Intermolecular Potential Function for Ammonia-Lithium Ion Based on Ab-Initio Calculations

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The intermolecular interaction for ammonia-lithium ion has been investigated based on the LCAO-MO-SCF method, with double zeta basis set including polarization. The potential functions were constructed firstly from 50 ammonia configuration. Then 50 additional random configurations were added to test the quality of the function. The results show that even 100 configurations are not enough to obtain convergency, but the quality of the function obtained by well-selected points of the surface is already sufficient for simulation purposes.

Introduction

Liquids at molecular level can be studied by Monte Carlo [1] and molecular dynamics [2] simulations. Interesting results have been obtained by the simulation of electrolytes [3]. On the other side, metal-ammonia solutions as non-electrolytes have been the subject of intensive investigations [4–10]. Basically, metal ammonia solutions show the characteristics of liquid metals containing nearly free electrons [1]. To deal with this problem by means of Monte Carlo and molecular dynamics methods, metal-ammonia potential functions are required.

In this work the intermolecular potential for ammonia-lithium ion is evaluated. The procedure proposed by Beveridge [11] is used to construct and test the quality of the function.

Method of Calculations

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

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(i) *Selection of geometries*

Lithium ion was placed at numerous positions within the space around ammonia, where $0° \leqq \Phi \leqq 180°$ and $0° \leqq \Theta \leqq 60°$ in Figure 1. First the ion was moved along the z-axis. Then the three trajectories corresponding to (Θ, Φ) values of (0, 90), (30, 60) and (30, 90) were chosen. Finally the potential function was determined by including $0° \leqq \Phi \leqq 180°$ and $0° \leqq \Theta \leqq 60°$ in steps of 30°.

(ii) *Performance of the SCF calculations*

Quantum chemical calculations were performed for the aforementioned configurations. The HONDO

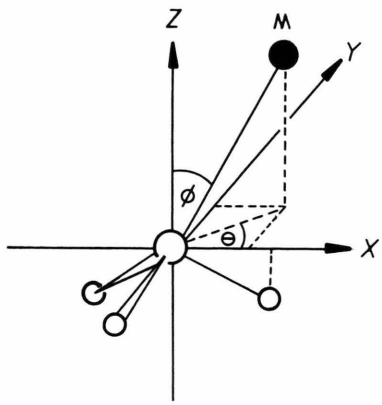

Fig. 1. Definition of geometric variables for configurations of ammonia-lithium ion.

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programme was used with the following choices of basis sets: GLO, STO-2G, STO-3G and DZP (Double Zeta with Polarization function of exponents (1.00), (0.21, 0.80) and (0.03) for N, H and Li (I), respectively). In agreement with the results of [12], the DZP basis set was found to give the best dimerization energy and dipole moment. Therefore this basis set was selected for the further calculations. The experimental geometry of ammonia was taken from [13] as N–H = 1.0124 Å and H–N–H = 106.7°. Ammonia molecules easily invert even in the gas phase but this mode does not occur in normal molecular dynamics simulations with a total time shorter than the inversion period of the ammonia molecule (21 ps) [14]. Therefore, for such simulations it is allowed to treat ammonia as being rigid. All calculation were performed on the IBM 3031/08 computer center of Chulalongkorn University.

(iii) Fitting of pair interaction energies to a functional form

After having calculated 50 ammonia-lithium configurations in the trajectories, where $(\Theta, \Phi) = (0, 0)$, (0, 90), (0, 180), (30, 90) and (30, 60), the interaction energies of the pair lower than 5 kcal/mol were fitted, using a multidimentional non-linear least-squares procedure by menas of the Marquard-Levenberg minimizing algorithm, to a functional of the form

$$\Delta E(r) = \sum_{i=1}^{4} (-A_{im}/r_{im}^6 + B_{im} \exp\{-C_{im} r_{im}\} + D\, q_i\, q_m / r_{im}),$$

where r_{im} is the distance between the i-th atom of ammonia and lithium ion. q_i and q_m are the net charges of an atom i of ammonia and lithium ion respectively, in atomic units, obtained from the Mulliken population analysis [14] in the SCF calculations of the isolated 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 and iterating until the standard deviation was minimized, whereby constancy of the fitting parameters was reached.

(iv) Testing the quality of the function

The function obtained from the first SCF-data set was tested using the procedure proposed by Beveridge [11]. This test consists in a choice of lithium-ammonia configurations outside the first set of data, but within the ranges $\Theta = 0°$ to 60° and $\Phi = 0°$ to 180° in 30° steps. The interaction energies ΔE_{FIT} for these additional configurations were eveluated 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% [15] and a sufficiently low standard deviation was reached.

Results and Discussion

Table 1 shows the iteration steps, number of configurations included in each step, standard deviations, σ, number of testing points used to test the previous function and σ_{test}. For the initial 50 data points, the standard deviation of the function was 1.22 kcal/mol. 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. 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.

As mentioned before, mostly the low energy range was chosen for the construction of our function. The

Table 1. Number of SCF-data points (N), standard deviation (σ in kcal/mol), 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	–	–

Table 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.

Atom	q	A	B	C	D
N	−0.74207	−0.4377216987 E+05	0.1071700000 E+05	0.4530000000 E+03	0.1025571898 E+04
H	0.24736	−0.3116480898 E+05	−0.5476518247 E+02	0.5783549897 E+00	0.1025571898 E+04

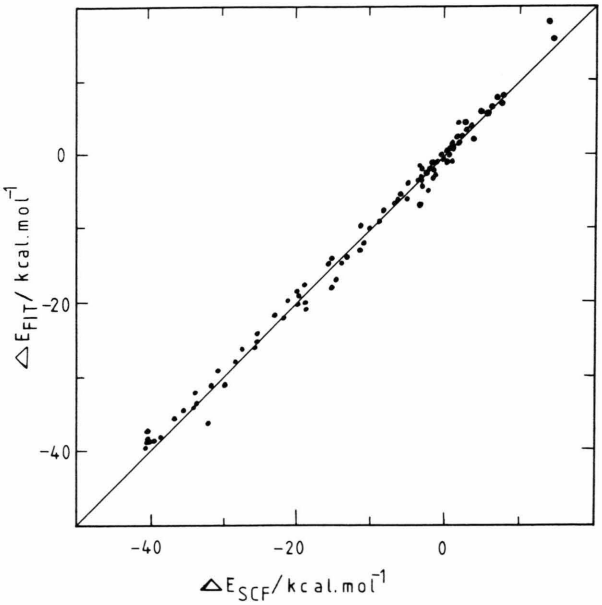

Fig. 2. Comparison of the stabilization energies from the DZP-ab initio data, ΔE_{SCF}, and the potential function with the final values of the fitting parameters given in Table 2, ΔE_{FIT}.

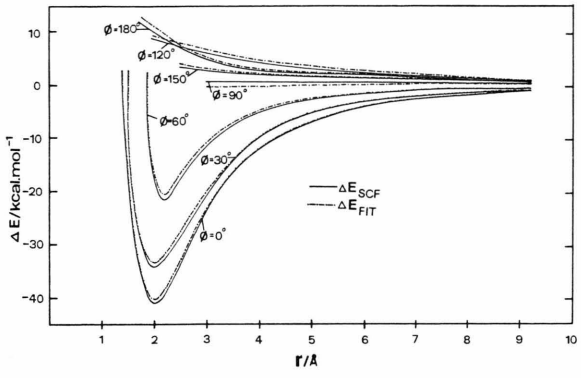

Fig. 3. Comparison of the Φ dependence ($\Theta = 0°$, see Fig. 1) between the DZP-ab initio energies (——), and the fitting analytical potential (– · – · –), ΔE_{FIT}.

75-th to 100-th configurations represent surface energies with rather weak ammonia-lithium interaction. Therefore, the test of the function for this data set led to a slightly higher but still acceptable value of σ_{test} (1.79 kcal/mol). 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. However, this standard deviation is still very good compared to other published functions [15, 16, 17].

In Figure 2, the stabilization energies obtained from the quantum chemical calculations ΔE_{SCF} were plotted versus those obtained from the function with the parameters summarized in Table 2. The good agreement between both is evident.

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. The results show the relation to be very satisfactory even in the repulsive region where $\Theta > 90°$, which does not contribute to the simulation results. As mentioned before, only the dimerization energies lower than 5 kcal/mol have been included in the fitting procedure [11, 18–20].

Finally, false minima of the function were searched with a program generating a square grid with an angular variation of 5° and a distence variation of 0.2 Å from 1 to 10 Å for the whole space around ammonia. No artificial minima were found for our function. This checking procedure is also essential, as unwanted minima may produce errors as reported by Jorgensen [20] where such a minimum with the dimerization energy of −115028 kcal was found in the

MCY (Matsuoka-Clementi-Yoshimine) water potential function [21] for a cyclic dimer with $r(00) = 1.122$ Å. Having performed this test procedure we can assume that our proposed pair potential function is a suitable tool for forthcoming simulation work.

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