First-principles study of water molecules at the electrified graphene surface

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INTRODUCTION

A detailed understanding of the atomic and electronic structures of electrified electrochemical interfaces has critical implications for the development of advanced energy conversion and storage devices. Here, graphene has been regarded as an ideal component for electrode materials due to its excellent mechanical, electrical, and chemical properties. Recently, for the improved understanding of electrified electrochemical interfaces, first-principles characterizations based on the approach combining density functional theory (DFT) and non-equilibrium Green's function (NEGF) have been utilized with much successes. However, due to the requirement of semi-infinite electrodes, the DFT-NEGF approach so far could not be applied to graphene-based electrochemical interface models. In this presentation, taking the advantage of the multi-space constrained-search DFT (MS-DFT) formalism [1-3] that can handle the electrified finite electrodes, we firstly investigate the total enthalpy change of the water molecule on the electrified graphene electrode surface in a fully first-principles manner. Moreover, by carrying out nonequilibrium molecular dynamics simulations with MS-DFT, we will study the bias-dependent configurations of water molecules at the electrified graphene-water interfaces. Comparing the interfacial water structures with those on metal electrodes, we extract important insight into the water at electrified electrochemical interfaces.

THEORETICAL BACKGROUND

In recent years, we presented a variational approach for non-equilibrium open quantum systems based on the viewpoint that maps quantum transport processes to multi-space excitation counterparts, and established as a practical ab initio computational scheme the multi-space constrained-search DFT (MS-DFT) formalism [1-3]. Within MS-DFT, the non-equilibrium state of a channel C established by the left electrode L and right electrode R at the electrochemical potentials μ_L and μ_R, respectively, is calculated by variationally minimizing the total energy functional within the constraint of an applied finite bias voltage $eV_b = \mu_L - \mu_R$. Here in, we applied MS-DFT to the electrode-water molecule interface system where a single water molecule, which corresponds to the C, was placed close to one side of the left electrode surface (L). In order to isolate the electrode-water interface from the direct interaction induced by the other side of the right electrode (R), the distance between two electrodes is set to 20 Å.

COMPUTATIONAL DETAILS

All calculations were performed within SIESTA package [4], in which MS-DFT is implemented, and we used the gradient-dependent exchange-correlation (XC) functionals which includes van der waals corrections (vdW) [5]. Double ζ-plus-polarization-level numerical atomic orbital basis sets were employed together with the Troullier-Martins type norm-conserving pseudopotentials [6]. The mesh cutoff of 800 Ry for the real-space integration, and $5 \times 5 \times 1$ and $8 \times 8 \times 1$ Monkhorst-Pack k-points grid of the Brillouin zone were sampled for the Au(111) slab and graphene monolayer electrode, respectively. The atomic geometries were optimized until the total residual force was below 0.005 eV/ Å using the conjugate gradient algorithm.

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