CHAPTER IV

Results for Zn^{2+} - Water function

4.1 Pair Potential

To construct the potential function by means of quantum chemical calculations the following steps were performed :

(i) selection of representative geometries of pairs ;

(ii) performance of the SCF calculation ;

(iii) fitting of the computed interaction energies to a functional form and testing of the function .

(i) Selection of Geometries

Zn^{2+} ion was placed at numerous positions around the fix water molecule, varying geometrical parameters $0° \leq \theta \leq 180°$ and $0° \leq \Phi \leq 135°$ (Figure 4.1). For each configuration, the zinc-oxygen internuclear distance was varied from 1.0 Å to 10.0 Å. The water molecule's geometry was kept fixed during all calculations at the experimental values (38) (O-H = 0.9572 Å and H-O-H = 104.52 Å). The fixed cartesian coordinates for water molecule are given in table 4.1 .

(ii) Performance of the SCF Calculations

The calculations were performs based on the LCAO-MO-SCF method, with double zeta basis set including polarization functions (DZP) and ECP (39) approximation, using a version of the HONDO (7.0) (40) program. For the oxygen atom of water, the basis set was taken from Stevens et al.(41) for both core and valence shell electrons, and was extended by a d-type polarization function of orbital exponent 1.154 (42). For the Zn^{2+} ion the original ECP-DZV basis set of Hay and

Wadt (43) had to be modified to a truncated form. The reason for that is that the original basis set does not describe correctly the behaviour of the system $Zn^{2+}...H_2O$ at larger distances. Contraction of the d-functions into one set, and removal of the softest functions (p,s) ensures that Zn^{2+} remains a Zn^{2+} at all Zn...O distances. In addition, with the original basis set charge transfer occurs to water at larger distances, leading to an electronic state closed to Zn^+. The original and the modified basis sets are given for comparison in tables 4.2 and 4.3 , repectively.

The LCAO-SCF calculations with the modified basis set have been carried out for numerous Zn^{2+}/ water configurations listed in table 4.4 . The zinc(II) ion / water stabilization energy, ΔE_{SCF} in kcal/mol can be calculated as

$$\Delta E_{SCF} \ (kcal/mol) = (E - E_{Zn^{2+}} - E_{H_2O}) \times 627.5$$

$$(4.1)$$

where

E = Total energy of the supermolecule

$E_{Zn^{2+}}$ = Total energy of Zn^{2+}

E_{H_2O} = Total energy of water

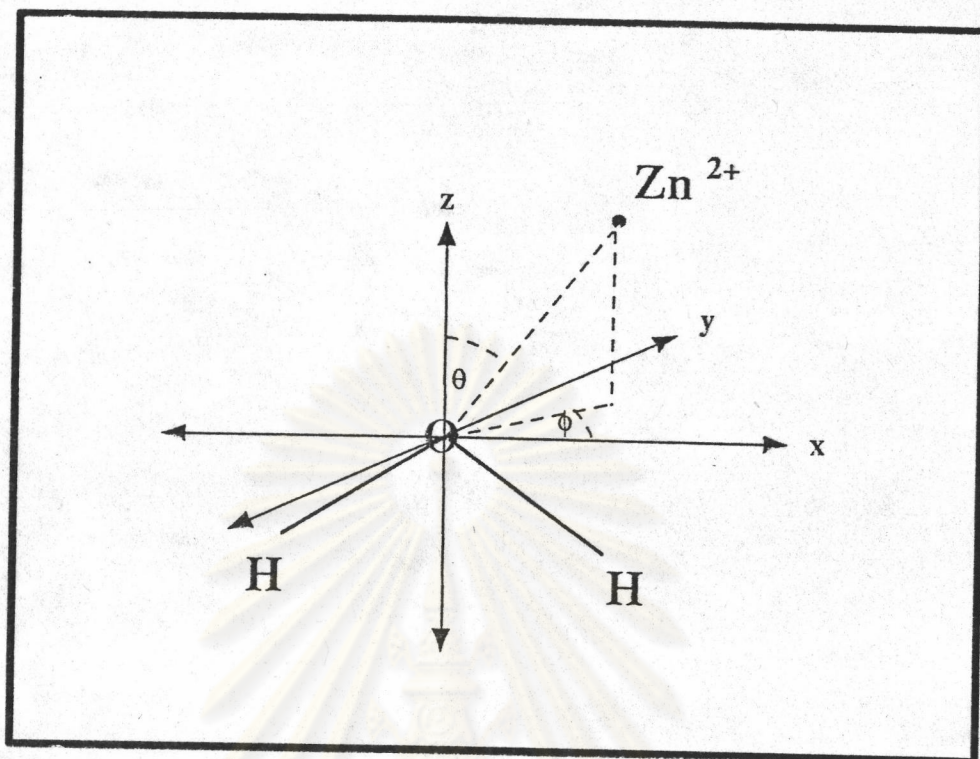The ab initio stabilization energies, for some important trajectories are reported in table 4.5 - table 4.9

Figure 4.1 : Definition of geometric variables for confiurations of zinc (II) ion - water surface.

Table 4.1 : Coordinates of water molecule (in Å)

atom	Coordinates		
	X	Y	Z
O	0.00000	0.00000	0.00000
H1	0.78830	0.00000	-0.57380
H3	-0.78830	0.00000	-0.57380

Table 4.2: Original basis set for Zn.

Function Type	α_i	c_i
1s	.79970	-0.2517637
	.17520	0.5099734
2s	.05560	0.6581327
3p	.12020	0.6130140
4p	.03510	0.4898007
5d	68.8500	0.0214335
	18.3200	0.1368916
	5.9220	0.3704352
	1.9270	0.4834232
6d	0.5528	0.3315150

Table 4.3: Modified basis set for Zn.

Function Type	α_i	c_i
s	.799700	-0.2517637
d	68.8500	0.0214335
	18.3200	0.1368916
	5.9220	0.3704352
	1.9270	0.4834232
	0.5528	0.3315150

α_i = gaussian orbital exponent

c_i = coefficient

Table 4.4: Spherical polar angles (degree) for the Zn^{2+} /water complex in different direction. (cf.figure.4.1)

Direction	ϕ	θ
1	0	0
2	0	30
3	0	60
4	0	90
5	0	150
6	0	180
7	30	30
8	30	60
9	30	90
10	30	150
11	30	180
12	60	0
13	60	30
14	60	60
15	60	90
16	60	150
17	60	180

Table 4.5 : Coordinates of the Zn^{2+} for Zn^{2+}/water adduct where $(\phi,\theta) = (0°,0°)$, Zn^{2+}-O distances (in Å) and computed interaction energies, ΔE_{SCF} , (in kcal.mol^{-1})

r	X	Y	Z	ΔE_{SCF}
1.80	0.0000	0.0000	1.8000	-80.711
1.85	0.0000	0.0000	1.8500	-82.396
1.90	0.0000	0.0000	1.9000	-82.947
2.00	0.0000	0.0000	2.0000	-81.621
2.20	0.0000	0.0000	2.2000	-73.697
4.00	0.0000	0.0000	4.0000	-14.482
6.00	0.0000	0.0000	6.0000	-1.723
7.00	0.0000	0.0000	7.0000	-0.718
9.00	0.0000	0.0000	9.0000	-0.215

Table 4.6 : Coordinates of the Zn^{2+} for Zn^{2+}/water adduct where $(\phi,\theta) = (0°,30°)$, Zn^{2+}-O distances (in Å) and computed interaction energies, ΔE_{SCF} , (in kcal.mol^{-1})

r	X	Y	Z	ΔE_{SCF}
1.60	0.8000	0.0000	1.3856	-41.095
1.80	0.9000	0.0000	1.5588	-67.895
2.00	1.0000	0.0000	1.7321	-69.925
4.00	2.0000	0.0000	3.4641	-11.178
9.00	4.5000	0.0000	7.7942	-3.887

Table 4.7 : Coordinates of the Zn^{2+} for Zn^{2+}/water adduct where $(\phi,\theta) = (0°,90°)$, Zn^{2+}-O distances (in Å) and computed interaction energies, ΔE_{SCF} , (in kcal.mol^{-1})

r	X	Y	Z	ΔE_{SCF}
1.60	1.6000	0.0000	0.0000	182.913
1.80	1.8000	0.0000	0.0000	76.034
2.00	2.0000	0.0000	0.0000	28.997
6.00	6.0000	0.0000	0.0000	8.765
9.00	9.0000	0.0000	0.0000	7.492

Table 4.8 : Coordinates of the Zn^{2+} for Zn^{2+}/water adduct where $(\phi,\theta) = (0°,150°)$, Zn^{2+}-O distances (in Å) and computed interaction energies, ΔE_{SCF} , (in kcal.mol^{-1})

r	X	Y	Z	ΔE_{SCF}
1.60	0.8000	0.0000	-1.3856	403.552
1.80	0.9000	0.0000	-1.5588	192.527
2.00	1.0000	0.0000	-1.7321	93.555
4.00	2.0000	0.0000	-3.4641	20.102
8.00	4.0000	0.0000	-6.9282	11.298
9.00	4.5000	0.0000	-7.7942	10.436

Table 4.9 : Coordinates of the Zn^{2+} for Zn^{2+}/water adduct where $(\phi,\theta) = (0°,180°)$, Zn^{2+}-O distances (in Å) and computed interaction energies, ΔE_{SCF} , (in kcal.mol^{-1})

r	X	Y	Z	ΔE_{SCF}
1 . 80	0 . 0000	0 . 0000	- 1 . 8000	77 . 556
2 . 00	0 . 0000	0 . 0000	- 2 . 0000	40 . 176
4 . 00	0 . 0000	0 . 0000	- 4 . 0000	20 . 739
8 . 00	0 . 0000	0 . 0000	- 8 . 0000	11 . 710
9 . 00	0 . 0000	0 . 0000	- 9 . 0000	10 . 786

(iii) Fitting of Pair Potential to a Functional Form

After having calculated 300 SCF-points of the energy surface in the geometries mentioned in section (i), the energy points of the differences less than 80 kcal.mole^{-1} were included in fitting using a multidimensional non-linear least-squares procedure, to a functional of the form

$$\Delta E = \sum_{i}^{3} \left[\frac{A_0 q_{Zn} q_i}{r_i} + A_{1i} r_i^{-3} + A_{2i} r_i^{-4} + A_{3i} \exp(-A_{4i} r_i) \right]$$

where r is the distance between the i-th atom of water and zinc(II) ion in Å, q_i and q_{Zn} are charges of hydrogen and oxygen of water and zinc(II) ion, respectively, obtained by Mulliken population analysis (44) in the SCF calculations of the isolated systems. These q-values were kept constant throughout the calculations. A_0, A_1,..., A_4 are the fitting parameters for the interactions between Zn^{2+} and oxygen or hydrogen of water. These parameters are shown in table 4.10 . Figure 4.2 illustrates the function obtained, showing the energy as a function of the location of a zinc(II) ion in the x-y plane around a water molecule lying in the same plane, where the uppermost part shows isoenergetic contours, the middle part shows the three-dimensional surface and the lower part shows areas of stabilization (dark) and destabilization (light).

The analytical potential function obtained was then tested for its quality by using the procedure proposed by Beveridge(45). The result was satisfactory and ensured by a plot of the SCF-energies versus the energies predicted by the function with the final parameters (figure 4.3).

Table 4.10 : Final optimized parameters for the interaction of O and H atoms of water with Zn^{2+}

Parameters	Atom	
	O	H
A_0	0.87647	0.87647
A_1	-1669.45	351.7161
A_2	1982.57	-82.2223
A_3	25672.89	-743.592
A_4	3.53504	1.7261

Figure 4.2 : Energy Surface for Zn^{2+} - water (Zn^{2+} appoaching water within its molecular plane). The uppermost part shows isoenergetic contours, the middle part the 3-dimensional surface and the lower part areas of stabilization (dark) and destabilization (light)
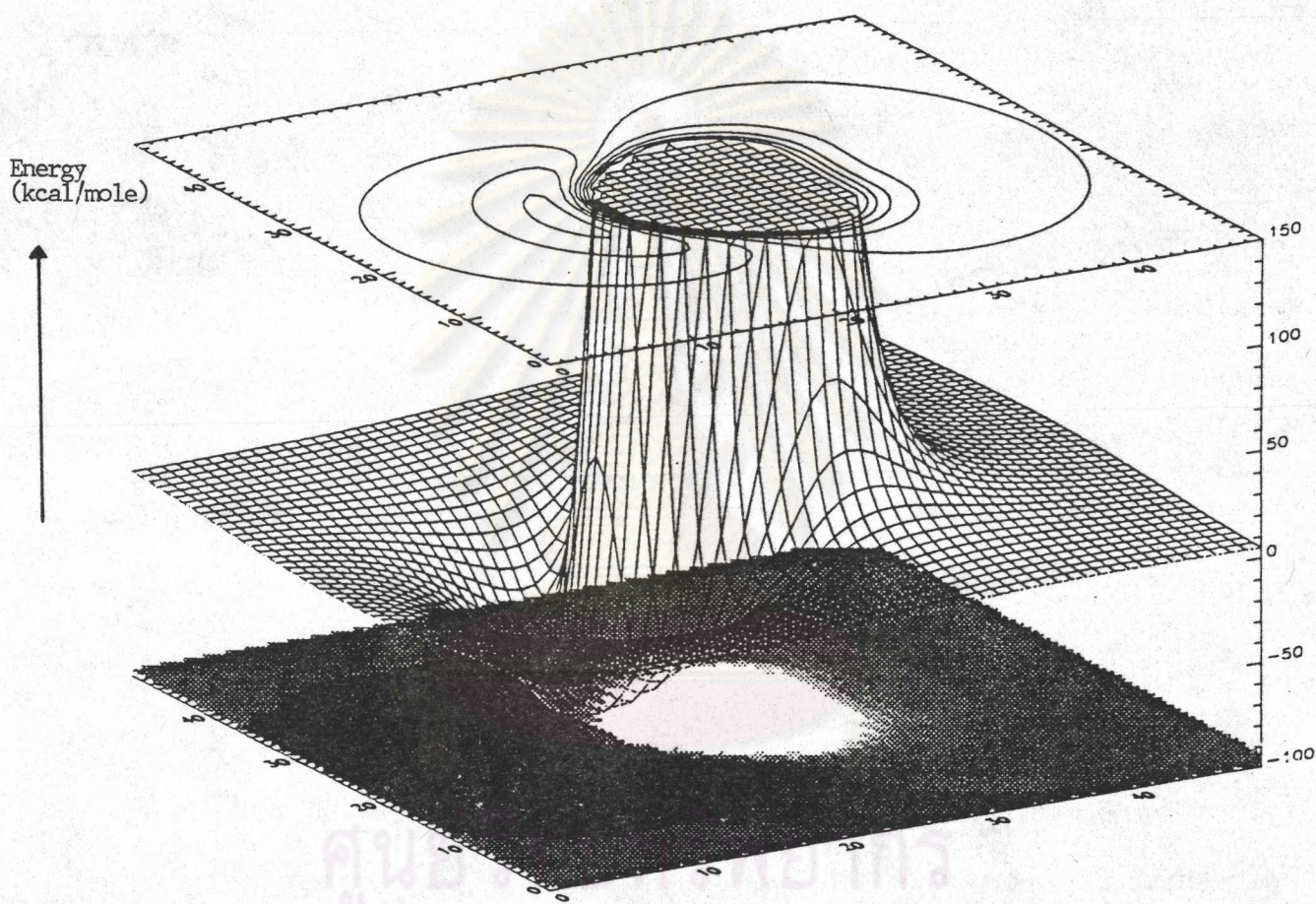
Energy
(kcal/mole)

Figure 4.3 : Scatterplot of fitted (x-axis) versus SCF calculated (y-axis) energy points of the Zn/H_2O energy surface.
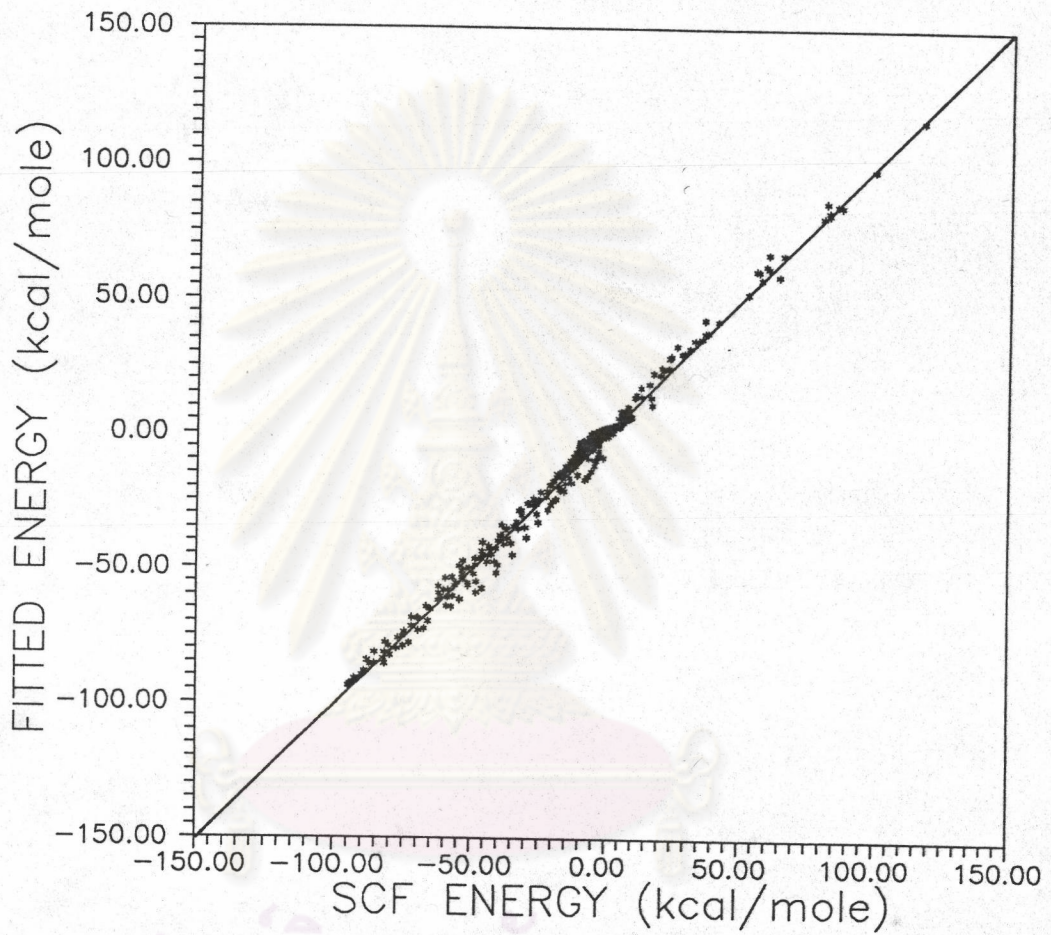
4.2 Monte Carlo Simulation with Pair Potential

A Monte Carlo simulation was carried out with this potential function, for infinitely dilute solution conditions represented by 1 Zn^{2+} and 200 water molecules in the elementary box, at a temperature of 25.0 °C and 1 atm. The Metropolis algorithm (24) was applied. For water-water interaction, the MCY (27) potential was used. The edge length L of the box was 18.143 Å , corresponding to the density of pure water, and a spherical cut-off for exponential terms of L/2 was employed. The starting configuration was obtained by random generation and in the following procedure one molecule was displaced randomly . Thus, new configurations were randomly generated, translation in all three cartesian directions and rotation about a randomly chosen angle were made. An acceptance rate of roughly 50 % for new configurations was obtained by using ranges of ± 0.1 Å for translations and ± 10 ° for rotation. After 1 million configulations, the system had reached energetic equilibrium. Heating up the system and reduction to the original temperature was performed in order to assure that the true equilibrium state had been reached. A further three million configurations were generated for the evaluation of radial distribution functions and other statistical data.

Results and Discussion

The radial distribution functions (RDF) $g_{\alpha\beta}$ for zinc-oxygen and zinc-hydrogen are presented in figure 4.4, together with the corresponding running integration numbers. In the Zn^{2+} -O RDF, the first peak is centered at 2.2 Å, 0.3 Å beyond the minimum of the SCF Zn^{2+} -water potential. Clearly separated, a second hydration sphere appears in the region between 2.8 and 5.8 Å . The average coordination number for the first hydration shell results as 8, in contrast to the value 6 expected from experimental x-ray data(46-48). This situation was similar to the result from a recent Monte Carlo simulation of Cu^{2+} hydration using conventional pair potential(49). As in case of Cu^{2+} , water-water repulsion alone is apparently not

sufficient to prevent accumulation of a larger number of water molecules in the first hydration sphere of Zn^{2+} , even at the price of the moderate enlargement of the Zn^{2+} -O distance. It was obvious that 3-body corrections had to be taken into account for further simulation work.

The second hydration shell contains about 16 water molecules. Since this value should strongly depend on the structure of the first hydration sphere, it should also not be considered too reliable.

Evaluation of a potential function taking into account 3-body effects exactly implies - besides the evaluation of the "conventional" pair potentail function - the performance of a large number of SCF calculations on $H_2O...Zn^{2+} ...H_2O$ and $H_2O...H_2O$ with wide variations of distances and angles, followed by a fitting of these data to a separate correction function. Although the first part of these efforts had already been performed (i.e. the pair potential evaluation), it seemed worthwhile to investigate the possibility of a different approach, allowing to obtain an improved ion-ligand function in one step by a less computer-intensive way. Such a function should also fulfill the requirements not to increase significantly the time needed for energy computations during statistical simulations. These considerations were finally realized in the correction algorithm outlined in the following Section 4.3
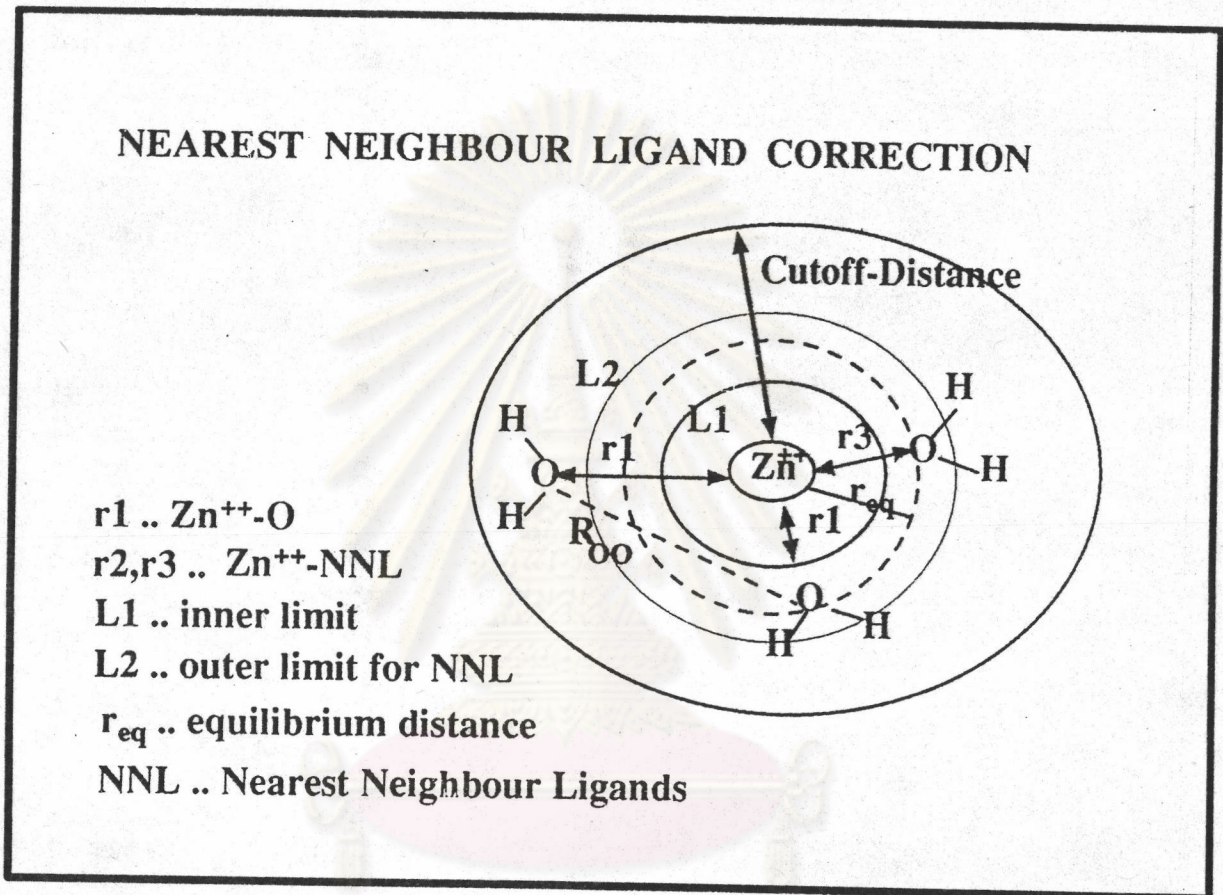
Figure 4.4 : Zn^{2+}-oxygen and Zn^{2+}-hydrogen radial distribution functions and running integration numbers obtained by pair potential.
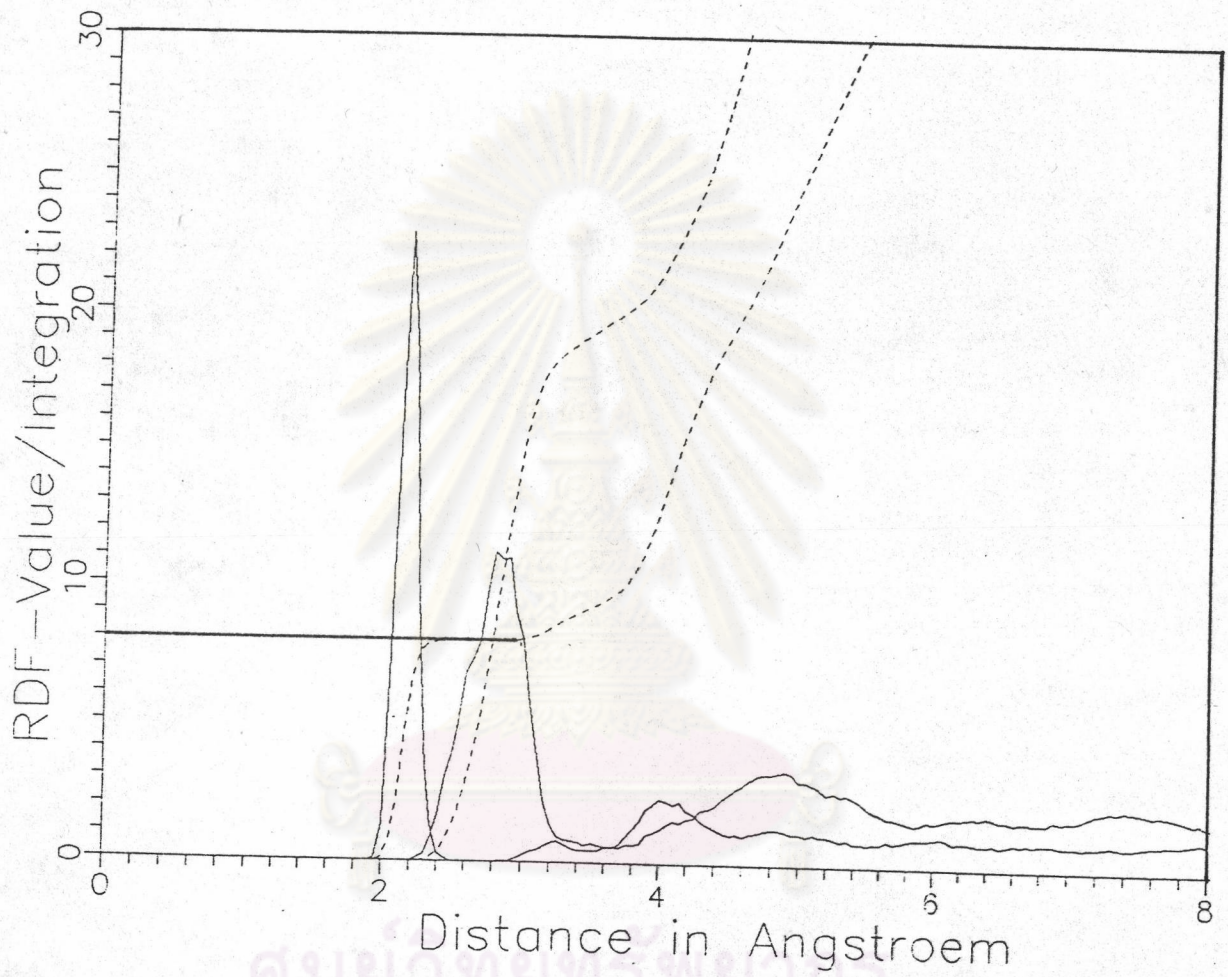
Figure 4.5 : Schematic illustration of correction method for Zn^{2+}-water potential.

4.3 Nearest Neighbour Ligand Correction (NNLC)

As the conventionally evaluated pair potential function for Zn^{2+} with H_2O leads to the wrong coordination number 8 for the ion at infinite dilution (simulated by a system of 1 Zn^{2+} and 200 water molecules), it was evident, that 3-body effects should play an important role in the ion-water interaction, as indicated by several literature data (4-6,12). Since the evaluation of a potential function taking into account exactly these 3-body effects implies the performance of a large number of SCF calculations on $H_2O..Zn^{2+}..H_2O$ and $H_2O...H_2O$ with wide variations of distances and angles, a less computer-intensive way was sought to obtain a potential function still describing most of the 3-body effects. Further, this function should also not increase significantly the time needed for energy computations during the statistical simulation. Thus a new approach which had been used successfully in the case of Cu^{2+} in water (49) was performed and tested for the case of Zn^{2+} in water. This procedure, referred to as " Nearest Neighbour Ligand Correction (NNLC) " hereafter, is based on the evaluation of an intermolecular pair potential function between an ion already bound to one water molecule, and a second water molecule at varying locations. A 3-body correction algorithm (the NNLC) contains the distance between the centres of both ligands as geometrical parameter, and is invoked in the simulation for all ligands residing already in the first hydration shell at or near the energetic minimum positions, whenever a metal-ion / ligand pair energy is evaluated.

Figure 4.5 illustrates the schematic picture of NNL correction. The large sphere indicates the area, where the correction is effective for the water molecule whose interaction with the central ion is under consideration. The two inner sphere limits mark the area, where nearest neighbour ligands are searched and included in the correction of the interaction energy.

Figure 4.6 : Evaluation of NNL corrected intermolecular potentail: characteristic radial and angular variations in SCF calculations.
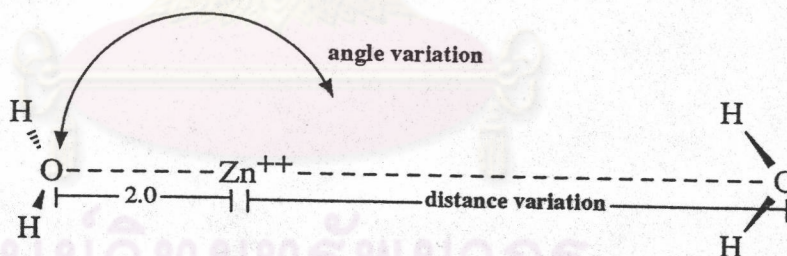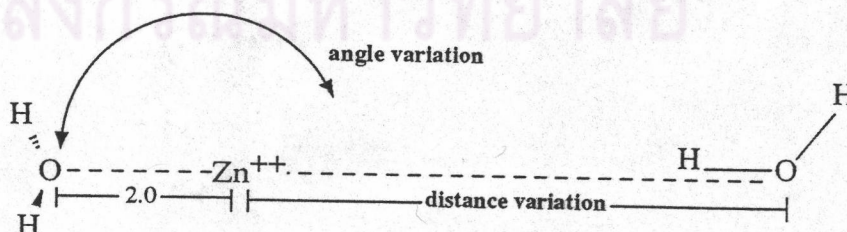
R(I.)
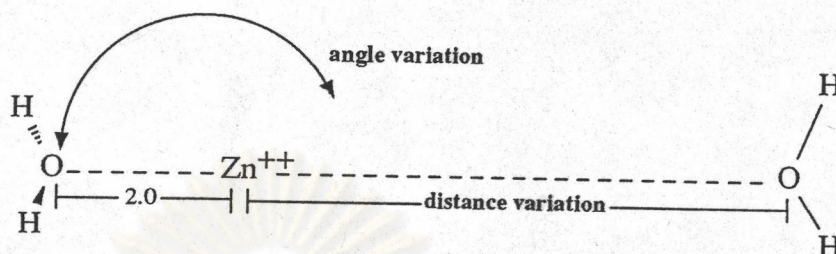
R(II.)
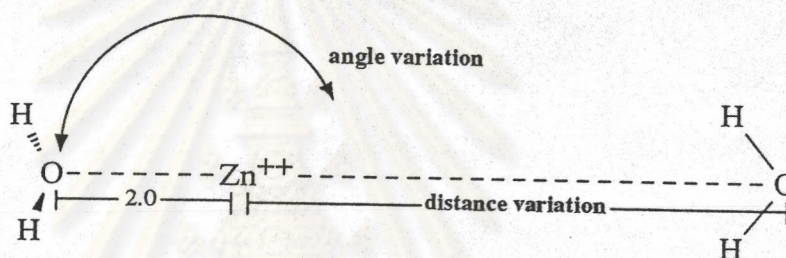
R(III.)

R(IV.)

The Angle Variation : 180 - 60 degree
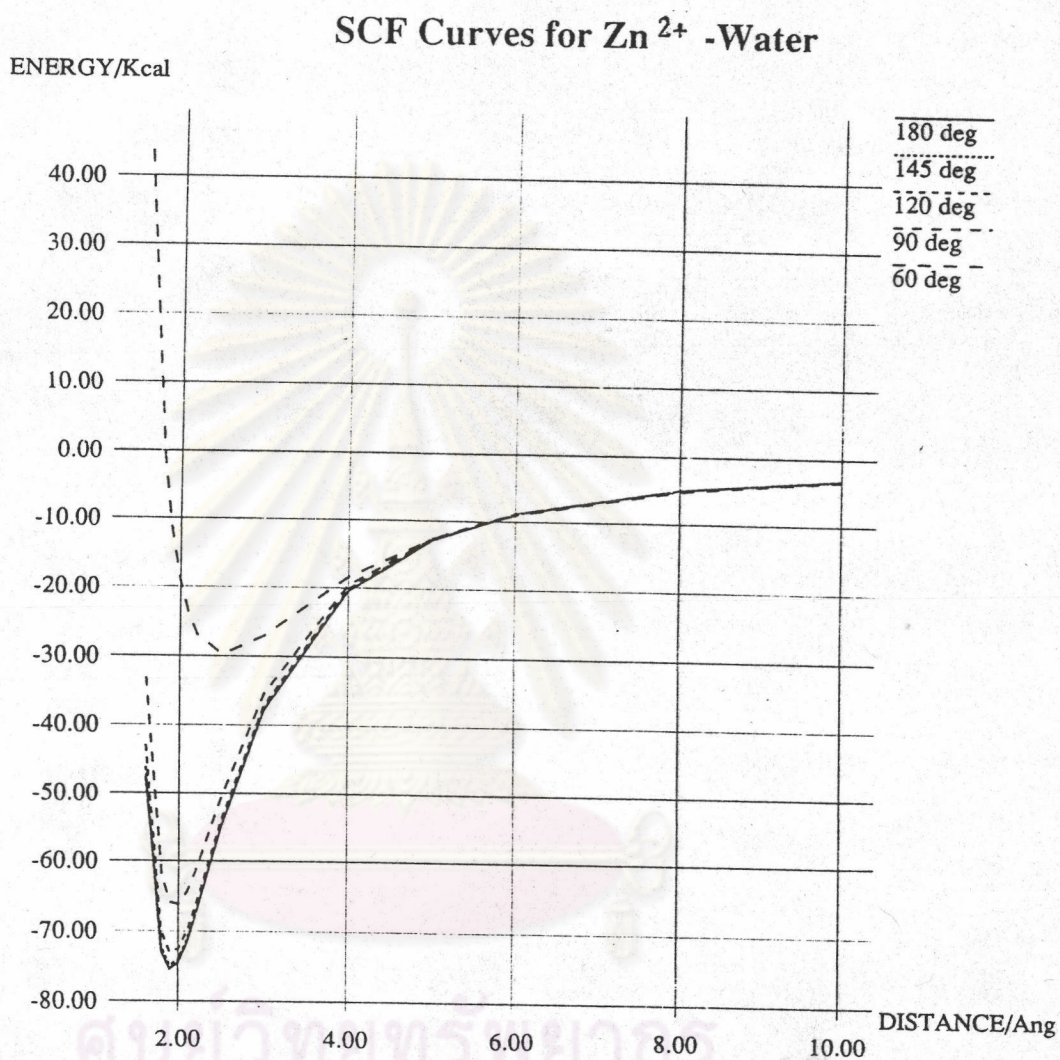
The Distance Variation : 1.6 - 10.0 Angtroem

Construction of the intermolecular potential function

Instead of SCF calculations on a Zn^{2+}/water energy surface, points were evaluated for the energy surface of a water molecule in the field of a fixed Zn^{2+}-H_2O system, where the Zn^{2+}-O distance of the fixed water molecule was 2.0 Å, corresponding to the average experimental value found for aqueous zinc solutions (46). A total of 260 points of the energy surface for system H_2O-Zn^{2+}...OH_2 have been considered, including the most characteristic directions of approach as illustrated in figure 4.6, and variations of the O/Zn/O angle from 180 to 60 degrees. The energy of these points was calculated by the ab initio SCF procedure involving a double zeta valence basis set for water (50) and an effective core potential (ECP) for oxygen (41).

The ECP for zinc was taken from ref. (43), but the valence basis set from this reference had to be modified to the same truncated outlined in the previous chapter, in order to describe ion-ligand corrections correctly also for intermediate distances, where unrealistic charge transfers would occur with the original basis set of ref. (43).

The absolute minimum found for the energy surface occurs at an O/Zn/O angle of 180°, when the second water molecule is 1.90 Å apart from Zn^{2+}, with a stabilization energy of -75.5 kcal/mole. The influence of the second water's orientation is demonstrated by the SCF energy curves in Figure 4.7, and this effect will be taken into account by the nearest-neighbour ligand correction term of the potential function.

Figure 4.7 : Influence of angular orientation of second water molecule on SCF energy curve(for dipole-oriented attractive configuration).

SCF Curves for Zn^{2+} -Water

4.4 Final Function including NNLC

Fitting of the resulting SCF interaction energies was performed to a potential function of the type :

$$\Delta E = \sum_i \left[\frac{q_{Zn} q_i}{r_i} + A_{1i} r_i^{-3} + A_{2i} r_i^{-4} + A_{3i} \exp(A_{4i} r_i) \right] + NNLC$$

$$NNLC = \sum_N (CL - r)^2 A_5 \exp(A_6 R_{OO})$$

r.....Zn^{2+} - O distance

i.....atoms in H_2O

N.....number of neighbour ligands within selected spherical area

R_{OO} ....O-O distance of water molecules

NNLC....nearest neighbour ligand correction

CL....Cut-off Limit for NNLC

The first part of this function is identical to the form of the conventional pair potential previously used for Zn^{2+}-H_2O. The second term (NNLC) corresponds to a "Nearest Neighbour Ligand Correction" and is related to the distance of the oxygens of other water molecule near Zn^{2+} and the moved water molecule. N is the number of these "nearest neighbour ligands" determined by a search algorithm in the simulation which evaluates number and position of other water molecules fulfilling the condition 2.0 Å $< r_{Zn-O} < 2.2$ Å. These narrow limits around the peak of the first hydration shell obtained by the pair potential have to be set, as the fitted function will be applicable only when the second water molecule is located at, or near the distance it had in the

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$$\Delta E = \sum_i \left[\frac{q_{Zn}q_i}{r_i} + A_{1i} r_i^{-3} + A_{2i} r_i^{-4} + A_{3i} \exp(A_{4i}r_i) \right] + NNLC$$

$$NNLC = \sum_N (CL - r)^2 A_5 \exp(A_6 R_{OO})$$

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SCF calculations.

A cutoff limit CL has also been introduced into the function, avoiding calculation of correction terms for larger Zn^{2+}-O distances, where also 3-body corrections become negligible. This limit was varied during the fitting procedure from 2.5 to 6 Å, and the best fit was obtained for CL = 4 Å . The implementation by the form $(CL - r)^2$ ensures that the function will be steady at the point of cutoff.

In Table 4.11, the final parameters of the fitting procedure are listed. Figure 4.8 shows the scatterplot of fitted versus SCF calculated energy data, showing the points closed to the theoretical 45° line, especially in the important attractive region.

Table 4.11: Final parameters of the NNL corrected intermolecular potential function for Zn^{2+} / H_2O

Atom	q_i (a.u.)	A_1 ($Å^3$kcal/mole)	A_2 ($Å^4$kcal/mole)	A_3 (kcal/mole)	A_4 ($Å^{-1}$)
O	-0.742	64.60	-848.465	911007.50	-4.0028
H	0.371	-6.7873	-48.494	381.480	-1.8452

For NNLC:

A_5 (kcal/mole)	A_6 ($Å^{-1}$)
827.7356	-2.0474

The effect of the NNL correction term as a function of Zn^{2+}...O and O...O distances is visualized in figure 4.9 . It shows a rather steep barrier near the ion without significant effects for the outer surroundings.
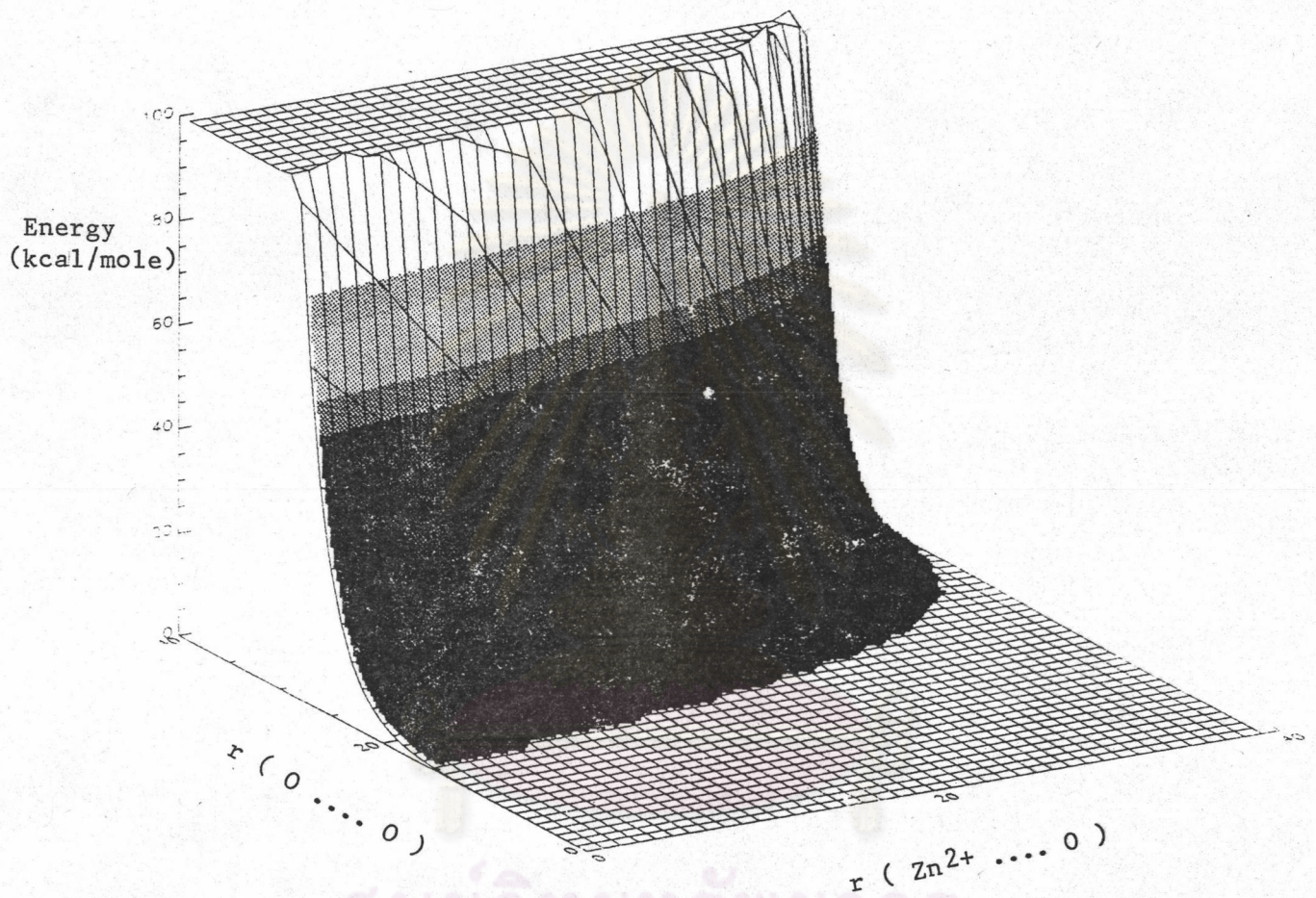
Figure 4.8 : Scatterplot of fitted (x-axis) versus SCF calculated (y-axis) energy points of the Zn^{2+}-H_2O / H_2O energy surface.
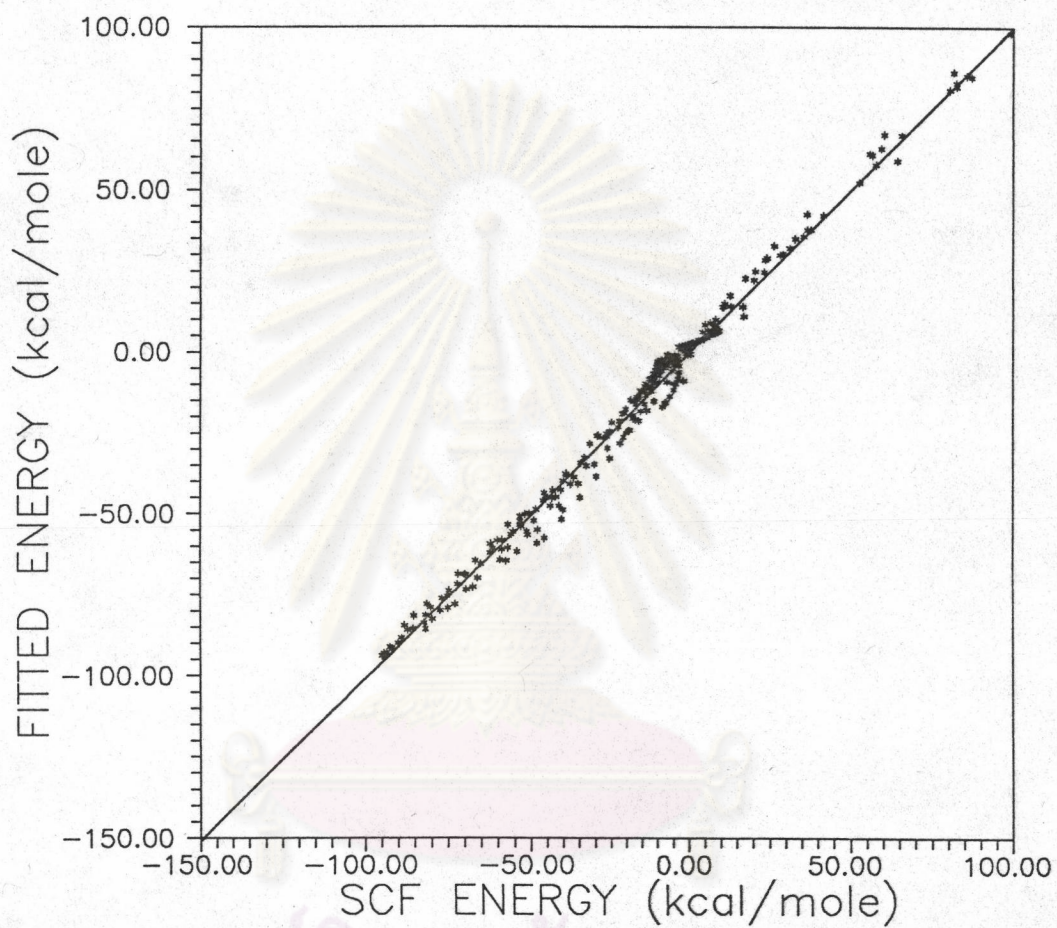
Figure 4.9 : Effect of the NNL correction term as a function of Zn^{2+}...O and O...O (ligand-ligand) distance.

4.5 Monte Carlo Simulation of Zn^{2+} in Water with NNL Corrected Function

4.5.1 Methodical Investigations

The system chosen for testing the corrected intermolecular function for Zn^{2+}/H_2O in MC simulations consisted of 1 Zn^{2+} and 200 water molecules, at the density of pure water. This leads to a box length of 18.143 Å, and for exponential terms a cutoff of half of this box length was applied. Periodic boundary conditions were assumed, the simulation temperature was 25° C and the Metropolis sampling algorithm was used. For water-water interactions, the MCY potential (27) was employed.

The previous simulation with the uncorrected pair potential function for Zn^{2+}/H_2O had led to a single sharp peak for the first coordination sphere, whose integration yielded a coordination number of 8.0 .

With the corrected function, a series of simulations was performed with varying conditions, in order to obtain also some more methodical informations about applicability and limitations of the nearest-neighbour ligand correction method.

Variations of the correction's cutoff limit CL as well as the range, within which neighbour ligands are considered, have been investigated first. They showed, that the results for structural data are sensitive to these parameters, especially to the range. If a wrong or too wide range is selected, RDF functions split up and coordination numbers can hardly been determined. The choice of CL = 4.0 Å, where the best function fitting characteristics are obtained, and restriction of the selection range for neighbour ligands to the narrow area of 2.0 to 2.2 Å, closely corresponding to the conditions of the SCF calculations seem, to be justified therefore not only theoretically, but also by practical results.

A second problem, which did not show up in the simulation of Cu^{2+} in water, was the number of nearest neighours to be considered. In the case of Cu^{2+} in water,

the number of eligible ligands never exceeded 1 in average. For Zn^{2+}, less strongly interacting with water and having a slightly larger equilibrium distance to oxygen, equilibrium was not yet established even after a considerable higher number of configurations than in the case of Cu^{2+}. During the process, up to 5 eligible ligands could be found within the limits. It seemed useful therefore, to investigate whether a limitation of the number N for the NNLC correction term should be applied, also because the error of multiple double-counting of ligand-ligand repulsion as outlined in (49) could become more significant, when several nearest-neighbour ligands are involved.

In the first simulation, starting from a random configuration, no such limitation was made, leading to an average of 3.5 ligands considered in the NNL correction after 1 million configurations. Sampling of 500000 further configurations was performed. A triple splitting of the first peak in the Zn-O radial distribution function (RDF) was observed, which smoothed only slightly after adding another 500000 configurations to the sampling. Even then, the system had not reached equilibrium. During the simulations, some of the water molecules in the first shell were scarcely moved, showing that too strong restrictions had been imposed by the immediate and full application of the correction algorithm.

In a second simulation, starting from the previously obtained configuration, the maximum number of eligible ligands was set to 2 for the correction, taking those two with the shortest distance to the one water molecule under consideration in the potential energy evaluation. The resulting Zn^{2+}-O RDF after 1 million configurations (Figure 4.10a) now displayed a dominating first peak at 2.05 Å, whose integration up to the first minimum yields 6 water molecules. A second sharp peak is closely attached to it, containing one further water molecule. The corresponding Zn^{2+}-H RDF shows by its main peak that the water molecules of the first peak are dipole-vector oriented, and its integration line displays a slight turn at the value 12, and at the end of the peak reaches the value 14, corresponding to 6 and 7 water molecules, respectively. This had to be regarded also as preliminary result, as energy was still decreasing after the 1 million configurations evaluated.

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Figure 4.10 : Radial distribution functions (RDF) and their integration from Monte Carlo testruns for Zn^{2+} in water: (a) restricted to correction for 2 nearest-neighbour ligands. (b) restricted to correction for 1 nearest-neighbour ligand.
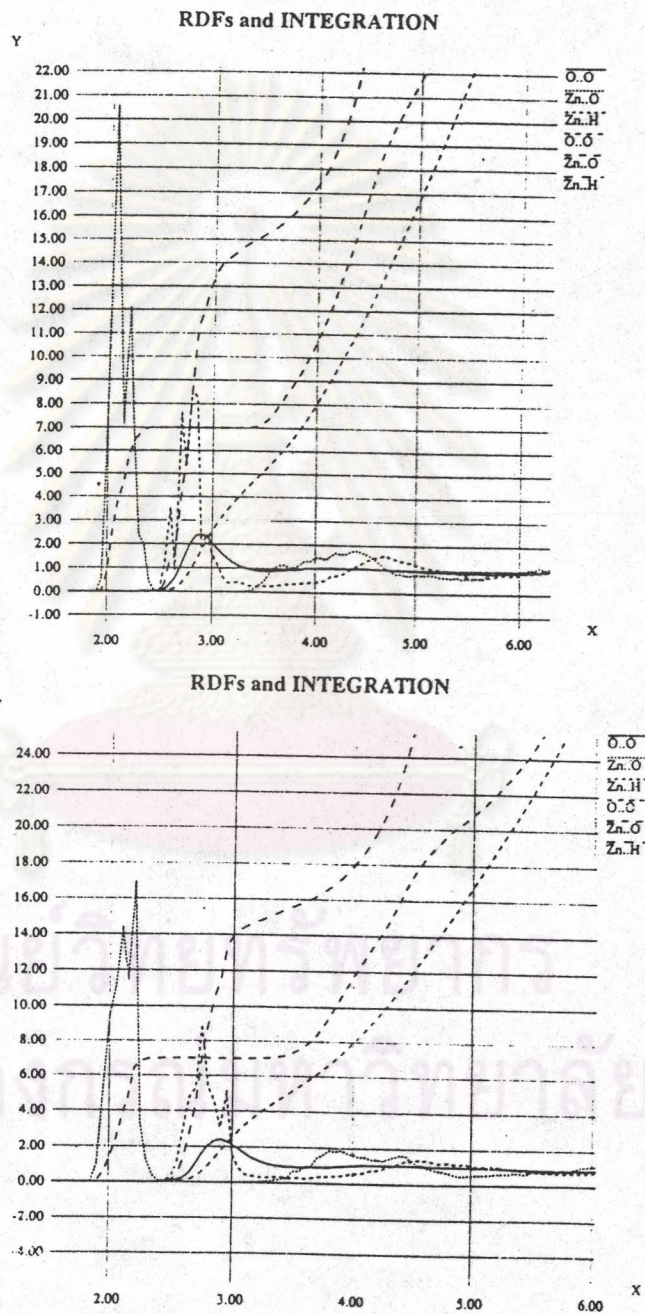
In a third run, the number of nearest neighbour ligands considered for the correction was restricted to only the one very nearest ligand, i.e. the one with the smallest O..O distance among all neighbours found within the 2.0 - 2.2 Å sphere around Zn^{2+}. Considerable changes in the Zn^{2+}-O RDF are observed (Figure 4.10b). The first hydration shell is now represented by a peak with minor splitting, showing the relative maximum at 2.2 Å, but centered around 2.1 Å far from the ion. Integration over the whole peak yields 7 water molecules up to 2.5 Å, which is identical to the integration value obtained at the same limit while considering a maximum of 2 neighbours. In this simulation, energy had reached equilibrium more readily and fluctuated around a constant value for the last 30% of the 1 million configurations performed.

Finally, it had to be examined, what would be the effect of applying the maximal correction -i.e. with consideration of all eligible neighbours- to this state of equilibrium.

Starting thus from the configuration obtained with 1- neighbour-correction, a simulation was carried out without limitation towards the number neighbour ligands included in the correction. Equilibrium in energy was reached after only 200,000 steps but due to strong fluctuations, another 2 million configurations were taken for the final sampling and evaluation.

For comparison, the testrun which had included all neighbour ligands from the beginning was restarted, and the further development of nearest-neighbour ligand number, RDF's and energy showed, that it would also converge to the same result, but after more than 5 million configurations,showing that the most appropriate and economic form of invoking the NNLC algorithm is a stepwise addition of the correction, obtaining first a good starting configuration by consideration of 1 neighbour only, and then applying the algorithm without restriction to the eligible

ligands' number.

It seemed also interesting, to compare the numbers of relevant neighbour ligands for the 3 simulation runs and the associated NNL energy correction values. These data are given below, where N_{max} denotes the limitation of considered neighbour ligands, n_{NNL} the average number of neighbours actually found within the boundaries, and E_{NNLC} the associated correction energy in kcal/mole :

N_{max}	n_{NNL}	E_{NNLC}	$n_{conf.}$
1	4.5	5.4	$1.5 \cdot 10^6$
2	3.4	11.1	$1.5 \cdot 10^6$
unlimited*	1.8	10.9	2.10^6

* starting from configuration obtained with 1-neighbour-correction

Full application of the correction algorithms strongly reduces the number of water molecules "allowed" to stay within the selected boundaries, and leads to a correction energy 80% higher than that for the Cu^{2+}/H_2O system under otherwise identical conditions.

It should be mentioned at this point that despite of the consideration of other ligands for the numerical evaluation of the correction energy term, the NNL correction supplies just a modification of a pair potential energy term and should not be mistaken or treated thus as a true 3-, 4- or n-body (according to the number of considered neighbour ligands) correction term. In the simulation, the evaluated ΔE has to be treated, therefore, strictly as in the case of an unmodified pair potential.

4.5.2 Results of final MC simulation

The resulting RDFs of the final run are shown in Figure 4.11 . The picture is quite similar to that obtained in the preliminary run with a maximum of 2 neighbours considered. The O-O RDF is almost identical to that of pure water.

Figure 4.11 : Radial distribution function (RDF) and their integration from final Monte Carlo simulation for Zn^{2+} in water.
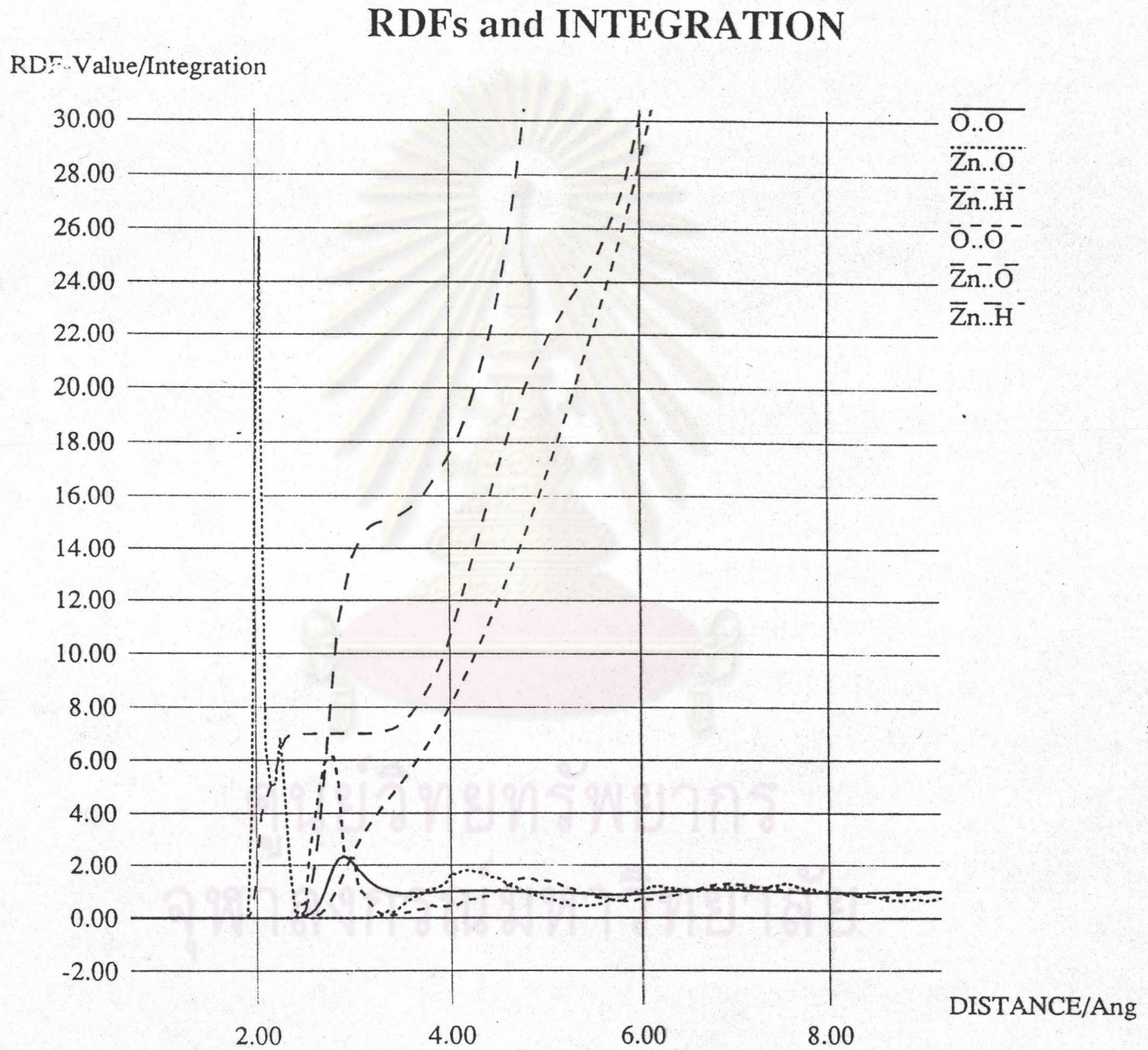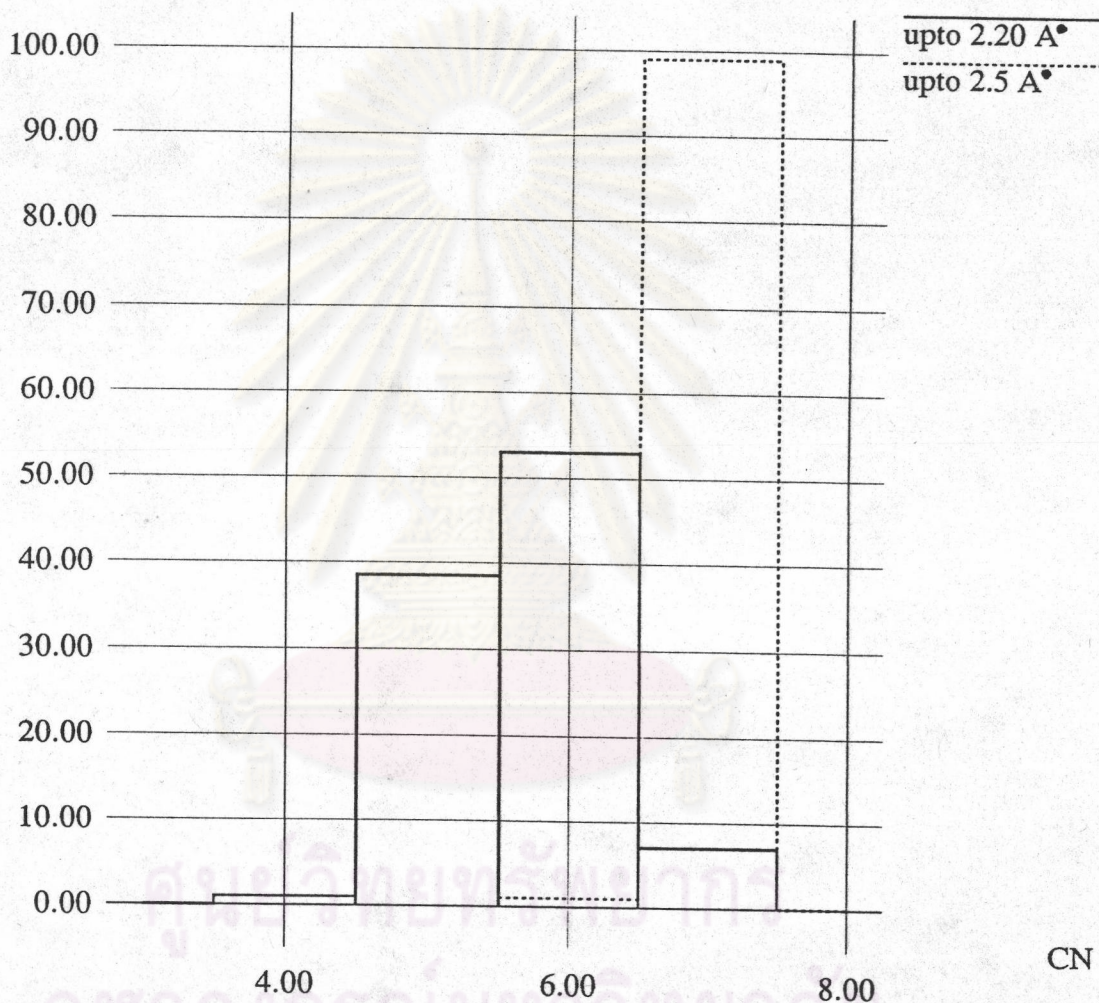

RDFs and INTEGRATION

Figure 4.12 : Distribution of water coordination numbers in 1st hydration shells of Zn^{2+} , for 2 different limits (cf.text).

Coordination Number Distribution Zinc(II) ion in Water

Figure 4.12 : Distribution of water coordination numbers in 1st hydration shells of Zn^{2+} , for 2 different limits (cf.text).

Coordination Number Distribution Zinc(II) ion in Water

Percent

upto 2.20 A°
upto 2.5 A°
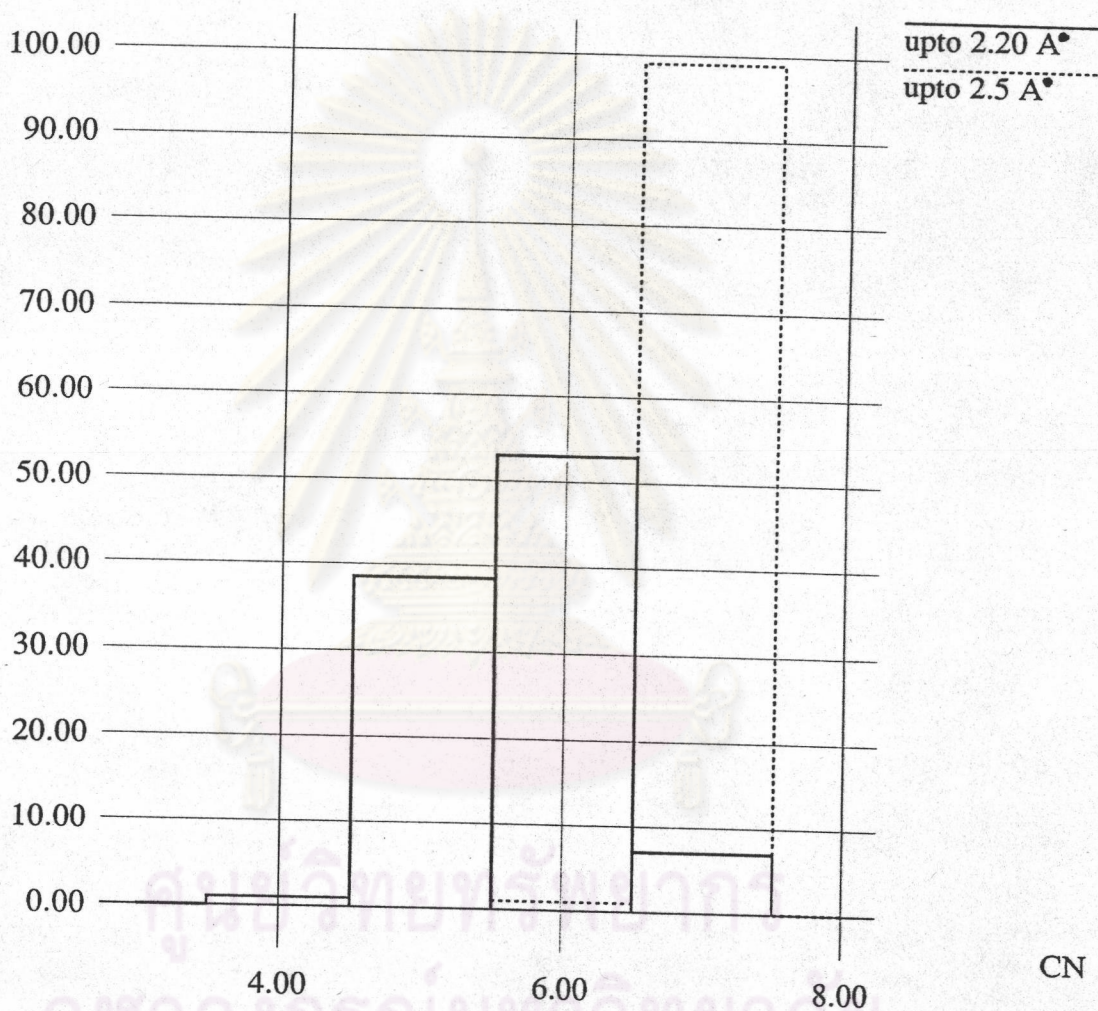
The average hydration energy for Zn^{2+} resulting from this final simulation is 848 kcal/mole, 32 kcal less than obtained for Cu^{2+}, where 100 % of the solvates are hexaquo-ions with waters of the first shell centered 1.95 Å away from the ion, i.e. 0.1 Å closer than in the case of Zn^{2+} (49).