

CHAPTER 5

DETAIL OF CALCULATIONS

5.1 Selection of Basis Set for SCF Calculations

It is known that results obtained from the simulations depend strongly on the quality of the potential functions, and hence the quality of the basis set used in quantum chemical calculations. However, a higher quality basis set frequently requires much more time and computer resources.

In this work the STO-3G, 6-31G, 6-311G, and DZP (Double Zeta including Polarization function) quality basis sets have been used. Their orbital exponents and coefficients are summarized in Appendix A. Calculations for the system of a calcium ion and ammonia molecule were for the arrangement shown in Figure 5.1. An error due to unbalance of the basis set, BSSE, has been analyzed using the counterpoise method. Also, there is a balance between accuracy and computing time.

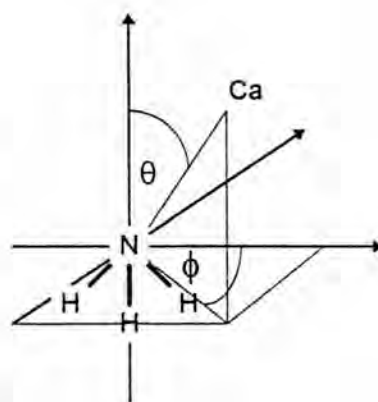


Figure 5.1 Geometry of Ca(II)-NH₃

5.2 Development of the Pair Potential Function

To develop the Ca(II)-NH₃ pair potential, more than 1700 Ca(II)-NH₃ configurations were generated. The Ca(II) was placed around the ammonia molecule as illustrated in Figure 5.1 varying $1.5 \text{ \AA} \leq r \leq 10.0 \text{ \AA}$, $0^\circ \leq \theta \leq 180^\circ$, and

$0^\circ \leq \phi \leq 60^\circ$. The experimental gas phase geometry of the ammonia molecule, with an N-H distance of 1.0124 Å and HNH angle of 106.67° , was taken from the literature [Benedict and Plyler 1985] and kept constant throughout. The pair interaction energies were computed via an *ab initio* SCF method using the Gaussian 92 program on the IBM RISC 6000 Workstation, and were fitted to an analytical function of the form

$$\Delta E_{pair}^{FIT} = \sum_{i=1}^4 \left[\frac{a_i}{r_i^4} + \frac{b_i}{r_i^3} + c_i \exp(-d_i r_i) + \frac{332.15 q_i q_{Ca}}{r_i} \right],$$

where ΔE_{pair} is the fitted energy in kcal.mol⁻¹, a_i , b_i , c_i and d_i are the fitting parameters, r_i is the distance in Å between the i -th atom of the ammonia molecule and the calcium ion, and q_i and q_{Ca} are their corresponding atomic net charges obtained from a Mulliken population analysis [Hannongbua 1997] in the SCF calculations. The factor 332.15 is used to convert coulombic interactions to units of kcal.mol⁻¹.

5.3 Development of Three-Body Correction Function

The complete three-body potential function can be developed based on quantum chemical calculation. The nitrogen atom of the first ammonia molecule, N1, was placed on the z-axis at the distance r_1 from the origin of system and the calcium ion was at the origin (Figure 5.2). The nitrogen atom of the second ammonia molecule, N2, was placed at the coordinates (r_2, θ, ϕ) .

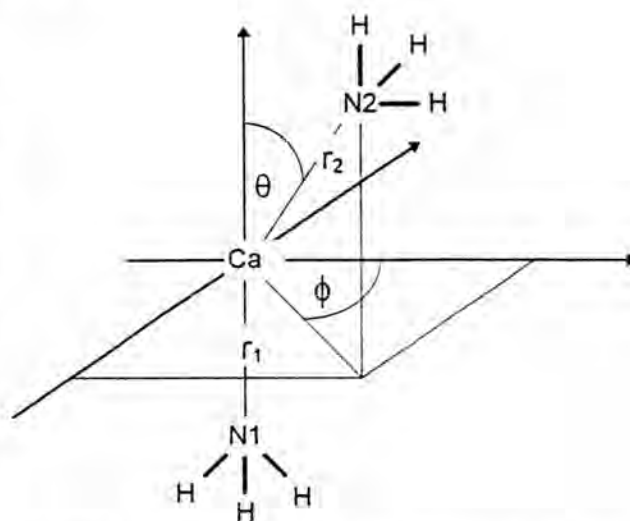


Figure 5.2 Geometry for the evaluation of the $\text{NH}_3\text{-Ca(II)-NH}_3$ potential for SCF calculations.

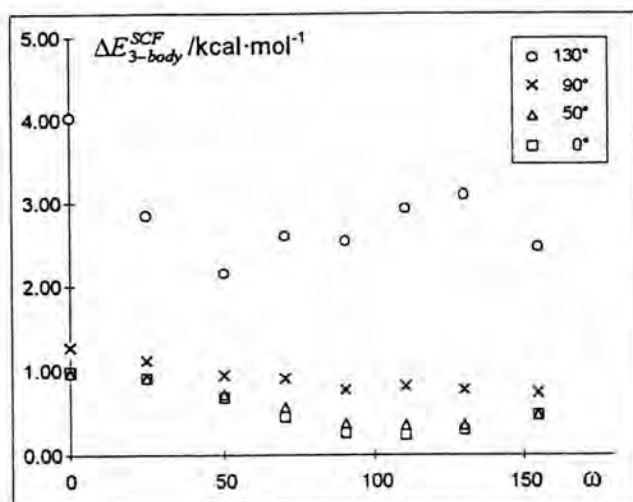


Figure 5.3 Example of dependence between three-body interaction energies and orientation of ammonia molecules. This figure shown for $\theta = 0^\circ, 50^\circ, 90^\circ,$ and 180° , the distance r_1 and r_2 are 3.3 and 3.9 Å. The symbol ω represents the angle between dipole moment of ammonia molecules and vectors pointing from calcium ion to the nitrogen atoms.

The three-body interaction energies of more than 7,000 configurations of $\text{NH}_3\text{-Ca(II)-NH}_3$ were calculated using the SCF method. We observed that the orientation of the ammonia molecules outside the first solvation shell slightly affected the three-body interaction energy (Figure 5.3). Also, the ammonia molecules in the first solvation shell generally point their dipole vectors away from the calcium ion (Figure 6.21). Therefore, we could greatly reduce the computation time by selecting the

$\text{NH}_3\text{-Ca(II)-NH}_3$ configurations in which the ammonia dipole vectors directly point away from the calcium ion. Four parameters were varied independently in the ranges $1.9 \text{ \AA} \leq r_i \leq 10.0 \text{ \AA}$, $0^\circ \leq \theta \leq 180^\circ$, and $0^\circ \leq \phi \leq 60^\circ$ in order to cover the whole spatial configuration of the $\text{NH}_3\text{-Ca(II)-NH}_3$ complex. Then the three-body interaction energy, ΔE_{3b} , for each configuration was computed from the SCF energies of the monomer, dimer, and trimer according to equation:

$$\begin{aligned} \Delta E_{3\text{-body}}^{SCF} = & \left[E\{ML_1L_2\} - E\{M\} - E\{L_1\} - E\{L_2\} \right] \\ & - \left[E\{ML_1\} - E\{M\} - E\{L_1\} \right] \\ & - \left[E\{ML_2\} - E\{M\} - E\{L_2\} \right] \\ & - \left[E\{L_1L_2\} - E\{L_1\} - E\{L_2\} \right], \end{aligned}$$

where M , L_1 , and L_2 denote the calcium ion and the first and second ammonia molecules, respectively. The three-body interaction energy was fitted using an analytical function of the form

$$\Delta E_{3\text{-body}}^{FIT} = \{R_1(r_1)R_2(r_2) + R_1(r_1)R_2(r_2)\}\Theta(\theta) ,$$

where

$$\begin{aligned} R_1(r_1) &= \left(a_0^{(1)} + a_1^{(1)}r_1 + a_2^{(1)}r_1^2 + a_3^{(1)}r_1^3\right)\exp\left(-c_1^{(1)}r_1\right) \\ R_2(r_2) &= \left(a_0^{(2)} + a_1^{(2)}r_2 + a_2^{(2)}r_2^2 + a_3^{(2)}r_2^3\right)\exp\left(-c_1^{(2)}r_2\right) \\ \Theta(\theta) &= \left(a_0^{(3)} + a_1^{(3)}\cos\theta + a_2^{(3)}\cos^2\theta + a_3^{(3)}\cos^3\theta\right), \end{aligned}$$

$a_j^{(i)}$ and $c_j^{(i)}$ are fitting constants and θ is the N_1 -Ca(II)- N_2 angle.

5.4 Molecular Dynamics Simulations

5.4.1 Dilute solutions

A flexible model has been employed for the ammonia molecules in the simulations. Both inter- and intra-molecular potentials of ammonia molecules, which are the same as those used in previous works [Hannongbua 1991, 1997; Hannongbua et al. 1992; Tongraar et al. 1997], were taken from the literature [Spirko 1983; Hannongbua et al. 1988].

Molecular dynamics simulations, with and without three-body corrections, were performed for the system consisting of one calcium ion and 215 ammonia molecules at an average temperature of 240 K and atmospheric pressure. The experimental density of pure liquid ammonia at the simulated temperature and pressure, $0.688 \text{ gm}\cdot\text{cm}^{-3}$ [Weast 1977], leads to the size of the periodic cube of 20.67 Å. The shifted force potential method [Strett, Tildesley, and Saville 1978] was employed to make short-range interactions vanish smoothly at the half-box length. The simulations were started from random configurations and were equilibrated for 10,000

timesteps. Then they were continued for 80,000 timesteps, corresponding to 10 picoseconds, with system configurations collected every 10 timesteps.

5.4.2 Concentrated solutions

Three simulations were performed, at the same environment as employed in the dilute solution, for the concentrated calcium-calcium solution using the total site-site interactions obtained from the three model of the pseudopotential.

- I. Ashcroft model with Gurskii dielectric function (see sections 4.3.4, 4.3.5).
- II. Ashcroft model with Ichimaru dielectric function (see sections 4.3.4, 4.3.5).
- III. Point ion model with Gurskii dielectric function (see sections 4.3.4, 4.3.5).

The interactions due to the pseudopotential were calculated via Equation (4.32) and (4.49)

$$V_{ind}(R) = \frac{\Omega_0}{\pi^2} \int_0^\infty F(q) \frac{\sin qR}{R} q dq, \quad (4.32)$$

and

$$F(\vec{q}) = -\frac{q^2 \Omega}{8\pi e^2} \left| \langle \vec{k} + \vec{q} | \mathbf{w}^0 | \vec{k} \rangle \right|^2 \frac{\varepsilon(q) - 1}{\varepsilon(q)}, \quad (4.49)$$

where $\varepsilon(q)$ is dielectric function and $\langle \vec{k} + \vec{q} | \mathbf{w}^0 | \vec{k} \rangle$ is form factor. The experimental density, taken from the literature [Wong 1966], is $0.642 \text{ gm}\cdot\text{cm}^{-3}$, at an average temperature of 240 K and atmospheric pressure. A simulation cube containing 18 calcium ions and 215 ammonia molecules corresponding to 7.73 mole percent yields the box length of 22.46 \AA .

Note that the simulations using model I and II lead to the collapse of the ammonia molecule. To avoid difficulty, simulations were carried out using rigid ammonia model. After equilibration, all particles, ammonia molecules and calcium ions, pull to center of the cube, therefore, simulations for these two pseudo potential models were finally given up. For the pseudopotential model III, simulation can be performed

properly with flexible model. The simulations were heated up to 2000 K for 10,000 timesteps. Then they were cooled down to 240 K and were equilibrated for 30,000 timesteps. Finally they were continued for 50,000 timesteps, corresponding to 6.25 picoseconds.

5.5 Calculation Apparatus

The SCF calculations in this work were accomplished by the Gaussian 92 program. Other calculations were performed using numerous program of FORTRAN 77 source code modified from previous work in the Austrian-Thai Center for Computer Assisted Chemical Education and Research (ATC) at Chulalongkorn University, Bangkok, Thailand..

All the calculations and simulations were performed on the IBM RISC 6000 and DEC 3100 Workstations at ATC and SGI Power Challenge XL at the High Performance Computing Center (HPCC), National Electronics and Computer Technology Center (NECTEC), Bangkok, Thailand.