CHAPTER 2

THEORETICAL BACKGROUND

2.1 Solution of Schrödinger Equation of Molecular Systems

2.1.1 The Schrödinger Wave Equation [24,25]

The energy and properties of the stationary state of a molecule can be obtained from the solution of the Schrödinger equation,

$$\hat{H}\Psi = E\Psi \tag{2.1}$$

Here $\hat{H}$ is the Hamiltonain operator. E is the eigenvalue representing the energy of the state. Ψ is the wavefunction which is the function of spatial and spin coordinates of all particles. The probability distribution of the particles within the molecule is interpreted by $|\Psi|^2$.

The Hamiltonian $\hat{H}$, like the energy in classical mechanics, is the sum of kinetic ($\hat{T}$) and potential ($\hat{V}$) operators,

$$\hat{H} = \hat{T} + \hat{V} \tag{2.2}$$

where for a molecule

$$\hat{T} = \hat{T}_n + \hat{T}_e$$

$$= -\sum_{A=1}^{N} \frac{1}{2M_A} \nabla_A^2 + \sum_{i=1}^{n} \frac{1}{2} \nabla_i^2 \qquad (2.3)$$

and

$$\hat{V} = \hat{V}_{ne} + \hat{V}_{ee} + \hat{V}_{nn}$$

$$= -\sum_{i=1}^{n} \sum_{A=1}^{N} \frac{Z_A}{r_{iA}} + \sum_{i=1}^{n} \sum_{j<i}^{n} \frac{1}{r_{ij}} + \sum_{A=1}^{N} \sum_{B<A}^{N} \frac{Z_A Z_B}{R_{AB}} \qquad (2.4)$$

The Hamiltonian described above is in the nonrelativistic form, which ceases to be appropriated as the velocities of the particles, particularly electrons, approach the velocity of light. Certain small magnetic effects, for example, spin-orbital coupling, spin-spin interactions, and so forth, are also omitted in this Hamiltonian.

2.1.2 The Born-Oppenheimer Approximation

From (2.2) to (2.4), the molecular Hamiltonian is,

$$\hat{H} = \sum_{i=1}^{n} \frac{1}{2} \nabla_i^2 - \sum_{A=1}^{N} \frac{1}{2M_A} \nabla_A^2 - \sum_{i=1}^{n} \sum_{A=1}^{N} \frac{Z_A}{r_{iA}} + \sum_{i=1}^{n} \sum_{j<i}^{n} \frac{1}{r_{ij}} + \sum_{A=1}^{N} \sum_{B<A}^{N} \frac{Z_A Z_B}{R_{AB}} \qquad (2.5)$$

where A and B refer to nuclei and i and j refer to electrons. The first term in (2.5) is the operator for the kinetic energy of the electrons. The second term is the operator for the kinetic energy of the nuclei. The third term is the electron-nuclear attraction where r_{iA} being the distance between electron i and nucleus A. The fourth term is the electron-electron repulsion where r_{ij} being the distance between electrons i and j. The last term is the nuclear-nuclear repulsion where R_{AB} being the distance between nuclei A and B with atomic numbers Z_A and Z_B.

Due to the complexity of the Schrödinger equation for molecular systems which involved both nuclear and electron coordinates, an approximation is, therefore, needed. Since nuclei are much heavier than electrons, they move more slowly. Hence, one can consider electrons in a molecule as moving in the field of fixed nuclei. Within this approximation, the second term of equation (2.5), that is the kinetic energy of the nuclei, can be neglected and the term representing the repulsion between nuclei can be considered as a parameter that its value depends on internuclear distance R. This approximation is called "*Born-Oppenheimer approximation*". The Hamiltonian that omits the nuclear kinetic energy terms from (2.5) is called "*purely electronic Hamiltonian*, $\hat{H}^{el}$ "

$$\hat{H}^{el} = \sum_{i=1}^{n} \frac{1}{2} \nabla_i^2 - \sum_{i=1}^{n} \sum_{A=1}^{N} \frac{Z_A}{r_{iA}} + \sum_{i=1}^{n} \sum_{j>i}^{n} \frac{1}{r_{ij}} \tag{2.6}$$

The solution of the Schrödinger equation involving the electronic Hamiltonian is given as

$$\hat{H}^{el} \Psi^{el} = E^{el} \Psi^{el} \tag{2.7}$$

Ψ^{el} is the electronic wavefunction, which describes the motion of electrons in the field of fixed nuclei. The total energy E^{total} of the system of a given set of internuclear distance is then given as

$$E^{total} = E^{el} + \sum_{A=1}^{N} \sum_{B<A}^{N} \frac{Z_A Z_B}{r_{AB}} \tag{2.8}$$

2.1.3 The Hartree-Fock Wavefunction

From the equation 2.6 the electronic Hamiltonian is the function of only spatial coordinates of the electrons. To specify electron spin, it is necessary to introduce two spin functions, $\alpha(\omega)$ and $\beta(\omega)$, corresponding to spin up and down, respectively. These two spin functions form complete set and are orthonormal. The wavefunction for an N-noninteracting-electron system or the Hartree product is given as

$$\psi = \chi_1(1)\chi_2(2)\cdots\chi_N(N),\qquad(2.9)$$

where $\chi_i(i)$ is the function of space and spin coordinates of electron i $\chi_i(\vec{r},\bar{\omega}_i)$, called the spin orbital. According to the antisymmetry principle, many-electron wavefunction must be antisymmetric with respect to the interchange of the coordinate of any two electrons,

$$\psi(\chi_1(1)\cdots\chi_i(i)\cdots\chi_j(j)\cdots\chi_N(N)) = -\psi(\chi_1(1)\cdots\chi_j(j)\cdots\chi_i(i)\cdots\chi_N(N))$$

$$(2.10).$$

This requirement is a very general statement of the Pauli exclusion principle. The wave function of (2.9) is not antisymmetric. Using properties of determinant, the Hartree-Fock wavefunction in which the exchange of any row or column changes the sign of determinant could be formed,

$$\psi = \frac{1}{\sqrt{(n)!}}\begin{vmatrix} \chi_1(1) & \chi_2(1) & \chi_3(1) & \cdots & \chi_n(1) \\ \chi_1(2) & \chi_2(2) & \chi_3(2) & \cdots & \chi_n(2) \\ \chi_1(3) & \chi_2(3) & \chi_3(3) & \cdots & \chi_n(3) \\ \vdots & \vdots & \vdots & \cdots & \vdots \\ \chi_1(n) & \chi_2(n) & \chi_3(n) & \cdots & \chi_n(n) \end{vmatrix}$$

or

$$= \frac{1}{\sqrt{(n)!}} \begin{vmatrix} \psi_1(1)\alpha(1) & \psi_1(1)\beta(1) & \psi_2(1)\alpha(1) & \cdots & \psi_{n/2}(1)\beta(1) \\ \psi_1(2)\alpha(2) & \psi_1(2)\beta(2) & \psi_2(1)\alpha(1) & \cdots & \psi_{n/2}(2)\beta(2) \\ \psi_1(3)\alpha(3) & \psi_1(3)\beta(3) & \psi_2(1)\alpha(1) & \cdots & \psi_{n/2}(3)\beta(3) \\ \vdots & \vdots & \vdots & \cdots & \vdots \\ \psi_1(n)\alpha(n) & \psi_1(n)\beta(n) & \psi_2(1)\alpha(1) & \cdots & \psi_{n/2}(n)\beta(n) \end{vmatrix} \qquad (2.11)$$

This determinant is also called "Slater determinant". Since $\chi_j(k)$ is the spin orbital j of electron k which called one-electron spin orbital. It is consisted of spatial part or molecular orbital (MO) and spin functions. For the spatial part, 2 different assignments of orbital can be made *i.e.* the restricted orbital where the paired α and β electrons are assigned the same spatial part and the unrestricted orbital where the paired α and β electrons are assigned different spatial part. The Hartree-Fock wavefunction that uses restricted orbitals is called "Restricted Hartree-Fock" (RHF) and that used unrestricted orbital is called "Unrestricted Hartree-Fock" (UHF).

2.1.4 Molecular Orbital and Introduction of Basis set

The molecular orbitals $\psi_1, \psi_2, \ldots$ in equation (2.11) can be written in term of the linear combinations of orthogonal function which forms the complete set.

$$\psi_i = \sum_{\mu=1}^{N} c_{\mu i} \phi_\mu \qquad (2.12)$$

The $\phi_1, \phi_2, \ldots, \phi_N$ are the orthogonal function with known expression. The set of this function is called "basis set".

The best solution to the approximation of MO could theoretically be obtained by the use of an infinite and complete set of basis functions. The most often used mathematical expressions for the basis functions are the Slater-type orbital (STO) and the Gaussian-type orbitals (GTO).

The Slater-type orbitals has the form

$$\phi^{STO} = r^{n-1} e^{-\varsigma r} Y_l^m(\theta, \phi) \qquad (2.13)$$

where n, l, m are quantum numbers and ς is orbital exponent. The r, θ, ϕ are the spherical polar coordinates. This Slater functions were introduced by Slater [26] and extremely close in form to the hydrogenic orbitals. In the past, they were mostly used for the calculations of small molecules. Their advantage is that only few functions are needed for a good description, but not suited to the numerical work, and their use in practical molecular orbital calculations has been limited.

The Gaussian-type orbitals has the form

$$\phi^{GTO} = x^a y^b z^c e^{-ar^2} \qquad (2.14)$$

where a, b, c are integer number and α is orbital exponent. The x, y, z are the Cartesian coordinates. The GTO were introduced into molecular orbital calculations by Boy [27]. They are less satisfactory than STO as representations of atomic orbital, particularly because they do not have a cusp at the origin (Figure 2.1). Due to this deficiency more than one GTOs are often required for a good description. At present, most calculation performed uses GTOs instead of STOs since the computation of GTO is much faster than that of the STO. So, as many GTO functions, which yields the same quality to the STO can be computed in the fraction of time.
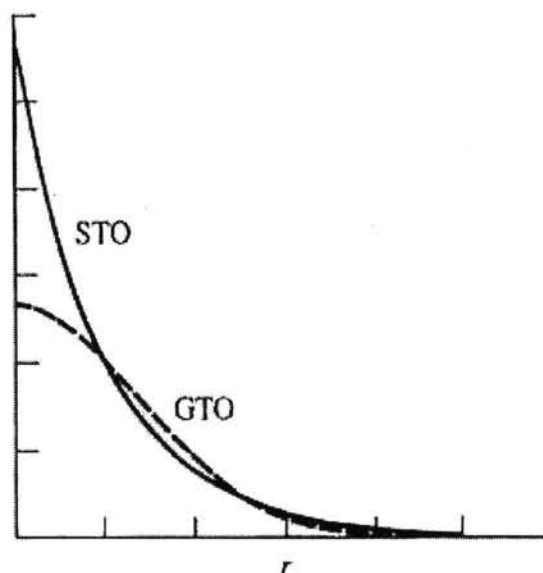
Figure 2.1 The cusp of Slater function.

2.2 Basis set [24,28]

2.2.1 Minimal Basis sets

A minimal basis set is a representation that contains just the number of functions that are required to accommodate all the filled orbitals in each atom. In practice, a minimal basis set normally includes all of the atomic orbitals in the shell. Thus, for hydrogen and helium a single s-type function would be required. For elements from lithium to neon the 1s, 2s and 2p functions are used and so on. The basis sets STO-nG for example, STO-3G, STO-4G, are all minimal basis sets in which n Gaussian functions are used to represent a Slater orbital. In fact, it is found that there is often a little difference between the result obtained with STO-3G basis set and the larger minimal basis set with more Gaussian functions. The only exception is for the case of where hydrogen-bonded complexes where STO-4G

performs significantly better. The minimal basis sets are well known to accompany with several deficiencies. There are particular problems with compounds containing atoms at the end of a period, such as oxygen or fluorine. Such atoms are described using the same number of basis functions as the atoms at the beginning of the period despite they have more electrons. A minimal basis set only contains one function per atomic orbital. Since the radial exponents are not allowed to vary during the calculation, the orbital cannot expand or contract in size in accordance with the molecular environment.

2.2.2 Extended Basis sets

The problems with minimal basis sets can be addressed if more than one function is used for each orbital. For STO, a basis set which doubles the number of functions in the minimal basis set is described as *double zeta* basis. The double or triple or more of STO minimal basis function allows the linear combination of the 'contracted' and the 'diffuse' functions which gives an overall result that is intermediate between the two. In other words, the size of orbital can be modified during the course of calculation. An alternative to the double zeta basis approach is to double the number of functions used to describe the valence electrons but to keep a single function for the inner shells called "split valence double zeta basis". For GTO, the similar notation like STO can also be used. The 3-21G exemplifies the notation used for such split valence double zeta basis sets. In this basis set, three Gaussian functions are used to describe the core orbitals. The valence electrons are also represented by three Gaussian; the contracted part by two Gaussian and the diffuse part by one Gaussian. The most commonly used split valence basis sets are 3-21G, 4-31G, and 6-31G. Other type of extended basis set is Dunning basis set [29] such as DZV and TZV.

2.2.3 Polarized basis set

Just simply increasing the number of basis functions does not necessarily improve the model. In fact, this possibly leads to a wholly erroneous result, particularly for molecules with strongly anisotropy charge distribution. All of the basis sets employed in modern quantum chemical calculations usually use functions that are centered on atomic nuclei. The use of split valence basis sets can help to overcome the problems with non-isolated atom. For instance, the electron cloud in an isolated hydrogen atom is symmetrical, but when the hydrogen atom is present in a molecule the electrons are drew towards the other nuclei. This distortion can be considered to correspond to mixing p-type character into the 1s orbital of the isolated atom, to give a form of sp hybrid. In a similar manner, the unoccupied d orbitals introduce asymmetry into p orbital. In other words, the addition of p function for H atom and d function for heavier atom enable orbitals on nuclei to polarize and form bond. These functions, p for hydrogen and d for 1st and 2nd row element, have a higher angular momentum and they are called the "polarization" function. An asterisk (*) indicates the use of polarization basis functions. Thus, 6-31G* refers to a 6-31G basis set with polarization functions on the heavy (non-hydrogen) atoms. Two asterisks, such as 6-31G** indicate the use of polarization functions on hydrogen and heavy atoms. For Dunning's type basis sets, the annexation of "P" at the end of basis set notation, for example DZVP and TZVP, is made to represent the polarized basis set.

2.2.4 Basis set incorporating diffuse function

Another deficiency of the basis sets is their inability to deal with species that have a significant amount of electron density away from the nuclear centers such as anions and molecules containing lone pair. This failure arises because the amplitudes of the Gaussian basis functions are rather low far from the nuclei. To

remedy this deficiency highly diffuse functions *i.e.* functions with very small exponent, is added to the basis set. These basis sets are denoted using a '+'; thus the 3-21G+ basis set contains an additional single set of diffuse s- and p-type Gaussian functions for heavy atoms. A '++' indicates that the diffuse functions are included also for hydrogen as well as for heavy atoms such 6-31G++.

2.3 Effective Core Potential (ECP) [30]

The tremendous cost of *ab initio* calculations, especially for atom with large atomic number, has motivated many attempts to find computational shortcuts. One such approach is based on the observation that core orbitals are relatively inert to changes in chemical bonding (the so called "frozen core approximation"). Another observation is that the effect of core electrons on the valence electron can be treated through the use of a potential energy term expressed as the sum of local functions multiplied by projection operators. Based on these two assumptions, effective core potentials (ECP's) or pseudopotentials, as they are sometimes called reduce the computational problems to deal with valence electron only. Most early results obtained from ECP's compared favorably with results obtained from all-electron calculations, although there was a tendency to find shorter bond lengths and somewhat deeper potential energy curves. An another advantage of ECP is that for atom with very high atomic number the quantum relativistic effect can be included to the ECP.

The generation of ECP's is performed as following:

1. The "core" orbitals to be replaced and the remaining "valence" orbitals are defined.

2. Numerical valence orbitals (ϕ'_l) are obtained from self-consistent Hartree-Fock calculations for $l = 0, 1, ..., L$, where L, in general, is one greater than the highest angular momentum quantum number of any core potential.

3. Smooth, nodeless pseudo-orbitals (ϕ'_l) are derived from the Hartree-Fock orbital (ϕ'_l) in a manner so that ϕ^i_l behaves as closely as possible to ϕ'_l in the outer, valence region of the atom.

4. Numerical effective core potentials U_l are derived for each l by demanding that ϕ_1 is a solution in the field of U_1 with the same orbital energy E_l as the orbital ϕ_1.

5. The numerical potentials are fitted in analytic form with Gaussian functions. The total potential is represented as

$$U(r) = U_L(r) + \sum_{l=0}^{L-1}[U_l(r) - U_L(r)]\hat{p}_l \tag{2.15}$$

where U_L, U_l is Gaussian functions,

$\hat{p}_l$ is projection operators,

r   is distance between atom.

6. The numerical pseudo-orbitals are also fitted to Gaussian functions to obtain basis sets for molecular calculations.

The example of ECP basis set is LANL2DZ [30] which uses full double zeta on first row element and Los Alamos ECP plus double zeta basis for Na-Bi.

2.4 Density Functional Theory [31]

The probability distribution of electrons which corresponds to the solution of the Schrödinger equation (2.1) can be presented as density matrix,

$$\gamma_N(x_1 x_2 \ldots x_N) = \Psi_N(x_1 x_2 \ldots x_N)\Psi_N^*(x_1 x_2 \ldots x_N) \qquad (2.16).$$

The general form of the equation (2.16) is

$$\gamma_N(x_1 x_2 \ldots x_N) = \Psi_N(x_1' x_2' \ldots x_N')\Psi_N^*(x_1 x_2 \ldots x_N) \qquad (2.17).$$

For normalized Ψ_N,

$$tr(\gamma_N) = \int |\Psi_N|^2 d\tau \qquad (2.18).$$

where $tr(\gamma_N)$ is the sum of the diagonal elements of the matrix γ_N. Equation (2.16) is called Nth order density matrix for a state of N-electrons system. The reduced density matrix of order p is then defined as

$$\gamma_N(x_1' x_2' \ldots x_p', x_1 x_2 \ldots x_p) = \binom{N}{p}\int \ldots \int \Psi_N \Psi_N^* dx_{p+1} \ldots dx_N \qquad (2.19).$$

where $\binom{N}{p}$ is a binomial coefficient. So

$$\gamma_2(x_1' x_2', x_1 x_2) = \frac{N(N-1)}{2} \int \ldots \int \Psi_N \Psi_N^* dx_3 \ldots dx_N \qquad (2.20)$$

$$\gamma_1(x_1', x_1) = N \int \ldots \int \Psi_N \Psi_N^* dx_2 \ldots dx_N \qquad (2.21).$$

From $E = \langle \Psi_N | \hat{H} | \Psi_N \rangle$ and the definition of the density matrix, we obtain

$$E = \int \Psi_N^* \hat{H} \Psi_N dx_1 dx_2 \ldots dx_N = tr(\hat{H} \gamma_N) \qquad (2.22)$$

$$E = \int \left[(-\frac{1}{2} \nabla_1^2 + \sum_{A=1}^{M} \frac{Z_A}{r_{1A}}) \gamma_1(x_1', x_1) \right]_{x_1'=x_1} dx_1 + \iint \frac{1}{r_{12}} \gamma_2(x_1 x_2, x_1 x_2) dx_1 dx_2 \qquad (2.23)$$

The first and 2nd order spinless density matrices are given as

$$\rho_1(r_1', r_1) = \int \gamma_1(r_1' s_1, r_1 s_1) ds_1$$

$$= N \int \ldots \int \Psi(r_1' s_1 x_2 \ldots x_N) \Psi^*(r_1 s_1 x_2 \ldots x_N) ds_1 dx_2 \ldots dx_N \qquad (2.24)$$

and

$$\rho_2(r_1' r_2', r_1 r_2) = \iint \gamma_2(r_1' s_1 r_2' s_2, r_1 s_1 r_2 s_2) ds_1 ds_2$$

$$= \frac{N(N-1)}{2} \int \ldots \int \Psi(r_1' s_1 r_2' s_2 x_3 \ldots x_N) \Psi^*(r_1 s_1 r_2 s_2 x_3 \ldots x_N) ds_1 ds_2 dx_3 \ldots dx_N$$

$$\qquad (2.25)$$

where s is the spin coordinate. The short form of the diagonal elements of ρ_2 can be written as

$$\rho_1(r_1, r_2) = \rho_2(r_1' r_2', r_1 r_2)$$

$$= \frac{N(N-1)}{2} \int \ldots \int |\Psi|^2 ds_1 ds_2 dx_3 \ldots dx_N \qquad (2.26)$$

and the diagonal element of $\rho_1(r_1,r_1)$ which is the electron density is

$$\rho_1(r_1) = \rho_2(r_1',r_1)$$

$$= N \int \dots \int |\Psi|^2 \, ds_1 dx_2 \dots dx_N \tag{2.27}$$

From equation (2.26) and (2.27) we get

$$\rho_1(r_1',r_1) = \frac{2}{N-1} \int \rho_2(r_1'r_2, r_1 r_2) dr_2 \tag{2.28}$$

and

$$\rho_1(r_1) = \frac{2}{N-1} \int \rho_2(r_1, r_2) dr_2 \tag{2.29}$$

Then the energy formula of equation (2.23) becomes

$$E = E[\rho_1(r_1',r_1), \rho_2(r_1,r_2)] = E[\rho_1(r_1'r_1, r_1 r_2)]$$

$$= \int \left[-\frac{1}{2} \nabla_r^2 \rho_1(r',r) \right]_{r'=r} dr + \int \sum_{A=1}^{M} \frac{Z_A}{r_{1A}} \rho(r) dr + \iint \frac{1}{r_{12}} \rho(r_1,r_2) dr_1 dr_2 \tag{2.30}$$

The three terms in equation (2.30) represent the electronic kinetic energy, nuclear-electron potential energy and the electron-electron potential energy respectively. The second order density can be expressed in terms of the first order density as

$$\rho_2(r_1,r_2) = \frac{1}{2} \rho(r_1)\rho(r_2)[1 + h(r_1,r_2)] \tag{2.31}$$

where $h(r_1,r_2)$ is the pair correlation function. Substitute equation (2.31) into the third term of equation (2.30), we obtain

$$\frac{1}{2} \iint \frac{1}{r_{12}} \rho(r_1)\rho(r_2)dr_1 dr_2 + \frac{1}{2} \iint \frac{1}{r_{12}} \rho(r_1)\rho(r_2)h(r_1,r_2)dr_1 dr_2$$

Looking very closely, the first term is recognized as the Coulomb integral in terms of $\rho(r)$ which is

$$J[\rho] = \frac{1}{2} \iint \frac{1}{r_{12}} \rho(r_1)\rho(r_2)dr_1 dr_2 \tag{2.32}$$

So the energy in density functional theory can be expressed by

$$E = \int \left[-\frac{1}{2}\nabla_r^2 \rho_1(r',r) \right]_{r'=r} dr + \int \sum_{A=1}^{M} \frac{Z_A}{r_{1A}} \rho(r)dr + \frac{1}{2}J[\rho] + \iint \frac{1}{2r_{12}} \rho(r_1)\rho_{xc}(r_1,r_2)dr_1 dr_2$$

$$\tag{2.33}$$

where the exchange correlation density $\rho_{xc}(r_1,r_2)$ is defined as

$$\rho_{xc}(r_1,r_2) = \rho(r_2)h(r_1,r_2) \tag{2.34}$$

The last term of equation 2.33 can not be determined since the exact expression for ρ_{xc} is not know. Thus, the approximation method are used.

One of the approximation for exchange energy in DFT is the local-density approximation (LDA) E_x^{LDA} which is given by

$$E_x^{LDA} = -C_x \sum_s \int \rho_s^{4/3} dr, \tag{2.35}$$

where
$$C_x = \frac{3}{2}\left(\frac{3}{4\pi}\right)^{1/3}$$

The LDA for the exchange correlation energy, E_{xc}^{LDA}, is [31]

$$E_{xc}^{LDA} = \int \frac{dk}{(2\pi)^2} \int dr \frac{1}{2} \int_0^1 d\lambda \frac{4\pi}{|k|^2} \rho(r) \left[S_\lambda^{LDA}(k; \rho(r)) - 1 \right], \qquad (2.36)$$

where $S_\lambda^{LDA}(k; \rho(r))$ is $S_\lambda(k)$ for a homogeneous electron gas with density $\rho(r)$. The S_λ, the density fluctuation, in r space is given as

$$NS_\lambda(r_1, r_2) = \left\langle \Psi_\rho^\lambda \left| \left[\hat{\rho}(r_1) - \rho(r_1) \right] \left[\hat{\rho}(r_2) - \rho(r_2) \right] \right| \Psi_\rho^\lambda \right\rangle \qquad (2.37)$$

where its transformation to the Fourier space k is

$$S_\lambda(k_1, k_2) = \int dr_1 \int dr_2 e^{-ik_1 \cdot r_1 + ik_2 \cdot r_2} S_\lambda(r_1, r_2) \qquad (2.38)$$

The other approximation for exchange energy is Becke's 1988 parameter denoted as ΔE_x^{B88}, given by

$$\Delta E_x^{B88} = E_x^{LDA} - \beta \sum_s \int \rho_s^{4/3} \frac{x_s^2}{1 + 6\beta x_s \sinh^{-1} x_s} dr \qquad (2.39)$$

where β is a constant, s is electron spin, and $x_s = \dfrac{|\nabla \rho_s|}{\rho_s^{4/3}}$.

Perdew and Wang proposed the gradient corrected correlation energy as

$$E_c^{PW91} = \int dr^3 n \left[\varepsilon_c(r_s, \zeta) + H(t, r_s, \zeta) \right] \qquad (2.40)$$

where $\varepsilon_c(r_s, \zeta)$ is the correlation energy per particle for a uniform electron gas,

$$\zeta = \frac{(\rho_\alpha - \rho_\beta)}{n} \text{ is the local polarization,}$$

$$r_s = (3/4\pi n)^{1/3} \text{ is the local Seitz radius,}$$

$$t = |\nabla n|/2gk_s n,$$

$$g = \left[(1+\zeta)^{2/3} + (1-\zeta)^{2/3}\right]/2,$$

$$k_s = (4k_F/\pi)^{1/2}, \; k_F = (3\pi^2 n)^{1/3}$$

The function H is the summation of H_0 and H_1 where

$$H_0 = g^3 \frac{\beta^2}{2\alpha} \ln\left[1 + \frac{2\alpha}{\beta} \frac{t^2 + At^4}{1 + At^2 + A^2 t^4}\right],$$

$$H_1 = \nu\left[C_c(r_s) - C_c(0) - 3C_x/7\right]g^3 t^2 \cdot \exp\left[-100g^4(k_s^2/k_F^2)t^2\right],$$

$\alpha = 0.09$, $\beta = \nu C_c(0)$, $\nu = (16/\pi)(3\pi^2)^{1/3}$, $C_c = 0.004235$, $C_x = -0.001667$, and

$$A = \frac{2\alpha}{\beta} \frac{1}{e^{-2\alpha\varepsilon_c(r_s,\zeta)/(g^3\beta^2)} - 1}$$

The correlation energy proposed by Lee *et al*, known as Lee-Yang-Parr correlation functional, for closed shell systems is expressed as [32]

$$E_c = -a\int \frac{1}{1+d\rho^{-1/3}}\left\{\rho + b\rho^{-2/3}\left[C_F\rho^{5/3} - 2t_W + (\frac{1}{9}t_W + \frac{1}{18}\nabla^2\rho)\right]e^{-c\rho^{-1/3}}\right\} \quad (2.41)$$

where

$$t_W(r) = \frac{1}{8}\frac{|\nabla\rho(r)|^2}{\rho(r)} - \frac{1}{8}\nabla^2\rho$$

is a local "Weizsacker" kinetic-energy density, a, b, c, and d are constants, and

$$C_F = \frac{3}{10}(3\pi^2)^{2/3}$$

A.D. Becke proposed the another approximation for E_{xc} which included three semi-empirical parameters, a_0, a_c, and a_x, as in the following, [33]

$$E_{xc} = E_{xc}^{LDA} + a_0(E_x^{exact} - E_x^{LDA}) + a_x\Delta E_x^{B88} + a_c\Delta E_c^{PW91} \qquad (2.42)$$

where E_x^{exact} is the exact exchange energy, ΔE_x^{B88} is Becke's 1988 exchange functional [34], and ΔE_x^{PW91} is Perdew and Wang's 1991 gradient correction for correlation [35]. Using E_{xc} of Becke's three parameter and E_c of Lee-Yang-Parr for the correlation term, this DFT method is called B3LYP,

$$E(B3LYP) = E_{xc}(Becke's\ threeparameter) + E_c(LYP) \qquad (2.43).$$

2.5 Molecular Mechanics [28]

Owing to the limit of the computer, many chemical problems involved large molecules are not feasible to be calculated using quantum mechanical methods. Since it incorporates both motion of electrons and nuclei and are time-consuming. The force field method or the molecular mechanic method, which based on empirical equations ignore the electronic motions and calculate the energy of a system as a function of the nuclear position only. The molecular mechanics potential is written as the summation of 4 kinds of the interactions within a system *i.e.* bond stretching, angle bending, bond torsion, and non-bonded interaction;

$$V(r^N) = \sum_{bonds} \frac{k_i}{2}(l_i - l_{i,0})^2 + \sum_{angles} \frac{k_i}{2}(\theta_i - \theta_{i,0})^2 + \sum_{torsions} \frac{V_n}{2}(1 + \cos(n\omega - \gamma))$$

$$+ \sum_{i=1}^{N} \sum_{j=i+1}^{N} \left(4\varepsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] + \frac{q_i q_j}{4\pi\varepsilon_0 r_{ij}} \right) \qquad (2.44).$$

$V(r^N)$ denotes molecular mechanics or sometime called "steric energy or steric strain" which is a function of the positions (r) of N particles. The first term, the bond stretching, is the interaction between pairs of bonded atoms modeling by the harmonic potential that gives the increase in energy as the bond length l_i deviates from the reference value $l_{i,0}$. The second term, angle bending, is summation over all valence angles in the molecule. The third term is a torsional potential that the energy changes as a bond rotates. The last term is the non-bonded term, which is calculated between all pairs of atoms (i and j) that are in different molecules or that are in the same molecule but separated by at least three bonds. In a sample force field, the non-bonded term is usually consisted of the Coulomb potential term for electrostatic interactions and Lennard-Jones potential for van der Waals interactions.

One type of molecular mechanic method is the Universal force field (UFF) [36]. The Universal force field describes the bond stretching, angle bending, torsion, van der Waals, and electrostatic same as the general molecular mechanics potential. However, it adds the inversion term, which described by the cosine Fourier expansion in ω for atoms I bonded exactly to three other atoms J, K, L,

$$E_\omega = K_{IJKL}(C_0 + C_1 \cos\omega_{IJKL} + C_2 \cos 2\omega_{IJKL}) \tag{2.45}$$

where K_{IJKL} is the force constant in kcal/mol and ω_{IJKL} is the angle between the IL axis and the IJK plane. $C_0 = 1, C_1 = -1, C_2 = 0$ for the carbon sp^2.

2.6 ONIOM Approach (our own n-layered integrated molecular orbital and molecular mechanics) [37]

Although the density functional theory obtained from the combination with coulomb and exchange integrals has led to theoretical methods which scaled almost linearly with the size of the system, the accurate *ab initio* modeling of chemical systems containing a large number of atoms is still a challenging task. Morokuma *et al.* [38] proposed the Integrated Molecular Orbital and Molecular Mechanics (IMOMM) method which partitioned the system into 2 parts where different levels of theory are treated. Thus, interesting or difficult part of the system is treated with more accurate method while the rest of the system is treated with the less accurate method. By this approach, a lot of computation time can be saved and "real" instead of "model" system can be studied. The crucial aspect in this and other hybrid schemes is the interaction between the inner and the outer part (higher level of theory)/(lower level of theory) of the system. The total energy $E(X-Y)$ of the entire system $X-Y$ where X is the inner region and Y is the outer region can be defined as

$$E(X-Y) = E_{low}(X-Y) - E_{low}(X) + E_{high}(X) \qquad (2.46)$$

where $E_{low}(X-Y)$ is the energy of the entire system $X-Y$ which X is inner region and Y is outer region which calculated at the low level of theory.

     $E_{low}(X)$ is the energy of the inner region which calculated at the low level of theory.

     $E_{high}(X)$ is the energy of the inner region which calculated at the high level of theory.

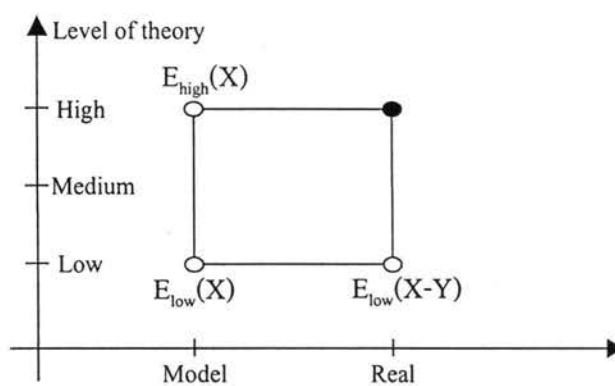The equation 2.46 is best described using the below diagram.

Figure 2.2 The ONIOM extrapolation scheme for a molecular system partitioned into two layers.

From the equation 2.46, there is no necessity for a special interaction Hamiltonian, since the interaction between the two layers is consistently treated at the low level of theory.

As mentioned before, an important and critical feature of all the combination schemes is the treatment of the link atoms. In Figure 2.3, the atoms present both in the model system (inner layer + link atom) and the real system (inner + outer layer) are call set 1 atoms and their coordinates are denoted by R_1. The set 2 atoms are the artificially introduced link atoms [38].

Model System = inner layer + linkatoms
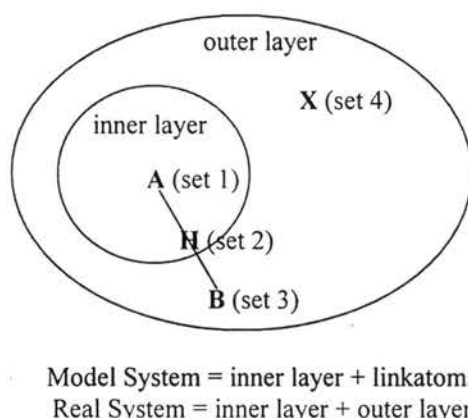Real System = inner layer + outer layer

Figure 2.3 Definition of different atom sets within the ONIOM scheme.

They only occur in the model system and their coordinates are described by R_2. In the real system they are replaced by the atoms described by R_3. Atoms that belong to the outer layer and not substituted by link atoms are called set 4 atoms with the coordinates R_4. The geometry of the real system is thus described by R_1, R_3 and R_4 and they are the independent coordinates for the ONIOM energy:

$$E_{ONIOM} = E_{ONIOM}(R_1, R_3, R_4) \qquad (2.47)$$

In order to generate the model system, described by R_1 and the link atoms R_2, we define R_2 as a function of R_1 and R_3:

$$R_2 = f(R_1, R_3) \qquad (2.48)$$

If atom **A** belongs to set 1 and atom **B** belongs to set 3, the set 2 link atom (symbolized by **H** in Figure 2.2) is placed onto the bond axis **A-B**. In terms of internal coordinates we choose the same bond angles and dihedral angles for set 2 atoms as for set 3. Therefore, in the model calculations the link atoms always aligned along the bond vector of the real system. For the exact position r_2 of a single **H** atom along an **A-B** bond $(r_3 - r_1)$, a fixed scale factor (or distance parameter) g is introduced. Hence,

$$r_2 = r_1 + g(r_3 - r_1) \qquad (2.49)$$

For example, the ethane molecule (CH_3-CH_3), we can divide the ethane molecule into two regions. The inner region is the methane molecule, which treated with the high level. The outer region is the methyl group, which treated with the low level. The link atom is hydrogen atom in high level and in low level is carbon atom as shown in Figure 2.4.

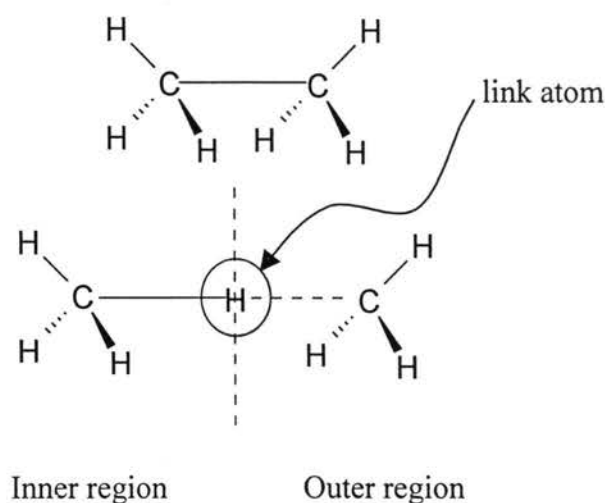Inner region   Outer region

Figure 2.4 Inner and outer regions using for partitioning of ethane molecule.

The expression of the ONIOM energy gradient along with a certain functional relationship between set 2 and set 1/3 atoms, is straightforward. For a two-layer ONIOM system, we obtain

$$\nabla E_{ONIOM2} = \nabla E_3 - \nabla E_1 * J(R_2; R_1, R_3) + \nabla E_2 * J(R_2; R_1, R_3) \qquad (2.50)$$

where J is the Jacobian matrix that projects the forces on *all* set 2 link atoms (R_2) onto set 1 (R_1) and set 3 atoms (R_3). The differentiation of the vector components of *one* set 2 atom r_2 with respect to components of r_1 and r_3 yields a very simple Jacobian:

$$\partial r_{2,a} / \partial r_{3,b} = g\delta_{a,b} \qquad (2.51)$$

$$\partial r_{2,a} / \partial r_{1,b} = (1-g)\delta_{a,b} \qquad (2.52)$$

where a and b denote the catesian components x, y, and z. δ is the Kronecker delta symbol.

The Hessian matrix, H_{ONIOM} is the definition of the second derivatives of the ONIOM total energy E_{ONIOM} can be achieved easily,

$$H_{ONIOM} = \nabla^2 E_{ONIOM} \qquad (2.53)$$

The force constant matrixes of the model system at low level (H_1) and high level (H_2) have to be transformed by applying the Jacobian J and its transposed J^T. Hence, we obtain for a two-layer ONIOM system:

$$H_{ONIOM2} = H_3 - J^T(R_2; R_1, R_3) \times *H_1 * J(R_2; R_1, R_3)$$

$$+ J^T(R_2; R_1, R_3) * H_2 * J(R_2; R_1, R_3) \qquad (2.54)$$

Similarly, gradient and second derivative expressions can be derived easily for the three or n-layer ONIOM partitioning [37].