
F	: Fock matrix
H^{core}	: Core Hamiltonian
P	: Density matrix
E_{xc}	: Exchange energy
D	: Dipole moment
ρ	: Electron density

LIST OF ABBREVIATIONS

Abbreviations

AOs	: Atomic Orbitals
MOT	: Molecular Orbital Theory
DFT	: Density Function Theory
HFT	: Hartree Fock Theory
LCAO	: Linear combination of atomic orbital
HOMO	: Higher Occupied Molecular Orbital
LUMO	: Lower Unoccupied Molecular Orbital
FMOs	: Frontier Molecular Orbitals
H_{aa} , H_{bb}	: Coulomb integral of electron
BMO	: Bonding Molecular Orbital
AMO	: Antibonding Molecular Orbital

1. INTRODUCTION

The theory of molecular orbital (MOT) was firstly developed by Robert Sanderson Mulliken and Friedrich Hermann Hund in 1932. In the MOT, molecular orbitals are formed by the combination of atomic orbital for different atoms, which are occupied by electrons according to the principle of Pauli exclusion and Hund's law [1-4]. The totality of atomic orbitals that can be obtained in each atom is equal to the entire number of molecular orbitals constructed [5, 6]. MOT has been used to predict the structure, the electronic properties of molecules, bond orders and shapes [7-9]. All atomic orbital that is obtainable after each atom is used to create molecular orbitals so as to determine the overall of the molecule energy [2, 10, 11]. The significant of atomic orbital used to illustrate a molecule for bonding objectives are derived from the valence or exterior shell of the separate atom. These external orbitals are known as frontier molecular orbitals (FMOs) [12-15]. The FMOs are composite the lowest unoccupied molecular orbital energy (LUMO or acceptor or acceptor orbitals) and the highest occupied molecular orbitals (HOMO or donor orbitals) [16-24].

In atoms that contain more than one electron, due to of the repulsion term in the potential energy, the Schrödinger wave equation cannot be analytically solved. An approximate numerical method such as Density Function and Hartree Fock Theory can be used to obtain eigenvalues and eigenfunctions Schrödinger wave equation that has greater than one electron.

In the density functional theory (DFT), the basis for the DFT is an indication from Hohenberg and Kohn that the electronic energy of the ground state is completely determined by the density of electron (ρ) [25-27]. In practice, computer codes DFT are used to analysis the electronic and magnetic properties of molecules, materials, and biological systems. The performance of modern DFT methods is focused on the suggestion by Kohn and Sham that the electron kinetic energy and exchange-correlation energy should be computed from an auxiliary collection of orbitals, the one used to explain the electron density [28]. The energy of correlation is a measure of how much one electron's movement is influenced by the presence of all other electrons [29-32].

In Hartree Fock Theory (HFT), a method of approximation in computational physics and chemistry is used to determine the wave function and the energy of the stationary multi-body quantum system. One of the benefits of this theory is that it breaks the Schrödinger multi-electron equation into many simpler one-electron equations.

This principle requires the electron's wave function to be antisymmetric when two electron positions are exchanged, which is to change the sign when the two electron's position is changed. the hartree fock method (HFT) explains that many electronic wave functions take the form of single electron wave functions, known as Slater determinant. A slater determinant is a demonstration of a multi-part wave function for a fermion system satisfying the need for antisymmetry [32-35].

Therefore, many researchers in physics, chemistry, biology, and many other fields have been working in MOT for finding electronic structure and properties of molecules by using density functional theory (DFT) and hartree fock theory (HFT) with different basis sets via Gaussian 09W package. This program is an electronic structure package capable of expecting many properties of atoms and molecules. The physicists (S Xavier, et.al, 2014) [36] worked on Propylbenzene molecules and calculated electronic properties. The biologists (Mohammad and Ridwan, 2015) in microbiology department were studied the chemical Reactivity and stability of Naproxen with the solvent effect [37] . The chemists in organic chemistry department (Luis R. Domingo, Mar Ríos-Gutiérrez, and et.al, 2016) are used the theoretical reactivity indices and stability based on the DFT study of organic reactivity [38]. The physicists (Bashar Jumaa Suraah, et.al, 2017) was studied of the electronic structure of (di-Cyclobutadiene) Molecule by Using DFT at B3LYP level with basis sets (6-31G (d, p)), and found the values of HOMO and LUMO energies[39] . The researchers in physics department (M. SARANYA, S. AYYAPPAN, and et.al, 2018) were calculated the HOMO-LUMO energy and thermodynamic properties of graphene by DFT [17]. The chemist and physicist (Aslisah, Seda, et.al, 2019) explored the Spectroscopic and electronic properties (HOMO-LUMO) energies of a copolymer [40].

The aim of this study is theoretical investigate structural and electronic properties for these molecules such as (Cyclobutadiene (C_4H_4), phosgene ($COCl_2$), Propylbenzene (C_9H_{12}), 2-chloro-5-(trifluoromethyl) aniline ($C_7F_3NH_5Cl$) by DFT and HFT with four different basis sets. As well as, highest occupied molecular orbitals (HOMO) and lowest unoccupied molecular orbitals (LUMO), Total energies, Molecular structure, Chemical potential (μ), Dipole moment (D), Electronegativity (χ), Hardness of molecules (η), Softness of molecules (S), Electrophilic (ω) and energy gap (E_g) are calculated.

2. CHEMICAL PROPERTIES OF STUDIED MOLECULES

The investigation of electronic chemical properties is significant to gather information about these compounds. Global chemical reactivity descriptors are important to understand the behaviour of these molecules about kinetic stability, chemical reactivity, and selectivity in biology.

2.1. Cyclobutadiene (C_4H_4)

Cyclobutadiene is an organic compound with the chemical structure C_4H_4. This compound includes 8 atoms and 28 electrons as shown in Figure 2.1. It is poor stability and higher reactivity. C_4H_4 has not color gas that can be easily condensed into a liquid. Also, this molecule involves a ligand in several organometallic molecules and is a part of various medication structures [41].

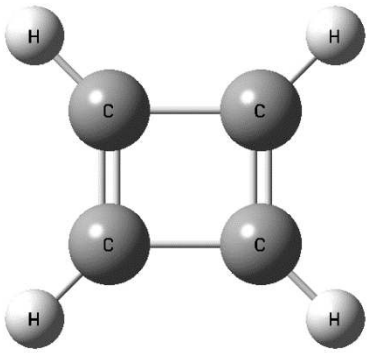


Figure 2.1. Cyclobutadiene structure (C_4H_4)

2.2. Propylbenzene (C_9H_{12})

Propylbenzene (Cumene) is an organic compound with the C_9H_{12} chemical structure and consist of 21 atoms and 66 electrons as shown in Figure 2.2. It is stable, low reactivity, colorless liquid, and combustible. Cumene is used to make of iron, steel, and rubber [42].

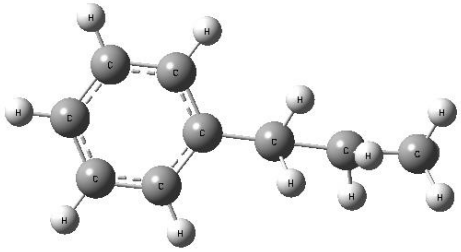


Figure 2.2. Propylbenzene structure (C_9H_{12}) (Cumene)

2.3. Phosgene (Carbonyl dichloride) ($COCl_2$)

Carbonyl dichloride is a colorless toxic gas produced by reactions to chlorine and carbon dioxide and is involves 4 atoms and 48 electrons as displayed in Figure 2.3. It is more stable, less reactivity, and colorless. Also, phosgene can be used in chemical industry to manufacture such precursors for additional cobalt compounds.

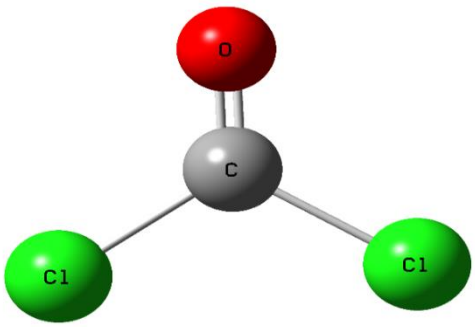


Figure 2.3. phosgene structure (Carbonyl dichloride) (COCl2)

2.4. 2-Chloro-5-(Trifluoromethyl) aniline ($C_7F_3NH_5Cl$)

2-chloro-5-(trifluoromethyl) aniline is a compound with the molecular formula ($C_7F_3NH_5Cl$) and by physical appearance, it is a colorless liquid, containing 17 atoms and 98 electrons as shown in Figure 2.4. It is commonly used for a variety of commercial industrial purposes, in the manufacturing of pesticides, and pharmaceuticals.

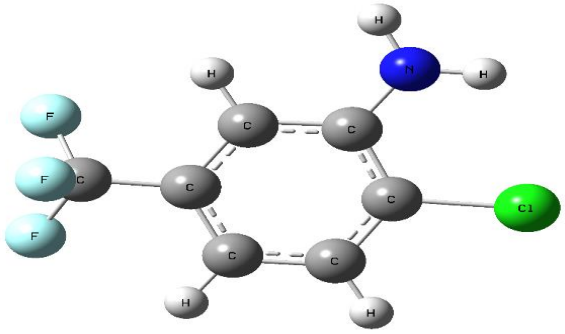


Figure 2.4. 2-chloro-5-(trifluoromethyl) aniline ($C_7F_3NH_5Cl$) structure

3. THEORY

Schrödinger wave equation cannot analytical solved for atoms containing greater than one electron. The approximation method such as, hartree fock theory (HFT) and density functional theory (DFT) can be used for achieving eigenvalues and eigenfunctions of Schrödinger wave equation that have higher than one electron.

3.1. Linear Combination of Atomic Orbitals (LCAO)

Atomic orbitals could be expressed as wave functions (Ψ_{mo}) illustrating the amplitude of electron waves agreeing to wave mechanics. Their values can be determined through the solution of Schrödinger's wave equation. An approximate method recognized by LCAO is used to treat the problems in Schrödinger's wave equation [43]. However, the quantum mechanically, system was treated within the context of the Born Oppenheimer approximation and LCAO in MOT. In LCAO, molecular orbitals (MOs) are created by combining atomic orbitals of the constituent atoms of the molecule (addition or subtraction). The atomic orbital of these atoms is represented by the highest occupied molecular orbitals (Ψ_H) and lowest unoccupied molecular orbitals (Ψ_L) [44]. Where the bonding molecular orbitals are created by additional of wave functions of atomic orbitals as display in Figure 3.1.

$$\psi_{mo} = \psi_H + \psi_L \tag{3.1}$$

Also, the Antibonding molecular orbitals are produced by subtraction of wave functions of atomic orbitals as shown in equation (3.2)

$$\psi^*_{mo} = \psi_H - \psi_L \tag{3.2}$$

The molecular orbitals of hydrogen are constructed by the combination of two atoms of hydrogen with 1s orbitals as illustrated below [45].

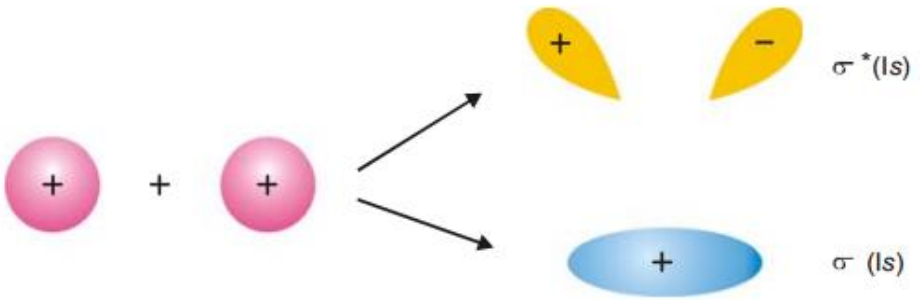


Figure 3.1. Creation of molecular orbitals from two 1s orbitals of hydrogen atoms [46]

The electron density of bonding and antibonding molecular orbitals is achieved by the square of the wave functions from equations (3.1& 3.2)[1, 47].

$$\psi_{mo}^{*2} = (\psi_H - \psi_L)^2 \tag{3.3}$$

$$\psi_{mo}^{*2} = (\psi_H - \psi_L)^2$$

$$\psi_{mo}^{2} = (\psi_H + \psi_L)^2$$

$$\psi_{mo}^{2} = \psi_H^2 + \psi_L^2 + 2\psi_H\psi_L \tag{3.4}$$

The probability of electron density of Antibonding molecular orbital (ABMO) from equation (3.3) is smaller than the entirety of the probability densities of separated atoms by $(2\psi_H\,\psi_L)$ factor. On the other hand, the probability density of electrons in BMOs from equation (3.4) is bigger than the total of the probability densities of separated atoms by $(2\psi_H\,\psi_L)$ factor [48, 49]. The molecular orbital of the H_2^+ is created by taking LCAO of the lowest atomic energy orbitals of the two 1s orbit hydrogen atoms as can be seen in Figure 3.2.

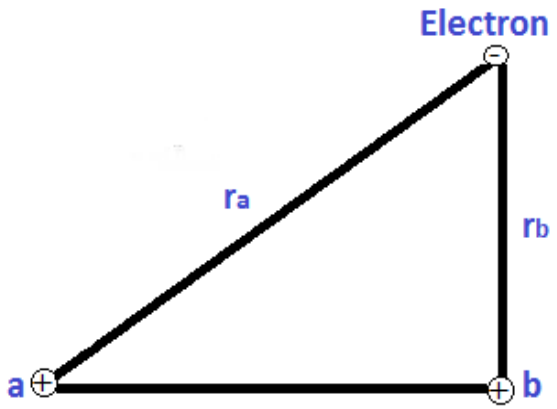


Figure 3.2. Hydrogen ion

$$\psi = \sum C_i\,\phi_i \tag{3.5}$$

Where, ψ Molecular orbital, C_i mixing coefficient and ϕ_i atomic orbital.

$$H = -\frac{1}{2}\nabla^2 - \frac{1}{r_a} - \frac{1}{r_b} + \frac{1}{R} \tag{3.6}$$

$$H = H_e + \frac{1}{R} \tag{3.7}$$

Where first term H_e is the Hamiltonian for the electronic motion and is equal to $\left(-\frac{1}{2}\nabla^2 - \frac{1}{r_a} - \frac{1}{r_b}\right)$.

Second term $\frac{1}{R}$ is the Hamiltonian for the nuclear – nuclear repulsion.

If $1S_a$ and $1S_b$ are the 1S orbitals associated with the nuclei **a** and **b**, respectively then

$$\psi_{mo} = C_1\, 1S_a + C_2\, 1S_b \tag{3.8}$$

The energy of hydrogen ion molecule is given by this formula:

$$\langle E\rangle = \frac{\langle \psi_{mo}|H|\psi_{mo}\rangle}{\langle \psi_{mo}|\psi_{mo}\rangle} \tag{3.9}$$

From equation (3.5) & (3.6)

$$E = \frac{(\langle C_1 1Sa + C_2 1S_b|H|C_1 1Sa + C_2 1S_b\rangle)}{(\langle C_1 1Sa + C_2 1S_b\ |C_1 1Sa + C_2 1S_b\rangle)} \tag{3.10}$$

If the equation (3.10) is

1- Expanded.

2- Differentiated with respected C_1 when C_2 is constant.

3- Differentiated with respected C_2 when $C_1$is constant.

4- $\left(\frac{\partial \mathrm{E}}{\partial \mathrm{C}_1}\right)$And $\left(\frac{\partial \mathrm{E}}{\partial \mathrm{C}_2}\right)$are equal to zero to get the condition for the minimum value of energy we arrive at the following secular equations.

Differentiation with respect to C_1 and setting the derivative equal to zero gives

$$C_1 (H_{aa} - ES_{aa}) + C_2 (H_{ab} - ES_{ab}) = 0 \tag{3.11}$$

Differentiation with respect to C_2 and setting the derivative equal to zero gives

$$C_1 (H_{ba} - ES_{ba}) + C_2 (H_{bb} - ES_{bb}) = 0 \tag{3.12}$$

Equations (3.11) and (3.12) are coinciding equations in C_1 and C_2, by secular equations.

These equations must be solved to gain the proper values for $C_1$and C_2.

Compare equation (3.11) and (3.12) with secular equations

$$C_1 (H_{11} - ES_{11}) + C_2 (H_{12} - ES_{12}) = 0$$

$$C_1 (H_{21} - ES_{21}) + C_2 (H_{22} - ES_{22}) = 0$$

For non-trivial solutions ($C_1 = C_2 = 0$), we need that the equivalent secular determinant be equal to zero:

$$\begin{vmatrix} H_{aa} - ES_{aa} & H_{ab} - ES_{ab} \\ H_{ba} - ES_{ba} & H_{bb} - ES_{bb} \end{vmatrix} = 0 \tag{3.13}$$

This equation can be solved by the following methods:

A) The Coulomb integral: it is equal to the energy of an electron in the corresponding atomic orbital.

$H_{aa} = \langle 1S_a|H_e|1S_a\rangle$

$H_{bb} = \langle 1S_b|H_e|1S_b\rangle$

B) The exchange integral: The strength of the bonding interaction due to the overlap of orbitals (a) and b).

$H_{ab} = \langle 1S_a|H_e|1S_b\rangle$

$H_{ba} = \langle 1S_b|H_e|1S_a\rangle$

C) Normalization

$S_{aa} = \langle 1S_a|1S_a\rangle$

$S_{bb} = \langle 1S_b|1S_b\rangle$

D) Overlap integrals: is a quantity of the effectiveness of overlap of the orbitals, and it's always equal to one.

$S_{ab} = \langle 1S_a|1S_b\rangle$

$S_{ba} = \langle 1S_b|1S_a\rangle$

Meanwhile, two nuclei are identical:

$(H_{aa}=H_{bb})$ and $(H_{ab} = H_{ba})$

$(S_{aa} = S_{bb} = 1)$ and $(S_{ab} = S_{ba} = S)$

Now the secular determinant of equation (3.11) becomes

$$\begin{vmatrix} H_{aa} - E & H_{ab} - ES \\ H_{ab} - ES & H_{aa} - E \end{vmatrix} \quad (3.14)$$

Expanding the equation of (3.14), and these results was gotten:

$(H_{aa} - E)^2 = (H_{ab} - E\,S)^2$ by taking roots for both sides

$$(H_{aa} - E) = \pm (H_{ab} - E\,S) \quad (3.15)$$

Firstly, taking the negative sign in equation (3.15)

$(H_{aa} - E) = -(H_{ab} - E\,S)$

$H_{aa} + H_{ab} = E(1 + S)$

$$E = \frac{H_{aa} + H_{ab}}{(1 + S)} \quad \text{or} \quad E_{e(1)} = \frac{H_{aa} + H_{ab}}{(1 + S)} \tag{3.16}$$

The symbol $E_{e(1)}$ is used to designate that the energy is only the Hamiltonian H_e due to electronic motion. Similarly, if we take the positive sign in equation (3.15)

$$E_{e(2)} = \frac{H_{aa} + H_{ab}}{(1 + S)} \tag{3.17}$$

The secular equations are

$$C_1 (H_{aa} - ES_{aa}) + C_2 (H_{ab} - ES_{ab}) = 0$$

$$C_1 (H_{ab} - ES_{ba}) + C_2 (H_{bb} - ES_{bb}) = 0$$

After simplification of equation (3.11) becomes

$$C_1(H_{aa} - E) + C_2 (H_{ab} - S) = 0 \tag{3.18}$$

By taking negative sign to equation (3.15)

$$(H_{aa} - E) = -(H_{ab} - ES) \tag{3.19}$$

Put the equation (3.13) in equation (3.18)

$$C_1(H_{aa} - E) - C_2 (H_{aa} - E) = 0$$

$$C_1(H_{aa} - E) = C_2 (H_{aa} - E) \quad or \quad C_1 = C_2, and\ C_1 = -C_2$$

By taking the positive sign to equation (3.18)

$\psi_m = C_1\, 1S_a + C_2\, 1S_b$

The molecular orbitals are corresponding to the two roots of E_1 and E_2

In equation (3.8) if $C_2 = C_1$, and $C_1 = C$

$$\psi_1 = C(1S_a + 1S_b) \tag{3.20}$$

Also, in equation (3.8) if $C_2 = -C_1$, and $C_1 = C$

$$\psi_1 = C(1S_a - 1S_b) \tag{3.21}$$

The normalization condition of equation (3.20)

$\psi_1 = C(1S_a + 1S_b)$

$\langle\psi_1|\psi_1\rangle = 1$

$\langle C(1S_a + 1S_b)|C(1S_a + 1S_b)\rangle = 1$

$C^2[\langle 1S_a|1S_a\rangle + \langle 1S_b|1S_b\rangle + 2\langle 1S_a|1S_b\rangle] = 1$

$\langle 1S_a|1S_a\rangle = 1$ $\langle 1S_b|1S_b\rangle = 1$ and $\langle 1S_a|1S_b\rangle = S$

The equation above becomes

$C^2[2+S] = 1$

$$or \quad C = \frac{1}{\sqrt{2+2S}} \quad (i)$$

Put the value (i) in equation (3.20) and (3.21)

$$\psi_1 = \frac{1Sa + 1Sb}{\sqrt{2+2S}} \tag{3.22}$$

$$\psi_2 = \frac{1Sa - 1Sb}{\sqrt{2-2S}} \tag{3.23}$$

More explicit expressions for E_1 and E_2

$$E_{e(1)} = \frac{H_{aa} + H_{ab}}{1+S} \tag{3.24}$$

Derive an explicit expression for H_{aa} and H_{bb} and put in equation (3.16)

$H_{aa} = \langle 1S_a|H_e|1S_a\rangle$

$$H_e = -\frac{1}{2}\nabla^2 - \frac{1}{r_a} - \frac{1}{r_b}$$

$$H_{aa} = \left\langle 1S_a\middle| -\frac{1}{2}\nabla^2 - \frac{1}{ra} - \frac{1}{r_b}\middle|1S_a\right\rangle$$

$$H_{aa} = \left\langle 1S_a\middle| -\frac{1}{2}\nabla^2 - \frac{1}{ra}\middle|1S_a\right\rangle - \left\langle 1S_a\middle|\frac{1}{r_b}\middle|1S_a\right\rangle \tag{3.25}$$

$-\frac{1}{2}\nabla^2 - \frac{1}{r_a}$ is the Hamiltonian for the H atom and the second integral denoted by P

The equation of (3.24) may be written as:

$$H_{aa} = E_H - P \tag{3.26}$$

$$H_{ab} = \left\langle 1S_a \middle| -\frac{1}{2}\nabla^2 - \frac{1}{ra} - \frac{1}{r_b} \middle| 1S_b \right\rangle$$

$$H_{ab} = \left\langle 1S_a \middle| -\frac{1}{2}\nabla^2 - \frac{1}{ra} - \frac{1}{r_b} \middle| 1S_b \right\rangle - \left\langle 1S_a \middle| \frac{1}{r_b} \middle| 1S_b \right\rangle \quad (3.27)$$

$-\frac{1}{2}\nabla^2 - \frac{1}{\mathrm{rb}}$ is the Hamiltonian for H atom, the equation of (3.27) may be written as:

$$H_{ab} = \langle 1S_a | E_H | 1S_b \rangle - \left\langle 1S_a \middle| \frac{1}{r_b} \middle| 1S_b \right\rangle$$

If the second integral is written as (Q), equation (3.27) becomes

$$H_{ab} = \langle 1S_a | E_H | 1S_b \rangle - Q$$

$$H_{ab} = E_H \, <1S_a \, | 1S_b> - Q$$

Since $<1S_a \, / 1S_b> = S$

$$H_{ab} = E_H \, S - Q \quad (3.28)$$

substitute equation (3.26) and (3.28) in equation (3.16)

$$E_{e(1)} = \frac{E_H - P + E_H S - Q}{1 + S}$$

$$E_{e(1)} = E_H - \frac{P + Q}{1 + S} \quad (3.29)$$

$$E_{e(2)} = E_H - \frac{P - Q}{1 - S} \quad (3.30)$$

According to the Oppenheimer approximation, nuclear repulsion is independent of the electronic coordinates and therefore the total energy E (R) can be written for a fixed nuclear framework.

$$E\,(R) = E_e + \frac{1}{R}$$

It follows therefore that

$$E_{e(1)}(R) = E_{e(1)} + \frac{1}{R} \quad (3.31)$$

Substitute equation (3.29) in equation (3.31) and we obtain,

$$E_{e(1)}\,(R) = E_H - \frac{P + Q}{1 + S} + \frac{1}{R} \quad (3.32)$$

Similarly

$$E_{e(2)}(R) = E_{e(2)} + \frac{1}{R} \tag{3.33}$$

Substitute equation (3.30) in equation (3.33) and the energy can be obtained:

$$E_{e(2)}(R) = E_H - \frac{P - Q}{1 - S} + \frac{1}{R} \tag{3.34}$$

Equation (3.31) and (3.33) P, Q and S are positive. Hence $E_{e(1)}$ (R) < $E_{e(2)}$ (R)

E_1 (R) is the ground state energy of the H_2^+ ion, and since $E_{e(1)}$ (R) corresponding to the molecular orbital.

$$\psi_1 = \frac{1S_a + 1S_b}{\sqrt{2 + 2S}}$$

Where, ψ_1 is the ground state of H_2^+ ion.

$$\psi_2 = = \frac{1Sa - 1S_b}{\sqrt{2 - 2S}}$$

Where the ψ_2 corresponds to higher energy E_2 (R) is the state molecular orbital of H_2^+ ion.

$$E_{e(1)}(R) = E_H - \frac{P + Q}{1 + S} + \frac{1}{R} \tag{3.35}$$

$$E_{e(2)}(R) = E_H - \frac{P - Q}{1 - S} + \frac{1}{R} \tag{3.36}$$

Using the 1*S* orbital for the hydrogen atom $1S = \frac{1}{\sqrt{\pi}}\, e^{-r}$, it is possible to derive an expression for the integrals *P, Q* and *S* in terms of internuclear distance *R* [11, 50, 51].

$$P = \frac{1}{R}[1 - (1 + R)]\, e^{-2R} \tag{3.37}$$

$$Q = (1 + R)\, e^{-R} \tag{3.38}$$

$$S = [1 + R + \frac{R^2}{3}]e^{-R} \tag{3.39}$$

3.2. Density Function Theory (DFT)

The theorem of Hohenberg-Kohn (HKT) is the foundation of DFT. The HKT notes that the electronic energy in the ground state can totally find out by the density of electrons. Computationally and conceptually, DFT is quite close to HFT theory. The electron-electron correlation is influenced by DFT, but this effect is ignored in HFT because DFT can produce much

better results as compared to HFT. The main goal in DFT is to find exchange-correlation functional [52, 53]. There are many different exchange-correlations functionalities to explain the electronic structure of the molecules in the literature. So, such various functions can give a good outcome or bad outcome based on which parameter could be measured. Exchange-correlation functionals are created by hypothetically and empirically, which is why there are so many different functionals [47, 54-58].

3.3. DFT from Hohenberg-Kohn Theory (HKT), and Kohn- Sham Theory

The Hohenberg-Kohn theory (HKT) includes two main ideas. The first theory is the electron density, which is the fundamental parameter for determining the system [59, 60]. The second theory is the ground state of the system. It can be gotten by introducing the variational principle [16, 22].

$$H_e = T_e + V_{ext} + V_{ee} \tag{3.40}$$

Where, T_e is the electronic kinetic energy, so V_{ext} is interaction with the exterior potential energy, and V_{ee} is the electron-electron interaction potential energy. The overall energy can be described

$$E[\rho] = F[\rho] + \int V_{ext}\,(r)\rho(r)dr \tag{3.41}$$

Where V_{ext} is the interaction with nuclei and any other field, and F[ρ] is universal function, and is

$$F[\rho] = T[\rho] + V[\rho] \tag{3.42}$$

$$F[\rho] = T_s[\rho] + \int \rho(r)\,\rho(\acute{r})drd\acute{r} + E_{exc}[\rho] \tag{3.43}$$

Now general energy expression for DFT can be written as:

$$E_{DFT}[\rho] = T_s[\rho] + E_{exc}[\rho] + J[\rho] + E_{ne}[\rho] \tag{3.44}$$

Where, $T_s[\rho]$ is non-interaction kinetic energy, $E_{exc}\ [\rho]$ is exchange-correlation energy $J[\rho]$ Coulomb energy, and $E_{ne}[\rho]$ is electron–nuclear potential energy.

3.4. Hartree-Fock Method (HFT)

The properties of systems from individual molecules to macroscopic structures consisting of tens of thousands of atoms can be studied with the power of modern computers [52]. Usually, one starts by solving the time-independent Schrödinger equation to describe an atomic system:

$H_{tot} * \Psi_{tot} = E_{tot} * \Psi_{tot}$

$$H_{tot} = H_e + T_n - \frac{1}{2M_{tot}}\left(\sum_{i}^{N_{elec}} \nabla_i\right)^2 \tag{3.45}$$

where, T_n is the kinetic energy operator of the nuclei, $\boldsymbol{\Psi}$ is the wave function to be solved and H_e is the electronic Hamiltonian operator. H_e represents the kinetic energy of the electrons and the interactions of nuclei to electrons. Also, from nuclei to nuclei and electrons to electrons is a function that depends on the nuclear positions then the equation can be written as:

$$H_e(R)\Psi_i(R,r) = E_i(R)\Psi_i(R,r), i = 1,2,3,\ldots,\infty \tag{3.46}$$

Where (R) denotes the positions of nuclei and (r) represents the positions of electrons. The Born-Oppenheimer approximation assumes that the motions of electrons and nuclei can be separated. The electronic Schrödinger wave equation can be solved exactly for one-electron systems such as (H_2^+) the hydrogen atom. The Pauli Exclusion Principle states that two electrons can't have the exact same quantum numbers and that requires the wave function to be antisymmetric. This is achieved by building the wave function from Slater determinants.

$$\phi_{SD} = \frac{1}{\sqrt{N!}}\begin{vmatrix} \phi_1(1) & \phi_2(2) & \cdots & \phi_N(N) \\ \phi_1(2) & \phi_2(2) & \cdots & \phi_N(N) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_1(N) & \phi_2(N) & \cdots & \phi_N(N) \end{vmatrix}, \langle\phi_i|\phi_j\rangle = \delta_{ij} \tag{3.47}$$

The columns in the Slater determinant are the single-electron wave functions or the so-called molecular orbitals (MO), which are the spatial orbitals multiplied with the spin orbitals α or β. In the HFT, the total wave function is a product of electron orbitals. The energies of the MOs can be written as the Hartree-Fock (HFT) equation:

$$F_i\phi_i = \varepsilon_i\,\phi_i \tag{3.48}$$

Where F_i is the Fock operator, which effectively describes the one-electron energy including the kinetic energy of an electron. HFT and LCAO approximations, taken together and applied to the electronic Schrödinger wave equation, lead to a set of matrix equations now known as the Roothaan–Hall equation:

Where *c* is the unidentified molecular orbital coefficients of orbital energies, *S* is the overlap

$$Fc = S\,c\,\varepsilon \tag{3.49}$$

matrix, and *F* is the Fock matrix, which is analogous to the Hamiltonian in the Schrödinger equation.

$$F_{\mu\nu} = H_{\mu\nu}^{core} + J_{\mu\nu} + K_{\mu\nu} \tag{3.50}$$

Where $H_{\mu\nu}^{core}$ the so-called is core Hamiltonian, the elements of which are given by

$$H_{\mu v}^{core} = \int \phi_1(1) \left[\frac{-\hbar^2}{2m_e}\nabla^2 - \frac{e^2}{4\pi\epsilon_0}\int_A^{nuclei} \frac{Z_A}{r_{1A}}\right] \phi_v(1) d\tau \quad (3.51)$$

Coulomb ($J_{\mu v}$) and exchange ($K_{\mu v}$) elements are given by:

$$J_{\mu v} = \sum_{\lambda}^{basis\ functions} \sum_{\sigma} P_{\lambda\sigma}\,(\mu v|\lambda\sigma) \quad (3.52)$$

$$K_{\mu v} = \frac{1}{2}\sum_{\lambda}^{basis\ functions} \sum_{\sigma} P_{\lambda\sigma}\,(\mu\lambda|v\sigma) \quad (3.53)$$

Where $P_{\lambda\sigma}$ is called the density matrix, the elements of which include a product of two molecular orbital coefficients summed over all occupied molecular orbitals:

$$P_{\lambda\sigma} = 2 \sum_{i}^{occupied\ molecular\ orbital} c_{\lambda i}\, c_{\sigma i} \quad (3.54)$$

Where $(\mu\lambda|v\sigma)$ and are two-electron integrals, the number of which increases as the fourth power of the number of basis functions. Therefore, the cost of a calculation:

$$(\mu\lambda|v\sigma) = \iint \phi_\mu(1)\,\phi_v(1) \left[\frac{1}{r_{12}}\right] \phi_\lambda \phi_\sigma d\tau_1 d\tau_2 \quad (3.55)$$

Methods resulting from the solution of the Roothaan–Hall equations are called (HFT) models. The corresponding energy in the limit of a complete basis set is called the (HFT) energy [52].

3.5. Molecular Orbital Energy

Molecular orbital energies can create by linear combination of atomic orbitals (LCAO). Highest occupied molecular orbitals (HOMO) are created by constructive interference while lowest unoccupied molecular orbitals (LUMO) are created by destructive interference.

3.5.1. Bonding Molecular Orbital (HOMO)

The Highest Occupied Molecular Orbital (HOMO or bonding molecular orbitals) is created by combining the additional wave function represented by ($\Psi_{HOMO} = \Psi_A + \Psi_B$). It is similar to the constructive interference taking place in phase because of which electron probability density increases resulting in the creation of bonding orbital [61, 62]. The probability of discovery electron between the two nuclei zone of the BMO is higher than that combining atomic orbitals [2, 63, 64]. The electrons are existing of the molecular orbital bond because of the attraction between two atoms. Because of attraction, it has lower energy and therefore greater stability than the

combination of atomic orbitals as shown in Figure 3.3. They are characterized by(σ, π, δ) [1, 65, 66].

3.5.2. Antibonding Molecular Orbital (LUMO)

The Lowest Unoccupied Molecular Orbital (LUMO or Antibonding Molecular Orbital (ABMO)) is produced by subtraction molecular orbital wave function and is signified by ($\Psi_{LUMO} = \Psi_A - \Psi_B$), they have greater energy than atomic orbitals as shown in Figure 3.3. It identical to destructive interference happening out of phase resulting in the creation ABMO [64, 67]. The electron presents in the ABMO cause repulsion between the two atoms. It has greater energy and low stability because of its repulsive force between two nuclei. They are denoted by$(\sigma^*, \pi^*, \delta^*)$. On the other side, the band gap energy is the difference between HOMO and LUMO energies orbitals as shown in equation (3.56) [1, 46, 66, 68].

$$E_g = (E_{LUMO} - E_{HOMO}) \tag{3.56}$$

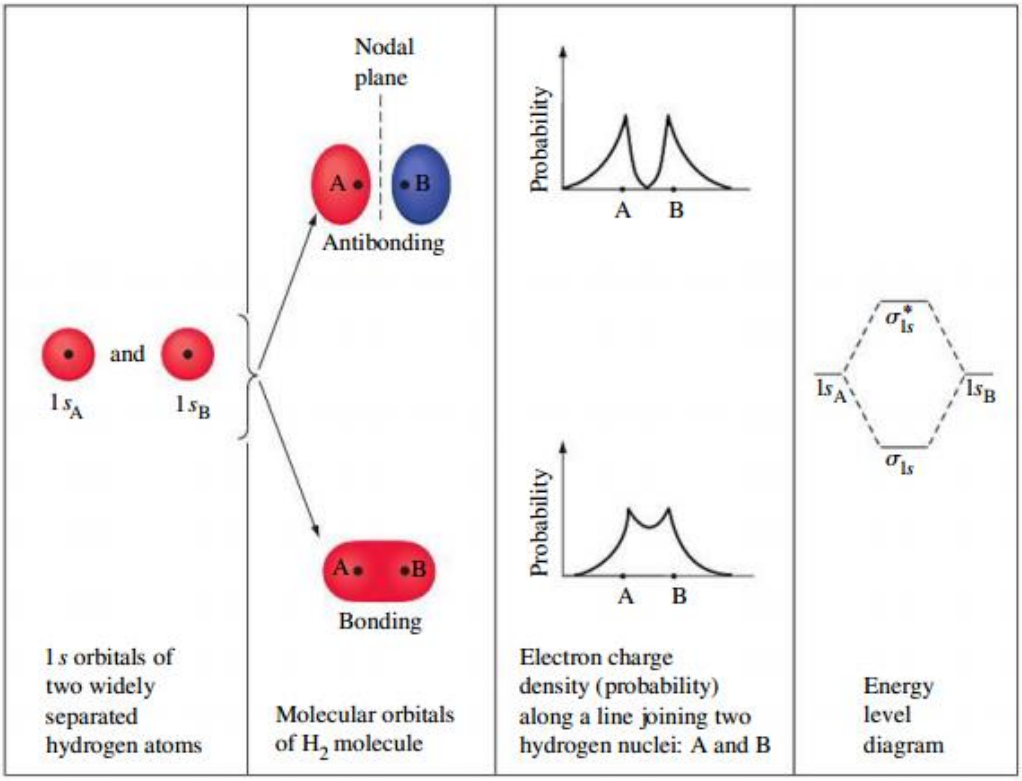


Figure 3.3 The interaction of two atoms of hydrogen by the molecular orbit diagram [2].

3.6. Global Reactivity

From the theorem of the Koopman, electron affinity (EA) and ionizing potential (IP) are the LUMO and HOMO's eigenvalues with change the sign. Some worldwide descriptors of molecules for chemical reactivity such as hardness (η), softness (S), electronegativity (χ), electrophilicity index (ω) and chemical potential (μ) [69, 70]. The chemical potential (μ) and global hardness (η) is defined as the second and first derivative of the energy (E), with respect to the number of electrons (N), when the external potential, v ($\vec{r}$) is constant [36, 41, 71].

$$IP \approx -E_{HOMO} \text{ and } EA \approx -E_{LUMO} \tag{3.57}$$

$$\text{Hardness } (\eta) = \frac{1}{2}\left(\frac{\partial^2 E}{\partial N}\right)_{v(\vec{r})} \text{ andchemical potential } (\mu) = \frac{1}{2}\left(\frac{\partial E}{\partial N}\right)_{v(\vec{r})} \tag{3.58}$$

From equation (3.58), E and v ($\vec{r}$) are external potential and electronic energy of an N-electron system individually. The reciprocal of hardness is called softness and electronegativity the tendency of a molecule to attract an electron. Softness is a property of molecules that measures the extent of chemical reactivity.

$$\text{Softness } (S) = \frac{1}{2\eta}, \text{and electronegativity } (\chi) = -\mu = \frac{1}{2}\left(\frac{\partial E}{\partial N}\right)_{v(\vec{r})} \tag{3.59}$$

Using Koopmans theorem [36, 41, 71] μ, η, and χ can be rewired as:

$$\eta = \frac{1}{2}(E_{LUMO} - E_{HOMO}) \tag{3.60}$$

$$\mu = \frac{1}{2}(E_{HOMO} + E_{LUMO}) \tag{3.61}$$

$$\chi = -\frac{1}{2}(E_{HOMO} + E_{LUMO}) \tag{3.62}$$

Electrophilicity is a valuable structural reactivity depicter and is often used in the analysis of mole cules of chemical reactivity.

$$\omega = \frac{\mu^2}{2\eta} \tag{3.63}$$

4. RESULTS AND DISCUSSION

In chemistry, the Frontier Molecular Orbitals (FMOs) is the application of MOT that explaining the interaction between (HOMO-donor orbital energy) and (LUMO-acceptor orbital energy). The HOMO energy orbital as an electron donor is the capacity to provide an electron, while the LUMO energy orbital as an electron acceptor denotes the ability to receive an electron. The global chemical reactivity descriptors such as (Bandgap energy, Electronegativity, Hardness, Softness, Electrophilicity index, and Chemical potential can be calculated from the value of HOMO-LUMO energy. Similarly, total energy and dipole moments can be achieved by Gaussian 09 software with the DFT and HFT methods in different basis sets such as (3-21G, 6-31G, 6-31+G (d, p), and 6-311G) for (Cyclobutadiene (C_4H_4), phosgene ($COCl_2$), Propylbenzene (C_9H_{12}), 2-*chloro*-5-(trifluoromethyl) aniline ($C_7F_3NH_5Cl$) molecules. Furthermore, there is a bit of dissimilarity between the figures of MOT for all molecules by using DFT and HFT, due to different basis sets.

4.1. Cyclobutadiene (C_4H_4)

For the cyclobutadiene (C_4H_4) molecule, DFT and HFT methods are used to calculate the HOMO and LUMO with the basis sets that mention above. Energy gap values for DFT including (E_g = 3.27eV (3-21G), 3.73eV (6-31G), 3.48eV (6-31+G(dp)), 3.73eV (6-311G)) and energy gap for HFT consist of (E_g = 4.90 eV (3-21G),4.82 eV (6-31G), 5.77 eV (6-31+G(dp)), 5.33 eV (6-311G)). The gap energy for this molecule is E_g = 3.48 eV (6-31+G(dp)) for the DFT method as shown in Figure 4.3. with Table 4.1. Bandgap energy is significant parameter to expect stability and reactivity of chemical compounds. The highest value of bandgap energy is signified to more stability and less reactivity. The results (3.27eV (3-21G), 3.73eV (6-31G), 3.48eV (6-31+G(dp)) are close to the energy gap in reference [39] having the value 3.488 and the calculated data in reference [72] having the values 3.972 eV (3-21G), 3.722 73eV (6-31G), 3.479 eV (6-31+G(dp). Entire calculations by HFT are not agreement with calculated data in reference [72].

The total energy of this molecule for DFT involving (E_t = -154 a.u (3-21G), -155 a.u (6-31G), -155 a.u (6-31+G(d,p)), -155 a.u (6-311G), and for HFT (E_t = -153 a.u (3-21G), -154 a.u (6-31G), -154 a.u (6-31+G(d,p)), -154 a.u (6-311G) as shown in Table 4.1. All calculation close to the results in reference [41, 72, 73] with the value of -154.7 a.u, and calculated data -154.69 a.u, respectively. The dipole moment is zero for DFT and HFT methods, because of this molecule nonpolar molecules. As well as, the value of this parameter identical to the reference result [74] having zero value. Therefore, the electronegativity is the essential parameter to expect the ability of compounds to attract electron toward itself. The highest value of this parameter indicates that

more ability to attract electron. The exact value of electronegativity calculated that χ = 3.62 eV (6-31+G (dp)) for DFT as made known in Table 4.1. Also, this outcome is close to the reference [41] value of 3.67 eV.

The chemical potential is a significant parameter in chemistry that describes the tendency of molecule for escaping electron from the molecule. Also, it related to electronegativity ($\mu = -\chi$), and the exact value is μ = - 3.62 eV (6-31+G (dp)) for DFT calculation. Also, the chemical potential parameter value for this molecule is near the result in reference [41].

The hardness of cyclobutadiene can be achieved which η = 1.74 eV (6-31+G (dp)) for DFT as shown in Table 4.1. The softness of cyclobutadiene (C_4H_4) is inversely proportional to hardness, S = 0.29 $(eV)^{-1}$(6-31+G (dp)) for DFT as shown in Table 4.1. Both chemical parameters are important to understand chemical stability and reactivity of molecules then both quantities are similar to the result in reference [41] having the value of 1.77 eV for hardness, and 0.28 eV for softness.

The last calculation is Electrophilicity (ω), this is an important essential parameter related to nucleophile and electrophile. The big value of ω signifies electrophile while small value of ω denotes to good nucleophile. The exact result of ω can be gotten by DFT which ω = 3.77 eV (6-31+G (dp)), and this value is like a result in reference [41].

Finally, as can be seen for all the calculations above, Density Function theory is suitable with (6-31+G (dp), and 6-311G) basis sets. So, DFT more accurate results than HFT. DFT depends on the electron density, while HFT depends on the wave function of the electrons.

Table 4.1. Calculating quantum chemistry parameters for Cyclobutadiene (C_4H_4) by DFT and HFT with different basis sets

Cyclobutadiene (C_4H_4)	Density Function Theory (DFT)				Hartree Fock Theory (HFT)			
Basis set	3-21G	6-31G	6-31+G (d, p)	6-311G	3-21G	6-31G	6-31+G (d, p)	6-311G
HOMO (eV)	-4.90	-5.12	-5.36	-5.41	-7.67	-7.56	-7.62	-7.73
LUMO (eV)	-1.63	-1.39	-1.88	-1.69	-2.78	-2.75	-1.85	-2.39
Band gap energy (E_g) (eV)	3.27	3.73	3.48	3.73	4.90	4.82	5.77	5.33
Total energy (E_t) (a.u)	-154	-155	-155	-155	-153	-154	-154	-154
Dipole moment (Debye)	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Electronegativity (χ) (eV)	3.27	3.27	3.62	3.56	5.22	5.17	4.73	5.06
Hardness (η) (eV)	1.63	1.86	1.74	1.86	2.45	2.41	2.88	2.67
Softness (S) $(eV)^{-1}$	0.31	0.27	0.29	0.27	0.21	0.21	0.18	0.19
Chemical potential (μ) (eV)	-3.27	-3.27	-3.62	-3.56	-5.22	-5.17	-4.73	-5.06
Electrophilicity (ω) (eV)	3.27	2.87	3.77	3.40	5.56	5.55	3.88	4.80

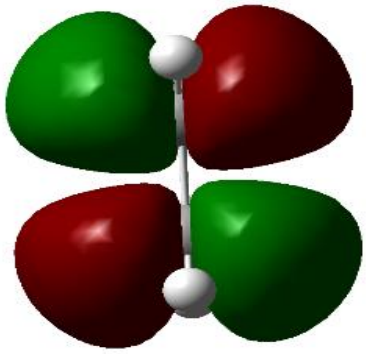
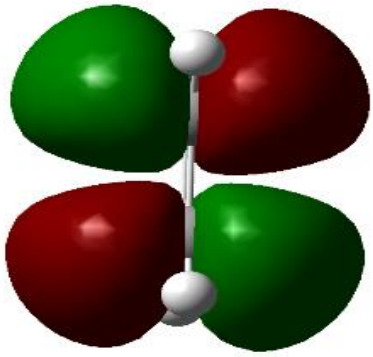
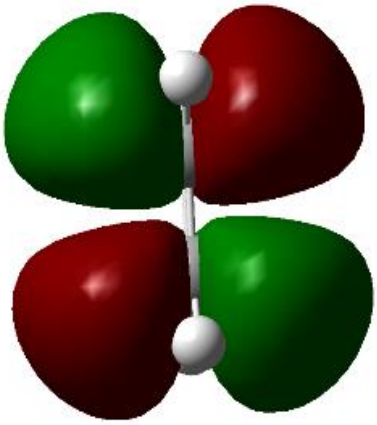
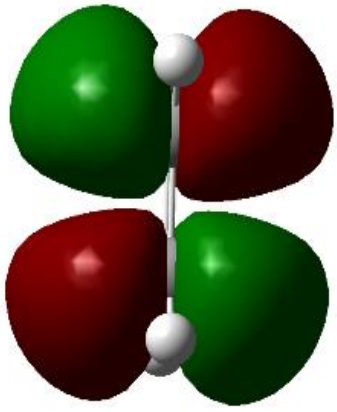
Basis set (3-21G) HFT	Basis set (3-21G) DFT
	
HOMO energy = -7.67 eV	HOMOenergy = -4.90 eV
Band gap energy = 4.90 eV	Band gap energy = 3.27 eV
LUMO energy = -2.78 eV	LUMO energy = -1.63 eV
	

Figure 4.1. Frontier Molecular Orbitals of cyclobutadiene with (3-21G) basis set by DFT and HFT methods

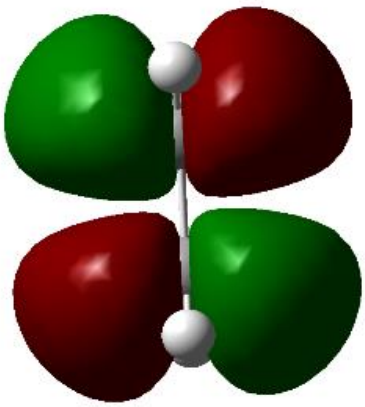
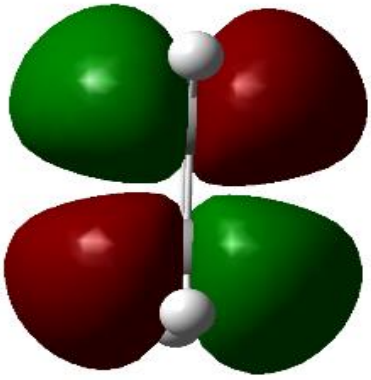
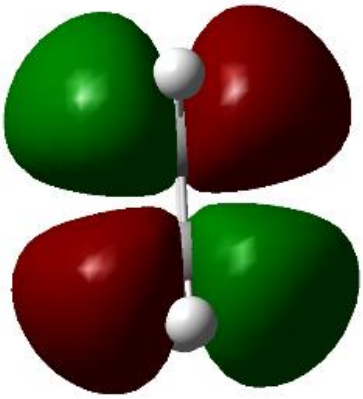
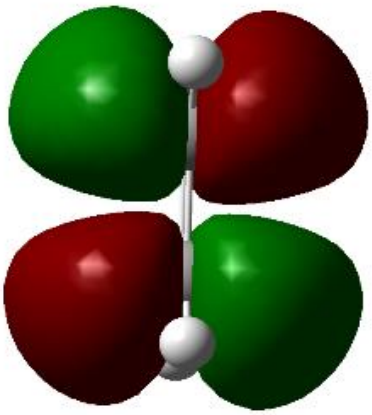
Basis set (6-31G) HFT	Basis set (6-31G) DFT
	
HOMO energy = -7.56 eV	HOMO energy = -5.12 eV
Band gap energy = 4.82 eV	Band gap energy = 3.73 eV
LUMO energy = -2.75 eV	LUMO energy = -1.39 eV
	

Figure 4.2. Frontier Molecular Orbitals of cyclobutadiene with (6-31G) basis set by DFT and HFT methods

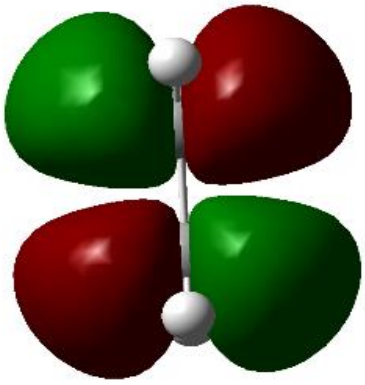
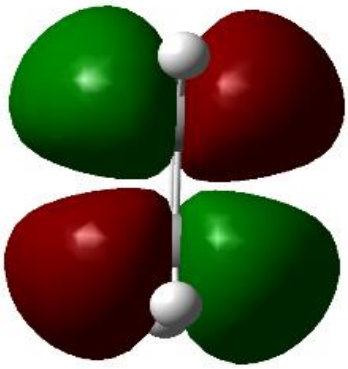
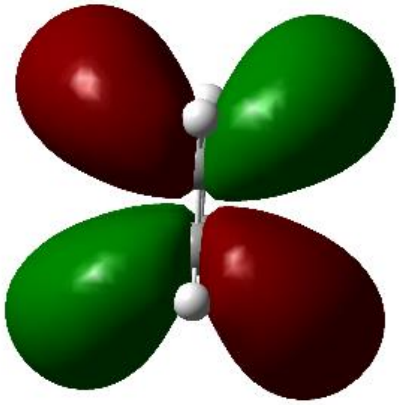
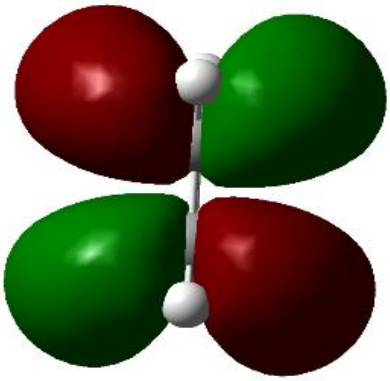
Basis set (6-31+G (d, p)) HFT	Basis set (6-31G+ (dp)) DFT
	
HOMO energy = -7.62 eV	HOMO energy = -5.35 eV
Band gap energy = 5.77 eV	Band gap energy = 3.48 eV
LUMO energy = -1.85 eV	LUMO energy = -1.88 eV
	

Figure 4.3. Frontier Molecular Orbitals of cyclobutadiene with (6-31+G (d, p)) basis sets by DFT and HFT methods

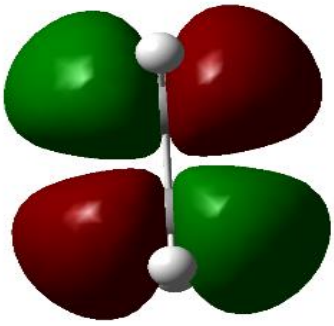
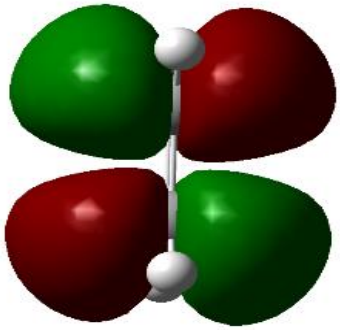
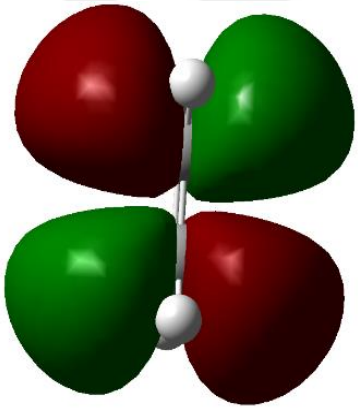
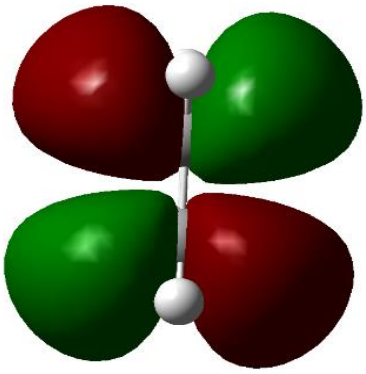
Basis set (6-311G) HFT	Basis set (6-311G) DFT
	
HOMO energy = -7.73 eV	HOMO energy = -5.41 eV
Band gap energy = 5.33 eV	Band gap energy = 3.73 eV
LUMO energy = -2.39 eV	LUMO energy = -1.69 eV
	

Figure 4.4. Frontier Molecular Orbitals of cyclobutadiene with (6-311G) basis sets by DFT and HFT methods

4.2. Propylbenzene (C_9H_{12})

The frontier energy orbitals (bandgap energy) for C_9H_{12} are an important factor in quantum chemistry that related to stability and reactivity. The lowest E_g is shown the maximum reactivity and lowest kinetic stability of Propylbenzene. The bandgap energy by DFT are comprises of (E_g = 12.96 eV (3-21G), 12.73eV (6-31G), 6.23eV (6-31+G(dp)), 6.5eV (6-311G)) and energy gap for HFT contains (E = 12.95 eV (3-21G),12.73 eV (6-31G), 8.53 eV (6-31+G(dp)), 12.49 eV (6-311G)). The precise energy gap for Propylbenzene is 6.23 eV for DFT method as illustrated in Figure 4.5 with Table 4.2. The outcome for DFT(6.23eV (6-31+G(dp)), 6.5eV (6-311G)) is too close same result in reference [36] having the value of 6.233 eV (6-311++G(d,p)) , and near the results in reference [71] having the value of 6.44 eV 6-31++G(d,p). Also, these results close to the calculated result 6.23eV (6-31+G(dp)) is near the calculated data in reference [72] having the value 6.33 eV 6-31+G(dp)). In different, due to far from the exact result all calculations by HFT were ignored.

The hardness is vital parameter to understand the chemical stability and reactivity of, and is directly proportional to the value of band gap energy ($\eta \propto E_g$). The hardness can be calculated from the magnitude of E_g by Density Function Theory, which includes (η = 6.48eV (3-21G), 6.37eV (6-31G), 3.12eV (6-31+G(d, p)), 3.25eV (6-311G)) and hardness for HFT consist of (η = 6.48 eV (3-21G), 6.37 eV (6-31G), 4.27 eV (6-31+G(d, p)), 6.25 eV (6-311G)) as can be seen from the Figure 4.5. The hardness values 3.12 eV and 3.25 eV for DFT is in agreement with the result in reference [36, 71] having the value of 3.12 eV, 3.17 eV, respectively, other value for HFT calculation is not agreements with the exact result.

Another calculation is softness, it has been obtained by HFT and DFT with four different basis set. The DFT calculations consist of (S = 0.08 $(eV)^{-1}$ (3-21G), 0.08 $(eV)^{-1}$ (6-31G), 0.16 $(eV)^{-1}$ (6-31+G(d, p)), 0.16 $(eV)^{-1}$ (6-311G)) and softness for HFT are including (S = 0.08 $(eV)^{-1}$ (3-21G),0.08 $(eV)^{-1}$ (6-31G), 0.12 $(eV)^{-1}$ (6-31+G(dp)), 0.08 $(eV)^{-1}$ (6-311G)). The positive softness value by DFT is 0.16 $(eV)^{-1}$, as seen in Table 4.2. The convenient result for this compound which has a value of 0.19 $(eV)^{-1}$ related to the result in reference[36].

The electronegativity parameter is characterizing the power of atoms or molecules to attract electrons. As display in the Table 4.2. ,the electronegativity of C_9H_{12} by DFT is contain (χ = 2.39 eV (3-21G), 2.37 eV (6-31G), 3.49 eV (6-31+G(d, p)), 3.44 eV (6-311G)) and electronegativity for HFT is involving (χ = 2.40 eV (3-21G), 2.37 eV (6-31G), 2.41 eV (6-31+G(d, p)), 2.60 eV (6-311G). The good outcomes of χ by DFT is 3.44 eV are suitable result compared to other calculations. Furthermore, this result is in agreement with the calculation in reference [36] having the value of 3.38 eV, and 3.52 eV in reference [71].

The dipole moment calculation of this molecule in the DFT (Dipole moment = 0.259 D (3-21G), 0.280 D (6-31G), 0.408 D (6-31+G(d, p), 0.317 D (6-311G) and for HFT (Dipole moment = 0.259 D (3-21G), 0.280 D (6-31G), 0.401 D (6-31+G(dp)), 0.345 D (6-311G) as exhibited in Table 4.2. The obtained value of this parameter by DFT has the 0.408 D is approaching the results in reference[71, 74] having the values of 0.47 eV, and experimental value 0.421 D (6-31+G (d, p).

The total energy for C_9H_{12} by the DFT and HFT was achieved from (E_t = -345.9 eV to -350.2 eV) with different basis sets. The E_t is changed due to changing basis sets and methods. Also, these results similar to calculated data in reference [72] having the values –345.88 to – 350.22 eV.

The electrophilicity index was used to evaluate the chemical reactivity for C_9H_{12}. Lowest value of this parameter specified that good nucleophile while highest value meant the good electrophile. Electrophilicity index of C_9H_{12} by DFT having (ω = 0.44 eV (3-21G), 0.44 eV (6-31G), 1.95 eV (6-31+G(dp)), 1.82 eV (6-311G)) and electrophilicity for HFT having (ω = 0.44 eV (3-21G), 0.44 eV (6-31G), 0.68 eV (6-31+G(dp)), 0.54 eV (6-311G) as shown in Table 4.2. The results for DFT calculation 1.95 eV, and 1.82 eV are comparable to other results in reference[36, 71] having the values of 1.98 eV, and 1.07 eV, separately.

Chemical potential is the last calculation for Propylbenzene. The μ of C_9H_{12} for the DFT and HFT has been found between (μ =-2.37 eV to -3.49 eV) with different basis sets as displayed in Table 4.2. It is the negative value of electronegativity. The results (μ = -3.49 eV, and -3.44 eV for DFT calculation are suitable than other calculation in the HFT calculations. Besides, these results are close to the calculations in reference[36, 71] having the value of -3.38 eV and -3.52 eV, respectively.

Table 4.2. Calculating quantum chemistry parameters for Propylbenzene (C_9H_{12}) by DFT and HFT with different basis sets

Propylbenzene (C_9H_{12})	Density Function Theory (DFT)				Hartree Fock Theory (HFT)			
Basis set	3-21G	6-31G	6-31+G (d, p)	6-311G	3-21G	6-31G	6-31+G (d, p)	6-311G
HOMO (eV)	-8.87	-8.73	-6.6	-6.69	-8.87	-8.73	-6.67	-8.84
LUMO (eV)	4.09	4.00	-0.37	-0.19	4.08	4.00	1.86	3.65
Band gap energy (E_g) (eV)	12.96	12.73	6.23	6.5	12.95	12.73	8.53	12.49
Total energy (E_t) (a.u)	-345.9	-347.7	-350.2	-350.2	-345.9	-347.7	-347.8	-347.7
Dipole moment (Debye)	0.259	0280	0.408	0.317	0.259	0.280	0.401	0.345
Electronegativity (χ) (eV)	2.39	2.37	3.49	3.44	2.40	2.37	2.41	2.60
Hardness (η) (eV)	6.48	6.37	3.12	3.25	6.48	6.37	4.27	6.25
Softness (S) $(eV)^{-1}$	0.08	0.08	0.16	0.16	0.08	0.08	0.12	0.08
Chemical potential (μ) (eV)	-2.39	-2.37	-3.49	-3.44	-2.40	-2.37	-2.41	-2.60
Electrophilicity (ω) (eV)	0.44	0.44	1.95	1.82	0.44	0.44	0.68	0.54

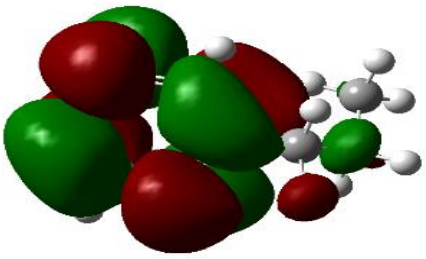
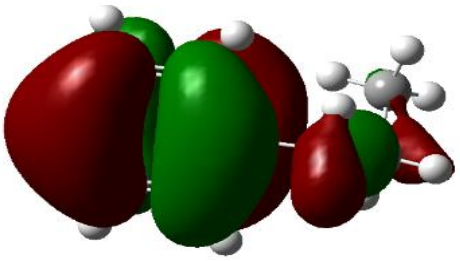
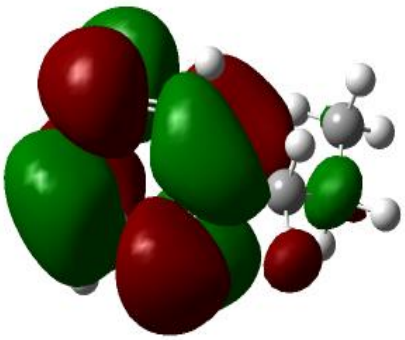
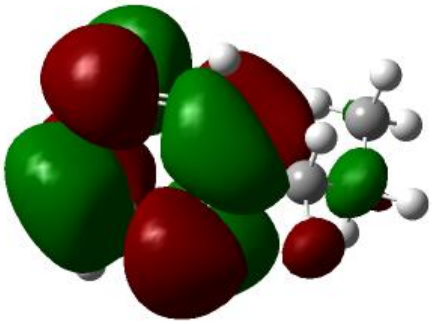
Basis set (3-21G) HFT	Basis set (3-21G) DFT
	
HOMO energy = -8.87 eV	HOMO energy = -8.87 eV
Band gap energy = 12.95 eV	Band gap energy = 12.96 eV
LUMO energy = 4.08 eV	LUMO energy = 4.09 eV
	

Figure 4.5. Frontier Molecular Orbitals of Propylbenzene with (3-21G) basis sets by DFT and HFT methods

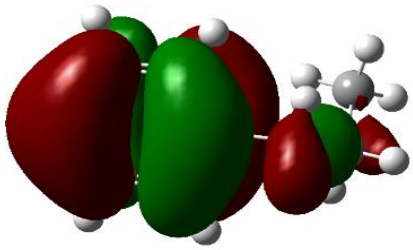
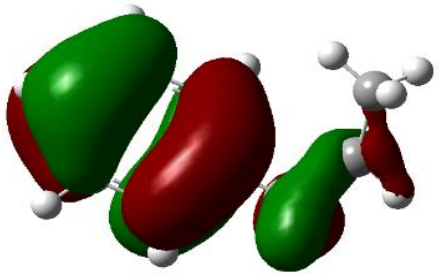
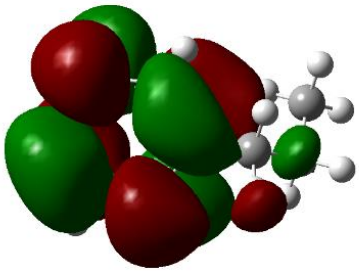
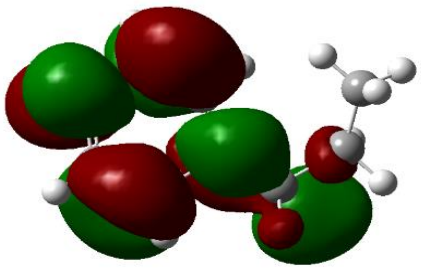
Basis set (6-31G) HFT	Basis set (6-31) DFT
	
HOMO energy = -8.73 eV	Homo energy = -8.73 eV
Band gap energy = 12.73 eV	Band gap energy = 12.73 eV
LUMO energy = 4.00 eV	LUMO energy = 4.00 eV
	

Figure 4.6. Frontier Molecular Orbitals of Propylbenzene with (6-31G) basis sets by DFT and HFT methods

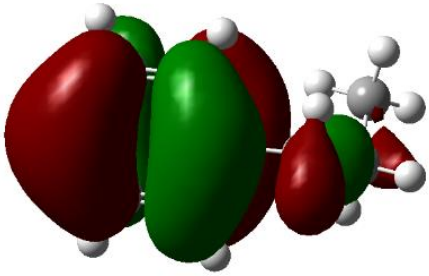
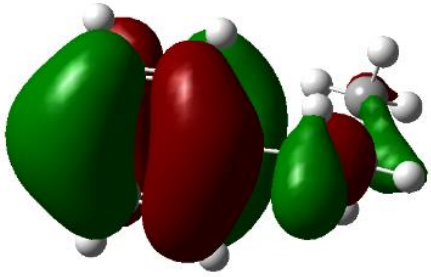
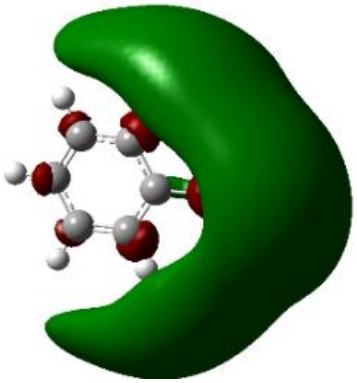
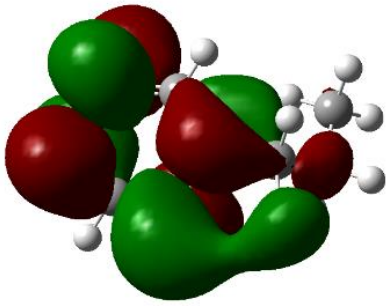
Basis set (6-31+G (d, p)) HFT	Basis set (6-31+G (d, p)) DFT
	
HOMO energy = -6.67 eV	HOMO energy = -6.6 eV
Band gap energy = 8.53 eV	Band gap energy = 6.23 eV
LUMO energy = 1.86 eV	LUMO energy = -0.37 eV
	

Figure 4.7. Frontier Molecular Orbitals of Propylbenzene with (6-31+G (d, p)) basis sets by DFT and HFT methods.

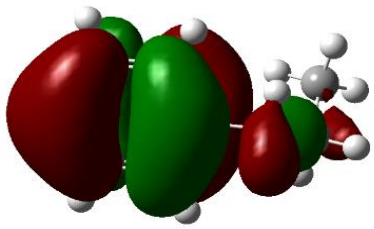
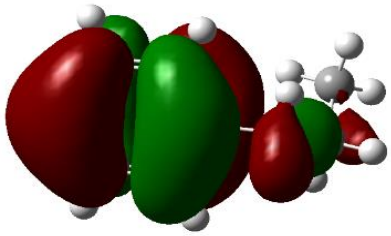
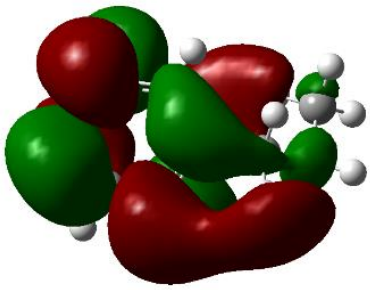
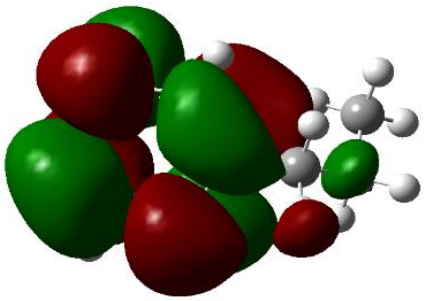
Basis set (6-311G) HFT	Basis set (6-311G) DFT
	
HOMO energy = -8.84 eV	HOMO energy = -6.69 eV
Band gap energy = 12.49 eV	Band gap energy = 6.5 eV
LUMO energy = 3.65 eV	LUMO energy = -0.19 eV
	

Figure 4.8. Frontier Molecular Orbitals of Propylbenzene with (6-311G) basis sets by DFT and HFT methods

4.3. Phosgene (Carbonyl dichloride) ($COCl_2$)

The energy difference between the donor orbital (HOMO) and acceptor orbital (LUMO) is vital to study the kinetic chemical stability and reactivity of carbonyl dichloride. The energy gap is a significant parameter to comprehend conductivity, stability, and chemical reactivity. The small value represented the greatest reactivity but the big value denoted to lowest reactivity. Energy gap of the DFT are counting (E_g = 6.42 eV (3-21G), 6.34 eV (6-31G), 6.34eV (6-31+G (d, p)), 6.32eV (6-311G)) and energy gap for HFT are including (E_g = 14.72 eV (3-21G),15.44 eV (6-31G), 14.75 eV (6-31+G (d, p)), 15.35 eV (6-311G)). The appropriate energy gap value as display in Figure 4.(9-13) by DFT for phosgene is 6.42 eV (3-21G), and close to the calculated data in reference [74] having the value of 6.44 eV (3-21G). Moreover, all calculation by HFT was disagreement by reason far from the exact result.

Molecular hardness is a concept for illustrating the behaviour of chemical structure of this molecule and depend on the value of band gap energy between HOMO and LUMO energies orbitals. The DFT values are comprising (η = 3.21 eV (3-21G), 3.17eV (6-31G), 3.17 eV (6-31+G (d, p)), 3.16 eV (6-311G)) and for HFT are containing (η = 7.36 eV (3-21G), 7.72 eV (6-31G), 7.38 eV (6-31+G(dp)), 7.68 eV (6-311G) as display in Table 4.3.

The softness is a suitable idea for demonstrating the properties of chemical structure of this molecule and depend on the value of hardness and band gap energy. It was achieved by DFT with four dissimilar (S = 0.311 $(eV)^{-1}$ (3-21G), 0.316 $(eV)^{-1}$ (6-31G), 0.316 $(eV)^{-1}$ (6-31+G (d, p)), 0.317 $(eV)^{-1}$ (6-311G)) basis sets and the softness for HFT contains of (S = 0.136 $(eV)^{-1}$ (3-21G),0.130 $(eV)^{-1}$ (6-31G), 0.136 $(eV)^{-1}$ (6-31+G (d, p)), 0.130 $(eV)^{-1}$ (6-311G).

The electronegativity (χ) parameter of this compound is representing the capacity to attract electrons toward themselves. It is significant to understand the reactivity of phosgene and inversely proportional to the magnitude of bandgap energy as shown in the Table4.3.

The electronegativity of carbonyl dichloride by DFT involves (χ = 5.4 eV (3-21G), 5.7 eV (6-31G), 5.7 eV (6-31+G (d, p)), 5.9 eV (6-311G)) and electronegativity by HFT includes (χ = 5.6 eV (3-21G), 5.6 eV (6-31G), 5.6 eV (6-31+G (d, p)), 5.7 eV (6-311G). lowest value signified the more reactivity.

The dipole moment parameter is an essential for comprehension of molecular polarity and directly proportional to electronegativity. It can be analyzed by the DFT (Dipole moment = 1.182 D (3-21G), 1.56 D (6-31G), 1.77 D (6-31+G (d, p), 1.59 D (6-311G) and the dipole moment for this molecule by HFT (Dipole moment = 0.66 D (3-21G),1.25 D (6-31G), 1.47 D (6-31+G(dp)), 1.15 D (6-311G). The right value is 1.182 D (3-21G) D by HFT which agreement with experimental data in reference [74] having the value of 1.17 D.

The total energy of this molecule with different basis sets for the DFT and HFT was found from (E_t =-1027 a.u to -1034 a.u). These results of the total energies for the DFT and HFT are close to the references result [74, 75] with values from – 1028.67 a.u to -1033.72 a.u.

The electrophilicity index is a more convenient parameter to forecast the chemical stability and reactivity of this molecule. A small value is specified more kinetic stability and low reactivity but big value is indicated that highest reactivity and less kinetic stability. This parameter depends on the values of hardness and chemical potential. It can be calculated (ω = 4.6 eV (3-21G), 5.1 eV (6-31G), 5.1 eV (6-31+G (d, p)), 5.5 eV (6-311G)) by Density Function Theory, and (ω = 2.2 eV (3-21G), 200 eV (6-31G), 2.1 eV (6-31+G (d, p)), 2.1 eV (6-311G) for Hartree Fock Theory.

The chemical potential can be gotten from the values of HOMO and LUMO energies orbitals, and is a negative value of electronegativity. The μ of phosgene for the DFT and HFT have been found from (μ =-5.4 eV to -5.9 eV) values with different basis sets as shown in Table4.3.

Table 4.3. Calculating quantum chemistry parameters for phosgene ($COCl_2$) by DFT and HFT with different basis set

phosgene ($COCl_2$)	Density Function Theory (DFT)				Hartree Fock Theory (HFT)			
Basis set	3-21G	6-31G	6-31+G (d, p)	6-311G	3-21G	6-31G	6-31+G (d, p)	6-311G
HOMO (eV)	-8.65	-8.84	-8.87	-9.03	-13.01	-13.31	-13.01	-13.36
LUMO (eV)	-2.23	-2.50	-2.53	-2.72	1.71	2.14	1.74	2.00
Band gap energy (E_g) (eV)	6.42	6.34	6.34	6.32	14.72	15.44	14.75	15.36
Total energy (E_t) (a.u)	-1029	-1034	-1034	-1034	-1027	-1032	-1032	-1032
Dipole moment (Debye)	1.182	1.56	1.77	1.59	0.66	1.25	1.47	1.15
Electronegativity (χ) (eV)	5.4	5.7	5.7	5.9	5.6	5.6	5.6	5.7
Hardness (η) (eV)	3.21	3.17	3.17	3.16	7.36	7.72	7.38	7.68
Softness (S) $(eV)^{-1}$	0.155	0.158	0.157	0.158	0.068	0.065	0.068	0.056
Chemical potential (μ) (eV)	-5.4	-5.7	-5.7	-5.9	-5.6	-5.6	-5.6	-5.7
Electrophilicity (ω) (eV)	4.6	5.1	5.1	5.5	2.2	2.0	2.1	2.1

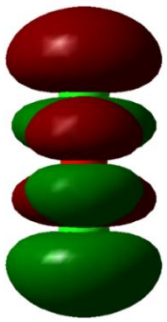
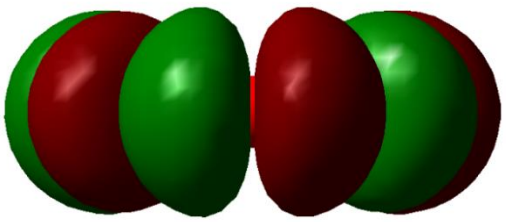
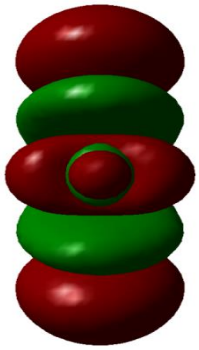
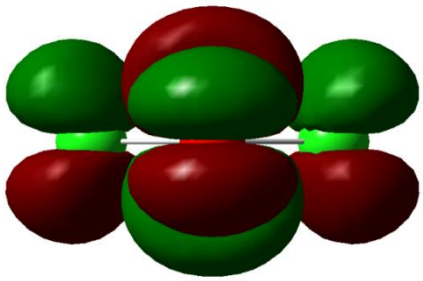
Basis set (3-21G) HFT	Basis set (3-21G) DFT
	
HOMO energy = -13.01 eV	HOMO energy = -8.87 eV
Band gap energy = 14.72 eV	Band gap energy = 6.42 eV
LUMO energy = - 1.71 eV	LUMO energy = - 2.23 eV
	

Figure 4.9. Frontier Molecular Orbitals of Phosgene with (6-31G) basis set by DFT and HFT methods

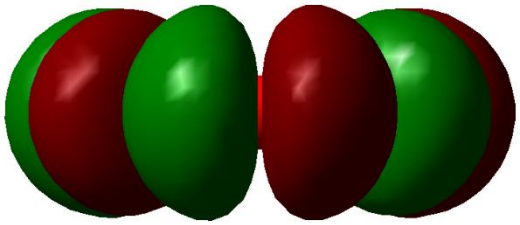
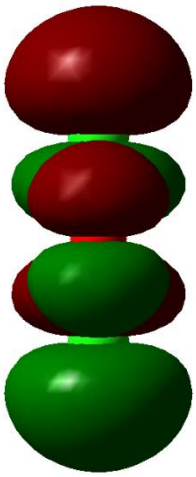
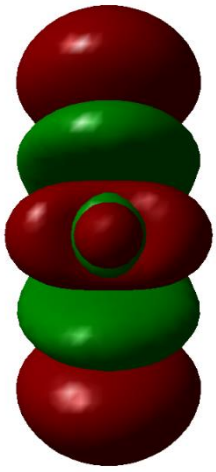
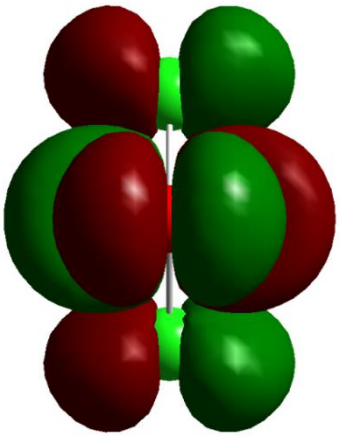
Basis set (6-31G) HFT	Basis set (6-31G) DFT
	
HOMO energy = -13.31 eV	HOMO energy = -8.84 eV
Band gap energy =15.44 eV	Band gap energy = 6.34 eV
LUMO energy = 2.14 eV	LUMO energy = -2.50 eV
	

Figure 4.10. Frontier Molecular Orbital energy of Phosgene with (6-31G) basis sets by DFT and HFT methods.

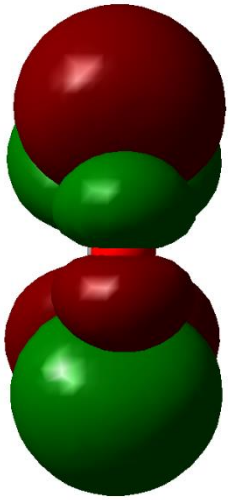
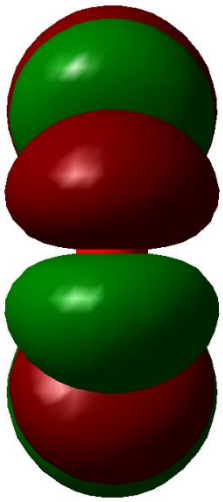
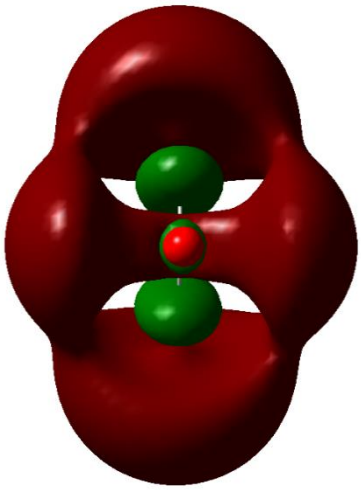
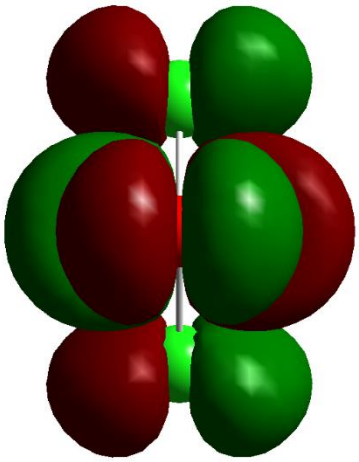
Basis set (6-31+G (d, p)) HFT	Basis set (6-31+G (d, p)) DFT
	
HOMO energy = -13.01 eV	HOMO energy = -8.87 eV
Band gap energy = 14.75 eV	Band gap energy = 6.34 eV
LUMO energy = 1.74 eV	LUMO energy = -2.53 eV
	

Figure 4.11. Frontier Molecular Orbital energy of Phosgene with (6-31+G (d, p)) basis sets by DFT and HFT methods.

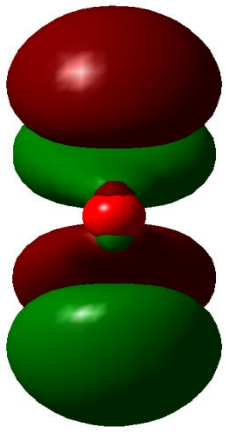
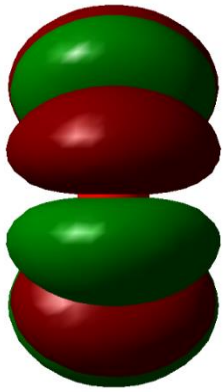
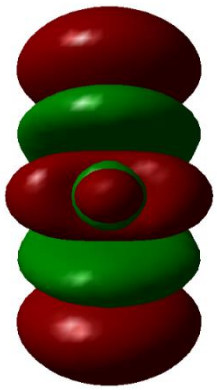
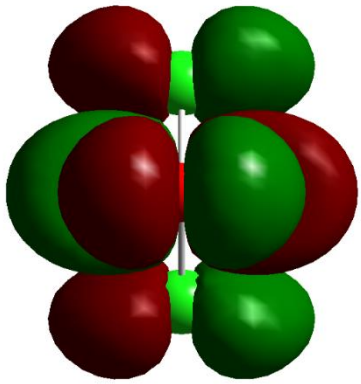
Basis set (6-311G) HFT	Basis set (6-311G) DFT
	
HOMO energy = -13.36 eV	HOMO energy = -9.03 eV
Band gap energy = 15.36 eV	Band gap energy = 6.32 eV
LUMO energy = 2.00 eV	LUMO energy = -2.72 eV
	

Figure 4.12. Frontier Molecular Orbital energy of Phosgene with (6-311G) basis sets by DFT and HFT methods

4.4. 2-Chloro-5-(trifluoromethyl) aniline ($C_7F_3NH_5Cl$)

The energy gap of $(C_7F_3NH_5Cl)$ was achieved by DFT and HFT with their basis sets that indicated above. The bandgap energy is an essential quantity to investigate the chemical reactivity and stability of this molecule. High or low values of the energy gap between LUMO and HOMO molecular orbital energy are correlated to the reactivity and stability of this molecule. The energy gap by DFT calculation are relating (E_g = 6.80 eV (3-21G), 5.14 eV (6-31G), 5.17 eV (6-31+G (d, p)), 5.09 eV (6-311G)) and for HFT are involving (E_g = 11.43 eV (3-21G), 11.37 eV (6-31G), 11.35 eV (6-31+G (d, p)), 11.27 eV (6-311G)) as illustrated in Figure 2.4 with Table 4.4. The exact value

of band gap energy is 5.09 eV, and this measurement is approaching the result in reference [76] with a value of 5.06 eV (6-31++G(3df,3pd)). As well as, other results of the bandgap energy by HFT are insignificant because of these results are not similar the exact result in reference [76].

The hardness is helpful parameter to estimation the reactivity, polarizable, and stability of this compound, and is associated to the energy gap. Harder molecule has the big energy gap. Also, the hardness of this molecule was calculated by DFT are calculating (η = 3.4 eV (3-21G), 2.6 eV (6-31G), 2.6 eV (6-31+G (d,p)), 2.5 eV (6-311G)), and hardness for HFT are counting (η = 5.7 eV (3-21G), 5.7 eV (6-31G), 5.7 eV (6-31+G (d, p)), 5.6 eV (6-311G)) as indicated Table 4.3.The chemical Softness is meaningful quantity to estimate the chemical properties of this molecule, and is connected to hardness. It is the reciprocal of hardness. The softness has been found by DFT with various basis set with (S = 0.15 $(eV)^{-1}$ (3-21G), 0.19 $(eV)^{-1}$ (6-31G), 0.19 $(eV)^{-1}$ (6-31+G (d, p)), 0.20 $(eV)^{-1}$ (6-311G)) and softness for HFT with (S = 0.09 $(eV)^{-1}$ (3-21G), 0.09 $(eV)^{-1}$ (6-31G), 0.09 $(eV)^{-1}$ (6-31+G (d, p)), 0.09 $(eV)^{-1}$ (6-311G)).

The magnitude of electronegativity is important to describe the reactivity and the tendency of this molecule to attract electron toward itself. As can be seen in the Table 4.3. below, the electronegativity of $C_7F_3NH_5Cl$ was computed by DFT are obtained as (χ = 4.2 eV (3-21G), 3.7 eV (6-31G), 3.9 eV (6-31+G (d, p)), 4.0 eV (6-311G)) and electronegativity for HFT are achieved as (χ = 3.0 eV (3-21G), 4.1 eV (6-31G), 4.1 eV (6-31+G (d, p)), 3.3 eV (6-311G).

The chemical potential for $(C_7F_3NH_5Cl)$ by DFT and HFT has been obtained from (μ = -3.0eV to -4.2 eV) with unlike basis sets as point out in Table 4.3. It is connected to the electronegativity. Greater value of this parameter is caused by increasing the reactivity and decreasing the stability of this compound.

Dipole moment is describing the charge distribution on the atoms of this molecule, and is directly proportional to electronegativity. The dipole moment was gotten for DFT (D = 2.67 eV (3-21G), 3.03 eV (6-31G), 2.97 eV (6-31+G (d, p)), 3.27 eV (6-311G)) and dipole moment (D = 2.67 eV (3-21G), 2.73 eV (6-31G), 0.98 eV (6-31+G (d, p)), 2.77 eV (6-311G) for HFT.

The total energy of this molecule for the DFT and HFT was achieved from (E_t =-1075 a.u to -1084 a.u) with different basis sets. total energy is changed due to changing basis sets and methods as shown in Table 4.3. The exact outcome is -1084 a.u and closes the result with the -1084 value in reference [76].

The electrophilicity is directly proportional to the square of chemical potential and inversely proportional to the hardness. The calculations by DFT are containing (ω = 2.6 eV (3-21G), 2.6 eV (6-31G), 3.0 eV (6-31+G (d, p)), 3.1 eV (6-311G)) and electrophilicity for HFT are containing (ω = 0.8 eV (3-21G), 1.5 eV (6-31G), 1.5 eV (6-31+G (d, p)), 1.0 eV (6-311G) as shown in Table 4.3.

Table 4.4.Calculating quantum chemistry parameters for ($C_7F_3NH_5Cl$) aniline by DFT and HFT with different basis sets.

($C_7F_3NH_5Cl$) aniline	Density function theory (DFT)				Hartree Fock theory (HFT)			
Basis set	3-21G	6-31G	6-31+G (d, p)	6-311G	3-21G	6-31G	6-31+G (d, p)	6-311G
HOMO (eV)	-7.6	-6.3	-6.5	-6.5	-8.7	-9.8	-9.8	-9.0
LUMO (eV)	-0.82	-1.12	-1.36	-1.44	2.72	1.58	1.55	2.29
Band gap energy (E_g) (eV)	6.80	5.14	5.17	5.09	11.43	11.37	11.35	11.27
Total energy (E_t) (a.u)	-1079	-1084	-1084	-1080	-1075	-1080	-1080	-1080
Dipole moment (Debye)	2.67	3.03	2.79	3.27	2.67	2.73	0.98	2.77
Electronegativity (χ) (eV)	4.2	3.7	3.9	4.0	3.0	4.1	4.1	3.3
Hardness (η) (eV)	3.4	2.6	2.6	2.5	5.7	5.7	5.7	5.6
Softness (S) $(eV)^{-1}$	0.15	0.19	0.19	0.20	0.09	0.09	0.09	0.09
Chemical potential (μ) (eV)	-4.2	-3.7	-3.9	-4.0	-3.0	-4.1	-4.1	-3.3
Electrophilicity (ω) (eV)	2.6	2.6	3.0	3.1	0.8	1.5	1.5	1.0

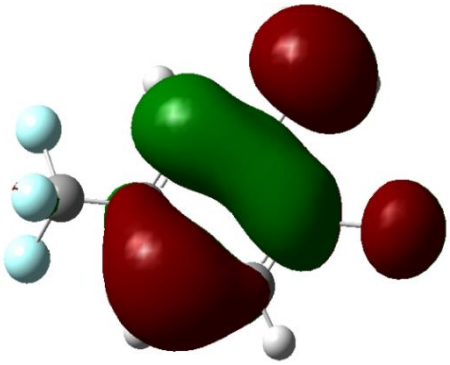
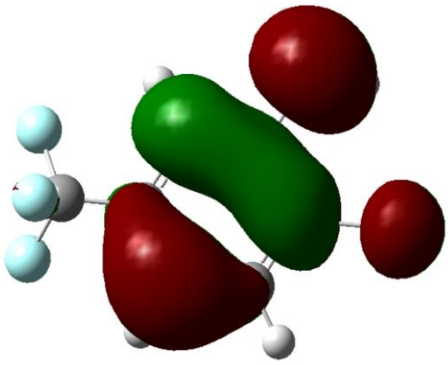
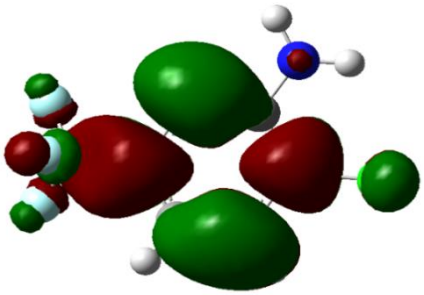
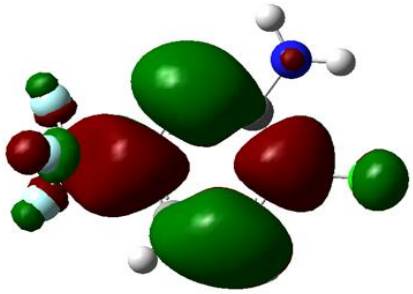
Basis set (3-21G) HFT	Basis set (3-21G) DFT
	
HOMO energy = - 8.7 eV	HOMO energy = -7.6 eV
Band gap energy = 11.43 eV	Band gap energy = 6.80 eV
LUMO energy = 2.72 eV	LUMO energy = -0.82 eV
	

Figure 4.13. Frontier Molecular Orbital energy of $C_7F_3NH_5Cl$ with (3-21G) basis set by DFT and HFT method

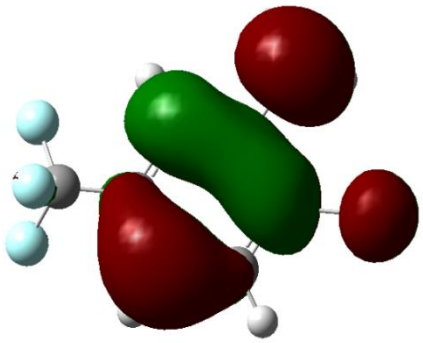
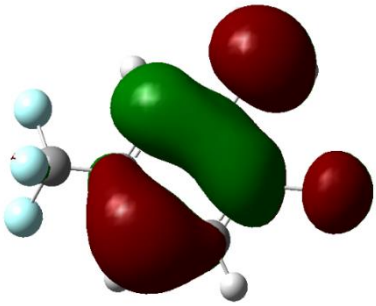
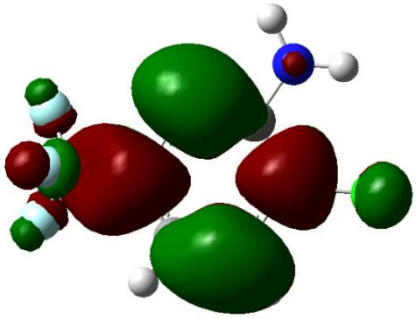
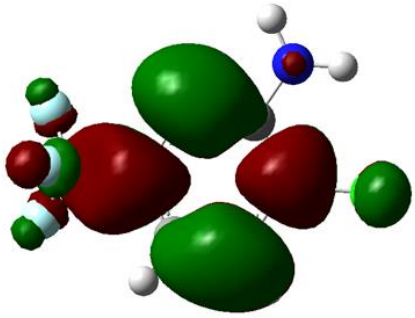
Basis set (6-31) HFT	Basis set (6-31G) DFT
	
HOMO energy = -9.8 eV	HOMO energy = -6.3 eV
Band gap energy = 11.37 eV	Band gap energy = 5.14 eV
LUMO energy = 1.58 eV	LUMO energy = -1.12 eV
	

Figure 4.14. Frontier Molecular Orbital energy of $C_7F_3NH_5Cl$ with (6-31+G (d, p)) basis sets by DFT and HFT methods

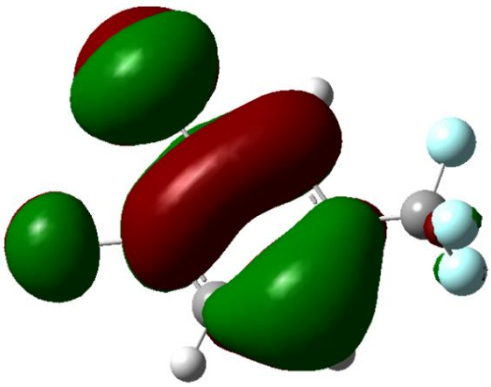
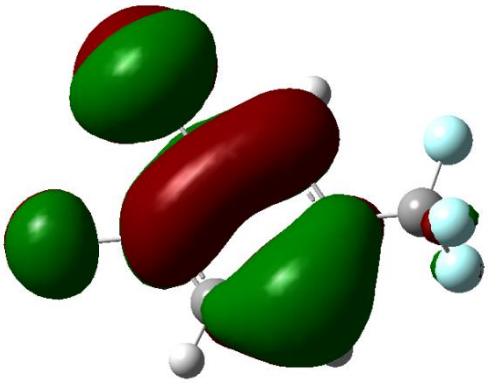
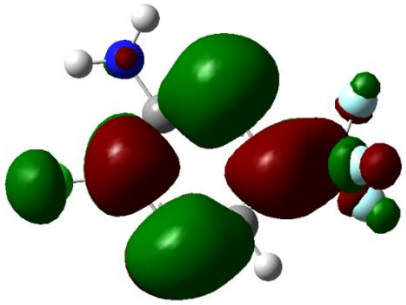
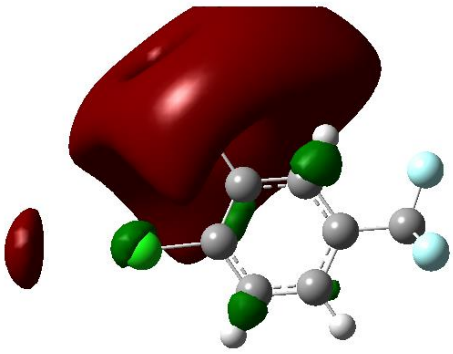
Basis set (6-31+G (dp)) HFT	Basis set (6-31+G (d, p)) DFT
	
HOMO energy = -9.8 eV	HOMO energy = -6.5 eV
Band gap energy = 11.35 eV	Band gap energy = 5.17 eV
LUMO energy = 1.55 eV	LUMO energy = -1.36 eV
	

Figure 4.15. Frontier Molecular Orbital energy of $C_7F_3NH_5Cl$ with (6-31G) basis sets by DFT and HFT methods

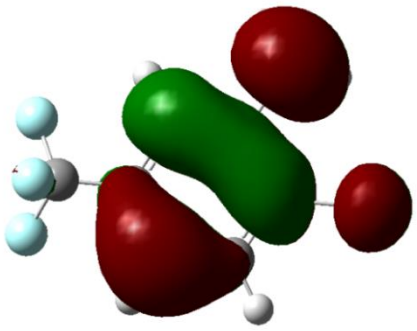
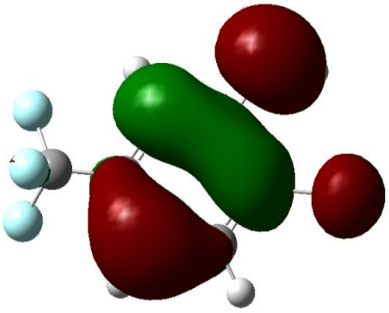
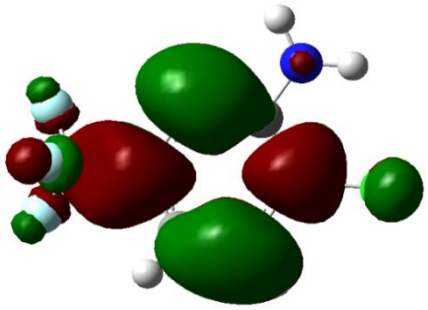
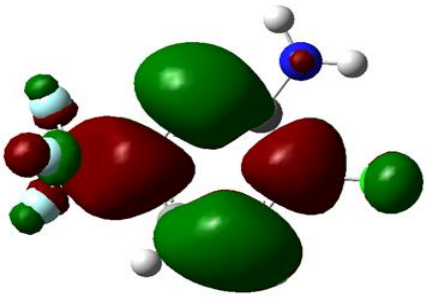
Basis set (6-311G) HFT	Basis set (6-311G) DFT
	
HOMO energy = -9.0 eV	HOMO energy = -6.5 eV
Band gap energy = 11.27 eV	Band gap energy = 5.09 eV
LUMO energy = 2.29 eV	LUMO energy = -1.44 eV
	

Figure 4.16. Frontier Molecular Orbital energy of $C_7F_3NH_5Cl$ with (6-311G) basis sets by DFT and HFT methods

5. CONCLUSION

In this work, density functional theory (DFT) and hartree fock theory (HFT) were used to investigate the structural and electronic properties of these molecules such as (Cyclobutadiene (C_4H_4), Carbonyl chloride (Phosgene) ($COCl_2$), Propylbenzene (C_9H_{12}), and 2-*chloro*-5-(trifluoromethyl) aniline ($C_7F_3NH_5Cl$). The frontier molecular orbital (LUMO, HOMO) energy, Energy gap (E_g), Total energies (E_t), Chemical potential (μ), Electronegativity (χ), Hardness (η), Softness (S), Dipole moment (D), and Electrophilic (ω) have been calculated by DFT and HFT with difference basis sets like (B3LYP/3-21G, 6-31+G(d, p), 6-31G,6-311G) via gaussian 09 software. The higher frontier orbital gaps specify that the molecules have more kinetic stability and low chemical reactivity. The calculations by the DFT are convenient result compared HFT, and the rate of accuracy increase by increasing the basis sets. The strong agreement was obtained for the dipole moments for the whole compounds between theoretical and experimental results.

RECOMMENDATION

This chapter presents the recommendation made as an outgrowth of this study. In our work about the investigation of quantum chemical parameters of some molecules, I will suggest that, for theoretical calculations density functional theory is proper method compared to hartree fock theory. As well as, quantum chemistry parameters of a larger molecules should be studied in future and these molecules must synthesize experimentally.

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ACADEMIC ACTIVITIES

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Second Article: I. N. QADER, A. Mohammed, Y. H. AZEEZ, Chemical Structural and Vibrational Analysis of Potassium Acetate: A Density Function Theory Study, 2019, J Journal of Physical Chemistry and Functional Materials, 2 (1), 22-24.