Self-Consistent Density Functional Calculation of Field Emission Currents from Metals

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We have developed a fully self-consistent method which is suitable to examine field emission currents, on the basis of the density functional theory. In our method, the nearby counterelectrode is not necessary. By using this method, we have investigated field emission currents from a biased metallic surface represented by the jellium model. We have found that the energy barrier between the jellium and vacuum becomes lower than the Fermi energy under strong electric fields (e.g., 10 V/nm for $r_s = 4$ bohr). In this situation, the slope of the Fowler-Nordheim plot becomes flatter than that under a weaker field.

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Recently, field emitters have attracted much attention as promising candidates of compact and controllable cold electron sources which are useful elements in vacuum microelectronic devices such as microwave amplifiers, flat panel displays, and others [1]. Since several applications such as amplifiers require strong electric currents, it is necessary to clarify the conditions to obtain high emission currents by using field emitters.

So far the Fowler-Nordheim (FN) theory [2] has been widely used to analyze field emission currents. In this theory emission currents are evaluated on the basis of the free-electron approximation and the Wentzel-Kramers-Brillouin (WKB) method [3], and thus any quantitative arguments based on the FN theory are highly questionable. Nevertheless, almost all of the experimental or engineering-oriented studies concerning field emission still rely on the theory. The most probable reason for this is that alternative quantitative theories have not been established yet. As an approach to improve the FN theory, modification of the theory by including the classical image potential [4] is well known. However, this approach cannot be an essential solution, because it still relies on the WKB method.

To go beyond the free-electron approximation, Jensen [5] analyzed field emission potential barriers on the basis of the electron distribution which is calculated non-self-consistently from the triangular potential as that considered in the original FN theory. By using this method, further improvement to the image-potential corrected FN theory can be derived, for example, in the form of a shift of the image plane. However, a change of the effective potential caused by redistribution of electrons due to applied fields is not taken into account self-consistently, and thus this method is still insufficient especially for high fields.

In another approach reported by Lang *et al.* [6], field emission currents were calculated self-consistently within the density functional theory (DFT) [7]. They considered a model similar to the configuration of scanning tunneling microscope (STM) experiments where there are two electrodes corresponding to a STM tip and a sample surface with a bias voltage between them. This model is not necessarily appropriate for analyses of field emission currents, because the distance between the two electrodes, 1.59 nm, is significantly shorter than a typical distance between an emission cathode and an anode in field emission experiments, the order of 10 cm. This short distance involves effects other than the electric field such as chemical interaction between the two electrodes [8]. To eliminate such undesirable effects, a self-consistent method without using a counterelectrode is desired, but such a method has not been established yet because of the difficulty in direct treatment of electronic states under unscreened electric fields in vacuum.

In this Letter, we propose a *single-electrode* method for fully self-consistent density functional calculation of field emission currents. In this method, the microscopic aspects of field emission are described without using a counterelectrode, in contrast with the previous DFT calculation [6]. Our results for metallic surfaces show that the potential barrier at the surface becomes lower than the Fermi energy under strong electric fields.

In the present calculation, a single metallic field emitter is modeled by a semi-infinite jellium, in which positive ions are replaced by a uniform background charge. Hereafter we take the semi-infinite jellium region to be $z \leq 0$. The positive background charge can be expressed by $\rho_+(z) = \rho_+ \Theta(-z)$, where Θ is the Heaviside step function. The density ρ_+ is related to the Wigner-Seitz radius r_s through $\frac{4}{3}\pi r_s^3 \rho_+ = 1$.

On the basis of the above model, we perform self-consistent DFT calculation to obtain the electron density and the potential barrier. Since there is no atomic structure in the direction parallel to the surface, the single-particle wave function can be expressed as $\Psi(\boldsymbol{r}) = \psi(z) \exp(i\boldsymbol{k}_\parallel \cdot \boldsymbol{r}_\parallel)$. Then the Schrödinger equation in the atomic unit can be written as

$$-\tfrac{1}{2}\psi''(z) + V(z)\psi(z) = (E - \tfrac{1}{2}|\boldsymbol{k}_\parallel|^2)\psi(z), \quad (1)$$

which should be solved for a given energy E and a given surface-parallel wave vector $\boldsymbol{k}_\parallel$. Within the DFT, the

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effective potential $V(z)$ in the above equation is a sum of the Hartree, exchange-correlation, and external electrostatic potentials. For the exchange-correlation potential, we adopt the one proposed by Ceperley and Alder [9] within the local density approximation. As for electrostatic potential (a sum of Hartree and external electrostatic potential), it is calculated by the Poisson equation. Here we would like to emphasize that in the single-electrode method we can treat the electric field F directly as a boundary condition of the Poisson equation.

In the present method, Eq. (1) is discretized along the z direction by taking mesh points z_i which satisfy $z_{i+1} - z_i = h$ for any i, and is expressed as

$$A_{i-1}\psi(z_{i-1}) - B_i\psi(z_i) + A_{i+1}\psi(z_{i+1}) = O(h^6). \quad (2)$$

Here A_i and B_i are determined on the basis of the Noumerov discretization method [10] and can be expressed by E, $\boldsymbol{k}_\parallel$, h, and $V(z_i)$. In addition, we divide the whole system into the following three regions: region I, the vacuum region far from the jellium where the electric field F is considered to be constant, region II, the region where the electron distribution should be self-consistently determined by using Eq. (2), and region III, the jellium region far from the vacuum where electron distribution is considered to be constant.

In region I, the solution of Eq. (1) is known to be the Airy functions $\mathrm{Ai}(-\zeta)$ and $\mathrm{Bi}(-\zeta)$ [11]. Since we are interested in field emission currents, we consider only an electron wave traveling toward $+\infty$. This wave can be expressed as

$$\psi(z) = tC[\mathrm{Bi}(-\zeta) + i\mathrm{Ai}(-\zeta)] \equiv tw(z). \quad (3)$$

Here t is an unknown transmission coefficient, C is a normalization constant, and $\zeta = (2F)^{1/3}[z - z_{\mathrm{I}} - (V(z_{\mathrm{I}}) - E + \frac{1}{2}|\boldsymbol{k}_\parallel|^2)/F]$, where z_{I} is an arbitrary-chosen point in region I. The unknown coefficient t can be eliminated by utilizing the continuation conditions for $\psi(z)$ and its derivative at the boundary between regions I and II [12]. Then we obtain a boundary condition to be satisfied as

$$\psi'(z) = \frac{w'(z)}{w(z)}\psi(z)[= tw'(z)]. \quad (4)$$

Furthermore, $\psi'(z)$ in this equation is discretized by the Noumerov method to obtain an algebraic expression. In region III, where both incident and reflected waves are expressed as plane waves, we can eliminate an unknown reflection coefficient similarly by using the continuation conditions at the boundary between regions II and III. Then, we can solve Eq. (2) in region II, and can calculate electric current density j_z:

$$j_z = \frac{2}{(2\pi)^3}\int d\boldsymbol{k}^{\mathrm{inc}}\,\mathrm{Im}[\psi^*(z)\psi'(z)], \quad (5)$$

where $\boldsymbol{k}^{\mathrm{inc}}$ is a wave vector of incident waves.

In the following calculation, the boundaries between regions I and II, and regions II and III are taken to be $z = 40$ and -20 bohr (1 bohr = 0.0529 nm), respectively. The mesh size of the z-axis grid h is taken to be 0.2 bohr.

In Fig. 1, we show the effective potential $V(z)$ for $r_s = 4$ bohr obtained from the present self-consistent calculation. Here $V(z)$ in the case of the applied field $F = 0$ and 10 V/nm (= 1 V/Å) are shown by dashed and solid lines, respectively. It should be mentioned that the slope of $V(z)$ for $F = 10$ V/nm is nearly constant in the region $z = \sim 35$–40 bohr which is not shown in Fig. 1. We have confirmed that the following results hardly change if the boundary between regions I and II is shifted to be $z = 50$ bohr. This confirms the validity of our assumption that F is constant in region I ($z > 40$ bohr) [13]. In the case of $F = 0$, the Fermi energy E_F of the jellium electrode which is represented by the dotted line is 3.13 eV, and the work function Φ is evaluated to be 2.91 eV. This value is almost the same as that of Perdew and Wang (2.90 eV) [14]. In the case of $F = 10$ V/nm, the Fermi energy is shifted upward by 0.01 eV compared to that of $F = 0$. Such a shift of E_F caused by applying an electric field has already been pointed out by Lang [15].

As has already been known, the potential barrier at the jellium-vacuum interface becomes smaller as the applied electric field ($F > 0$) becomes larger. An interesting finding in our results is that this barrier height $V_{\max}$ is only 0.02 eV higher than E_F in the case of $F = 10$ V/nm. In other words, the barrier for electrons with energy of $\sim E_F$ nearly disappears due to the strong field $F = 10$ V/nm, which can be realized in practical experiments. Such disappearance of the potential barrier under realizable strength of an electric field has already been found in the case where an adsorbate is attached on the jellium [6] and where the chemical interaction between an electrode and a counterelectrode may be significant [8,15]. Here we would like to emphasize that this phenomenon can occur by the pure effect of the electric field in field emission. This is shown in the present calculation for the first time as far as we know.

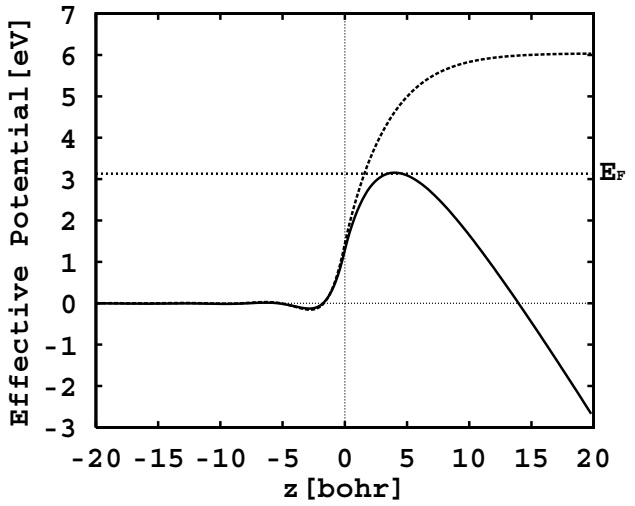

FIG. 1. Effective potential $V(z)$ calculated self-consistently in the case of $r_s = 4$ bohr for $F = 10$ V/nm (solid line) and $F = 0$ (dashed line). Jellium edge is $z = 0$. Dotted line (3.13 eV) denotes the Fermi energy E_F for $F = 0$.

In Fig. 2, we show calculated electron densities for $r_s = 4$ bohr. The electron density profile for $F = 0$ (dashed line) is nearly the same as that calculated by Lang and Kohn [16] except for a slight discrepancy caused by the difference in the adopted exchange-correlation potential. Both for $F = 10$ V/nm (solid line) and $F = 0$, the electron density changes exponentially in the region $z = \sim 0-10$ bohr. The reason for this feature is that many electrons with energy E_F are reflected at the jellium-vacuum interface. From Fig. 2, we can see several differences between the density profiles for $F = 0$ and 10 V/nm as follows. First, in the region $z = \sim 0-10$ bohr, the electron density for $F = 10$ V/nm becomes higher than that for $F = 0$. This contributes mainly to the induced electronic charge of $\int \delta\rho\, dz = -0.0886$ C/m^2, which agrees well with an estimation for an ideal metal based on classical electromagnetism, $\int \delta\rho\, dz = -0.0885$ C/m^2. Next, the magnitude of Friedel oscillation inside the jellium decreases for $F = 10$ V/nm. It should be noted that such a decrease is not clearly seen for higher density jellium (e.g., $r_s = 2$ bohr). This difference between the lower and higher density jellium can be caused by different degrees of the screening capacity.

In Fig. 3, we plot the calculated tunneling probability t^2 of an electron with the energy E_F for $F = 10$ V/nm as a function of the work function for $F = 0$, Φ [17]. Here results of the present calculation are denoted by filled circles. For comparison, we also show t^2 calculated on the basis of the FN theory (solid line) [2] and the corrected FN theory (dashed line) where the image potential is taken into account [4]. From this figure, we can say that these three theories give qualitatively similar results: The smaller the work function, the larger the tunneling probability. However, quantitative discrepancy among them is significant. In the present theory, t^2 is considerably smaller than unity even if $\Phi < 2.9$ eV, where $V_{\max}$ is lower than E_F, because of the wave nature of electrons. The FN theory gives a considerably smaller value of t^2 than that of the present theory, because the reduction of the potential barrier due to an applied field is not taken into account. On the other hand, the corrected FN theory, where the reduction of the barrier is taken into account in the form of the image potential, gives too large a value of t^2 [18]. In particular, t^2 becomes unity in the case of $\Phi = 3.79$ eV where E_F equals the maximum of the barrier. This can be attributed to the fact that the WKB scheme is not valid in this case.

In Fig. 4, the calculated electronic current density j_z is shown in the form of the Fowler-Nordheim plot [$1/F$ versus $\log(j_z/F^2)$]. As is well known, j_z calculated by the FN theory has a constant slope in the FN plot. On the other hand, the slope is not constant in the case of j_z calculated by the present theory and by the corrected FN theory, as can be seen in this figure. However, the present results can be regarded to be aligned in the region $F < 5$ V/nm, and the slope of the plot is similar to that predicted by the FN theory for the corresponding r_s. As well as the FN theory, the slope of the plot predicted by the corrected FN theory is similar to that predicted by the present theory for weak fields. As a result, if the zero-field work function Φ is estimated by using the FN plot [19], the difference between Φ estimated by using the present and the FN theories is less than 10%, even though there is tremendous quantitative disagreement in the calculated values of j_z [20]. This explains why the work function can be reasonably estimated by the analyses based on the FN plot, in spite of the deficiency of the FN theory mentioned before.

As can be seen in Fig. 4, discrepancy between the present and the FN theories becomes more significant even qualitatively, as the electric field becomes larger: Our theory predicts that the stronger the electric field, the flatter the slope of the FN plot. In fact, similar nonlinear behavior of the FN plot has already been reported on the

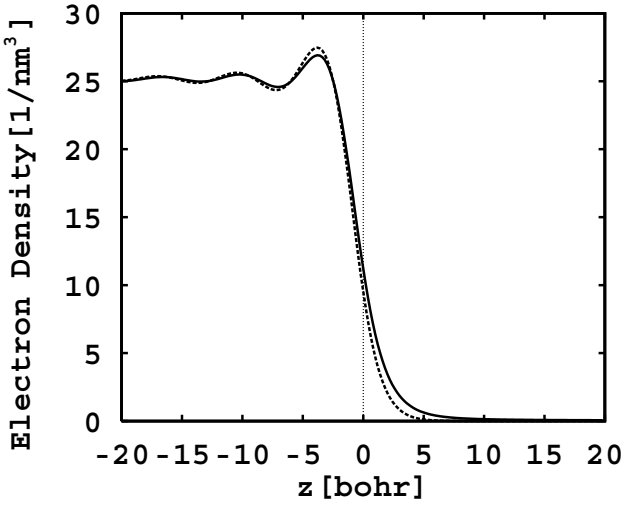

FIG. 2. Electron density distribution in the case of $r_s = 4$ bohr for $F = 10$ V/nm (solid line) and $F = 0$ (dashed line). Note that $\rho_+ = 25.2$ nm^{-3}.

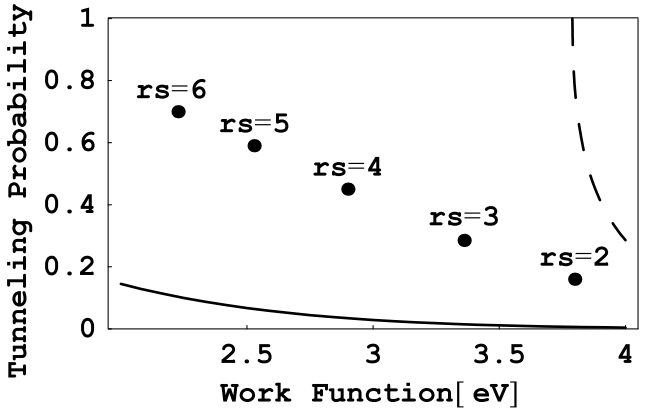

FIG. 3. Tunneling probability of an electron having the energy E_F in the case of $F = 10$ V/nm, calculated by the present method (filled circles), by the Fowler-Nordheim (FN) theory (solid line) [2], and by the corrected FN theory (dashed line) where the image potential is considered [4]. Here the values of the work function are for $F = 0$.

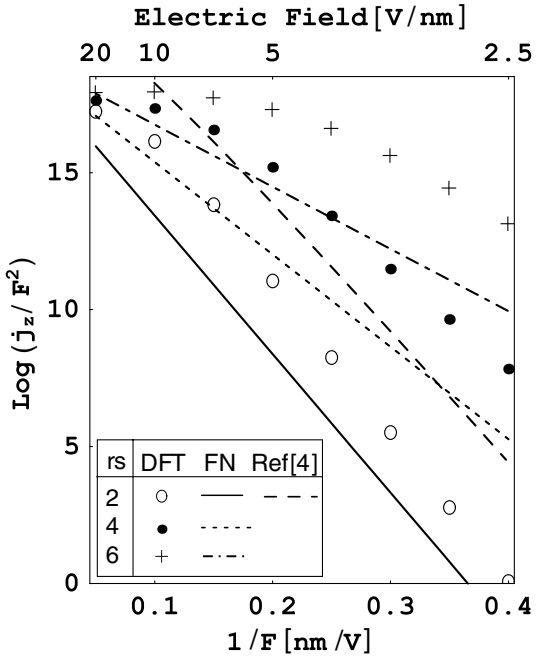

FIG. 4. The FN plot calculated by the present theory (open and filled circles for $r_s = 2$ and 4 bohr, respectively, and crosses for $r_s = 6$ bohr), by the FN theory (solid, dotted, and dash-dotted lines for $r_s = 2$, 4, and 6 bohr, respectively) [2], and by the corrected FN theory (dashed line for $r_s = 2$ bohr) [4].

basis of the corrected FN theory with modified image potential [21]. However, it is of great importance that the previous results have been confirmed by our self-consistent method, which does not have any adjustable parameters and is much more reliable than the WKB method. Consequently, density functional treatment for emission currents, such as the present method, is essentially important to analyze field emission in strong electric fields. It should be noted that this flattening is caused by several factors such as a finite reflection coefficient, i.e., $t^2 < 1$, a finite energy width of emitted electrons, i.e., $0 < E < E_F$, especially for low density jellium (e.g., $0 < E < 1.39$ eV for $r_s = 6$ bohr), and space charge effects.

In conclusion, we have developed a fully self-consistent method which is suitable to examine field emission currents, on the basis of the density functional theory. By using this method, we have investigated field emission currents from a biased metallic surface represented by the jellium model. We have found that the energy barrier between the jellium and vacuum becomes lower than the Fermi energy under strong electric fields. In this situation, finite reflection of ballistic electrons causes the flattening of the FN plot. It should be noted that an extension of the present method to include realistic atomic structures is straightforward. Such an extension is of great use in quantitative analyses of field emission currents in actual materials, and will be done in the near future.

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