Comparative Study of Time-Dependent and Scattering-State Ab Initio Calculations for Field Emission

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We perform time-dependent (TD) and scattering-state (SS) ab-initio calculations for simulating the field emission (FE) of Na surfaces to explore the applicability of the two schemes. The amplitude of emission current is evaluated more reliably by SS than TD methods, because the former treats the steady-state electron tunneling faithfully but the latter utilizes transient electron dynamics. In contrast with the evaluation of current amplitude, the TD method is more suitable than the SS one for revealing the electronic-state origin of FE, because the TD method can directly determine the time evolution of all wave functions caused by an electric field. Thus, the TD and SS methods are found to play a complementary role in the FE study. [DOI: 10.1380/ejssnt.2005.457]

Keywords: Density functional calculations; Field emission; Metallic surfaces; TD-DFT

I. INTRODUCTION

Electron field emission (FE) from nanostructures has attracted much attention from the viewpoints of fundamental science and technological applications. On the practical side, FE can be used in display applications. Unlike the cathode-ray tube display with a bulky electron gun, the field-emission display (FED) [1-3] consists of an array of field emitters and is easily flattened and thinned. Since the FED operates at low temperatures, it consumes far less energy than the conventional display with a cathode-ray tube that is based on thermal emission. Moreover, it can be expected that the imaging speed of the FED is faster than that of liquid crystal displays. From these potential merits, the FED is the most promising candidate for next-generation displays. As regards the theoretical aspect, the Fowler-Nordheim (F-N) theory [4, 5] has been formulated and often used in the analysis of FE properties thus far. The F-N theory is suitable for the study of FE from flat jellium surfaces, and cannot correctly describe the emission process of real nanostructures. Therefore, more rigorous methods that take into account atomic geometry, atomic species and electronic structures are necessary for realization of the FED and other applications related to FE.

There are some first-principles calculations based on the density-functional theory (DFT) for the study of FE. In the present study, we adopt two different methods. One is the time-dependent density-functional theory (TD-DFT) method [6-8] and the other is the scattering-state method [9-12]. In the TD-DFT calculation, emission currents are obtained from temporal wave functions, and the TD-DFT method is found from our previous studies to be suitable for clarifying the electronic-state origin responsible for the FE of covalent-bond nanostructures [7, 8, 13]. In the scattering-state calculation, on the other hand, current-carrying states are obtained by connecting wave functions in the vicinity of the surface to the Airy functions that are the solutions of Schrödinger equations in vacuum under an electric field. Both methods have been successfully applied to explain some FE properties of metal surfaces and carbon nanostructures. However, a direct comparison between the TD-DFT and scattering-state methods for the FE of a particular system has not been made thus far.

Our objective in this study is to clarify the advantages and drawbacks of both the TD-DFT and scattering-state schemes through the analysis of FE from Na surfaces. Since we focus on the methodological aspect in this article, we adopt a Na surface as a simple metal surface.

II. METHOD AND MODEL

A brief description of two approaches, the TD-DFT method [7, 14] and the recursion-transfer-matrix (RTM) method [11, 15] for the scattering-state calculation and model systems calculated in this study are given in this section. We begin with a computational procedure of the TD-DFT calculation for FE. First, we determine the ground-state electronic structures using a conventional DFT calculation [16] in a zero electric field. Next, we apply an electric field and calculate the time evolution of the wave function by applying the TD-DFT scheme. Finally, FE current is evaluated from the linear slope in the curve of the number of emitted electrons as a function of time [7]. In the calculation of the time evolution of wave functions we adopt the sixth-order Taylor expansion method [17], and the electronic wave functions are expanded in terms of a plane wave basis set [18]. See Refs. 6 and 7 for details of the TD-DFT method for FE.

In the RTM method for FE [11], we consider a system consisting of a few atomic layers on a semi-infinite metallic jellium electrode and a vacuum region. The wave functions deep inside the jellium electrode are plane waves. The wave functions in the vacuum region under the applied electric field are expressed by Airy functions. In the surface region with some atomic structures, the electronic states are expressed as scattering waves that are determined self-consistently for given incident energies in the framework of the DFT method. The wave function

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FIG. 1: Schematic diagrams of Na surface models used in (a) time-dependent density-functional (TD-DFT) and (b) recursion-transfer-matrix (RTM) calculations for field emission (FE). The rectangle in (a) is the unit cell and that in (b) is the surface region repeated in the $x$ and $y$ directions. Gray circles are Na atoms and the dark area in (b) denotes a semi-infinite jellium electrode. Electrons are emitted from the surface toward the vacuum.

is expanded with plane waves in the direction parallel to the surface on which a periodic boundary condition is imposed. In solving Kohn-Sham equations, wave functions in the surface region are connected to plane waves at the surface-electrode boundary and to the Airy functions at the surface-vacuum boundary. FE current is calculated from the transmission probability. See Ref. 11 for details of the RTM method for FE.

In the present study, we investigate Na (001) surfaces, as shown in Fig. 1. The models shown in Figs. 1(a) and 1(b) are for the TD-DFT and RTM methods, respectively. The $x$, $y$ and $z$ axes are defined as shown in Fig. 1. The unit cell size of Fig. 1(a) is 4.28 Å $\times$ 4.28 Å $\times$ 209.8 Å, and Na slabs with ten and twenty atomic layers are investigated. The unit cell size shown in Fig. 1(b) is 4.28 Å $\times$ 4.28 Å $\times$ 78.9 Å, and two Na layers are placed 1.59 Å above the jellium electrode. In these systems, the bond lengths between Na atoms are 3.71 Å and electric fields are applied in the $z$ direction. We choose 4 points in the $k_x$-$k_y$ plane in the first Brillouin zone for the TD-DFT calculation and 36 points for the RTM calculation. The empty-core pseudopotential developed by Ashcroft [19] is adopted for the ionic potential of Na and the Ceperly-Alder form [20] as parameterized by Perdew and Zunger for the exchange-correlation potential [21]. The cutoff energy is 9.7 Ry for both calculations.

FIG. 2: Field-emission energy-distributions (FEEDs) under applied field of 2.5 V/nm by (a) TD-DFT and (b) RTM calculations. The solid and broken lines in (a) indicate the FEEDs from Na slab with 20 and 10 atomic layers, respectively. Both FEEDs are drawn by the Gaussian broadening with a parameter of 0.2 eV.

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III. RESULT AND DISCUSSION

First of all, note that the type of model systems we can use depend on the calculation methods by which we evaluate FE current. The TD-DFT method simulates the FE from a finite slab with atomic structures. (Fig. 1(a).) The slab could approach a realistic electrode with increasing thickness. On the other hand, in the RTM method, two Na layers are sufficient for the surface structure because a semi-infinite jellium electrode is attached to the Na layers. The difference in the model surface results in the difference in work function. The work functions of surfaces in Figs. 1(a) and 1(b) are $\phi_{\text{DFT}} = 2.06$ eV and $\phi_{\text{RTM}} = 2.69$ eV, respectively.

We describe the results on the field-emission energy-distributions (FEEDs) under an applied field of 2.5 V/nm calculated by the TD-DFT and RTM methods in Figs. 2(a) and 2(b), respectively. The solid and broken...
The solid and broken lines connected by dots (A and C) are calculated results obtained by the TD-DFT and RTM methods, respectively. The solid and broken straight lines (B and D) are the F-N lines of the work functions, $\phi_{\text{DFT}}$ and $\phi_{\text{RTM}}$, respectively.

![Diagram](image)

**FIG. 3:** Fowler-Nordheim (F-N) plots. The solid and broken lines are the FEEDs of the Na slab with 20 and 10 atomic layers calculated by TD-DFT, respectively. The multipeak feature merges into a single-peak spectrum as the slab thickness increases from 10 to 20 atomic layers. The change in the spectra reflects the decrease in the discreteness of the energy band due to the increase in slab thickness. This result means that the slab should be sufficiently thick for evaluating a physically reasonable emission current from a bulk electrode when we employ the TD-DFT method. On the other hand, the RTM method generates a single peak in the FEED, as seen in Fig. 2(b). It is also known from a theoretical study [4, 22] that flat metallic surfaces without imperfections or large clusters produce a single peak in the FEED spectrum. Accordingly, both the TD-DFT method and RTM method seem to be suitable for the analysis of FE.

However, the absolute values of the two peaks are very different from each other. That is, the ratio of the peak height determined by the TD-DFT method (Fig. 2(a)) to that by the RTM method (Fig. 2(b)) is $\sim 10^3$ and the ratio of width of the two peaks is approximately two. There are two reasons why the present calculation by the TD-DFT method overestimates the FE current. One of the reasons is the low work function of 2.06 eV determined by the DFT method compared with 2.69 eV by the RTM method. The difference in work function, however, is not sufficiently large for explaining the large difference in FE current. The other, which is the main reason for overestimation, is an abrupt switching of electric field to the vacuum. This is not a steady-state but transient electron tunneling. Therefore, both switching time and simulation time have to be sufficiently large for attaining steady-state electron emission by the TD-DFT method.

The F-N plots of total emission current obtained by the two methods are given in Fig. 3. The solid line A and broken line C are the results calculated by the TD-DFT (with 20 Na layers) and RTM methods, respectively. The solid straight line B and broken straight line D are plotted by the F-N formula with work functions of $\phi_{\text{DFT}}$ and $\phi_{\text{RTM}}$, respectively. The large difference between the TD-DFT (A) and RTM (C) methods originates from two factors. One is the difference in the work function between $\phi_{\text{DFT}}$ and $\phi_{\text{RTM}}$, leading to the difference in the vertical value between B and D. The other is overestimation of emission current by the TD-DFT method due to incomplete screening of the external field, as discussed in the previous paragraph. This effect is roughly estimated as the difference between A and B.

Now, the drawback of the TD-DFT method for the study of FE becomes clear through the present analyses. Incomplete screening of external electric field due to abrupt switching generates an unexpectedly large emission current even from the states far below the Fermi level. To overcome this, a new technique for external-field switching should be devised in addition to a long-time simulation [6]. On the contrary, the TD-DFT method has advantages over the RTM method for FE study. When the system has weakly bound states, for instance caused by surface states or impurity states, these might be a source of FE. We found from previous studies of FE from defects of covalent-bond nanostructures [8, 13] that the electron emission from such states can be captured straightforwardly by the TD-DFT method. FE from localized states such as dangling-bond states of graphitic nanostructures is also observed by the TD-DFT method [7, 8]. In marked contrast with TD-DFT, the RTM method is unsuitable for investigating FE from these localized states, because the incident energy of an electron injected from the bulk electrode does not always hit such a narrow energy band as that originating from some of the defects described above.

**IV. SUMMARY**

We carried out a comparative study of the TD-DFT and RTM methods through the FE of Na surfaces to explore the advantages and drawbacks of the two schemes. While the RTM method evaluates the magnitude of FE currents correctly and efficiently, the TD-DFT method overestimates the values. On the other hand, the TD-DFT method is more suitable than the RTM method for obtaining the electronic-state origin of FE, even if the states are weakly localized. Therefore, the complementary use of the TD-DFT and RTM methods would be ideal toward complete understanding of the FE mechanism.

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