CHAPTER 2

MODEL OF SOLUTION :THE INTERMOLECULAR
POTENTIALS

2.1 Introduction

Chapter 1 has indicated how computer simulations can be a powerful tool for developing our understanding of molecular systems at the atomic/molecular level. However, there are two major limitations preventing computer simulations from fulfilling their true potential in providing scientific insights and aiding the industrial development of new materials. The first problem is that simulations require considerable computing resources; this limitation is rapidly being overcome by the hardware and software development. The second one is the accuracy of the fundamental input into the simulations, i.e., the intermolecular model potential, which quantifies the forces acting between the particles.

Since the quality of the results from the simulations definitely depend on the quality of the input, it is important to be able to assess the likely accuracy of an intermolecular potential. Intermolecular potentials are well known with very high accuracy for the rare gases. Much current work on deriving accurate intermolecular potentials is concentrating on small rigid polyatomic molecules. Due to the shortage of reasonable intermolecular potentials, the development in the field of solution research by means of computer simulations seem to be slower than it should be according to technological advances.

Early simulation works were aimed at understanding general features of, for example, liquid behaviour, and so idealised model potentials were appropriate. Nowadays, many simulations are undertaken in order to model real systems. The simulations seek to produce results which are in agreement with experiment. The first stage in such a computer simulation is to find a model for the intermolecular interactions in the chosen system, which is sufficiently realistic to give worthwhile results. There are, of course, difficulties to do so since there are no generally reliable simple procedures for developing intermolecular potentials. Mostly, one must choose which potentials are suitable for the intended simulation by considering the nature of the system. In order to improve this situation, more accurate intermolecular potentials, which are reliably transferable from study to study, must be constructed.

2.2 Definitions and Approximations

2.2.1 Pairwise Additive Approximation

An intermolecular pair potential $U(R,\Omega)$ is defined as the energy of interaction of a pair of molecules as a function of their relative separation R and orientation Ω. To approach the intermolecular potential with pairwise additive approximation, some assumptions have been made as followings.

(a) First, molecules are treated as rigid molecules, which is usually a good approximation for small molecules. Sometimes the potential is also a function of the intramolecular bond-lengths and bond-angles for studying the transfer of energy between translational and vibrational motions. Organic molecules are not usually rigid, so it is usual to model their intermolecular forces by

approximating the molecule as a set of fragments and assuming that contributions from each fragment do not depend on the molecular conformation. This assumption will only be valid if the charge density associated with each fragment does not change with the conformation of the molecule.

(b) The total interaction energy of a many-(N-) molecule system based upon the pairwise additive approximation can be calculated as

$$U \approx \sum_{i<j}^{N} U_{ij}(R_{ij}, \Omega_{ij})$$

Indeed, an exact interaction energy of the system does not only sum over all possible pairs, but also other higher-order non-additive terms. The exact interaction energy of a system consisting of N rigid molecules is given by

$$U = \sum_{i<j}^{N} U_{ij} + \sum_{i<j<k}^{N} U_{ijk} + \sum_{i<j<k<l}^{N} U_{ijkl} + \dots + U_{ijk\dots N}$$

where U_{ij} is the previously outlined intermolecular pair potential describing the interaction of two molecules, and U_{ijk}, U_{ijkl}, $U_{i,j,k,\dots N}$ are the 3-, 4-, and N-body terms whose energy reflects the error in the pairwise additive approximation. Many-body terms certainly play a role and their importance depends on the system, especially when ions in solution are concerned.

2.2.2 The Isotropic Atom-Atom Approximation

The intermolecular interaction energy between a pair of molecules is assumed as a sum of interactions between every intermolecular pair of atoms, and these interactions thus depend only on the separation of the atoms. A typical model is

$$U_{ij} = \sum_{kl} B_{\kappa\lambda} \exp(-C_{\kappa\lambda} R_{kl}) - A_{\kappa\lambda}/R_{kl}^6 + q_\kappa q_\lambda/R_{kl} \qquad (2.2)$$

where atom k, of atomic type κ belongs to molecule i at a distance R_{kl} from atom l of type λ in molecule j. This model has an exponential term for the repulsion, a R^{-6} dispersion term, and a point charge electrostatic term, which are quantified by the parameters $B_{\kappa\lambda}$ and $C_{\kappa\lambda}$, $A_{\kappa\lambda}$, and charges q_κ and q_λ respectively. Other potentials may have a variety of other terms, where atom-atom potential can be a more complex function of R_{kl} [41]. With regard to the aforementioned definition of the intermolecular pair potential as a function of molecule pair separations and orientation, the orientation dependence is implicit in the use of an isotropic atom-atom assumption. The isotropic atom-atom approximation is a fairly good approximation considering its convenience and reliability, which recognises just the relative positions of the atoms within the molecule as the major factor in determining the interaction energy between pairs of molecules. In addition, the isotropic atom-atom approach may allow transfering the potential parameters for a particular atom in a molecule to others. This assumption completely neglects the effects of attached atoms, which implies that every atom is treated as spherical shape. Therefore, errors may occur somehow, but these errors can be partly absorbed into the

parameters, according to which parts of the intermolecular potential are sampled in fitting. There is considerable cancellation of errors between different components of the potentials, so taking some parts of potentials, and combining them with other terms, can make the overall scheme be useable. Hence, it is not possible to state that a given parameter set is best, except in the sense that it has been fitted and tested against the widest range of data. The only way of establishing which potential will be best for the purposes of a given simulation is by trying a variety of functional forms.

2.2.3 Contributions to the Intermolecular Potential

The intermolecular forces all have an electronic origin and are fundamentally the same as the forces involved in chemical bonding; although magnetic and gravitational effects do exist, they can normally be neglected. There is no general description of what components are composed in a potential. Thus, it is dependent upon how it has been established. An intermolecular potential which is derived from empirical data may contain different parts from one derived by fitting quantum-mechanical energies. In principle, each intermolecular potential consists of an attractive and a repulsive potential. The attractive potential reflects the long-range interaction, while the repulsion dominates the short-range interaction. In general, most intermolecular potentials are usually described by a repulsive potential, a dispersion term, point-charge Coulombic interaction, and sometimes general polarization terms. Morokuma [42] has successfully developed a method of separating the Hartree-Fock energy into several components, including electrostatic, exchange repulsion, charge-transfer, and polarization components. The importance of what components represent the main interaction varies from system to system. In hydrocarbon systems, the hydrogen-hydrogen repulsive forces dominate the

interaction energy [43]. On contrary, hydrogen bonding interaction is most important in water.

2.3 Classification of Intermolecular Potentials

Intermolecular potentials fall roughly into three classes namely, model potential, empirical potential, and quantum-mechanical potential. The model potential is the most simple one, but it has also the specific intention of showing that the structure of simple liquids is more or less universal and could be well approximated by the interaction of rigid spherical particles. It dominated in the early literature of Molecular Dynamics [44,45] Monte Carlo [46,47] simulations as presented in the work of van der Waals and also in the hard-sphere glasses built from ball bearings by Bernal [48]. As time went on and computers became more powerful, the focus of such simulations shifted away from the general properties of liquids to the more specific, leading to the need of more realistic models to an increasing extent. At present, intermolecular potentials employed in most simulations are empirical and quantum-mechanical intermolecular potentials. The latter one seem to be of advantage in both aspects of its accuracy and transferability.

2.3.1 Model Intermolecular Potentials

Model intermolecular potentials have been also known as "idealized" intermolecular potentials for the reason that they do not represent realistic interactions between molecules pair. For the purpose of investigating general properties of liquids and solutions and for comparison with theory, they may be, however, of value. Thus, it is very common to use them in computer simulations. There are three forms of the

model intermolecular potentials; the hard-sphere potential, the square-well potential, and the soft-sphere potential. Because of their simple mathematical form, many of the empirical intermolecular potentials are derived from them with refining of experimental data.

(a) hard-sphere potential

This model represents molecules as rigid spheres of diameter σ: two such molecules will bounce off each other elastically if their centers approach to a distance σ, but otherwise do not interact at all. The potential can be written in the form

$$V(r) = \infty \quad (r \leq \sigma)$$
$$V(r) = 0 \quad (r > \sigma)$$

as shown in Fig. 2.1(a). This model takes account of only the short-range repulsion which is always infinitely large in the inner space of the molecule sphere. Due to its simplest form, it has the greatest advantage compared to other model potentials, so that simulations with this model can be carried out with relative ease. In many cases such simulations give a good qualitative picture of the effects of molecular collisions. This is especially true at relatively high temperatures, where molecules have enough kinetic energy that they encounter mainly the upper portion of the repulsive curve. Most of the principles of kinetic theory can be developed with only this model.
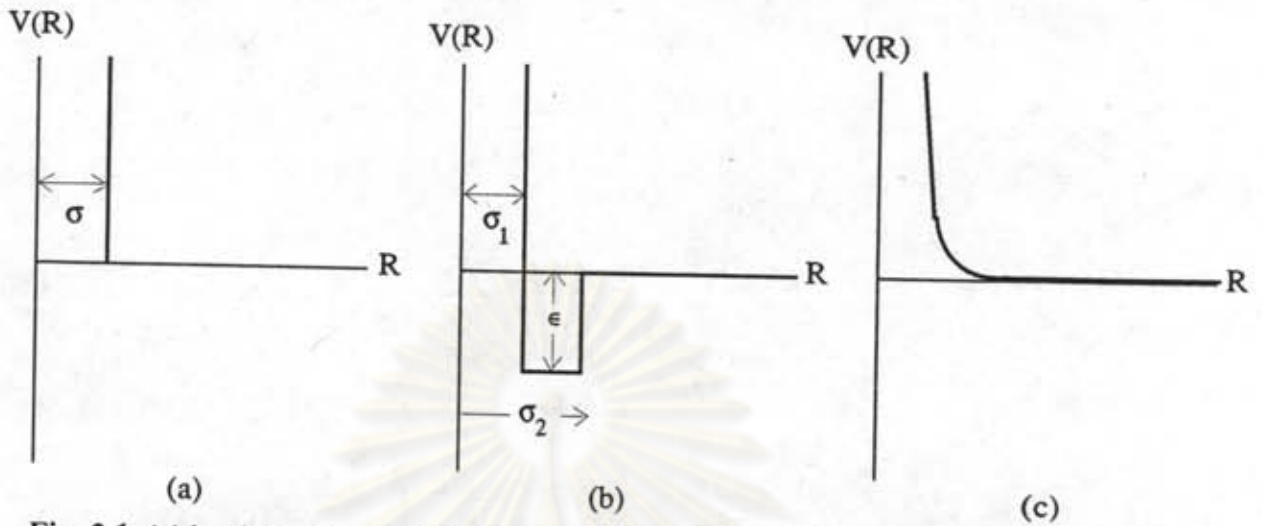
Fig. 2.1 (a) hard-sphere model (b) square-well model (c) soft-sphere model

(b) Square-well potential

This is one of the simplest potential including both attractive and repulsive contributions, as shown in Fig. 2.1(b), a hard-sphere surrounded by an attractive well of constant depth. The square-well potential is defined by the equations

$$V(R) = \infty \quad (R \leq \sigma_1)$$
$$V(R) = -\epsilon \quad (\sigma_1 < R < \sigma_2)$$
$$V(R) = 0 \quad (R \geq \sigma_2)$$

with the three adjustable parameters σ_1, σ_2 and ϵ. This model is a good compromise between mathematical simplicity and realism.

(c) Soft-sphere model

A somewhat more realistic representation of the repulsive energy is given by the potential

$$V(R) \quad = cR^{-\delta},$$

Fig. 2.1(c), where c is a positive constant and the index of repulsion δ must be larger than 3 (values between 9 and 15 are usually found) [49]. This model recognizes the fact that more energetic molecules can approach each other more closely before being repelled, and thus can represent some of the temperature dependence of properties. But it again neglects the attractive part of the molecular interaction, and has mainly just mathematical convenience to recommend it.

2.3.2 Empirical Intermolecular Potentials

The empirical model for intermolecular potentials has been developed in order to fix the problems of non-realistic model intermolecular potential for many years before the ab-initio calculations became possible for calculating molecular energies with high accuracy. Most empirical intermolecular potentials are derived by fitting only one observed property, such as lattice constants [50], or vibrational spectra [51], to a potential function. Those potentials are usually not sufficient to describe the interaction energies when the system enhances its complexity. However, fitting a wide variety of experimental data is very difficult because the observed properties sometimes does not correlate altogether. Limited attempts have been made to combine several different types of properties in one potential [51,52], but this has been done only for a small class of systems. Need of a large amount of experimental data for highly accurate potential hinders development of the empirical model. Moreover, there are no experimental data available for large classes of systems.

To determine an empirical intermolecular potential requires,

(i) some experimental data for some properties of the molecular solid, liquid

or gas, which is sensitive to the intermolecular potential,

(ii) a quantitative theory to forward those properties to be an intermolecular potential, and

(iii) an assumed functional form for the intermolecular potential which contains some adjustable parameters.

Most of the early models were based on the Lennard-Jones potential of the form

$$U(R) \quad = \quad \epsilon \left[\, [\frac{\rho}{R}]^{12} \, - \, 2 \, [\frac{\rho}{R}]^{6} \, \right]$$

which has only two parameters, the minimum energy separation ρ and the well depth ϵ. It has a reasonable functional form at long range, as the dominant term in the dispersion energy is R^{-6}. The R^{-12} term for the repulsive wall was chosen purely for mathematical convenience (an exponential one would be sometimes more realistic). This model potential is then fitted to the experimental data by first guessing initial values for ϵ and ρ, calculating the property from the guessed potential, comparing with the experimental values, and thereby deriving an improved estimate of ϵ and ρ, using some fitting criteria such as a least squares minimization. The set of parameters which gives the 'best' agreement with experiment defines the potential, which can then be used in the simulation.

2.3.3 Quantum Mechanical Intermolecular Potentials

According to difficulties in obtaining highly accurate empirical intermolecular potentials, the advantages of modern and fast computers is utilized

more and more for the energy calculations of chemical systems, and quantum-mechanical intermolecular potentials now become a helpful tool to computer simulations. In the view of quantum mechanics, the intermolecular energy is assumed to be the difference of the supermolecule (dimer or complex) energy and the energies of its constituents.

$$E(intermolecular) = E(supermolecule) - E(constituents)$$

Since the intermolecular potentials employed in the simulations of this study have been derived by quantum chemical method, in the following two sections some details of quantum mechanics as well as the construction procedure are presented.

2.4 Quantum Mechanical Method

The principle of quantum mechanics is to calculate physical quantities by solving Schrödinger equation,

$$H\Psi = E\Psi .$$

The total energy is thus obtained, as expectative value of H, i.e.

$$E = < \Psi|H|\Psi > ,$$

where Ψ is the normalized total wave function of the system. To calculate the energy of a chemical system by means of quantum-mechanics method in practice, the following is done:

a) defining an approximate Hamiltonian operator for the system,

b) selecting some mathematical function $\Psi(q_1, q_2, q_3, ...)$ as trial wave function, where $q_1, q_2, q_3, ...$ are finitely variable parameters,

c) minimizing the total energy, with respect to variations of the parameters until the change of energy is lower than a given limit (e.g. 10^{-5} Hartree).

This procedure finally leads to the ab-initio or Hartree-Fock SCF method [53,54].

2.4.1 Hartree-Fock approximation

The total Hamiltonian operator (H) of the many electron system can be given as sum of all possible Coulombic energy operator and kinetic energy operators of the electrons and nuclei of the form,

$$H = -\sum_A \frac{1}{2} M_A \nabla^2 - \frac{1}{2} \sum_i \nabla_i^2 - \sum_A \sum_i Z_A / r_{Ai} + \sum_{i<j} \sum 1/r_{ij} + \sum_{A<B} \sum Z_A Z_B / r_{AB}$$

where $\nabla^2 = \partial^2/\partial x^2 + \partial^2/\partial y^2 + \partial^2/\partial z^2$, r and M are distance and mass, respectively. A and B are nuclei, and i and j represent electrons. The first approximation of this approach is a non-relativistic model of electrons in the system. The first term of the above equation, the kinetic energy of the nuclei, can be neglected according to the Born-Oppenheimer approximation which assumes that the nuclei are so heavy that their motions are very slow relative to those of the electrons. The last term, the repulsion between the nuclei, thus becomes constant and can be separately calculated. Consequently, only the remaining terms form the electronic Hamiltonian, H^{el}.

2.4.2 Independent Particle Model, Molecular Orbitals and Linear Combination of Atomic Orbitals (LCAO) Approximation

Even the simplified n-electron equation resulting from the BO approximation is still beyond practical useability for molecular systems. This gave rise to a much more drastic simplification, known as Independant Particle Model or Orbital Approximation. The basic principle of it is the assumption of independent electron movement, i.e. that any single electron is moving independent in the field of the others, without having its movement correlated to the movement of the others (for this reason the error in the total energy obtained at this level of approximation compared to the Born-Oppenheimer level is refered to as "correlation energy"). For the Hamiltonian, this means a splitting of the n-electron Hamiltonian into n 1-electron Hamiltonians:

$$H^{el} = \sum_i H^{core}(i) + \sum_{i<j} \frac{1}{r_{ij}}$$

where

$$H^{core}(i) = \frac{1}{2} \nabla_i^2 - \sum_A \frac{Z_A}{r_{iA}}$$

$H^{core}(i)$ is the core Hamiltonian operator of an electron that represents the kinetic energy of an electron and its interaction with all nuclei of the system.

For the wavefunction, this approximation is equivalent to setting up the n-electron probability function as a product of n 1-electron functions, i.e.

$$\Psi^{n\text{-}el.} = \Psi_{(1)}\Psi_{(2)}\Psi_{(3)}\Psi_{(4)}........\Psi_{(n)},$$

the so-called Hartree Product.

However, since this form of function does not guarantee that it correctly follows the Pauli antisymmetry principle (electrons are fermions), the Hartree product must be antisymmetrized. This Hartree-Fock ansatz leads to the form of determinantal functions for the n-electron system, which is widely known as Slater determinants:

$$\Psi^{n\text{-}el.} = \frac{1}{\sqrt{n!}} \begin{vmatrix} \psi_1(1) & \psi_2(1) & .... & \psi_n(1) \\ \psi_1(2) & \psi_2(2) & .... & \psi_n(2) \\ .... & .... & .... & .... \\ \psi_1(n) & \psi_2(n) & .... & \psi_n(n) \end{vmatrix}$$

The 1-electron functions, consisting of a spatial part and a spinfunction α or β are known as spin orbitals or molecular orbitals. They are still fairly complicated functions and thus an appropriate method to obtain them is to construct them from a set of simple basis functions, which are usually assigned to all atoms of the system and thus known as atomic orbitals (ϕ). A molecular orbital (ψ) is then obtained by a linear combination of these atomic orbitals (LCAO-MO method), as

$$\psi_i = \Sigma_\mu c_{\mu i}\phi_\mu$$

where $c_{\mu i}$ are the linear combination coefficients. The quality of the molecular orbitals is related to the quality of the basis set used. The early STO basis functions (Slater Type Orbital) introduced by Slater [55], is based on approximations of hydrogen-like

atomic orbitals according to empirical rules. They were mostly used for the calculations of small molecules. Although the advantage of using a few functions of STO satisfies us for its simplicity and more accurate representation of atomic orbitals, the integrations of the functions are very time-consuming. The typical form of STO is denoted by the expression;

$$\phi^{STO} = Nr^{(n-1)} \exp(-\beta r)Y_{l,m}(\theta,\Phi),$$

where β, n, $Y_{l,m}$ are the exponent coefficient, principle quantum number and the angular part of the wave function, respectively.

An alternative to the STOs is the use of a GTO (Gaussian Type Orbital) basis set [56], which represents a STO by a sum of Gaussian functions of the form

$$\phi^{GTO} = \alpha_i N \exp(-\beta_i r^2)Y_{l,m}(\theta,\Phi)$$

where α and β are the appropriate coefficients and exponents, respectively.

According to the assumption above, the larger the expansion of GTOs, the more equivalence to a STO is obtained. Another type of atomic orbital is the GLO (Gaussian Lobe Orbital) [57,58] which is the simplest form of basis functions. Its form is

$$\phi^{GLO} = N \exp(-\beta r^2)$$

The angular part is omitted. Instead, GLOs are combined together to reproduce the conventional orbital shapes.

2.4.3 Minimization of the Total Energy (Self-Consistent Field Procedure)

The Hartree-Fock equations for spinorbitals as outlined in the previous chapter, in combination with the construction of the spin orbitals by the LCAO-MO method allows a convenient variation ansatz for optimizing the spin orbitals with respect to total energy:

$$\delta E^{HF} / \delta c_{\mu i} = 0$$

Solving this variation ansatz under the condition of preservation of orthonormality of the spin orbitals leads to the Roothaan equation, which is the fundamental equation for all *ab initio* molecular orbital calculations:

$$F\,C = S\,C\,E$$

where F is the matrix of the Fock operator, C the matrix of the linear combination coefficients, S the overlap matrix and E the matrix of the 1-electron-energy eigenvalues.

Optimization of the total energy is performed by varying the values of the coefficient, $c_{\mu i}$. The minimization procedure begins with the use of an initial guess of c 's to create a first matrix of the Fock operator F. The elements of the matrix F are :

$$F_{\mu v} = H_{\mu v}^{core} + \Sigma_{\lambda,\sigma}(P_{\lambda\sigma}(\mu v|\lambda\sigma)-1/2(\mu\lambda|v\sigma))$$

The matrix of the elements of the core Hamiltonian contains the one-electron Hamiltonian, H^c.

$$H_{\mu\nu}^{\ core} = <\phi_\mu(i)|H^c|\phi_\nu(i)>$$

In the first one of two previous equations, the second term is the two-electron part. The elements of the density matrix $P_{\lambda\sigma}$ and the two-electron integrals, $(\mu\nu|\lambda\sigma)$ and $(\mu\lambda|\nu\sigma)$, are given by

$$P_{\lambda\sigma} = 2\sum_1^{occ} c_{\lambda i}\ c_{\sigma i}$$

$$(\mu\nu|\lambda\sigma) = \iint\phi_\mu^*(1)\phi_\nu(1)\ 1/r_{12}\ \phi_\lambda^*(2)\phi_\sigma(2)\ d\tau_1 d\tau_2,$$

and,

$$(\mu\lambda|\nu\sigma) = \iint\phi_\mu^*(1)\phi_\lambda(1)\ 1/r_{12}\ \phi_\nu^*(2)\phi_\sigma(2)\ d\tau_1 d\tau_2.$$

From the first approximation of the Fock operator matrix F, a second set of elements, C, can be obtained by solving of the Roothaan equation.

2.5 Intermolecular Potentials in this Study

Since the system consisting of one Zn(II) in liquid ammonia was chosen for this study, two kinds of intermolecular potentials, namely Zn(II)-ammonia and ammonia-ammonia, are required. The ammonia-ammonia intermolecular potential was taken from literature [33] and details are given in Table 2.1. In order to allow studying intramolecular properties of ammonia, a flexible model for ammonia by

Spirko [59] was chosen.

Table 2.1 Ammonia-ammonia intermolecular potential; energies are gieven in units of 10^{-19} J and distances in Å.

$V_{NN}(R) = 14.85/R + 55719/R^{12} - 13.6/R^6$

$V_{NH}(R) = -4.95/R + 0.01042\{\exp[-4.6(R-2.4)] - 2\exp[-2.3(R-2.4)]\}$

The Zn(II)-ammonia intermolecular potential, had to be newly constructed by quantum-mechanical method.

2.5.1 Construction of the Zn(II)-NH$_3$ Intermolecular Pair Potential

To construct the Zn(II)-ammonia intermolecular pair potential by means of quantum-mechanical calculations, the following steps are required: (i) selection of representative geometries of the pairs, (ii) performance of the SCF calculations, (iii) fit of the computed interaction energies to a functional form, and (iv) test of the function.

(i) Selection of geometries

The ammonia with the bond lengths and angles from experiment [60] (N-H = 1.0124 Å and H-N-H angle = 106.7°) was fixed at the origin of Cartesian coordinate system Then, Zn(II) was placed at numerous positions within the space

around ammonia, where $0° \leq \Theta \leq 180°$ and $0° \leq \Phi \leq 60°$ (according to its C_{3v} symmetry) as shown in Fig. 2.2.

The number of energy points needed to construct the intermolecular potential is determined by the complexity of the system. Due to the C_{3v} symmetry of the ammonia molecule, it is unnecessary to place Zn(II) around the whole space, only one-sixth is required. Indeed, there are many possible ways to arrange the positions of the Zn(II) around the ammonia molecule. The points may be chosen by gridding the three-dimensional space like a network lattice. However, it is easier to evaluate the potential keeping some variables constant while varying another. For instance, in this study the angles Θ and Φ were kept constant while varying the distance. The frequency of chosen points in the space is also dependent on the "chemical importance" of those regions. A region around the minimum energy has a strong influence not only for the potential function, but also for the simulation results, therefore more points are needed in that zone. To where the distances should be extended to depends on the strength of the interaction energy. In fact, it is necessary to extend the points to a distance where interaction energy approaches zero. Normally, the longest distance should be at least equal to the cut-off limit employed in the simulation, except cases where the interactions approach zero before reaching this cut-off limit.

On contrary, the nearest distance is related to interparticle repulsion. In general, any energy points above 50 kcal/mol are unnecessary for low-temperature simulations for the reason that molecules can never reach such configurations.

(ii) Performance of the SCF calculations

SCF calculations were performed for the aforementioned configurations by

using the HONDO VII program [61]. A modified ECP basis set was selected for Zn(II) [62], and the DZP basis set of Dunning [63] was used for hydrogen. For nitrogen, the basis set was taken from literature [64] for both core and valence shell electrons and was augmented by a d-type polarization function with orbital exponent 0.864 [65]. The interaction energies obtained by the equation in section 2.3.3 were used in the fitting procedure.
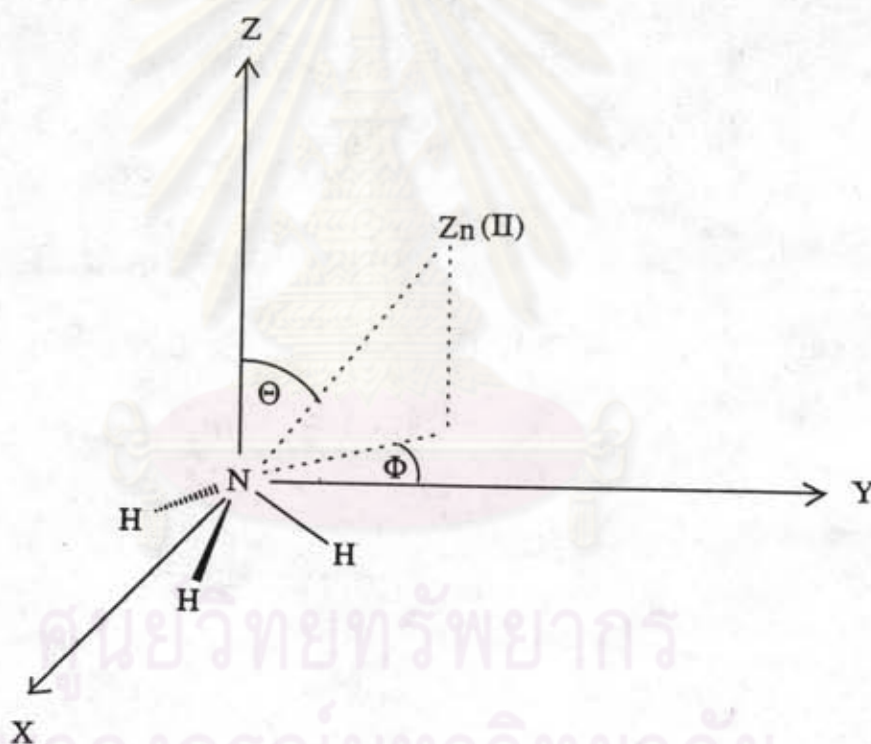

Fig 2.2 Definition of geometric variables for configurations of Zn(II)-ammonia

(iii) Fit of the computed interaction energies

After having calculated a number of Zn(II)-ammonia configurations, the interaction energies of the pair were fitted (ΔE_{FIT}), using a multidimensional

non-linear least-square procedure, to an analytical function of the form,

$$\Delta E_{FIT} = \sum_{i=1}^{4} f(r_i)$$

where $f(r_i)$ denotes for potential energy function of r_i, the distance between the i-th atom of ammonia and Zn(II). This analytical function can be any mathematical equation. Each component of the form should have, if possible, a reasonable physical meaning.

Details of the functions, including typical forms and adjustable parameters will be given in CHAPTER 4.

(iv) Test and improvement of the function

The function obtained from the first SCF-data set was tested using the procedure suggested by Beveridge et.al [66]. Interaction energies by means of SCF method, ΔE_{SCF}, for Zn(II)-ammonia configurations outside the first set of data were calculated and compared with those obtained from the optimized function, ΔE_{FIT}. Standard deviation, σ_{test}, of the two sets expresses the quality of the function. To improve the quality of the function, the additional SCF points were then included in the fitting procedure. An improved set of the parameters being obtained, additional configurations were tested and included in the function in the same way until constancy of the fitting parameters within a range of ± 5 % [67] and a sufficiently low standard deviation was reached.

In addition, the energy points around a local minimum of a energy-distance

curve crucially determine the quality of the function. The fitting and SCF energy at each minimum may differ slightly, while the equilibrium distances for the minima have to be equal.

2.5.2 Construction of the $Zn(II)$-NH_3 Intermolecular Potential with Three-body Correction

The intermolecular pair potential obtained form section 2.5.1 was examined by Monte Carlo simulations. The results implied that the pairwise additive approximation of the potentials are not sufficient to represent the interactions between $Zn(II)$ and ammonia molecules in condensed phase, as a wrong coordination number of 9 was predicted. Therefore, at least the first non-additive term, i.e. the three-body term, had to be taken into account.

2.5.2.1 Evaluation of Many-body Effects

To evaluate how much the three-body effect influences the intermolecular potential, SCF calculations for $Zn(II)$-$(NH_3)_n$ complexes with n=1,2,3,4 and 6 were performed. Ammonia molecules were positioned so that-with respect to nitrogen atoms- C_∞, D_{3h},T_d and O_h symmetry for n=2,3,4 and 6, was established. The $Zn(II)$-nitrogen distances were energy optimized. The average binding energy per ammonia molecule, ΔE_{av1}, is computed as:

$$\Delta E_{av1} = \{ E[ML_n] - E[M] - E[L_n] \} /n ,$$

where M and L denotes $Zn(II)$ and ammonia molecule, respectively. All energies on

the right hand side of the above equation are total energies, ligand-ligand repulsions are already eliminated in this definition.

In order to evaluate possible errors of the assumption of pairwise additivity of interaction due to many-body effects, average pair interaction energies between Zn(II) and ammonia molecules in Zn(II)-(NH$_3$)$_n$ configuration were calculated and defined as :

$$\Delta E_{2FCN} = \sum_{i=1}^{n} \{E[ML_i] - E[M] - E[L_i]\} /n$$

where ML$_i$ denotes any of the Zn(II)-NH$_3$ pairs in the Zn(II)-(NH$_3$)$_n$ complexes.

The results of this evaluation are reported and discussed in CHAPTER 4.

2.5.2.2 Construction of the Three-body Correction Function

A second ammonia molecule was placed at numerous postions around the Zn(II)-NH$_3$ complex, varying geometrical parameters $0° \leq \Theta \leq 180°$ and $0° \leq \Phi \leq 60°$ and 1.5 Å $\leq r2 \leq 10.0$ Å as illustrated in Fig 2.3. The Zn(II)-N1 distance (r1) of 1.5 Å and configurations of the first ammonia were kept fixed and SCF calculations were performed for these Zn(II)-(NH$_3$)$_2$ clusters. In order to develop the complete three-body function, the same procedure was repeated for r1 = $1.8, 1.95, 2.2, 2.4, 3.0, 4.0, 6.0$ and 8.0 Å, thus leading to a total of more than 1,500 configurations of the Zn(II)-(NH$_3$)$_2$ system and 4,500 Zn(II)-NH$_3$ and NH$_3$-NH$_3$ pair interactions. The definition of orientation is shown in Fig. 2.3 .

The three-body interaction energies were calculated according to

$$\Delta E_{3bd} = \{ E[ML_1L_2] - E[M] - E[L_1] - E[L_2] \}$$
$$- \{ E[L_1L_2] - E[L_1] - E[L_2] \}$$
$$- \Sigma^2_{i=1} \{ E[ML_i] - E[M] - E[L_i] \}$$

and these energies were fitted then to an analytical function. Details of this three-body correction function are also reported and discussed in CHAPTER 4.
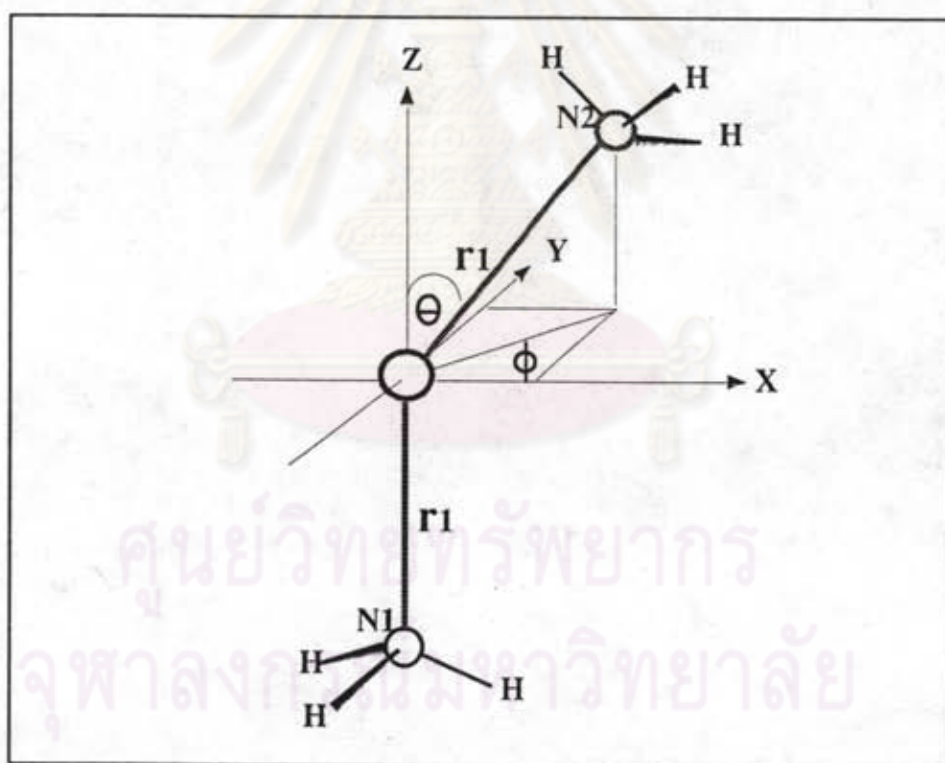

Fig. 2.3 Definition of orientaion of two ammonia with Zn(II)