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Potential Energy Surfaces for Liquid Ammonia: An Estimation of ab initio Calculations for Molecular Simulations

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Hydrogen-bond-enhanced interactions were generated for ammonia pairs by ab initio calculations using tempered basis sets. The potential function obtained by the generation of interaction energies was applied to a Monte Carlo simulation for the liquid state of ammonia. The simulated bulk properties were considered compared with a previous ab initio STO-3G based simulation. The thermodynamic properties were obtained in the simulation and compared with those of a liquid water system to which the same manner of enhancement for the hydrogen bond was applied. The qualitative difference between the two liquids was reproduced.

Many kinds of experimental studies have been carried out for ammonia to explain this simplest hydrogen-bonded molecule. Theoretical studies for this system, therefore, have been examined as quality tests to ensure that the calculation methods or the proposed models agree with the experimental results. The intermolecular properties as geometrical parameters for the dimer configurations were obtained by ab initio molecular orbital calculations,[1—6] and the bulk properties for the molecular assembly were obtained by Monte Carlo and molecular dynamics simulations.[7—9] Many more studies for water than for ammonia have been carried out as evaluation tests, because the importance of water as the standard molecule of the hydrogen-bonding system is well established. It is known that the experimentally observed stable structure of the water dimer has a linear configuration:[10] One O–H bond of a molecule faces one lone pair of the other molecule. The configuration is also suggested by early ab initio studies[11] within the Hartree–Fock level of theory, and has been confirmed by successive studies regardless of the used basis sets and the used electron correlations on the calculations.[12] The units of the linear dimers are inherent in liquid and solid phases: The structures in these phases can be modeled by stacking bricks of the units. Even in the liquid phase, a feature of the dimer structure remains in the pair correlation function at close molecular separations. The structural character obtained by simulations[13] agrees well with that obtained by the neutron-diffraction experiment.[14] For water, the experimentally observed results prove the accuracy of the methods and the validity of the models.

The major difference in the studies between ammonia and water is that we have not yet reached qualitative agreements concerning both the dimer and liquid structures, and they are the unsolved problems for ammonia. Because hydrogen-bonding systems continue to appeal to experimentalists, successive simulations could be carried out if new experimental results are reported. This is true for ammonia. We, however, should not only use the latest experimental results to fit the simulations to them, but should also use the latest methods for a substantial understanding of the phenomena. The use of the empirical potential function is very economical in computational time, but has a difficulty to generate the function. A nonempirical method, called ab initio molecular dynamics simulation,[15] based on density functional theory, on the other hand, may be a reasonable solution. However, even now it is difficult to obtain the intermolecular interaction accurately for a weak hydrogen-bonding system like ammonia. The estimation procedure of the dispersion-force interaction is not well established by density functional theory,[16] while it is a suggestive result by traditional molecular orbital theory that the electron correlation has a considerable contribution to the system and it effects the determination of the stable dimer configuration.[4]

We believe that a consistent way to predict the properties obtained from simulations is to use the information from intermolecular interaction nonempirically. Two investigations must be taken into account in this case: One is the capability of potential functions to correctly reproduce reference interaction energies; the other is the quality of the interaction energies. In previous studies, the parameter-fitting step of the potential function to ab initio energy surfaces had difficulty concerning the reproducibility of the interaction energies. We resolved this problem by proposing the potential energy function (PEF[17]). The characteristic of the PEF is not only the accuracy of the function to reference energies, but the ease of generating its parameters, because the function is based on the theory of intermolecular interactions.

Our previous Monte Carlo study for liquid ammonia[18] was used for the PEF, and is free from the problem involving the reproducibility of the ab initio energy surfaces by potential functions. The use of the Hartree–Fock energies with the STO-3G basis set, however, had drawbacks: the shorter N–N separation of the pair correlation function and the un-

derestimated internal energy compared with the experiment. The inclusion of electric correlation with larger basis sets, therefore, is necessary in order to accurately evaluate the interaction energies so as to improve the simulated results.

In our short report for liquid water,[19] selections of the basis set and the electron correlation were proposed. In the report, we concluded that an enhanced water–water interaction must be taken into account for the simulation. Without using the emphasized interaction between the water molecules, the characteristic structure of liquid water disappeared and a simple liquid-like structure was incorrectly observed. An extension of the study has been applied to this weaker hydrogen-bonding system, liquid ammonia. An important argument is that the enhanced interaction treatment may or may not be valid for not only the structure, but also the thermodynamic properties of liquid ammonia. The main subject of this study is consistent simulations for hydrogen-bonding systems.

Results and Discussion

Calculation of the ab initio Reference Energy. To obtain reference energy surfaces, we need to examine what size of the basis sets is suitable and how the electronic correlation must be taken into account to reproduce the bulk properties, liquid structure and thermodynamic properties by simulations. For water, a proposal we made was to use the MIDI4[20] basis sets with polarization functions (MIDI4*) on O atoms and the minimal sets on H atoms, and the second-order Møller–Preset perturbation level of the theory (MP2). The potential energy curve of the dimer shifted to the shorter O–O separation; about 0.2 Å was required to produce the O–O pair correlation function correctly. Although we did not succeed in explaining the reason for the condition, we found that the enhancement of hydrogen bonding in the liquid state characterizes the structure of water. If this effect is common for hydrogen-bonding systems, the same performance in the simulations would be expected for other hydrogen-bonding species. In this study, we use the MIDI4* basis sets on N atoms and the minimal sets on H atoms, from now on referred to as MIDI4*/MINI, and the MP2 level of theory for electron correlation. To avoid an artificial electron correlations from the inner-core orbitals, the frozen-core treatment has been applied to the system in the same manner as to the liquid water system. Reference energies and the optimized structure of the dimer were calculated using the HONDO[21] and Gaussian 92[22] programs, respectively.

The Basis Set Selection and the Functional Form for Potential Function. A feature of the PEF is the function of overlap integrals between localized molecular orbitals,[23] each of which corresponds to a bond or lone pair of a molecule. The PEF, therefore, requires the basis set to express bonds or lone pairs. The minimal basis set, MINI2,[20] is used for easy localization of the orbitals and saving computational time. The selection of the basis set also follows the study of liquid water.

Localized molecular orbitals generated by the minimal basis set are easily identified as bond or antibond or lone-pair orbitals, but a difficulty arises in producing the present ab initio reference energies. There are two reasons for the insufficiency of the function: One is that the function lacks the ability to polarize the molecule; the other is that it does not explicitly include the functional form for a dispersion interaction. The PEF reproduces ab initio reference interaction energies well if the minimal basis set is consistently used to evaluate the references. The use of a limited small basis set as the energy reference, however, is inappropriate, and larger basis sets are required to perform realistic simulations. This enables molecules to polarize sufficiently so as to significantly affect the energy profile. The limited functional spaces of the PEF using only the bond and lone-pair orbitals restrict the reproducibility of the function. The second problem of the functional form regarding dispersion interactions, which has already been suggested,[24] is that the interaction of the ammonia dimer can be hardly expressed by the traditional form with R^{-6} (R is the interatomic distance). This demands the introduction of another functional form for dispersion interactions.

These problems are resolved by introducing augmented parameters for overlap integrals over diffuse p-type orbitals. The polarization effect should essentially be treated with the many body interaction, which means that the energies should not be estimated pairwise because the electronic field on a molecule is determined by the configuration of all surrounding molecules. First, however, we would like to resolve the polarization effect as the simple form. The procedure is similar to that of liquid water, but here the direction of the p-type orbitals is different by depending on the molecular shape.

The final expression of the PEF for this study is shown as follows:

$$V_{A,B} = V^{min}_{A,B} + V^{aug}_{A,B} \tag{1}$$

$$V^{min}_{A,B} = C_{b,b}\sum_{\substack{i\in b\\ j\in b}} S^2_{ij} + C_{b,lp}\left(\sum_{\substack{i\in b\\ l\in lp}} S^2_{il} + \sum_{\substack{k\in lp\\ j\in b}} S^2_{kj}\right) + C_{lp,lp}\sum_{\substack{k\in lp\\ l\in lp}} S^2_{kl} + C'_{b^*,b}\left(\sum_{\substack{i^*\in b^*\\ j\in b}} S^2_{i^*j} + \sum_{\substack{i\in b\\ j^*\in b^*}} S^2_{ij^*}\right) + C'_{b^*,lp}\left(\sum_{\substack{i^*\in b^*\\ l\in lp}} S^2_{i^*l} + \sum_{\substack{k\in lp\\ j^*\in b^*}} S^2_{kj^*}\right) + \sum \frac{Q_r Q_s}{R_{rs}} \tag{2}$$

$$V^{aug}_{A,B} = \sum_u C_{lp,p^*_u}\left(\sum_{\substack{k\in lp\\ n\in p^*_u}} S^2_{kn} + \sum_{\substack{m\in p^*_u\\ l\in lp}} S^2_{ml}\right) + \sum_u C_{b,p^*_u}\left(\sum_{\substack{i\in b\\ n\in p^*_u}} S^2_{in} + \sum_{\substack{m\in p^*_u\\ j\in b}} S^2_{mj}\right) \tag{3}$$

The potential energy, V, of molecules A and B is expressed as Eq. 1, where the term $V^{min}_{A,B}$ is a function of the overlap integrals using the minimal basis set, MINI2, and the term $V^{aug}_{A,B}$ is a function of those related to the diffuse p-type orbitals. In Eq. 2, the fitting parameters of the PEF to reproduce ab initio reference energies are the coefficients (C, C') for the overlap integrals (S) which are summed over bond (b), antibond (b*), and lone pair (lp) and fractional point charges (Q) on atoms r and s for Coulomb interactions between the

interatomic distance, R_{rs}. For diffuse p-type orbitals, the notation P_u^* is used in Eq. 3, where a diffuse p-type orbital with a single exponent along with the C_{3v} axis of the ammonia molecule refers to P_z^* and two other orbitals, which are perpendicular to P_z^*, to P_x^* and P_y^* (see Fig. 1). The running index, u, is not over the Cartesian coordinates (x, y, and z) independently, because the energy invariance for rotating along the C_{3v} axis is not conserved if the coefficients for the overlap integrals to P_x^* and to P_y^* are not equivalent. The $V_{A,B}^{aug}$, therefore, is a function related to one P_z^* and two degenerated P_{xy}^* orbitals. A former part of Eq. 3 consists of the coefficient C_{lp,p_u^*} and the overlap integrals between the lone pair and diffuse p-type orbitals, which were previously proposed for water.[19] Unfortunately, for ammonia only the inclusion of these terms fails to fit the potential energy surface, especially for the repulsive energy region. It is found that the disagreement comes from the lack of an attractive interaction for the nonhydrogen bonding configuration of the dimer. A further improvement is made by adding a function related to the bond and diffuse p-type orbitals as a latter part, the coefficient C_{b,p_u^*} and the overlap integrals, in Eq. 3. These additional attractive terms of the latter part to the potential function must be prepared for ammonia because a considerable contribution comes from the dispersion interaction by electron correlation. For water, such a type of function, on the other hand, is unnecessary because the dominant interaction is the hydrogen bond. Therefore, it is confirmed, even for ammonia dimers, that the Hartree–Fock interaction energies, which do not include any contribution from the electron correlation, can be described by the PEF without using the latter part in Eq. 3. The parameters of the potential function are summarized in Table 1 where the 94 configurations of the dimer are evaluated for the fitting process. As has been shown in previous work, the magnitude of the fractional point charges, Q, is chosen so as to reproduce the dipole moment of an isolated ammonia molecule.

The exchange-repulsion-type parameters, C, between the bond orbitals and between the bond and lone-pair orbitals, should be positive due to the theory of intermolecular interaction, while the charge-transfer-type parameters, C', between the bond and antibond orbitals or between the lone-pair and antibond orbitals should be negative. From Table 1, an undesirable coefficient is only a pair between the NH bond and the NH antibond. The contribution from the bond pair to the interaction energy, however, is small, and we can say that the function in $V_{A,B}^{min}$ has acceptable performance from the view point of the theory of intermolecular interaction, while no rule about the coefficients is found in $V_{A,B}^{aug}$. In the current study, although the introduction of the functions causes the best results, a further improvement in the functions is still needed.

Optimized Structure of the Ammonia Dimer. The optimized geometrical parameters and interaction energies determined by ab initio calculations are listed in Table 2 where the configurations, shown in Fig. 2, are frequently examined as standard ones. The eclipsed configuration, Fig. 2a, is distinguished from the cyclic one by the number of geometrical parameters: two parameters, θ_1 and θ_2, for the eclipsed one and a θ under the restriction of $\theta_1 = \theta_2$ for the cyclic one. The staggered linear configuration, Fig. 2b, which cannot be not transformed to the cyclic one within its geometrical parameters, was believed to be the most stable one in early studies[1] using the Hartree–Fock level of theory and also in an experiment[25] as an analogy of the water dimer. The later study by ab initio calculations reports on the importance of the cyclic configuration,[2] however, the unexpected configuration shown in Fig. 2c with the measured values is a new proposal based on an experiment by Nelson et al.[26] No theoretical study, including the work of Tao and Klemperer,[6] coworkers of the experiment, predicts the configuration shown in Fig. 2c, and even now it is not concluded that the difference is due to problems in the accuracy of the ab initio calculations or those in the experiment.

Rapid progress in computational power permits more accurate evaluations using larger basis sets and by including the electron correlation for molecular pairs.[3–6] These studies

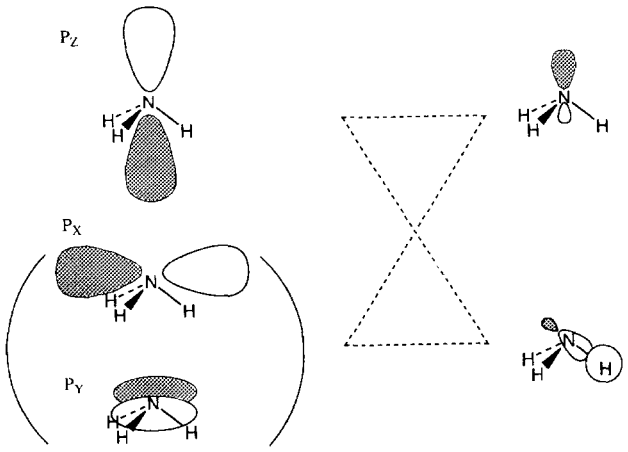

Fig. 1. Augmented interactions between the diffuse P_u^* type orbitals and lone pair orbitals and between the diffuse orbitals and bond orbitals.

Table 1. Parameters of the PEF for the NH_3 Dimer

Q_N	−1.0146
Q_H [a]	(0.3382)
$C_{NH,NH}$ [b]	1.2005
$C_{NH,LP}$ [b]	1.6426
$C_{LP,LP}$ [b]	3.1429
$C_{NH^*,NH}$ [b]	0.11952
$C_{NH^*,LP}$ [b]	−0.47525
C_{LP,p_z^*} [b]	0.078681
C_{LP,p_{xy}^*} [b]	−0.048621
C_{NH,p_z^*} [b]	−0.044268
C_{NH,p_{xy}^*} [b]	−0.035790
σ [c]	1.29

a) Determined by neutrality of charges. b) Units of parameters are taken to be $10^3 \times$ kJ mol^{-1}. c) Least-square deviation in kJ mol^{-1}. The value of 0.08 is used for the exponent of p_u^* orbitals.

Table 2. The Geometrical Parameters for the Optimized Ammonia Dimer

Method	PEF	ab initio	PEF	ab initio	ab initio
Level of theory		MP2		SCF	QCISD
Basis set	MIDI4/MINI	MIDI4/MINI	STO-3G	STO-3G	6−311+G (2d′, p)[a]
Configuration[b]					
Eclipsed					
R	3.194	3.165	3.044	3.065	3.318
θ_1	5	5	−2	−1	13
θ_2	98	95	104	104	85
E	−15.25	−16.24	−15.23	−15.89	−12.40
Cyclic					
R	3.17	3.111	3.333	3.251	
θ	68	70	43	43	
E	−12.57	−12.61	−6.77	−6.83	−12.07
Staggered Linear					
R	3.198	3.184	3.043	3.066	
θ	0	2	5	4	
E	−14.91	−15.61	−15.09	−15.67	

a) Ref. 5. b) For the configurations of the dimer, see Fig. 2.

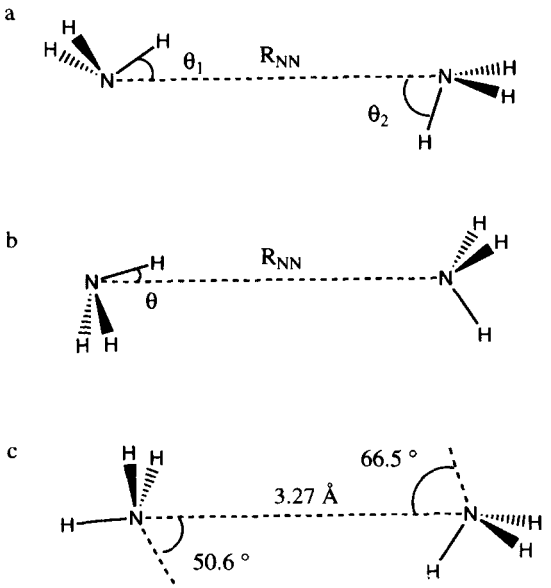

Fig. 2. The geometrical parameters for ammonia dimers: a the eclipsed (the cyclic), b staggered, and c experimentally observed configurations with the observed values.

spotlight the eclipsed configurations and the cyclic one in Fig. 2a, which can be converted to each other within given geometrical parameters. An eclipsed configuration where the θ_1 is close to 0 degree and θ_2 to 112 degrees, for example, has a typical hydrogen bond like the staggered linear one (one hydrogen atom of a molecule faces toward the nitrogen atom of the other molecule), which is easily stabilized only using the Hartree–Fock level of theory. The cyclic configuration, on the other hand, becomes stable with the help of the contribution of the electron correlation. Although the most stable configuration has one set of geometrical parameters between the eclipsed one and the cyclic one shown in Fig. 2a, the considerable contribution of the electron correlation makes the determination difficult. Various studies, even now, do not provide any conclusive results, and only agree with the too-small energy difference between the two configurations and with the possibility for the coexistence of the configurations.

Density functional theory is an alternative to the Hartree–Fock and its extended theories for all molecular systems. The succession using the theory gives a reestimation for the ammonia dimer,[27] and the results recall the staggered linear configuration. Unfortunately, there is no panacea for molecular calculations: The theory has the drawback of producing van der Waals interactions, and it is now under development for both exchange functional and correlation functional.[28] It may therefore be safe to exclude the results from the theory until the procedure for the interactions is well established.

To return to the results given in Table 2, the QCISD study by Hassett et al.[5] using a carefully selected basis set without including effective, but sometimes unmanageable, bond functions[6] concluded that the eclipsed configuration is the most stable structure. Our result qualitatively agrees with their study, but it is seen from the geometrical parameters, θ's, that the structure leans strongly toward the hydrogen-bonded dimer. This tendency is expected because the enhancement for hydrogen-bonding configurations is the characteristic using MIDI4*/MINI. Although the same enhancement is also observed by the Hartree–Fock calculation with the STO-3G basis set, the inclusion of the MP2 contribution in the present study improves the weaker bonding for the cyclic configuration by the STO-3G calculation. For the N–N separation, R_{NN}, the enhancement also affects the shorter distance compared with the QCISD study. In Table 2, our results give an intermediate value of the distance between the STO-3G and the QCISD studies for the eclipsed configuration. The longer N–N separation of the cyclic dimer than the eclipsed and the staggered configurations by the STO-3G results, however, is not observed.

The optimized structures and energies using the PEF are also given in Table 2; they closely agree with those using the reference ab initio calculations. Therefore, the discussion about the dimer structure previously described is also adopted for that about the PEF. The guarantee for the agreement is very important, because this excludes the extra problems which come from any inappropriate reproducibility of the function. The relationship between the summarized results in dimer configurations and the liquid properties are discussed in the following section.

MC Simulation. MC simulations[29] of the N, P, T ensemble using the PEF were carried out for 125 molecules in the basic cell. The volume-fluctuation procedure was inserted every 5 canonical steps, which are equal to 125 random trials under 0.5 MPa at 277 K. A total of 150×10^3 steps were used to evaluate the statistical properties, and their errors were estimated by three partial means of every 50×10^3 steps.

Pair Correlation Function. In Fig. 3, the N–N pair correlation function obtained by the present simulation is shown along with those by the STO-3G simulation and by Narten's X-ray experiment.[30] First, we mention the first peak in the N–N pair correlation function. The split first peak in the X-ray experiment suggests that an ammonia molecule has two different surroundings, as in the solid phase.[31] After Narten's study, successive experiments were carried out by neutron diffraction.[32] It is still difficult to completely deny that the split comes from an artifact due to truncation errors by a transformation from the structure factor to the pair correlation function. Although the recent neutron-diffraction experiment by Ricci et al.[33] does not show the split first peak, this does not determine the structure, because their intervals of data points seem to be loose. Against these experiments, the present study gives no specific structure around the first peak, which is the common result for most previous simulations. The first peak with the broad shoulder of the previous STO-3G simulation is an exception. The weaker interaction energy and the longer N–N separation for the STO-3G cyclic dimer than the staggered linear and the eclipsed configurations (Table 2) gives the broad region on the N–N correlation function: the region is constituted of interstitial cyclic configurations to the stronger bindings by the staggered linear and eclipsed ones. The interactions between ammonia molecules which we used in this study are enhanced for hydrogen-bonding configurations due to the consistent estimation for that of water. A comparable interaction energy and the shorter N–N separation of the cyclic configuration, however, gives no great difference among configurations. This is a general feature when using the larger basis set and the higher level of theory for including the electron correlation. The current improvement of the cyclic configuration makes the broad region shown in the STO-3G simulation disappear. There is an empirical potential function which produces the split first peak.[8] According to the discussion mentioned above, the calculated split first peak does not become evidence for the validity of the simulations. As a result, the ammonia system cannot be modeled by the extension of the solid phase, and the difference with the water system is exposed.

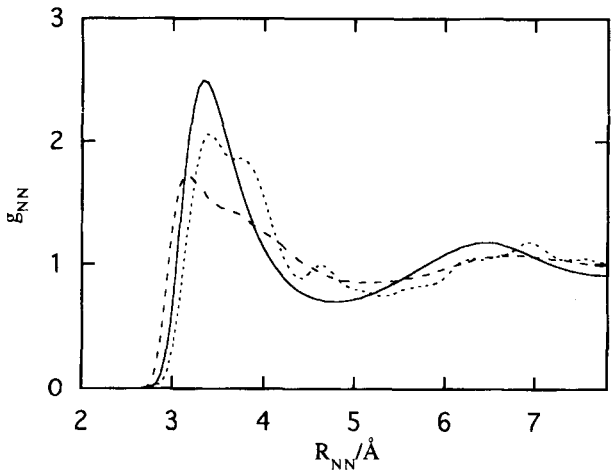

Fig. 3. The N–N pair correlation functions of liquid ammonia obtained from the present (solid line) and the STO-3G (dashed line) simulations and from the X-ray experiment (dotted line).

Next, the peak location of the N–N pair correlation function is discussed. The value of 3.4 Å obtained by the X-ray experiment is consistent with that by the neutron-diffraction experiment estimated in the figure given by Ricci et al. (The diffraction experiment gives no numerical data in the paper, but the whole feature of the N–N pair correlation function agrees with the X-ray experiment, except for the shape of the first peak. A comparable discussion between the function obtained by simulations and by the X-ray experiment, therefore, is reasonable.) The calculated N–N pair correlation function has a shorter peak of 3.3 Å. The difference in the first peak of 0.1 Å may be seen to be small. The total evaluation of the pair correlation function, however, is difficult, except at peak points. Actually, Fig. 3 shows a feature of the calculated function, which excessively shifts to a shorter N–N separation. It is very natural that the tendency toward a shorter N–N separation of the dimer is observed as a feature of the pair correlation function. A careful consideration, however, is required concerning the relationship between the property of the dimer structure and that of the liquid structure. For liquid water, the same estimation of ab initio reference energies, MIDI4*/MINI with MP2, gives a shorter O–O distance for the dimer, but a good agreement concerning the pair correlation functions. The strong cooperativity of the bulk system for water enhances the hydrogen-bond interactions, and the PEF used in the simulation effectively includes an enhancement of the interactions. In the case of ammonia, there is a considerable contribution to the interaction energy from the van der Waals interaction. An enhanced estimation of MIDI4*/MINI with MP2, therefore, overestimates the liquid structure for such a van der Waals subdominant system.

For a feature of the N–N function, it is worth comparing our results with the work of Gao et al.[9] Their results are very close to ours at the points of the single first peak and the short N–N separation for the function. However, in their

work, the empirical potential function which is generated to reproduce the experimentally obtained properties was used. There was, therefore, room to improve the performance of the pair correlation function. This result shows that the enhancement, which affects the liquid structure too much, must be taken into account to reproduce the other properties appropriately.

Thermodynamic Properties. In Table 3, the calculated thermodynamic properties are listed together with the experimental values. The density is a fundamental thermodynamic property in the N,P,T ensemble because other properties are estimated under the condition of the given value; a quantitative consideration by comparing the calculated values with the experimental ones has no meaning if any other properties are measured at very condense or disperse states. The calculated density shifts toward the higher value of 0.690 g cm^{-3} from the experimental one at 277 K and gives an error of 0.057 g cm^{-3}, while an error of 0.041 g cm^{-3} at 240 K was previously reported based on a simulation using an empirical potential function.[9] Comparing these results, it can be concluded that our simulation produces the density of the liquid reasonably well because our nonempirical simulation has the same order of magnitude of error as the empirical one.

The statistically averaged energy of the system is also a fundamental property because the energy in each step is monitored and used to determine whether the next trial is accepted or rejected. The internal energy was only a calculated thermodynamic property in the STO-3G simulation, −7.4 kJ mol^{-1}, which is underestimated with a significant error of 8.2 kJ mol^{-1} from the experimental value. In this study, the enthalpy is estimated instead of the internal energy. Including the dispersion interactions by evaluating electronic correlation gives an overestimated value this time, but the error is reduced to 1.65 kJ mol^{-1}. The heat capacity, isothermal compressibility, and coefficient of thermal expansion are estimated based on the fluctuations of enthalpy, volume, and enthalpy and volume, respectively. The estimation of thermodynamic properties using the fluctuations causes large statistical errors; it is, therefore, difficult to have any precise discussions. The orders of magnitudes for these properties, however, have been successfully produced, and there are no great differences from the experimental values.

A consistent proposal of the simulation for a series of hydrogen-bonding systems is another purpose of our studies. In our short letter on liquid water,[19] the internal energy of the system was stated to be a calculated thermodynamic property because we concentrated only on the liquid structure. The thermodynamic properties for liquid water, therefore, were recalculated using the N,P,T ensemble, and are given in Table 3. The calculation procedure is the same as that for liquid ammonia, but longer MC steps, 300×10^3, are required for the lower convergence of the calculated volume. This may be due to the smaller compressibility of liquid water than that of liquid ammonia. The statistical errors of the thermodynamic properties are estimated by the partial average of 100×10^3 steps. The agreement of the reproduced density is not very excellent compared with that using the famous empirical potential functions.[37] The density, however, is frequently taken into account in trials for generating empirical potential functions. It is, therefore, a foregone conclusion that the calculated densities using empirical functions closely agree with the experimental values. Among simulations which were carried out by a nonempirical procedure, our potential function gave a reasonable performance to reproduce the thermodynamic properties; it is concluded that our simulations succeed to produce the difference between liquid ammonia and liquid water qualitatively.

Concluding Remarks

Using the enhanced interactions for hydrogen-bonding configurations as the reference energies, the PEF was generated and applied to a Monte Carlo simulation. The calculated properties (liquid structure and thermodynamic properties) gave totally acceptable performances within nonempirical simulations. The term 'enhancement' means that the trials to generate empirical potential functions for simulations are expressed by an equal method which modifies the reference energies by the choice of the basis set and by including the electron correlation. A question remains as to how the interaction for hydrogen-bonding systems should be treated for molecular simulations. Many body effects, such as the cooperativity by hydrogen bonding and the polarizability of molecules by the surrounding electronic fields, are missing terms of the potential function for explicit evaluations. Although numerous attempts have been made to deal with the many body interaction, none of those studies have reported

Table 3. Thermodynamic Properties of Liquid Ammonia and Liquid Water

	NH_3		H_2O	
	MC	expt	MC	Expt
ρ/g cm^{-3}	0.690±0.008	0.63298[a)]	0.95±0.03	0.9970[b)]
H/kJ mol^{-1}	−14.31±0.11	−12.664[a)]	−37.85±0.44	
E_i/kJ mol^{-1}	−14.33±0.11	−12.677[a)]	−37.85±0.44	−41.51[c)]
C_p/J K^{-1} mol^{-1}	115±14	79.082[a)]	104±18	75.29[b)]
$\alpha_p\times10^3$/K^{-1}	4±1	2.21[d)]	0.5±0.7	0.257[b)]
$\varkappa_T\times10^{10}$/Pa^{-1}	20±8	12.6[a)]	6±2	4.52[b)]

a) The experimental vales are taken from Ref. 34 at 277.28 K, 0.5 Mpa. b) The experimental vales are taken from Ref. 35 at 298 K, 0.1013 Mpa. c) Ref. 36. d) The value is estimated by the relationship $\alpha^2=(C_p-C_v)\varkappa_T/(TV)$.

any obvious influences. There is obviously insufficiency which arises in generating the empirical potential function, but it is also concluded that perfect pair interactions give poor agreement with the bulk properties, especially for hydrogen-bonding systems. Based on hints about the difference between pair and bulk properties, we plan to carry out the most suitable simulations to treat many body interactions effectively.

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References

1 W. A. Lathan, L. A. Curtiss, W. J. Hehre, J. B. Lisle, and J. A. Pople, *Prog. Phys. Org. Chem. Soc.*, **11**, 175 (1974); P. A. Kollman and L. C. Allen, *J. Am. Chem. Soc.*, **93**, 4991 (1971).

2 K. Hirao, T. Fujikawa, H. Konishi, and S. Yamabe, *Chem. Phys. Lett.*, **104**, 184 (1984).

3 Z. Latajka and S. Scheiner, *J. Chem. Phys.*, **81**, 407 (1984); M. J. Frisch, J. A. Pople, and J. E. Del Bene, *J. Phys. Chem.*, **89**, 3664 (1985); M. J. Frisch, J. E. Del Bene, J. S. Binkley, and H. F. Schaefer, III, *J. Chem. Phys.*, **84**, 2279 (1986); K. P. Sagarik, R. Ahlrichs, and S. Brode, *Mol. Phys.*, **57**, 1247 (1986); S. M. Cybulski, *Chem. Phys. Lett.*, **228**, 451 (1994).

4 Z. Latajka and S. Scheiner, *J. Chem. Phys.*, **84**, 341 (1986).

5 D. M. Hassett, C. J. Marsden, and B. J. Smith, *Chem. Phys. Lett.*, **183**, 449 (1991).

6 F.-M. Tao and W. Klemperer, *J. Chem. Phys.*, **99**, 5976 (1993).

7 W. L. Jorgensen and M. Ibrahim, *J. Am. Chem. Soc.*, **102**, 3309 (1980); A. Hinchliffe, D. G. Bounds, M. L. Klein, I. R. Mcdonald, and R. Righini, *J. Chem. Phys.*, **74**, 1211 (1981); R. H. Kincaid and H. A. Scheraga, *J. Phys. Chem.*, **86**, 833 (1982); A. L. Kielpinski, K. Mansour, and S. Murad, *Int. J. Thermophys.*, **7**, 421 (1986); J. M. Caillol, D. Levesque, J. J. Weis, J. S. Perkyns, and G. N. Patey, *Mol. Phys.*, **62**, 1225 (1987); M. Ferrario, M. Haughney, I. R. McDonald, and M. L. Klein, *J. Chem. Phys.*, **93**, 5156 (1990).

8 M. L. Klein, I. R. Mcdonald, and R. Righini, *J. Chem. Phys.*, **71**, 3673 (1979).

9 J. Gao, X. Xia, and T. F. George, *J. Phys. Chem.*, **97**, 9241 (1993).

10 T. R. Dyke and J. S. Muenter, *J. Chem. Phys.*, **66**, 2929 (1974).

11 K. Morokuma and L. Pedersen, *J. Chem. Phys.*, **48**, 3275 (1968); P. A. Kollman and L. C. Allen, *J. Chem. Phys.*, **51**, 3286 (1969); K. Morokuma and J. R. Winnick, *J. Chem. Phys.*, **52**, 1301 (1970); J. Del Bene and J. A. Pople, *J. Chem. Phys.*, **52**, 4858 (1970).

12 J. G. C. M. van Duijneveldt-van de Rijdt and F. B. van Duijneveldt, *J. Chem. Phys.*, **97**, 5019 (1992); M. W. Feyereisen, D. Feller, and D. A. Dixon, *J. Phys. Chem.*, **100**, 2993 (1996); E. M. Mass and K. Szalewicz, *J. Chem. Phys.*, **104**, 7606 (1996); A. Halkier, H. Koch, P Jørgensen, O. Christiansen, I. M. B. Nielsen, and T. Helgaker, *Theor. Chem. Acc.*, **97**, 150 (1997).

13 M. Sprik and M. L. Klein, *J. Chem. Phys.*, **89**, 7556 (1988); Y.-P Liu, K. Kim, B. J. Berne, R. A. Friesner, and S. W. Rick, *J. Chem. Phys.*, **108**, 4739 (1998).

14 A. K. Soper and M. G. Phillips, *Chem. Phys.*, **107**, 47 (1986).

15 K. Laasonen, M. Sprik, M. Parrinello, and R. Car, *J. Chem. Phys.*, **99**, 9080 (1993); U. Röthlisberger and M. Parrinello, *J. Chem. Phys.*, **106**, 4658 (1997).

16 S. Kristyán and P. Pulay, *Chem. Phys. Lett.*, **229**, 175 (1994); J. E. Del Bene, W. B. Person, and K. Szczepaniak, *J. Phys. Chem.*, **99**, 10705 (1995); J. J. Novoa and C. Sosa, *J. Phys. Chem.*, **99**, 15837 (1995); P. Hobza, J. Šponer, and T. Reschel, *J. Comput. Chem.*, **16**, 1315 (1995).

17 K. Honda and K. Kitaura, *Chem. Phys. Lett.*, **140**, 53 (1987).

18 K. Honda, K. Kitaura, and K. Nishimoto, *Bull. Chem. Soc. Jpn.*, **67**, 2679 (1994).

19 K. Honda and K. Kato, *Chem. Phys. Lett.*, **229**, 65 (1994).

20 H. Tatewaki and S. Huzinaga, *J. Comput. Chem.*, **1**, 205 (1980).

21 M. Dupuis, J. D. Watts, H. O. Villar, and H. B. Hurst, *QCPE Library*, Program No.544.

22 M. J. Frisch, G. W. Trucks, M. Head-Gordon, P. M. W. Gill, M. W. Wong, J. B. Foresman, B. G. Johnson, H. B. Schlegel, M. A. Robb, E. S. Replogle, R. Gomperts, J. L. Andres, K. Raghavachari, J. S. Binkley, C. Gonzalez, R. L. Martin, D. J. Fox, D. J. Defrees, J. Baker, J. J. P. Stewart, and J. A. Pople, Gaussian, Inc., Pittsburgh, PA (1992).

23 J. M. Foster and S. F. Boys, *Rev. Mod. Phys.*, **32**, 300 (1960).

24 K. Kitaura, *Fluid Phase Equilib.*, **104**, 57 (1995).

25 J. A. Odutola, T. R. Dyke, B. J. Howard, and J. S. Muenter, *J. Chem. Phys.*, **70**, 4884 (1979).

26 D. D. Nelson, Jr., G. T. Fraser, and W. Klemperer, *J. Chem. Phys.*, **83**, 6201 (1985); D. D. Nelson, Jr., W. Klemperer, G. T. Fraser, F. J. Lovas, and R. D. Suenram, *J. Chem. Phys.*, **87**, 6364 (1987).

27 T. Zhu and W. Yang, *Int. J. Quant. Chem.*, **49**, 613 (1994); M. Kieninger and S. Suhai, *J. Comput. Chem.*, **17**, 1508 (1996).

28 Y. Zhang, W. Pan, and W. Yang, *J. Chem. Phys.*, **107**, 7921 (1997).

29 N. Metropolis, A. W. Rosenbluth, M. N. Rosenbluth, A. H. Teller, and E. Teller, *J. Chem. Phys.*, **21**, 1087 (1953).

30 A. H. Narten, *J. Chem. Phys.*, **66**, 3117 (1977).

31 I. Olovsson and D. H. Templeton, *Acta Crystallogr.*, **12**, 832 (1959); J. W. Reed and P. M. Harris, *J. Chem. Phys.*, **35**, 1730 (1961).

32 P. Chieux and H. Bertagnolli, *J. Phys. Chem.*, **88**, 3726 (1984).

33 M. A. Ricci, M. Nardone, F. P. Ricci, C. Andreani, and A. K. Soper, *J. Chem. Phys.*, **102**, 7650 (1995).

34 L. Haar and J. S. Gallagher, *J. Chem. Phys. Ref. Data*, **7**, 635 (1978).

35 G. S. Kell, *J. Chem. Eng. Data*, **20**, 97 (1975). G. S. Kell, in "Water, a Comprehensive Treatise," ed by F. Franks, Plenum Press, New York, N.Y. (1972), Vol. I, Chap. 10.

36 W. L. Jorgensen, *J. Chem. Phys.*, **77**, 4156 (1982).

37 W. L. Jorgensen, J. Chandrasekhar, J. D. Madura, R. W. Impey, and M. L. Klein, *J. Chem. Phys.*, **79**, 926 (1983).