Kekulé pattern on conductance images between two STM probes

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The conductance image between two probes of scanning-tunneling-microscopy (STM) is calculated in a zigzag carbon nanotube within a tight-binding model and a realistic model for STM probes. A Kekulé-type pattern usually appears due to interference of states at K and K' points.

1 Introduction Carbon nanotubes are regarded as ballistic conductors. In metallic nanotubes, in particular, the backward scattering is entirely suppressed for scatterers with potential range larger than the lattice constant of a two-dimensional graphite and the conductance is quantized into $2e^2/\pi\hbar$ [1,2]. When several bands are occupied, a perfectly conducting channel transmitting through the system without being scattered back is present [3]. It is known that scanning tunneling microscopy (STM) and spectroscopy (STS) are a powerful technique for directly viewing electronic wave functions at the atomic level. Quite recently multi-probe STM was developed [4]. The purpose of this paper is to explicitly visualize interference effects in two-probe STM images in ballistic carbon nanotubes.

STM measurements have been conducted in order to observe the electronic wavefunctions in carbon nanotubes [5,6]. Energy-dependent interference patterns in the wavefunctions were observed in nanotubes shortened to less than 40 nm [6]. Numerical calculations were made on electronic states and STM images in a finite carbon nanotube [7]. Topographical STM images have been calculated within a tight-binding model and the appearance of the honeycomb structure has been demonstrated in infinitely long nanotubes [8]. Electron transmission has been studied between two STM tips as leads which contact the nanotube via single carbon atoms [9]. Recently, we have shown a Kekulé type pattern in two-probe STM images in armchair carbon nanotubes due to interference of states at K and K' point except in special cases [10]. In this paper, we calculate the conductance in a zigzag nanotube and discuss the robustness of the Kekulé pattern for arbitrary chirality.

2 Formulation

2.1 Preliminaries Figure 1 (a) shows the structure of two–dimensional (2D) graphite or graphene, two primitive translation vectors $\mathbf{a}$ and $\mathbf{b}$, and three vectors $\boldsymbol{\tau}_l$ ($l = 1, 2, 3$) connecting nearest-neighbor atoms. A unit cell contains two carbon atoms denoted as A (open circle) and B (closed circle). The origin of the coordinates is chosen at a B site, *i.e.*, a B site is given by $\mathbf{R}_B = n_a\mathbf{a} + n_b\mathbf{b}$ and an A site is $\mathbf{R}_A = n_a\mathbf{a} + n_b\mathbf{b} + \boldsymbol{\tau}$ with n_a and n_b being integers and $\boldsymbol{\tau} \equiv \boldsymbol{\tau}_1 = (\mathbf{a}+2\mathbf{b})/3$. In the coordinate system (x', y') fixed onto the graphene sheet, we have $\mathbf{a} = a(1,\, 0)$, $\mathbf{b} = a(1/2,\, \sqrt{3}/2)$, and $\boldsymbol{\tau} = a(0,\, 1/\sqrt{3})$, where $a = 0.246$ nm is the lattice constant. In the following we use a tight–binding model with a nearest–neighbor hopping integral $-\gamma_0$.

In a 2D graphite, two bands having approximately a linear dispersion cross the Fermi level at corner K and K' points of the first Brillouin zone. The wave vectors of the K and K' points are given by $\mathbf{K} = (2\pi/a)(1/3,\, 1/\sqrt{3})$ and $\mathbf{K}' = (2\pi/a)(2/3,\, 0)$. For states in the vicinity of the Fermi level $\varepsilon = 0$, the wavefunction is written as [11]

$$\psi_A(\mathbf{R}_A) = e^{\mathrm{i}\mathbf{K}\cdot\mathbf{R}_A} F_A^K(\mathbf{R}_A) + e^{\mathrm{i}\eta} e^{\mathrm{i}\mathbf{K}'\cdot\mathbf{R}_A} F_A^{K'}(\mathbf{R}_A), \quad (1)$$

$$\psi_B(\mathbf{R}_B) = -\omega e^{\mathrm{i}\eta} e^{\mathrm{i}\mathbf{K}\cdot\mathbf{R}_B} F_B^K(\mathbf{R}_B) + e^{\mathrm{i}\mathbf{K}'\cdot\mathbf{R}_B} F_B^{K'}(\mathbf{R}_B), \quad (2)$$

with $\omega = \mathrm{e}^{2\pi\mathrm{i}/3}$ in terms of the slowly–varying envelope functions F_A^K, F_B^K, $F_A^{K'}$, and $F_B^{K'}$ with chiral angle η.

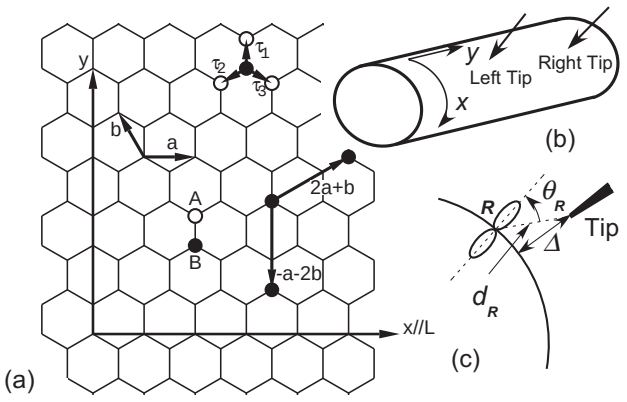

Figure 1 (a) Lattice structure of a two–dimensional graphite sheet. The coordinates are chosen in such a way that x is along the circumference of a nanotube and y is along the axis. (b) A schematic view of a carbon nanotube with two STM tips modeled by 1D wires. (c) A model of the STM tip and the carbon nanotube with a π orbital on a carbon atom at $\mathbf{R}$. Δ is the normal distance of the STM tip to the nanotube.

Then, in the vicinity of the K point, for example, they satisfy the **k**·**p** equation:

$$\gamma(\boldsymbol{\sigma}\cdot\hat{\mathbf{k}})\mathbf{F}^K(\mathbf{r})=\varepsilon\mathbf{F}^K(\mathbf{r}), \tag{3}$$

$$\mathbf{F}^K(\mathbf{r})=\begin{pmatrix} F_A^K(\mathbf{r}) \\ F_B^K(\mathbf{r}) \end{pmatrix}, \tag{4}$$

where $\gamma=\sqrt{3}a\gamma_0/2$ is the band parameter with γ_0 being a nearest-neighbor hopping integral, $\hat{\mathbf{k}}=(\hat{k}_x,\hat{k}_y)=-\mathrm{i}\boldsymbol{\nabla}$ is a wave vector operator, ε is the energy, and σ_x and σ_y are the Pauli spin matrices.

In nanotubes, the coordinate system (x,y) will be chosen in such a way that the x axis is in the chiral direction, *i.e.*, the direction along the circumference or the chiral vector $\mathbf{L}$, and the y axis in the direction of the axis. In metallic nanotubes, the **k**·**p** equation is solved under a periodic boundary condition in the x direction. The wave function for the linear bands at $\varepsilon=0$ is independent of the position and given by

$$\mathbf{F}^{K\pm}(\mathbf{r}) = \frac{1}{\sqrt{2LA}}\begin{pmatrix} \mp\mathrm{i} \\ 1 \end{pmatrix}, \tag{5}$$

$$\mathbf{F}^{K'\pm}(\mathbf{r}) = \frac{1}{\sqrt{2LA}}\begin{pmatrix} \pm\mathrm{i} \\ 1 \end{pmatrix}, \tag{6}$$

where $L=|\mathbf{L}|$, A is the length of the nanotube, and the upper and lower signs correspond to right and left-going waves, respectively.

2.2 Interference between K and K' Points We consider the conductance between two STM tips in an infinitely long metallic nanotube as illustrated in Fig. 1 (b). First, we consider traveling wave with $\varepsilon\approx 0$ injected from the B site $\mathbf{R}_B=0$. We may approximately take the lowest order of the coupling between the STM tip and carbon atoms, because the coupling is usually very weak. The injected electron equally propagates to both right and left directions, because of the symmetry of the configuration. Further, the wavefunction of the injected electron is decomposed into those at the K and K' point with the same amplitude. Then, eq. (2) shows that on the right hand side of the injection point $\mathbf{R}_B=0$, the envelope functions become

$$\mathbf{F}^K(\mathbf{r}) = -\omega^{-1}\mathrm{e}^{-\mathrm{i}\eta}\delta\mathbf{F}^{K+}(\mathbf{r}), \tag{7}$$

$$\mathbf{F}^{K'}(\mathbf{r}) = \delta\mathbf{F}^{K'+}(\mathbf{r}), \tag{8}$$

with δ being the amplitude. Upon substitution of the above into eq. (2), we have

$$\psi_A(\mathbf{R_A}) = \mathrm{i}\frac{\delta}{\sqrt{2LA}}(\omega^{-1}\mathrm{e}^{-\mathrm{i}\eta}\mathrm{e}^{\mathrm{i}\mathbf{K}\cdot\mathbf{R}_A}+\mathrm{e}^{\mathrm{i}\eta}\mathrm{e}^{\mathrm{i}\mathbf{K}'\cdot\mathbf{R}_A}), \tag{9}$$

$$= \mathrm{i}\sqrt{\frac{2}{LA}}\delta\,\mathrm{e}^{\mathrm{i}\pi n_a}\cos\Big[\frac{\pi}{3}(n_a-2n_b)+\eta\Big], \tag{10}$$

$$\psi_B(\mathbf{R_B}) = \frac{\delta}{\sqrt{2LA}}(\mathrm{e}^{\mathrm{i}\mathbf{K}\cdot\mathbf{R}_B}+\mathrm{e}^{\mathrm{i}\mathbf{K}'\cdot\mathbf{R}_B}), \tag{11}$$

$$= \sqrt{\frac{2}{LA}}\delta\,\mathrm{e}^{\mathrm{i}\pi n_a}\cos\Big[\frac{\pi}{3}(n_a-2n_b)\Big]. \tag{12}$$

The conductance between the STM probe at the origin and that at $\mathbf{R_B}$ is approximately proportional to the probability density $|\psi_B(\mathbf{R_B})|^2$. It becomes the maximum $\propto 2\delta^2$ for $n_a-2n_b=3m$ with an integer m and becomes $\propto(1/2)\delta^2$ for $n_a-2n_b=3m\pm1$. The probability density at A sites depends on the chirality. For zigzag nanotubes $\eta=0$, it becomes the maximum $\propto 2\delta^2$ for $n_a-2n_b=3m$ and $\propto(1/2)\delta^2$ for $n_a-2n_b=3m\pm1$.

The sites $\tilde{\mathbf{R}}=n_a\mathbf{a}+n_b\mathbf{b}$ satisfying $n_a-2n_b=3m$ with integer m form a honeycomb lattice. Its basis vectors can be chosen as $\tilde{\mathbf{a}}=-\mathbf{a}-2\mathbf{b}$ and $\tilde{\mathbf{b}}=2\mathbf{a}+\mathbf{b}$ as shown in Fig. 1 (a), for example, and therefore the lattice constant is $\sqrt{3}a$ and the area of the unit cell is $3\Omega_0$ with $\Omega_0=(\sqrt{3}/2)a^2$ being the area of the original honeycomb lattice spanned by the basis vectors $\mathbf{a}$ and $\mathbf{b}$. The maximum conductance is observed when two STM probes couple to atoms on this enlarged lattice for both A and B sublattices. This so-called Kekulé pattern is a result of the interference of traveling waves at the K and K' points as clearly shown in eq. (12). The pattern also appears in the wavefunction around a single vacancy [12,13].

2.3 Tip Model We consider a more realistic model of a nanotube with curvature and an STM tip with coupling to several carbon atoms. The hopping integral between the tip s atom and a π orbital at $\mathbf{R}$ of the tube is given by sp Slater–Koster form [8]:

$$t_{\mathbf{R}} = t_0 w_{\mathbf{R}}\exp\Big(-\frac{d_{\mathbf{R}}}{\lambda}\Big)\cos\theta_{\mathbf{R}}, \tag{13}$$

$$w_{\mathbf{R}} = \exp(-\alpha^2 d_{\mathbf{R}}^2)\Big[\sum_{\mathbf{R}'}\exp(-\alpha^2 d_{\mathbf{R}'}^2)\Big]^{-1}, \tag{14}$$

where $d_{\mathbf{R}}$ is the distance between the tip atom and the carbon atom, $\theta_{\mathbf{R}}$ is the angle with the orientation of the π

Table 1 The coordinates of the left STM tip shown in Fig. 2 (a) and the maximum values of the conductance, $G_{\max}$, used for plotting Figs. 2.

	$3\Delta x/a$	$\sqrt{3}\Delta y/a$	$G_{\max}$ ($10^{-10}e^2/\pi\hbar$)
(b)	0	0	15
(c)	0	-0.5	9.5
(d)	0	-1	1.3
(e)	0.4	-0.6	4.8
(f)	0.75	-0.25	5.7
(g)	1.1	0.1	4.8
(h)	-0.4	-1.19	2.1
(i)	0.4	-1.19	2.1

orbital as shown in Fig. 1 (c). This model hopping integral with parameters $\lambda = 0.085$ nm, $\alpha^{-1} \approx 0.13$ nm, and $\Delta = 0.5$ nm has been introduced in previous works [8, 10]. The STM tip is modeled by a chain of s-like atoms with nearest neighbor hopping integral $-t$ and the Fermi energy being fixed at the center of the one-dimensional band.

In order to deal rigorously with the infinite nanotube, we solve numerically a scattering problem in a finite nanotube between two STM probes connected at both ends to semi-infinite nanotubes. We calculate the transmission probability between these two STM tips. In terms of the transmission probability T, the conductance G is given by $G = (e^2/\pi\hbar)T$ using the Landauer formula. In actual calculations we consider the so-called (15,0) zigzag nanotube with $L = 15a$, and choose fixed parameters $t_0/\gamma_0 = -10$, $t/\gamma_0 = 1$. The Fermi energy is chosen at $\varepsilon = 0.05(2\pi\gamma/L)$ in such a way that the Fermi wave-length is much longer than the distance of STM tips, which enable us to clearly see the Kekulé pattern. Even if Fermi wave length is shorter than the tip distance and thus the Fermi energy is higher, the calculated conductance images exhibit the same behavior except for an interference-like modulation due to the finite wave length.

3 Numerical Results In the following, the left STM tip is fixed at several points marked by open circles in Fig. 2 (a) and the right tip is continuously swept over the wide region. The actual coordinates of the left tip are given in Table 1.

Figure 2 shows the conductance for varying the position of the right STM tip when the left tip is fixed at points 'b' to 'i' shown in Fig. 2 (a). The position of the left tip is denoted by an open circle, but its actual position is shifted by $(0,\ -26\sqrt{3})a$ in the coordinate system (x, y) shown in the Fig. 1 (a) and therefore is quite far from the right tip position. Because the distance between two tips is much larger than the circumference, the contribution only of traveling modes is dominant and therefore the conductance varies periodically in all the cases.

When the left tip is on top of site B_1 denoted by 'b' in Fig. 2 (b), the conductance exhibits a clear Kekulé pattern and follows the simplified estimation presented in §2. In fact, the conductance is largest at B sites $\tilde{\mathbf{R}}_B$ and A sites $\tilde{\mathbf{R}}_B + \tau$ related to the left-tip atom by the basis vectors $\tilde{\mathbf{a}}$ and $\tilde{\mathbf{b}}$. Further, it is small at the other A and B sites. With the increase in the displacement 'c' to the hexagon center 'd' along the axis corresponding to (c) and (d), respectively, the same image appears with the Kekulé pattern. Actually, the same image always emerges while the left-tip is on the line along tube axis, including on top of A site, where a total phase factor is the only difference of wavefunctions injected from B site $\tilde{\mathbf{R}}_B$ and A site $\tilde{\mathbf{R}}_B + \tau$. With the increase in the deviation from the hexagon center, the image varies continuously from (d) to (f) toward the same one as Fig. 2 (d) but shifted by $\mathbf{a} + \mathbf{b}$, when the left tip is on another hexagon center at 'd′'.

We have demonstrated in armchair nanotubes that the Kekulé pattern disappears for special cases and original periodicity recovered in the conductance images, due to the lack of interference between K and K' states [10]. In the special case, the electron is injected into a single traveling state at one of Fermi points, if a wave is injected from three carbon atoms in the specific ratio shown in our previous work for arbitrary chirality, because the injected wavefunction is orthogonal to that of traveling waves at the other Fermi point.

For zigzag nanotube, the ratio is given as $\sqrt{3} : 2 : 1$, when the left tip couples to three carbon atoms denoted as $\mathrm{B}_2 : \mathrm{A}_4 : \mathrm{A}_2$ in Fig. 2 (a) for the injection into K state and $\mathrm{B}_3 : \mathrm{A}_4 : \mathrm{A}_3$ for K' state. Figures 2 (h) and (i) show the conductance, when the left tip position is precisely chosen to satisfy the ratio for the injection into K and K' state, respectively. The Kekulé pattern almost disappears but is weakly seen, because the coupling to the fourth site at B_1 can not be ignored and thus weak interference remains, within our model of the hopping integral eq. (14). Actually the coupling strength to the fourth B_1 site is 70% of that to the third sites (h) A_2 and (i) A_3.

4 Conclusions We have calculated numerically the conductance between two STM probes in a metallic zigzag nanotube. The STM probes have been modeled with sp Slater-Koster hopping terms. It has been shown that a Kekulé pattern usually appears due to interference between traveling waves at K and K' points.

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References

[1] T. Ando and T. Nakanishi, J. Phys. Soc. Jpn. **67**, 1704 (1998).

[2] T. Ando, T. Nakanishi, and R. Saito, J. Phys. Soc. Jpn. **67**, 2857 (1998).

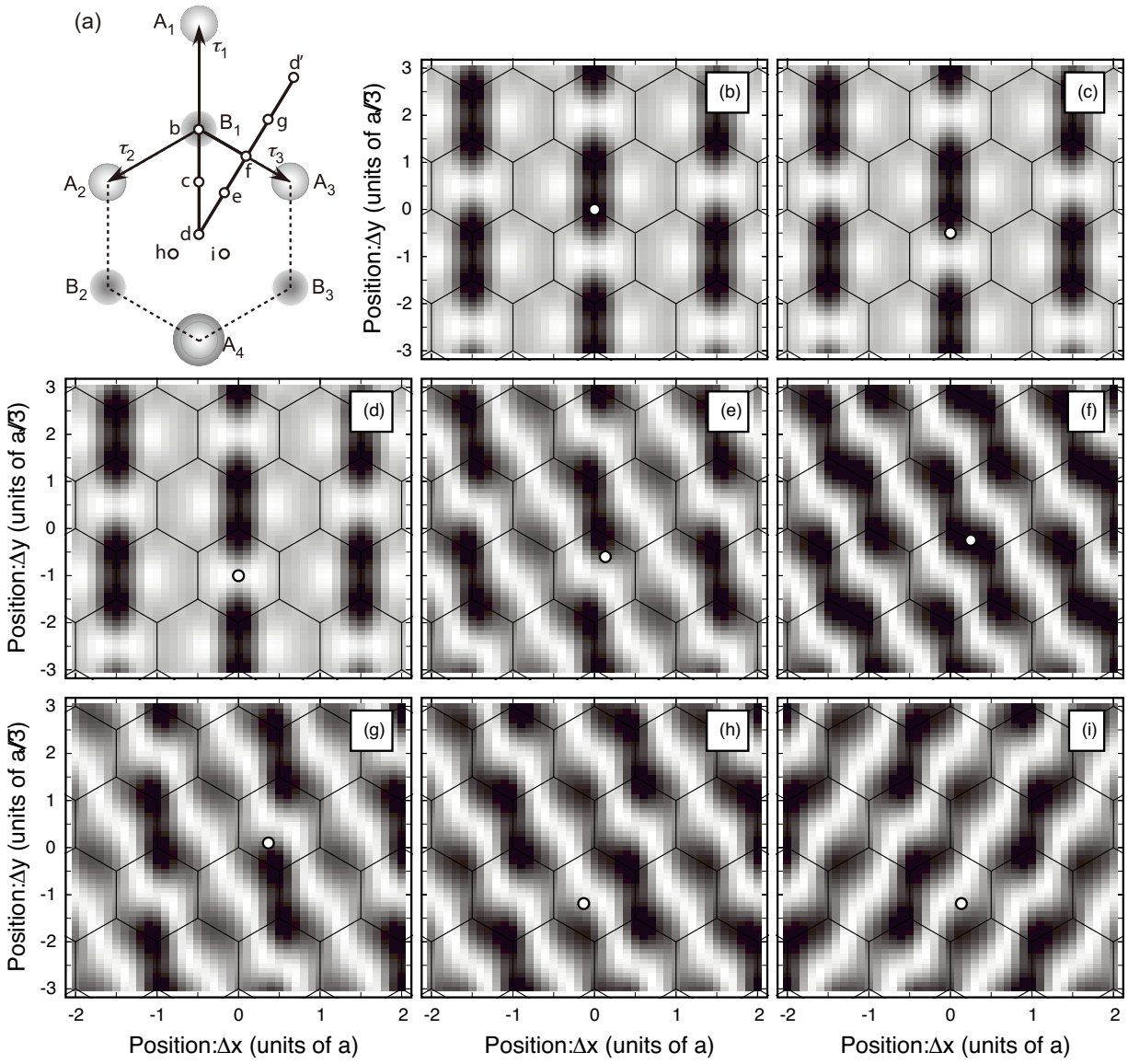

Figure 2 (a) The left STM-tip positions for which the STM image of the right tip is calculated. The actual coordinates are given in Table 1. Calculated conductance as a function of right STM tip position for the left-tip position from 'b' to 'i' of (a). The left STM tip is fixed above a position denoted by a open circle, but its actual position is at $(0, -26\sqrt{3})a$ in the coordinate system and therefore is quite far from the right tip. The conductance is shown by the density in the maximum listed in a Table 1 as plot range.

[3] T. Ando and H. Suzuura, J. Phys. Soc. Jpn. **71**, 2753 (2002).

[4] O. Kubo, Y. Shingaya, M. Nakaya, M. Aono, and T. Nakayama, Appl. Phys. Lett. **88**, 254101 (2006).

[5] L. C. Venema, J. W. G. Wildoer, J. W. Janssen, S. J. Tans, H. L. J. T. Tuinstra, L. P. Kouwenhoven, and C. Dekker, Science **283**, 52 (1999).

[6] S. G. Lemay, J. W. Janssen, M. van den Hout, M. Mooij, M. J. Bronikowski, P. A. Willis, R. E. Smalley, L. P. Kouwenhoven, and C. Dekker, Nature **412**, 617 (2001).

[7] A. Rubio, D. Sanchez-Portal, E. Artacho, P. Ordejon, and J. M. Soler, Phys. Rev. Lett. **82**, 3520 (1999).

[8] V. Meunier and Ph. Lambin, Phys. Rev. Lett. **81**, 5588 (1998).

[9] L. F. Chibotaru, S. Compernolle, and A. Ceulemans, Phys. Rev. **B 68**, 125412 (2003).

[10] T. Nakanishi and T. Ando, J. Phys. Soc. Jpn. **77**, 024703 (2008).

[11] T. Ando, J. Phys. Soc. Jpn. **74**, 777 (2005).

[12] M. Igami, T. Nakanishi, and T. Ando, J. Phys. Soc. Jpn.**68**,716 (1999).

[13] P. Ruffieux, M. Melle-Franco, O. Gröning, M. Bielmann, F. Zerbetto, and P. Gröning, Phys. Rev. **B 71**, 153403 (2005).