CHAPTER II
THEORETICAL BACKGROUND

In this chapter, a brief concept of quantum mechanics (QM) in computational chemistry is overviewed.

2.1 Introduction to Quantum Mechanics

The word quantum comes from Latin (quautus, "how much?") and is first used by Max Plank in 1900 to donate the constrained quantities or amounts in which energy can be emitted or absorbed. "Mechanics" as used in physics is traditionally the study of the behavior of bodies under the action of forces. The term "quantum mechanics" is apparently first used by Born (of the Born-Oppenheimer approximation) in 1924. Because of molecules are consisted of nuclei and electrons, quantum chemistry deals with the motion of electrons under the influence of the electromagnetic force exerted by nuclear charges. An understanding of the behavior of electrons in molecules, structures and reactions of molecules, reset on quantum mechanics and in particular on the adornment of quantum chemistry, the Schrödinger equation.

Quantum mechanics mean that energy is quantized, absorbed and emitted in discrete packets of magnitude $h\nu$, where h is Plank's constant and ν is the frequency associated with the energy. The QM grows out of studies of blackbody radiation and of the photoelectric effect, which contribute to the transition from classical to modern physics. The Rutherford nuclear atom suffers from the deficiency that Maxwell's electromagnetic theory demands which its orbit electrons radiate energy away and swiftly fall into the nucleus. This problem is countered by Bohr's quantum atom, in which an electron can orbit stably if its angular momentum is an integral multiple of $h/2\pi$. However, the Bohr model contains several problems and works only for the hydrogen atom. The deficiencies of the Bohr atom are surmounted by Schrödinger's wavefunction which is based on a combination of classical wave theory.

In summary, by solving the electronic Schrödinger equation at a variety of geometry, one can find stable structure of molecule. The *potential energy surfaces (PES)* are the solutions of the electronic Schrödinger equation. The interesting part of PES is a nuclear arrangement which has the lowest energy. An example of such surface is shown in Figure 2.1 which is a plot of one particle energy against two geometrical coordinates. There appears to be three minima which corresponded to geometries of stable molecular structures. The surface also displays two transition structures connected to the three minima, labeled as transition structure A and B. It can be observed that Figure 2.1 shows just one of the energy surfaces, due to each molecule has a ground-state surface as well as an infinite number of excited-state surfaces. Chemical reactions are described by locating the lowest energy path leading from one minimum on the PES to another.

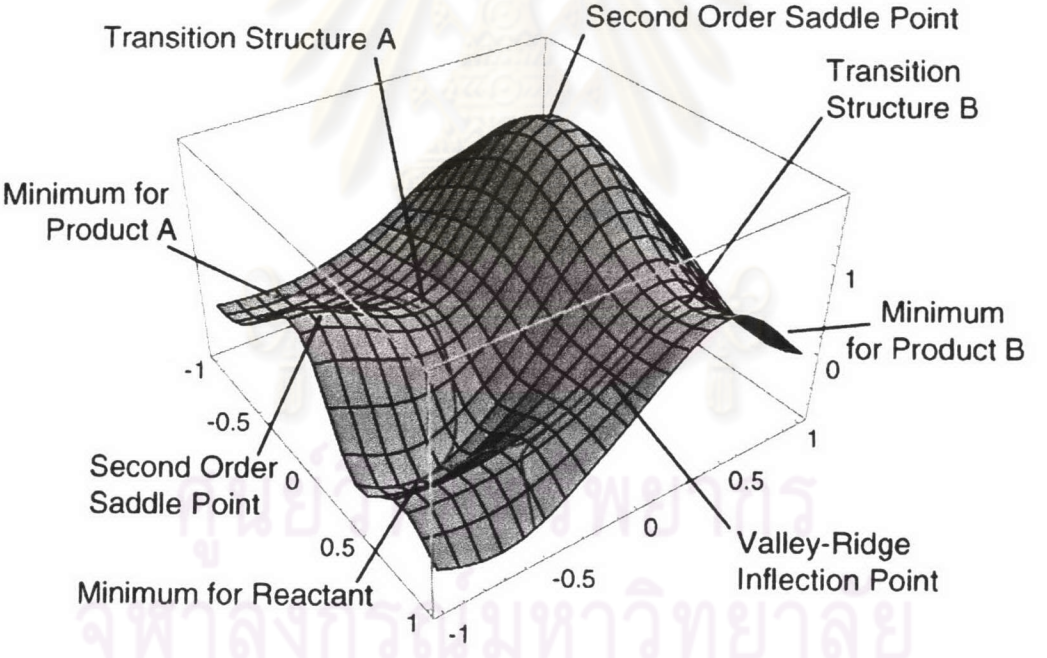

Figure 2.1 Two-dimensional potential energy surface shown local minima, transition states and paths connected them *[49]*.

2.2 Solution of the Schrödinger Equation of Molecular Systems

2.2.1 The Schrödinger Wave Equation

The Schrödinger equation is a fundamental equation of quantum mechanics. The solution to the Schrödinger equation is called wavefunctions.

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

Here $\hat{H}$ is the Hamiltonian operator represented the total energy, E is the numerical value of the energy of the state in which the constituent particles (nuclei and electrons) are infinitely separated. And the last one, Ψ is the wavefunctions which depended on not only Cartesian coordinates of all particles but also on the spin coordination. The square of wavefunction, Ψ^2 , is interpreted as a measure of the probability distribution of the particles within the molecule. The Hamiltonian operator $\hat{H}$, in general,

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

where for a molecule,

$$\hat{T} = \hat{T}_n + \hat{T}_e = -\sum_{A=1}^{N} \frac{1}{2M_A}\nabla^2{}_A - \sum \frac{1}{2}\nabla_i^2 \tag{2.3}$$

where $\nabla^2{}_A$ and $\nabla^2{}_i$ are the Laplacian operators acted on nuclei and electrons, respectively.

$$\hat{V} = \hat{V}_{ne} + \hat{V}_{ee} + \hat{V}_{nn} = -\sum_{i=1}^{n}\sum_{A=1}^{N} \frac{Z}{r_{iA}} + \sum_{i=1}^{n}\sum_{j<1}^{n} \frac{1}{r_{ij}} + \sum_{A=1}^{N}\sum_{B<A}^{N} \frac{Z_A Z_B}{R_{AB}} \tag{2.4}$$

From (2.3) to (2.4), the molecular Hamiltonian is,

$$\hat{H} = -\sum \frac{1}{2}\nabla_i^2 - \sum_{A=1}^{N} \frac{1}{2M_A}\nabla^2{}_A - \sum_{i=1}^{n}\sum_{A=1}^{N} \frac{Z}{r_{iA}} + \sum_{i=1}^{n}\sum_{j<1}^{n} \frac{1}{r_{ij}} + \sum_{A=1}^{N}\sum_{B<A}^{N} \frac{Z_A Z_B}{R_{AB}} \tag{2.5}$$

in which A and B referred to nuclei and i and j referred to electrons. The first and second terms in equation 2.5 are the operators for the kinetic energy of the electrons and nuclei, respectively. The third term is the electron-nuclear attraction where r_{iA} is the distance between electron i and nucleus A. The fourth term is the electron-electron

repulsion where r_{ij} is the distance between electron i and j. The last term is the nuclear-nuclear repulsion where R_{AB} is the distance between nuclei A and B with atomic number Z_A and Z_B, respectively. This formation is time-independent. Additional terms can appear in the Hamiltonian operator where relativity or interaction or fields are taken into account. Furthermore, small magnetic effects, for example, spin-orbit coupling, spin-spin interactions, etc., are also omitted in this Hamiltonian.

In summary, whenever the Hamiltonian does not depend on time, one can solve the time-independent Schrödinger equation first and then obtain the time-dependent equation when the energy E is known. In the case of molecular structure theory, it is a quite daunting task even to approximately solve the full Schrödinger equation because it is a partial differential equation depending on all of the coordinates of the electrons and nuclei in the molecule. For these reason, there are various approximations that one usually implements when attempts to study molecular structure using quantum mechanics.

2.2.2 Born-Oppenheimer Approximation

The general molecular problem in quantum mechanics is the separation of the nuclear and electronic motions. This is possible because the nuclear masses are much greater than those of the electrons, therefore, nuclei move much more slowly. As a consequence, the electrons in a molecule adjust their distribution to change nuclear position rapidly. This makes its reasonable approximation to suppose that the electron distribution depends only on the instantaneous positions of the nuclei but not on their velocities. The separation of general problem into two parts is frequency called the adiabatic or *Born-Oppenheimer approximation*. It is examined quantitatively by Born-Oppenheimer, who reveal that it is valid, provided that the mass ratio of electron to nuclear is sufficiently. The approximation states that the Schrödinger equation for a molecule may be separated into an electronic and nuclear equation. The Born-Oppenheimer approximation is formulated by writing down the Schrödinger equation for electrons in the field of fixed nuclei.

$$\hat{H}^{elec}\Psi^{elec}(r,R) = E^{eff}(R)\Psi^{elec}(r,R) \tag{2.6}$$

Here, Ψ^{elec} is the electronic wavefunction which depended on the electronic coordinates, r, as well as on the nuclear coordinates, R. The electronic Hamiltonian, $\hat{H}^{elec}$, corresponds to motion of electrons only in the field of fixed nuclei and is

$$\hat{H}^{elec} = -\sum_{i}^{elec}\frac{\nabla_i^2}{2} - \sum_{A}^{n}\sum_{i}^{elec}\frac{Z_i}{r_{iA}} + \sum_{i<j}^{elec}\sum\frac{1}{r_{ij}} \tag{2.7}$$

The first part of equation 2.7 is corresponded to the kinetic energy of the electrons only. The next term is the attraction of electron to nuclei. The last term is the repulsion between electrons.

The main task of theoretical studies of electronics structure is to solve, at least approximately, the electronic Schrödinger equation (equation 2.6), and then find the effective nuclear potential function, $E^{eff}(R)$. From this point, the superscripts in equation 2.5 are omitted. It is assumed that the Hamiltonian operator, wavefunction and energy referred to electronic motion only, each quantity being implicitly a function of the relative nuclear coordination.

2.3 Ab Initio Methods

A quantum mechanical approach that does not rely on calibration against measured chemical parameter is called *ab initio*. The term *ab initio* is a Latin for "from the beginning". This is an approximate mathematical calculation which is based on a fundamental physical equation, the Schrödinger equation. The nature of the necessary approximations determines the level of the calculation. The most common type of *ab initio* calculation is *Hartree Fock approximation* (HF).

The HF approximation is the basis of molecular orbital theory, which posits that each electron's motion can be described by a single-particle function (orbital) which not depended on the instantaneous motions of the other electrons. The calculation of Hartree wavefunctions and energy level of atom are prompted by the impossible of analytic solution to polyelectronic systems. The Hartree method is to write a plausible approximation polyelectronic wavefunction for an atom as the product of one electron wavefunctions:

$$\Psi_o = \psi_o(1)\psi_o(2)\psi_o(3)...\psi_o(n) \tag{2.8}$$

This function is called a Hartree product. Here ψ_o is a function of the coordinates of all the electrons in the atom, $\psi_o(1)$ is a function of the coordinates of electron 1, $\psi_o(2)$ is a function of the coordinates of electron 2, etc. The one-electron functions, $\psi_o(1)$, $\psi_o(2)$, etc., are called *atomic orbital*. The first Hartree process applies to solve Schrödinger equation for electron 1. A one-electron Schrödinger equation in which the electron-electron repulsion comes from electron 1 and an average smeared out electrostatic field calculated from $\psi_o(2)$, $\psi_o(3)$, ..., $\psi_o(n)$, due to all the other electrons. The only moving particle in this equation is electron 1. Solving this equation gives $\psi_1(1)$, an improved version of $\psi_o(1)$. The next solution for electron 2 is a one-electron Schrödinger equation with electron 2 moving in an average field due to the electron of $\psi_1(1), \psi_o(3), ..., \psi_o(n)$, continued to electron *n* moving in a field due to $\psi_1(1), \psi_1(2), ..., \psi_1(n-1)$. This completes the first cycle of calculation and given

$$\Psi_1 = \psi_1(1)\psi_1(2)\psi_1(3)...\psi_1(n) \tag{2.9}$$

Repetition of the cycle given

$$\Psi_2 = \psi_2(1)\psi_2(2)\psi_2(3)...\psi_2(n) \tag{2.10}$$

The process is continued for *k* cycles till the energy calculated from ψ_k that is essentially the same as the wavefunction energy from the previous cycle (*k-1*). It is "consistent with" this previous field, and so the Hartree procedure is called the *self-consistent-field-procedure,* which is usually abbreviated as the SCF procedure.

There are problems with the Hartree product. Electrons are indistinguishable and have a property called spin, which not more than two electrons can occupy one atomic or molecular orbital (this is one of the *Pauli exclusion principle*). If switch the positions of two of the particles, i.e. exchange their coordinates, then a wavefunction of the coordinates of indistinguishable particles must either unchanged or changed its sign. If switch the coordinates of the two particles leave the function unchanged, it is said to be symmetric with respect to particle exchange, while if the function changes

its sign, it is said to be antisymmetric with respect to particle exchange. The comparison between the prediction of theory and the results of experiment exposes that electronic wavefunctions are actually antisymmetric with respect to exchange, while Hartree product is symmetric rather than antisymmetric. These defects of the Hartree are corrected by Fock and Slater. The Slater wavefunction is composed of spin orbitals rather than just spatial orbitals. In the fact that Slater wavefunction is not a simple product of one-electron wavefunctions, but rather a determinant which those functions are its element. A spin orbital $\psi(spin)$ is the product of a spatial orbital and a spin function, α or β. The Slater determinant enforces the Pauli exclusion principle, which forbids any two electrons in a system to have all quantum numbers the same, and it ensures that wavefunction is antisymmetric since its sign is changed by switch two electron amounts to exchange two rows of the determinant. For *2n* electrons, the general form of a Slater determinant is clearly the *2n* x *2n* determinant.

$$\Psi_{2n} = \frac{1}{\sqrt{(2n)!}} \begin{vmatrix} \psi_1(1)\alpha(1) & \psi_1(1)\beta(1) & \psi_2(1)\alpha(1) & \psi_2(1)\beta(1) & \cdots & \psi_n(2)\beta(2) \\ \psi_1(2)\alpha(2) & \psi_1(2)\beta(2) & \psi_2(2)\alpha(2) & \psi_2(2)\beta(2) & \cdots & \psi_n(2)\beta(2) \\ \vdots & \vdots & \vdots & \vdots & & \\ \psi_1(2n)\alpha(2n) & \psi_1(2n)\beta(2n) & \psi_2(2n)\alpha(2n) & \psi_2(2n)\beta(n2) & \cdots & \psi_n(2n)\beta(2n) \end{vmatrix} \quad (2.11)$$

Again, the Hartree-Fock method seeks to approximately solve the electronic Schrödinger equation. It assumes that the wavefunction can be approximated by a single Slater determinant made up of one spin orbital per electron. One limit of HF is that it does not treat electron correlation property. For example, each electron is considered to move in an electrostatic field represented by the average positions of the other electrons, whereas in fact electrons avoid each other better than this model predicts. Since any electron A sees any other electron B as a moving particle and the two electrons adjust their motion to minimize their interaction energy. Electron correlation is treated better in post-HF methods, such as *Møller-Plesset perturbation theory* (MPn, where n is the order of correction), *configuration interaction* (CI) and *coupled cluster theory* (CC), etc. Those methods avoid electron-electron interaction energy by allowed the electron to reside not only in conventionally occupied molecular orbitals, but also in formally unoccupied molecular orbitals.

The main use of the HF methods is calculating molecular geometries, energies, vibrational frequencies, spectra (IR, UV, and NMR), ionization potentials and electron affinities. And properties like dipole moments, which are directly connected with electron distribution, are also calculated.

2.4 Basis Sets

The approximate treatment of electron-electron distribution and motion assigns individual electrons to one-electron function, termed *spin orbital*. These consist of a product of spatial functions, termed *molecular orbitals (MO)*, $\psi_1(x,y,z)$, $\psi_2(x,y,z)$, $\psi_3(x,y,z)$, ..., and either α or β spin components. The spin orbitals are allowed complete freedom to spread throughout the molecule. Their exact forms are determined to minimize the total energy. In the simplest level of theory, a single assignment of electron to orbital is made by used ψ as atomic orbital wavefunction based on the Schrödinger equation for the hydrogen atom. This is not a suitable approach for molecular calculation. This problem can be solved by representing MO as linear combination of basis functions.

In practical calculation, the molecular orbitals $\psi 1$, $\psi 2$, ..., are further restricted to be linear combinations of a set of N known one-electron function $\phi_1(x,y,z)$, $\phi_2(x,y,z)$, ..., $\phi_N(x,y,z)$:

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

The functions ϕ_1, ϕ_2, ..., ϕ_N, which are defined in the specification of the model, are known as one-electron basis function called basis function. The set of basis functions is called basis set. If the basis functions are the atomic orbitals for the atoms making up the molecule, function in equation 2.12 is often described as the *linear combination of atomic orbitals* (LCAO). There are two types of basis function which commonly used in the electronic structure calculations, *Slater type orbitals* (STO) and *Gaussian type orbitals* (GTO).

The Slater orbitals are primarily used for atomic and diatomic systems where high accuracy is required and semiempirical calculations where all three- and four-center integrals are neglected. The Slater type orbitals have the function form

$$b = Ae^{-\zeta r} r^{n^*-1} Y_{lm}(\theta,\phi) \tag{2.13}$$

where parameter n^* and ξ are chosen to make the larger part of the orbitals look like atomic Hartree-Fock orbitals. There are a lot like hydrogen orbitals, but without the complicated nodal structure.

The Gaussian type orbitals can be written in terms of polar or cartesian coordinates

$$g = x^a y^b z^c e^{-\alpha r^2} Y_{lm}(\theta,\phi) \tag{2.14}$$

in which *a*, *b*, and *c* are integers and α is a parameter that is usually fixed. Primitive Gaussian function is shown in equation 2.14. Normally, several of these Gaussian functions are summed to define more realistic atomic orbitals basis functions, as shown below.

$$b_\mu = \sum_p k_{\mu p} g_p \tag{2.15}$$

The coefficients $k_{\mu p}$ in this expansion are chosen to make the basis functions look as much like Slater orbitals as possible. Slater functions are good approximation to atomic wavefunctions but required excessive computer time more than Gaussian functions, while single-Gaussian functions are a poor approximation to the nearly ideal description of an atomic wavefunction that Slater function provides. The solution to the problem of this poor functional behavior is to use several Gaussians to approximate a Slater function. In the simplest version of this basis, n Gaussian functions are superimposed with fixed coefficients to form one-Slater type orbital. Such a basis is denoted STO-nG, and n = 3, 4, …, etc.

The limit of quantum mechanics involves an infinite set of basis function. This is clearly impractical since the computational expanse of molecular orbital calculations is proportional to the power of the total number of basis functions. Therefore, ultimate choice of basis set size demands on a compromise between accuracy and efficiency. The classification of basis sets is given below.

2.4.1 Minimal Basis Sets

The minimum basis set is a selected basis function for every atomic orbital that is required to describe the free atom. For hydrogen atom, the minimum basis set is just one *1s* orbital. But for carbon atom, the minimum basis set consisted of a *1s* orbital, a *2s* orbital and the full set of three *2p* orbitals. For example, the minimum basis set for the methane molecule consists of 4 *1s* orbitals, one per hydrogen atom, and the set of *1s*, *2s* and *2p* orbitals described above for carbon. Thus, total basis set comprises of 9 basis functions.

Several minimum basis sets are used as common basis sets especially the STO-nG basis sets because they are available for almost all elements in the periodic table. The most common of minimum basis sets is STO-3G, where a linear combination of three Gaussian type orbitals (GTOs) is fitted to a Slater-type orbital (STO). The individual GTOs are called primitive orbitals, while the combined functions are called contracted functions. For example, the STO-3G basis set for methane consists of a total of 9 contracted functions built from 27 primitive functions. Other commonly uses of STO-nG basis sets are STO-4G and STO-6G where each STO is fitted to 4 and 6 GTOs, respectively.

2.4.2 Scaled Orbital by Splitting the Minimum Basis Sets

In the early calculation on the hydrogen molecule, it is discovered that the STO *1s* orbitals do not give the best result in the molecular environment when the Schrödinger equation is solved, because electron is attracted to both nuclei rather than just one nucleus. In each molecular orbital, both large and small sets of orbital appear and they are mixed in the ratio that gives the lowest energy. The combination of a large orbital and a small orbital is essentially equivalent to an orbital of intermediate size. The result orbital is a size that best fit for the molecular environment since it is obtained from minimizing the energy. The advantage of this procedure is that the mixing coefficients in the molecular orbitals appear in a linear function. This simple dodge is equivalent to scaling the single minimal basis set orbitals. The minimum basis set can scaled not only the valence orbitals of the minimal basis set (split valence basis set), but also all the orbitals of the minimal basis set (double zeta basis sets).

a) Split the Valence Orbitals (Split Valence Basis Sets)

The split valence basis sets mean that each valence orbital is spited into two parts, an inner shell and an outer shell. For example, the 3-21G basis set is referred to basis function of the inner shell represented by two Gaussian functions and that of the outer shell represented by one Gaussian function(hence the "21"). The core orbitals are represented by one basis function and each function composes of three Gaussian functions (hence the "3"). The purpose of splitting the valence shell is to give the SCF algorithm more flexibility in adjusting the contributions of the basis function to the molecular orbitals, achieving a more realistic simulated electron distribution.

b) Split all Orbitals (Double Zeta Basis Sets)

Double zeta basis set is a member of minimum basis set replaced by two functions. In this way both core and valence orbitals are scaled in size. For some heavier atoms, double zeta basis sets may have slightly less than double the number of minimum basis set orbitals. For example, some double zeta basis sets for the atoms Ga - Br have 7 rather than 8 *s* basis functions, and 5 rather than 6 *p* basis functions.

The term "*double zeta*" arises from the fact that the exponent in a STO is often referred by the Greek letter "*zeta*". Since it takes two orbitals with different exponents, it is called "*double zeta*". The minimum basis set is "*single zeta*". The normal abbreviation for a double zeta basis set is DZ. It is also quite common to use split valence basis sets where the valence orbitals are spitted into three functions. Basis sets where this is done for all functions are called triple zeta functions and referred to as TZ, TZP, TZ2P etc.

2.4.3 Polarized Basis Sets

In the discussion on the scaling of the hydrogen orbitals in the H_2 molecule, it is argued that the orbital on one atom in the molecule becomes smaller because of the attraction of the other nucleus. However, it is also clear that the influence of the other nucleus may distort or polarize the electron density near the nucleus. This problem desires 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 add basis functions of higher

angular momentum quantum number. Thus, the spherical *1s* orbital on hydrogen is distorted by mixing in an orbital with *p* symmetry. The positive lobe at one side increases the value of the orbital while the negative lobe at the other side decreases the orbital. The orbital has overall "moved" sideways. It has been polarized. Similarly, the *p* orbital can polarize if it mixes in an orbital of *d* symmetry. These additional basis functions are called polarization functions. The polarization functions are added to the 6-31G basis set as follows:

6-31G* - added a set of d orbitals to the atoms in the first and second rows (Li-Cl).

6-31G** - added a set of d orbitals to the atoms in the first and second rows (Li-Cl) and a set of *p* functions to hydrogen.

The nomenclature above is slowly being replaced. The 6-31G* is called 6-31G(d), while the 6-31G** is called 6-31G(d,p). This new nomenclature allows the possibility of adding several polarization functions. Thus 6-31G(3df,pd) added 3 *d*-type GTOs and 1 *f*-type GTO to atoms Li-Cl and added 1 *p*-type and 1 *d*-type function to H.

2.4.4 Diffuse Function Basis Sets

In some cases the normal basis functions are not adequate. This is particular the case in excited states and in anions where the electronic density is spread out more over the molecule. This model has correctly by using some basis functions which themselves are more spread out. This means that small exponents are added to GTOs. These additional basis functions are called diffuse functions. The diffuse functions added to the 6-31G basis set as follows:

6-31+G - added a set of diffuse *s* and *p* orbitals to the atoms in the first and second rows (Li-Cl).

6-31++G - added a set of diffuse *s* and *p* orbitals to the atoms in the first and second rows (Li-Cl) and a set of diffuse *s* functions to hydrogen.

Diffuse functions can be added along with polarization functions also. Some examples of these functions are 6-31+G*, 6-31++G*, 6-31+G** and 6-31++G** basis sets.

2.5 Semiempirical Methods

Semiempirical calculations are set up with the same general structure as a HF calculation in that they have Hamiltonian and wavefunction, but they have approximated some information. For example, the core electrons are not included in the calculation and only a minimal basis set is used. In order to correct for the errors introduced by omitting part of the calculation, the method is parameterized. Parameters to estimate the omitted values are obtained by fitting the results to experimental data or *ab initio* calculations. Semiempirical methods are parameterized to reproduce various results such as geometry and energy, dipole moments, heats of reaction, and ionization potentials.

The advantage of semiempirical calculations is that they are faster than *ab initio* calculation. The disadvantage of these calculations is that the results can be erratic and fewer properties can be predicted reliably. If the molecule being computed is similar to the molecules in the database used to parameterize the method, then the results may be very good. If the computed molecule is significant different from the parameterization sets, the answer may be very poor. Semiempirical calculations have been very successful in the description of organic chemistry, where there are only a few elements and the sizes of molecules are moderate. Some semiempirical methods have been devised specifically for the description of inorganic chemistry as well.

2.6 Density Functional Theory (DFT)

The *ab initio* methods described above all start with the Hartree-Fock approximation. The HF methods are widely used by quantum chemists but they have limitations, in particular the computational difficulty of performing accurate calculations with large basis sets on molecules containing many atoms. An alternative to the HF methods that have been growing in popularity over the past decade is density functional theory. In contrast to the methods described above, the concept of DFT is the electron probability density. The basic idea behind DFT is that the energy

of an electronic system can be written in terms of the electron probability density. The electronic energy E is said to be a function of the electron density. The DFT is based on Hohenberg-Kohn theorem, which states that the ground-state properties of an atom or molecule are determined by its electron density function. An application of this theory is developed by Kohn-Sham theory which formulates a method that has structure similar to the HF method. In DFT formulation, the electron density is expressed as a linear combination of a basis function similar in mathematical form to the HF orbital. A determination is then formed these function, called Kohn-Sham orbital. It is electron density from this determination of orbital that is used to compute the energy. A density function is used to obtain the energy for the electron density.

Solving the energy for a given wavefunction is similar to HF methods but difference of using the electron density. The total energy of the system can be expressed by the equation below.

$$E_{DFT[\rho]} = T_{s[\rho]} + E_{ne[\rho]} + J_{[\rho]} + E_{xc[\rho]} \tag{2.16}$$

Where $T_{s[\rho]}$ is described the kinetic energy calculated from a Slater determinant, $E_{ne[\rho]}$ is the term accounting for nuclear-electron interactions, $J_{[\rho]}$ is the Coulomb integral and $E_{xc[\rho]}$ is the exchange-correlation term which is the part that remains after subtraction of the non-interacting kinetic energy, and $J_{[\rho]}$.

$$E_{xc[\rho]} = (T_{[\rho]} - T_{s[\rho]}) + (E_{ee[\rho]} - J_{[\rho]}) \tag{2.17}$$

The first parenthesis in equation 2.17 may be considered the kinetic correlation energy which mean that $E_{xc[\rho]}$ is included the remaining kinetic energy due to correlation effects of the electrons. The second parenthesis contains both exchange and potential correlation energy. The first term is exchange-correlation, $E_{ee[\rho]}$ which is the true interaction between two electrons and subtracting the $J_{[\rho]}$ operator gives the exchange energy.

The advantage of using electron density is that the integrals of coulombic repulsion are done only over the electron density, which is a three dimensional function. Furthermore, at least some electron correlation can be included in the calculation. This result is faster than HF calculation and more accurate as well. The better DFT functions give results with accuracy similar to that of an MP2 calculation.

The simplest version of DFT is the *local density approximation* (LDA), which treats the electron density as constant or only varying from point to point in an atom or molecule. It has been replaced by method which used gradient-corrected (nonlocal) functions and assigns one set of spatial orbitals to α-spin electrons, and another set of orbitals to β-electrons; this latter "unrestricted" assignment of electron constituted the *local spin density approximation* (LSDA). The results appear to come from so-called hybrid functions, which some contributions from HF type exchange are included in Kohn-Sham orbitals. The most popular current DFT method is the LSDA gradient-corrected hybrid method which used the B3LYP (Beck-three-Lee-Yang-Parr) function. The accuracy of results from DFT calculations can be poor to fairly good, depending on the choice of basis set and density function.

2.7 Transition State Theory and Statistical Mechanics

Transition state theory (TST) assumes that a reaction proceeded from one energy minimum to another via an intermediate maximum. The *transition state* is the configuration which divides the reactant and product parts of surface. For example, a molecule which has reached the transition state is continuing to product. The geometrical configuration of the energy maximum is called the *transition structure*. Within standard TST, the transition state and transition structure are identical, but this is not necessarily for more refined models. The direction of reaction coordinate is started from the reactant to product along a path where the energies are as low as possible and the TS is the point where the energy has a maximum. In the multidimensional case, TS is a first-order point on the potential energy surface as a maximum in the reaction coordinate direction and a minimum along all other coordinates, shown in Figure 2.2.

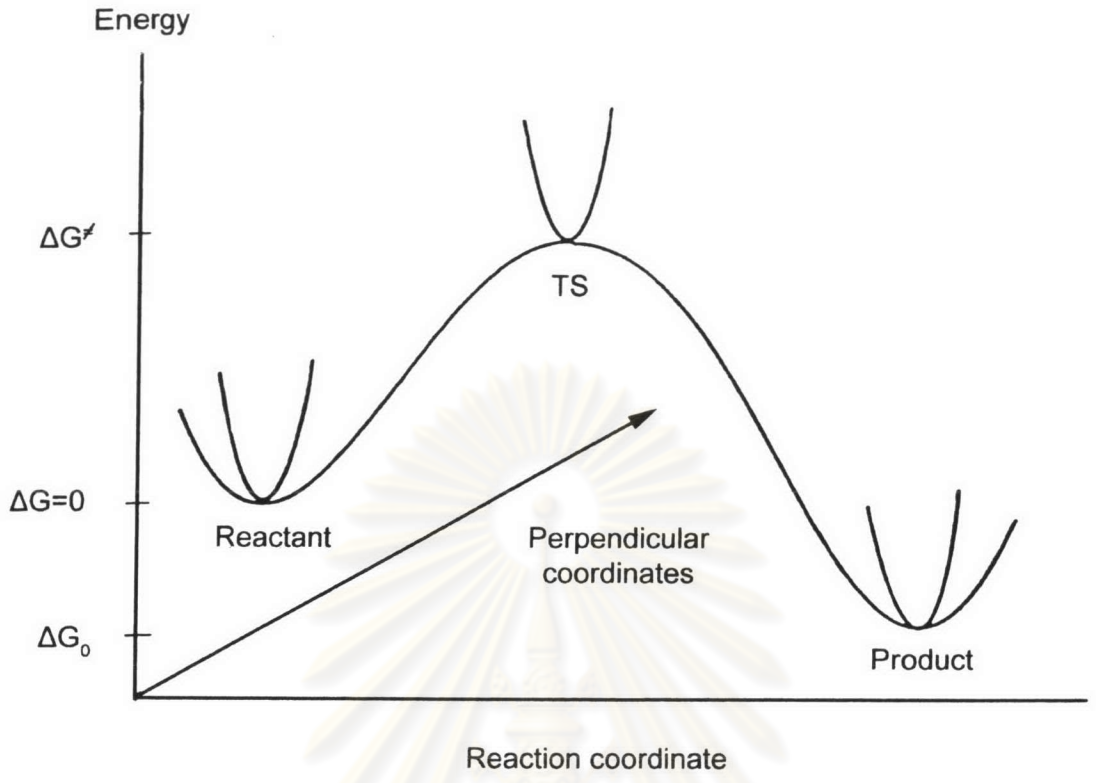

Figure 2.2 Schematic illustration of reaction path *[50]*.

Transition state theory assumes equilibrium energy distribution among all possible quantum states at all points along the reaction coordinates. The probability of finding a molecular in a given quantum state is proportional to $e^{-\Delta E / k_B T}$, which is Boltzman distribution. Assuming that the molecule at the TS is in equilibrium with the reactant, the macroscopic rate constant can be expressed as

$$k = \frac{k_B T e^{-\Delta G^{\neq} / RT}}{h} \tag{2.18}$$

in which $\Delta G^{\neq}$ is the Gibbs free energy difference between the TS and reactant, T is absolute temperature and k_B is Boltzmann's constant. It is clear that if the free energy of the reactant and TS can be calculated, the reactant rate follows trivially. The equilibrium constant for a reaction can be calculated from the free energy difference between the reactant and product.

$$K_{eq} = e^{-\Delta G_0 / RT} \tag{2.19}$$

The Gibbs free energy is given in terms of the enthalpy and entropy, $G = H - TS$. The enthalpy and entropy for a macroscopic ensemble of particles maybe calculated from properties of the individual molecules by means of statistical mechanics. The difference between rate constant and equilibrium constant is shown in Figure 2.3.

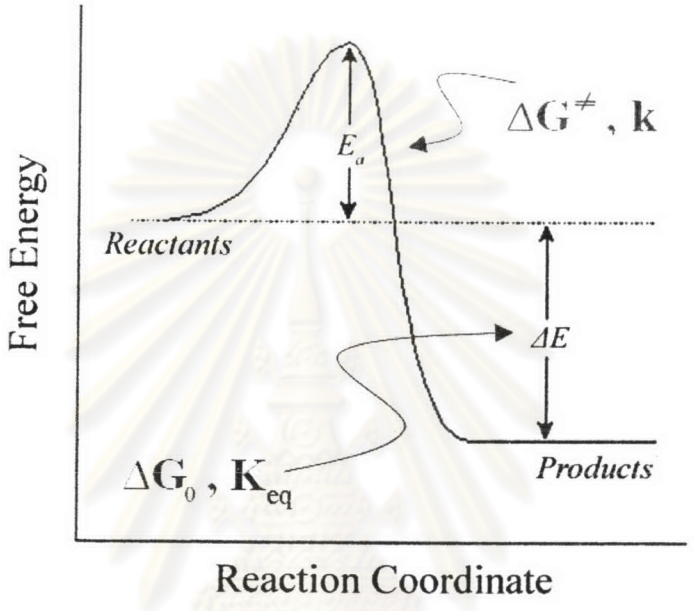

Figure 2.3 The difference between rate constant (k) and equilibrium constant (K).

2.8 Hammond's Postulate

The energy of transition states is of crucial importance for the rate of chemical reactions. However, the vary nature of transition states means that it is not possible to observe them directly. Hammond's Postulate allows to making assumption about the structure of transition states. In a publication in the Journal of the American Chemical Society, Hammond postulated that "If two states, as for example a transition state and an unstable intermediate, occur consecutively during a reaction process and have nearly the same energy content, their interconversion will only involve a small reorganization of molecular structure" *[51-52]*. That is, along the reaction coordinate, species with similar energies also have similar structures. Hammond postulated that in highly exothermic reactions the transition state is structurally similar to the reactant,

but that in highly endothermic reactions the product is a better model of the transition state. The caution against using the postulate is that if reactions are more thermoneutral or slightly exothermic reaction, the transition is resembled neither reactant nor product.

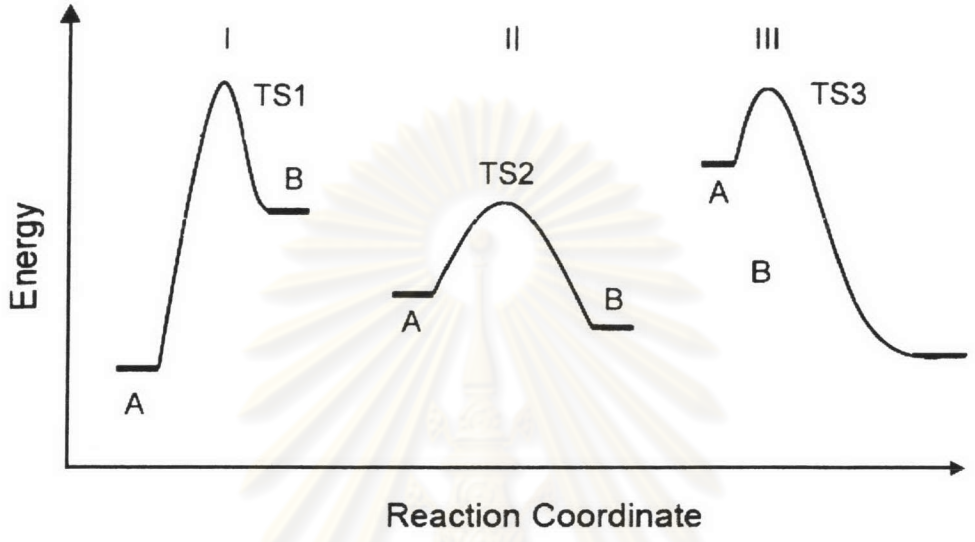

Figure 2.4 The schematic conclusion of Hammond's postulate.

Hammond's Postulate can be considered the following three scenarios, according to Figure 2.4. Case I, if reaction is a highly endothermic, the structure of TS1 resembles the product B. For case II, if reaction is a slightly exothermic with relatively high activation energy, the TS2 resemble neither reactant A nor product B. And the last one, case III, if reaction is a highly exothermic, the structure of TS3 resembles the reactant A.