CHAPTER III

ANALYTICAL PAIR POTENTIAL FUNCTION

The Monte Carlo (MC) and molecular dynamics (MD) simulation techniques have been well established and are used by numerous scientists at present. The most important factor, the results of such calculations depend undoubtedly on the potential function in used. At the same time, it is necessary to evaluate energy and force values as rapidly as possible in the course of the simulation, due to economy of CPU time.

Potential functions which have been used so far are obtained from two sources , namely , non-empirical and empirical methods. The former type is usually based on molecular orbital calculations. Numerous non-empirical functions have been presented so far , for example the MCY (Matsuoka-Clementi-Yoshimine) water dimer pair potential (41) which was frequently used for the simulation of liquid water and aqueous solutions (5-7,9-12,14,16-17). With respect to the water pair potential, the functions were parametrized to reproduce quantum mechanical results accounted for water, the central force potential including consideration of vibrational motion (20,42) has applied succesfully as well (41,43,61,65). For the latter one, the first empirical potential for water dimer was presented by Rowlinson (44), and has afterwards been modified by Raman and Stillinger (45) and named ST2 potential. One of merits of using empirical potentials is the feasibility of incorporating higher order interactions into the effective pair potential (46). Since this type of potential function is determined to reflect experimental properties, data obtained from simulation should be in good agreement with those from experiment. However, it was found that this functions, sometimes, produce discrepant structural results for electrolyte solutions (47).

Recently, potential function derived through ab initio MO calculations has been become prevalent because it is easy to determine without considering experimental values such as internal energy, vibrational modes, or second virial coefficients. Accordingly, the stabilization interaction energies for many different configurations of adduct are calculated, as only sum of the pair potentials are taken into account, but not higher order interactions, in usual simulations. The function has been adopted and disposable parameters for suitable function has been obtained with least square concept. However, many problems of non-empirical potentials remain ,e.g. the selection of basis set, the neglect of dispersion forces and the functional form of the potential.

In this chapter, the lithium ion/ammonia potential function will be constructed. Details of the calculation will be briefly presented, the quality of the function will also be tested using an effective procedure (56).

Construction of Lithium Ion/Ammonia Potential Function

3.1 Detail of Calculations

To obtain the potential function by means of quantum chemical calculations, the four consecutive steps are required : (i) selection of representative geometries of pairs : (ii) performance the SCF calculations : (iii) fitting of computed interaction energies to a functional form and (iv) testing the function.

3.1.1 Selection of Geometries

To select adduct geometries, two principal ways, which were generaly used up to now have been presented. The first one is to use a tridimensional grid (with a pass of ⩽ 1 atomic units) system defined by a combination of certain numbers of orientation types and distances surrounding the molecule (48). In this way, a reasonable assurance of having scanned the potential hypersurface with inclusion of all the minima is obtained and the potential surface can be clearly characterized. A problem arose, however, from the number of resultant geometries becoming rapidly too large and form absolute adduct configurations not occuring in the actual simulations of the condensed phase.

Another alternative way is to use adduct geometries taken by random choice (49). The curve fitting procedure is started with an initial set of geometries, and the procedure will be repeated, adding newly sampled geometries until the standard deviation of the " trial function " will have reached a quality for which the predictive ability of the potential function converges. Since adduct geometries generated randomly do not often produce important configurations from the viewpoint of energy, especially in polar molecular systems, a modified method has been employed in order to avoid this problem.

In this work lithium ion was placed at numerous positions within the space around ammonia for fifteen directions as the spherical polar angles shown in figure 3.1. The selected interaction trajectories are given in table 3.2. The relevant positions of lithium ion were generated as follows and summarized in tables 3.5-3.19.

First , ion was moved along the z-axis , then the three trajectories corresponding to (θ, ϕ) values of $(0^{\circ}, 90^{\circ})$, $(30^{\circ}, 60^{\circ})$ and $(30^{\circ}, 90^{\circ})$ were chosen. Finally the potential function was determined by including $0^{\circ} \leqslant \phi \leqslant 180^{\circ}$ and $0^{\circ} \leqslant \theta \leqslant 60^{\circ}$ in steps of 30°. For all directions $r_{Li(I)-N}$ was varied from 1 to 10 Å.

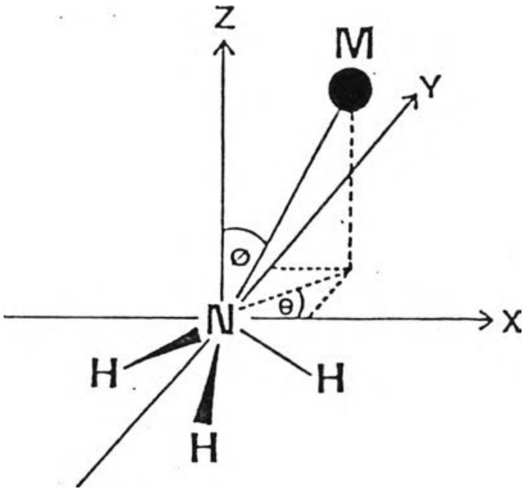

Figure 3.1 Definition of geometric variables for configurations of lithium ion-ammonia surface.

3.1.2 Performance the SCF Calculations

3.1.2.1 Ammonia Monomer

The total energy (electronic energy plus nuclear repulsion energy) of ammonia monomer has been examined by means of ab-initio molecular orbital calculations at different levels of basis set , and compared with literature data (table 3.4). The HONDO program was used throughout the calculations. The geometry of ammonia was taken from experimental data (50) with N-H bond length = 1.0124 Å and ∢HNH angle = 106.7° . The fixed cartesian coordinates for ammonia molecule are given in table 3.1. Ammonia molecules are easily invert even in the gas phase. However , the inversion period of the ammonia molecule is about 21 ps which is quite long. Therefore , the function obtained from this data would be reliable not only for Monte Carlo but also for the normal molecular dynamics simulations by neglecting this mode of vibration. As shown in table 3.3 the GLO basis set gives rather high total energy for ammonia monomer, the dipole moment value is, however, quite acceptable. The STO-3G basis set applied in this work gives a similar dipole moment, while it still displays a considerably high total energy compared with other data. The calculation with DZP was found to give a much improved total energy, but not a better dipole moment. For reasons of better polarization feasibility, however, this basis set was selected for further calculations. This type of basis set was discussed and recommened in the litterlature reviews (63).

3.1.2.2 Lithium ion/Ammmonia Adduct

SCF-LCAO calculations with the DZP basis set , as listed in table 3.4 , have been performed for several lithium ion/-ammonia configurations selected in (3.1.1). The lithium ion/ammonia stabilization energy,ΔE_{scf}in kcal.mol^{-1} is calculated as

$$\Delta E_{SCF}(\text{kcal.mol}^{-1}) = (E - E_{Li(I)} - E_{NH3}) \times 627.5 \ ,$$

where E is the total energy of the supermolecule and $E_{Li(I)}$ and E_{NH3} are those of lithium ion and ammonia at infinite seperation. The ab-initio stabilization energies are also reported in table 3.5 - table 3.19.

Table 3.1 Coordinates of ammonia molecule (in atomic units).

atom	Coordinates X	 Y	 Z
N	0.00000	0.00000	0.00000
H1	1.77214	0.00000	-0.72089
H2	-0.88607	-1.53472	-0.72089
H3	-0.88607	1.53472	-0.72089

Table 3.2 Spherical polar angles (degree) for the lithium ion in different directions.

Direction	θ	ø
1	0	0
2	0	30
3	0	60
4	0	90
5	0	120
6	0	150
7	0	180
8	30	60
9	30	90
10	30	120
11	60	30
12	60	60
13	60	90
14	60	120
15	60	150

Table 3.3 Comparison of total energies and dipole moments of ammonia monomer.

basis set	total energy	μ	ref.
4-31 G	-56.10269	2.28	51
6-31 G	-56.18404	1.93	52
Ext (a)	-56.16223	2.15	53
Ext (b)	-56.14545	2.16	53
Ext (c)	-56.16355	1.52	53
Exptl..	-	1.47	54
this work			
GLO	-47.72130	1.82	
STO-3G	-55.45408	1.79	
DZV	-56.17558	2.35	
DZP	-56.20907	1.89	

units are given in a.u. for total energies and Debye for dipole moments. (a) uncontracted, (b) contracted, (c) with polarization functions.

Table 3.4 Orbital exponents for the DZP basis sets of atoms.

	N	H	Li(I)
1s	5909.000000	19.238400	921.300000
2s	887.500000	2.898720	138.700000
3s	204.700000	0.653472	31.940000
4s	59.840000	0.163064	9.353000
5s	20.000000	-	3.158000
6s	7.193000	-	1.157000
7s	2.686000	-	0.444600
8s	7.193000	-	0.444600
9s	0.700000	-	0.076660
10s	0.213300	-	0.028640
1p	26.790000	1.000000	1.488000
2p	5.956000	-	0.266700
3p	1.707000	-	0.072010
4p	0.531400	-	0.023700
5p	0.165400	-	-
1d	0.800000	-	-

Table 3.5 Coordinates of the lithium ion for Lithium ion/ammonia adduct where (θ,ϕ) = (0^{o},0^{o}) , Li(I)-N distances (in Å) and computed interaction energies,Δ E_{SCF} , (in kcal.mol^{-1}).

r	X	Y	Z	ΔE_{SCF}
1.40	0.0000	0.0000	2.6457	21.8
1.60	0.0000	0.0000	3.0236	-20.3
1.90	0.0000	0.0000	3.5906	-39.5
1.96	0.0000	0.0000	3.7039	-40.3
1.98	0.0000	0.0000	3.7417	-40.5
1.99	0.0000	0.0000	3.7606	-40.5
2.00	0.0000	0.0000	3.7795	-40.5
2.10	0.0000	0.0000	3.9685	-40.3
2.50	0.0000	0.0000	4.7244	-33.7
3.00	0.0000	0.0000	5.6693	-23.8
5.00	0.0000	0.0000	9.4488	- 7.1
7.00	0.0000	0.0000	13.2283	- 3.3
9.00	0.0000	0.0000	17.0079	- 1.9

Table 3.6 Coordinates of the lithium ion for lithium ion/ammonia adduct where (θ , ϕ) = (0°,30°) , Li(I)-N distances (in Å) and computed interaction energies, ΔE_{SCF} , (in kcal.mol^{-1}).

r	X	Y	Z	ΔE_{SCF}
1.50	1.4173	0.0000	2.4549	- 1.9
1.80	1.7008	0.0000	2.9459	-29.8
1.99	1.8803	0.0000	3.2568	-34.0
2.00	1.8897	0.0000	3.2732	-34.1
2.10	1.9843	0.0000	3.4368	-34.1
2.20	2.0787	0.0000	3.6005	-33.3
3.00	2.8346	0.0000	4.9098	-20.2
5.00	4.7241	0.0000	8.1829	- 5.9
7.00	6.6142	0.0000	11.4561	- 2.7
9.00	8.5039	0.0000	14.7292	- 1.6

Table 3.7 Coordinates of the lithium ion for lithium ion/ammonia adduct where (θ,ϕ) = (0^{o},60^{o}) , Li(I)-N distances (in Å) and computed interaction energies, ΔE_{SCF} , (in kcal.mol^{-1}).

r	X	Y	Z	ΔE_{SCF}
2.00	3.2731	0.0000	1.8898	-13.1
2.60	4.2551	0.0000	2.4567	-13.9
3.00	4.9098	0.0000	2.8346	-10.5
5.00	8.1829	0.0000	4.7241	- 3.0
7.00	11.4561	0.0000	6.6142	- 1.4

Table 3.8 Coordinates of the lithium ion for lithium ion/ammonia adduct where (θ , ϕ) = (0^{o},90^{o}) , Li(I)-N distances (in Å) and computed interaction energies, ΔE_{SCF} , (in kcal.mol^{-1}).

r	X	Y	Z	ΔE_{SCF}
3.00	5.6693	0.0000	0.0000	0.5
3.60	6.8032	0.0000	0.0000	0.4
3.80	7.1811	0.0000	0.0000	0.4
4.00	7.5591	0.0000	0.0000	0.5
6.00	11.3386	0.0000	0.0000	0.3
9.00	17.0079	0.0000	0.0000	0.1

Table 3.9 Coordinates of the lithium ion for lithium ion/ammonia adduct where (θ , ϕ) = (0^{o},120^{o}) , Li(I)-N distances (in Å) and computed interaction energies, ΔE_{SCF} , (in $kcal.mol^{-1}$).

r	X	Y	Z	ΔE_{SCF}
3.00	4.9098	0.0000	- 2.8346	5.2
5.00	8.1829	0.0000	- 4.7241	2.2
7.00	11.4561	0.0000	- 6.1642	1.3
9.50	15.5475	0.0000	- 8.9764	0.7

Table 3.10 Coordinates of the lithium ion for lithium ion/ammonia adduct where (θ , ϕ) = (0^{o},150^{o}), Li(I)-N distances (in Å) and computed interaction energies, ΔE_{SCF}, (in $kcal.mol^{-1}$).

r	X	Y	Z	ΔE_{SCF}
3.00	2.8346	0.0000	- 4.9098	2.6
5.00	4.7241	0.0000	- 8.1829	2.9
7.00	6.6142	0.0000	-11.4561	- 2.7
9.50	8.9764	0.0000	-15.5475	1.1

Table 3.11 Coordinates of the lithium ion for lithium ion/ammonia adduct where (θ, ϕ) = (0^o,180^o), Li(I)-N distances (in Å) and computed interaction energies, ΔE_{SCF}, (in $kcal.mol^{-1}$).

r	X	Y	Z	ΔE_{SCF}
2.00	0.0000	0.0000	- 3.7795	8.3
2.50	0.0000	0.0000	- 4.7244	0.1
3.00	0.0000	0.0000	- 5.6693	0.8
4.00	0.0000	0.0000	- 7.5591	3.0
5.00	0.0000	0.0000	- 9.4488	2.9
7.00	0.0000	0.0000	-13.2283	2.0
9.00	0.0000	0.0000	-17.0079	1.3

Table 3.12 Coordinates of the lithium ion for lithium ion/ammonia adduct where (θ , ϕ) = (30^o,60^o), Li(I)-N distances (in Å) and computed interaction energies, ΔE_{SCF}, (in $kcal.mol^{-1}$).

r	X	Y	Z	ΔE_{SCF}
2.00	2.8346	0.0000	1.8898	-16.4
3.00	4.2519	0.0000	2.8346	-10.9
5.00	7.0866	0.0000	4.7244	- 3.0
7.00	9.9213	0.0000	6.6142	- 1.4
8.00	11.3386	0.0000	7.5591	- 1.1

Table 3.13 Coordinates of the lithium ion for lithium ion/ammonia adduct where (θ,ϕ) = (30°,90°), Li(I)-N distances (in Å) and computed interaction energies, ΔE_{SCF}, (in kcal.mol^{-1}).

r	X	Y	Z	ΔE_{SCF}
2.40	3.9278	2.2677	0.0000	1.0
3.00	4.9098	2.8346	0.0000	- 0.7
3.40	5.5644	3.2126	0.0000	- 0.3
5.00	8.1829	4.7244	0.0000	0.2
7.00	11.4561	6.6142	0.0000	0.1
9.00	14.7292	8.5039	0.0000	0.1

Table 3.14 Coordinates of the lithium ion for lithium ion/ammonia adduct where (θ , ϕ) = (30°,120°), Li(I)-N distances(in Å) and computed interaction energies, ΔE_{SCF}, (in kcal.mol^{-1}).

r	X	Y	Z	ΔE_{SCF}
3.00	4.2519	2.4549	- 2.8346	4.0
4.00	5.6693	3.2732	- 3.7799	3.1
5.00	7.0866	4.0915	- 4.7244	2.3
6.00	8.5039	4.9098	- 5.6693	1.7
7.00	9.9213	5.7280	- 6.6142	1.3
9.00	12.7559	7.36462	- 8.5039	0.6

Table 3.15 Coordinates of the lithium ion for lithium ion/ammonia adduct where (θ , ϕ) = (60°,30°), Li(I)-N distances(in Å) and computed interaction energies, ΔE_{SCF}, (in $kcal.mol^{-1}$).

r	X	Y	Z	ΔE_{SCF}
1.60	0.7559	1.3093	2.6185	-15.1
2.00	0.9449	1.6366	3.2732	-34.6
2.40	1.1339	1.9639	3.9278	-30.6
3.00	1.4173	2.4549	4.9098	-20.3
5.00	2.3622	4.0915	8.1829	- 6.0
7.00	3.3071	5.7280	11.4561	- 2.7
9.00	4.2519	7.3646	14.7292	- 1.6

Table 3.16 Coordinates of the lithium ion for lithium ion/ammonia adduct where (θ, ϕ) = (60^o,60^o) , Li(I)-N distances(in Å) and computed interaction energies, ΔE_{SCF}, (in $kcal.mol^{-1}$).

r	X	Y	Z	ΔE_{SCF}
1.80	1.4729	2.5512	1.7008	-14.6
2.00	1.6366	2.8346	1.8898	-19.2
2.20	1.8002	3.1181	2.0787	-19.3
2.60	2.1276	3.6850	2.4567	-15.4
3.00	2.4549	4.2519	2.8346	-11.3
4.00	3.2732	5.6693	3.7795	- 5.4
5.00	4.0915	7.0866	4.7244	- 3.1
9.00	7.3646	12.7559	8.5039	- 1.4

Table 3.17 Coordinates of the lithium ion for lithium ion/ammonia adduct where (θ , φ) = (60^o,90^o) , Li(I)-N distances(in Å) and computed interaction energies, ΔE_{SCF}, (in kcal.mol^{-1}).

r	X	Y	Z	ΔE_{SCF}
1.80	1.7008	2.9459	0.0000	7.9
2.00	1.8898	3.2732	0.0000	- 2.5
2.60	2.4567	4.2551	0.0000	- 2.8
2.80	2.6457	4.5824	0.0000	- 2.3
3.00	2.8346	4.9098	0.0000	- 1.7
3.40	3.2126	5.5644	0.0000	- 0.9
3.60	3.4016	5.8917	0.0000	- 0.6
5.00	4.7244	8.1829	0.0000	0.0
7.00	6.6142	11.4561	0.0000	0.1
9.00	8.5039	14.7292	0.0000	0.1

Table 3.18 Coordinates of the lithium ion for lithium ion/ammonia adduct where (θ, ϕ) = (60^{o},120^{o}), Li(I)-N distances(in Å) and computed interaction energies, ΔE_{SCF}, (in kcal.mol^{-1}).

r	X	Y	Z	ΔE_{SCF}
2.40	1.9639	3.4016	- 2.2677	4.8
3.00	2.4549	4.2519	- 2.8346	2.9
4.00	3.2732	5.6693	- 3.7795	2.8
5.00	4.0915	7.0866	- 4.7244	2.2
7.00	5.7280	9.9213	- 6.6142	1.3
9.00	7.3646	12.7559	- 8.5039	0.8

Table 3.19 Coordinates of the lithium ion for lithium ion/ammonia adduct where (θ, ϕ) = (60^{o},150^{o}), Li(I)-N distances(in Å) and computed interaction energies, ΔE_{SCF}, (in kcal.mol^{-1}).

r	X	Y	Z	ΔE_{SCF}
2.00	0.9449	1.6366	- 3.2731	13.9
3.00	1.4173	2.4549	- 4.9098	2.1
4.00	1.8898	3.2732	- 6.5463	3.3
5.00	2.3622	4.0915	- 8.1829	2.9
7.00	3.3071	5.7280	-11.4561	1.8
9.00	4.2519	7.3646	-14.7292	1.2

3.1.3 Fitting of Pair Interaction Energies to the Functional Form

After having calculated 50 lithium ion/ammonia configurations in the trajectories, where $(\theta, \phi) = (0^\circ,0^\circ)$, $(0^\circ,180^\circ)$, $(0^\circ,90^\circ)$, $(30^\circ,60^\circ)$ and $(30^\circ,90^\circ)$, the interaction energies of pairs lower than 5 kcal.mol^{-1} were fitted, using a multidimensional nonlinear least-squares procedure by means of the Marquard-Levenberg minimizing algorithm to a functional consisting of Lennard-Jones and Coulombic terms ;

$$\Delta E_{FIT} = \sum_{i=1}^{4} (-A_{im}/r_{im}^{6} + B_{im}\exp(-C_{im}r_{im}) + Dq_i q_m/r_{im})$$

where r_{im} is the distance between the ith atom of ammonia and lithium ion, q_i and q_m are the net charges of an atom i of ammonia and lithium ion in atomic units, obtained from the Mulliken population analysis (55) in the SCF calculations of the monomers. These values were kept constant throughout the calculations. A_{im} , B_{im} , C_{im} and D are the fitting parameters for the interaction between Li(I) and N or H atoms of ammonia. Only one value for the first order Coulombic parameter D was used, valid for both Li(I)-N and Li(I)-H interactions.

The fitting procedure was performed starting from an initial guess of the parameters. The process is iterated until the standard deviation was minimized, whereby constancy of the fitting parameters was reached.

3.1.4 Testing the Quality of the Function.

The function obtained from the first SCF-data set was tested using the procedure proposed by Beveridge (56). This test consists of a choice of lithium ion/ammonia configurations outside the first set of data, but within the $\theta = 0^{\circ}$ to 60° and $\phi = 0^{\circ}$ to 180° in 30° steps. The interaction energies ΔE_{FIT} for these additional configurations, N_{test} points, were evaluated from the optimized function, followed by quantum chemical calculation for the same configurational points, giving the energy ΔE_{SCF}. The quality of the intermolecular potential function is then indicated by comparing all ΔE_{FIT} and ΔE_{SCF} values and their deviations from each other in the set σ_{test}.

To improve the quality of the function, the additional SCF points were then included in the fitting procedure. An improved set of the parameters being obtained, additional configurations were tested and included in the function in the same way until constancy of the fitting parameters within a range of ±5% (57) and a sufficiently low standard deviation was reached.

3.2 Results and Discussion

In Table 3.20 ,the iteration steps , number of configurations included in each step ,standard deviations , σ , number of testing points, N_{test} used to test the previous function and σ_{test} are summarized. For the initial 50 data points , the standard deviation of the function was 1.22 $kcal.mol^{-1}$. The standard deviation of the values predicted by the function from the corresponding ab-initio calculated values for further 25 chosen test points was 1.04 kcal.mol^{-1}. This result indicates that the interaction of ammonia and lithium ion is already well represented by this function. After inclusion of these points, the standard deviation reduces to 1.13 kcal.mol^{-1}.

As mentioned before , most of the low energy ranges were chosen for the construction of the function. The 75th to 100th configurations represent surface energies with rather weak lithium ion/ammonia interactions. Therefore, the test of the function for this data set lead to a slightly higher but still acceptable value of σ_{test} (1.79 kcal.mol^{-1}). Apparently the function is somewhat less suitable to describe the weak interaction range. This can be seen also after inclusion of these additional points to the function, whereby the standard deviation changes to 1.32 kcal.mol^{-1}. However , this standard deviation is still very good compared to similar published functions (58-59).

In figure 3.2, the stabilization energies obtained from quantum chemical calculations (ΔE_{SCF}) were plotted versus those obtained from the function with the parameters summarized in Table 3.20, good agreement between both of them can be seen clearly.

Structural results of Monte Carlo or molecular dynamics simulations depend rather on the shape of the function than on the absolute interaction energies. Sometimes even a function with higher standard deviations may give more accurate results , especially for the information about the intermolecular distances. An important parameter indicating the quality of the function is the correlation between the position of the energy minima of ΔE_{SCF} and ΔE_{FIT}. To illustrate this agreement , potential curves for some directions were plotted in figure 3.3. The results show the relation to be very satisfactory even in the repulsive region where $\phi > 90^{o}$ which does not contribute to the simulation results.

Finally, false minima of the function were searched with a program generating a tridimensional grid with an angular variation of 5^{o} and a distance variation of 0.2 Å from 1 to 10 Å for the whole space around ammonia. No artificial minima was found for the reported function. This checking procedure is also essential, as unwanted minima may produce errors as reported by Jorgensen (61) where such a minimum with a dimerization energy of -112058 kcal.mol^{-1} was found in the MCY water potential (41) for a cyclic dimer with r(OO)=1.122 Å. Having performed this test procedure the proposed pair potential function would be a suitable tool for further statistical simulations.

Table 3.20 Final optimized parameters for the interaction of H and N atoms of ammonia with lithium ion. Interaction energies and r are given in kcal.mol^{-1} and atomic units, repectively. (q_N=-0.74207 a.u. and q_H=0.24736)

Optimized Parameters	Atom N	Atom H
A	-0.4377216987E+05	-0.3116480890E+05
B	0.1071700000E+05	-0.5476518247E+02
C	0.4530000000E+03	0.5783549897E+00
D	0.1025571898E+04	0.1025571898E+04

Table 3.21 Number of SCF-data points (N) , standard deviation (σ) (in $\mathrm{kcal.mol}^{-1}$) , number of testing points (N_{test}) and σ_{test} (see text) for each optimization step.

Step	N	σ	N_{test}	σ_{test}
1	50	1.22	25	1.04
2	75	1.13	25	1.79
3	100	1.32	-	-

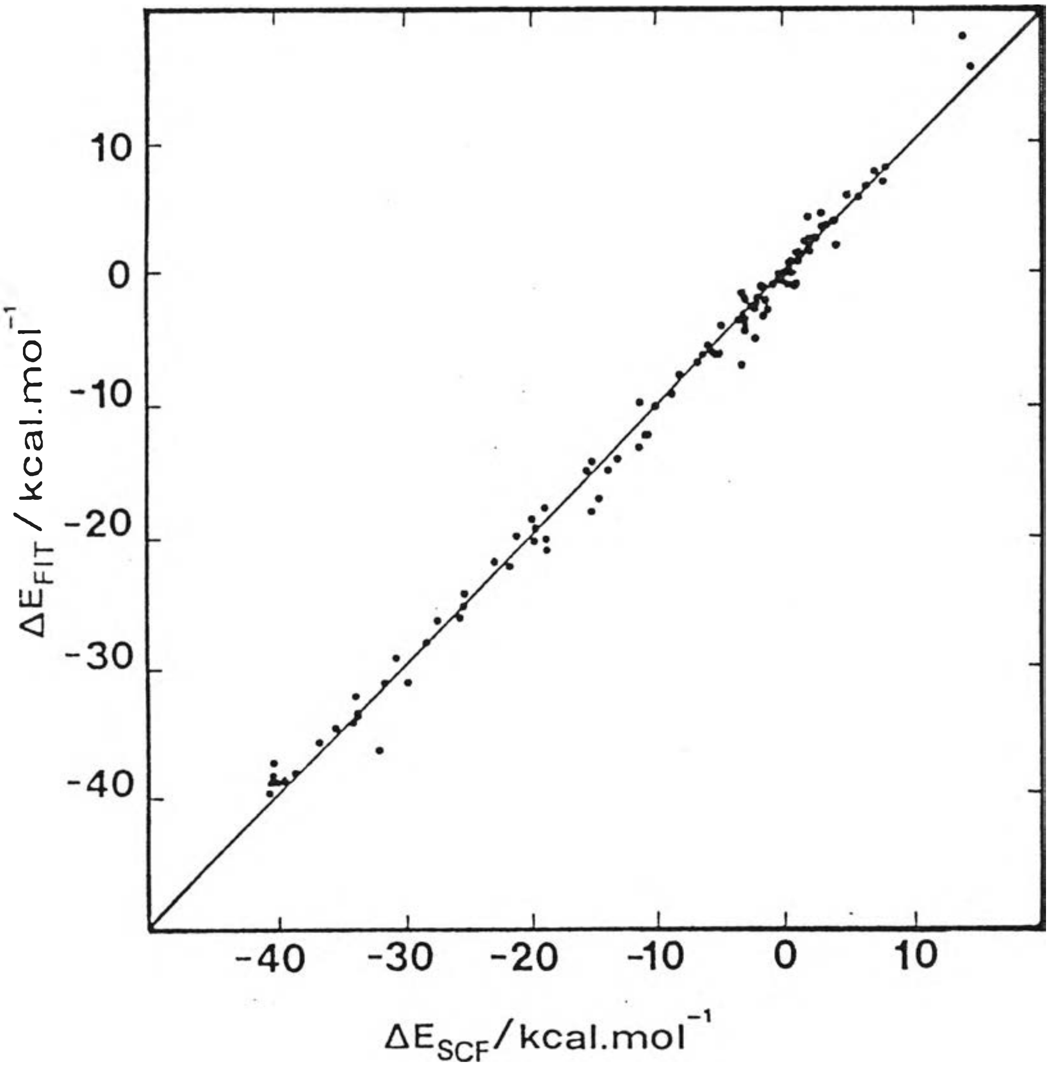

Figure 3.2 Comparison of the model calculated (ΔE_{FIT}) with the quantum mechanically calculated energies (ΔE_{SCF}). The line of unit slope represents perfect agreement between the model and the quantum mechanical calculations.

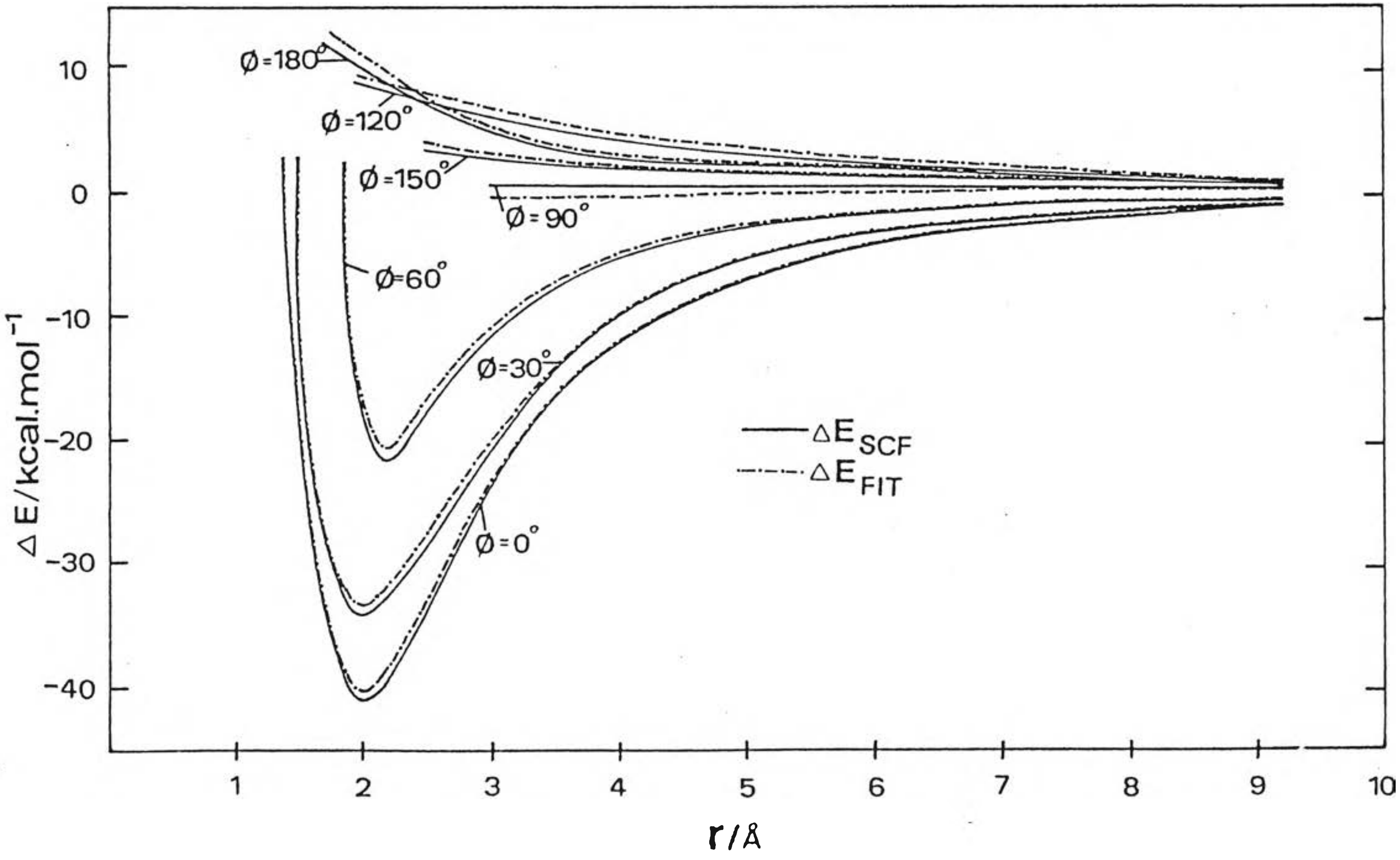

Figure 3.3 Comparison between the DZP ab-initio energies (-·-·-), ΔE_{SCF} and the fited analytical potential (——), ΔE_{FIT}, where $\theta = 180^{\circ}$