3.6 Software Advancement Projects and Workshop Support

Improvement of Quantum ESPRESSO implementing the ESM-RISM method

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In this project, we modified the source code of the Quantum ESPRESSO (QE) package, a popular open-source code for studying the electronic structure of materials with the density functional theory (DFT).

Before starting the project, we implemented several simulation techniques to elucidate a microscopic detail of an electrochemical reaction and atomic geometry under an electrochemical environment at the electrode and electrolyte interface, called the electrochemical interface. To reduce the calculation time for obtaining the equilibrium electrolyte distribution, we utilized the classical liquid theory, called the reference interaction site model (RISM), in a particular part of the electrolyte region [1]. The RISM region can describe the electric double layer near the interface, which includes the accumulation and depletion of the counter-ions in the electrolyte when introducing an excess charge on the electrode surface by applying a bias voltage. These techniques are made possible by introducing a grand canonical ensemble for both electrons on the electrode [2] and ions in the electrolyte [1] and solving the Poisson equation of the system under the open boundary condition along the perpendicular direction of the interface [3]. We call this hybrid simulation technique applicable to interfacial electrochemistry the ESM-RISM method.

In the ESM-RISM method, we need to solve the Laue represented Poisson and RISM equations.

$$\{\partial_z^2 - g_\parallel^2\}V(\boldsymbol{g}_\parallel, z) = -4\pi\rho(\boldsymbol{g}_\parallel, z), \qquad (1)$$

$$h_\gamma(\boldsymbol{g}_\parallel, z) = \sum_\alpha \int \mathrm{d}z' c_\alpha(\boldsymbol{g}_\parallel, z') \times \chi_{\alpha\gamma}(\boldsymbol{g}_\parallel, |z - z'|), \qquad (2)$$

where $\boldsymbol{g}_\parallel$, $g_\parallel$, ρ, h, c, χ, α, and γ represent, respectively, a wave vector parallel to the interface, the absolute value of $\boldsymbol{g}_\parallel$, the total charge density, the total correlation function, the direct correlation function, the solution susceptibility, the atomic sites of implicit and explicit solutions. These two equations are related through the electrostatic potential $V(\boldsymbol{g}_\parallel, z)$ [1]. In the first implementation of ESM-RISM, we used a common z mesh points for both Eqs. (1) and (2). Figure 1(a) shows the schematic illustration of the z mesh in the calculation cell. Since the mesh points along the z direction are common, the electrostatic potential can be easily shared in the equations, and this model is relevant for the thin electric double layer (EDL) system. However, we need to solve the RISM equation in a wide range of solution regions at low electrolyte concentrations because the EDL becomes thicker according to the Debye-Hückel theory. In this situation, it is more versatile to be able to solve the Eqs. (1) and (2) with different mesh spacing and different unit cell along z direction, L_z^{DFT} and L_z^{RISM} (see Fig. 1(c)). Thus we modify our ESM-RISM code from the original common mesh to an individual one.

To accomplish the goal, we need to map an arbitrary function f on the common mesh onto $\tilde{f}$ on the individual mesh. As seen in the figure. 1(d), we employ the Fourier interpolation

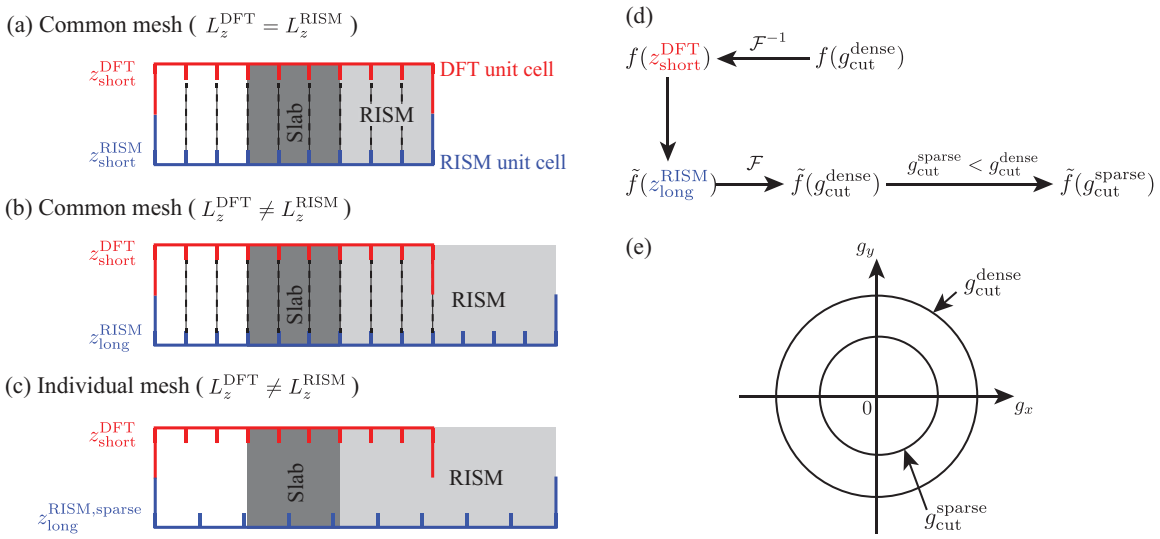

Figure 1: Schematic illustrations of a calculation cell. The z-mesh points used in DFT and RISM calculations for (a) a common mesh with same cell sizes along z-direction ($L_z^{\mathrm{DFT}} = L_z^{\mathrm{RISM}}$), (b) a common mesh with different cell sizes, and (c) an individual mesh with different cell size. The horizontal red and blue lines with grids represent the unit cell size along the z-direction for the DFT and RISM calculations. Conceptually, the $z_{\mathrm{x}}^{\mathrm{y}}$ indicates a grid point of x (= long or short) unit cell for y (= DFT or RISM) calculation. (d) The mapping sequence of an arbitrary function $f(g_{\mathrm{cut}}^{\mathrm{dense}})$ to $\tilde{f}(g_{\mathrm{cut}}^{\mathrm{sparce}})$, where $\mathcal{F}$ and $\mathcal{F}^{-1}$ are the forward and backward Fourier transform, respectively. (e) Schematic illustration of cutoff radii in the reciprocal space ($g_{\mathrm{cut}}^{\mathrm{dense}}$ and $g_{\mathrm{cut}}^{\mathrm{sparse}}$). The "sparse" in (c) means a sparse mesh with a small cutoff radius, $g_{\mathrm{cut}}^{\mathrm{sparce}}$.

scheme. First, we did the backward Fourier transform from $f(g_{\mathrm{cut}}^{\mathrm{dense}})$ to $f(z_{\mathrm{short}}^{\mathrm{DFT}})$, and then we map the f in the DFT cell onto the $\tilde{f}$ in the RISM cell by the following condition:

$$\tilde{f}(z) = \begin{cases} f(z) & z = z_{\mathrm{short}}^{\mathrm{DFT}}, \\ 0 & z \neq z_{\mathrm{short}}^{\mathrm{DFT}}. \end{cases} \tag{3}$$

After the forward Fourier transformation, the dense FFT grids $g_{\mathrm{cut}}^{\mathrm{dense}}$ is reduced to the sparse FFT grids $g_{\mathrm{cut}}^{\mathrm{sparse}}$ (see Fig. 1(e)). In the program, we first apply the mapping sequence from ρ to $\tilde{\rho}$. Secondly, by solving the Eq. (1) with $\tilde{\rho}$, the electrostatic potential in the RISM cell can include the contribution from the DFT charge. Finally, we solve the RISM equation Eq. (2) on the sparse grids $z_{\mathrm{long}}^{\mathrm{RISM,sparse}}$.

After finishing the code development, we checked the validity of our implementation by comparing the total energy and the force acting on atoms between the two calculations with Figs. 1 (a) and (c) configurations.

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Unified platform of experiment-data analysis for 2D material structure

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In a PASUMS project at FY2021, an open-source data-analysis framework 2DMAT [1-4] has been developed for experimental measurements of two-dimensional material structures. The present project is the successor of one at FY2020. The current version of 2DMAT is an unified platform for the analysis of different experimental measurement techniques, total-reflection high-energy positron diffraction (TRHEPD) [5], surface X-ray diffraction (SXRD), and low-energy electron diffraction (LEED) experiments by installing corresponding forward problem solvers that generate diffraction intensity data from a given dataset of the atomic positions. Among them, SXRD and LEED were supported as a result of the present project. The current version of 2DMAT offers five analysis methods: (i) Nelder-Mead optimization, (ii) grid search, (iii) Bayesian optimization, (iv) replica exchange Monte Carlo (REMC) method, and (v) population-annealing Monte Carlo (PAMC) method. Methods (ii) through (v) are implemented by parallel computation, which is efficient not only for personal computers but also for supercomputers. Among the above five methods, the PAMC method was implemented in the present project. In addition, the forward problem solver of TRHEPD was also published as an open-source software package by the present project [6,7].

2DMAT was applied to the structure analysis of $Si_4O_5N_3$ / 6H-SiC(0001)-($\sqrt{3} \times \sqrt{3}$)R30° surface, a novel two-dimensional semiconductor, by TRHEPD experiment [2]. A data-driven sensitivity analysis was proposed for the quantitative analysis of experimental uncertainties. The variation over individual fitting parameters was analyzed by solving the eigenvalue problem of the variance-covariance matrix. 2DMAT was used also in other application studies by TRHEPD experiment and the study by T. Takeda (Waseda U.) *et al*. won a poster-session prize [8]. The analysis methods in 2DMAT are general and can be applied also to other problems and was applied to a performance prediction of massively parallel computation by Bayesian inference [4].

As activities to promote 2DMAT, hands-on workshops were held in April 2021 and April

2022, and a study group was held in September 2021. Test calculations in massively parallel computations by the Fugaku supercomputer are underway (hp210228, hp210267).

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Report of CCMS hands-on sessions in the 2021 fiscal year

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In the 2021 fiscal year, Center for Computational Materials Science (CCMS) in the Institute for Solid State Physics (ISSP) held three hands-on sessions where the ISSP supercomputer was used [1-3]. In this report, we briefly summarize the hands-on sessions.

Table 1 shows the list of the hands-on sessions in the 2021 fiscal year. Software used in the hands-on sessions are 2DMAT, PHYSBO, and HΦ: 2DMAT is a Python package to search an optimal result by applying a search algorithm to a direct-problem solver [4], PHYSBO is a Python library to perform a fast and scalable Bayesian optimization [5], and HΦ is a package of solvers for quantum many body systems [6]. Development of these software was supported by “Project for advancement of software usability in materials science” (PASUMS) [7]. In all of the hands-on sessions, lecturers explained the basics of each software and gave its tutorial. Materials of these hands-on sessions are available on each official page (in Japanese) [8-10].

Table 1: List of CCMS hands-on sessions where the ISSP supercomputer was used in the 2021 fiscal year.

Date	Lecturer	Software
Apr. 20	T. Hoshi et al.	2DMAT[4]
May 24	K. Tsuda et al.	PHYSBO[5]
Oct. 1	Y. Yamaji et al.	HΦ[6]

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[3] https://ccms.issp.u-tokyo.ac.jp/event/5078

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[5] https://www.pasums.issp.u-tokyo.ac.jp/physbo/

[6] https://www.pasums.issp.u-tokyo.ac.jp/hphi/

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[8] https://www.pasums.issp.u-tokyo.ac.jp/2dmat/doc/paper/

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Supercomputer course of Computational Materials Design (CMD®) workshop

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The 39th Computational Materials Design (CMD®) workshop (CMD39) has been held from September 6th to September 10th and the 40th CMD® workshop (CMD40) has been done from February 21st to February 25th. Both were held online. In this workshop we have the supercomputer course to train up human resources to advance research by using system B supercomputer of ISSP, the University of Tokyo.

In CMD39 eight participants took the supercomputer course and got a tutorial on STATE-Senri developed by Y. Morikawa. After giving the introductory lecture of large-scale computing by M. Geshi and explaining how to use the supercomputer of ISSP, participants started constructing calculation models of their own research subjects with the help of the lecturers. Then they carried out calculations using supercomputers. Concrete themes were molecular adsorption on solid surfaces, chemical reactions at electrode interfaces, oxygen reduction reaction on carbon electrodes, and so on. The participants performed the calculations and examined the results.

In CMD38 two participants took the supercomputer course and used the supercomputer of ISSP. They got a tutorial on RSPACE developed by T. Ono. After giving the introductory lecture of large-scale computing by M. Geshi and introducing the calculation method of electronic states and electron conduction property using RSPACE, exercises instructed in the manual were carried out. Then, electronic structure calculations were carried out for various molecules, and the electronic density distribution was visualized. The attendees also performed massively parallel calculations to confirm the efficiency for parallel computing. Finally, the electron conduction property of molecules connected to atomic wires was analyzed.