Theory of Electric Enthalpy of Formation in Electrified Interface

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INTRODUCTION

The recent developments in the modern theory of polarization or density polarization functional theory have derived a well-established concept of the electric enthalpy providing a detailed understanding of the electrified interfaces in the field of electromechanics [1-3]. Despite their success, including the electrode potential effects on first-principles calculations remains a significant challenge due to the difficulty of incorporating the non-equilibrium electrostatic potential condition. While the non-equilibrium Green's function (NEGF) formalism coupled with density-functional theory (DFT) is adopted as a standard approach to finite-bias calculations, it has fundamental limitations raised from the grand-canonical condition which yields an ill-defined quantity of total energy. In this work, we establish a theory of the electric enthalpy based on the multi-space constrained-search DFT (MS-DFT) formalism [4] which allows the variational total energy of non-equilibrium states employing the microcanonical viewpoint. Within MS-DFT, we formulate the non-equilibrium electric enthalpy of the interface systems consisting of electrode and channel systems. Our framework is tested with gold and graphene-based nanocapacitor models by evaluating the biased-induced changes in electric enthalpy. This study will provide a quantitative understanding of the electrified interface's energetics which has critical implications for the development of advanced energy conversion and storage devices.

METHOD

As an alternative to DFT-NEGF scheme, the MS-DFT formalism is based on the microcanonical viewpoint which maps quantum transport processes to multi-space excitation counterparts that allows the variational total energy of a non-equilibrium state of a junction model consisting of channel (C), left electrode (L), and right electrode (R), where their electrodes are at different electrochemical potentials of μ_L and μ_R.

In this study, we utilize the MS-DFT formalism to obtain L/C/R electron densities of total junction system under applied bias V_b, and thus we can formulate the electric field ($\boldsymbol{\mathcal{E}}_{L+R}^V$) of the electrodes and dipole moment ($\boldsymbol{p}_C^V$) of C regions. We then calculate the non-equilibrium electric enthalpy of junction according to

$$\mathcal{F}_{L+C+R}^V = E_{L+C+R}^V - \boldsymbol{\mathcal{E}}_{L+R}^V \cdot \boldsymbol{p}_C^V, \qquad (1)$$

where E_{L+C+R}^V is the non-equilibrium total energy of the junction.

RESULTS

We first evaluate the capability of MS-DFT calculations to properly decompose the total electron densities of junction system into the L/C/R electron densities. As shown in Fig. 1, the electron density of nanocapacitor models are separated into electrode's and channel's electron densities. These quantities can properly reproduce the dielectric profiles obtain from the conventional finite-field approach (Fig. 2). We then apply our method to calculate the non-equilibrium enthalpy for a single water molecule placed next to Au(111) electrode and graphene surface (Fig. 3).

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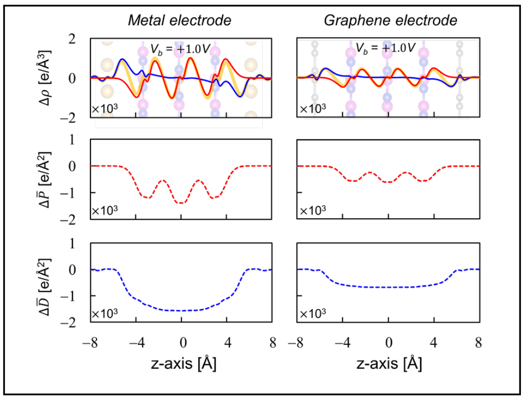

Fig. 1. Electric displacement and polarization of Au/hexagonal boron nitrides (hBN)/Au and graphene/hBN/graphene models

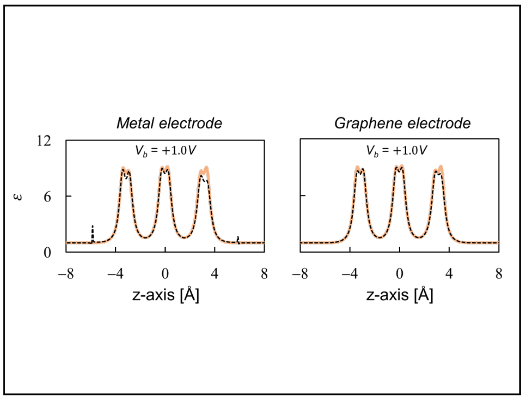

Fig. 2. Comparison of the dielectric profiles obtained through Fig. 1 (black dotted) and the finite field method (yellow).

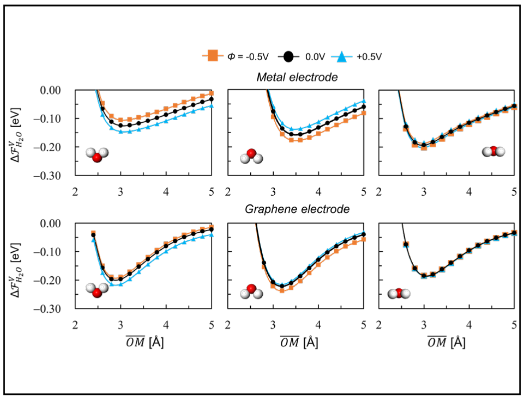

Fig. 3. The formation of enthalpy for single water molecule with difference configurations placed next to Au electrode (top) and graphene surface (bottom).