Ab Initio Integrated Multi-Center Molecular Orbitals Method for Large Cluster Systems: Total Energy and Normal Vibration

Shogo Sakai* and Shoji Morita

Department of Chemistry, Faculty of Engineering, Gifu University, Yanagido, Gifu 501-1193, Japan

Received: May 25, 2005; In Final Form: July 8, 2005

A new computational scheme integrating multi-center ab initio molecular orbitals for determining total energy and normal vibration of large cluster systems is presented. This method can be used to treat large cluster systems such as solvents by quantum mechanics. The geometry parameters, the total energies, the relative energies, and the normal vibrations for four models of water cluster, the hydrated hydronium ion complex, and the transition state of proton transfer are calculated by the present method and are compared with those obtained by the full ab initio MO method. The results agree very well. The scheme proposed in this article is also intended to be used in modeling computer cluster systems using parallel algorithms.

1. Introduction

It has been recognized that solvent effects would be a central topic in the theoretical physical chemistry.[1−5] Therefore, the development of predictive quantum chemistry based methods to study conformational energies, molecular stabilities, electronic properties, chemical reactivity, and dynamical behavior of molecules in large cluster systems as solvent is a high priority. Several approaches for treating quantum chemistry processes for large cluster systems have been proposed.[6−14] On the other hand, molecular dynamics methods[15−17] have become important investigation tools for modeling chemical phenomena in large cluster systems. The forces in molecular dynamics calculations can be evaluated using an empirical function with parameters determined by experience,[18−22] quantum mechanics (QM) methods,[15,23−25] quantum mechanical methods such as combined quantum mechanical and molecular mechanical (QM/MM) methods,[6−11] or fragment molecular orbital (FMO) methods.[12−14] Especially for chemical reactions and solvent effects, it is difficult to evaluate potential fields using empirical functions with parameters determined by experience. Therefore, the QM, QM/MM, and FMO methods are used for this application. However, enormous CPU computation time is necessary when using QM methods for evaluating potential fields. Accordingly, such analysis is limited to small systems. For molecular dynamics calculations of large cluster systems involving solvents, the QM/MM method, the fragment MO method, or methods including dielectric field models are used. In some chemical reactions in solvent, the solvents act as reagents in the reaction. For example, it is known that proton or hydronium ion in water solvent has an important role for some biological reaction systems. In this case, with treatment by the QM/MM method, some solvent molecules are treated by QM, and other solvent molecules are treated by MM. In the treatment of systems including solvent molecules by QM/MM, however, there are many cases in which the solvent molecules treated by MM become involved in the important region of the reaction according to molecular trajectories. The use of QM/MM methods for trajectory calculations presents important problems from a theoretical viewpoint in that the accuracy of the QM/MM method does not hold during molecular movement as pointed out in the previous paper.[26] For the fragment MO method, the molecules relating to reaction have to include the same fragment group. However, if the solvents act as reagents in the reaction, at the beginning of the trajectory we cannot distinguish which solvent molecules act as reagents during the simulation process. Accordingly, the treatment of solvent molecules by the QM/MM method and/or the fragment MO method is unsuitable for such molecular dynamics calculations.

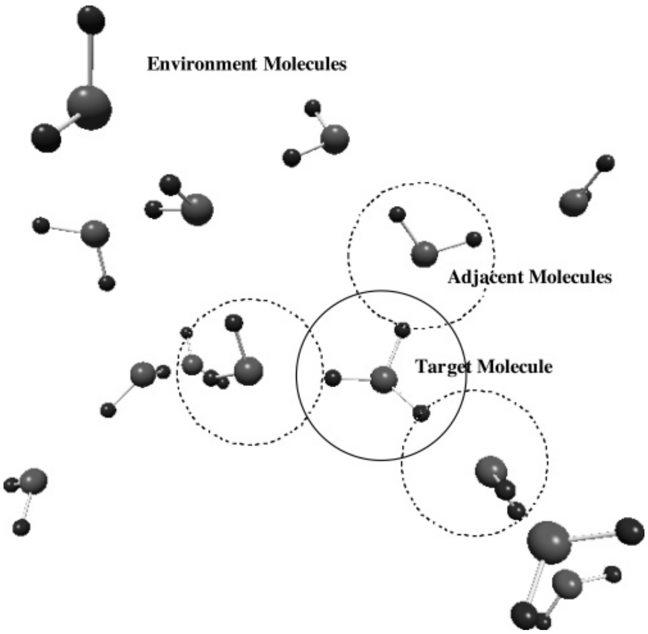
Recently, in light of this, we have proposed an approximation method (integrated multi-center molecular orbital: IMiC MO)[26,27] by which the forces of all atoms of the solute and the solvent are evaluated at the level of the QM method. This method evaluates the force of every atom in each molecule necessary for trajectory calculation. The calculated geometry parameters by the IMiC MO exhibit very good correspondence with those by the full ab initio MO method as shown in the previous papers. In the present paper, we report the development of the IMiC MO method for the approximate representation of total energy and the second derivative matrix, namely normal vibrational frequencies for an entire system. This scheme is applied for some small water clusters and hydration systems of hydronium ion.

2. Theoretical Treatments

2.1. IMiC MO Model and Validation. The IMiC MO method was proposed as an approximation technique to evaluate the force of each atom at the ab initio MO level in order to perform a molecular dynamic calculation and a geometry optimization in large cluster systems as solvent. The basic idea behind our IMiC MO approach can be explained most easily when it is considered as an evaluation scheme of the force of each atom for a molecule unit. For a molecule unit, we define that a bond exists between atoms if the distance between any given atoms is less than 1.5 times the sum of the covalent bond radii of those atoms. Thus, we define atom groups connected by bonds as molecules. Namely this method divides the entire system into units of molecules, and calculates the force of each atom in the unit. To reduce the number of orbitals to allow the system to be resolved in a single QM calculation, the system is divided into three regions (see Scheme 1): the molecule for which the force is calculated (target molecule), the region of molecules surrounding the target molecule (adjacent molecular region), and all other molecules (environment molecular region). Adjacent molecules are defined as follows. We compare the

10.1021/jp0527453 CCC: $30.25

SCHEME 1



distances (r_{ab}) between each atom of the target molecule and each atom of other molecules with their respective van der Waals bond distances (d_{ab}). The subscripts a and b in r_{ab} and d_{ab} denote atoms of the target molecule and of other molecules, respectively. If r_{ab} is shorter than d_{ab}, the molecule including the atom of b is regarded as an adjacent molecule. Environment molecules are all molecules other than the target molecule and the adjacent molecules. The target molecule and molecules belonging to the adjacent molecular region are treated by QM, and molecules belonging to the environment molecular region are included in the electrostatic field calculation as a point-charge approximation. The force of each atom in the system is evaluated by repeating this process for all molecules. The algorithm for computation by the IMiC MO method was described in the previous paper.[26] In our method, the number of atoms constituting a molecule can be changed during the calculation process of molecular dynamics calculation or geometry optimization. Therefore, when a chemical reaction occurs in the system, molecules recombine.

For this method, the computational time increases only linearly with the number of molecules in the system as shown in the previous paper.[26] It is important to note that the repetition does not need to be performed sequentially. Accordingly, these repetition operations can be calculate in parallel using more than one computer. The real time of computation can be distributed if parallel processing is used. We implemented a program by taking the ab initio (QM) component from the GAMESS program.[28]

2.2. Evaluation of Total Energy for IMiC MO. In the IMiC MO method the system is divided into three regions, and the electronic energies (E_{TAe}) for one molecule unit, which are included in the QM calculation of the target molecule and the adjacent molecules with the electrostatic potential of environment molecules, are calculated. The subscript capital letters and small letters indicate the treatments by QM and by the static potential calculations for molecules in three regions (T and t: target molecule; A and a: adjacent molecules; and e: environment molecules), respectively. To evaluate the total energy of a whole system, we calculate two extra type QM calculations for one target molecule. One is the QM calculation (E_{tAe}) for the adjacent molecules including the electrostatic potential for the target molecule and environment molecules. Another is the QM calculation (E_{Tae}) for only the target molecule including the electrostatic potential for the adjacent and the environment molecules. The electrostatic potential energy between the target molecule and the environment molecules is evaluated approximately as eq 1

$$E_{te} \cong \sum_{i\in t}\sum_{j\in e} \frac{V_i V_j}{|R_i - R_j|} \tag{1}$$

where V_i and R_i are the electrostatic point charge and the coordination for the ith atom, respectively. Then the electronic energy for one target molecule in the whole system is evaluated as eq 2

$$\begin{aligned} E_T^{ele} &= E_{TAe} - E_{tAe} - {}^1/_2(E_{TAe} - E_{Tae} - E_{tAe}) - {}^1/_2E_{te} \\ &= {}^1/_2(E_{TAe} + E_{Tae} - E_{tAe} - E_{te}) \end{aligned} \tag{2}$$

where eq 2 can be represented as the following. If the energy terms such as E_{TAe} are decomposed as eq 3,

$$E_{TAe} = E(T) + E(A) + E(T-A) + E(T-e) + E(A-e) \tag{3}$$

the terms ($E_{TAe} - E_{tAe}$) and ($E_{TAe} - E_{Tae} - E_{tAe}$) in eq 2 are represented as eqs 4 and 5, respectively, where E(T) and E(A) are electronic energies of each T and A, and E(T−A), E(T−e), and E(A−e) are each the interaction energy between T and A, T and e, and A and e.

$$E_{TAe} - E_{tAe} = E(T) + E(T-A) + E(T-e) - E(A-t) \tag{4}$$

$$E_{TAe} - E_{Tae} - E_{tAe} = E(T-A) - E(T-a) - E(A-t) \tag{5}$$

Then eq 2 can be represented as the following,

$$\begin{aligned} E_T^{ele} = E(T) + E(T-e) + {}^1/_2(E(T-A) + \\ E(T-a) - E(A-t)) - {}^1/_2E(t-e) \end{aligned} \tag{6}$$

If the energy terms such as E(T−A) are also decomposed as eq 7,

$$\begin{aligned} E(T-A) = E(t-a) + E(t{:}oth-a) + \\ E(t-a{:}oth) + E(t{:}oth-a{:}oth) \end{aligned} \tag{7}$$

eq 2 can be represented as eq 8

$$\begin{aligned} E_T^{ele} = E(T) + E(t{:}oth-a) + E(t{:}oth-e) + \\ {}^1/_2(E(t-a) + E(t{:}oth-a{:}oth) + E(t-e)) \end{aligned} \tag{8}$$

where E(t:oth−a) indicates the interaction energy between T and the electrostatic potential of a except for the electrostatic interaction energy between t and a, and E(t:oth−a:oth) is the interaction energy between T and A except for the electrostatic interaction energy between t and a. The interaction of the inter-regions except for E(t:oth−a) and E(t:oth−e) includes a half of each term to avoid the double count of the energies.

The nuclear repulsion energy for one target molecule unit can be calculated by eq 9

$$E_T^{nuc} = \sum_{i<j, i\in T, j\in T} \frac{Z_i Z_j}{|R_i - R_j|} + \frac{1}{2}\sum_{i\in T, j\notin T} \frac{Z_i Z_j}{|R_i - R_j|} \tag{9}$$

where Z_i is nuclear charge of the ith atom. Then the total energy

SCHEME 2

	Mol 1	Mol 2	Mol 3	
Mol 1	$\dfrac{\partial^2 E_{\mathrm{TAe}}^{\mathrm{mol\,1}}}{\partial i\,\partial j}$ i,j ∈ mol 1	$\dfrac{1}{2}\left(\dfrac{\partial^2 E_{\mathrm{TAe}}^{\mathrm{mol\,1}}}{\partial i\,\partial j}+\dfrac{\partial^2 E_{\mathrm{TAe}}^{\mathrm{mol\,2}}}{\partial i\,\partial j}\right)$ i ∈ mol 1, j ∈ mol 2	$\dfrac{1}{2}\left(\dfrac{\partial^2 E_{\mathrm{TAe}}^{\mathrm{mol\,1}}}{\partial i\,\partial j}+\dfrac{\partial^2 E_{\mathrm{TAe}}^{\mathrm{mol\,3}}}{\partial i\,\partial j}\right)$ i ∈ mol 1, j ∈ mol 3	
Mol 2		$\dfrac{\partial^2 E_{\mathrm{TAe}}^{\mathrm{mol\,2}}}{\partial i\,\partial j}$ i,j ∈ mol 2	$\dfrac{1}{2}\left(\dfrac{\partial^2 E_{\mathrm{TAe}}^{\mathrm{mol\,2}}}{\partial i\,\partial j}+\dfrac{\partial^2 E_{\mathrm{TAe}}^{\mathrm{mol\,3}}}{\partial i\,\partial j}\right)$ i ∈ mol 2, j ∈ mol 3	
Mol 3			$\dfrac{\partial^2 E_{\mathrm{TAe}}^{\mathrm{mol\,3}}}{\partial i\,\partial j}$ i,j ∈ mol 3	

for the whole system can be obtained approximately as eq 10 from eq 11.

$$E_{\mathrm{T}} = E_{\mathrm{T}}^{\mathrm{ele}} + E_{\mathrm{T}}^{\mathrm{nuc}} \tag{10}$$

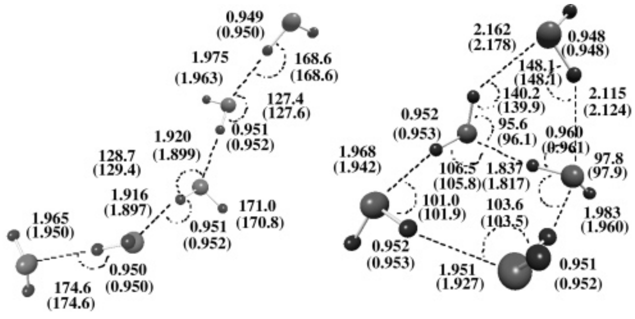
$$E_{\mathrm{total}} = \sum_{N}^{\text{all molecules}} E_{\mathrm{T}} \tag{11}$$

2.3. Hessian Matrix Definition for the IMiC MO Model. To evaluate the Hessian matrix of the IMiC MO model, we divide the matrix into the block of each molecule unit. Accordingly there are two types of blocks in the Hessian matrix: the diagonal block and the off-diagonal block. The elements of the diagonal block for each molecule unit are evaluated by the second derivative of the energy of E_{TAe}, which is obtained with the evaluation of the Hessian of the target molecule. The elements of the off-diagonal block are evaluated simply by the addition of each half of the off-diagonal element of each Hessian matrix between these target molecules. The evaluation of each block of the Hessian matrix is shown in Scheme 2. The evaluation of the Hessian matrix for the IMiC MO model is very simple and can also be calculated with a parallel procedure in computation.

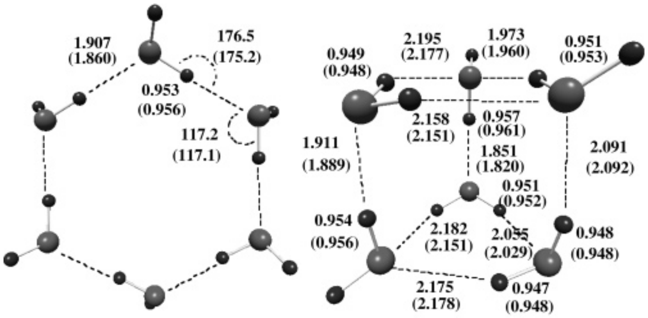
3. Applications

The geometry parameters of some small clusters obtained by the present method were already tested in the previous papers. Briefly, however, the equilibrium geometries of some small clusters obtained by the IMiC MO method are compared with those from the full ab initio MO method. We should focus on the calculation of energies and vibrational frequencies in comparison with the corresponding full ab initio MO calculations.

3.1. $(H_2O)_5$ and $(H_2O)_6$ Clusters. The geometry parameters of a system are considered to be the classification of the geometrical isomerization of water clusters of $(H_2O)_5$ and $(H_2O)_6$, respectively: (A) linear $(H_2O)_5$, (B) boat $(H_2O)_5$, (C) ring $(H_2O)_6$, and (D) block $(H_2O)_6$. The geometry parameters for four models were obtained by both our method and the full ab initio MO method at the HF/6-31G(d,p) level.[29,30] The calculated geometry parameters are shown in Figure 1: the values in parentheses were obtained by full ab initio MO calculations. From the figure the geometry parameters obtained by the present method exhibit very good correspondence with those obtained by the full ab initio MO method.



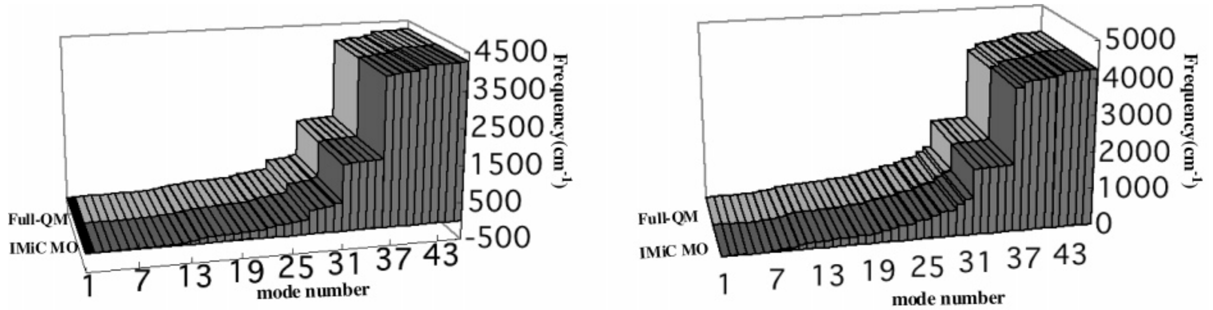
(A) Linear $(H_2O)_5$ (B) Boat $(H_2O)_5$



(C) Ring $(H_2O)_6$ (D) Block $(H_2O)_6$

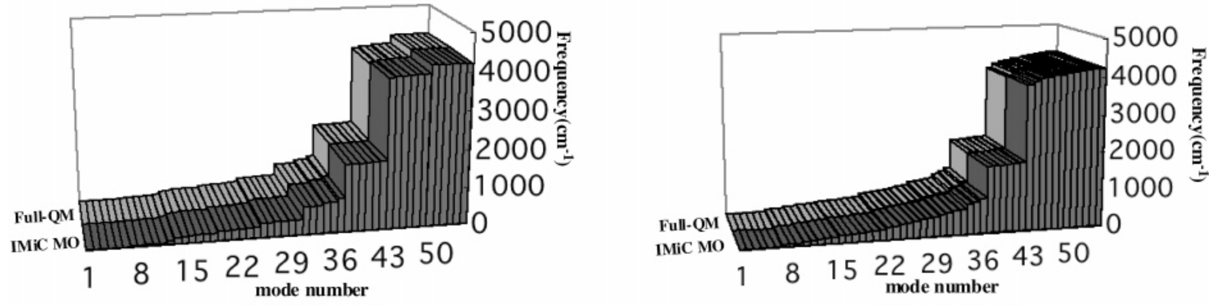
Figure 1. Structures for four models of water clusters calculated by the IMiC MO method and the full ab initio MO method with the HF/6-31G(d) level. The values in parentheses were obtained by the full ab initio MO method.

The vibrational frequencies for four models of water clusters were obtained by both our method and the full ab initio MO method. The calculated vibrational frequencies are shown in Figure 2, with the numerical table shown in the Supporting Information. For the model (A) of linear $(H_2O)_5$, the largest difference in each frequency obtained by both methods is 4.8 cm^{-1} and the mode corresponds to the O−H symmetric-stretching mode (4022.1 cm^{-1} by the IMiC MO and 4017.3 cm^{-1} by the full QM), and is only 0.1% in error. One imaginary frequency for the linear model is also obtained (−8.1 and −8.3 cm^{-1}) by both methods, corresponding to the bending mode of the entire system relating to the formation of a ring. The average error of the frequencies obtained by the present method is only 1.1 cm^{-1}, and the correspondence is quite good. For the model (B) of boat $(H_2O)_5$, the correspondence of the frequencies calculated by both methods is slightly worse than that of the above linear model. The largest difference in each frequency obtained by both methods is 30.1 cm^{-1} and the mode corresponds to the O−H symmetric-stretching mode (3869.6 cm^{-1} by the IMiC MO and 3839.5 cm^{-1} by the full QM), and is only 0.8% in error. The average error of the frequencies obtained by the present method is only 6.8 cm^{-1}. For models (C) and (D) of $(H_2O)_6$ clusters, the largest difference in each frequency obtained by both methods is 36.5 and 37.5 cm^{-1}, respectively. These frequencies correspond to the O−H symmetric-stretching mode (3943.3 cm^{-1} by the IMiC MO and 3906.8 cm^{-1} by the full QM for model (C) and 3871.4 and 3833.9 cm^{-1} for model (D)), and the errors are under 1%. The average error of the frequencies calculated by the present method is only 8.0 and 7.9 cm^{-1} for models (C) and (D), respectively. In the above four models of water clusters, the largest difference in each frequency obtained by both methods relates to the O−H symmetric-stretching mode and their errors are only under 1%. The average error of frequencies by the present method is in



(A) Linear of $(H_2O)_5$

(B) Boat of $(H_2O)_5$



(C) Ring of $(H_2O)_6$

(D) Block of $(H_2O)_6$

Figure 2. Normal vibrational frequencies of (A) linear $(H_2O)_5$, (B) boat $(H_2O)_5$, (C) ring $(H_2O)_6$, and (D) block $(H_2O)_6$ calculated by the IMiC MO method and the full ab initio MO method.

TABLE 1: Total Energy and Relative Energy for $(H_2O)_5$, $(H_2O)_6$, and $H^+(H_2O)_{14}$ Cluster Systems by IMiC MO and Full QM Calculations atthe HF/6-31G(d,p) Level

	total energy (hartree)			relative energy (kcal/mol)	
	full QM	IMiC MO	diff (kcal/mol)	full QM	IMiC MO
$(H_2O)_5$					
linear type	−380.160 512	−380.160 479	−0.02		
boat type	−380.175 470	−380.174 606	−0.54	−9.39	−8.86
$(H_2O)_6$					
ring type	−456.215 907	−456.215 264	−0. 40		
block type	−456.220 669	−456.219 349	−0.83	−2.99	−2.56
$H^+(H_2O)_{14}$					
complex	−1 064.920 267	−1 064.919 420	−0.53		
TS	−1 064.897 976	−1 064.897 800	−0.11	13.99	13.57

the range between 1 and 8 cm^{-1}, and the correspondence of the vibrational frequencies by both methods is fairly good.

Total energies and the isomerization energies of the water clusters, $(H_2O)_5$ and $(H_2O)_6$, are listed in Table 1. From the table, the total energy obtained by the IMiC MO method is slightly higher than that by the full ab initio MO method. The largest difference between total energies calculated by both our method and the full ab initio MO method is only 0.83 kcal/mol for the block type of $(H_2O)_6$. For the linear model, the difference of total energies calculated by both methods is only 0.02 kcal/mol, and is quite small. The differences of the relative energies of the isomerization for $(H_2O)_5$ and $(H_2O)_6$ models are only 0.53 and 0.43 kcal/mol, respectively. Thus, the agreement of energies calculated by both methods is also fairly good.

3.2. Hydration of Hydronium Ion and Transition State of Proton Shift. To check the accuracy of geometrical parameters, energies, and vibrational frequencies for larger cluster systems than those in the previous section, these properties of the hydration complex of hydronium ion and the transition state of proton shift of the $H^+(H_2O)_{14}$ cluster were calculated by both the present method and the full ab initio MO method with the HF/6-31G(d,p) level. For the complex and the transition state structures, the correlation between the bond distances obtained by the present method and the full ab initio MO method is shown in Figure 3 (complex (A) and transition state (B)). From the figure, it can be seen that the geometry parameters obtained by the present method exhibit very good correspondence with those by the full ab initio MO method.

The vibrational frequencies of the complex and the transition state obtained by both the present method and the full ab initio MO method are shown in Figure 4, with the numerical table shown in the Supporting Information. From the figure, the frequencies obtained by the present method indicate very good correspondence with those by the full ab initio MO method. For the complex, the largest difference in each frequency obtained by both methods is 83.4 cm^{-1} corresponding to the bending mode of hydronium ion (1456.8 cm^{-1} by the IMiC MO and 1373.3 cm^{-1} by the full QM), and the second one is 65.7 cm^{-1} corresponding to the mode of the O−H streaching hydronium ion (3077.3 cm^{-1} by the IMiC MO and 3011.6 cm^{-1} by the full QM). For the transition state, the largest difference in each frequency obtained by both methods is 50.3 cm^{-1} corresponding to the reaction path (−548.1 cm^{-1} by the IMiC MO and −598.4 cm^{-1} by the full QM) and the second one is 18.9 cm^{-1} with the mode corresponding to the O−H symmetric-streaching mode (3706.8 and 3687.9 cm^{-1}). The average errors of frequencies obtained by the present method are 7.0 and 4.4 cm^{-1} for the complex and the transition state systems, respectively. From comparison of the average errors of frequencies

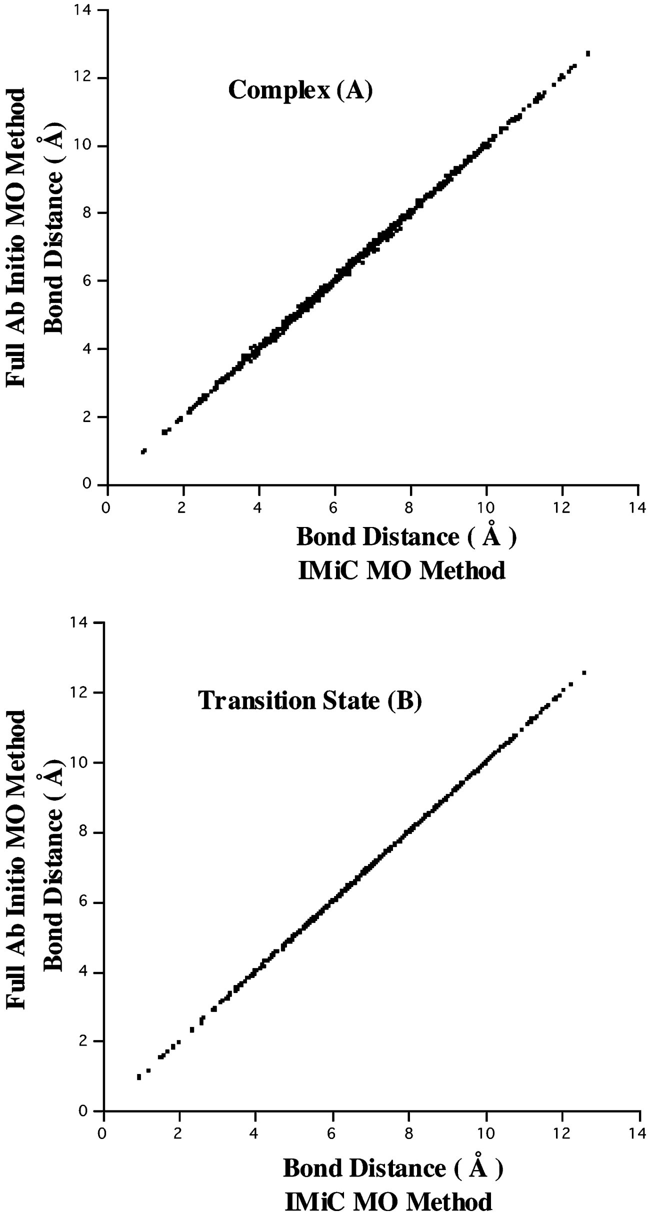
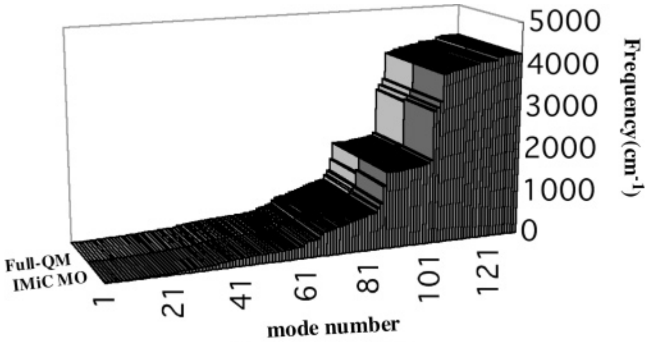


Figure 3. Bond distances of complex (A) and transition state (B) of hydration ion, $H^+(H_2O)_{14}$, obtained by the IMiC MO method against those by the full ab initio MO method.

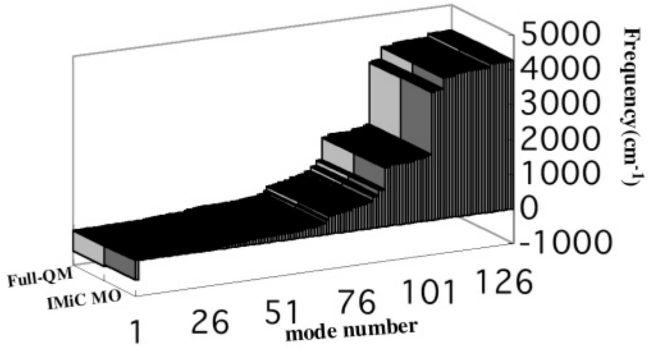
for the $H^+(H_2O)_{14}$ system and small clusters in the previous section, the average error does not depend on the system size.

The total energies of the complex and transition state of $H^+(H_2O)_{14}$ and the relative energies between the $H^+(H_2O)_{14}$ systems calculated by both methods are also listed in Table 1. The difference of total energies obtained by both methods is 0.11 and 0.53 kcal/mol for the transition state and the complex, and is almost the same level with that of small clusters. The difference of the relative energies is 0.42 kcal/mol, and is also quite small. From the above facts, it is considered that the difference errors for energies and normal vibrational frequencies obtained by our method do not depend on the system size.

3.3. Computation Times. To evaluate the variation in processing time for the number of CPU (central processing units) from 1 to 18 by the present method at the HF/6-31G(d,p) level, the real computation times for determining the force in the cluster system of 100 water molecules were observed with a shared memory computer including 18 CPU (SGI Power Challenge). The efficiency of parallel processing against the number of CPU is shown in Figure 5. As shown in the figure, the efficiency of parallel processing by the present method increases linearly against the number of CPU. Therefore, the present method is very suitable for full use of parallel processing and/or grid computing.



(A) Complex of $H^+(H_2O)_{14}$



(B) Transition State of $H^+(H_2O)_{14}$

Figure 4. Normal vibrational frequencies of the complex and transition state of $H^+(H_2O)_{14}$ calculated by the IMiC MO method and the full ab initio MO method.

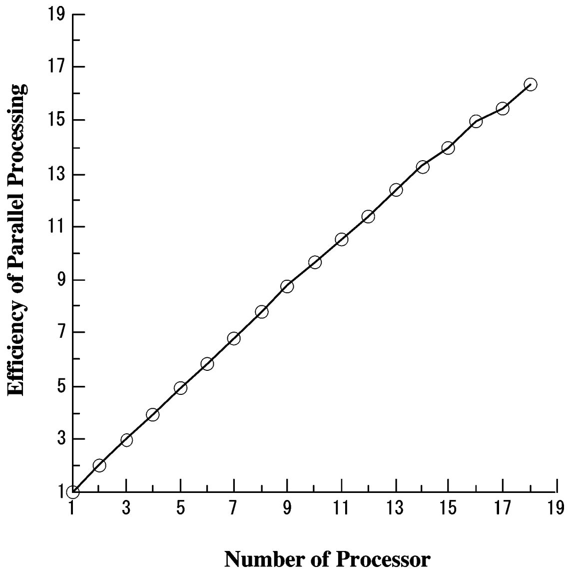


Figure 5. Efficiency of parallel processing against the number of processors.

4. Conclusions

We have developed the procedure (IMiC MO: ab initio integrated multicenter molecular orbital) for calculations of the total energy and the vibrational frequency of large cluster systems at the ab initio MO calculation level. To test the accuracy of the present method, the total energy and the vibrational frequency calculations for some water clusters, the hydrated hydronium ion cluster, and the transition state of proton shift were calculated by both the present method and the full ab initio MO method. The total energies calculated by the present method correspond well under 1 kcal/mol for all systems treated here with those by the full ab initio MO method. The vibrational frequencies calculated by the present method correspond very well with those by the full ab initio MO method. The average error of frequencies obtained by the present method is only under 8 cm^{-1} for all models and does not depend on the size of the systems. The accuracy of the energies and the vibrational frequencies obtained by the present method is fairly good. The algorithm of the present method can also make use of parallel processing and/or grid computing. As shown in the previous paper,[26] the computation time by the full ab initio MO method increases exponentially with the number of molecules, whereas for the present method the time increases linearly. The computation time for the cluster including over several molecules by the present method is less than that by the full ab initio MO method. Therefore, it is considered that only the present method can perform a "real simulation" without a model by assuming of activation points for a large cluster system at the ab initio MO level.

Acknowledgment. The present research has been supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture. The computer time was made available by the Computer Center of the Institute for Molecular Science and by Osaka Sangyo University with its SGI Power Challenge computer.

Supporting Information Available: Listing of vibrational frequencies. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Reichardt, C. *Solvents and Solvent Effects in Organic Chemistry*; Verlag-Chemie: Weinheim, Germany, 1979.

(2) Amis, E. S.; Hinton, J. F. *Solvent Effects on Chemical Phenomena*; Academic Press: New York, 1973; Vol. 1.

(3) Beak, P. *Acc. Chem. Res.* **1977**, *10*, 186.

(4) Nicol, M. F. *Appl. Spectrosc. Rev.* **1974**, *8*, 183.

(5) Bayliss, N. S.; McRae, E. G. *J. Phys. Chem.* **1954**, *58*, 1002.

(6) Warshed, A.; Levitt, M. *J. Mol. Biol.* **1976**, *103*, 227.

(7) Singi, U. C.; Kollmann, P. A. *J. Comput. Chem.* **1986**, *7*, 718.

(8) Field, M. J.; Bash, P. A.; Karplus, M. *J. Comput. Chem.* **1990**, *11*, 700.

(9) Maseras, F.; Morokuma, K. *J. Comput. Chem.* **1995**, *16*, 1170.

(10) Monard, G.; Merz, K.M., Jr. *Acc. Chem. Res.* **1999**, *32*, 904.

(11) Dapprich S.; Komaromi, I.; Byun, K. S.; Morokuma, K.; Frisch, M. J. *J. Mol. Struct.* (*THEOCHEM*) **1999**, *461*−*462*, 1.

(12) Day, P. N.; Jensen, J. H.; Gordon, M. S.; Webb, S. P.; Stevens, W. J.; Krauss, M.; Garmer, D.; Basch, H.; Cohen, D. *J. Phys. Chem.* **1996**, *100*, 1968.

(13) Kitaura, K.; Sawai, T.; Asada, T.; Nakano, T.; Uebayasi, M. *Chem. Phys. Lett.* **1999**, *312*, 319.

(14) Fedorov, D. G.; Kitaura, K. *J. Chem. Phys. A.* Submitted for publication.

(15) *Dynamics of Molecules and Chemical Reactions*; Wyatt, R. E., Zhang, J. Z. H., Eds; Marcel Dekker: New York, 1996.

(16) Puhovski, Y. P.; Rode, B. M. *J. Phys. Chem.* **1995**, *99*, 1566.

(17) Puhovski, Y. P.; Rode, B. M. *J. Chem. Phys.* **1995**, *102*, 2920.

(18) Craw, J. S.; Guest, J. M.; Cooper, M. D.; Burton, N. A.; Hillier, I. H. *J. Phys. Chem.* **1996**, *100*, 6304.

(19) Burton, N. A.; Chiu, S. S.-L.; Davidson, M. M.; Green, D. V.; Hillier, I. H.; McDouall, J. W.; Vincent, M. A. *J. Chem. Soc., Faraday Trans.* **1993**, *89*, 2631.

(20) Wong, M. W.; Wiberg, K. B.; Frisch, M. J. *J. Am. Chem. Soc.* **1992**, *114*, 1645.

(21) Adamo, C.; Cossi, M.; Barone, V. *J. Comput. Chem.* **1997**, *18*, 1993.

(22) Wong, M. W.; Wiberg, K. B.; Frisch, M. J. *J. Am. Chem. Soc.* **1992**, *114*, 1645.

(23) Car, R.; Parrinello, M. *Phys. Chem. Lett.* **1985**, *55*, 2471.

(24) Schinke, R. *Photodissociation Dynamics*; Cambridge University Press: Cambridge, UK, 1993.

(25) Kaledin, A. L.; Morokuma, K. *J. Chem. Phys.* **2000**, *113*, 5750.

(26) Morita, S.; Sakai, S. *J. Comput. Chem.* **2001**, *22*, 1107.

(27) Morita, S.; Sakai, S. Submitted for publication.

(28) Schmidt, M. W.; Buldridge, K. K.; Boatz, J. A.; Jensen, J. H.; Koseki, Gordon, M. S.; Nguyen, K. A.; Windus, T. L.; Elbert, S. T. *QCPE Bull.* **1990**, *10*, 52.

(29) Haviharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213.

(30) Gordon, M. S. *Chem. Phys. Lett.* **1980**, *76*, 163.