

# Localized valence states characteristics and work function of single-walled carbon nanotubes: A first-principles study

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The localized valence states characteristics of single-walled carbon nanotubes (SWNT's) are described by virtue of the discrete energy levels within first-principles calculations. We find that the contributions of the localized valence states to field emission are sensitively dependent on their spatial orientations and deduce that the electron emission in one individual SWNT is not a continuum as in conventional metallic emitters. The work function of SWNT's is defined and calculated within the framework of the linear combination of atomic orbitals for the molecular orbital cluster method, and its localized features are discussed.

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## I. INTRODUCTION

Recently the main potential applications of carbon nanotubes in commerce and science fields are that they can be used as ultimate field emitters for flat panel displays<sup>1</sup> and as tips for atomic force microscopy<sup>2</sup> due to their sharp geometry, intrinsic electrical conductivity, and mechanical resilience. Field emission studies<sup>3</sup> of single-walled carbon nanotubes (SWNT's) bundles and multiwalled carbon nanotubes (MWNT's) showed that the tip plays an important role in this process. The current-voltage ( $I$ - $V$ ) characteristics of carbon nanotubes in field emission could obey the well-known Fowler-Nordheim tunneling equation at low currents, whereas their systematic and significant deviations from the Fowler-Nordheim model are also observed at high currents. In addition, the energy spread (about 0.2 eV) of the electron emission from carbon nanotubes is typically half that of metallic emitters.<sup>4</sup> This evidence strongly suggests that carbon nanotubes cannot be simply considered as ordinary conventional metallic emitters, but rather unique conducting molecules. Up to now, some theoretical works<sup>5-7</sup> have also demonstrated that the excellent field emission properties of carbon nanotubes are attributed to the presence of localized electronic states at the emitting regions. But except for the local density of states (LDOS), to our knowledge, less other information about the localized electronic states characteristics is provided in the prior studies, especially in quantitative analytic aspects. Furthermore, the LDOS cannot give a reasonable and clear interpretation of the above phenomena in these theoretical studies.

In term of the emission process, we know that the work function  $\phi$  and the amplification factor  $\beta$  of the emitting region constitute the link between the structure and the field emission property, and the work function  $\phi$  is related to the localized electronic structure of carbon nanotubes.<sup>7</sup> Recently, some investigators obtained work functions of about 5.7 eV (Ref. 8) and 4.3 eV (Ref. 9) for MWNT and 4.8 eV (Ref. 10) for SWNT bundles using ultraviolet photoemission spectroscopy. These above distinct experimental values show that an accurate measurement of the work function  $\phi$  of carbon nanotubes has been very difficult until now. Owing to the hollow tubular geometrical structure, one SWNT can be regarded as a one-dimensional crystal as well as a unique

simple huge molecule. This unique feature will significantly simplify the resolutions of some problems of the chemical and physical properties of the SWNT surface. For example, within the framework of the cluster method, the theoretical prediction of the work function  $\phi$  of the SWNT, which is equal to the energy required to remove one electron from the carbon nanotube surface to the vacuum, becomes possible without spending many computational time. Moreover, the characteristics of the discrete energy levels corresponding to the localized valence electronic states can be conveniently illuminated.

In this paper, we systematically study the localized valence states characteristics of SWNT's using first-principles calculations and attempt to explore the correction between the localized valence states and the field emission property by virtue of the discrete energy levels. Moreover, as a quantitative description, the work function  $\phi$  of carbon nanotubes is defined and calculated within the framework of the linear combination of atomic orbitals for molecular orbital (LCAO-MO) cluster model, and the corresponding physical background is further discussed.

## II. CALCULATIONAL MODEL AND METHOD

In our present calculations, a finite-length cylindrical sealed carbon cluster consisting of 420 carbon atoms is chosen to represent an armchair C(5,5) capped carbon nanotube, where both ends are closed by fullerene-like cap (i.e., half C<sub>60</sub> molecule). According to the different contributions to field emission, we classify the carbon nanotube as two regions and label them as tip and body as shown in Fig. 1. In what follows we emphasize the link, belonging to the tip, between the tip and body because its physical and chemical properties

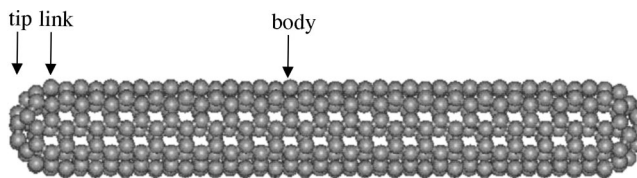


FIG. 1. Geometrical structure of one capped C(5,5) single-walled carbon nanotube in the present calculation. Tip, link, and body are shown by arrows.

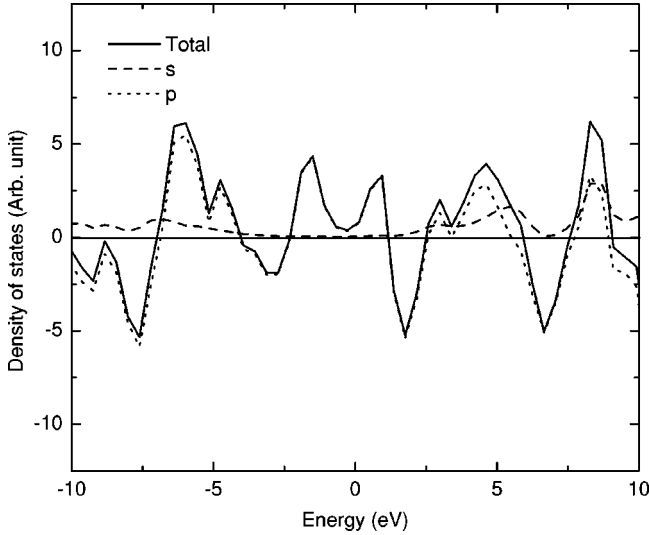


FIG. 2. Local density of states (LDOS) difference between the tip and body (solid line),  $s$  electronic states (dashed line), and  $p$  electronic states (dotted line), respectively, for one capped SWNT. The Fermi level is set to zero.

are more significantly different from those of the body in comparison with other atoms at the tip. The LCAO-MO cluster method using the discrete variational scheme within the framework of the local density approximation is employed.<sup>11</sup> The numerical free-atom variational basis sets selected are  $2s2p$  atomic orbitals for the C atom.

### III. RESULTS AND DISCUSSION

In order to clearly describe the localized electronic states characteristics, the LDOS difference  $\Delta D_{nl}^{v_1-v_2}(E)$  between two spatial locations  $v_1$  and  $v_2$  is represented as

$$\Delta D_{nl}^{v_1-v_2}(E) = \sum_{v_1, n, l} \sum_i f_{nl, i}^{v_1} \frac{\gamma}{\pi[(\varepsilon - \varepsilon_i)^2 + \gamma^2]} - \sum_{v_2, n, l} \sum_i f_{nl, i}^{v_2} \frac{\gamma}{\pi[(\varepsilon - \varepsilon_i)^2 + \gamma^2]}, \quad (1)$$

where  $f_{nl, i}^{v_1}$ , and  $f_{nl, i}^{v_2}$  are the Mulliken population contributions from atoms localized at the spatial locations  $v_1$  and  $v_2$ , state  $(n, l)$  to the  $i$ th molecular orbital,  $\varepsilon_i$  is energy level of the  $i$ th molecular orbital, and  $\gamma$  is the Lorentzian width parameter.

The LDOS difference between the body and tip is illustrated in Fig. 2. Comparing with the LDOS of the tube body, we find that that of the tip exhibits a bit significant features as follows: (i) the values of the DOS at the Fermi level are positive; (ii) two sharp positive peaks occur at both sides of the Fermi level, along with two negative peaks located at the energy levels far from the Fermi level; (iii) the minimum of the DOS shifts from the Fermi level to the lower-energy level. These features indicate that sharp localized resonant electronic states, comprised of  $p$  valence electrons, exist at the tip, and valence electrons at the tip are more easily emit-

ted in comparison with those at the body under an electric field, which are in good agreement with the experimental cases<sup>3</sup> and the previous theoretical predictions.<sup>7,12</sup>

In order to more particularly illuminate the localized valence states characteristics, we suggest that it is very important to establish the concept of localized states (i.e., “tip states”) from the spatial location, which faithfully reflects the electronic structure at one special spatial location (i.e., the tip) in this limit carbon cage. Our previous study<sup>13</sup> showed that one SWNT has the same bonding characteristics as those of a graphite sheet: the bonding is predominantly a  $\sigma$  bond, and a  $\pi$  bond perpendicular to the cylindrical surface takes an additional effect. The nature of the covalent bond between carbon atoms determines that valence electrons only circle in the vicinity of the host carbon atoms. Therefore, the “tip states” are only related to the interaction behaviors of valence electrons situated at the tip and are easy to be realized by the approach as mentioned below.

Within the framework of LCAO-MO calculations, one MO  $\Psi_j$  to the one-electron Hamiltonian can be approximated by a linear combination of atomic orbitals from the various atoms that compose the molecule. We further classify the atomic orbitals  $\phi$  as “localized” atomic orbitals and “delocalized” atomic orbitals in term of the atomic spatial location. For example, the electronic states in carbon nanotubes are naturally classified as the tip states and body states according to the field emission effects. When we regard the tip electronic states contributed from the atoms at the tip as the “localized states” in the consideration, the body electronic states originating from the atoms at the body are the “delocalized states.” Consequently, the molecular orbital  $\Psi_j$  can be rewritten as

$$\Psi_j = \sum_{i=localized} C_{ij} \phi_i + \sum_{i=delocalized} C_{ij} \phi_i, \quad (2)$$

where  $C_{ij}$  is the mixing coefficient of the atomic orbital, while the square of absolute value  $|C_{ij}|^2$  for the mixing coefficient represents the contribution of the atomic orbital  $\phi_i$  to the molecular orbital  $\Psi_j$ . Comparing the sum of mixing coefficient  $|C_{ij}|^2$  of “localized” atomic orbitals with that of “delocalized” atomic orbitals, we can easily clarify the characteristics of one molecular orbital and realize the localized electronic states at one spatial location. Herein, we stipulate that when the sum of mixing coefficients  $|C_{ij}|^2$  of atomic orbitals  $\phi_i$  belonging to atoms at one spatial location (e.g., tip) obviously exceeds the corresponding atomic ratio between this spatial location (e.g., tip) and the globe tube, the characteristics of the localized molecular orbital  $\Psi_j$  can represent those of the localized electronic states at the same spatial location (e.g., tip). This stipulation seems more effective and reasonable in the LCAO-MO framework.

The reality that valence electrons at the tip participate in field emission shows that the number of emitted electrons must be finite and further implies that the electronic states in the vicinity of the Fermi level correspond to the discrete energy levels, which is in accordance with the above experimental observations.<sup>4</sup> We suggest that only the valence electronic states play the role in the field emission process of

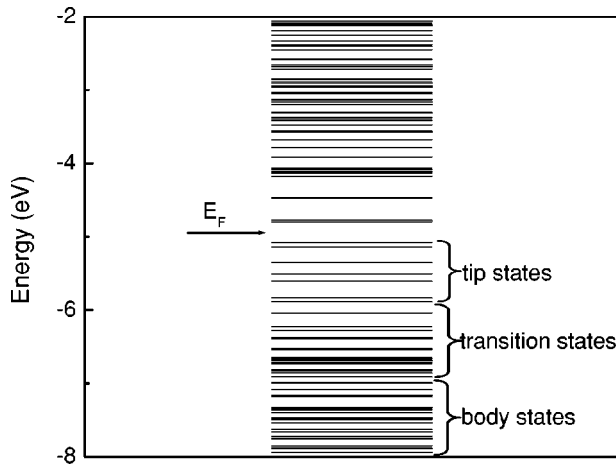


FIG. 3. Distributions of energy levels in the vicinity of the Fermi level in one capped SWNT. Arrow represents the Fermi level.

nanotubes, not the valence band and conduction band states in conventional emitters. In what follows we emphasize expatiating upon the characteristics of the valence electronic states.

According to formula (2) and the related stipulation, we analyze the compositions of molecular orbitals near the Fermi level and naturally classify the occupied molecular orbitals (i.e., valence states) as three regions as shown in Fig. 3 that are the tip states, the transition states, and the body states in the sequence. Comparing with the scheme of the LDOS difference between the body and tip (i.e., Fig. 2), we confirm that the tip states correspond to the electronic states in the range from the Fermi level to the first positive peak, the body states correspond to the electronic states in the vicinity of the first negative peak, and the transition states maybe correspond to the electronic states between the positive peak and the negative peak. In these valence states,  $\pi$ -electronic states originating from  $p$  atomic orbitals of carbon atoms make the predominant contributions, especially in the tip states.

From this figure, we can see that the number of energy levels in the tip states is far fewer than that in the body states, whereas the energy difference between two neighbor energy levels in the tip states is larger than that in the body states. It is easily understood that the former is relative to the finite number of emitted electrons at the tip, and the latter corresponds to the nonhomogeneous distribution of the localized electronic states at the tip. With these discrete energy levels, we can affirm that the emission probability of  $\pi$  electrons at the tip is sensitively dependent on the spatial orientation of the corresponding  $\pi$ -electronic states (i.e., the localized bond network). In details,  $\pi$  electrons corresponding to the electronic states with the node plane perpendicular to the tube axis (i.e.,  $\pi$ -electronic states localized at the link between the body and tip) can be easily emitted by virtue of the yielding donor states due to the higher occupied energy levels, whereas  $\pi$  electrons corresponding to the electronic states with the node plane parallel to the tube axis (i.e.,  $\pi$ -electronic states localized at the top of the hemisphere) are hardly emitted due to the lower occupied energy levels. This

contradicts the conclusions by Han and Ihm<sup>14</sup> who suggest that  $\pi$  electrons at the top of the hemisphere have a large emission probability because they point to the anode side, and the overlap integral with the lobe of the wave function from the anode side of the barrier is relatively large. With the different contributions to the different localized molecular orbitals from carbon atoms at the different spatial locations, we not only confirm that the spatial charge distributions of the emitting states in the individual capped carbon nanotube are nonhomogeneous, which is consistent with the field emission microscopy (FEM) experiments of MWNT's,<sup>4</sup> but also deduce that the  $I$ - $V$  characteristics in the field emission process cannot obey the Fowler-Nordheim equation for the individual SWNT at neither low currents nor high currents. We can affirmatively point out that these experimental cases (i.e., the  $I$ - $V$  characteristics) observed in SWNT bundles are false phenomena and attributed to the bundles effects. Furthermore, these viewpoints about the discrete energy levels of the individual SWNT are very important in the following applications of SWNT's used as tips for atomic force microscopy.

Figure 4 displays the highest occupied molecular orbital (HOMO) plots at the link and body. From this figure, we find these features: (i) the charge distribution at the link is just the reverse of that at the body despite the same  $\pi$  molecular orbital, which indicates that valence electrons have different spatial distributions at the tip and body; in other words, the bond network is varied with the spatial location; (ii) the charge density at the link is far larger than that at the body, which indicates that valence electrons located at the Fermi level mostly originate from the link, and we deduce that valence electrons at the link are more easily emitted. Table I listing the composition of HOMO further demonstrates the conclusions drawn from Fig. 4.

With Fig. 3, we also note that the energy difference between the HOMO and the lowest unoccupied molecular orbital (LUMO) is up to 0.29 eV. This visible energy gap indicates that this carbon cage in our consideration is semiconducting, which is not in agreement with the scanning tunneling microscopy and spectroscopy measurement results<sup>15</sup> that armchair carbon nanotubes do not have the energy gap between the conduction band and valence band, and are metallic. We speculate that the electric properties of carbon nanotubes obtained in these measurements only represent those of the tube body and the tip effects are neglected. Haddon *et al.*<sup>16</sup> had reported that the energy gap of the  $C_{60}$  molecule is up to 0.67 eV and claimed that the  $C_{60}$  molecule is not metallic. So we certify that the reason for the existence of an energy gap in the finite-length sealed armchair carbon cage is attributed to tip effects, not finite-length effects. The nonmetallic feature of the tube tip is not only verified by the composition of the HOMO, but the characteristics of localized molecular orbitals near the Fermi level and LDOS as mentioned above, but also consistent with the experimental cases.<sup>4</sup>

The work function  $\phi$  is conventionally defined as the distance between the average of the HOMO and LUMO (i.e., the arrow in Fig. 3) and the vacuum potential, and it is 4.95 eV in our calculations. From the field emission process and

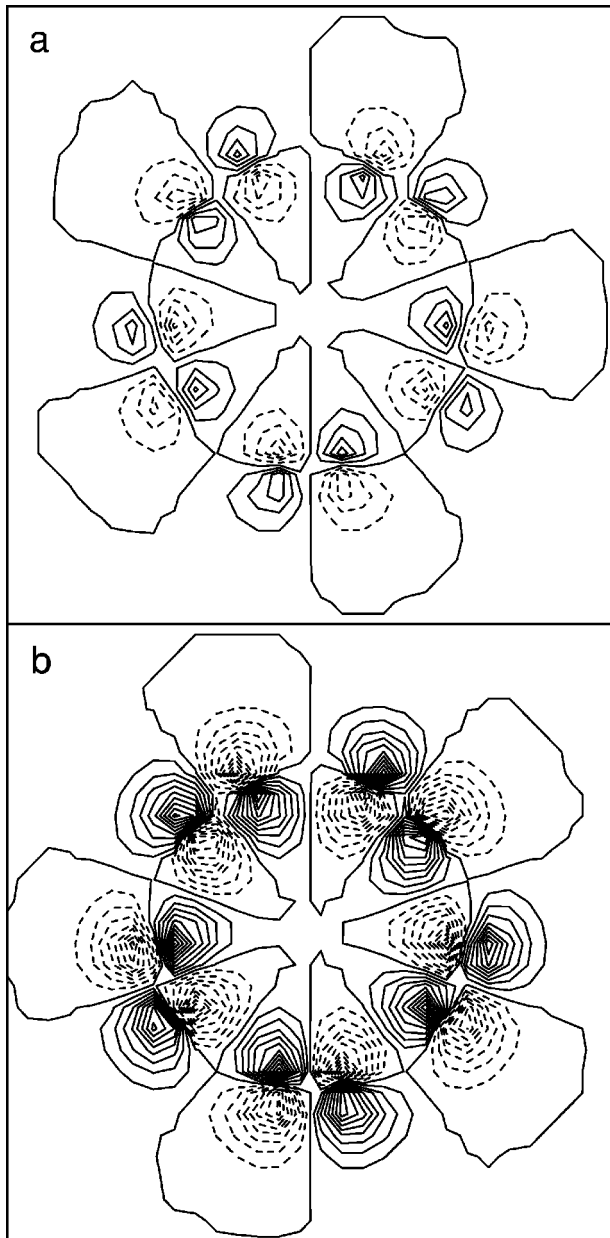


FIG. 4. Contour plots of charge density of the highest localized molecular orbital (HOMO) at the body (a) and link (b) in one capped SWNT, respectively. Solid (dotted) contours denote contours of increased (decreased) density [in units of  $0.003 e/(\text{a.u.})^3$ ].

mechanism, it is maybe more reasonable that one SWNT is considered as a unique big hollow molecule like  $C_{60}$  rather than a one-dimension crystal. For one molecule, the Fermi level does not have any practical meaning, is only a datum. Consequently, we suggest that the conventional definition of the work function is a lack of enough physical background and meaning for SWNT's.

In terms of the above analyses on “localized states” and the related information given, we find that the HOMO belongs to the tip states in carbon nanotubes and suggest that the field emission process is that valence electrons at the discrete energy levels are removed from the tip to the vacuum under the electric field, and the energy required cor-

TABLE I. State, energy level (eV), composition (%), and atomic ratio (%) of the highest occupied molecular orbital (HOMO) in one capped SWNT. Symbols “link” and “body” mean the link between tip and body, and the body, respectively.

State	Energy level	Composition		Atomic ratio	
		Link	Body	Link	Body
186 A1	-5.08	11.06	81.23	4.76	85.72

responds to the work function. Due to the correction between the emission probability of  $\pi$  electrons at the tip and the spatial orientation of the corresponding  $\pi$ -electronic states, we deduce that the work function is varied with the spatial location in nanotubes, as is the case in conventional metallic emitters. In other words, the work function in carbon nanotubes has also localized features as the localized valence electronic states. Here we define the localized work function as the potential energy difference of one electron between the highest occupied molecular orbital in the “tip states” and vacuum level. From Fig. 3, we obtain the localized work function  $\phi$  of carbon nanotubes (i.e., the tip), which is 5.08 eV, which is very close to the values of Lovall *et al.*<sup>17</sup> (5.10 eV) and the values of Shiraishi and Ata<sup>18</sup> (5.05 eV) for SWNT's. Moreover, it is larger than that of the open-ended states,<sup>7</sup> but smaller than that of the body,<sup>7</sup> which also attests to these cases that the emission property of one capped nanotube is weaker than that of one open-ended nanotube, and the electrons at the tip are more easily emitted than those at the body in nanotubes.

In comparison with the conventional definition of the work function, that of the localized work function has a vivid physical background and meaning that is the minimum energy spent to remove one electron localized at the occupied electronic states of the tip to the vacuum level. It reflects the electron emission process and characteristics in essence. Furthermore, we predict that these two work function values are maybe approached and not identical with each other along with the increase of the tube length owing to the nonmetallic tips.

#### IV. CONCLUSIONS

In this paper, we systematically study the localized valence states characteristics of single-walled carbon nanotubes by use of first-principles calculations. The localized valence states characteristics can be conveniently and clearly described by virtue of the discrete energy levels (i.e., localized molecular orbitals). With this approach, we not only find that the contributions of  $\pi$ -electronic states to field emission are sensitive to their spatial orientations ( $\pi$ -electronic states localized at the link between the body and tip make a predominant contribution to the field emission), but also affirm that the electron emission in one SWNT is not a continuum as in the usual metallic emitters. Furthermore, we define and calculate the localized work function of carbon nanotubes within the framework of the LCAO-MO cluster model. The calculated value of the localized work function is 5.08 eV, which is very close to the experimental values.

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