First-Principles Study of Field-Effect Doping in Nano-Scale Systems by the Enforced Fermi-Energy Difference Method *

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We propose a method for investigating the field-effect doping and the capacitance in nano-scale systems by first-principles calculations. Utilizing this method, we demonstrated the field-effect doping into the water bi-layer (channel) sandwiched by a pair of gate electrodes. We found that the H2O molecules rotated around the O atoms artificially pinned, accompanied by the bias application between the channel and gate electrodes. We confirmed that $Q-\mu$ relation (capacitance) was also modified through this rotation of the molecule. We believe that this kind of bias-induced structural modifications of the channel materials can be utilized for designing nano-electronic devices with a variety of novel and functional characteristics.

Keywords: First-principles calculation; Enforced Fermi-Energy Difference Method; Field-effect doping; Water; Bias-induced structural modifications; capacitance; nano-scale capacitor

I. INTRODUCTION

Remarkable progresses in the recent experimental technologies drive us to investigate nano-scale electronics, from scientific and applicational points of view. Many theoretical studies discussing the conductance in nano-scale systems have been already performed [1]. However, theoretical investigations of the capacitance in nano-scale systems have just began lately [2–7], in spite of the manifestly important roles of the “gate capacitors” in practical type of electronic devices, such as the field-effect transistors (FETs) and the single-electron transistors (SETs).

In this study, as one of the first steps for investigating the field-effect doping (gate capacitor) and the capacitance in nano-scale systems, we propose a first-principles method for calculating the electronic states of the charge-accumulated capacitors. Utilizing this method, as an example, we demonstrate the field-effect doping into the water bi-layer (channel) sandwiched by a pair of Si slabs coated with Al atoms (gate electrodes) under the repeated boundary condition (See the schematic illustration in Fig. 1).

We show that the H2O molecule rotates around the O atom artificially pinned, accompanied by the bias application between the channel and gate electrodes. It is also shown that the $Q-\mu$ relation (in other words, capacitance) varies through this rotation of the molecule. We believe that this kind of bias-induced structural modifications of the channel materials can be utilized for developing nano-electronic devices with a variety of novel and functional characteristics.

II. METHODOLOGY

To obtain the electronic states of the charge-accumulated capacitor, we define a free energy to be minimized:

$$F = E_{\text{DFT}}[\rho(r)] - \mu N[\rho(r)]$$

in place of the usual energy minimized in the conventional first-principles calculations. This free energy represents the situation where the bias voltage $\mu$ is applied [8] between the one electrode (channel, region $-\text{II}$ of Fig. 1) and the other electrode (gate electrode, region $-\text{I}$ and $-\text{I}'$) of the capacitor. Minimizing this free-energy, we can obtain the electronic state of the charge-accumulated capacitor, in which the inter-electrode difference of the chemical potentials of electrons is matched with this $\mu$,

$$\epsilon_F|_{\text{I}(\text{I}')} - \epsilon_F|_{\text{II}} = \mu :$$

FIG. 1: The water bi-layer sandwiched by a pair of gate electrodes (Si slabs coated with Al Atoms) is schematically illustrated. Vacuum regions separate these sub-systems. Due to the repeated boundary condition, the present model corresponds to the double-gate configuration. We apply the finite bias voltage between the gate electrodes and the water bi-layer, so that holes ($+Q$) and electrons ($-Q$) are injected into them respectively. Total charge neutrality of the unit cell is maintained throughout this work ($+Q - Q = 0$).

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Here, \( N[\rho(r)] \) is the amount of electrons transferred from the one electrode (channel, -I) to the other electrode (gate electrode, -I and -I'), calculated by

\[
N[\rho(r)] = \int_{\text{Region I+I'}} \Delta \rho(r) \, dr,
\]

where

\[
\Delta \rho(r) = \rho(r) - \rho_{\mu=0}(r)
\]

shows the variation of the electron density due to the bias application. The boundary planes between the region -I/I' and -I I (See Fig. 1) are placed at the middle of the vacuum regions, where the tails of the wave functions of the electrons bound in the electrodes are sufficiently dampened.

The electron density is calculated by

\[
\rho(r) = \sum_{\epsilon_n \leq \epsilon_{p\text{Fermi}}} |\phi_n(r)|^2,
\]

with the pseudo-Fermi level \( \epsilon_{p\text{Fermi}} \) chosen as

\[
\epsilon_{p\text{Fermi}} = \begin{cases} 
\epsilon_{\text{Fermi}|I} - \mu, & \text{for } r \in \text{Region I (I')} \\
\epsilon_{\text{Fermi}|II}, & \text{for } r \in \text{Region II}
\end{cases}
\]

Kohn-Sham’s equation is also modified as

\[
[\hat{H}_{\text{KS}} + w(r)] \phi_n(r) = \epsilon_n \phi_n(r),
\]

where

\[
w(r) = \begin{cases} 
-\mu, & \text{for } r \in \text{Region I (I')} \\
0, & \text{for } r \in \text{Region II}
\end{cases}
\]

effectively describes the biased chemical potentials of the electrons applied to the system.

In summary, we formulated a first-principles method for investigating the field-effect doping and the capacitance in nano-scale systems, by the minimization of the free energy defined by Eq. (1). After the self-consistent calculation with the bias voltage \( \mu \), the electronic state of the capacitor charged by \( \pm Q = \mp N[\rho(r)] \) is obtained. In this way, we can discuss the \( Q-\mu \) and \( \Delta \rho(r)-\mu \) relations (in a word, capacitance) of the nano-scale capacitors considering their atomic and electronic structures by the first-principles calculations.

By the minimization of the total free energy added by the Ewald term,

\[
F' = E_{\text{Ewald}} + F,
\]

\[
= E_{\text{Ewald}} + E_{\text{DFT}}[\rho(r)] - \mu N[\rho(r)],
\]

we can also calculate the optimized atomic structure after the bias application. We named our formalism the “EFED” method, because the obtained electronic states are characterized by the Enforced Fermi-Energy Difference between the sub-systems.

\[\text{FIG. 2: After the bias application, the H}_2\text{O molecule rotated around the O atom artificially pinned. (A) and (B) are the accumulated electron density calculated under the structure (a) and (b) respectively.}\]

III. DEMONSTRATION

Following calculations were performed with the ultra-soft pseudo-potential method [9], and the exchange-correlation energy density of PW91-type [10]. The cut-off energy for describing the electronic states was chosen at 36Ry. \( 6 \times 6 \times 3 \) k-points were sampled for the integrations in the first Brillouin zone. For simplicity, in the present work, only the H atoms in the H\(_2\)O molecules were allowed to relax in the structural optimizations before and after the bias application.

First, we calculated the optimized atomic structure before the bias application (See (a) of Fig. 2). Under this structure, as drawn by the red line (A), we estimated the accumulated electron density calculated under the structure (a) and (b) respectively.
FIG. 3: The $Q$-$\mu$ relations were calculated, with the atomic structures of the system fixed at either (a) or (b) of Fig. 2. Analyzing these data, we can discuss the capacitance, and its quantum effects.

The bi-layer was positively (+$Q$) charged due to the counter holes. Total charge neutrality was maintained regardless of this electron transfer (+$Q$ – $Q$ = 0). We can also confirm the penetrations of the accumulated charges into the vacuum region, from this figure.

We also calculated the optimized atomic structure under this bias, $\mu$=0.40Hartree. We found that the H$_2$O molecules rotated around the O atoms artificially pinned and accompanied by the charging (See (b) of Fig. 2). Accumulated electron density calculated under this structure is also shown by the green line (B) in Fig. 2. Total amount of the accumulated charge was larger than that of the (A).

Next, in Fig. 3, we plot the calculated $Q$-$\mu$ relations over the range of $-0.4$Hartree $\leq \mu \leq +0.4$Hartree. Here, the atomic structures were fixed at either (a) or (b) of Fig. 2. We can confirm that the $Q$-$\mu$ relation is modified by the rotation of the H$_2$O molecule. In other words, atomic-scale structural modification of the channel material strongly affected the capacitance $C_{\mu}$ = $Q/\mu$, or the differential capacitance $C_{\mu}$ = $dQ/d\mu$, of the system, which is one of the features of the nano-scale capacitors with the very small inter-electrode distances.

The capacitance is zero around $\mu \sim 0$. Considering our formulation, this zero-capacitance region corresponds to the band-gap width of the water bi-layer. Thus, the variation of the latter due to the rotation of the H$_2$O molecule also results in that of the former. This is one of the origins of the variation of the $Q$-$\mu$ relation (capacitance) brought about by the structural modification of the nano-scale systems, beyond the simple effect merely due to the variation of the inter-subsystem distance.

As roughly demonstrated above, we have shown that our method is working well. Detailed analyses of the capacitance and its quantum effects will be shown elsewhere [11].

IV. CONCLUSION

In conclusion, we proposed the EFED method for investigating the field-effect doping and the capacitance in nano-scale systems by the first-principles calculations. We demonstrated the field-effect doping into the water bi-layer sandwiched by the gate electrodes. Accompanied by the charge injections into the water bi-layer, the H$_2$O molecules rotated around the O atoms artificially pinned. The $Q$-$\mu$ relation, i.e., capacitance, also varied through this deformation of the molecule. We believe that this kind of structural modifications of the channel materials can be utilized for designing novel nano-electronic devices with a variety of functional characteristics.

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[8] In the classical electro-static limit, the energy of the capacitance charged by $\pm Q$ can be written with a constant $C_0$:

$$E = \frac{Q^2}{2C_0},$$

while the free energy defined here is

$$F = \frac{Q^2}{2C_0} - VQ.$$
while only un-charged energetically ground state can be obtained by the minimization of the energy:\n\[
\frac{dE}{dQ} = 0 \rightarrow Q = 0 \text{ (un-charged state)}.
\]

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