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สถาบันวิทยบริการ

จุฬาลงกรณ์มหาวิทยาลัย

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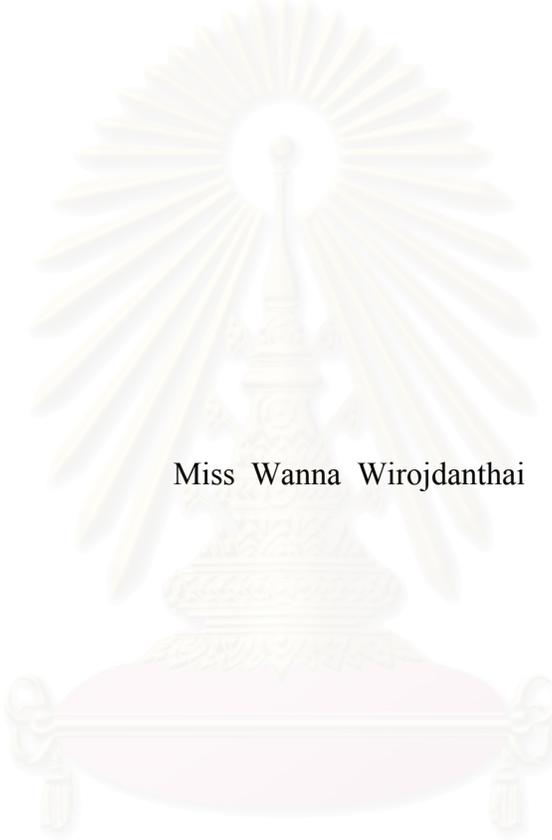
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ลิขสิทธิ์ของ จุฬาลงกรณ์มหาวิทยาลัย

THREE-BODY EFFECT IN MONTE CARLO SIMULATION FOR METAL ION-  
AMMONIA SOLUTION



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สถาบันวิทยบริการ

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ได้ทำการศึกษาโครงสร้างของลิเทียมและแมกนีเซียมในสารละลายแอมโมเนียโดยวิธีมอนติ  
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The solvation structures of  $Li^+$  and  $Mg^{2+}$  in liquid ammonia have been investigated using the Metropolis Monte Carlo scheme. Including three-body correction functions. The systems under investigation contain one  $Li^+$  in 201  $NH_3$  and one  $Mg^{2+}$  in 201  $NH_3$ . The three-body correction includes functions representing orientations the ammonia molecules. From the experimental density for pure liquid ammonia at 277 K and 1 atm of  $0.690 \text{ g.cm}^{-3}$ , a periodic cubic volume of side length  $20.99 \text{ \AA}$  was constructed. The  $Li^+ - NH_3$  and  $Mg^{2+} - NH_3$  three-body correction functions have been developed based on *Hatree-Fock* calculations with Dunning's double zeta plus polarizations (DZP) basis set. The simulations yielded the first shell coordination of six for both  $Li^+$  and  $Mg^{2+}$  systems. The results are in agreement with the previous work whose no molecular orientation was taken in to account. A clear and useful conclusion is that the orientation of the solvent molecules can be neglected from consideration, at least when dealing with structural properties of the solution.

Department.....Mathematics.....	Student's signature.....
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# CONTENTS

	Pages
ABSTRACT IN THAI.....	iv
ABSTRACT IN ENGLISH.....	v
ACKNOWLEDGEMENTS.....	vi
LIST OF FIGURES.....	ix
LIST OF TABLES.....	xi
CHAPTER 1 INTRODUCTION.....	1
1.1. Computer Simulations.....	1
1.2. Metal-Ammonia Solutions and Infinite Dilute Solutions....	2
1.3. Computer Simulations based on the Pair Approximation....	3
1.4. Computer Simulations including Three-body Correction Functions.....	4
1.5. What is new in This Study?.....	6
CHAPTER 2 THE MONTE CARLO METHODS.....	9
2.1. Basic Principles of Monte Carlo Method.....	9
2.2. Conditions of Calculations.....	10
2.2.1 Metropolis Monte Carlo Method.....	10
2.2.2 Defining the cube size.....	11
2.2.3 The Amount of Particles for Simulation.....	12
2.2.4 Defining the Starting Configuration.....	12
2.2.5 Periodic Boundary Condition.....	12

	Pages
2.2.6 Spherical Cut-off.....	14
2.2.7 Long-range Interactions.....	15
2.3. Steps of Calculations.....	15
2.4. Radial Distribution Functions and the Integration Numbers	18
<b>CHAPTER 3 DETAIL OF CALCULATIONS.....</b>	<b>19</b>
3.1. Pair Potentials.....	19
3.2. Three-body Correction Functions.....	20
3.3. Monte Carlo Simulations.....	25
<b>CHAPTER 4 RESULT AND DISCUSSION.....</b>	<b>26</b>
4.1. Three-body Correction Functions.....	26
4.2. Monte Carlo Simulations:Radial Distribution Functions and Running Integration Numbers.....	31
4.3. Conclusion.....	36
<b>REFERENCES.....</b>	<b>37</b>
<b>CURRICULUM VITAE.....</b>	<b>40</b>

## LIST OF FIGURES

	Pages
Figure 1.1 The connection between experiment, theory, and computer simulation (taken from [1]).....	1
Figure 1.2 Geometrical parameter definitions in the evaluation of the in $M-(NH_3)_2$ potentials, used for the SCF calculations.....	8
Figure 2.1 A two-dimensional periodic system.....	14
Figure 2.2 The calculating steps of Monte Carlo simulations.....	17
Figure 3.1 Geometrical parameter definitions in the evaluation of the in $M-(NH_3)_2$ potentials, used for the SCF calculations.....	21
Figure 3.2 All 24 distances (a) M-N and N-N, (b) M-H, (c) H-H and (d) N-H distances, which are included in the three-body correction functions (dark sphere denotes $Li^+$ or $Mg^{2+}$ )....	22
Figure 4.1 Comparison of the three-body interaction energies of the $Li^+-NH_3$ obtained from the SCF calculations, $\Delta E_{3bd}^{SCF}$ , and from the fit, $\Delta E_{3bd}^{FIT}$ , for the generated configurations.....	26
Figure 4.2 Comparison of the three-body interaction energies of the $Mg^{2+}-NH_3$ obtained from the SCF calculations, $\Delta E_{3bd}^{SCF}$ , and from the fit, $\Delta E_{3bd}^{FIT}$ , for the generated configurations...	27
Figure 4.3 $\Delta E_{3bd}^{SCF}$ and $\Delta E_{3bd}^{FIT}$ as a function of $Li^+-N_2$ distance. In which only 3 distances (above) and all 24 distances (below) have been taken into accounted (more details see text).....	28

	Pages
Figure 4.4 $\Delta E_{3bd}^{SCF}$ and $\Delta E_{3bd}^{FIT}$ as a function of $Mg^{2+}$ - $N_2$ distance. In which only 3 distances (above) and all 24 distances (below) have been taken into accounted (more details see text).....	29
Figure 4.5 $Mg^{2+}$ -N and $Mg^{2+}$ -H radial distribution functions and corresponding running coordination number obtained from the simulations with three-body corrections. All 24 distances (a and b) and only 3 distances (c and d).....	33
Figure 4.6 $Li^+$ -N and $Li^+$ -H radial distribution functions and corresponding running coordination number obtained from the simulations with three-body corrections. All 24 distances (a and b) and only 3 distances (c and d).....	34
Figure 4.7 N-N, N-H and H-H radial distribution functions and corresponding running coordination number.....	35

## LIST OF TABLES

		Pages
Table 1.1	The three-body corrections reduce their first shell coordination number in liquid ammonia.....	4
Table 1.2	The assumption of pairwise additivity leads to an error of interaction energies in cation-water.....	5
Table 1.3	The errors in the two-body approximation in the octahedral complexes of metal-ammonia.....	5
Table 1.4	Analytical forms of the three-body interaction energies for ions in liquid ammonia.....	7
Table 3.1	Final optimized parameters for the interaction of H and N atoms of ammonia with lithium ion. Interaction energies and r have been evaluated in kcal/mol and atomic length units, respectively.....	19
Table 3.2	Final optimized parameters for the interaction of H and N atoms of ammonia with lithium ion. Interaction energies and r have been evaluated in kcal/mol and atomic length units, respectively.....	20
Table 3.3	Optimized parameter for the $\text{NH}_3\text{-Mg}^{2+}\text{-NH}_3$ three-body correction functions (equations (3.5-3.9)).....	23
Table 3.4	Optimized parameter for the $\text{NH}_3\text{-Li}^+\text{-NH}_3$ three-body correction functions (equations (3.11-3.15)).....	24
Table 3.5	Definition of the distances (in Å) between atoms in the three-body correction functions where M, N and H represent metal ions, nitrogen atoms and hydrogen atoms, respectively.....	25

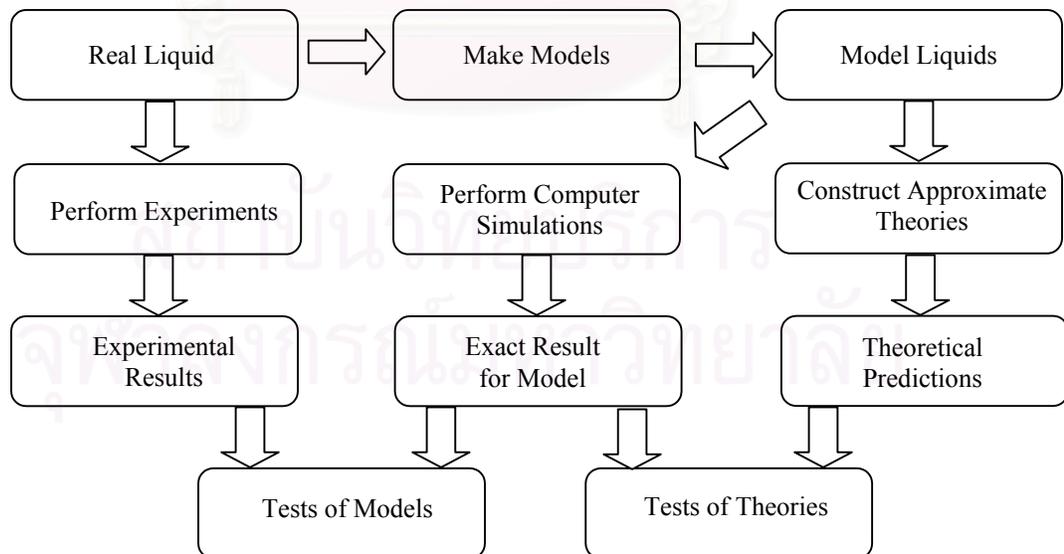
# CHAPTER 1

## INTRODUCTION

### 1.1 Computer Simulations

Computers play significant roles in many fields of science, “Computational science makes use of computer simulations instead of experiments for evaluating interesting information of systems, particularly, of those systems for which experiments cannot be easily performed”.

The connection between experiment, theory and computer simulation is exhibited in Figure 1.1. If the model is a good one, the simulator hopes to offer insights to the experimentalist, as a bridge between models and theoretical predictions on one hand, and between models and experimental results on the other. Because of this connecting role and the way in which simulations are conducted and analysed, these techniques are often termed “computer experiments”.



**Figure 1.1** The connection between experiment, theory, and computer simulation (taken from [1]).

Computer simulation methods, such as Monte Carlo practically introduced by Metropolis [2], and molecular dynamics by Alder [3], are important tools for studying statistical and dynamical properties of liquids and solutions. The results from Monte Carlo and molecular dynamics simulations overcome some limitations of the experimental approach and the availability of high processing capacities of computers simulations of rather large number of molecules are now possible. Numerous studies based on these methods for solution have been published [4-18]. Most of the investigations were, however, based on the structural and dynamic properties concerning the first solvation shell of ions in pure solvents.

Monte Carlo simulation allows not only to evaluate solvation numbers and solute-solvent distances from computed radial distribution functions, but also gives access to data not available from any experimental technique for example an analysis of the perceptual contribution of various coordination numbers to the average solvation of ions or solvent molecules. The access to the angular distribution of neighbour molecules is also an important means of these methods for the evaluation of structural factors in solution.

## **1.2 Metal-Ammonia Solutions and Infinite Dilute Solutions**

The study of metal-ammonia solutions has a long and venerable history [19-21]. Most study has focused on the solution of alkaline or alkaline earth metal in liquid ammonia because of their remarkable properties such as high electrical conductivity. Alkaline and alkaline earth metals can be dissolved to large amounts in liquid ammonia, showing the characteristics of liquid metals. As a result, alkaline and alkaline earth metals in liquid ammonia are the subject of extensive research by means of both experimental and theoretical methods.

The solution of one metal ion in a solvent serves as a good model for an infinitely dilute solution. In addition, infinitely dilute solution is a useful tool to understand the effect of a cation or an anion to the solvent species around it, without

perturbation by any other ion field. However, the study of infinitely dilute solution is impossible in the view of experimental investigations as the experimental apparatus is not capable of giving results for very dilute solution.

### 1.3 Computer Simulations based on the Pair Approximation

The reliability of results obtained from Monte Carlo or molecular dynamics simulations depends strongly on the quality of the potential functions used. A potential function describes the interaction energy among particles in that system. In general, the total interaction energy of  $N$  particles of the system can be written as

$$\Delta E = \sum_i^N v_1(r_i) + \sum_i^N \sum_{j>i}^N v_2(r_i, r_j) + \sum_i^N \sum_{j>i}^N \sum_{k>j>i}^N v_3(r_i, r_j, r_k) + \dots \quad (1.1),$$

where the first term in equation (1.1),  $v_1(r_i)$ , represents the effect of an external field (e.g. the container walls) on the system. The second term,  $v_2$ , called the pair potential gives the highest contribution to the energy. In practice, one assumes  $\Delta E$  to be approximately equal to this term only. This approach is known as the pair-wise additive approximation, whereas the remaining terms are often referred to as non-additive corrections. The third term,  $v_3$ , called three-body connecting interaction which sometimes becomes very significant in case of condensed systems, especially electrolyte solution. In most of published simulation, however, they were not included, due to the large computer time needed and normally are neglected. The four-body and higher terms are expected to be small in comparison to  $v_2$  and  $v_3$ .

As mentioned above, most published works on the Monte Carlo or molecular dynamics simulations simply  $\Delta E$  using only up to the pair potential term. So far, there have been several types of pair potentials used in computer simulations. The most commonly used is the Lennard-Jones 12-6 pair potential [22].

## 1.4 Computer Simulation including Three-body Correction Functions

According to Tables 1.1-1.3, it was observed that the conventional pair potential fails to predict structural data of metal ion-ammonia solutions, while the approximate three-body correction was sufficient to establish full agreement with experimental results [18,23,25,26,27]. An error of the pair interactions for the metal ion-ammonia complex is about two times higher than those of metal-water system. Include the three-body correction energy, in which the  $\text{NH}_3\text{-M-NH}_3$  complex is in the configuration shown in Figure 1.2, leads to a decrease of an error of the pair approximation from 23% to 10.6% for  $\text{Li}^+\text{-NH}_3$  and from 30% to 10% for  $\text{Mg}^{2+}\text{-NH}_3$  systems.

**Table 1.1** The three-body corrections reduce their first shell coordination number in liquid ammonia.

Metal-ammonia	Coordination Number		Reference
	Without three-body	With three-body	
$\text{Li}^+$	6	6	[26]
$\text{Na}^+$	9	8	[25]
$\text{Mg}^{2+}$	10	6	[25]
$\text{Ca}^{2+}$	9	8	[27]
$\text{Zn}^{2+}$	9	6	[18]

**Table 1.2** The errors in the two-body approximation in the octahedral complexes of cation-water.

Cation-water	Error of interaction energies	Reference
$Li^+$	10 %	[23]
$Mg^{2+}$	15 %	[23]
$Al^{3+}$	20 %	[23]

**Table 1.3** The errors in the two-body approximation in the octahedral complexes of cation-ammonia.

Cation-ammonia	Errors in the two-body approximation in the octahedral complexes	Reference
$Na^+$	17 %	[25]
$Li^+$	23 %	[26]
$Zn^{2+}$	18 %	[18]
$Ca^{2+}$	20 %	[27]
$Mg^{2+}$	30 %	[25]
$Be^{2+}$	43 %	[23]
$Al^{3+}$	43 %	[23]

## 1.5 What is new in This Study?

In order to develop the complete three-body correction function, a second ammonia molecule was placed at numerous positions around the ammonia-metal complex, and the configuration of the first ammonia were kept fixed and SCF calculations were performed for these metal-ammonia cluster. More detailed investigations were given in Figure 1.2.

The three-body interaction energies were calculated as:

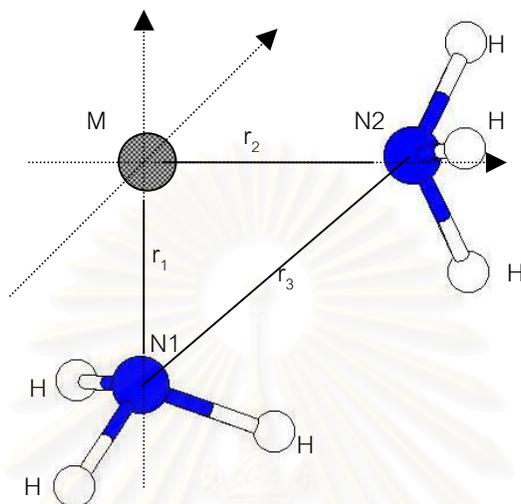
$$\begin{aligned} \Delta E_{3bd} = & [E\{ML_1L_2\} - E\{M\} - E\{L_1\} - E\{L_2\}] \\ & - [E\{ML_1\} - E\{M\} - E\{L_1\}] \\ & - [E\{ML_2\} - E\{M\} - E\{L_2\}] \\ & - [E\{L_1L_2\} - E\{L_1\} - E\{L_2\}] \end{aligned} \quad (1.2)$$

All energies on the right-hand side of equation (1.2) are the total energies of the system in brackets, where M, L<sub>1</sub> and L<sub>2</sub> denote the metal ion and the first and second ammonia molecules, respectively. This energy was then fitted to the and given in Table 1.4.

**Table 1.4** Analytical forms of the three-body interaction energies for ions in liquid ammonia

System	Function	Reference:
$Li^+ - NH_3$	$\Delta E_{3bd} = a e^{-b(r_1+r_2)} e^{-cr_3}$	[26]
$Mg^{2+} - NH_3$	$\Delta E_{3bd}^{Mg-NH_3} = 0.40573 \exp(-0.024808 r_{Mg-N_1}^2)$ $* \exp(-0.024808 r_{Mg-N_2}^2)$ $* \exp(-0.077318 r_{N_1-N_2}) T_{Mg}$ $T_{Mg} = [1 - \exp\{0.1(5.5 - r_{Mg-N_1})^2\}]$ $* [1 - \exp\{0.1(5.5 - r_{Mg-N_2})^2\}] [r_{Mg-N_1}^2 r_{Mg-N_2}^2]$	[25]
$Na^+ - NH_3$	$\Delta E_{3bd}^{Na-NH_3} = 1.79488 \exp(-0.0156885 r_{Na-N_1})$ $* \exp(-0.0156885 r_{Na-N_2})$ $* \exp(-0.237606 r_{N_1-N_2}) T_{Na}$ $T_{Na} = [1 - \exp\{0.2(6.0 - r_{Na-N_1})\}]$ $* [1 - \exp\{0.2(6.0 - r_{Na-N_2})\}] [r_{Na-N_1} r_{Na-N_2}]$	[25]
$Zn^{2+} - NH_3$	$\Delta E_{3bd} = a\{b\beta + c[1 - \cos(2\alpha)]\} \exp[-d(r_1^2 + r_2^2)]$	[18]

In the previous works on the three-body effect, only coordinates of the two N atoms Figure 1.2. were taken into consideration in the development of the three-body correction function (Table 1.4). That means that orientation of the two ammonia molecules does not change the three-body energies. In order to improve quality of the three-body correction function, all coordinate of atoms in both ammonia molecules will be included in the functions. Quality of the obtained function will be examined by performing Monte Carlo simulations. The simulated systems are infinite dilute solutions of  $Li^+$  and  $Mg^{2+}$  in Liquid ammonia.



**Figure 1.2** Geometrical parameter definitions in the evaluation of the  $M-(NH_3)_2$  potentials, used for the SCF calculations.

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## CHAPTER 2

### The Monte Carlo Methods

This technique was called Monte Carlo (MC) after the name of the famous casino city because the method of calculation involves the generation of random numbers, the computation of multidimensional integrals which are too difficult to solve by analytical methods. This method can also be applied to study properties of condensed matters, where the thermodynamical averages obtained over probability distributions are of interest.

The goal of Monte Carlo simulations is to study the microscopic properties of the solution, such as the structural and energetic properties, based on the knowledge of potential functions; e.g. to study, how a solute influences the solvent structure or how a solute is solvated by solvent molecules in the solution. Such structural and energetic information are very difficult to obtain from spectroscopic measurements, especially in dilute solutions.

#### 2.1 Basic Principles of Monte Carlo Method

Classical Monte Carlo calculations are based on pair potential functions, and it assumes that only two-body forces are to be considered, i.e. linear additivity is given for the total configurational energy,  $E(\mathbf{v})$ , of the system.  $E(\mathbf{v})$  can be written thus as a sum of pairwise interaction energies between the individual particles  $E_{ij}(\mathbf{v})$  of the system,

$$E(\mathbf{v}) = \sum_{i=1}^N \sum_{j=1}^N E_{ij}(\mathbf{v}) \quad (2.1)$$

where  $\mathbf{v}$  is a configurational coordinate of the particles in a system.

In order to calculate the properties of the system, a canonical ensemble with  $N$  particles in a volume  $V$  at a constant temperature  $T$  must be considered, and to eliminate surface effects, periodic boundary conditions are required. The average of any quantity of interest  $\langle F \rangle$  can be written as

$$\langle F \rangle = \frac{\int \dots \int F \exp(-E(v)/kT) dv}{\int \dots \int \exp(-E(v)/kT) dv} \quad (2.2)$$

where  $dv$  is a volume element in the multi-dimensional configuration space and  $k$  denotes Boltzmann constant. If the starting configuration is generated randomly in three dimensional space, integration over many orders of magnitude would be needed for the integrand  $\exp(-E(v)/kT)$  shown in equation (2.2). This is the main principle of the general Monte Carlo method, which is however, not practicable.

## 2.2 Conditions of Calculations

### 2.2.1 Metropolis Monte Carlo Method

The above principle was modified by Metropolis et al. In 1953 [2] based on the idea of importance sampling. In this method, the  $N$  configurations are randomly generated but accepted with respect to their probability,  $P(v)$  and they are evenly weighted with  $P(v)$ . After taking a quite large number of space points  $M$ . equation (2.2), can be approximated by the sum

$$\langle F \rangle \cong \bar{F} = \frac{\sum_{i=1}^M F(v) P^{-1}(v) \exp(-E(v)/kT)}{\sum_{i=1}^M P^{-1}(v) \exp(-E(v)/kT)} \quad (2.3)$$

The probability  $P(v)$  in this Metropolis Monte Carlo method is given by a Boltzmann factor,

$$P(v) = \exp(-E(v)/kT) \quad (2.4)$$

Then equation (2.3) can be reduced to a simple form of

$$\bar{F} = \frac{1}{M} \sum_{i=1}^M F_i \quad (2.5)$$

where  $F_i$  is the value of the property  $F$  of the system after the  $i^{\text{th}}$  configuration changes and  $M$  is a large number of space points.

### 2.2.2 Defining the cube size

The cubic box is duplicated throughout space to form an infinite lattice. It contains all investigated particles. This box simply forms a convenient axis system for measuring the particles. The length of the cubic box  $L(A)$ , which holds  $N_p$  particles for  $m$  species can be calculated as

$$L^3 = \frac{\sum_{p=1}^m N_p M_p}{0.602D} \quad (2.6)$$

where  $D$  denotes the experimental density of the solution in  $g/cm^3$  at the temperature and pressure which the simulations have been considered.  $M_p$  is the ionic or atomic weight of species  $p$ .

### 2.2.3 The Amount of Particles for Simulation

The number of particle in the system investigated depends on the computer efficiency. The result will be more accurate whenever an increasing number of particle is performed. In addition, the Central Processing Unit (CPU) time has to be considered between accuracy and time cost. For several studies, they have been shown that the system would consist of at least 200 particles for the most suitable condition.

### 2.2.4 Defining the Starting Configuration

In the first step of the Monte Carlo simulation, the starting coordinates of all particles have often been generated randomly. However, the particles should be throughout the cube so that the system will be equilibrated so fast. Therefore, the shortest distance between particles  $l_{\min}$  can be calculated by

$$l_{\min} = \sqrt[3]{\frac{L^3}{N}} \quad (2.7)$$

If the simulations are long enough, differences between the results obtained from different starting configurations are found to be negligible. However, the random one is more often used.

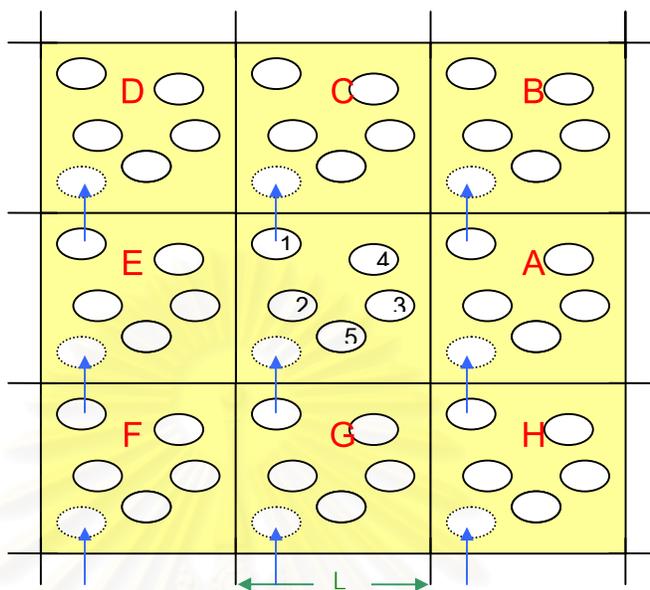
### 2.2.5 Periodic Boundary Condition

An idea of the computer simulation is to enhance the ability of small systems to simulate the behavior of large systems. This technique considers a certain basis region, usually a cube contains a certain number,  $N$ , of molecules. Then imagines

that all space is filled by periodic images of this basic unit. In this way, one can consider configurations of an infinite ( which must of course be periodic ) while only considering a limited number of molecules,  $N$ . The problem of surface effects can be also overcome.

The problem of surface effects can be overcome by implementing periodic boundary conditions. The cubic box is replicated throughout space to form an infinite “lattice”. In the simulation, as a molecule moves in the original box, its periodic image in each of the neighboring boxes moves in exactly the same way. Thus, as a molecule leaves the central box, one of its images will enter through the opposite face. There are no walls at the boundary of the central box, and no surface molecules. This box simply forms a convenient axis system for measuring the coordinates of the  $N$  molecules. A two-dimensional version of such a periodic system is shown in Figure 2.1.

The duplicate boxes are labeled  $A, B, C$ , etc. As particle 1 moves through a boundary, its images,  $1_A, 1_B$  etc. (where the subscript specifies in which box the image lies) move across their corresponding boundaries. The number density in the central box (and hence in the entire system) is conserved. It is not necessary to store the coordinates of all the images in a simulation (an infinite number), just that of the molecules in the central box. When a molecule leaves the box by crossing a boundary, attention may be switched to the image just entering. It is sometimes useful to picture the basic simulation box (in the two dimensional examples) as being rolled up to form the surface of a three-dimensional doughnut, when there is no need to consider an infinite number of replicas of the system nor any image particles. This correctly represents the topology of the system. A similar analogy exists for a three-dimensional periodic system.



**Figure 2.1** A two-dimensional periodic system.

### 2.2.6 Spherical Cut-off

In the minimal image convention, then, the calculation of the potential energy due to pairwise-additive interactions involves  $\frac{1}{2}N(N-1)$  terms. This may still be a very substantial calculation for a system of 1,000 particles. A further approximation significantly improves this situation. The largest contribution to the potential comes from neighbours close to the molecule of interest, and for short-range interactions, a spherical cut-off can be applied. This means setting the pair potential  $E(r_{ij})$  to zero for  $r_{ij} \geq r_c$ , where  $r_c$  is the cut-off distance. The cut-off distance must be no greater than  $\frac{1}{2}L$  for consistency with the minimal image convention, and it is applicable only to rapidly decreasing potential terms, e.g.  $\frac{1}{r^6}$  or exponential terms.

## 2.2.7 Long-range Interactions

The long-range interaction is defined as one in which the spatial interaction falls off no faster than  $r^{-d}$  where  $d$  is the dimensionality of the system. In another meaning, the long-range interaction is the one in which all the particles lying outside the cut-off sphere of a given particle. The charge-charge, charge-dipole, dipole-dipole and charge-quadrupole interactions are the examples of such a long interaction. Long-range interactions are a serious problem for the computer simulator, since their range is greater than half the box length. So far, The Ewald summations [22,28] and the reaction field method [22,29] have been two widely used methods, which can be employed to handle this problem. The Ewald summations procedure which is perfectly consistent with periodic boundary conditions is a technique for efficiently summing the interaction between a particle and all its periodic images. The reaction field method introduce without the assumption of the periodicity. It treats all molecules beyond the cut-off sphere of radius from a center charge as forming a continuum with a given dielectric constant; therefore, any charge lying inside the spherical cut-off will polarize the continuum and create a reaction field at the center.

## 2.3 Steps of Calculations

Assuming  $N$  particles in a given configuration and in a given volume at temperature  $T$  Kelvin, the Monte Carlo algorithm consists essentially in iterating the following steps which are illustrated in Figure 2.2.

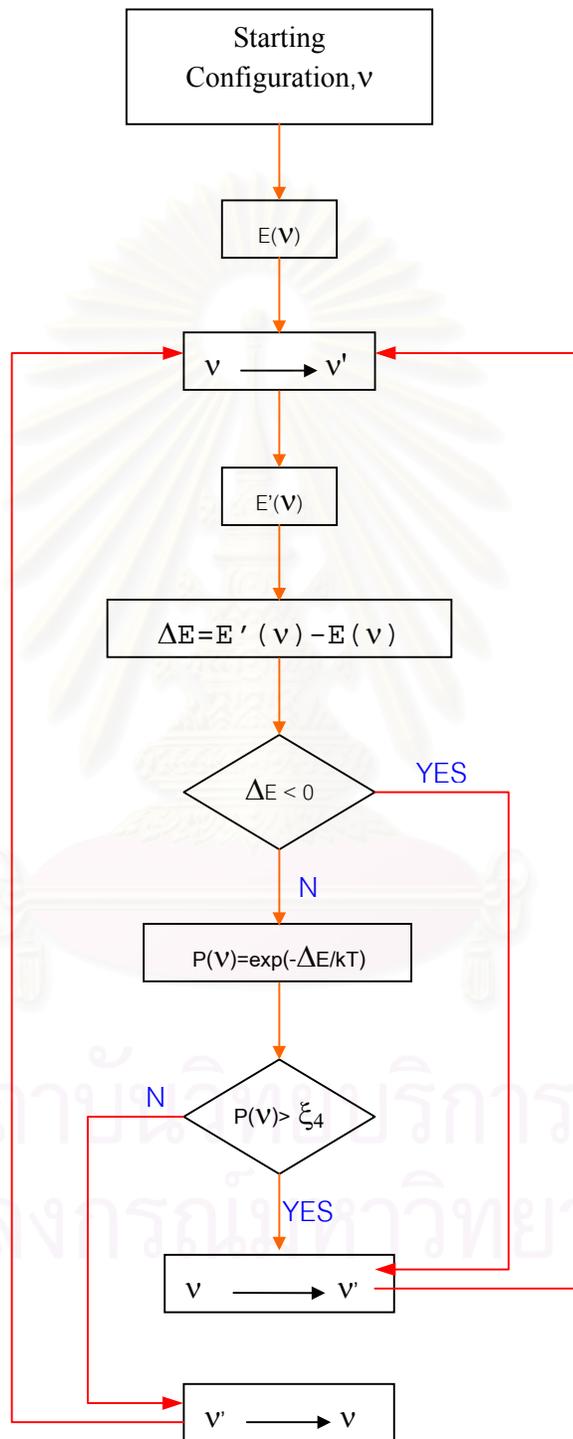
- 1) Determine an initial configuration,  $v$ , that is chosen by which the position of the  $N$  particles are generated randomly or from a previous simulation.
- 2) Calculate the interaction energy of this configuration,  $E(v)$ , according to equation (2.1) based on the potential function.

- 3) Choose randomly an integer from 1 to  $N$  and the particles will be determined to move. Then, move the labeling particles,  $v \rightarrow v'$  in succession according to the following prescription:

$$\begin{aligned} X &\rightarrow X + a\xi_1 \\ Y &\rightarrow Y + a\xi_2 \\ Z &\rightarrow Z + a\xi_3 \end{aligned} \quad (2.8)$$

where  $a$  is the maximum allowed displacement, which for the sake of this argument is arbitrary, and  $\xi_1$ ,  $\xi_2$  and  $\xi_3$  are random numbers between (-1) and 1. If the maximal displacement is too large, most of the moves will be forbidden, if too small, the configuration will not change enough. In later case it would take longer to reach equilibrium. For the first case, the equilibrium may not be reached.

- 4) Calculate the new the configuration energy  $E'(v)$  and the change in energy of the system  $\Delta E = E'(v) - E(v)$ , which is caused by the move.
- 4.1) If  $\Delta E < 0$ , the move bring the system to a state of lower energy, the move is allowed and put the particle in its new configuration.
  - 4.2) If  $\Delta E > 0$ , the move is allowed with the probability  $P(v) = \exp(-\Delta E / kT)$ , where  $k$  is the Boltzmann constant and  $T$  is the temperature in Kelvin. A random number  $\xi_4$  is taken between 0 and 1.
    - 4.2.1) If  $P(v) > \xi_4$ , move the particle to its new position, the next procedure is performed by returning to step 3
    - 4.2.2) If  $P(v) < \xi_4$ , return it to its old position. Then, having attempted to move a particle again by repeating step 3.



**Figure 2.2** The calculating steps of Monte Carlo simulations.

## 2.4 Radial Distribution Functions and the Integration Numbers

The most common way to analyze the structure of solution is to employ the radial distribution function,  $g(r)$  and the corresponding-running integration number  $n(r)$  around various atoms. The radial distribution gives information about the configurationally averaged deviation of the local environment of particle from the values characteristic for the bulk. This function for the  $N$  particle system in configuration  $\nu$  is obtained with  $r_{ij}$  as:

$$g(r) = \frac{N(r)}{\rho 4\pi r^2 dr} \quad (2.9)$$

where  $N(r)$  is the average number of particles in the spherical shell of width  $dr$  at a radial distance  $r$  from the central particle. The  $\rho$  is the number density of the system of the pair of the particle in the cubic volume  $V$ . Based on the radial distribution functions, solvation shells can be derived from the peaks pronounced over the standard level, and the first solvation number is obtained by the integration of the function up to the first minimum.

The average number of particles  $\rho$  within a sphere of a given radius can be determined by :

$$n(r) = \rho \int_0^{r_m} g(r) 4\pi r^2 dr \quad (2.10)$$

where  $r_m$  is often chosen as the radial value of the first or second minimum in  $g(r)$ .

## CHAPTER 3

### DETAIL OF CALCULATIONS

#### 3.1 Pair Potentials

The  $Mg^{2+}$ - $NH_3$  pair potential used in this study was taken from literature [25]. The analytical form and the corresponding parameters are:

$$\Delta E_{2bd}^{Mg^{2+}-NH_3} = \frac{A}{r} - \frac{B}{r^4} + \frac{C}{r^8} + D * \exp(E * r) \quad (3.1)$$

**Table 3.1** Final optimized parameters for the interaction of H and N atoms of ammonia with Magnesium ion. Interaction energies and r are in kcal/mol and atomic length unit, respectively.

Atom	A	B	C	D	E
N	-532.7448	-3064.6533	1898.6624	47496.2148	-2.8936
H	177.5816	0	0	3972.0449	-3.51697

The  $Li^+$ - $NH_3$  pair potential taken from [30] are:

$$\Delta E_{2bd}^{Li^+-NH_3} = \sum_{i=1}^4 \left( \frac{A_{im}}{r_{im}^6} + B_{im} * \exp\{C_{im} * r_{im}\} + \frac{D}{r_{im}} \right) \quad (3.2)$$

**Table 3.2** Final optimized parameters for the interaction of H and N atoms of ammonia with lithium ion. Interaction energies and r are in kcal/mol and atomic length unit, respectively.

Atom	A	B	C	D
N	-43772.1698	10714.0	-453.0	-188.25237
H	-31164.8089	-54.7651824	-0.57635498	-188.25237

### 3.2 Three-body Correction Functions

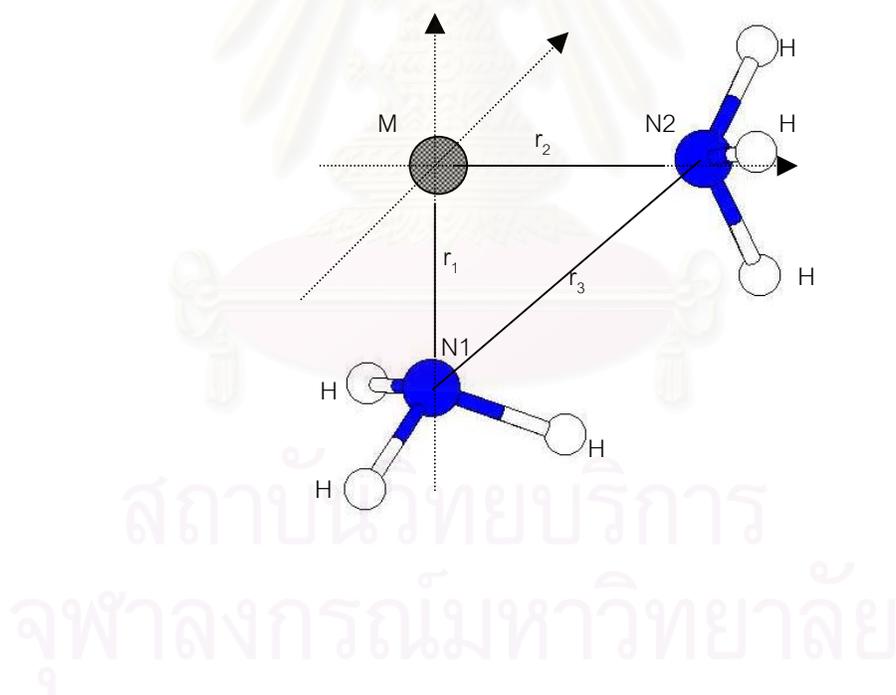
The three-body interaction energy,  $\Delta E_{3bd}$ , for each configuration was computed from 13 terms of the SCF energies on the right side of equation (3.3),

$$\begin{aligned}
 \Delta E_{3bd} = & [E\{ML_1L_2\} - E\{M\} - E\{L_1\} - E\{L_2\}] \\
 & - [E\{ML_1\} - E\{M\} - E\{L_1\}] \\
 & - [E\{ML_2\} - E\{M\} - E\{L_2\}] \\
 & - [E\{L_1L_2\} - E\{L_1\} - E\{L_2\}]
 \end{aligned} \tag{3.3}$$

where M is the Lithium or Magnesium ion,  $L_1$  and  $L_2$  are the first and second ammonia molecules. Then, 1,500 configurations of the  $L_1$ -M- $L_2$  complex in which  $\Delta E_{3bd}$  is function of M-N distances and orientation of the two ammonia molecules, have been generated. Here, the complex was positioned in orientation given in Figure 3.1, where  $r_{M-N_1} = 1.5, 1.8, 1.9, 2.2, 2.4, 3.0, 4.0, 6.0$  and  $8.0 \text{ \AA}$ . At each  $r_{M-N_1}$  distance, second ammonia ( $L_2$ ) was positioned at  $r_{M-N_2} = 1.5, 1.8, 1.9, 2.2, 2.4, 3.0, 4.0, 6.0$  and  $8.0 \text{ \AA}$ , it was also rotated around M- $N_2$  axis with rotational step of  $90^\circ$ .

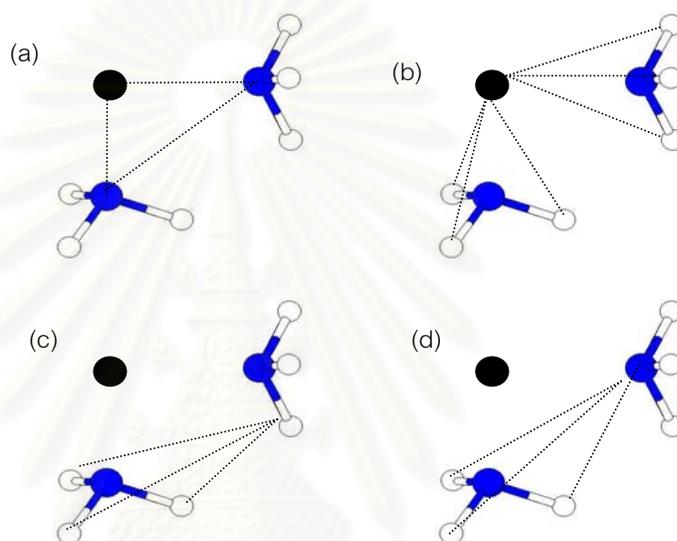
All three-body data points were calculated using quantum chemical calculations with the basis sets of double zeta quality. They were, then, fitted to an analytical function of exponential form. By means of a nonlinear Marquard-Levenberg fitting procedure [31]

In the previous work [25,26], only 3 distances,  $r_1$ ,  $r_2$ , and  $r_3$  in Figure 3.1, were included into the three-body correction functions (see Table 1.4). Therefore, the  $\Delta E_{3bd}$  obtained from such a function does not change when the two ammonia molecules ( $L_1$  and  $L_2$ ) rotate.



**Figure 3.1** Geometrical parameter definitions in the evaluation of the  $M-(NH_3)_2$  potentials, used for the SCF calculations.

In this study, the orientation of two ammonia molecules was included into the three-body correction functions, i.e., all 24 distances shown in Figure 3.2 have been taken into consideration.



**Figure 3.2** All 24 distances (a) M-N and N-N, (b) M-H, (c) H-H and (d) N-H distances, which are included in the three-body correction functions (dark sphere denotes  $\text{Li}^+$  or  $\text{Mg}^{2+}$ ).

The optimal form and final values of the parameters for the three-body correction function are given below, where the energy and the distance are in kcal/mol and Å, respectively.

$$\Delta E_{3bd}^{\text{Mg}^{2+}} = AA_1A_2A_3 + LA_4A_5 \quad (3.4)$$

where

$$A_1 = \prod_{i=1}^2 \exp\left(-B * r_i + \frac{G}{r_i^3}\right) \quad (3.5)$$

$$A_2 = \exp(-C * r_3 + \frac{H}{r_3^3}) \quad (3.6)$$

$$A_3 = \prod_{j=4}^9 \exp(-D * r_j + \frac{I}{r_j^3}) \quad (3.7)$$

$$A_4 = + L \prod_{k=10}^{15} \exp(-E * r_k^2 + \frac{J}{r_k^5} + \frac{M}{r_k^3}) \quad (3.8)$$

$$A_5 = \prod_{l=16}^{24} \exp(-F * r_l^2 + \frac{K}{r_l^5} + \frac{N}{r_l^3}) \quad (3.9)$$

**Table 3.3** Optimal parameters for the  $\text{NH}_3\text{-Mg}^{2+}\text{-NH}_3$  three-body correction function (equations. (3.5-3.9)).

A(kca/mol)	381.7760	H(Å <sup>3</sup> )	-2.896576
B(1/Å)	0.888677	I(Å <sup>3</sup> )	-0.2104110
C(1/Å <sup>2</sup> )	0.419310	J(Å <sup>5</sup> )	0.6576194
D(1/Å <sup>2</sup> )	-0.204817	K(Å <sup>5</sup> )	3.539369
E(1/Å <sup>2</sup> )	-0.255172	L(kcal/mol)	165.65300
F(1/Å <sup>2</sup> )	0.3872960	M(Å <sup>3</sup> )	-0.445206
G(Å <sup>3</sup> )	-0.659569	N(Å <sup>3</sup> )	-3.219359

$$\Delta E_{3bd}^{Li^+} = AA_1A_2A_3A_4A_5 \quad (3.10)$$

where

$$A_1 = \prod_{i=1}^2 (\exp(-B * r_i) + G * r_i^2) \quad (3.11)$$

$$A_2 = (\exp(-C * r_3) + H * r_3^2) \quad (3.12)$$

$$A_3 = \prod_{j=4}^9 (\exp(-D * r_j) + I * r_j^2) \quad (3.13)$$

$$A_4 = \prod_{k=10}^{15} (\exp(-E * r_k^2)) \quad (3.14)$$

$$A_5 = \prod_{l=16}^{24} (\exp(-F * r_l^2)) \quad (3.15)$$

**Table 3.4** Optimal parameters for the NH<sub>3</sub>-Li<sup>+</sup>-NH<sub>3</sub> three-body correction function (equations. (3.11-3.15)).

A(kcal/mol)	49.3063	D(1/Å)	0.03738	G(1/Å <sup>2</sup> )	-1.02519
B(1/Å)	0.54260	E(1/Å <sup>2</sup> )	0.08618	H(1/Å <sup>2</sup> )	114.00211
C(1/Å)	-0.49805	F(1/Å <sup>2</sup> )	-0.04322	I(1/Å <sup>2</sup> )	-0.35827

**Table 3.5** Definition of the distances (in Å) between atoms in the three-body correction functions where M, N and H represent metal ions, nitrogen atoms and hydrogen atoms, respectively.

$r_i$	i=1-2	$M - N_i$	-
$r_j$	j=3	$N_1 - N_2$	-
$r_k$	k=4-9	$M - H_k$	-
$r_l$	l=10-15	$N_i - H_k$	i=1, k=7-9 i=2, k=4-6
$r_m$	m=16-24	$H_n - H_o$	n=4, o=7-9 n=5, o=7-9 n=6, o= 7-9

### 3.3 Monte Carlo Simulations

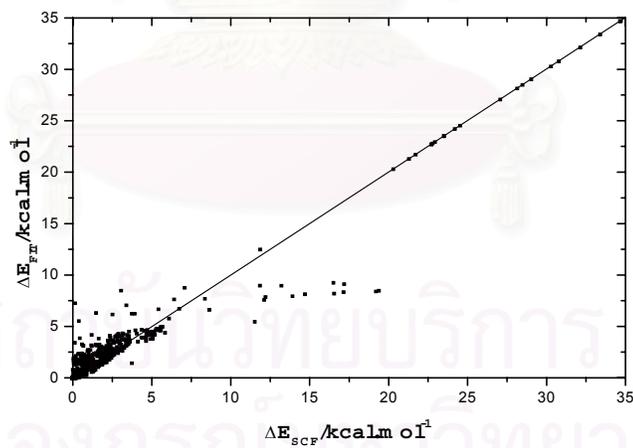
Monte Carlo simulations have been performed for the system consisting of one  $Mg^{2+}$  in 201  $NH_3$  and one  $Li^+$  in 201  $NH_3$ , using the pair potentials and the newly developed three-body correction functions as described above. The experimental density of pure liquid ammonia at 277 K and 1 atm ( $0.618 \text{ g cm}^{-3}$ ) leads to a periodic box length of 20.989 Å. The starting configuration was randomly generated and further 3 million configurations after equilibration were used to evaluate structural properties of the solution.

# CHAPTER 4

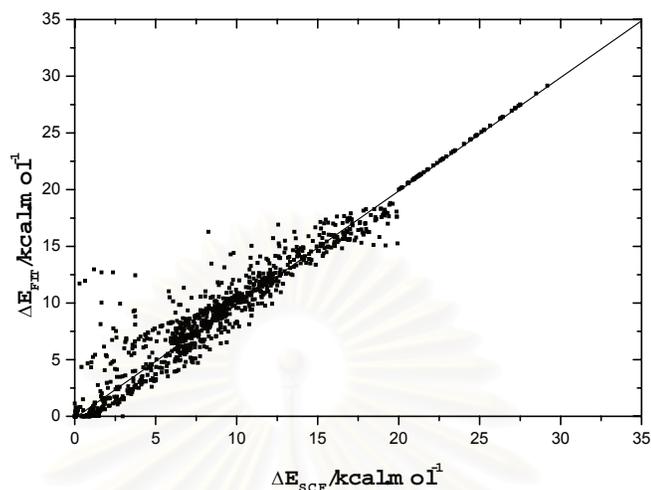
## RESULT AND DISCUSSION

### 4.1 Three-body Correction Functions

The SCF three-body interactions,  $\Delta E_{3bd}^{SCF}$ , and fitted energies,  $\Delta E_{3bd}^{FIT}$ , are compared in Figure 4.1-4.2. Perfect agreement would have implies a straight line of unit slope, and the scatter about this line gives a graphical measure of the quality of the fit. The plot indicates a good agreement between both data, especially for the attractive ranges, which is important for prediction of the simulation results. The obtained chi-square for the  $\text{Li}^+$ - $\text{NH}_3$  and  $\text{Mg}^{2+}$ - $\text{NH}_3$  systems are 0.12 and 0.88 kcal/mol, respectively.

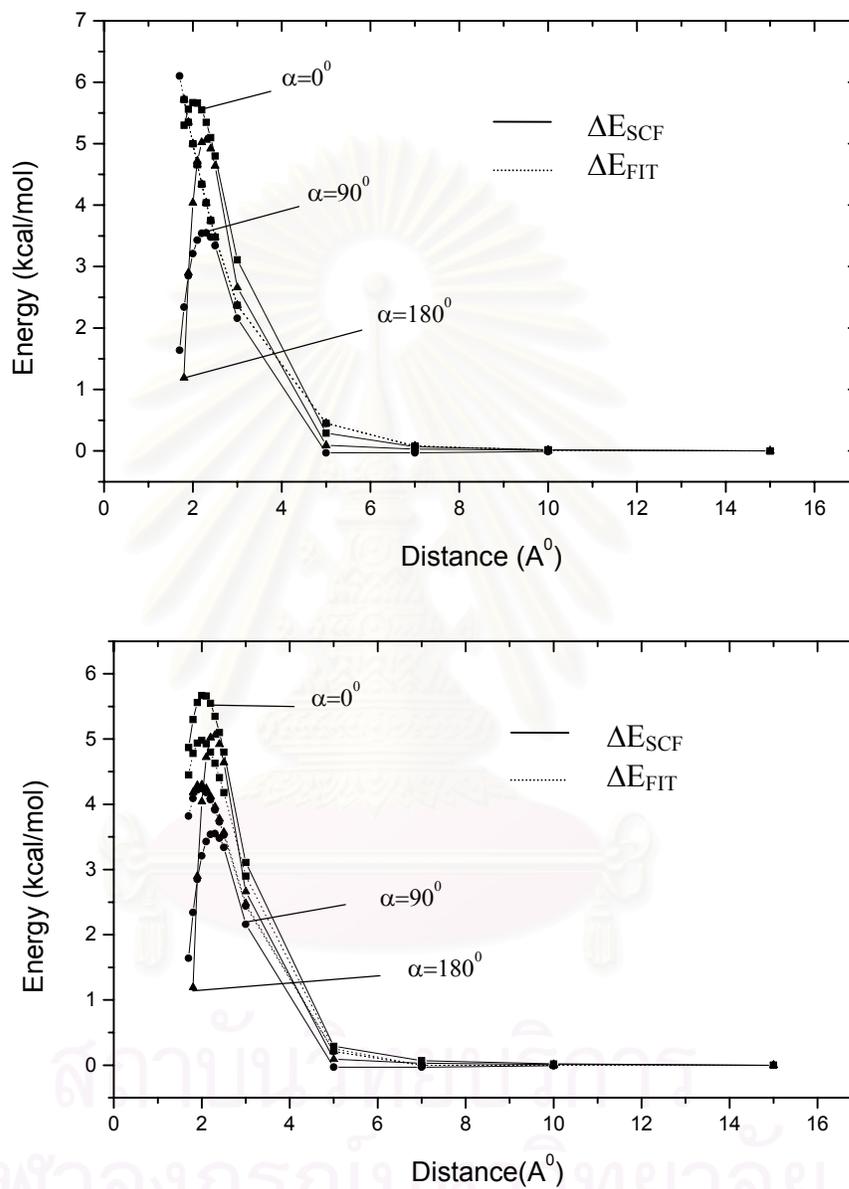


**Figure 4.1** Comparison of the three-body interaction energies of the  $\text{Li}^+$ - $\text{NH}_3$  obtained from the SCF calculations,  $\Delta E_{3bd}^{SCF}$ , and from the fit,  $\Delta E_{3bd}^{FIT}$ , for the generated configurations.

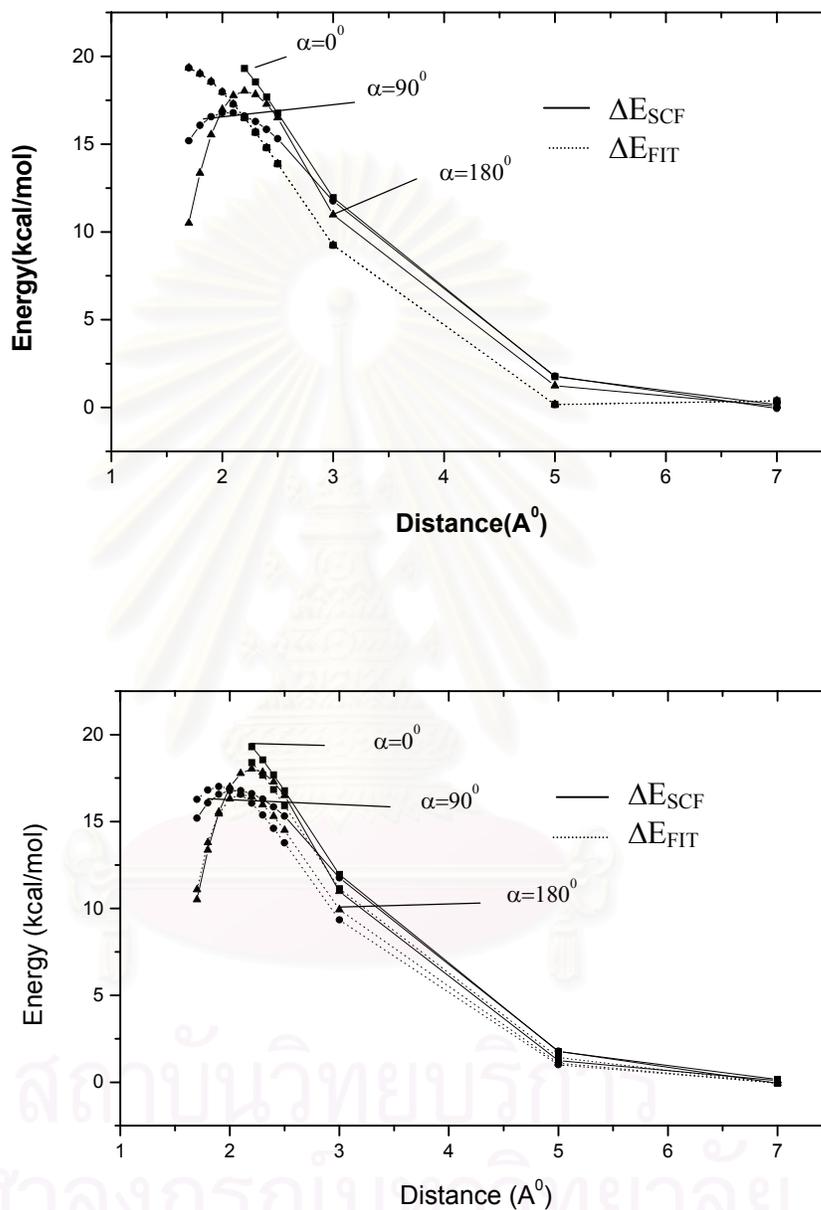


**Figure 4.2** Comparison of the three-body interaction energies of the  $\text{Mg}^{2+}$ - $\text{NH}_3$  obtained from the SCF calculations,  $\Delta E_{3bd}^{SCF}$ , and from the fit,  $\Delta E_{3bd}^{FIT}$ , for the generated configurations.

To evaluate in more details the angular dependence of the three-body correction functions, the  $\Delta E_{3bd}^{SCF}$  and  $\Delta E_{3bd}^{FIT}$  for certain configurations were again compared. The M (where M is the  $\text{Mg}^{2+}$  or  $\text{Li}^+$ ) are placed at the origin of the coordinate system. The nitrogen atom of the first ammonia molecule ( $N_1$ ) was positioned in the  $z$ -axis (see Figure 3.1) at an M- $N_1$  distance ( $r_1$ ) = 1.5 Å (distance where the minimum of the M- $\text{NH}_3$  pair potential takes place). The second ammonia was positioned on M- $N_1$  = 1.5, 1.8, 1.9, 2.2, 3.0, 4.0, 6.0 and 8.0 Å and the  $N_1$ -M- $N_2$  angle was fixed at  $90^\circ$ . The hydrogen atoms of both ammonia molecules are in the configuration shown in Figure 3.1. These configurations are used as reference orientation ( $\alpha = 0^\circ$ ). The same procedures were repeated for  $\alpha = 90^\circ, 180^\circ, 270^\circ$ , where  $\alpha$  is the angle of rotation of the second ammonia around its dipole axis. The results are displayed in Figure 4.3 and Figure 4.4. The data obtained from the previous works [25,26] where orientation of the two ammonia molecules was not taken into consideration, were also given for comparison.



**Figure 4.3**  $\Delta E_{3bd}^{SCF}$  and  $\Delta E_{3bd}^{FIT}$  as a function of  $Li^+ - N_2$  distance. In which only 3 distances (above) and all 24 distances (below) have been taken into accounted (more details see text).



**Figure 4.4**  $\Delta E_{3bd}^{SCF}$  and  $\Delta E_{3bd}^{FIT}$  as a function of  $Mg^{2+}$ - $N_2$  distance. In which only distances (above) and all 24 distances (below) have been taken into accounted (more details see text).

As mentioned before, the three-body interaction energy obtained from quantum chemical calculations depends on the orientation of the two ammonia molecules. In the previous work [25,26] this change did not include in the three-body correction functions as only 3 distances ( $r_{M-N1}$ ,  $r_{M-N2}$  and  $r_{N1-N2}$ ; see Figure 3.1) were taken into consideration (Table 1.4). Therefore, the three curves of the SCF three-body energies,  $\Delta E_{3bd}^{SCF}$ , in Figures 4.3 and 4.4 (above) have been represented only by one  $\Delta E_{3bd}^{FIT}$  line, i.e., rotation of the two ammonia molecules does not effect the  $\Delta E_{3bd}^{FIT}$ . Situation is different for the newly developed functions where all 24 distances have been included. The three curves of the,  $\Delta E_{3bd}^{SCF}$ , in Figures 4.3 and 4.4 (below) have been nicely represented by the  $\Delta E_{3bd}^{FIT}$  curves.

Some comments could be made concerning the sensitivity of the simulation results on the three-body correction energy. Each metal-ammonia pair interaction must be added by N-1 terms of the  $\Delta E_{3bd}^{FIT}$  obtained from the three-body correction functions, where N is total number of solvent molecules in the simulation box. For example, each M-L<sub>1</sub> pair energy must be added by the L<sub>1</sub>-M-L<sub>i</sub> (i = 1, 2, 3, ..., N-1) three-body energies where M and L denote metal ion and ammonia molecule, respectively. In another word, total energy of the simulation box must be added by (N-1)N(N-1)/2 terms of the three-body correction energy. Therefore, little discrepancy between the  $\Delta E_{3bd}^{SCF}$  and the  $\Delta E_{3bd}^{FIT}$  would have led to significant change of the total energy of the system due to the summation of numerous  $\Delta E_{3bd}^{FIT}$  terms (for example N = 201 for this study).

## 4.2 Monte Carlo Simulations: Radial Distribution Functions and Running Integration Numbers

The atom-atom radial distribution functions (RDFs) and corresponding integration numbers for the two simulations,  $\text{Li}^+$  and  $\text{Mg}^{2+}$  with the three-body correction functions, have been illustrated in Figures 4.5 and 4.6. RDFs taken from the previous work [25,26] with and without the three-body correction functions (with only 3 distances, M-N<sub>1</sub>, M-N<sub>2</sub> and N<sub>1</sub>-N<sub>2</sub>) have been also given for comparison.

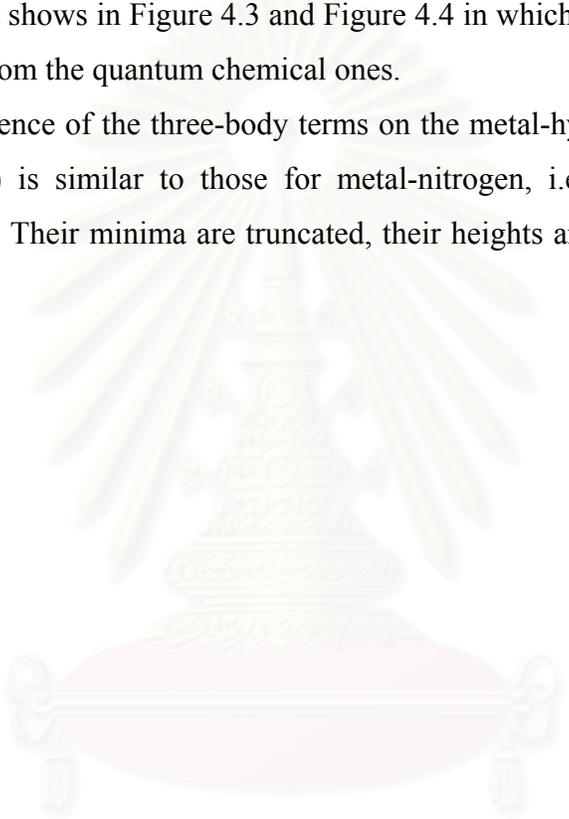
It can be clearly seen from the Figures that the influence of the three-body corrections is more visible in the  $\text{Mg}^{2+}$  system than in the  $\text{Li}^+$  case. Although, the energies obtained incorporating the three-body correction functions including only 3 and all distance are obviously different. The characteristic of the metal-ammonia RDFs obtained from this work are almost the same as those of the previous works [25,26]. Significant change can be observed only in terms of the height of the first  $\text{Mg}^{2+}$ -N and  $\text{Mg}^{2+}$ -H RDFs. The  $\text{Mg}^{2+}$ -N RDFs for all three cases, without three-body corrections and with 3r and 24r three-body corrections, showed the first peak at 2.26 Å. The corresponding integration numbers up to the first minimum for both corrections (3r and 24r) is 6 ammonia molecules. In addition the  $\text{Mg}^{2+}$ -N RDF without the three-body corrections displays also a small peak beyond the first maximum. The number of ammonia molecules under the first and small peaks of this RDF is 8 and 10, respectively. The  $\text{Mg}^{2+}$ -H RDFs for all cases agree well with the  $\text{Mg}^{2+}$ -N RDFs by showing the first peak integration number of 18 and 24 for the simulations with both 3r and 24r and without three-body corrections, respectively.

For the  $\text{Li}^+$ -NH<sub>3</sub> system the difference of the first peak position for all RDFs is almost negligible. The first solvation sphere for all 3 cases is represented by a sharp peak centered at 2.20 Å. The corresponding coordination numbers integrated up to the first minima of the all  $\text{Li}^+$ -N RDFs is 6.

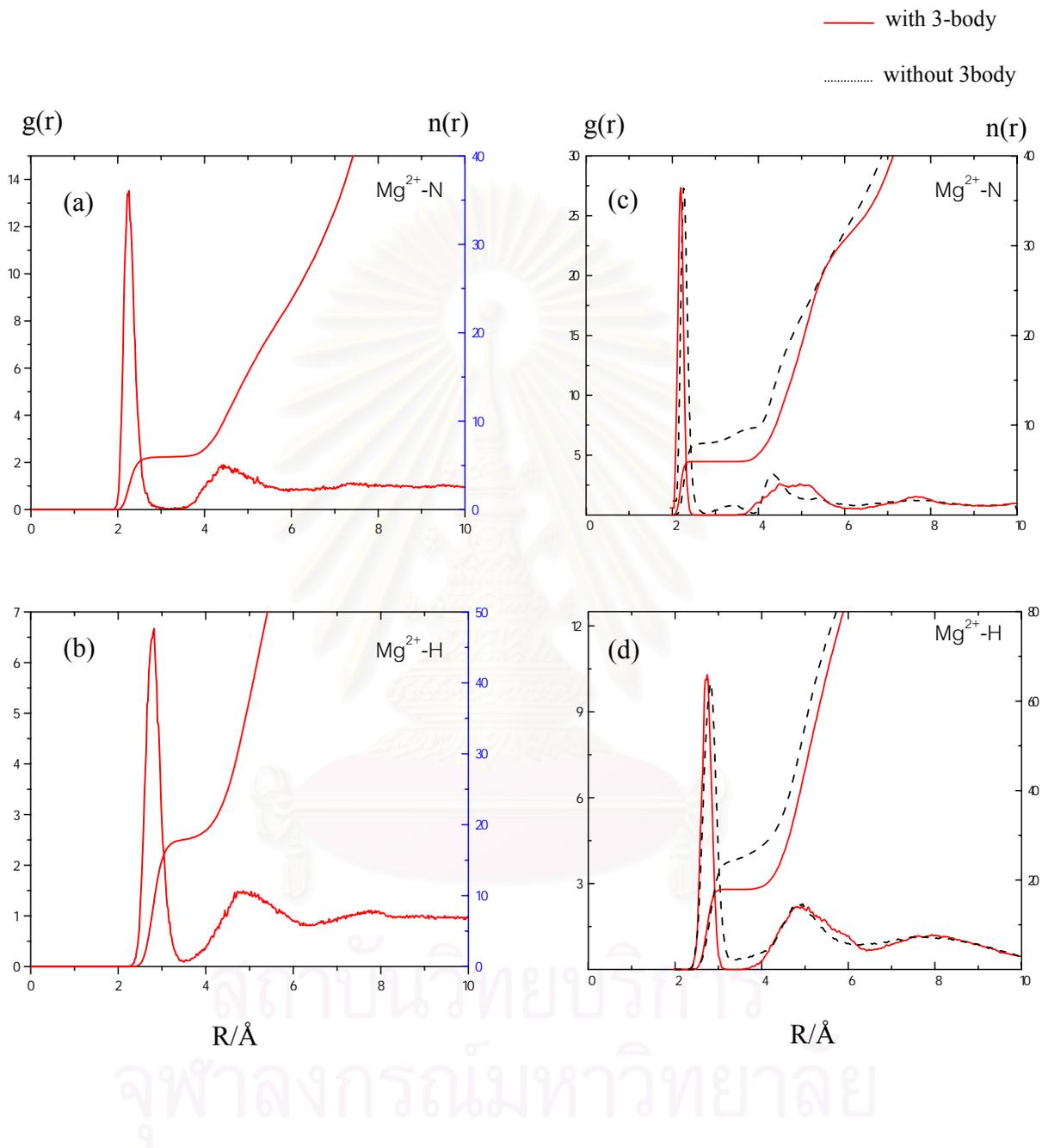
Some comments could be made concerning the simulation data given above. The three-body interaction energies yielded from quantum chemical calculations are much

better represented by the 24r potential function than the 3r one while the simulation results obtained from the two functions are, somehow, identical. This fact can be understood by an error cancellations due to the position and negative deviations of the quantum calculation energies in relation with the fitted energies. This statement confirms the plot shows in Figure 4.3 and Figure 4.4 in which the fitted curve is supposed to be averaged from the quantum chemical ones.

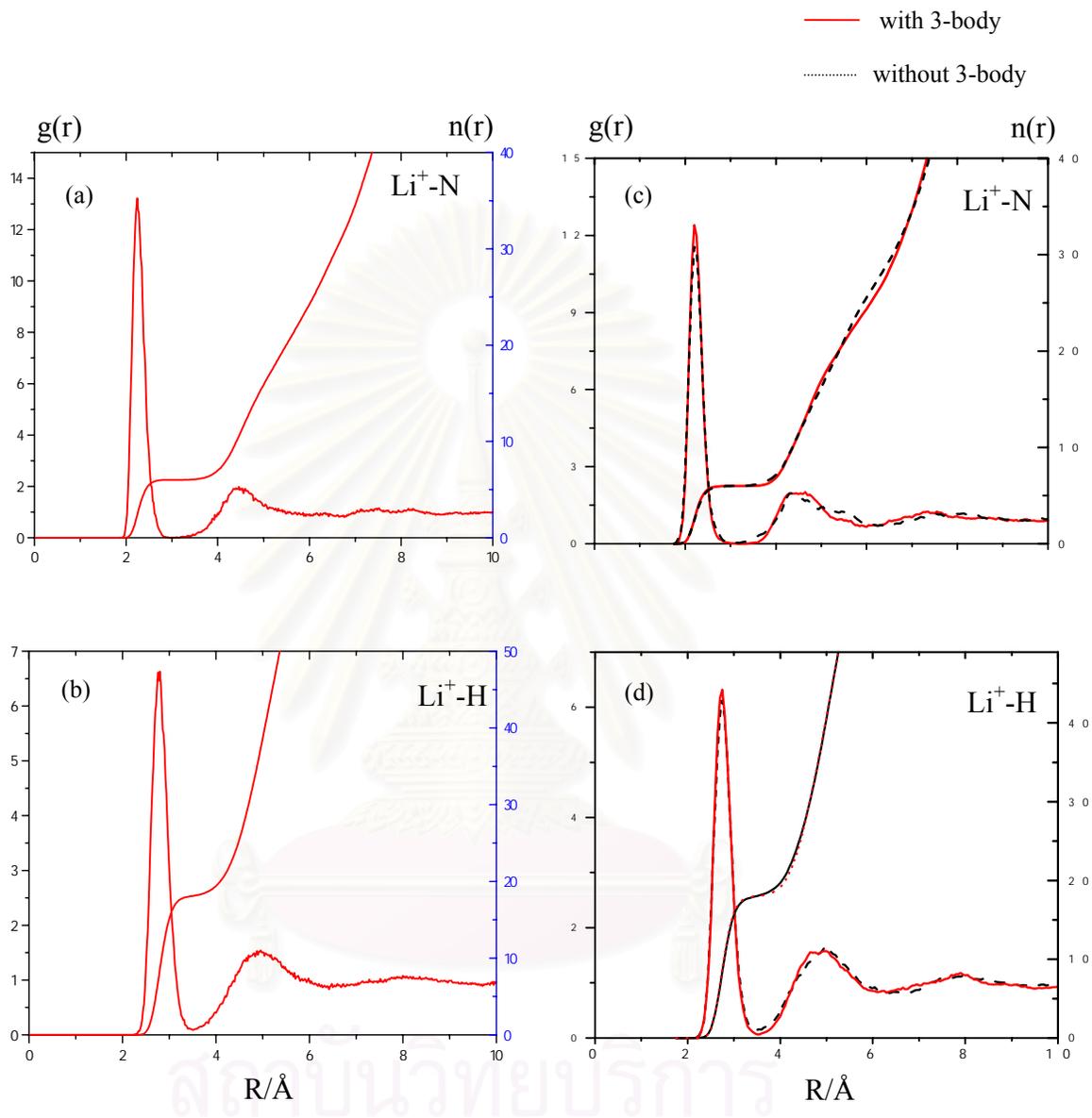
The influence of the three-body terms on the metal-hydrogen RDFs (Figure 4.5. and Figure 4.6.) is similar to those for metal-nitrogen, i.e. the first peak positions increase slightly. Their minima are truncated, their heights and integration numbers are lower.



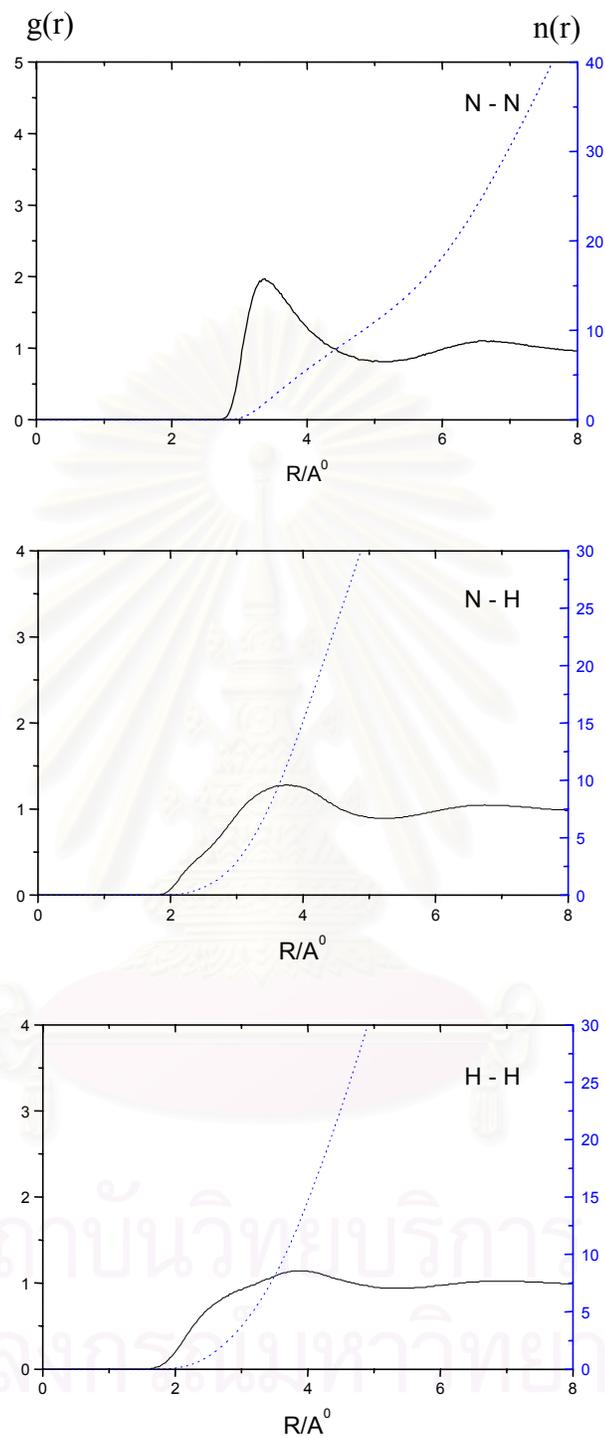
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**Figure 4.5**  $\text{Mg}^{2+}$ -N and  $\text{Mg}^{2+}$ -H radial distribution functions and corresponding running coordination number obtain from the simulations with three-body corrections. All 24 distance (a and b) and only 3 distance (c and d).



**Figure 4.6**  $\text{Li}^+\text{-N}$  and  $\text{Li}^+\text{-H}$  radial distribution functions and corresponding running coordination number obtain from the simulations with three-body corrections. All 24 distance (a and b) and only 3 distance (c and d).



**Figure 4.7** N-N, N-H and H-H radial distribution functions and corresponding running coordination number.

Due to the fact that there is only one ion in 201 ammonia molecules, the observed solvent properties are, somehow, identical to those of pure liquid ammonia. The N-N RDF from the X-ray measurements by Narten [32] at 277 K exhibits a maximum at 3.37 Å and minimum at 5.3 Å leading to the coordination number of 12. The MC results agree well with these X-ray data, especially for the coordination number and height of the first RDF. The N-N, N-H and H-H RDFs are also in consistence with those observed theoretically [33-36].

### 4.3 Conclusion

It has been already conclude from the previous works [25,26] that three-body effects play significant role in the prediction of structural, dynamics and thermodynamic properties of the solution. Additional conclusion which is the result of this study is that the orientation of the solvent molecules can be neglected from consideration, at least in dealing with structural properties of the solution. This conclusion leads to numerous reduction of computational efforts in including of three-body effects in computer simulations.

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## REFERENCES

1. Allen, M. P. and Tildesley, D. J. (1987). Computer Simulation of Liquids. New York: Oxford University Press.
2. Metropolis, N., Rosenbluth, A. W., Rosenbluth, M. N., Teller, A. H., and Teller, E. (1953). Equation of state calculation by fast computing machines. J. Chem. Phys. 21 (6): 1087-1092.
3. Alder, B. J. and Wainwright, T. E. (1960). Studies in molecular dynamics. II. Behaviour of a small number of elastic spheres. J. Chem. Phys. 33: 1439-1451.
4. Lie, G. C., Clementi, E. and Yoshimine, M. (1975). Study of the structural of molecular complexes XIII: Monte Carlo simulation of liquid water with a configuration interaction pair potential. J. Chem. Phys. 64(6): 2314-2323.
5. Swaminathan, S., Harrison, S. W. and Beveridge, D. L. (1977). Monte Carlo studies on the structure of a dilute aqueous solution of methane. J. Am. Chem. Soc. 100(8): 5705-5712.
6. Jorgensen, W. L. and Ibrahim, M. (1980). Structure and properties of liquid ammonia. J. Am. Chem. Soc. 102(10): 3309-3315.
7. Jorgensen, W. L. (1981). Simulation of liquid ethanol including internal rotation. J. Am. Chem. Soc. 103(2): 345-350.
8. Bolis, G., Corongiu, G. and Clementi, E. (1981). Methanol in water solution at 300 K. Chem. Phys. Lett. 6(3): 299-306.
9. Jorgensen, W. L. and Madura, J. D. (1983). Solvation and conformation of methanol in water. J. Am. Chem. Soc. 105(6): 863-869.
10. Linse, P., Karlstrom, G. and Jonsson, B. (1984). Monte Carlo studies of a dilute aqueous solution of benzene. J. Am. Chem. Soc. 106(15): 4096-4102.
11. Byrnes, J. M. and Sandler, S. I. (1984). Monte Carlo simulation of liquid ethane. J. Chem. Phys. 80(2): 881-885.
12. Dietz, W. and Heinzinger, K. (1984). Structure of liquid chloroform: A comparison between computer simulation and neutron scattering results. Ber. Bunsenges. Phys. Chem. 88: 543-546.

13. Okazaki, S., Touhara, H. and Nakanishi, K. (1984). Computer experiments of aqueous solutions V: Monte Carlo calculation on the hydrophobic interaction in 5 mol % methanol solution. J. Chem. Phys. 81(2): 890-894.
14. Alagona, G., Ghio, C., and Kollman, P.A. (1985). Monte Carlo Simulations of the Solvation of the Dimethyl Phosphate Anion. J. Am. Chem. Soc. 107(8): 2229-2238.
15. Tanabe, Y., and Rode, B. M. (1988). Monte Carlo Simulation of an 18.45 mol % Aqueous Ammonia Solution. J. Chem. Soc. Faraday. Trans. II 84: 679-692.
16. Hannongbua, S., Ishida, T., Spohr, E., and Heinzinger, K. (1988). Molecular Dynamics Study of a Lithium Ion in Ammonia. Z. Naturforsch. 43a: 572-582.
17. Kheawsrikul, S., Hannongbua, S. V., Kokpol, S. U. and Rode, B. M. (1989). A Monte Carlo Study on Preference Solvation of Lithium (I) in Aqueous Ammonia. J. Chem. Soc. Faraday. Trans. II. 85: 643-649.
18. Hannongbua, S., Kerdcharoen, T., and Rode, B. M. (1992). Zinc (II) in Liquid Ammonia: Intermolecular Potential Including Three-Body Terms and Monte Carlo Simulation. J. Chem. Phys. 96: 6945-6949.
19. Lepoutre, G. and Seinko, M. J. (1964). Metal-ammonia solutions, New York: Benjamin, Collogue Weyl I.
20. Lagowski, J. J. and Seinko, M. J. (1970). Metal-ammonia solutions, London: Butterworths, Collogue Weyl II.
21. Jortner, J. and Kertner, N. R. (1973). Electrons in fluids, Springer, Berlin Collogue Weyl III.
22. Leach, A. R. (1996). Molecular Modelling: Principles and Applications. 1<sup>st</sup> ed. Essex: Addison Wesley Longman Limited.
23. M. M. Probst, (1987). Chem. Phys. Lett. 137: 229.
24. Kerdcharoen T. (1995). Hot-spot molecular dynamics, Ph. D. Thesis, University of Innsbruck.
25. Hannongbua, S. (1997). The role of nonadditive effects in the first solvation shell of Na<sup>+</sup> and Mg<sup>2+</sup> in liquid ammonia: Monte Carlo studies including three-body corrections. J. Chem. Phys. 106(14): 6076-6081.

26. Hannongbua, S. (1998). On the solvation of lithium ions in liquid ammonia: Monte Carlo simulations with a three-body potential. Chemical Physics Letters. 288: 663-668.
27. Sidhisoradej, W., Hannongbua, S., and Ruffolo, D. (1998). Three-body Effects in Calcium(II)-ammonia Solutions: Molecular Dynamics Simulations. Z. Naturforsch. 53a: 208-216.
28. Ewald, P. (1921). Die Berechnung Optischer und Elektrostatischer Gitterpotentiale. Ann. Phys. 64: 253-287.
29. Friedman, H. L. (1975). Image Approximation to the Reaction Field. Molecular Physics. 29: 1533-1543.
30. Hannongbua, S., Sirirat U. Kokpol, Suchada Kreawsrikul, Supa Polman, and Bernd M. Rode (1988). Intermolecular Potential Function for Ammonia-Lithium Ion Based on Ab-Initio Calculations. Z. Naturforsch. 43a: 143-146.
31. H. P. William, P. F. Brian, A. T. Saul, and T. V. William, (1989). Numerical Recipes, New York: Cambridge University Press.
32. Narten, A. H. (1977). Liquid ammonia: Molecular correlation functions from X-ray diffraction. J. Chem. Phys. 66: 3117.
33. Hannongbua, S. S. (1991). A molecular dynamics simulation of the structure of sodium ion in liquid ammonia. Aust. J. Chem. 44: 447.
34. Klein, M. L., and McDonald, I.R. (1981). J. Chem. Phys. 74: 4214.
35. Rode, B. M., Islam, S. M. and Yongyai, Y. (1991). Pure Appl. Chem. 63: 1894.
36. Yongyai, Y., Kokpol, S. and Rode, B. M. (1991). Chem. Phys. 156: 403.

# CURRICULUM VITAE

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