# Development of Experiment Integrated Computational Chemistry and Its Application to Advanced Materials

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### 1. Introduction

Needless to say, developments of new advanced materials are of great importance for not only advance in the present technology but also the new technologies, e.g. the next-generation electronic devices. In order to accelerate the developments of advanced materials, the findings detailed in both electronic and atomic levels are indispensable. However, there still exist difficulties in accessing electronic and atomic levels for materials, and hence theoretical investigation is demanded. In this sense, the first-principles molecular dynamics (FPMD) method is powerful tool in order to understand a dynamics of matter from the electronic and atomistic points of view. However, FPMD method requires extremely huge computation cost. Our group has developed tight-binding quantum chemical molecular dynamics (TB-QCMD) simulator [1, 2]. It has been successfully applied to the electronic structure calculations of advanced materials [3]. Based on the above TB-QCMD simulator and our original MD simulator [4], a novel QCMD simulator (UA-QCMD) was developed recently [5-7]. This simulator can perform electronic structure calculations for large-scale systems consisted of a few thousands atoms.

On the basis of these simulators, measurement simulators for x-ray diffraction (XRD), neutron diffraction (ND), and vibrational spectroscopy were recently developed. Combining these simulators and precise experiments, we recently proposed a novel concept, "experiment integrated computational chemistry approach". In this paper, the developments of the above novel simulators and their applications to advanced materials will be summarized.

## 2. Methods

#### XRD and ND Simulators

The developed XRD and ND simulators calculate scattering angles based on Bragg's law and scattering intensities. Atomic scattering factors for XRD simulators and scattering amplitudes for ND simulators are taken from experimental values. These simulators are available for system consisted of more than 10,000 atoms.

Vibrational Spectroscopy Simulators

Vibrational spectroscopy simulator was developed based on the conventional  $F_X$  matrix method which is equivalent to the conventional GF matrix method [8]. Vibrational wavenumbers,  $n_j$ , of the jth vibrational mode, are proportinal to square root values of the eigenvalues,  $l_j$ , which are obtained by solving the secular determinant including a force constant matrix **F** and Cartesian coordinates **X**, as shown in eq. (1),

$$\boldsymbol{n}_{j} = \frac{\boldsymbol{l}_{j}}{\sqrt{2\boldsymbol{p}\,\boldsymbol{c}}} \tag{1},$$

where c is the speed of light in vacuum. In order to solve the secular determinant, the dsygv subroutine for generalized eigenvalue problems in LAPACK [9] was used. A force constant matrix, **F**, is determined by applying the finite difference method to the forces acting on atoms. The vibrational spectroscopy simulator is applicable for both our QCMD simulator and MD simulator.

#### 3. Results and Discussion

Validations of XRD and ND Simulators

The spectroscopic characterization simulators, XRD and ND, were attempted their validation by comparing the calculated XRD and ND patterns for H<sub>2</sub>O with the experimental ones. Fig. 1(a) and 1(b) shows the XRD and ND pattern for the water model consisted of 1620 molecules obtained by our XRD and ND simulator, respectively.By comparing with the experimental results [10, 11], it was found that our present results were in line with the experimental ones. Thus, our XRD and ND simulators were justified.



Fig. 1 Structure analysis results of 1620 H<sub>2</sub>O molecules: (a) calculated XRD and (b) calculated ND pattern.

#### Validations of Vibrational Spectroscopy Simulators

The calculated vibrational spectrum of H<sub>2</sub>O molecules by using our simulator was compared with the experimental result. Major two peaks at, *ca.* 3500 and 600 cm<sup>-1</sup>, were observed and agreed with the two bands, the stretching vibration mode (starting from *ca.* 3300 to 3500 cm<sup>-1</sup>) and to the libration mode (starting from *ca.* 500 to 800 cm<sup>-1</sup>), respectively, obtained by experiment [12]. The other characteristic peaks were observed at *ca.* 200 and 1550 cm<sup>-1</sup>, which corresponds to the intermolecular mode and the bending mode, respectively. These were also in agreement with the experimental result [12]. Thus, our vibrational spectroscopy simulators were validated.

#### Examples: Modeling of amorphous SiO<sub>2</sub>

Amorphous SiO<sub>2</sub> is important material as a gate dielectric one in CMOS. Now we are attempting to construct a realistic model of amorphous SiO<sub>2</sub> using our measurement simulators, on the basis of experimental XRD data. Fig. 2 shows an example for a constructed model for amorphous SiO<sub>2</sub> and its calculated XRD pattern. From the inspection of Fig. 2(a), it was seen there exists two regions in the constructed model for amorphous SiO<sub>2</sub>, namely 'boundary' region and 'crystalline-like' region. By applying our XRD simulator to this model, XRD pattern as shown in Fig. 2(b) was obtained. In this figure, it was confirmed that a highest peak appears to  $2q = 21^{\circ}$ , which was in qualitatively agreement with experimental results. This preliminary result implies the importance of consideration of two regions in the determination of atomic structures of SiO<sub>2</sub>.



Fig. 2 A constructed model for amorphous SiO<sub>2</sub>: (a) its computer graphics image and (b) calculated XRD pattern.

#### References

- K. Kasahara, H. Tsuboi, M. Koyama, A. Endou, M. Kubo, C. A. Del Carpio, A. Miyamoto, Electrochem. Solid-State Lett. 9 (2006) A490.
- [2] A. Endou, H. Onuma, S. Jung, R. Ishimoto, H Tsuboi, M. Koyama, H. Takaba, M. Kubo, C. A. Del Carpio, and A. Miyamoto, Jpn. J. Appl. Phys., 46 (2007) 2505.
- [3] H. Onuma, H. Tsuboi, M. Koyama, A. Endou, H. Takaba, M. Kubo, C. A. Del Carpio, P. Selvam, and A. Miyamoto, Jpn. J. Appl. Phys. 46 (2007) 2534.
- [4] P. Selvam, H. Tsuboi, M. Koyama, A. Endou, H. Takaba, M. Kubo, C. A. Del Carpio, and A. Miyamoto, Rev. Chem. Eng. 22 (2006) 377.
- [5] A. Endou, T. Onodera, S. Nara, A. Suzuki, M. Koyama, H. Tsuboi, N. Hatakeyama, H. Takaba, C. A. Del Carpio, M. Kubo, and A. Miyamoto, Tribol. Online 3 (2008) 280.
- [6] Md. K. Alam, F. Ahmed, K. Nakamura, A. Suzuki, R. Sahnoun, H. Tsuboi, M. Koyama, N. Hatakeyama, A. Endou, H. Takaba, C. A. Del Carpio, M. Kubo, and A. Miyamoto, J. Phys. Chem. C, in press.
- [7] A. Endou, H. Onuma, H. Kikuchi, I. Yamashita, K. Serizawa, K. Inaba, R. Sato, M. Koyama, H. Tsuboi, N. Hatakeyama, H. Takaba, C. A. Del Carpio, M. Kubo, H. Kajiyama, and A. Miyamoto, Jpn. J. Appl. Phys. 48 (2009) 04C126.
- [8] E. B. Wilson, Jr., J. Chem. Phys. 7 (1939) 1047.
- [9] http://www.netlib.org/lapack/
- [10] G. Hura, J. M. Sorenson, R. M. Glaeser, T. Head-Gordon, J. Chem. Phys. **113** (2000) 9140.
- [11] A. K. Soper, J. Phys.: Condens. Matt. 19 (2007) 335206.
- [12] J.-B. Brubach, A. Mermet, A. Filabozzi, A. Gershcel, P. Roy, J. Chem. Phys. **122** (2005) 184509.