IN THE NAME OF GOD

Ab initio Studies of Atomic and Molecular Properties

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THESIS

SUBMITTED TO THE SCHOOL OF GRADUATE STUDIES IN
PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE
DEGREE OF DOCTOR OF PHYLOSOPHY (Ph.D.)

IN
PHYSICAL CHEMISTRY
SHIRAZ UNIVERSITY
SHIRAZ, IRAN

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January 2003

To

My Parents

My husband

&

My Son

ACKNOWLEDGMENT

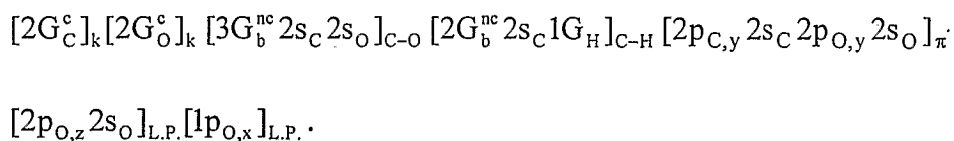# ABSTRACT

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In the first part of this research, chapter two, the improvement of π-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. Formaldeyhde (H_2CO) in which a non-symmetric π-system C=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:

$$[2G_C^c]_k [2G_O^c]_k [3G_b^{nc} 2s_C 2s_O]_{C-O} [2G_b^{nc} 2s_C 1G_H]_{C-H} [2p_{C,y} 2s_C 2p_{O,y} 2s_O]_\pi$$

$$[2p_{O,z} 2s_O]_{L.P.} [1p_{O,x}]_{L.P.}.$$

In the second part, the concept of localization and delocalization of π-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, $FO\,(^2\Pi), O_2^-\,(^2\Pi_g)$, $NO\,(^2\Pi), O_2^+\,(^2\Pi_g)$ and N_2O, 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 SiH_4 and NH_4^+ can make six possible kind of multi dihydrogen bonds, while the interaction of SiH_4 with H_3O^+ gives two and with FH_2^+ yields only one

kind of MDHB. We also found that BH_3 cannot make multi dihydrogen bond with NH_3, although it may form with 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

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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:

$$\Psi = \Psi(x_1, x_2, ... x_n, t) \qquad (1\text{-}2\text{-}1)$$

where $(x_1, x_2, ... x_n)$ 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 ($dv = dx_1, ... dx_n$).

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