

## CHAPTER II

### THEORETICAL BACKGROUND

#### 2.1 Introduction to quantum mechanics in computational chemistry

Quantum mechanics (QM) is the correct mathematical description of the behavior of electrons and thus of chemistry. In theory, QM can predict any property of an individual atom or molecule exactly. In practice, the QM equations have only been solved exactly for one electron systems. A collection of methods has been developed for approximating the solution for multiple electron systems.

Two equivalent formulations of QM were devised by Schrödinger and Heisenberg. The Schrödinger equation is

$$\hat{H}\psi = E\psi \quad (2.1)$$

where  $\hat{H}$  is the Hamiltonian operator,  $\psi$  a wave function, and  $E$  the energy [15].

#### 2.2 Ab initio method

Ab initio methods are computational chemistry methods based on quantum chemistry. The term ab initio indicates that the calculation is from first principles and that no empirical data is used. Robert Parr claims in an interview that the term was first used in a letter to him by David Craig and was put into the manuscript of their paper on the excited states of benzene published in 1950. The simplest type of ab initio electronic structure calculation is the Hartree-Fock (HF), in which the instantaneous coulombic electron-electron repulsion is not specifically taken into account.

### 2.2.1 The Hartree-Fock method

The Hartree-Fock (HF) method seeks to approximately solve the electronic Schrödinger equation, and it assumes that the wavefunction can be approximated by a single Slater determinant made up of one spin orbital per electron. Since the energy expression is symmetric, the variation theorem holds, and so we know that the Slater determinant with the lowest energy is as close as we can get to the true wavefunction for the assumed functional form of the single determinant. The Hartree-Fock equation determines the set of spin orbitals which minimize the energy and gives us this best single determinant. So, we need to minimize the Hartree-Fock energy expression with respect to changes in the orbitals:

$$\chi_i \rightarrow \chi_i + \delta \chi_i \quad (2.2)$$

We have also been assuming that the orbitals are orthonormal, and we want to ensure that our variation procedure leaves them orthonormal. The Hartree-Fock equation can be solved numerically, or they can be solved in the space spanned by a set of basis set functions (Hartree-Fock-Roothaan equation). In either case, note that the solution depends on the orbitals. Hence, we need to guess some initial orbitals and then refine our guess iteratively. For this reason, HF is called self-consistent-field (SCF) approach.

The first term above in the square brackets:

$$\sum_{j \neq i} \left[ \int dx_2 |\chi_j(x_2)|^2 r_{12}^{-1} \right] \chi_i(x_1) \quad (2.3)$$

gives the coulomb interaction of an electron in spin orbital  $\chi_i$  with the average charge distribution of the other electrons. Here we see in what sense HF is a mean field theory. This is called coulomb term and it is convenient to define a coulomb operator as:

$$J_j(x_1) \int dx_2 |\chi_j(x_2)|^2 r_{12}^{-1} \quad (2.4)$$

this gives the average local potential point  $x_l$  due to the charge distribution from the electron in orbital  $\chi_j$ . We can define an exchange integrals in terms of its action on an arbitrary spin orbital  $\chi_i$ :

$$K_j(x_1)\chi_i(x_1) = \left[ \int dx_2 \chi_j^*(x_2) r_{12}^{-1} \chi_i(x_2) \right] \chi_j(x_1) \quad (2.5)$$

Introducing a basis set transforms the HF equation into the Roothaan equation. Denoting the atomic orbital basis functions as  $\bar{\chi}$ , we have the expression:

$$\chi_i = \sum_{\mu=1}^K c_{\mu i} \bar{\chi}_{\mu} \quad (2.6)$$

for each spin orbital  $i$ . This leads to:

$$f(x_1) \sum_{\nu} c_{\nu i} \tilde{\chi}_{\nu}(x_1) = \epsilon_i \sum_{\nu} c_{\nu i} \tilde{\chi}_{\nu}(x_1) \quad (2.7)$$

This can be simplified by introducing the matrix element notation:

$$S_{\mu\nu} = \int dx_1 \bar{\chi}_{\mu}^*(x_1) \bar{\chi}_{\nu}(x_1) \quad (2.8)$$

$$F_{\mu\nu} = \int dx_1 \bar{\chi}_{\nu}^*(x_1) \bar{\chi}_{\mu}(x_1) \quad (2.9)$$

Now the Hartree-Fock-Roothaan equation can be written in matrix form as:

$$\sum_{\nu} F_{\mu\nu} C_{\nu i} = \epsilon_i \sum_{\nu} S_{\mu\nu} C_{\nu i} \quad (2.10)$$

or even more simply as matrices:

$$\mathbf{FC} = \mathbf{SC}\epsilon \quad (2.11)$$

where  $\epsilon$  is a diagonal matrix of orbital energies  $\epsilon_i$ . This is like an eigenvalue equation except for the overlap matrix S. One performs a transformation of basis to go to an orthogonal basis to make S vanish. Then it's just a matter of solving an

eigenvalue equation well, not quite. Since  $F$  depends on its own solution (through the orbitals), the process must be done iteratively. This is why the solution of Hartree-Fock-Roothaan equation is often called the SCF.

## **2.2.2 The Post-Hartree-Fock method**

In computational chemistry, Post-Hartree-Fock methods are the set of methods developed to improve on the HF, or SCF method. They add electron correlation which is a more accurate way of including the repulsions between electrons than in the HF method where repulsions are only averaged.

### **2.2.2.1 Electron correlation**

Electron correlation is the phenomenon of the motion of pairs of electrons in atoms or molecules being connected. The purpose of post-HF calculations is to treat such correlated motion better than does the HF method. In the HF treatment, electron-electron repulsion is handled by having each electron move in a smeared-out, average electrostatic field due to all the other electrons and the probability that an electron will have a particular set of spatial coordinates is independent of the coordinates of the other electrons.

There are basically three approaches to dealing with electron correlation: explicit use of the interelectronic distances as variables in the Schrödinger equation, treatment of the real molecule as a perturbed HF system, and explicit inclusion in the wavefunction of electronic configurations other than the ground-state one. The other two methods are general and very important: the perturbation approach is used in the very popular Møller-Plesset methods and the use of higher electronic configurations in the wavefunction forms the basis of configuration interaction, which in various forms is employed in some of the most advanced ab initio methods currently used for dealing with electron correlation.

#### **2.2.2.2 The Møller-Plesset approach to electron correlation**

The Møller-Plesset (MP) treatment of electron correlation is based on perturbation theory, a very general approach used in physics to treat complex systems;

this particular approach was described by Møller and Plesset in 1934 and developed into a practical molecular computational method by Binkley and Pople in 1975. Møller-Plesset calculations are denoted as MP, MPPT (MP perturbation theory) or MBPT (many-body perturbation theory) calculations. The derivation of the MP method is complicated, and only the flavor of the approach will be given here. There is a hierarchy of MP energy levels: MP0, MP1, MP2, etc..., which successively account more thoroughly for interelectronic repulsion.

“MP0” would use the electronic energy obtained by simply summing the HF one-electron energies. This ignores interelectronic repulsion except for refusing to allow more than two electrons in the same spatial MO. “MP1” corresponds to MP0 corrected with the columb and exchange integrals  $J$  and  $K$  (equations (2.4) and (2.5)).

“MP2” is the first MP level to go beyond the HF treatment. The MP2 energy is the HF energy plus a correction term that represents a lowering of energy brought about by allowing the electrons to avoid one another better than in the HF treatment:

$$E_{MP2} = E_{HF}^{total} + E^{(2)} \quad (2.12)$$

The HF term includes internuclear repulsions, and the perturbation correction  $E^{(2)}$  is a purely electronic term.  $E^{(2)}$  is a sum of terms each of which models the promotion of pairs of electrons from occupied to unoccupied MOs.

The MP2 energy correction for a closed-shell two-electron/two-MO system is:

$$E^{(2)} = \frac{\left[ \iint \psi_1(1)\psi_1(2)(1/r_{12})\psi_2(1)\psi_2(2)dv_1dv_2 \right]^2}{2(\varepsilon_1 - \varepsilon_2)} \quad (2.13)$$

The equation shows that the absolute value (the correction is negative since  $\varepsilon_1$  is smaller than  $\varepsilon_2$  – the occupied MO has a lower energy than the virtual one) of the correlation correction increases, with the magnitude of the integral. This integral represents the decrease in energy arising from allowing an electron pair in the occupied MO ( $\psi_1$ ) to spill over into the virtual MO ( $\psi_2$ ):



$\psi_1(1)$  represents electron 1 in  $\psi_1$  and  $\psi_1(2)$  represents electron 2 in  $\psi_1$ .  
 $\psi_2(1)$  represents electron 1 in  $\psi_2$  and  $\psi_2(2)$  represents electron 2 in  $\psi_2$ .

The operator  $1/r_{12}$  brings in coulombic interaction: the coulombic repulsion energy between infinitesimal volume elements  $\psi_1(1)\psi_1(2)dv_1$  and  $\psi_2(1)\psi_2(2)dv_2$  separated by a distance  $r_{12}$  is  $(\psi_1(1)\psi_1(2)dv_1)(\psi_2(1)\psi_2(2)dv_2)/r_{12}$ , and the integral is simply the sum over all such volume elements [16].

### 2.3 Basis sets

The approximate treatment of electron-electron distribution and motion assigns individual electron to one-electron function, termed spin orbital. These consist of 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  $\alpha$  or  $\beta$  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  $\psi$  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  $\psi_1, \psi_2, \dots, \psi_N$  are further restricted to be linear combinations of a set of N known one-electron function  $\phi_1(x,y,z)$ ,  $\phi_2(x,y,z)$ ,  $\phi_3(x,y,z)$ ,...,  $\phi_N(x,y,z)$ :

$$\psi_i = \sum_{\mu=1}^N c_{\mu i} \phi_{\mu} \quad (2.14)$$

The functions  $\phi_1, \phi_2, \dots, \phi_N$  which are defined in the specification of the model, are known as one-electron basis function called basis function. The set of basis function is called basis set. If the basis functions are the atomic orbitals for the atoms making up the molecule, function is equation (2.13) is often described as 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 semi empirical calculations where all three- and four-center integrals are neglected. The Slater type orbitals have the function form:

$$b = Ae^{-\zeta r} r^{n^*-1} Y_{lm}(\theta, \phi) \quad (2.15)$$

where parameter  $n^*$  and  $\zeta$  are chosen to make the larger part of the orbitals look like atomic HF 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:

$$g = x^a y^b z^c e^{-\alpha r^2} Y_{lm}(\theta, \phi) \quad (2.16)$$

in which  $a, b, c$  are integers and  $\alpha$  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 defined more realistic atomic orbital basis functions, as shown below:

$$b_\mu = \sum_p k_{\mu p} g_p \quad (2.17)$$

The coefficient  $k_{\mu p}$  in this expression 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 poor approximation to 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 Slater type orbital. Such a basis is denoted STO- $n$ G, and  $n = 3, 4$ .

The limit of quantum mechanics involves an infinite set of basis function. This is clearly impractical since the computational expense 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.

### 2.3.1 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 consists of a  $1s$ ,  $2s$  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 set comprises of 9 basis functions.

Several minimum basis sets are used as common basis sets especially the STO- $n$ G basis sets because they are available for almost all elements in the periodic table. The most common of basis sets is STO-3G, where a linear combination of three Gaussian type orbitals (GTOs) is fitted to 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 total of 9 contracted functions built from 27 primitive functions.

### 2.3.2 Split the valence orbitals (Split valence basis sets)

In the early calculation on the hydrogen molecule, it is discovered that 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.



The split valence basis sets mean that each valence orbital is split 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. The core orbitals are represented by one basis function and each function composes of three Gaussian functions. 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.

### 2.3.3 Polarized basis sets

In the discussion on the scaling of the hydrogen orbitals in the hydrogen 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.

6-31G\*\* added a set of *d* orbitals to the atoms in the first and second rows 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 and added 1 *p*-type and 1 *d*-type function to hydrogen.

### 2.3.4 Diffuse basis sets

Species with significant electron density far from removed from the nuclear centers *e.g.* anions, lone pairs and excited states require diffuse functions to account for the outermost weaker bound electrons. Diffuse basis sets are recommended for calculations of electron affinities, proton affinities, inversion barriers and bond angle in anions. The addition of diffuse *s*- and *p*-type Gaussian functions to non-hydrogen atoms is denoted by plus sign—as 6-31+G. Further addition of diffuse functions to both hydrogen and larger atoms is indicated by a double plus. 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 [17, 18].

## 2.4 Density functional theory (DFT)

The basis for density functional theory (DFT) is the proof by Hohenberg and Kohn that the ground-state electronic energy is determined completely by the electron density  $\rho$ . In other words, there exists a one-to-one correspondence between the electron density of a system and the energy. The significance of this is perhaps best illustrated by comparing to the wave function approach. A wave function for an  $N$ -electron system contains  $3N$  coordinates, three for each electron (four if spin is included). The electron density is the square of the wave function, integrated over  $N-1$  electron coordinates, this only depends on three coordinates, independently of the number of electrons. While the complexity of a wave function increases with the number of electrons, the electron density has the same number of variables, independently of the system size. The “only” problem is that although it has been proven that each different density yields a different ground-state energy, the functional connection these two quantities is not known. The goal of DFT methods is to design functionals connecting the electron density with the energy.

The foundation for the use of DFT methods in computational chemistry was the introduction of orbitals by Kohn and Sham. The basic idea in the Kohn and Sham (KS) formalism is splitting the kinetic energy functional into two parts, one of which can be calculated exactly, and a small correction term.

### 2.4.1 The Kohn-Sham energy

The ideal energy is that of an ideal system, a fictitious non-interacting reference system, defined as one in which the electrons do not interact and in which the ground state electron density  $\rho_r$  is exactly the same as in our real ground state system,  $\rho_r = \rho_0$ . The electronic energy of the molecule is the total internal “frozen-nuclei” energy can be found by adding the internuclear repulsions, and the 0 K total internal energy by further adding the zero-point energy.

The ground state electronic energy of our real molecule is the sum of the electron kinetic energy, the nucleus-electron attraction potential energies, and the electron-electron repulsion potential energies and each is a functional of the ground-state electron density.

$$E_0 = \langle T[\rho_0] \rangle + \langle V_{ne}[\rho_0] \rangle + \langle V_{ee}[\rho_0] \rangle \quad (2.18)$$

Focusing on the middle term, the nucleus-electron potential energy is the sum over all  $2n$  electrons of the potential corresponding to attraction of an electron for all the nuclei A

$$\langle V_{ne} \rangle = \sum_{i=1}^{2n} \sum_{\text{nuclei } A} -\frac{Z_A}{r_{iA}} = \sum_{i=1}^{2n} v(r_i) \quad (2.19)$$

where  $v(r_i)$  is the external potential for the attraction of electron  $i$  to the nuclei. The density function  $\rho$  can be introduced into  $\langle V_{ne} \rangle$  by using that

$$\int \psi \sum_{i=1}^{2n} f(r_i) \psi dt = \int \rho(r) f(r) dr \quad (2.20)$$

where  $f(r_i)$  is a function of the coordinates of the  $2n$  electrons of a system and  $\psi$  is the total wavefunction from equations (2.19) and (2.20), invoking the concept of expectation value  $\langle V_{ne} \rangle = \left\langle \psi \left| \hat{V}_{ne} \right| \psi \right\rangle$ , and since  $\hat{V} = V_x$ , and get,

$$E_0 = \int \rho_0(r)v(r)dr + \langle T[\rho_0] \rangle + \langle V_{ee}[\rho_0] \rangle \quad (2.21)$$

that can not known the function in  $\langle T[\rho_0] \rangle$  and  $\langle V_{ee}[\rho_0] \rangle$ . The Kohn and Sham to introduced the idea of a reference system of non-interacting electrons. Let us to define the quantity  $\Delta\langle T[\rho_0] \rangle$  as the deviation of the real kinetic energy from that of the reference system.

$$\Delta\langle T[\rho_0] \rangle \equiv \langle T[\rho_0] \rangle - \langle T_r[\rho_0] \rangle \quad (2.22)$$

Let us next define  $\Delta\langle V_{ee} \rangle$  as the deviation of the real electron-electron repulsion energy from classical charged-cloud coulomb repulsion energy. This classical electrostatic repulsion energy is the summation of the repulsion energies for pairs of infinitesimal volume elements  $\rho(r_1)dr_1$  and  $\rho(r_2)dr_2$  separated by distance  $r_{12}$ , multiplied by one-half. The sum infinitesimals is and integral and so

$$\Delta\langle V_{ee}[\rho_0] \rangle = \langle V_{ee}[\rho_0] \rangle - \frac{1}{2} \iint \frac{\rho_0(r_1)\rho_0(r_2)}{r_{12}} dr_1 dr_2 \quad (2.23)$$

Actually, the classical charged-cloud repulsion is somewhat inappropriate foe electrons in that smearing an electron out into a cloud forces it to repel itself, as any two regions of the cloud interact repulsively. This physically incorrect electro self-interacting will be compensated for by a good exchange-correlation functional can be written as

$$E_0 = \int \rho_0(r)v(r)dr + \langle T_r[\rho_0] \rangle + \frac{1}{2} \iint \frac{\rho_0(r_1)\rho_0(r_2)}{r_{12}} + \Delta\langle T[\rho_0] \rangle + \Delta\langle V_{ee}[\rho_0] \rangle \quad (2.24)$$

The sum of the kinetic energy deviation from the reference system and the electron-electron repulsion energy deviation from the classical system is called the exchange-correlation energy,  $E_{xc}$

$$E_{xc}[\rho_0] \equiv \Delta\langle T[\rho_0] \rangle + \Delta\langle V_{ee}[\rho_0] \rangle \quad (2.25)$$

The  $\Delta\langle T \rangle$  term represents the kinetic correlation energy of the electrons and the  $\langle \Delta V_{ee} \rangle$  term the potential correlation energy and the exchange energy, although exchange and correlation energy in DFT do have exactly.

#### 2.4.2 The Kohn-Sham equations

The Kohn-Sham (KS) equations are theorem obtained by utilizing the variation principle, which the second Hohenberg-Kohn theorem assures applies to DFT. We use the fact that the electron density of the reference system, which is the same as that of our real system, is given by

$$\rho_0 = \rho_r = \sum_{i=1}^{2n} |\psi_i^{KS}(1)|^2 \quad (2.26)$$

where the  $\psi_i^{KS}$  are the KS spatial orbital. Substituting the above expression for the orbitals into the energy and varying  $E_0$  with respect to the  $\psi_i^{KS}$  subject to the constraint that these remain orthonormal lead to the KS equations, procedure is similar to that used in deriving the HF equations,

$$\left[ -\frac{1}{2} \nabla_i^2 - \sum_{\text{nuclei } A} \frac{Z_A}{r_{iA}} + \int \frac{\rho(r_2)}{r_{12}} dr_2 + v_{xc}(1) \right] \psi_i^{KS}(1) = \epsilon_i^{KS} \psi_i^{KS}(1) \quad (2.27)$$

where  $\epsilon_i^{KS}$  are the KS energy levels and  $v_{xc}(1)$  is the exchange correlation potential, arbitrarily designated here for electron number 1, since the KS equations are a set of one-electron equations with the subscript  $i$  running from 1 to  $n$ , over all the  $2n$  electron in the system. The exchange correlation potential is defined as the functional derivative of  $E_{xc}[\rho_0(r)]$  with respect to  $\rho(r)$

$$v_{xc}(r) = \frac{\delta E_{xc}[\rho(r)]}{\delta \rho(r)} \quad (2.28)$$



We need the derivative  $v_{xc}$  for the KS equations, and the exchange-correlation function itself for the energy equation. The KS equations can be written as

$$\hat{h}^{KS} \psi_i^{KS} = \varepsilon_i^{KS} \psi_i^{KS} \quad (2.29)$$

The KS operator  $\hat{h}^{KS}$  is defined by equation (2.28). The difference between DFT method is the choice of the functional from of the exchange-correlation energy. Functional forms are often designed to have a certain limiting behavior, and fitting parameters to known accurate data. Which functional is the better will have to be settled by comparing the performance with experiments or high-level wave mechanics calculations.

### 2.4.3 DFT exchange and correlations

The form of  $E_{xc}$  is generally unknown and its exact value has been calculated only for a few very simple systems. In the density functional theory, the exchange energy is defined as

$$E_x[\rho] = \langle \phi[\rho] | \hat{V}_{ee} | \phi[\rho] \rangle - U[\rho] \quad (2.30)$$

When  $U[\rho]$  is the Hartree piece of the columbic potential. The correlation term is defined as the remaining unknown piece of the energy:

$$E_c[\rho] = F[\rho] - T_s[\rho] - U[\rho] - E_x[\rho] \quad (2.31)$$

Due to the definition of  $F[\rho]$ , the correlation energy consists of two separate contributions:

$$E_c[\rho] = T_c[\rho] + U[\rho] \quad (2.32)$$

when  $T_C[\rho]$  and  $U_C[\rho]$  are respectively the kinetic contribution and the potential contribution of the correlation energy.

In electronic structure calculations,  $E_{XC}$  is the most commonly approximation within the local density approximation or generalized–gradient approximation. In the local density approximation (LDA), the value of  $E_{XC}[\rho(r)]$  is approximated by exchange–correlation energy of an electron in homogeneous electron gas of the same density  $\rho(r)$ , *i.e.*

$$E_{XC}^{LDA}[\rho(r)] = \int \epsilon_{XC}(\rho(r))\rho(r)dr \quad (2.33)$$

The most accurate data for  $\epsilon_{XC}(\rho(r))$  is calculated from Quantum Monte Carlo calculation. For the systems with slowly varying charge densities, this approximation generally gives very good results. An obvious approach to improve the LDA, so called generalized gradient approximation (GGA), is to include gradient corrections by making  $E_{XC}$  a function of the density and its gradient as shown below

$$E_{XC}^{GGA}[\rho(r)] = \int \epsilon_{XC}(\rho(r))\rho(r)dr + \int F_{XC}[\rho(r), |\nabla\rho(r)|]dr \quad (2.34)$$

where  $F_{XC}$  is a correction chosen to satisfy one or several known limits for  $E_{XC}$ . Clearly, there is no unique equation for the  $F_{XC}$ , and several functions have been proposed. The development of the improved functions is currently a very active area of research although incremental improvements are likely. It is ambiguous whether the research will be successful in providing the substantial increase in accuracy that is desired.

#### 2.4.4 Hybrid functions

Hybrid functional augment the DFT exchange–correlation energy with a term calculated from Hartree-Fock theory. The Kohn-Sham orbitals are quit similar to the HF orbitals, give an expression, based on Kohn-Sham orbitals, for the HF exchange energy.

$$E_x^{HF} = - \sum_{i=1}^n \sum_{j=1}^n \left\langle \psi_i^{KS}(1) \psi_i^{KS}(2) \left| \frac{1}{r_{ij}} \right| \psi_j^{KS}(2) \psi_j^{KS}(1) \right\rangle \quad (2.35)$$

Since the KS Slater determinant is an exact representation of the wavefunction of the noninteracting electron reference system,  $E_x^{HF}$  is the exact exchange energy for a system of noninteracting electron with electron density equal to real system.

Including in a LSDA gradient-corrected DFT expression for  $E_{xc}$  ( $E_{xc} = E_x + E_c$ ) a weighted contribution of the expression for  $E_x^{HF}$  give a FH/DFT exchange-correlation functional, commonly called a hybrid DFT functional. The most popular hybrid functional at present is based on an exchange-energy functional developed by Becke, and modified Steven *et al.* by introduction of the LYP correlation-energy functional. This exchange-correlation functional, called the Becke3 LYP or B3LYP functional is

$$E_{xc}^{B3LYP} = (1 - a_0 - a_x) E_x^{LSDA} + a_0 E_x^{HF} + a_x E_x^{B88} + (1 - a_c) E_x^{VWN} + a_c E_c^{LYP} \quad (2.36)$$

Here  $E_x^{LSDA}$  is the kind accurate pure DFT LSDA non-gradient-corrected exchange functional,  $E_x^{HF}$  is the Kohn-Sham orbitals based HF exchange energy functional,  $E_x^{B88}$  is the Becke 88 exchange functional

$$\begin{aligned} E_x^{B88} &= E_x^{LDA} + \Delta E_x^{B88} \\ \Delta E_x^{B88} &= -\beta \rho^{1/3} \frac{x^2}{1 + 6\beta x \sinh^{-1} x} \end{aligned} \quad (2.37)$$

The  $\beta$  parameter is determined by fitting to known atomic data and  $x$  is a dimension gradient variable. The  $E_x^{VWN}$  is the Vosko, Wilk, Nusair function (VWN) can be written

$$\begin{aligned} E_x^{VWN} &= E_x^{LDA} (1 + ax^2 + bx^4 + cx^6)^{1/5} \\ x &= \frac{|\nabla \rho|}{\rho^{4/3}} \end{aligned} \quad (2.38)$$

which forms part of the accurate functional for the homogeneous electron gas of the LDA and LSDA, and  $E_c^{LYP}$  is the LYP correlation functional. The parameters  $a_0$ ,  $a_x$  and  $a_c$  are those that give the best fit of the calculated energy to molecular atomization energies. This is thus gradient-corrected hybrid functional [17].

## 2.5 Transition state theory

Transition state theory (TST) or activated complex theory provides a simple formalism for obtaining thermal rate constant by mixing the important features of the potential energy surface with a statistical representation of the dynamics. In addition to the Born- Oppenheimer approximation, TST is based on three assumptions:

- Classically there exists a surface in phase space that divides it into a reactant region and a product region. It is assumed that this dividing surface is located at the transition state, which is defined as the maximum value on the minimum energy path (MEP) of the potential energy surface that connects the reactant(s) and product(s). Any trajectory passing through the dividing surface (or bottleneck) from the reactant side is assumed to eventually form products. This is often referred to as the nonrecrossing rule.

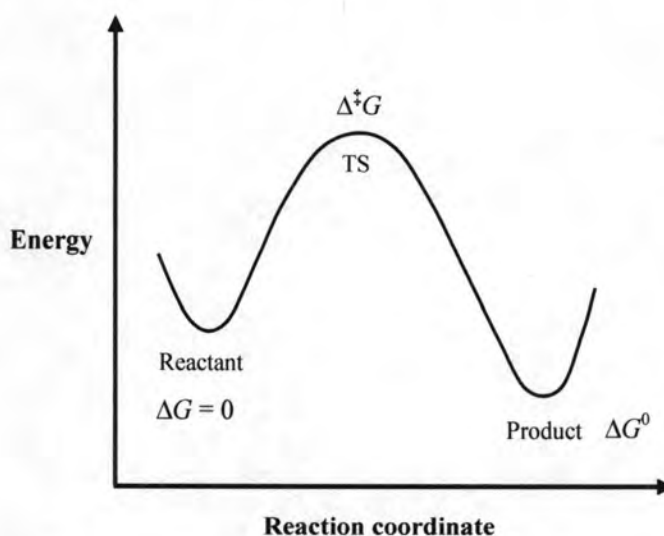
- The reactant equilibrium is assumed to maintain a Boltzmann energy distribution.

- Activated complexes are assumed to have Boltzmann energy distributions corresponding to the temperature of the reacting system. These activated complexes are defined as super-molecules having configurations located in the vicinity of the transition state.

In chemistry, transition state theory is a conception of chemical reactions or other processes involving rearrangement of matter as proceeding through a continuous change or "transition state" in the relative positions and potential energies of the constituent atoms and molecules. The theory was first developed by R. Marcelin in 1915, then continued by Henry Eyring and Michael Polanyi (Eyring equation) in 1931, with their construction of a potential energy surface for a chemical reaction, and

later, in 1935, by H. Pelzer and Eugene Wigner. Meredith Evans, working in coordination with Polanyi, also contributed significantly to this 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 will continue on 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, shown in Figure 2.1.



**Figure 2.1** Schematic illustration of reaction path.

TST assumes equilibrium energy distribution among all possible quantum states at all points along the reaction coordinates. The probability of finding a molecule 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

$$k = \frac{k_B T}{h c^0} e^{-\Delta^\ddagger G / RT} \quad (2.39)$$



$\Delta^\ddagger G$  is the Gibbs free energy difference between the TS and reactant,  $T$  is absolute temperature and  $k_B$  is Boltzmann's constant and  $c^0$  is concentration factor. From the TST expression (2.39) it is clear that if the free energy of the reactant and TS can be calculated, the reaction rate follows trivially. The equilibrium constant for a reaction can be calculated from the free energy difference between the reactant(s) and product(s).

$$K_{eq} = e^{-\Delta G_0 / RT} \quad (2.40)$$

The Gibbs free energy is given in terms of the enthalpy and entropy,  $G = H - TS$ .

### 2.5.1 Partition functions

The first step in determining the thermal contributions to the enthalpies and entropies of a molecule is to determine its partition function,  $q$  which is a measure of the number of accessible to the molecule (translational, rotational, vibrational and electronic states) at a particular temperature.

It is assumed that the translational ( $T$ ), rotational ( $R$ ), vibrational ( $V$ ) and electronic ( $E$ ) modes of the system can be separated, thus allowing the energy of each level,  $E_i$ , to be separated into  $T$ ,  $R$ ,  $V$  and  $E$  contributions as

$$E = E_i^T + E_i^R + E_i^V + E_i^E \quad (2.41)$$

While the translational modes are truly independent from the rest, the separations of other modes are based on an approximation, in particular the Born-Oppenheimer approximation for electronic and vibrational motion and the rigid rotor approximation which assumes (that the geometry of the molecule does not change as it rotates) for vibrational and rotational modes. Within these approximations, the total molecular partition function can therefore be factorized into translational, rotational, vibrational and electronic contributions:

$$q = q_{trans} q_{vib} q_{rot} q_{elect} \quad (2.42)$$

### 2.5.1.1 Translational partition function

For bimolecular reactions, the ratio of the translational partition functions may be simplified to yield the relative translational partition in per unit volume as

$$q_{trans} = \frac{V}{\Lambda^3} \quad (2.43)$$

$$\Lambda = h \left( \frac{\beta}{2\pi m} \right)^{1/2} \quad (2.44)$$

where  $h$  is Planck's constants,  $m$  is the mass of the molecule and  $V$  is the available volume to it. For a gas phase system this is the molar volume (usually determined by the ideal gas equation) at the specific temperature and pressure.

### 2.5.1.2 Vibrational partition function

The vibrational partition functions are calculated quantum mechanically within the framework of the harmonic approximation. The harmonic oscillator partition function is given by:

$$q_{trans} = \prod_i \frac{1}{1 - e^{-\beta h c \tilde{\nu}_i}} \quad (2.45)$$

where  $\tilde{\nu}_i$  is the vibrational frequency in  $\text{cm}^{-1}$  for mode  $i$ . The product is over all vibrational modes.

### 2.5.1.3 Rotational partition function

The formulation for rotational partition functions depends on whether or not the molecule is linear. For linear molecules

$$q_{rot} = \frac{k_B T}{\sigma h c B} \quad (2.46)$$

and for non linear

$$q_{rot} = \frac{1}{\sigma} \left( \frac{k_B T}{hc} \right)^{3/2} \left( \frac{\pi}{ABC} \right)^{1/2} \quad (2.47)$$

where  $\sigma$  is the rotational symmetry number of the molecule,  $c$  is the speed of light and  $A, B, C$  are the rotational constants.

#### 2.5.1.4 Electronic partition function

For the electronic partition function, an adiabatic potential energy surface is assumed. The electronic degeneracies along the MEP are assumed to be the same as at the transition state. The formula employed is

$$q_{elect} = \omega_{e1} + \omega_{e1} \exp(-\beta \Delta \varepsilon_{12}) + \dots \quad (2.48)$$

where  $\Delta \varepsilon_{1j}$  is the energy of the  $j^{th}$  electronic level relative to the ground state and  $\omega_{ej}$  is the corresponding degeneracy.

#### 2.5.2 Molecular vibrational frequencies

The total molecular energy  $E$  is approximately the sum of translation, rotational, vibrational, and electronic energies. In the harmonic oscillator approximation, the vibrational energy of an N-atom molecule is the sum of  $3N-6$  normal mode vibrational energies ( $3N-5$  for a linear molecule):

$$E_{vib} \approx \sum_{k=1}^{3N-6} \left( \nu_k + \frac{1}{2} \right) h \nu_k \quad (2.49)$$

where  $\nu_k$  is the harmonic vibrational frequency for the  $k^{th}$  normal mode and each vibrational quantum number  $\nu_k$  has the possible values 0, 1, 2, ..., independent of the value of the order vibrational quantum numbers.

The harmonic vibrational frequencies of a molecule are calculated as follows.

(1) Solve the electronic Schrödinger equation  $(\hat{H}_{el} + V_{NN})\psi_{el} = U\psi_{el}$  for several molecular geometries to find the equilibrium geometry of the molecule. (2) Calculate the set of second derivatives  $(\partial^2 U / \partial X_i \partial X_j)_e$  of the molecular electronic energy  $U$  with respect to the  $3N$  nuclear Cartesian coordinates of a coordinate system with origin at the center of mass. (3) Form the mass-weighted force-constant matrix elements

$$F_{ij} = \frac{1}{(m_i m_j)^{1/2}} \left( \frac{\partial^2 U}{\partial X_i \partial X_j} \right)_e \quad (2.50)$$

where  $i$  and  $j$  each go from 1 to  $3N$  and  $m_i$  is the mass of the atom corresponding to coordinate  $X_i$ . (4) Solve the following set of  $3N$  linear equations in  $3N$  unknowns

$$\sum_{j=1}^{3N} (F_{ij} - \delta_{ij} \lambda_k) l_{jk} = 0 \quad i = 1, 2, \dots, 3N \quad (2.51)$$

In this set of equations,  $\delta_{ij}$  is the Kronecker delta, and  $\lambda_k$  and the  $l_{jk}$ 's are as-yet unknown parameters whose significance will be seen shortly. In order that this set of homogeneous equations has a nontrivial solution, the coefficient determinant must vanish

$$\det(F_{ij} - \delta_{ij} \lambda_k) = 0 \quad (2.52)$$

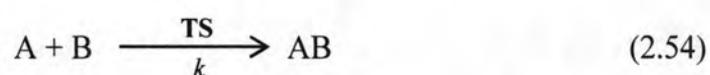
This determinant is of order  $3N$  and when expanded gives a polynomial whose highest power of  $\lambda_k$  is  $\lambda_k^{3N}$ . The molecular harmonic vibrational frequencies are then calculated from

$$\nu_k = \lambda_k^{1/2} / 2\pi \quad (2.53)$$

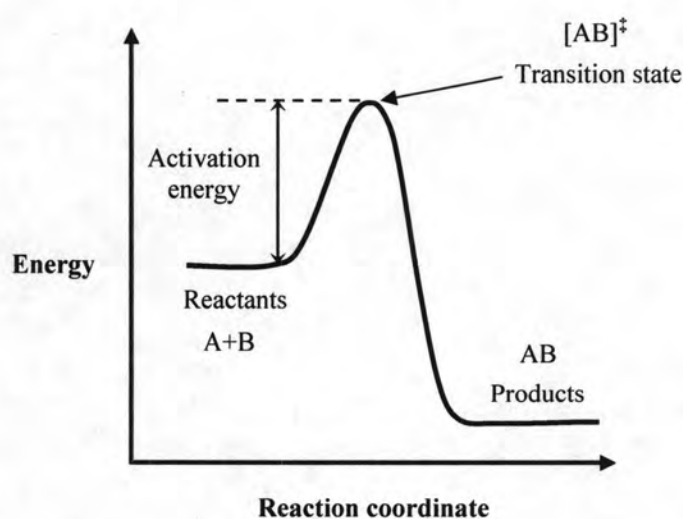
Six of the  $\lambda_k$  values found by solving will be zero, yielding six frequencies with value zero, corresponding to the three translational and three rotational degrees of freedom of the molecule. The remaining  $3N-6$  vibrational frequencies are the molecular harmonic vibrational frequencies [20].

## 2.6 Rate constant

An activated complex  $[AB]^\ddagger$  or transition state is formed at the potential energy maximum as shown in Figure 2.2. The high-energy complex represents an unstable molecular arrangement, in which bonds break and form to generate the product AB or to degenerate back to the reactants A and B as shown in equation (2.54). In the simple form of transition state theory, it is supposed that the transition state (TS) is in equilibrium with the reactants, and that its abundance in the reaction mixture can be expressed in terms of an equilibrium constants, which is normally denoted  $K$ :



$$K = \frac{[AB]}{[A][B]} \quad (2.55)$$



**Figure 2.2** Energy profile: Potential energy reaction coordinate for A and B via TS  $[AB]^\ddagger$ .



Then, if we supposed that the rate at which products are formed is proportional to the concentration of the TS, we can write

$$\text{Rate of formation of products} = k[\text{TS}]$$

We see that the rate constant  $k$  is proportional to the equilibrium constants  $K^\ddagger$  for the formation of the TS. We have already seen that an equilibrium constant may be expressed in terms of the standard reaction Gibbs energy, which in this case is the activation Gibbs energy,  $\Delta^\ddagger G$ , for the formation of the TS from the reactants. It follows from the equation (2.54) that

$$K = e^{-\Delta^\ddagger G / RT} \quad (2.56)$$

Furthermore  $\Delta^\ddagger G$  is given by

$$\Delta^\ddagger G = \Delta^\ddagger H - T\Delta^\ddagger S \quad (2.57)$$

Combining equation (2.56) and the equation (2.57) and solving for  $\ln K$  yields

$$\ln K = \frac{-\Delta^\ddagger H}{RT} + \frac{-\Delta^\ddagger S}{R} \quad (2.58)$$

The *Eyring equation*: is found by substituting equation (2.58) into equation (2.56)

$$k = \frac{k_B T}{hc^0} e^{-\frac{\Delta^\ddagger H}{RT}} e^{\frac{\Delta^\ddagger S}{R}} \quad \text{or} \quad k = \frac{k_B T}{hc^0} e^{-\frac{\Delta^\ddagger G}{RT}} \quad (2.59)$$

## 2.7 Tunneling corrections

Tunneling corrections were calculated using the Wigner [21], Eckart [22], the multi-dimensional zero-curvature (ZCT) [23] and centrifugal-dominant small-curvature (SCT) [24] methods. The Wigner method is a simple, zeroth-order tunneling approximation and only depends on the curvature at transition state. The Eckart method is believed to be one of the more accurate approximate one dimensional tunneling corrections. The Eckart tunneling factor is calculated by fitting

an Eckart potential to the MEP using the curvature at the transition state, the zero-point energy inclusive energy barrier, and the reaction energy. The ZCT method is a minimum-energy-path, semiclassical adiabatic ground-state (MEPSAG) method which takes into account tunneling along the MEP. Reaction path curvature and coupling to modes orthogonal to the MEP are neglected. The SCT method is a centrifugal-dominant small-curvature semi-classical adiabatic ground-state (CD-SCSAG) method which accounts for the curvature of the reaction path and approximately incorporates tunneling paths other than the MEP.

Reaction rate coefficients were calculated using the

$$k = \kappa \left[ \frac{k_B T}{h} \right] \left[ \frac{Q_{TS}}{Q_{Complex}} \right] e^{-\Delta^\ddagger E / RT} \quad (2.60)$$

where tunneling factor,  $\kappa = 1 + (1/24)(h\nu_i c / k_B T)^2$ ,  $k_B$  is Boltzman constant,  $T$  is absolute temperature,  $Q_{TS}$  and  $Q_{Complex}$  are the partition functions of transition state and complex, respectively,  $h$  is Plank constant,  $c$  is speed of light and  $\nu_i$  is imaginary frequency of transition state.

## 2.8 Thermochemistry

The term energy in chemistry can mean potential energy, enthalpy, or Gibbs free energy. The potential energy on a computed Born-Oppenheimer surface represents 0 K enthalpy difference without ZPE. Enthalpy difference  $\Delta H$  and free energy difference  $\Delta G$  are related through the entropy difference:

$$\Delta G = \Delta H - T\Delta S \quad (2.61)$$

To get  $\Delta H$ ,  $\Delta G$  and  $\Delta S$  we can regard it as essentially measure of the reaction enthalpy between product and reactant:

$$\Delta H = H_{product} - H_{reactant} \quad (2.62)$$

$$\Delta G = G_{product} - G_{reactant} \quad (2.63)$$

$$\Delta S = S_{product} - S_{reactant} \quad (2.64)$$