Density functional calculation of work function using charged slab systems

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Abstract. To check the relevance of charged-slab calculation, work functions of Al(111), Si(111) and TiO$_2$(110) surfaces are calculated using repeated charged slabs in density functional theory. It is shown that the charged-slab calculation can provide work functions which are in agreement with those by the conventional density-functional method using neutral surfaces. Moreover, it is shown that the charged-slab calculation is sensitive to the boundary condition; the charged surfaces often induces a non-uniform electric field in a vacuum region, which produces unphysical interactions between repeated charged slabs and errors in calculated results unless the vacuum thickness is enough large.

1. Introduction

Density Functional (DF) calculation is a powerful tool to explore ground-state properties of materials. Combined with the repeated-slab geometry in a periodic boundary condition, this calculation has been applied to a variety of surfaces and succeeded in clarifying their static and dynamic properties such as reconstructed structures and chemical reactions. Almost all these studies are concerned with neutral surface systems. On the other hand, the surface changes into a charged surface when the system is connected to an electrode and some voltage is applied to the system. This situation is commonly realized in the electrochemistry and scanning tunneling microscopy experiments. The charged surfaces show interesting phenomena such as the field-induced reconstruction for some metal surfaces[1, 2] and the variation of admolecular amount[3]. To approach these phenomena, the total-energy DF calculations have been extended to the methods using charged-slab systems[4, 5]. However, the application of these methods is limited to a few systems at present[4, 6] and there is no appropriate physical quantities that can be compared directly with charged-surface experiments. Thus, the reliability of these methods is still unclear. The purpose of this work is to examine the relevance of charged-slab calculation method, especially focusing on the boundary condition. This is because a charged two-dimensional slab produces an electric field that never decays at the boundary and thus the calculated results are sensitive to the boundary condition.

One of effective ways to check the suitability of boundary condition in charged-slab methods is to evaluate the work function. This is because one can compare the calculated work function by the charged-slab method with not only the observed work function but also the work...
function calculated by the conventional DF method using the neutral surface. In fact, based on Koopman’s theorem, the work function, $\phi$, can be evaluated by a total-energy difference between neutral and charged systems as $\phi = \lim_{n \to 0} (E(0) - E(n))/n$, where $E(n)$ is a total energy of the surface having a deficit charge of $n \leq 0$. On the other hand, in the conventional DF method, the work function is obtained as $\phi = V(\infty) - \epsilon_F$, where $V(\infty)$ and $\epsilon_F$ are the electronic potential in a vacuum region far from the neutral surface and the Fermi energy of the neutral surface system, respectively. In this work, we adopt three representative surfaces of Al(111), Si(111), and TiO$_2$(110), and evaluate their work functions using the charged-slab method to compare the results with those by experiments and conventional DF method.

2. Calculation method

The calculation of work function using charged slabs is divided into three steps. First, to simulate the charged surface system, we prepare the unit cell made of material-slab layers, which have $+n$ net charge and are located at the center of unit cell, and a vacuum region around the unit-cell boundary. It is well known that the total energy of such unit cell becomes divergent because the electronic field originating from the charged slab does not vanish in a vacuum region far from the surface and there appear an infinite number of Coulomb interactions among unit cells. To avoid such divergence, we employ the recipe proposed by Lozovoi et.al.[5], where the uniform background compensating charge, $n_{\text{comp}} = -n$, is artificially introduced in an unit cell such that there is no electric field at the unit-cell boundary. Using this neutral unit cell, we perform standard DF calculation to obtain the total energy of unit cell, $E(n,n_{\text{comp}})$.

At the second step, to obtain the charged unit-cell energy, $E(n)$, we subtract from calculated $E(n,n_{\text{comp}})$ the electrostatic energy due to artificial uniform background charge, $E_{\text{corr}}(n_{\text{comp}})$, as $E(n) = E(n,n_{\text{comp}}) - E_{\text{corr}}(n_{\text{comp}})$. In the case of uniform background charge, if we assume that the potential zero is located at the cell boundary such as $V(L) = 0$, $E_{\text{corr}}$ is expressed by

$$E_{\text{corr}} = \int_{\text{unitcell}} d\mathbf{r} \rho_{\text{comp}} (V(\mathbf{r}) - V(L)) + \frac{2\pi n^2}{3 \Omega} L^2,$$

(1)

where $\rho_{\text{comp}} = n_{\text{comp}}/\Omega$ is the background charge density, $\Omega$ the unit-cell volume, and $L$ the unit-cell length perpendicular to the slab. By this choice of the potential-zero position, $E(n)$ becomes equivalent to the total energy of the unit cell that is made of two charged slabs; (i) material layers, which are located at the center of unit cell and have $+n$ net charge, and (ii) a thin flat electrode, which is connected to the earth at the unit-cell boundary and has $-n$ compensating charge.

Since the energy, $E(n)$, includes the electrostatic energy between charged material layers and a charged electrode, $E(n)$ depends on not only $n$ but also the unit-cell length, $L$. Hereafter, we denote $E(n)$ as $E(n,L)$. $E(n,L)$ is, in general, represented as an expansion series of $n$ as

$$E(n,L) = E(n = 0,L) + \phi \cdot n + n^2 \cdot f(n,L),$$

(2)

where $f(n,L)$ is a regular function of $n$ and $L$. Work function, $\phi$, is obtained as a $n \to 0_-$ limit of $(E(n = 0,L) - E(n,L))/n$. Therefore, at the third step, we realize such limit by calculating $E(n,L)$ for various finite values of $n$, ranging from $n = -0.25$ to $-0.05$, and then fitting them as a quadratic polynomial to obtain the work function. We found that the calculated work functions have at most 0.1 eV error by this extrapolation.

Al(111), Si(111) and TiO$_2$(110) $(1 \times 1)$ surface-slab systems, which are respectively made of nine, eight atomic layers, and five trilayers, are employed to evaluate the work functions. The atomic positions of surfaces are obtained by total-energy optimization in case of neutral ($n = 0$) slabs, while those are fixed to the neutral positions in case of charged ($n < 0$) slabs. Standard DF total-energy calculations are performed for these systems using ultra-soft pseudopotentials and
Figure 1. Calculated work functions of (a) Al(111), (b) Si(111) and (c) TiO$_2$(110) surfaces, as a function of the vacuum thickness in the repeated-slab unit cell. Open circles are obtained by the charged-slab method, while solid circles by the conventional method.

Table 1. Work functions of Al(111), Si(111) and TiO$_2$(110) surfaces calculated by the charged-slab and conventional methods, together with observed values.

| Surface      | Charged-slab Method | Conventional Method | Experiment |
|--------------|---------------------|---------------------|------------|
| Al(111)      | 4.13                | 4.16                | 4.24 [7]   |
| Si(111)      | 4.71                | 4.71                | 4.56 [8]   |
| TiO$_2$(110) | 7.16                | 7.18                | 7.3 [9]    |

Tokyo Ab-initio Program Package (TAPP) code. The local density approximation is employed, where the exchange-correlation functional by Perdew-Wang-92 for Al and Si, while that by Perdew-Burke-Ernzerhof-96 for TiO$_2$. The wavefunctions are expanded by plane waves with cut-off energies of 16, 16, and 25 Rydberg for Al, Si, and TiO$_2$ systems, respectively.

3. Results and Discussion

As shown in Eq.(2), the calculated total energy of $E(n, L)$, in general, depends on the boundary condition, i.e., the unit-cell length $L$ or equivalently the thickness of vacuum region. In fact, it is well known that the thickness of vacuum region should be enough thick in the repeated-slab calculation to avoid unphysical interactions between nearest neighboring cells and realize the isolated surfaces. We show in Figs.1(a) to 1(c) the calculated work functions of Al(111), Si(111) and TiO$_2$(110) surfaces as a function of vacuum thickness. In case of Al(111) and Si(111), the work functions show rapid convergence with increasing the vacuum thickness; they have convergent values above 30 to 40 a.u. On the other hand, in case of TiO$_2$(110), we needs the vacuum thickness larger than about 80 a.u. to obtain the convergent value of work function.

First, we compare the calculated work functions by the present charged-slab method with those obtained by the conventional method and experiments. These data are shown in Table 1, where the calculated values are obtained as convergent ones from Fig.1. Good agreement is seen between calculated values by two methods. Mathematically, one can naturally expect such agreement because both methods are based on the same DF theory and $n \to 0$ limits of fundamental equations in two methods coincide with each other. However, the finite values of $n$ are used in the real numerical calculations in the charged-slab method. In this sense, the present agreement suggests that the charged slab method provides reliable results to simulate charged surface systems, especially the total energy of charged unit cell, $E(n)$. On the other hand, considering that calculations are performed in the local density approximation, one can
see reasonable agreement between calculated work functions and measured ones.

Then, we consider the reason why the convergence speed of work-function values with increasing vacuum thickness strongly depends on the material kinds in the present method. For comparison, the convergence feature of the conventional method is also shown in Fig.1. One can see that the convergence speed is similar between two methods for Al(111) and Si(111) cases. In case of TiO$_2$(110), however, the convergence is obtained at similar vacuum thickness around 40 a.u. for the conventional method, while the convergence is much slower for the charged-slab method. This result indicates that something unexpected happens for charged TiO$_2$ surfaces.

To understand the reason of this, we examined how the deficit ($n < 0$) charge is distributed on the surface. We found that, in cases of Al(111) and Si(111) surfaces, the deficit charge is uniformly distributed along on the surface. On the other hand, in case of TiO$_2$(110), since TiO$_2$ has a highly ionic character, the deficit charge is localized not around surface Ti but around atop oxygen on the surface. This non-uniform charge distribution induces in a vacuum region an electric field that is tilted from the perpendicular direction to the surface. When the vacuum thickness is not enough large, such electric field does not cancel out with the electric field originating from the compensating uniform background charge, thus producing unphysical interactions between neighboring unit cells and resulting in large error in calculated total energy.

From the above analysis, one can clearly recognize the sensitivity of the total-energy calculation of charged slabs to the boundary condition. Namely, when the charge density is expected non-uniform for charged surfaces such as surfaces of ionic materials or geometrically rough surfaces, one needs larger unit-cell size perpendicular to the surface in the charged-slab calculations compared to the case of neutral surface calculations. It should be noted that the convergence situation is almost the same when one adopts the other recipe of the charged-slab calculation that uses Gaussian-type charged sheet at cell boundary as compensating charge.[4]

4. Conclusion
In this paper, to examine the relevance of charged-slab calculation method, the work functions of Al(111), Si(111) and TiO$_2$(110) surfaces were calculated using repeated charged slabs, based on the density functional theory. Comparing with results by the conventional method using neutral surfaces, it was shown that the charged-slab calculation provides qualitatively reliable total energies of charged surface systems. We found that the charged surface of ionic materials induces non-uniform electric field in a vacuum region. Therefore, unless the vacuum thickness is enough large, such electric field produces unphysical interactions between repeated charged slabs and errors in calculated total energy.

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