CHAPTER ONE

Introduction and

Quantum Mechanics Background

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1-1 General Introduction

With the development of quantum mechanics, an amazing change occurred in chemistry. The application of quantum mechanics to chemistry leads to a new subdiscipline in chemistry-quantum chemistry, as foretold by Dirac's famous statement:

> "The underlying physical laws necessary for the mathematical theory of a large part of physics and whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble. It therefore becomes desirable that approximate practical methods of applying quantum mechanics should be developed, which can lead to an explanation of the main features of complex atomic systems without too much computation." [1]

The development of quantum chemistry enables us to study larger and larger chemical systems with the aid of computational tools. As the fundamental basis of quantum chemistry, Schrödinger's equation uses the N-electron wave function contains all the information we can possibly know about the system it describes.

Chemical structures and reactions are simulated numerically by computational algorithms that are based on the fundamental laws of physics. Chemists can study a chemical event by running calculations on computers rather than by doing reactions and synthesizing compounds experimentally. Unstable intermediates and transition states can be modeled by computational chemistry, which can provide information about molecules and reactions that is impossible to obtain through observation alone.

If we are interested in describing the electron distribution in detail, there is no way other than quantum mechanics. Electronic structure methods use quantum mechanics rather than classical physics. Electrons are very light particles and cannot be described correctly by classical mechanics. Quantum mechanics implies that the energy and the other properties of a molecule can be obtained by solving the Schrödinger equation [2-4].

1-2 The Schrödinger Equation

The Austrian physicist Erwin Schrödinger proposed an equation to find the wavefunction and energy of any system in 1926. The Schrödinger equation for a particle of mass m moving in one dimension with energy E is given in eq 1.1.

$$-\frac{\eta^2}{2m}\frac{d^2\Psi}{dx^2} + V(x)\Psi = E\Psi \qquad (1.1)$$

$V(x)$ is the potential energy of the particle and depends on the position x; ħ (ħ $=h/2\pi$, h is Planck's constant) and Ψ is the wave function of the system with respect to time.

The energy and many other properties of the particle can be obtained by solving the Schrödinger equation. For many real-world problems, the energy distribution does not change with time t, and it is useful to determine how the stationary states change with position x (independent of the time t). For every time-independent Hamiltonian Ĥ, there exist a set of quantum states, Ψ_n, known as energy eigenstates and corresponding real numbers E_n. Such a state has a definite total energy, whose value E_n is the eigenvalue of the state vector with the Hamiltonian Ĥ. This eigenvalue equation is referred to as the time-independent Schrödinger equation. Equation 1.1 is a non-relativistic description of the system, which is not valid when the velocities of particles approach the speed of light.

1-3 The Born-Oppenheimer Approximation

As nuclei are much heavier than electrons, their velocities are much smaller. Therefore, the Schrödinger equation can be separated into two parts; one part describes the electronic wave function for a fixed nuclear geometry, and another part describes the nuclear wave function, where the energy from the electronic wave function plays the role of a potential energy. This separation is called the Born-Oppenheimer (BO) approximation [2,3]. In another way, the nuclei look fixed to the electrons because they are heavier than electrons, and electronic motion can be described as occurring in a field of fixed nuclei in BO approximation.

The full Hamiltonian for the molecular system can be written as given in eq 1.2.

$$\hat{H} = \hat{T}_{elec} + \hat{T}_{nucl} + \hat{V}_{nucl-elec} + \hat{V}_{elec} + \hat{V}_{nucl} \tag{1.2}$$

T and V terms are kinetic and potential energy terms, respectively. The BO approximation allows solving two parts of the problem independently, so we can construct an electronic Hamiltonian which neglects the kinetic energy term from the nuclei as given in eq 1.3.

$$\hat{H}_{elec} = \hat{T}_{elec} + \hat{V}_{nucl-elec} + \hat{V}_{elec} + \hat{V}_{nucl} \tag{1.3}$$

This Hamiltonian is used in the Schrödinger equation to describe the motion of electrons in the field of fixed nuclei shown in eq 1.4.

$$\hat{H}_{elec} \Psi_{elec} = E_{eff} \Psi_{elec} \qquad (1.4)$$

Solving this equation for the electronic wavefunction will produce the effective nuclear potential function E_{eff}. It depends on the nuclear coordinates and describes the potential energy surface for the system. E_{eff} is also used as the effective potential for the nuclear Hamiltonian, shown in eq 1.5.

$$\hat{H}_{nucl} = T_{nucl} + E_{eff} \qquad (1.5)$$

This Hamiltonian is used in the Schrödinger equation for nuclear motion, to describe the vibrational, rotational, and translational states of the nuclei. Solving the nuclear Schrödinger equation approximately is necessary for predicting the vibrational spectra of molecules.

1-4 The Approximation Methods

The exact solutions for the Schrödinger equation are not computationally practical, due to repulsion terms and two-electron integrals. Therefore, various mathematical approximations are applied to solve the Schrödinger equation. There are three major classes of electronic structure methods: semiempirical methods [5,6], ab initio methods [7] and density functional methods [8].

a) Semiempirical methods: These methods use parameters derived from experimental data to simplify the computation. They solve an approximate form of the Schrödinger equation. Different semi-empirical

methods are classified by their approximations and parameter sets. Semi-empirical calculations are relatively inexpensive compared to ab initio calculations, and provide reasonable descriptions of molecular systems and fairly accurate in predictions of energies and structures for many systems. In this thesis, we didn't apply semiempirical methods at all.

b) Ab initio methods: These methods use no experimental parameters in their computations. Their computations depend on the laws of quantum mechanics. Ab initio computations provide high quality predictions for many systems.

c) Density functional methods: A third class of electronic structure methods used widely are called density functional methods (DFT). DFT methods are similar to ab initio methods. DFT methods are less expensive than the corresponding ab initio methods. Since they include the effects of electron correlation, they can give the benefits of some more expensive ab initio methods at a lower cost. In this thesis we applied this method, which are briefly discussed in the next chapter. The simplest way for Ab initio computation is Hartree-Fock that is described here.

1-5 Hartree-Fock Theory

Hartree-Fock theory [2,3] is one of the fundamental concepts of electronic structure theory. It depends on molecular orbital (MO) theory that uses one-

electron wave function to construct the full wave function. Hartree-Fock theory is not an exact theory: it is an approximation to the electronic Schrödinger equation. The approximation is that we assume that each electron feels only the average Coulomb repulsion of all the other electrons. This approximation makes Hartree-Fock theory much simpler than the real problem, which is an N-body problem. The advantage of this method is that it breaks the many-electron Schrödinger equation into many simpler one-electron equations. Each one electron equation is solved to yield a single-electron wave function, called an orbital, and energy, called an orbital energy. The orbital describes the behavior of an electron in the net field of all the other electrons.

The Hartee-Fock method generates solutions to the Schrödinger equation where the real electron-electron interaction is replaced by an average interaction. With sufficiently large basis sets, the HF wave function is able to account for 99% of the total energy, but the remaining 1% is often very important for describing chemical phenomena. The difference in energy between the HF and the lowest possible energy in a given basis set is called the Electron Correlation (EC) energy. The approximation can be corrected by explicitly accounting for electron correlation by density functional theory (DFT), many-body perturbation theory (MBPT) [9], configuration interaction (CI) [10,11], and other methods.

It is important to remember that these orbitals are mathematical constructions which approximate the reality. Only for hydrogen atom (or other one-electron systems, like He^+) orbitals are exact eigenfunctions of the full electronic Hamiltonian. As long as we consider molecules near their equilibrium geometry, Hartree-Fock theory often provides a good starting point for more elaborate theoretical methods which are better approximations to the electronic Schrödinger equation.

1-6 Restricted and Unrestricted Hartree-Fock

If the system has an even number of electrons and a singlet type of wave function (a closed-shell system), such wave function is known as Restricted Hartree-Fock (RHF) [12]. Open-shell systems may also be described by the restricted type wave functions where the doubly occupied orbitals is forced to be the same: this is known as Restricted Open-shell Hartree-Fock (ROHF) [12]. In other words, it uses doubly occupied molecular orbitals as far as possible and then singly occupied orbitals for the unpaired electrons

For open-shell systems, an unrestricted method [12], capable of treating unpaired electrons is needed. For this case, the alpha and beta electrons are in different orbitals, resulting in two sets of molecular orbital expansion coefficients. The two sets of coefficients result in two sets of Fock matrices and ultimately to a solution producing two sets of orbitals. These separate

orbitals produce proper dissociation to separate atoms, correct delocalized orbitals for resonant systems, and other attributes characteristic of open-shell systems. However eigenfunctions are not pure spin states, but contain some amount of spin contamination from higher states (for example, doublets are contaminated to some degree by states corresponding to quartets and higher states).

1-7 Basis Set

The approximation involves expressing the molecular orbitals as linear combination of a pre-defined set of one-electron functions known as basis functions [13]. These basis functions are usually centered on the atomic nuclei and so bear some resemblance to atomic orbitals. Larger basis sets more accurately approximate the orbitals by imposing fewer restrictions on the locations of the electrons in space. An individual molecular orbital is defined in eq 1.6,

$$\phi_i = \sum_{\mu=1}^{N} c_{\mu i} \chi_\mu \qquad (1.6)$$

where the coefficients $c_{\mu i}$ are known as the molecular orbital expansion coefficients. χ_μ refers to an arbitrary function in the same way ϕ_i refers to an arbitrary molecular orbital.

Ab initio methods try to derive information by solving the Schrödinger equation without fitting parameters to experimental data. Actually, ab initio methods also make use of experimental data, but in a somewhat more subtle fashion. Many different approximate methods exist for solving the Schrödinger equation, and the one to use for a specific problem is usually chosen by comparing the performance against known experimental data. Therefore, experimental data guides selection of the computational model, rather than directly entering the computational procedure.

Basis sets [3] are one of the approximations inherent in essentially all ab initio methods. Expanding an unknown function, such as a molecular orbital, in a set of known functions is not an approximation, if the basis set is complete. However, a complete basis set means that an infinite number of functions must be used, which is impossible in actual calculations. The smaller the basis, the poorer the representation.

There are two types of basis functions commonly used in quantum mechanical calculations. These are Slater-type orbitals (STO) [14] and Gaussian-type orbitals (GTO) [2,3]. STOs are not appropriate for numerical computations of multi-centered integrals for solving the Schrödinger equation due to high cost in computer time. Therefore their practical use in quantum-mechanical calculations is now limited. Even though most quantum mechanics programs use GTOs as basis functions, GTOs have difficulty in describing the

proper behavior near the nucleus. Nevertheless, GTOs have the important advantage that evaluating a GTO integral while solving the Schrödinger equation takes much less computer time than a STO integral evaluation. Therefore, GTOs are preferred and are generally used in computational calculations. STOs and GTOs functional forms are given in eq 1.7 and eq 1.8, respectively.

$$\phi_{\zeta,n,l,m}(r,\theta,\varphi) = NY_{l,m}(\theta,\varphi)r^{n-1}e^{-\zeta r} \qquad (1.7)$$

$$\phi_{\zeta,n,l,m}(r,\theta,\varphi) = NY_{l,m}(\theta,\varphi)r^{2n-2-l}e^{-\zeta r^2} \qquad (1.8)$$

N is a normalization constants and $Y_{l,m}$ are the usual spherical harmonic functions. The exponential dependence on the distance between the nucleus and the electron mirrors the exact orbitals for hydrogen atom. However, STOs do not have any radial nodes, nodes in the radial part are introduced by making linear combinations of STOs. The exponential dependence ensures a fairly rapid convergence with increasing number of functions, however, the calculations of three- and four-centre two- electron integrals cannot be performed analytically. After deciding the type of function (STO/GTO) and the location (nuclei), the most important factor is the number of functions to be used. Here, it is brief explanation of different basis sets.

a) **Minimal Basis Set:** The smallest number of functions possible is a minimum basis set that assigns one function to each orbital. For hydrogen and helium this means a single s-function. For the first row in the periodic table it means two s-functions (1s and 2s) and one set of p-functions ($2p_x$, $2p_y$ and $2p_z$).

For the second-row elements, three s-functions (1s, 2s and 3s) and two sets of p-functions (2p and 3p) are used.

b) Double Zeta Basis Sets: A minimal basis set has rather limited variational flexibility particularly if the exponents are not optimized. The first step in improving the minimal basis set involves using two functions for each of atomic orbitals, i.e. a double zeta set. The best orbital exponents of the two functions are commonly slightly above and slightly below the optimal exponent of the minimal $n = $ basis function. This allows effective expansion of the basis functions by variation of linear parameters rather than non linear exponents.

c) Split-valence basis sets: The split-valence basis sets are not exactly a double zeta basis since only the valence functions are doubled.

- 3-21G: The valence functions are split into one basis function with two GTOs, and one basis function with only one GTO. The core consists of three primitive GTOs contracted into one basis function.

- 6-31G: The core consists of six GTOs which are not split, while the valence orbitals are described by one orbital constructed from three primitive GTOs and one that is a single GTO.

d) Extended basis sets: The next step in improving basis sets could be adding polarization and diffusion functions. In the case of the scaling of the hydrogen

orbitals in the H_2 molecule, it was argued that the orbital on one other nucleus. However, it is also clear that the influence of the other nucleus. We clearly need orbitals that have more flexible shapes in a molecule than the s, p, d, etc. shapes in the free atoms. This is best accomplished by adding in basis functions of higher angular momentum quantum number. Thus, we can distort the spherical 1s orbital on hydrogen by mixing in an orbital with p symmetry. The positive lobe at one side increases the size of the orbital while the negative lobe at the other side decreases. The orbital has overally moved sideways and it has been polarized. Similarly we can polarize the p orbitals if we mix in an orbital of d symmetry. We can add polarization functions to the 6-31G basis set as follows:

- 6-31G*: adds a set of d functions to the atoms in the first and second rows (Li-Cl). For other rows, adds a set of additional basis functions with L = X+1, where X is the largest quantum number L in the basis set.

- 6-31G**: for example, adds a set of d functions to the atoms in the first and second rows (Li-Cl) and a set of p functions to hydrogen. For other rows the same as 6-31G*, but a set of additional functions are added to all atoms, including hydrogen.

Sometimes the normal basis functions we use are not adequate. This is particularly the case in excited states and in anions where the electronic density

is more spread out over the molecule. To model this correctly we have to use some basis functions which themselves are more spared out. This means GTOs with small exponents. These additional basis functions are called diffuse functions and cause increasing in the interaction board of different atoms. We normally add these as single GTOs, not contracting them together. We can add diffuse functions to the 6-31G basis set as follows:

- 6-31+G: adds a set of diffuse functions, for example, adds a set of s and p orbitals to the atoms in the first and second rows (Li-Cl). For other rows, adds a set of additional basis functions with $L = X+1$.

- 6-31++G: adds a set of diffuse functions, for example, adds a set of s and p orbitals to the atoms in the first and second rows (for other rows the same as 6-31+G) and a set of diffuse s functions to hydrogen.

Diffuse functions can also be added along with polarization functions. This leads, for example, to the 6-31+G*, 6-31++G*, 6-31+G** and 6-31++G** basis sets.

Basis sets for atoms beyond the third row of the periodic table are handled differently. For these very large nuclei, electrons near the nucleus are treated in an approximate way, via effective core potentials (ECPs) [12]. This treatment includes some relativistic effects, which are important in these atoms.

The ECPs and associated basis sets of Hay-Wadt [15], Stevens and co-workers [16], and Stuttgart-Dresden ECP [17] are widely used and implemented in many computational chemistry packages.

CHAPTER TWO

Theoretical Methods

Theoretical Methods

2-1 Quantum Theory of Atoms in Molecules

The quantum theory of atoms in molecules (QTAIM) [18] provides a connection between experimental chemistry and the quantum theory of electronic structure. In fact, the theory through its dependence on the important theorems of quantum mechanics provides a basis for many models whose origins are rooted in experimental chemistry. The theory of atoms in molecules enables one to take advantage of the single most important observation of chemistry, that of a functional group with a characteristic set of properties. In this document, we have shown that the topological analysis of $\rho(r)$, its first derivative (gradient field) $\nabla\rho(r)$, second derivative (Laplacian) $\nabla^2\rho(r)$ and energy of atoms in molecules reveals helpful information about the electronic structure of a molecule.

2-1-1 The Topology of the Electron Density

The QTAIM theory is based on a direct partitioning of the electron density in the physical space. The chemical bonds can also be characterized by various features of the electronic charge density [19].

Bader [20] could show that the virial theorem holds for defined atomic basins, which can be considered as a rigorous quantum theoretical proof that the model of discussing the chemical behavior of a molecule in terms of atomic properties is justified. The position of the atomic nucleus is defined in the QTAIM model as a critical point in the three-dimensional space where the first derivatives $\nabla\rho(r)$ are zero and the principle curvatures (eigenvalues) of the associated second derivatives of $\rho(r)$ are all negative. Other critical points at which the gradient of the electron density $\nabla\rho(r)$ vanishes define bonds, rings, and cages. The zero-flux surfaces which separate the atomic basins are defined as the gradient vector field whose trajectories of $\nabla\rho(r)$ do not vanish at the atomic nuclei but at the bond critical point. A bond critical point (BCP) has two negative and one positive eigenvalues of the second derivatives of $\rho(r)$. The trajectory which belongs to the positive eigenvalue connects the BCP and the bonded atomic nuclei. It is called the bond path and thus gives a physically sound description of the skeletal structure of the molecule in terms of atomic nuclei and chemical bonds.

The Laplacian at the BCP is the sum of the three curvatures of the density at the critical point, the two perpendicular to the bond path, being negative whereas the third, lying along the bond path, is positive. The negative curvatures measure the extent to which the density is concentrated along the bond path and the positive curvature measures the extent to which it is depleted in the region of the interatomic surface and concentrated in the individual atomic basins.

In covalent bonding the two negative curvatures are dominant and $\nabla^2\rho(r) \langle 0$. In contrast, in closed-shell bonding the interaction is characterized by a depletion of density in the region of contact of the two atoms and $\nabla^2\rho(r) \rangle 0$. In strongly polar bonding there is a significant accumulation of electron density between the nuclei, as in all shared interactions, but the Laplacian in this type of bonding can be of either sign.

2-1-2 The Energy of an Atom in Molecule

Energy densities require information contained in the one-electron density matrix (and not just the density, its diagonal elements). The energy densities (potential, kinetic, and total) are used to summarize the mechanics of a bonding interaction. The potential energy density, V(r), also known as the virial field, is the average effective potential field experienced by a single electron at point r in a many particle system. The virial field evaluated at any