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
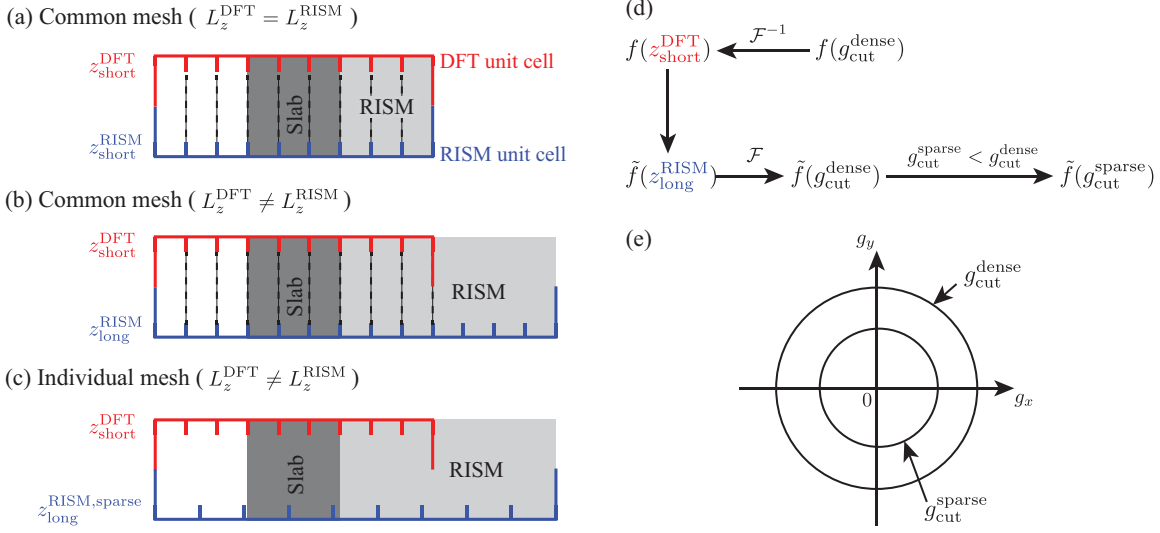
Figure 1: Schematic illustrations of a calculation cell. The z-mesh points used in DFT and RISM calculations for (a) a common mesh with same cell sizes along z-direction ($L_z^{\mathrm{DFT}} = L_z^{\mathrm{RISM}}$), (b) a common mesh with different cell sizes, and (c) an individual mesh with different 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_x^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:

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

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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