

IN THE NAME OF GOD

**Ab initio Studies of Atomic and Molecular Properties**

BY  
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To

My Parents

My husband

&

My Son

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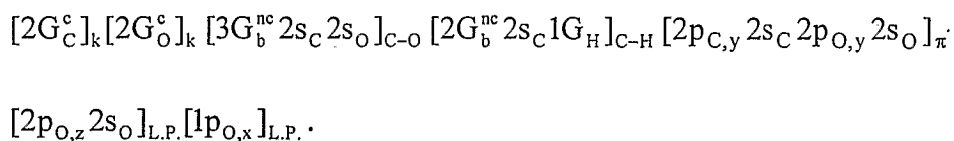
## *ABSTRACT*

### *Ab initio Studies of Atomic and Molecular Properties*

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In the first part of this research, chapter two, the improvement of  $\pi$ -molecular orbital description is the center of attention. The floating spherical gaussian orbital (FSGO) is found to be appropriate method for this type of investigation. Formaldehyde ( $\text{H}_2\text{CO}$ ) in which a non-symmetric  $\pi$ -system  $\text{C}=\text{O}$  is adjacent to lone pairs on oxygen has been chosen for this part. The best orbital description for different molecular orbitals in formaldehyde is:



In the second part, the concept of localization and delocalization of  $\pi$ -MOs has been examined in FSGO and SCF method. This part clearly

demonstrates that SCF method can only consider the delocalization phenomena, while FSGO can handle pictures, localization and delocalization. Cyclobutadiene has been chosen as a test for this section.

In Chapter three the application of density functional theory (DFT), on FSGO method is introduced for the first time. In this chapter our principal objective is to apply a combination of energy functionals to the FSGO densities. The functionals used are separated into exchange and correlation parts. For the exchange part the Becke exchange that includes gradient correction is used. The correlation part has been carried out using Lee, Yang and Parr gradient-corrected functional.

Three goals have been investigated in this chapter. First, is it possible to apply DFT in FSGO procedure to obtain electronic structure of chemical species? Second, is it stable condition from variational point of view during optimization of exponent and coefficient of gaussians? Third, when the above two questions are encouraging, are the results in consistent with other results in the literature? In this research we are looking for the acceptable answers to the above questions. The results demonstrate the possibility of combination of the FSGO method and DFT to have DFT-FSGO procedure. This new approach is stable variationally for the fully optimized electronic structure. Finally the results are in good agreement with other results in the literature and also the exact values.

Chapter four presents two subjects. The study of the electronic structure of some chemical species, such as,  $\text{FO} (^2\Pi)$ ,  $\text{O}_2 (^2\Pi_g)$ ,  $\text{NO} (^2\Pi)$ ,  $\text{O}_2^+ (^2\Pi_g)$  and  $\text{N}_2\text{O}$ , which have three or five electrons in their bonds is the first subject. We have found that it is difficult to represent the electronic structure of these molecules by current theories such as Lewis's, Pauling's and Linnett's. Hence, the second subject, as a first step, is to introduce a new representation (notation) for electronic structure of chemical species based on modern quantum chemistry, which represents the nature of electronic density of chemical compounds correctly. The importance of this new representation leads the chemists to make appropriate decisions for reactions mechanisms.

In chapter five we are interested in studying the possibility of association of different molecules having multi dihydrogen bonds (MDHB). In this research, this possibility was investigated using theoretical evidence. Three *ab initio* methods, RHF, B3LYP and MP2, have been applied in this study in which the basis set superposition error (BSSE) correction is also considered. The interaction of  $\text{SiH}_4$  and  $\text{NH}_4^+$  can make six possible kind of multi dihydrogen bonds, while the interaction of  $\text{SiH}_4$  with  $\text{H}_3\text{O}^+$  gives two and with  $\text{FH}_2^+$  yields only one

kind of MDHB. We also found that  $\text{BH}_3$  cannot make multi dihydrogen bond with  $\text{NH}_3$ , although it may form with  $\text{NH}_4^+$ .

In chapter six the theory of perturbational self-consistent field procedure are presented. This approach will ease the theory of configuration interaction (CI) by looking the problem in single particle approach. In this research the second and the third order of perturbation energies are added to the HF energy. Applying the HF procedure, constructing the functional  $J$  with the orthogonality constraint and minimizing the energy by  $\delta J = 0$ , yields the Fock operator, which includes perturbational terms (second and third order). This new approach has been programmed and were applied for three atoms and three molecules

## TABLE OF CONTENTS

Content	Page
LIST OF TABLES	XI
LIST OF FIGURES	XIII
CHAPTER 1. INTRODUCTION AND QUANTUM CHEMISTRY BACKGROUND	
1-1. Introduction	1
1-2. Schrödinger Equation	2
1-3. <i>Ab initio</i> Methods	5
1-3-1. Hartree-Fock Method	5
1-3-2. Post Hartree-Fock Methods	7
1-3-2-1. Configuration Interaction (CI)	8
1-3-2-2. Møller-Plesset Perturbation Theory (MPPT)	11
1-3-3. Density Functional Theory (DFT)	12
1-3-4. Basis Sets	14
1-3-5. Floating Spherical Gaussian Orbital(FSGO) Method	18
1-3-5-1. Basis set nomenclature in FSGO method	26
CHAPTER 2. LOCALIZATION AND DELOCALIZATION PROBLEM	
2-1. Introduction	29
2-2. Literature Survey	31
2-3. Objective	33
2-4. Definitions	34
2-5. Non-Symmetric $\pi$ -Bond Adjacent to Lone Pair	37
2-6. Study of Localization and Delocalization of $\pi$ -Bond in Cyclobutadiene	43
2-7. Conclusion	49
CHAPTER 3. DENSITY FUNCTIONAL THEORY ON FSGO METHOD	
3-1. Introduction	55



Content	Page
3-2. Energy expression in quantum chemistry	58
3-3. Historical background of density functional theory	60
3-3-1. The original idea: Thomas-Fermi model	60
3-3-2. The Hohenberg-Kohn theorem	62
3-3-3. The Kohn-Sham method	65
3-3-4. The $v$ - and $N$ -representability of an electron density	67
3-4. Local density approximation	69
3-5. Gradient corrections to LDA	70
3-6. Lee-Yang-Parr correlation energy	71
3-7. Application of density functional theory on FSGO method	73
3-7-1. Procedure	74
3-7-2. Numerical integration	75
3-8. Results and Discussions	81
3-9. Conclusion	84
CHAPTER 4. <i>AB INITIO</i> STUDY OF THREE- AND FIVE-ELECTRON BOND MOLECULES; AND INTRODUCING A NEW CHEMICAL REPRESENTATION	
4-1. Introduction	85
4-2. Part 1. <i>Ab initio</i> study of three- and five-electron bonds molecule	86
4-2-1. Literature review	86
4-2-2. Results and discussion	88
4-3. Part2. Introducing a new chemical representation	101
4-3-1. Literature review	101
4-3-2. Chemical representation	106
4-4. Conclusion	109
CHAPTER 5. <i>AB INITIO</i> STUDY OF MULTI DIHYDROGEN BONDS	
5-1. Introduction	111
5-2. Historical Perspective	112
5-3. Computational method	115
5-4. Results and discussions	115
5-4-1. Geometries	118
5-4-2. Basis set superposition error (BSSE)	120

<b>Content</b>	<b>Page</b>
5-4-3. Interaction energies	121
5-5. Conclusion	125
<b>CHAPTER 6. PERTURBATIONAL SELF-CONSISTENT FIELD THEORY</b>	
6-1. Introduction	126
6-2. The formalism of perturbation theory	129
6-3. Fock operator in HF method	130
6-4. Fock operator in perturbational HF method	132
6-5. Results and discussions	138
REFERENCES	140
ABSTRACT AND TITLE PAGE IN PERSIAN	150

## LIST OF TABLES

Table	Page
Table 2-1. Delocalization of Formaldehyde obtained at HF/6-311G** level of theory	40
Table 2-2. Comparison of our results with different calculations and experiment in Formaldehyde	41
Table 2-3. The results of optimized exponents, positions and coefficients of gaussians for model 5 in H <sub>2</sub> CO	42
Table 2-4. The results of different calculations on cyclobutadiene	51
Table 2-5. The results of optimized exponents, positions and coefficients of gaussians for FSGO/Square on cyclobutadiene	52
Table 2-6. The results of optimized exponents, positions and coefficients of gaussians for FSGO/Rectangle on cyclobutadiene	53
Table 2-7. The results of optimized exponents, positions and coefficients of gaussians for delocalized FSGO/Rectangle in cyclobutadiene	54
Table 3-1. Becke exchange energy ( $E_x^B$ ), LYP correlation energy ( $E_c^{LYP}$ ) and total energy ( $E_T$ ) of some atomic and ionic species	81
Table 4-1. The results of optimized exponents, positions and coefficients of gaussians of $\alpha$ -set in FO	92
Table 4-2. The results of optimized exponents, positions and coefficients of gaussians of $\beta$ -set in FO	93
Table 4-3. The results of optimized exponents, positions and coefficients of gaussians of $\alpha$ -set in O <sub>2</sub> <sup>-</sup>	94

<b>Table</b>	<b>Page</b>
Table 4-4. The results of optimized exponents, positions and coefficients of gaussians of $\beta$ -set in $O_2^-$	95
Table 4-5. The results of optimized exponents, positions and coefficients of gaussians of $\alpha$ -set in NO	96
Table 4-6. The results of optimized exponents, positions and coefficients of gaussians of $\beta$ -set in NO	97
Table 4-7. The results of optimized exponents, positions and coefficients of gaussians of $\alpha$ -set in $O_2^+$	98
Table 4-8. The results of optimized exponents, positions and coefficients of gaussians of $\beta$ -set in $O_2^+$	99
Table 4-9. Energy, bond length, dipole moment and order of $\alpha$ - and $\beta$ -orbital energy for FO, $O_2^-$ , NO, $O_2^+$	100
Table 4-10. Bond order of different spin and the chemical representation for FO, $O_2^-$ , NO, $O_2^+$ at B3LYP/6-311G** level	110
Table 5-1. Optimized geometry of different multi-hydrogen bond interactions	119
Table 5-2. Total energies, basis set superposition error (BSSE) and the corrected-interaction energies of different multi-hydrogen bond interactions by three methods	123
Table 5-3. Total energies of the interactiong species in different method by 6-311G**	124
Table 6-1. Second and third order Goldstone diagram	133
Table 6-2. The calculated HF and second order perturbational HF Energy (SPHF) (in Hartree)	139

## *LIST of FIGURES*

<b>Figure</b>	<b>Page</b>
Figure 2-1. Different structures of cyclobutadiene	46
Figure 4-1. Arrangement of seven electrons as two tetrahedral with a common apex	102
Figure 4-2. Arrangement of six electrons as two tetrahedral having a common edge	102
Figure 4-3. Arrangement of five electrons as two tetrahedral with a common face	102
Figure 5-1. The structure of different multi dihydrogen bond interactions	117

## *Chapter 1*

### *Introduction and quantum mechanics background*

#### *1-1 Introduction*

Chemistry is a science dealing with construction, transformation and properties of molecules. Theoretical chemistry techniques, especially quantum mechanics based methods can in principle be applied to these issues at very high accuracy if the appropriate calculations could be carried out. On the other hand, the concepts introduced by quantum mechanics have given the chemist a new and powerful language with which to interpret chemical observations. This language has continued to grow in volume and usefulness.

Some concepts such as zero point energy, atomic and molecular orbitals, electronic structures and *etc* are used in the every day work of a chemist. None of these concepts can be adequately understood without a good grasp of quantum mechanics. Computational chemistry is a generic phrase which covers a wide range of computational methods, approximations and procedures to calculate structure, reactivity, and

many other properties of atomic and molecular systems. These methods apply to atoms, small molecules, macromolecules and polymers and solids.

### *1-2 Schrödinger equation*

Every quantum particle is described by a wave function. In 1925 Erwin Schrödinger developed the differential equation, which governs the dynamical behavior of quantum mechanical systems. By solving the Schrödinger's equation, one can find a series of valuable and useful information about the system in hand.

Atom is a system of  $n$  electrons, interacting with each other and moving in the coulomb field of the nucleus. The state of the system is described by a state function:

$$\Psi = \Psi(x_1, x_2, \dots, x_n, t) \quad (1-2-1)$$

where  $(x_1, x_2, \dots, x_n)$  are the particle coordinates, and  $t$  is the time. The state function is such that  $\Psi^* \Psi dv$  gives the probability that at time  $t$ , electron 1 exists in the  $x_1$  position within the volume element  $dx_1$  and so forth ( $dv = dx_1, \dots, dx_n$ ).

The time dependent Schrödinger equation for the development of the state function is: