

Graduate School of Advanced Science and Engineering  
Waseda University

# 博士論文概要

## Doctoral Thesis Synopsis

論文題目  
Thesis Theme

Quantum Molecular Dynamics Study  
on Proton Transfer and Chemical Reaction  
in Condensed Phase

凝縮系のプロトン移動と化学反応に関する  
量子分子動力学研究

申請者  
(Applicant Name)

|               |            |
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| Aditya Wibawa | SAKTI      |
| サクテイ          | アディチャ ウィバワ |

Department of Chemistry and Biochemistry  
Research on Electronic State Theory

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In the global era, the necessity to maintain a severe environmental issue related to global warming and climate change is not avoidable. Global warming is observable elevation of average temperature of the earth, which is caused by the emission of greenhouse gases. One of the greenhouse gases that has been a concern since a few decades is carbon dioxide ( $\text{CO}_2$ ). Therefore, as an effort to reduce the emission of  $\text{CO}_2$  to atmosphere, there exists a technology so-called carbon capture and storage (CCS). In order to capture a gaseous  $\text{CO}_2$ , one of absorbents, namely, aqueous amine solution has been widely used in industry. The efficiency of the amine solution to absorb  $\text{CO}_2$  depends on physicochemical properties and composition of the amines. As one of the contributions to resolve such emergence environmental issue, this doctoral thesis proposes that a systematic computational study begins with a fundamental aspect of a pure water solvent up to a kinetics analysis of aqueous amine solution model. Amine is an alkaline compound that captures a proton from the environment, so that hydroxide ion ( $\text{OH}^-$ ) is formed. Diffusion of  $\text{OH}^-$  ion has an essential role to promote the formation of carbamate anion as one of the products in  $\text{CO}_2$  absorption process. Hence, as an initial study, the  $\text{OH}^-$  diffusion in the liquid water was investigated. As an initial study, more fundamental aspects of the excess proton in various configurations of water molecules were studied. By introducing one excess proton in a liquid water, one hydronium ion ( $\text{H}_3\text{O}^+$ ) is formed. Diffusivity of hydronium ion ( $\text{H}_3\text{O}^+$ ) in liquid and solid (ice) phases of water were comprehensively investigated in a spirit of molecular dynamics (MD) simulation.

This doctoral thesis consists of 8 chapters, as described as follows. Chapter 1 briefly introduces fundamental aspects of anomalous hydronium and hydroxide diffusion processes in condensed phase systems. The previous experimental and theoretical attempts to reveal a mechanism of  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$  ions diffusion in the liquid and solid water, as well as recent progress on the CCS technology using aqueous amine solutions. In an aqueous solution, hydrogen bonds play a role to stabilize a bulk structure and promoting proton transfer events between  $\text{H}_3\text{O}^+$  and water moieties. In the case of  $\text{OH}^-$  in the liquid water, hydrogen bonds have a slightly different role from the  $\text{H}_3\text{O}^+$  one, which is explained with more details in Chapter 4. A challenge on the current computational method for investigating the chemical reaction in the aqueous solution systems is also discussed, until finally an efficient computational method was used to reduce the computational cost while keeping the chemical accuracy.

Chapter 2 explains the computational and analysis methods used in this study. At first, an approximate density-functional theory method, namely, density-functional tight-binding (DFTB) formalism is briefly introduced. An enhanced version of that method, namely, divide-and-conquer type DFTB (DC-DFTB) is also explained. The MD method used for simulations is briefly discussed. A technique to improve the repulsive potential of DFTB parameter specifically, iterative Boltzmann inversion (IBI) is also explained. The IBI technique is reasonably useful to refine the structural property of a system, since it utilizes a fitting scheme for the two-body radial distribution function. Other chemical issue that is encountered is a high-barrier chemical reaction, so that a long simulation time will be necessary to observe a chemical reaction. In the present work, an enhance sampling method was adopted in order to reach a high-barrier chemical reaction by artificially adding Gaussian bias potentials, namely, metadynamics. Finally, routine analysis techniques, e.g. radial distribution

function and diffusion constants calculation, are also explained.

A first study is discussed in Chapter 3, namely, proton diffusion in a liquid water system, where the  $\text{H}_3\text{O}^+$  ion freely moves via Grotthuss mechanism, by means of structural diffusion. A large diffusivity of  $\text{H}_3\text{O}^+$  ion in the liquid water environment cannot be described correctly in a small unit-cell system containing 128 water molecules. It has been found that a vehicular diffusion, namely, a self-diffusion of water molecules dominates the overall diffusion process due to a large temperature fluctuation. As a result, structural diffusion is unphysically suppressed, which leads to a low contribution of the Grotthuss diffusion compared with the total  $\text{H}_3\text{O}^+$  ion diffusion. In order to minimize the temperature fluctuation, systems containing 523 water molecules were adopted. It led to reasonable Grotthuss diffusion constants as well as the Grotthuss diffusion barrier estimated via Arrhenius relationship. Both values are in good agreement with the experimental results.

Proton diffusion processes in ordered water configurations, namely, ice phases, are discussed in Chapter 4. The structures of ice  $\text{I}_h$ ,  $\text{I}_c$ , and III, as well as the melted ice VI phases were adopted. An excess proton was inserted to each ice structure, so that a structural defect was created. Once  $\text{H}_3\text{O}^+$  ion was created from such structural defect, it disrupts continuous hydrogen bond networks in ice structures. The effect of different degree of hexagonal and cubical symmetries in each structure was investigated. A loss of hexagonal symmetry was found to decrease the proton diffusivity significantly, rather than the cubical one. As decreasing the mass density, the hexagonal symmetry decreases, thus it decreases the proton diffusivity in ice III and the melted ice VI. Estimated Grotthuss diffusion barrier in the low-density ice phases are shown to be extremely lower than those of ice III and the melted VI phases.

In Chapter 5, the diffusivity of  $\text{OH}^-$  ion is comprehensively discussed. Previous theoretical study on  $\text{OH}^-$  diffusion process gives an idea to reveal the importance of the first hydration shell of  $\text{OH}^-$  ion to lead Grotthuss diffusion of  $\text{OH}^-$  ion. Different from the  $\text{H}_3\text{O}^+$  diffusion, which is triggered by the second hydration pattern, the first hydration shell is more important in case of  $\text{OH}^-$  ion. The first two mechanisms, i.e. static and dynamical hypercoordination mechanisms (SHM and DHM), were introduced. Both mechanisms highlight the role of the first hydration shell. In the case of SHM, the first hydration shell hyper-stabilized the OH ion, so that the proton transfer is inhibited. On the other hand, the DHM proposes a dynamical behavior of the first hydration shell for promoting the proton transfer. Another proposed mechanism, which is called as mirror image mechanism (MIM), describes an analogous mechanism with the  $\text{H}_3\text{O}^+$  ion. In the MIM, the second hydration shell is more important. Before further investigating the mechanism, however, it was found that the formation of water voids during the DFTB-MD simulation was unavoidable. The overbinding of the first hydration shell led to the formation of such water voids. In order to overcome this issue, the IBI method was used to improve the quality of the oxygen pair (O–O) repulsive potential. The O–O pair repulsive potential was improved so that the overbinding of the first solvation shell was reduced. Interestingly, by improving the structural property of the bulk water system, it also boosts the diffusivity of  $\text{OH}^-$  ion, which agrees well with the experimental value. A great advantage of the DC-DFTB-MD simulation to treat a large size simulations, i.e. to elongate the hydrogen bond networks is also shown in this chapter.

In Chapters 6 and 7, the application of DFTB-MD simulations on CCS is discussed. Chapter 6 discusses the evaluation of the degree of acidity,  $pK_a$  of 34 amine species as a test of the chemical accuracy of the DFTB method. The  $pK_a$  values were estimated using metadynamics sampling technique. Estimated values are in agreement with the experimental results. In Chapter 7, the chemical absorption between  $CO_2$  and amine species was studied via DC-DFTB-MD simulations. The initial condition was an aqueous amine mixture with different  $CO_2$  concentration, which was defined as the initial mole fraction between  $CO_2$  and amine moieties (neutral and protonated amines). Time-course changes of the number of species were investigated and fitted to the kinetic model derived from kinetic equations based on the elementary reactions. A direct kinetic property, namely, rate constants were estimated based on the fitting results. As a quantitative comparison to the experimental result,  $pK_a$  values were estimated based on the obtained rate constants. The estimated  $pK_a$  values are consistent with the one obtained from metadynamics simulations, as well as the experimental results.

Finally, in Chapter 8, general conclusions are deduced based on the present studies as well as the evaluation for future application of the DC-DFTB-MD simulations. Additionally, the future perspectives for applications of the DC-DFTB method on battery and heterogenous catalyst are also discussed in the next chapter.

## 早稲田大学 博士（理学） 学位申請 研究業績書

(List of research achievements for application of doctorate (Dr. of Science), Waseda University)

氏名 Aditya Wibawa Sakti 印

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|---------------------|---|
| Academic paper<br>○ | <ol style="list-style-type: none"> <li data-bbox="296 584 1453 734">1. “Divide-and-Conquer-Type Density-Functional Tight-Binding Molecular Dynamics Simulations of Proton Diffusion in a Bulk Water System”<br/><i>J. Phys. Chem. B</i>, <b>120</b> (1), 217 (2016).<br/><u>Hiromi Nakai</u>, <u>Aditya Wibawa Sakti</u>, and Yoshifumi Nishimura</li> <li data-bbox="296 779 1453 929">2. “Divide-and-Conquer-Type Density-Functional Tight-Binding Simulations of Hydroxide Ion Diffusion in Bulk Water”<br/><i>J. Phys. Chem. B</i>, <b>121</b> (6), 1362 (2017).<br/><u>Aditya Wibawa Sakti</u>, Yoshifumi Nishimura, and Hiromi Nakai</li> <li data-bbox="296 974 1453 1124">3. “Divide-and-Conquer Density-Functional Tight-Binding Molecular Dynamics Study on the Formation of Carbamate Ions during CO<sub>2</sub> Chemical Absorption in Aqueous Amine Solution”<br/><i>Bull. Chem. Soc. Jpn.</i>, <b>90</b> (11), 1230 (2017).<br/><u>Aditya Wibawa Sakti</u>, Yoshifumi Nishimura, Hiroshi Sato, and Hiromi Nakai</li> <li data-bbox="296 1169 1453 1319">4. “Rigorous pK<sub>a</sub> Estimation of Amine Species Using Density-Functional Tight-Binding-Based Metadynamics Simulations”<br/><i>J. Chem. Theory Comput.</i>, <b>14</b>, 351 (2018).<br/><u>Aditya Wibawa Sakti</u>, Yoshifumi Nishimura, and Hiromi Nakai</li> <li data-bbox="296 1364 1453 1514">5. “Density-Funtional Tight-Binding Molecular Dynamics Simulations of Excess Proton in Ice I<sub>h</sub>, Ice I<sub>c</sub>, Ice III, and Melted Ice VI Phases”<br/><i>J. Phys. Chem. A.</i>, <b>122</b>, 33 (2018).<br/><u>Aditya Wibawa Sakti</u>, Yoshifumi Nishimura, Chien-Pin Chou, and Hiromi Nakai</li> </ol> |

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|-----------------------------|--|
| International<br>Conference | <ol style="list-style-type: none"> <li data-bbox="312 427 1455 613">1. “Application of divide-and-conquer type density-functional tight-binding simulation for proton diffusion in bulk water system”<br/>Seventh Asia-Pacific Conference of Theoretical and Computational Chemistry (APCTCC 7), Kaohsiung (Taiwan), January 25–28, 2016.<br/><u>Aditya Wibawa Sakti</u>, Yoshifumi Nishimura, and Hiromi Nakai</li> <li data-bbox="312 658 1455 844">2. “Divide-and-Conquer Type DFTB Application for Hydronium and Hydroxide Ions Diffusion in the Bulk Water System”<br/>International CECAM-Workshop and Tutorial on Approximate Quantum Methods in the Ab Initio World, Beijing (China), November 6–13, 2016.<br/><u>Aditya Wibawa Sakti</u>, Yoshifumi Nishimura, and Hiromi Nakai</li> <li data-bbox="312 889 1455 1075">3. “Density-Functional Tight-Binding Molecular Dynamics Simulations of Proton Diffusion in the Bulk Ices and Liquid Water”<br/>11<sup>th</sup> Triennial Congress of the World Association of Theoretical and Computational Chemists (WATOC 2017), Munich (Germany), August 27–September 1, 2017.<br/><u>Aditya Wibawa Sakti</u>, Yoshifumi Nishimura, Chien-Pin Chou, and Hiromi Nakai</li> <li data-bbox="312 1120 1455 1305">4. “A Linear-Scaling Approximate DFT Method for Quantum Mechanical Molecular Dynamics Simulations of Large Systems”<br/>17<sup>th</sup> International Conference of Density-Functional Theory and Its Application (DFT 2017), Tallberg (Sweden), August 21–25, 2017.<br/>Yoshifumi Nishimura, <u>Aditya Wibawa Sakti</u>, and Hiromi Nakai</li> <li data-bbox="312 1350 1455 1536">5. “Development of Large-Scale Quantum Mechanical Molecular Dynamics Simulation: Divide-and-Conquer Density-Functional Tight-Binding Approach”<br/>First International Workshop on Advanced Methods for Nano Materials Design, Gyeonggi-do (Korea), July 14, 2017.<br/>Yoshifumi Nishimura, <u>Aditya Wibawa Sakti</u>, and Hiromi Nakai</li> <li data-bbox="312 1581 1455 1767">6. “Fast excess proton diffusion in ice phases: A molecular dynamics study at approximate density-functional level”<br/>Car-Parrinello Molecular Dynamics in 2017 (CPMD2017), Tsukuba (Japan), October 18–20, 2017.<br/><u>Aditya Wibawa Sakti</u>, Yoshifumi Nishimura, Chien-Pin Chou, and Hiromi Nakai</li> </ol> |

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|---------------------|---|
| Domestic conference | <ol style="list-style-type: none"> <li data-bbox="288 427 1455 577">1. “Divide-and-Conquer type Density-Functional based Tight-Binding Molecular Dynamics (DC-DFTB-MD) Simulation of Proton Transfer in Bulk Water System.”<br/>The 9<sup>th</sup> Molecular Science Symposium, Tokyo, September 16–19, 2015.<br/><u>Aditya Wibawa Sakti</u>, Yoshifumi Nishimura, and Hiromi Nakai</li> <li data-bbox="288 618 1455 768">2. “ナノスケール化学反応系に対する分割統治型密度汎関数強束縛分子動力学 (DC-DFTB-MD) シミュレーション”<br/>The 9<sup>th</sup> Molecular Science Symposium, Tokyo, September 16–19, 2015.<br/>Yoshifumi Nishimura, <u>Aditya Wibawa Sakti</u>, and Hiromi Nakai</li> <li data-bbox="288 808 1455 981">3. “分割統治型密度汎関数強束縛分子動力学(DC-DFTB-MD)法によるプロトン拡散シミュレーション”<br/>第6回 CMSI 研究会（戦プロ最終成果報告会）, Tokyo, December 7–8, 2015.<br/>Yoshifumi Nishimura, <u>Aditya Wibawa Sakti</u>, and Hiromi Nakai</li> <li data-bbox="288 1021 1455 1234">4. “分割統治型密度汎関数強束縛分子動力学(DC-DFTB-MD)法によるプロトン拡散シミュレーション”<br/>TCCI 第6回研究会, Okazaki Conference Center for Natural Science Research Organization, March 14–15, 2016.<br/>Yoshifumi Nishimura, <u>Aditya Wibawa Sakti</u>, Hiromi Nakai</li> <li data-bbox="288 1274 1455 1424">5. “Linear-scaling quantum mechanical molecular dynamics simulation with divide-and-conquer density-functional tight-binding method”<br/>日本化学会 第97春季年会, Tokyo, March 16–19, 2017.<br/>Yoshifumi Nishimura, <u>Aditya Wibawa Sakti</u>, and Hiromi Nakai</li> </ol> |
| Award               | <p data-bbox="288 1552 1455 1664">“Accurate <math>pK_a</math> Evaluation by Metadynamics Simulation at the Density-Functional Tight-Binding Level”<br/>日本コンピュータ化学会 (SCCJ) 奨学賞, Tokyo, June 9, 2017.</p>   |