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THE INTERMOLECULAR POTENTIAL FUNCTION FOR AMMONIA–MAGNESIUM ION BASED ON AB–INITIO CALCULATIONS

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ABSTRACT

An intermolecular potential function for ammonia–magnesium ion ($NH_3/Mg(II)$) *has been derived based on the data from ab–initio molecular orbital calculations with a minimal Gausian Lobe (GLO) basis set. The 120 interaction energies,* ΔE, *between two monomers were fitted to an analytical potential of the form*

$$\Delta E(kcal.mol^{-1}) = \sum_{i=1}^{4} [-A_{im}.exp(-B_{im}r_{im}) - C_{im}/r^{6}_{im} + D_{im}/r^{4}_{im} + Fq_iq_m/r_{im}]$$

where 4 is number of atoms in ammonia, A_{im} , B_{im} , C_{im} ,D_{im} *and F are constants and* r_{im} *is distance between the* i^{th} *atom of ammonia and magnesium ion.* q_i *and* q_m *are atomic charges of ammonia and magnesium ion, respectively. The resulting function is tested by searching for unwanted minima. In comparison with other ions in an identical solvent, based on a more extended basis set, Monte Carlo simulations using this function have led to encouraging results.*

INTRODUCTION

To model molecules and complexes in the liquid or solution state, information of solvation effects are needed. The advent of computer simulation techniques has provided the possibility of obtaining detailed structural and energy descriptions of complex liquids at molecular level. Progress has been made, on simple liquids and aqueous solutions of small solute molecules, through Monte Carlo[1] and Molecular Dynamics[2] simulations as well as X–ray and neutron diffractions and NMR experiments.[3] The rapid development of computer technology has led to the increasing in simulations and the research in this field.

The theoretical methods are capable of providing more details of the structural, energetic and dynamic characteristics of solute and solvent in solution. However, a critical factor which determines the significance and reliability of the result of such simulations is the quality of the intermolecular potential functions describing all solute/solute, solute/solvent and solvent/solvent interactions in the solution. The progress of knowledge in this area particularly depends on the development of such, improved functions.

The parameters included in the analytical pair potential may be obtained experimentally (empirical pair potentials),[4] theoretically based on quantum chemical calculations (ab–initio pair potentials)[5,6] or semi–empirically.[7] One major advantage of the ab–initio pair potentials, compared to others, is that information concerning any point on the potential hypersurface is accesible from calculations but not always from experiments.[8]

In this paper we present an intermolecular potential function for ammonia–magnesium ion based on ab–initio molecular orbital calculations with the well–tested minimal Gaussian Lobe (GLO) basis set, which was successfully employed in the previous derivation of cyclen–water potential function[9] and other evaluation of metal–ligand complexes.[10-12] As generally known, small basis sets give too high binding energies. However, Jorgenson[13] reported that results of simulations with potential functions based on ab–initio calculations with a small basis set are sufficiently accurate.

METHOD OF CALCULATION

The geometry of ammonia molecule was taken from experimental data[14] as $r_{NH} = 1.0124$ Å, $\sphericalangle$ HNH $= 106.67°$ and held rigid in all aspects of this work. In selecting geometrical configurations we fixed ammonia molecule in a coordinated frame with N at the origin, as the cartesian coordinates shown in table 1. We then let the magnesium ion approach the ammonia molecule from different directions within $0° < \Theta < 60°$, $0° < \phi < 180°$, in steps of 30°. For all directions r_{MgN} spand 1–10 Å.

The total energies (ΔE^t) of ammonia–magnesium ion dimer were computed for the aforementioned configurations using the HONDO programme.

The interaction energy of the dimer, evaluated by employing the supermolecule approach for each relative position is thus :

$$\Delta E = E^t_{\text{dimer}} - E^t_{\text{ammonia}} - E^t_{\text{magnesium ion}}$$

All ab–initio molecular orbital calculations and least–square fitting of the function were performed on the IBM 3031/08 system of the Computer Science Center of Chulalongkorn University.

RESULTS AND DISCUSSION

1. Construction of the potential function

For Monte Carlo or Molecular Dynamic simulations, it is particularly important to have the low – energy regions of the surface well represented. Therefore, only the interaction energy points with lower than 5 kcal.mol^{-1} will be included in the least – square procedure.

After having calculated a sufficiently large number of ab – initio energies, (which generally depend on the size and symmetry of the molecules), the geometries and energies were stored for use by non – linear least – square programme to obtain fits to trial potentials. A variety of functional forms were considered. The Lenard – Jones 6:12 form or exponential function ($e^{-\beta r}$) are usually employed. In the second step, the 120 interaction energies between ammonia and magnesium ion were fitted to an analytical potential of the form

$$\Delta E(\text{kcal.mol}^{-1}) = \sum_{i=1}^{4} [-A_{im}.\exp(-B_{im}r_{im}) - C_{im}/r^6_{im} + D_{im}/r^4_{im} + Fq_iq_m/r_{im}]$$

where 4 is the number of atoms in ammonia, r is distance between the i^{th} atom of ammonia and magnesium ion, q_i and q_m are atomic charges of ammonia and magnesium ion, respectively. These charges were obtained from Mulliken populations[15] of SCF wave functions of the isolated molecules. ΔE is the interaction energy in kcal.mol^{-1} A_{im} , B_{im} , C_{im} and D_{im} are fitting constants representing an interaction between magnesium ion and the i^{th} atom of ammonia. The first two terms represent the repulsive and attractive interactions for both molecules at short range. The third and the fouth terms account for the intermediate distance interactions and the long – range Coulombic interactions, respectively. For the parameter F in the last Coulombic term, only one value was used to represent an interaction between magnesium ion with both hydrogen and oxygen atoms of ammonia, in order to keep ammonia molecule always neutral.

The fitting procedure was performed starting from an initial guess of parameters, as iterative process minimizing the standard deviation, until constancy of the fitting parameters was reached.

A lower standard deviation doesn't always give better simulation results. The centre of the potential minima (the distance where the strongest attractive interaction for each orientation occurs) is also particularly important. Therefore, both the standard deviation and the position of the potential minima are used as criteria to decide the quality of our function.

To achieve this goal, further indications of the quality of the potential function are given in figures 2 and 3. The former illustration compares the interaction energies obtained from ab – initio molecular orbital calculations and from the analytical potential function using the parameters shown in table 2. The picture shows the best fit with a mean – square deviation of 2.28 kcal.mol^{-1}. One potential energy curve is shown in figure 3; the stabilization energies for the strongest attractive interaction of the two monomers (the trajectory where the magnesium ion is in the three – fold axis of ammonia) computed from ab – initio and from our function are compared. It can be seen that good agreement is obtained for both figures.

In the final step of the construction of the function, the FORTRAN programme, generating a square grid with an angular variation of 5° and a distance variation of 0.2 Å from 1 to 10 Å for the whole space around ammonia, was written. False minima of the function were searched for, but no artificial minima were found. This checking procedure was suggested by Jorgensen[13] and was successfully used in our previous lithium ion/ammonia potential function.[7]

2. Performing the Monte Carlo simulations

The analytical pair potentials obtained in the above section was used in the Monte Carlo simulations. One magnesium ion in 18.45 mole % of aqueous ammonia solution, respectively corresponding to 164 and 37 rigid water and ammonia molecules, was simulated. Experimental density of the mixture (0.9307 $g.cm^{-3}$) was used. The starting configuration taken from our previous Li(I) in aqueous ammonia solution was employed. More details of the simulations are given elsewhere.[16]

The solute/solvent structure can be well characterized through partial radial distribution functions, which are given by

$$g_{xy}(r) = \frac{N(r)}{\rho 4\pi r^2 dr}$$

where N(r) is the average numer of particles in the spherical shell of width Δr at a radial distance r from the central particle, x.ρ is the number density of particle y. Then, the corresponding integration number, obtained from

$$n_{xy}(r) = \rho \int_{0}^{r_m} g(r) 4\pi r^2 dr$$

can be determined. The distribution of solvent molecules around magnesium ion and the corresponding integration numbers are given in figure 4. Their RDF characteristics as well as those of lithium and sodium ions in identical solvents are given in table 3.

The radial distribution function where one can find the partial population of water and ammonia molecules surrounding the magnesium ion, is characterized by a well pronounced peak at 2.05 and 2.1 Å, respectively, leading to the total coordination number of 7 solvent molecules. This value is in relative agreement with the quantitative concept of the atomic radii and the atomic charges of the metal ions in identical solvents,[17,18] i.e., the relative solvation radii, to oxygen atom of water in a mixed solvent, of Li(I) > Mg(II) > Na(I)[17,18] is in good agreement with that of pure water[19-25] (*cf.* table 4). Unfortunately, there is no data available for Mg(II) in liquid ammonia.

As illustrated above, the generally satisfactory agreement between the structural results obtained from our function and other functions based on extended basis sets, leads us to believe that the potential function resulting from minimal basis set is a reasonable approach to the study of solution structure. If dealing with such problems using a more extended basis set, an unreasonable computation time would be required in order to calculate several SCF data points. This finding supports, Jorgenson's suggestions for water/water potential function.

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บทคัดย่อ

ทำการสร้างสมการศักย์ฟังก์ชันระหว่างแอมโมเนียและไอออนแมกนีเซียมโดยใช้ข้อมูลจากการคำนวณด้วยวิธีแอบ-อินนิชิโอ และเบสิสเซ็ทชนิดเกาสเซียนลูป 120 จุด สมการที่ได้อยู่ในรูปของ

$$\Delta E(\text{kcal.mol}^{-1}) = \sum_{i=1}^{4} [-A_{im}.\exp(-B_{im}r_{im}) - C_{im}/r^6_{im} + D_{im}/r^4_{im} + Fq_iq_m/r_{im}]$$

เมื่อ 4 คือ จำนวนอะตอมในแอมโมเนีย A_{im} B_{im} C_{im} D_{im} และ F คือค่าคงที่ r_{im} คือระยะทางระหว่างอะตอมในแอมโมเนียและไอออนแมกนีเซียม q_i และ q_m คือประจุบนอะตอมในแอมโมเนียและไอออนแมกนีเซียมตามลำดับ จากการทดสอบสมการศักย์ฟังก์ชันพบว่าไม่มีจุดต่ำสุดที่ไม่ต้องการเกิดขึ้นและเมื่อใช้ศักย์ฟังก์ชันนี้ในการคำนวณโดยวิธีมอนติ คาร์โล พบว่าผลที่ได้สอดคล้องกับผลการคำนวณสำหรับไอออนชนิดอื่น ๆ ในตัวทำละลายชนิดเดียวกันที่ใช้สมการศักย์ฟังก์ชันที่ได้จากเบสิสเซ็ทที่ใหญ่กว่า

TABLE 1 Cartesian coordinates of atoms in ammonia molecule, a.u.(atomic unit)

Atom	X	Y	Z
N	0.00000	0.00000	0.00000
H_1	1.77214	0.00000	−0.72089
H_2	−0.88607	−1.53472	−0.72089
H_3	−0.88607	1.53472	−0.72089

TABLE 2 Final Optimization parameters values of the fitted ammonia−magnesium ion pair potential. Interaction energies and r have been evaluated in kcal.mol^{-1} and atomic units, respectively (q_N = − 0.74207 ; q_H = 0.24736)

Parameters	Mg−N	Mg−H
A	-4.28579×10^5	9.24319×10^4
B	2.16937	2.29236
C	4.32547×10^5	1.11814×10^5
D	3.37469×10^3	-4.49597×10^3
F	8.10193×10^2	8.10193×10^2

TABLE 3 Characteristic values of the radial distribution functions and coordination number (n) for ions in 18.45 mol % aqueous ammonia solutions

	Min/Å	Max/Å	n	Ref.
Mg(II)−O	2.05	3.00	4	this work
Mg(II)−N	2.15	2.95	3	this work
Li (I)−O	1.95	2.75	4	18
Li (I)−N	2.50(3.35)	2.85(3.80)	2	18
Na (I)−O	2.36	2.95	4	17
Na (I)−N	2.35	2.80	2	17

TABLE 4 Solvation radii of ions in pure solvents

Ions	Solvation radii in/Å		Ref.
	H_2O	NH_3	
Mg(II)	2.00	–	22
Li (I)	1.90	2.29	23,24
Na (I)	2.10	2.42	19,25

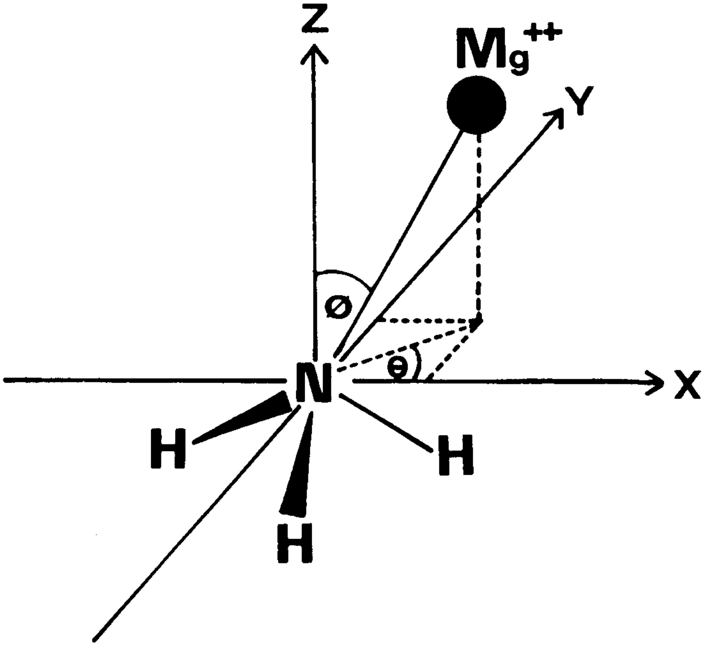

Fig. 1 Definition of geometric variables for configurations of $NH_3-Mg(II)$.

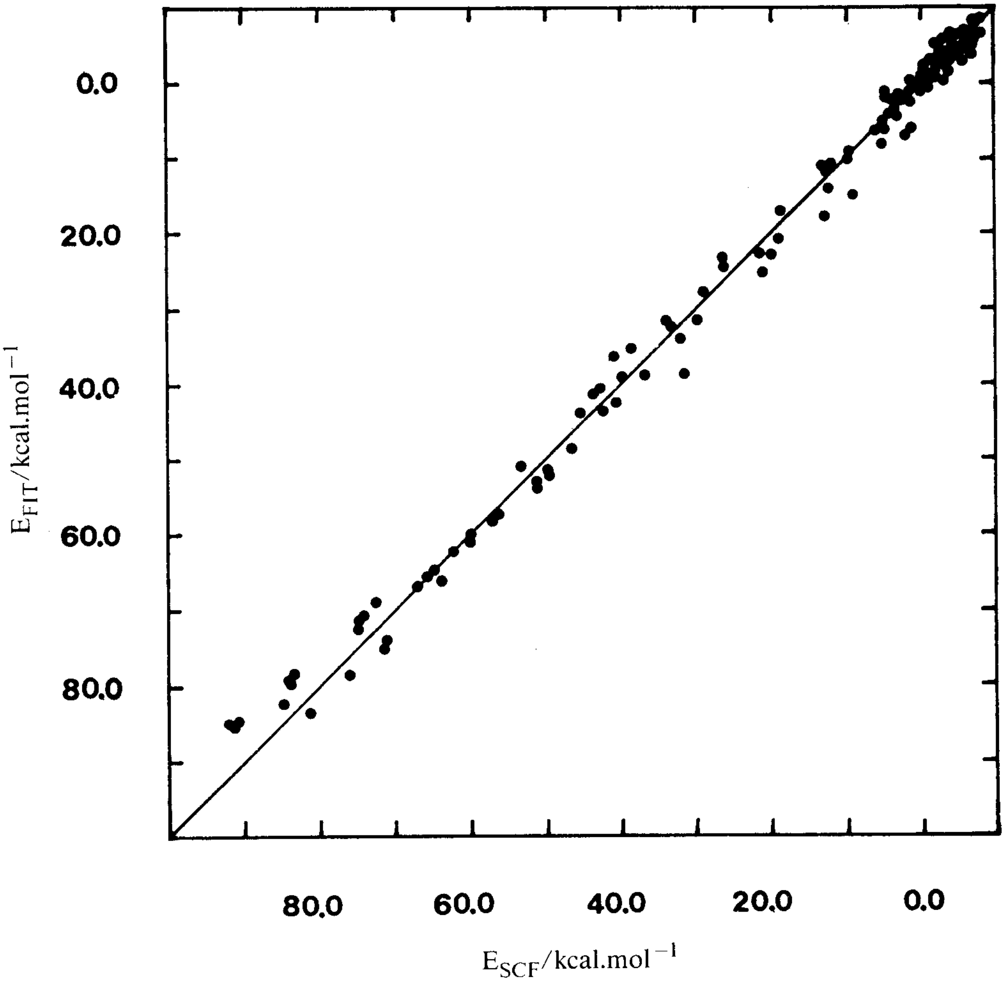

Fig. 2 Comparison of the energies from ab-initio molecular orbital calculations (E_{SCF}) with those obtained from the analytical potential function (E_{FIT}) with optimized parameters in table 1. The line is of unit slope and represent perfect agreement between the fitting and the ab-initio molecular orbital calculations.

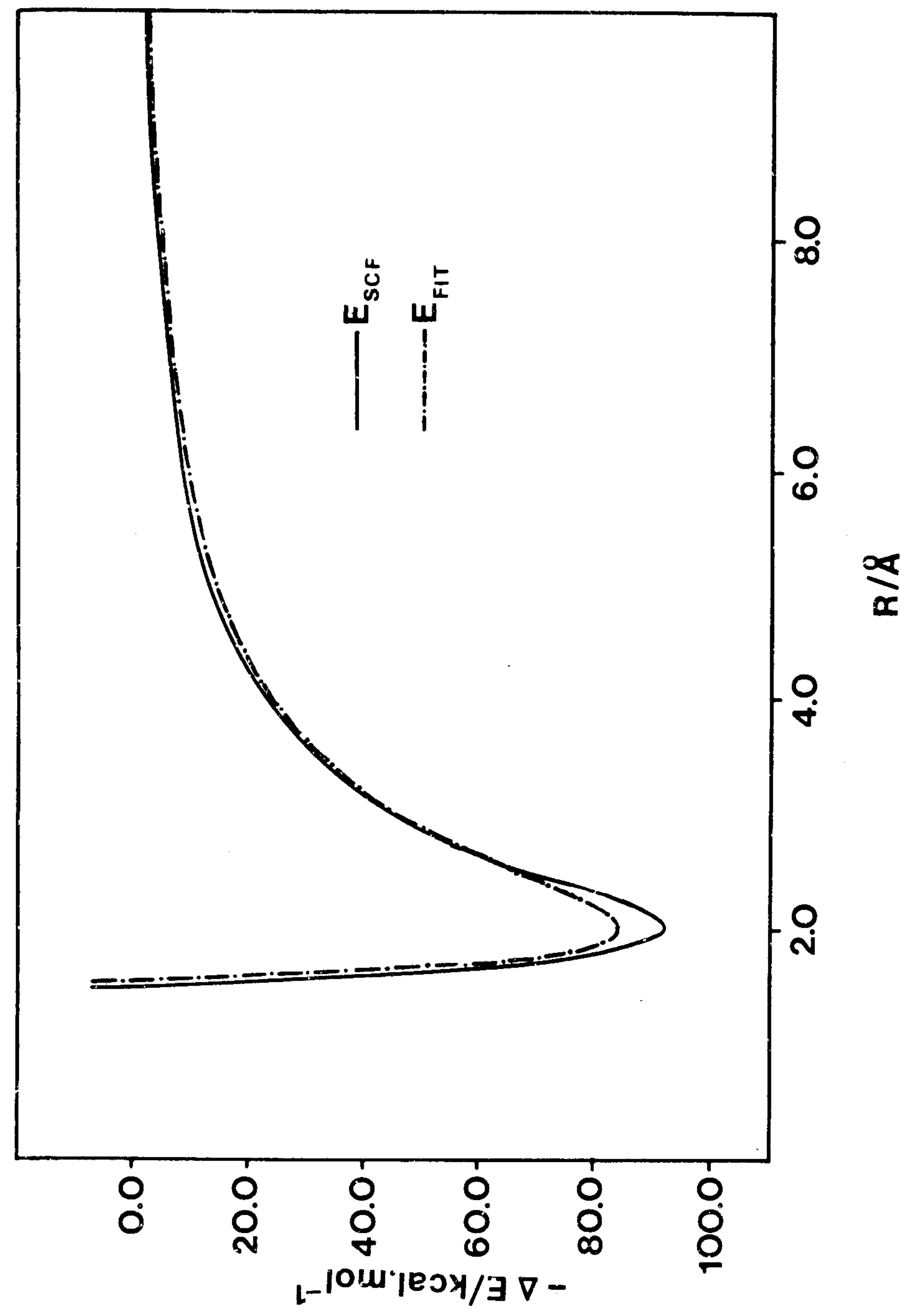

Fig. 3 The lowest distance dependent of a stabilization curve (along the three – fold axis of ammonia) resulted from the ab – initio molecular orbital calculations and analytical potential function with optimized parameters.

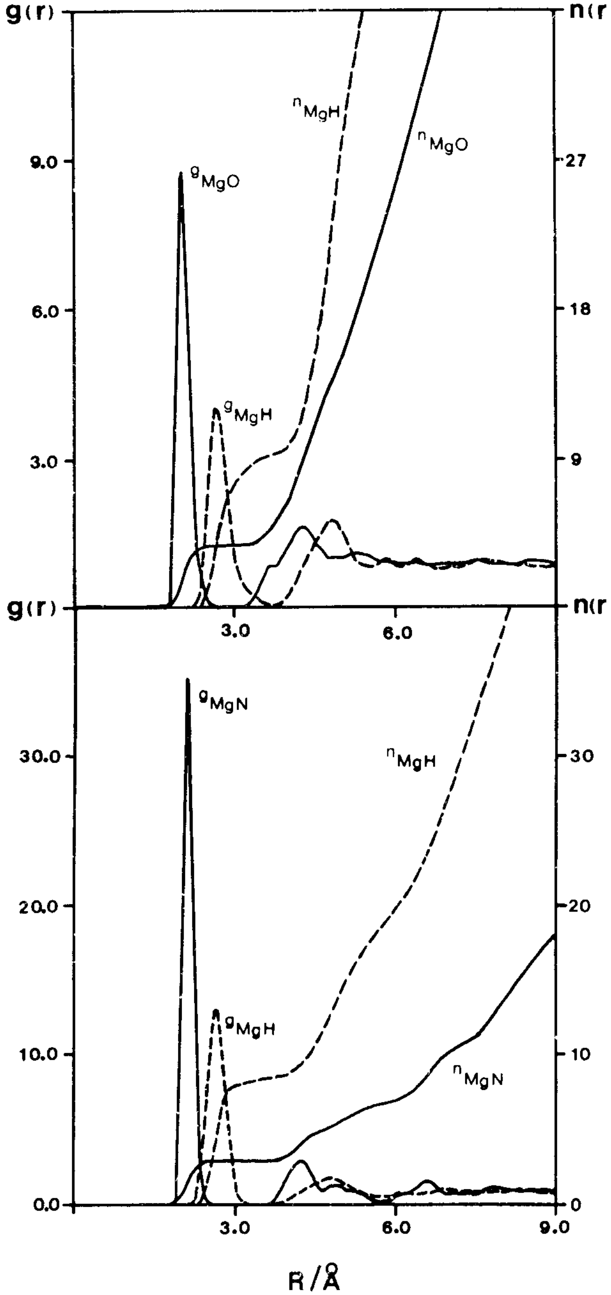

Fig. 4 Calculated radial distribution functions for Mg(II) – water (above) and Mg(II) – ammonia (below) and their corresponding integration numbers (right ordinate).