Localized Eigenstates in Carbon Nanotube Caps

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Localized cap states are discussed in caps consisting of \( q \) graphene sheets of regular triangles (1 \( \leq q \leq 6 \)) attached to a metallic nanotube both analytically and numerically in an effective-mass approximation. There are cap states at \( \varepsilon = 0 \) (the energy of a carbon \( \pi \)-orbital) associated with first excited conduction band and highest valence band. Cap states associated with other bands lie in the vicinity of the corresponding band edges. The wave function behaves as \( r^{1/2} \) in the vicinity of a five-membered ring for states with \( \varepsilon = 0 \), where \( r \) is the distance from the ring.

\section{1. Introduction}

Carbon nanotubes (CNs) are often closed by a structure called a cap at the end.\(^1\)\(^2\) A cap, according to Euler’s theorem, contains six five-membered rings if the cap is constructed of only six- and five-membered rings. The presence of localized states in some caps was predicted theoretically by the study of local density of states in a tight-binding model.\(^3\) Experiments using scanning tunneling microscopy (STM) gave some evidence for the presence of such localized states.\(^4\)\(^5\) Further, patterns associated with the presence of six five-membered rings were observed by a field emission microscopy.\(^6\) The purpose of this paper is to study localized cap states in some representative caps attached to an infinitely long nanotube in an effective-mass approximation.

Capped nanotubes are deeply related to graphitic cones\(^7\)\(^8\) or nano-horns.\(^9\) The graphitic cones consist of only caps. The nano-horns are caps with five five-membered rings at the tip, have a cone angle of 20°, and are occasionally attached to CNs. There have been several theoretical studies on the local density of states of these systems.\(^10\)\(^11\)\(^12\) The local density of states on the graphitic cone with one five-membered ring at its tip around the Fermi level was suggested to behave as \( r^{-2/5} \), where \( r \) is the distance from the tip.\(^13\)\(^14\)\(^15\)\(^16\)

There are many systems with topological defects such as five- and seven-membered rings. One interesting system is a junction connecting two nanotubes with different structures through a pair of five- and seven-membered rings.\(^1\)\(^17\) The conductance of the junction systems was calculated in a tight-binding model and shown to exhibit a universal power-law dependence on the ratio of the circumference of two nanotubes.\(^18\)\(^19\)\(^20\) The universal behavior was ascribed to unique boundary conditions for envelope functions in an effective-mass approximation, associated with the topological defects pair.\(^21\)\(^22\) The conductance of the junction systems has been calculated as a function of energy\(^23\)\(^24\) and also in magnetic fields.\(^25\)\(^26\) using the boundary conditions.

In previous study a phase shift for scattering of an electron wave on several different caps was calculated in a tight-binding model\(^27\) and using an effective-mass approximation.\(^28\) A discrete 2\(\pi\) jump occurs in the energy dependence of the phase shift in several less symmetric caps due to resonance with states localized in a cap.\(^27\) Energy levels of such cap states were calculated in nanotubes with different diameters in a tight-binding model.\(^29\) This paper, we discuss both analytically and numerically the energy levels and the wave functions for localized cap states in the effective-mass approximation.

This paper is organized as follows: In §2 a review is given on the effective-mass treatment of electronic states in capped nanotubes. In §3 the method to determine energy levels and wave functions of localized cap states based on plane wave expansion is introduced and discussed. In §4 explicit numerical results are presented. A discussion and summary are given in §5 and 6, respectively.

\section{2. Localized Cap States}

\subsection{2.1 Effective-Mass Theory}

In a two-dimensional (2D) graphite, two kinds of sublattice points are present in a unit cell denoted by A and B as shown in Fig. 1. The \( \pi \) bands where the Fermi level lies have almost linear dispersion and cross at K and K’ points of the Brillouin zone. The effective-mass equation in the vicinity of the K and K’ point is given by\(^30\)

\[ H\mathbf{F}(\mathbf{r}) = \varepsilon \mathbf{F}(\mathbf{r}), \] (2.1)

with

\[ H = \gamma \begin{pmatrix} 0 & \hat{k}_x - i\hat{k}_y & 0 \cr \hat{k}_x + i\hat{k}_y & 0 & 0 \cr 0 & 0 & \hat{k}_x - i\hat{k}_y \end{pmatrix}, \] (2.2)

\[ \hat{k}_x = -i\nabla + \frac{e\mathbf{A}}{\hbar c}, \] (2.3)

and

\[ \mathbf{F}(\mathbf{r}) = \begin{pmatrix} F_A^K(\mathbf{r}) \\ F_B^K(\mathbf{r}) \\ F_A^K(\mathbf{r}) \\ F_B^K(\mathbf{r}) \end{pmatrix}, \] (2.4)

where \( \gamma \) is a band parameter and \( \mathbf{A} \) is a vector potential. In the above equations, \( k_x \) and \( k_y \) are wave number
operators in the $x$ direction along the circumference and in the $y$ direction along the axis of CN, respectively, and $F(r)$ is an envelope function. The origin of $\varepsilon$ is chosen at the energy of a $\pi$ orbital of a carbon.

In the case of a nearest-neighbor tight-binding model, we have $\gamma = \sqrt{\pi}a\theta_0/2$ where $a$ is the lattice constant of 2D graphite and $\theta_0$ is the transfer integral between the nearest-neighbor carbon sites. The envelope function is related to a tight-binding wave function through \[ \psi_{\pm}(R_A) = e^{iK R_A}F_{\pm}(R_A) + e^{i\eta}e^{iK R_A}F_{\pm}^*(R_A), \]
(2.5)
with $\omega = e^{2\pi i/3}$ and $\eta$ being a chiral angle between a chiral vector $L = n_a a + n_b b$ and the $x$ axis, where $R_A$ and $R_B$ denote positions of A and B sites, respectively, and $\psi_A(R_A)$ and $\psi_B(R_B)$ are the amplitudes of the $\pi$ orbital.

### 2.2 Nanotube Caps with Magnetic Flux

In this paper, we consider only an armchair nanotube with $\eta = \pi/6$ and caps consisting of $q$ graphene sheets of regular triangles. A cap with $q = 6$ has been called a pencil cap and one with $q = 5$ a bowl cap. These caps have six five-membered rings as shown in Figs. 2 (a) and (b). Other caps with $1 \leq q \leq 4$ have $q$-fold rotation symmetry around the CN axis. Let $r_0$ be the side of an equilateral triangle. Then, we have
\[ L = qr_0, \]
\[ r_0 = \sqrt{3}pa, \]
(2.6)
(2.7)
with integer $p$ and $L = |L|$ being the circumference of the nanotube. We consider a situation that a magnetic flux $\phi$ parallel to the CN axis passes through the $q$-membered ring as shown in Fig. 3.

The effective-mass equation is written in terms of polar coordinates with the origin at the cap center as
\[ \hat{k}_x \pm i\hat{k}_y = e^{i\pm \theta}(\hat{k}_x \pm i\hat{k}_y), \]
\[ \hat{k}_x = -\frac{\partial}{\partial r} + \frac{eA_e}{\hbar c}, \]
\[ \hat{k}_y = -\frac{\partial}{\partial \theta} + \frac{eA_b}{\hbar c}, \]
(2.8)
(2.9)
(2.10)
where the vector potential is given by
\[ (A_e, A_b) = \left(0, \frac{6\phi}{q} \frac{1}{2\pi r} \right). \]
(2.11)
In the cap region, the wave function should satisfy
\[ F(R^q r) = e^{2\pi i \phi_0 / q} \frac{T_{\pi/3}^q}{T_{\pi/3}^q} F(r), \]
(2.12)
where $R$ denotes the $\pi/3$ rotation around the origin ($R^q$ denotes the $q\pi/3$ rotation), $\phi_0 = ch/e$ is the magnetic flux quantum, and
\[ T_{\pi/3} = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & -\omega^{-1} \\ \omega & 0 & 0 \end{pmatrix}, \]
(2.13)
which has been obtained for a junction system. In the tube region the vector potential is $(A_e, A_b) = (\phi/L, 0)$. The wave function should satisfy the periodic boundary condition of the circumference:
\[ F(x + L, y) = e^{2\pi i \phi_0 / q} F(x, y). \]
(2.14)

The present capped nanotube has $q$-fold rotation symmetry around the axis and therefore states are specified by discrete “angular momentum” $\sigma$ with $\sigma = 0, \ldots, q-1$. In the tube region it is defined as
\[ F(x + r_0, y) = e^{2\pi i \sigma / q} F(x, y), \]
(2.15)
with
\[ \sigma_0 = \sigma + \frac{\phi}{\phi_0}. \]
(2.16)

In the cap region it is given by
\[ F(Rr) = e^{2\pi i \sigma / q} F(r). \]
(2.17)

It is sufficient to connect for given $\sigma_0$ the wave functions only along the line $-r_0/2 < x < r_0/2$ at the boundary between the tube and cap regions.

It is now clear that the wave functions are determined by specifying $\sigma_0 \equiv \sigma / q$ independent of individual values of $\sigma_0$ and $q$. In fact, there is a one-to-one correspondence between the wave function for a state with $\sigma_0$ in a nanotube capped by $q'$ equilateral triangles and the present wave function when the following condition is satisfied:
\[ \frac{\sigma_0'}{q'} = \frac{\sigma_0}{q}. \]
(2.18)
This is valid also in a tight-binding model as noted previously. For example, a state with $\sigma = 1$ of a bowl cap ($q = 5$) in the absence of magnetic flux corresponds to $\sigma_0 = 6/5$ of a pencil cap ($q = 6$). This means that it is sufficient to consider only a pencil cap in the presence of magnetic flux $\phi$ in the range $-3 < \sigma_0 \leq 3$.

The same is applicable to energy levels. In fact, the energy levels of capped tubes with same $\sigma_0 / q$ are all equal if being scaled by $2\pi \gamma / r_0 = (2\pi \gamma / L)q$. This shows that for capped nanotubes with same circumference $L$, energy levels $\varepsilon(\sigma_0, q)$ for $\sigma_0$ and $q$ and $\varepsilon(\sigma_0', q')$ for $\sigma_0'$ and $q'$ are related to each other through
\[ \frac{\varepsilon(\sigma_0, q)}{q} = \frac{\varepsilon(\sigma_0', q')}{q'}, \]
(2.19)
when eq. (2.18) is satisfied.

In the present capped nanotubes there exists a mirror symmetry plane containing the axis. As is shown in Appendix A states with $\sigma_0$ are transformed into those with $-\sigma_0$ by the mirror reflection. Therefore, it is sufficient to consider only the region $0 \leq \sigma_0 \leq 3$.

### 2.3 Wave Function in Nanotube Region

The envelope functions in the tube region are given
by a plane wave $\exp(\imath k x + i k y)$ under the boundary condition (2.15) of the $q$-fold rotation symmetry. Therefore, we have the wave number in the $x$ direction
\begin{equation}
\kappa(j) = \frac{2\pi}{L}(q_j + \sigma_\phi),
\end{equation}
where $j$ is an integer. Localized eigenstates consist only of evanescent modes which decay away from the cap. The wave number of the evanescent mode with $\kappa(j)$ with energy $\varepsilon$ in the range $|\varepsilon| < \gamma |\kappa(j)|$ becomes a pure imaginary number $k = -\imath k_j$ with
\begin{equation}
        k_j = \sqrt{\kappa(j)^2 - (\varepsilon/\gamma)^2}.
\end{equation}

The corresponding wave functions are given by
\begin{align}
F_{j}^{K-} &= \frac{1}{\sqrt{L}} f^{K-}_j \exp[\imath(\varepsilon)_j x + k_j y], \\
F_{j}^{K'} &= \frac{1}{\sqrt{L}} f^{K'}_j \exp[\imath(\varepsilon)_j x + k_j y],
\end{align}
with
\begin{align}
f^{K-}_j &= \frac{1}{\sqrt{2}} \left( \begin{array}{c}
\text{sgn}(\varepsilon) u^{-}_j \\
\text{sgn}(q_j + \sigma_\phi) u^{+}_j \\
0 \\
0
\end{array} \right), \\
f^{K'}_j &= \frac{1}{\sqrt{2}} \left( \begin{array}{c}
0 \\
0 \\
\text{sgn}(\varepsilon) u^{+}_j \\
\text{sgn}(q_j + \sigma_\phi) u^{-}_j
\end{array} \right),
\end{align}
and
\begin{equation}
u^{\pm}_j = \sqrt{1 \pm k_j/|\kappa(j)|},
\end{equation}
where
\begin{equation} \text{sgn}(t) = \begin{cases} +1 & (t > 0); \\ 0 & (t = 0); \\ -1 & (t < 0). \end{cases} \end{equation}

2.4 Wave Function in Cap Region

Under the boundary condition (2.17), we have the wave functions
\begin{equation}
F_{\mu+}(r, \theta) = \begin{pmatrix} Z_{\mu+}(\tilde{\varepsilon} r) \\
\text{sgn}(\varepsilon) i Z_{\mu+ + 1}(\tilde{\varepsilon} r) \exp(\imath \phi) \\
-(-1)^m \exp(\imath \phi/3) \text{sgn}(\varepsilon) Z_{\mu+ + 1}(\tilde{\varepsilon} r) \exp(\imath \phi/3) \\
-(-1)^m \exp(\imath \phi/3) Z_{\mu-}(\tilde{\varepsilon} r) \end{pmatrix} \frac{\exp(i \mu \theta)}{D_{\mu+}},
\end{equation}
and
\begin{equation}
F_{\mu-}(r, \theta) = \begin{pmatrix} \text{sgn}(\varepsilon) Z_{\mu- + 1}(\tilde{\varepsilon} r) \exp(\imath \phi) \\
\exp(\imath \phi) Z_{\mu-}(\tilde{\varepsilon} r) \\
-(-1)^m \exp(\imath \phi/3) Z_{\mu- + 1}(\tilde{\varepsilon} r) \exp(\imath \phi/3) \\
-(-1)^m \exp(\imath \phi/3) \text{sgn}(\varepsilon) Z_{\mu- + 1}(\tilde{\varepsilon} r) \exp(\imath \phi/3)
\end{pmatrix} \frac{\exp(-i \mu \theta)}{D_{\mu-}},
\end{equation}
with
\begin{align}
\mu_+ &= 3m + 1 + 6\sigma_\phi/q, \\
\mu_- &= 3m + 1 - 6\sigma_\phi/q,
\end{align}
where $m$ is an integer, $\tilde{\varepsilon} = |\varepsilon|/\gamma$, $Z_{\mu}(\tilde{\varepsilon} r)$ denotes the Bessel $J_{\mu}(\tilde{\varepsilon} r)$ and Neumann $N_{\mu}(\tilde{\varepsilon} r)$ function, and $D_{\mu\mp}$ is a normalization coefficient defined by
\begin{equation}
D_{\mu\pm} = \int_0^{2\pi} d\theta r_0 |Z_{\mu\pm}(\tilde{\varepsilon} r_0)|^2.
\end{equation}

The wave functions at $\varepsilon = 0$ are defined by the limit $\varepsilon \to 0$ and are given by
\begin{align}
F_{\mu+}(r, \theta) &= \frac{(r/r_0)^m \exp(\imath \phi)}{\sqrt{2\pi r_0}} \begin{pmatrix} 1 \\
0 \\
0 \\
(-1)^m \exp(\imath \phi/3) \end{pmatrix}, \\
F_{\mu-}(r, \theta) &= \frac{(r/r_0)^m \exp(\imath \phi)}{\sqrt{2\pi r_0}} \begin{pmatrix} i \\
0 \\
0 \\
(-1)^m \exp(\imath \phi/3) \end{pmatrix}.
\end{align}
These wave functions are continuous as a function of $\varepsilon$ except at $r = 0$ as has been discussed previously.28

There are various restrictions on the possible values of $\mu_\pm$. First, the wave function should be normalizable, i.e.,
\begin{equation} \int r dr d\theta |F_{\mu}|^2 < \infty. \end{equation}

This shows that the Neumann functions $N_{\mu}$ are not allowed and the Bessel functions $J_{\mu}$ should satisfy $\mu > 0$. Consider an area surrounded by a contour $C$, next. A partial integration gives
\begin{align}
&\int_C dr dr' [H F_{\mu}(r) - \int_C dr' [H F_{\mu'}(r')]^\dagger F_{\mu'}(r)] \\
&= -\imath \gamma \int_C F_{\mu}^\dagger \tilde{S} F_{\mu} \times ds = -\imath \gamma \int_C F_{\mu}^\dagger |\tilde{S} \cdot n| F_{\mu} ds,
\end{align}
where $s$ is the vector along the contour, $n$ is a unit vector in the outward direction perpendicular to the contour, and $\tilde{S} = (\Sigma_x, \Sigma_y)$, with
\begin{equation}
\Sigma_x = \begin{pmatrix} \sigma_x & 0 \\
0 & \sigma_x \end{pmatrix}, \quad \Sigma_y = \begin{pmatrix} 0 & -\sigma_y \\
\sigma_y & 0 \end{pmatrix}.
\end{equation}
That $H$ should be Hermitian requires that the boundary integral in the right hand side of eq. (2.34) should at least be well-defined. For a contour passing the origin $r = 0$, therefore, we obtain another condition $\mu + \mu' > 0$ for $\mu = \mu_+$ and $\mu' = \mu_-$ or $\mu = \mu_-$ and $\mu' = \mu_+$. If it is combined with the condition that there should not be remarkable unbalance between the choice of the minimum values of $\mu_+$ and $\mu_-$, we have the more severe condition
\begin{equation}
\mu_+ > -\frac{1}{2}.
\end{equation}
This condition is same as that obtained previously for graphite cones.13,15

Figure 4 shows allowed values of $\mu_\pm$ in the vicinity of such lower bounds. In the region $\sigma_\phi < 3/2$, $\mu_+ = \sigma_\phi$ and $\mu_+ = 1 - \sigma_\phi$, and in the region $\sigma_\phi > 3/2$, $\mu_+ = \sigma_\phi - 3$ and $\mu_+ = -\sigma_\phi + 3$, where $\mu_\pm$ is the minimum allowed value of $\mu_\pm$. Exactly at $\sigma_\phi = 3/2$, a discrete jump occurs in $\mu_\pm$ and therefore $\mu_\pm$ is undefined. The present choice
of $\mu_{\text{min}}$ shows that the wave function in the vicinity of a five-membered ring at the tip of a bowl cap in the absence of a flux behaves as $\propto r^{-1/5}$ in contrast to $\propto r^{-3/5}$ discussed earlier\textsuperscript{21,26,28} without consideration of the condition (2.36), where $r$ is the distance from the five-membered ring.

§3. Localized Cap States

3.1 Plane Wave Expansion

We formulate the method to obtain the localized eigenstates in the pencil cap with $q = 6$ in the presence of a magnetic flux $\phi$. As has been discussed in the previous section, results for caps with $q \neq 6$ can be obtained immediately by using the relation given by eqs. (2.18) and (2.19). They can exist in the energy range $|\varepsilon| < 2\pi|\sigma_\phi|/L$ with $-3 < \sigma_\phi \leq 3$. The wave functions $F_T(x)$ in the tube region and $F_C(x)$ in the cap region are expanded as

$$F_T(x) = \frac{1}{\sqrt{L}} \sum_{j = N_2}^{N_1} [C_j^{K'} f_j f_j^{K'} + C_j^{K} f_j^{K'}] e^{i(x + k_j)\phi}, \quad (3.1)$$

$$F_C(x) = \sum_{m = -M_2}^{M_1} A_m F_{\mu_+}(x, y) + \sum_{m = -M_2'}^{M_1'} B_m F_{\mu_-}(x, y), \quad (3.2)$$

where $C_j^{K'}$, $C_j^{K}$, $A_m$, and $B_m$ are expansion coefficients. It is sufficient to connect the above functions in the range $-r_0/2 \leq x \leq r_0/2$ on the boundary $y = -\sqrt{3}r_0/2$ because of the rotation symmetry as mentioned in the previous section.

To obtain the solution, we expand the wave functions into Fourier series. Then, the coefficients should satisfy the matching conditions:

$$C_j^{K'} f_j f_j^{K'} + C_j^{K} f_j^{K'} = \sum_{m = -M_1}^{M_1} A_m G_{j,m} + \sum_{m = -M_2'}^{M_2'} B_m H_{j,m}, \quad (3.3)$$

where $G_{j,m}$ and $H_{j,m}$ are given by

$$G_{j,m} = \sqrt{L} \left( \begin{array}{c} \text{sgn}(\varepsilon) I_2^{0+} \\ \text{sgn}(\varepsilon) I_2^{10+} \\ -i(-1)^{m+1} e^{\pi/3} I_2^{10+} \\ (-1)^m e^{\pi/3} \text{sgn}(\varepsilon) I_2^{0-} \end{array} \right), \quad (3.4)$$

and

$$H_{j,m} = \sqrt{L} \left( \begin{array}{c} \text{sgn}(\varepsilon) I_2^{0+} \\ -i(-1)^{m+1} e^{\pi/3} I_2^{10+} \\ \text{sgn}(\varepsilon) I_2^{0-} \\ (-1)^m e^{\pi/3} \text{sgn}(\varepsilon) I_2^{10+} \end{array} \right), \quad (3.5)$$

with

$$I_1^{0+} = \int_{-1/2}^{1/2} dt J_{\mu_+} \left( \varepsilon r_0 \sqrt{t^2 + 3/4} \right) e^{-i2\pi(6j + \sigma_\phi)t/q} \left( t - i\sqrt{3}/2 \right)^{\pm\mu_+} / \sqrt{t^2 + 3/4}, \quad (3.6)$$

$$I_2^{0+} = \int_{-1/2}^{1/2} dt J_{\mu_+} \left( \varepsilon r_0 \sqrt{t^2 + 3/4} \right) e^{-i2\pi(6j + \sigma_\phi)t/q} \left( t - i\sqrt{3}/2 \right)^{\pm\mu_+ + 1} / \sqrt{t^2 + 3/4}. \quad (3.7)$$

The total number of the equations is $4(N_1 + N_2 + 1)$ and the total number of the coefficients is $2(N_1 + N_2 + 1) + M_1 + M_2 + M_1' + M_2' + 2$. They should be chosen such that there should be a unique solution for an outgoing traveling wave in the presence of an incoming traveling wave. The localized states are obtained when such equations have a nontrivial solution even in the absence of incoming traveling wave. This automatically gives a relation between the number of modes in the tube and cap region. This condition leads immediately to the relation

$$2(N_1 + N_2) = M_1 + M_2 + M_1' + M_2'. \quad (3.8)$$

First, $M_2$ and $M_2'$ are given by the minimum of $\mu$ and $\mu'$ as has been discussed in the previous section. Next, there should not be so much difference between $M_1$ and $M_1'$, and between $N_1$ and $N_2$. This condition determines $M_1$ and $M_1'$ almost uniquely if we specify a cutoff energy $\varepsilon_c$ or wave number $k_c = \varepsilon_c/\gamma$ and $N_1$ and $N_2$ are determined by the maximum and minimum value of $j$ satisfying the condition that $\gamma |\kappa(j)| \leq \varepsilon_c$. It turns out, however, that the results do not converge with the increase of the cutoff energy but oscillate almost periodically as a function of $\varepsilon_c$ when $\varepsilon_c$ is increased continuously. Therefore, the cutoff should be chosen carefully in an appropriate manner.

Figure 5 shows $\gamma |\kappa(j)| = 2\pi|\sigma_\phi|/L$ as a function of $\sigma_\phi$. First, the total number of independent modes should not change even if the flux is varied. This condition alone uniquely specifies $\varepsilon_c = \varepsilon_{c2}(j)$ or $\varepsilon_c = \varepsilon_{c1}(j)$, with

$$\varepsilon_{c1}(j) = \frac{2\pi\gamma(6j + 3)}{L} = \frac{2\pi\gamma (j + 1/2)}{r_0}, \quad \varepsilon_{c2}(j) = \frac{2\pi\gamma(6j)}{L} = \frac{2\pi\gamma}{r_0 j}. \quad (3.9)$$

The cutoff $\varepsilon_{c1}(j)$ corresponds to the cutoff of the mode number $N_1 = N_2 = j$ and $\varepsilon_{c2}(j)$ to $N_1 = N_2 - 1 = j$. Further, Fig. 5 shows that the choice $\varepsilon_c = \varepsilon_{c1}(j)$ is more reasonable near $\sigma_\phi = 0$ and $\varepsilon_c = \varepsilon_{c2}(j)$ near $\sigma_\phi = 3$ because the cutoff lies between wave vectors far apart from each other. In the following, therefore, we shall choose $\varepsilon_c = \varepsilon_{c2}(j)$ for $0 \leq \sigma_\phi < 3/2$ and $\varepsilon_c = \varepsilon_{c1}(j)$ for $3/2 < \sigma_\phi \leq 3$. This causes a discrete jump at $\sigma_\phi = 3/2$. Near $\sigma_\phi = 3/2$ there is no clear reason to select $\varepsilon_{c1}(j)$ or $\varepsilon_{c2}(j)$ and this region will be marked as a gray zone in the following.

The method introduced above can sometimes provide spurious solutions as will be discussed later in §5. In order to remove such inappropriate states we should confirm the matching of the actual wave functions. For
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this purpose we consider the dependence of $\Delta$ on the basis number $j$, where

$$\Delta = \frac{\int_{-r_{1}/2}^{r_{1}/2} dx |F_{\sigma}(x) - F_{\sigma}(x)|^2}{\int_{-r_{1}/2}^{r_{1}/2} dx \left[|F_{\sigma}(x)|^2 + |F_{\sigma}(x)|^2\right]/2}. \quad (3.10)$$

3.2 Lowest-Modes Approximation

For simplicity, we consider first the region $0 < \sigma_{\phi} < 3/2$ in a lowest-modes approximation in which only modes $N_{1} = 0$ and $N_{2} = 0$ are included corresponding to $\varepsilon_{c} = \varepsilon_{c1}(j)$ with $j = 1$. In this case the matching condition is

$$C_{0}^{K_{-}} f_{0}^{K_{-}} + C_{0}^{K_{+}} f_{0}^{K_{+}} - A_{0} G_{0,0} - B_{0} H_{0,0} = 0. \quad (3.11)$$

This gives only a trivial solution $A_{0} = B_{0} = C_{0}^{K_{-}} = C_{0}^{K_{+}} = 0$ except at $\varepsilon = 0$. At $\varepsilon = 0$ we have a nontrivial solution

$$A_{0} = 0,$$

$$C_{0}^{K_{-}} = i e^{i\pi/3} B_{0} \sqrt{L} I_{1}^{0,1-\sigma_{\phi}},$$

$$C_{0}^{K_{+}} = -i B_{0} \sqrt{L} I_{1}^{0,1-\sigma_{\phi}},$$

with nonzero $B_{0}$ and

$$I_{1}^{3m+1-\sigma_{\phi}} = \frac{i}{\sqrt{2\pi r_{0}(3m+1)}} \left[e^{i(3m+1)/3} - e^{i2(3m+1)/3}\right]. \quad (3.13)$$

This shows that the amplitude of the wave function in the cap region is proportional to $r^{-\mu_{\sigma}^{\min}} = r^{1-\sigma_{\phi}}$. In the case of $\sigma = 1$ for a pencil cap in the absence of a magnetic flux ($\sigma_{\phi} = 1$), in particular, the wave function is independent of $r$ in the cap. In a bowl cap, on the other hand, the amplitude for $\sigma = 1$ and $\phi = 0$ is proportional to $r^{-1/5}$ and becomes singular at the five-membered ring at the cap tip. In both cases, the wave function in the tube region decays exponentially away from the cap, i.e.,

$$\alpha \exp(-2\pi r_{0}/|\mu_{\sigma_{\phi}}|/L).$$

This state is not spurious because $\Delta$ decreases monotonically with the increase of $\varepsilon_{c1}$ as will be shown explicitly in the next section.

§ 4. Numerical Results

Figure 6 (a) shows an example of calculated energy levels of localized states as a function of $\sigma_{\phi}$. The solid lines represent the present results and the dotted line those in a tight-binding model. In the vicinity of $\sigma_{\phi} = 3/2$ there remains uncertainty in the choice of the cutoff energy and the gray region indicates that the results may not be so reliable in the range. In this example the cutoff has been chosen such that $N_{1} = N_{2} = 8$ in the region $0 \leq \sigma_{\phi} < 3/2$ and $N_{1} = N_{2} = 8$ in the region $3/2 < \sigma_{\phi} \leq 3$.

In the region $0 < \sigma_{\phi} < 3/2$, we obtain the energy levels at $\varepsilon = 0$ in agreement with the results of the lowest modes approximation discussed in the last section. In the region $3/2 < \sigma_{\phi}$, the energy levels jump from $\varepsilon = 0$ to $\varepsilon$ near the edges of the corresponding valence and the conduction band. This discrete jump is due to an abrupt change of the bases in the cap region, i.e., the change of $\mu_{\sigma_{\phi}}^{\min}$ at $\sigma_{\phi} = 3/2$ discussed in the previous section. The change in the cutoff between $\varepsilon_{c1}$ and $\varepsilon_{c2}$ is less responsible to the jump as will be discussed in § 5.

In the vicinity of $\sigma_{\phi} = 3$, two new states appear below the bottom of the conduction band and above the top of the valence band. These states have weak interaction with traveling continuum states and therefore become resonance states when they merge into the continuum. Figure 6 (b) shows a blowup of the results near the conduction-band bottom in the vicinity of $\sigma_{\phi} = 3$.

At $\sigma_{\phi} = 3$, these new localized states become degenerate with the other states present in the whole region $3/2 < \sigma_{\phi} < 3$. As is shown in Appendix A, the states for $\sigma_{\phi} = 3$ can be chosen as eigen states of the mirror reflection and specified by the corresponding parity $\pm 1$. Moreover, in the effective-mass approximation there exists a unitary transformation which converts an eigen function of the mirror reflection with parity +1 into that with −1 and vice versa as is shown in Appendix B. This leads to the degeneracy at $\sigma_{\phi} = 3$. Under such circumstances the appearance of the new states in the vicinity of $\sigma_{\phi} = 3$ is quite natural.

Figure 7 shows the dependence of $\Delta$ and the energy levels on the number of modes $N = N_{1} + N_{2} + 1$ for $\sigma_{\phi} = 1$ and 2. It shows that $\Delta$ decreases and approaches zero although slowly and that the energy levels are essentially independent of $N$. The results are qualitatively same for different values of $\sigma_{\phi}$, demonstrating that the states shown in Fig. 6 can be regarded as real cap states and are not spurious.

The energy levels of localized cap states were first obtained in a tight-binding model for several types of nanotubes with small diameters. The results show that they are quite asymmetric about $\varepsilon = 0$. A study was extended to thicker nanotubes and showed that the energy levels become more and more symmetric about $\varepsilon = 0$ with the increase of the radius. Figure 6 contains tight-binding results for a thick pencil cap with $L/a = 30\sqrt{3}$. The present energy levels are in agreement with the tight-binding results except in the gray region close to $\sigma_{\phi} = 3/2$ and in the vicinity of $\sigma_{\phi} = 3$. In the gray region, the tight-binding energy levels are quite asymmetric about $\varepsilon = 0$ and vary continuously as a function of $\sigma_{\phi}$, exhibiting a considerable deviation from the present results. At $\sigma_{\phi} = 3$ the degeneracy present in the effective-mass result is slightly lifted in a tight-binding model.

In actual nanotubes the presence of five-membered rings destroy the symmetry between the positive and negative energies, giving rise to an asymmetry around $\varepsilon = 0$. This asymmetry is strongest for thin nanotubes and decreases with the increase of the tube thickness. In the effective-mass approximation this symmetry is not destroyed although the resulting wave function is not symmetric.

In Fig. 6 (a) the arrows with (q, $\sigma_{\phi}$) denote the energy levels of cap states with $\sigma$ in the absence of a flux for a pencil ($q = 6$) and a bowl ($q = 5$) cap. Note that actual energy levels for a bowl cap should be obtained from those for a pencil cap by using eq. (2.19). In Table I the energy levels are compared with those obtained in a tight-binding model for a pencil cap with $L/a = 30\sqrt{3}$ and a bowl cap with $L/a = 25\sqrt{3}$.

Figure 8 compares the average amplitude of the
wave function in the cap region with corresponding tight-binding results. The amplitude is defined by

$$\tilde{\psi}(y) = \frac{\sqrt{3}y^{\sqrt{3}}}{2|y|^{3}r_{0}^{2}} \int_{-y^{3}}^{y^{3}} dx [|\psi_{A}(x,y)| + |\psi_{B}(x,y)|],$$

(4.1)

with $y_{0} = -(\sqrt{3}/2)r_{0}$. Figure 8 (a) shows the amplitudes in the range $0 < \sigma_{\phi} < 3/2$ ($\epsilon \sim 0$) and (b) shows those in the range $3/2 < \sigma_{\phi} < 3$ ($\epsilon \neq 0$). They show clearly the overall and good agreement between the present and tight-binding results except in the vicinity of $\sigma_{\phi} = 3/2$. A sizable disagreement for $\sigma_{\phi} = 1.4$ in Fig. 8 (a) and for $\sigma_{\phi} = 1.6$ in (b) appears presumably because the singularity of the wave function in the vicinity of the tip of the cap becomes critical ($\propto r^{-1/2}$ at $\sigma_{\phi} = 3/2$) and the state cannot be described well by the effective-mass approximation.

In the region $0 < \sigma_{\phi} < 3/2$, the wave functions show the dependence $|y|^{1-\sigma_{\phi}}$ as has been obtained analytically in the lowest modes discussed in the previous section. The amplitude shown in Fig. 8 (b) oscillates as a function of the position. The oscillation is due to interference of rapidly oscillating part of the Bloch function at K and K’ points. This oscillation disappears at $\epsilon = 0$ because wave functions consist only of a K point or a K’ point depending on sublattice A and B.

§5. Discussion

It is possible to calculate energy levels using $\epsilon_{c} = \epsilon_{c1}(j)$ or $\epsilon_{c} = \epsilon_{c2}(j)$ in the whole region of $\sigma_{\phi}$. Figure 9 shows such results. The dotted lines represent spurious energy levels which satisfy the matching conditions given by eq. (3.3) but give $\Delta$ not converging to zero with the energy levels which satisfy the matching conditions given in the previous section. The dotted lines represent spurious states. Apart from such spurious states, the cutoff $\epsilon_{c} = \epsilon_{c1}(j)$ gives the results almost same as those for the cutoff used in the previous section except in the vicinity of $\sigma_{\phi} = 3$. The reason of the failure is the absence of the mirror symmetry at $\sigma_{\phi} = 3$ for this choice of the cutoff. The cutoff $\epsilon_{c} = \epsilon_{c2}(j)$ completely fails to describe localized states in the vicinity of $\epsilon = 0$ in the range $0 < \sigma_{\phi} < 3/2$.

In STM experiments measured tunneling current is expected to depict the local density of states in the vicinity of an STM tip. The localized cap states at $\epsilon = 0$ give a sharp $\delta$-function peak $C(r)\delta(\epsilon)$ to the local density of states in the cap region with $C(r)$ being a coefficient dependent on the position. In a pencil cap, the amplitude $C(r)$ is nearly independent of the position, because the amplitude of the wave function is well approximated by a constant. In a bowl cap, on the other hand, a similar cap state gives $C(r) \propto r^{-1/5}$ in the vicinity of the five-membered ring at the tip because of the singularity of the wave function $\propto r^{-1/5}$. Further, the similar singular increase is expected in the vicinity of all five-membered rings in many different caps when localized cap states are present at $\epsilon = 0$. This dependence is consistent with that predicted for a tip of the graphitic cone,\textsuperscript{13,15,16}.

§6. Summary and Conclusion

Localized cap states of capped metallic armchair nanotubes have been studied by the effective-mass theory. We have explicitly considered the situation that a pencil cap consisting of six graphene sheets of regular triangles is attached to the tube and a magnetic flux passes through the center of the cap. By the magnetic flux, other caps with $q$ regular triangles with $1 \leq q \leq 5$ can be considered also.

In the absence of a magnetic flux, cap states associated with bands with angular momentum $\sigma = 1$ lie at $\epsilon = 0$ and those associated with bands with other $\sigma$ lie slightly below the bottom of the lowest conduction band and slightly above the top of the highest valence band with corresponding $\sigma$. For the level at $\epsilon = 0$, in particular, the amplitude of the wave function is almost constant in a pencil cap and $\propto r^{-1/5}$ in a bowl cap where $r$ is the distance from the tip of the cap.

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Appendix A: Mirror Symmetry

An armchair nanotube closed by a pencil cap ($q=6$) as shown in Fig. 2 (a) has the mirror symmetry on the plane containing the axis and therefore the wave functions are classified accordingly. The mirror-reflection operation II is given by\textsuperscript{21,28}

$$\Pi F(r) = PF(\Pi^{-1}r),$$

(A1)

where $\Pi r = \bar{r}$ with $\bar{r} = (-x, y)$ for $r = (x, y)$, and $P$ is given by

$$P = P^{-1} = \begin{pmatrix} 0 & i & 0 & 0 \\ -i & 0 & 0 & 0 \\ 0 & 0 & 0 & i \\ 0 & 0 & -i & 0 \end{pmatrix}. \quad (A2)$$

Let $R$ be the $\pi/3$ rotation around the origin (the tip of the cap). A straightforward calculation shows that

$$T_{\pi/3}PT_{\pi/3} = P,$$

leading to

$$RIIR = \Pi. \quad (A4)$$

Consider $F(r)$ in the cap region with $\sigma_{\phi}$, i.e.,

$$RF(r) = F(R^{-1}r) = \exp\left(-\frac{2\pi i \sigma_{\phi}r}{6}\right)F(r). \quad (A5)$$
With the use of eq. (2.17), we have
\[ RIF(r) = RIRR^{-1}F(r) = \exp\left(\pm \frac{2\pi \sigma i}{6}\right)IF(r). \]
\[ \Pi R F(r) = \exp\left(-\frac{2\pi \sigma i}{6}\right)\Pi F(r). \]

This shows that the wave function with \( \sigma \) is transformed to one with \(-\sigma\) in the cap region. The same is applicable to the wave function in the tube region although not shown explicitly. Therefore, it is sufficient to study the states with \( 0 \leq \sigma \leq 3 \). The above shows also that the mirror-reflection operation \( \Pi \) and the \( \pi/3 \) rotation commute each other only for states with \( \sigma = 0 \) and 3.

**Appendix B: Degenerate States at \( \sigma = 3 \)**

To understand the origin of the degenerate states at \( \sigma = 3 \), we define a matrix as
\[
\Omega = \begin{pmatrix}
0 & 0 & 0 & \sqrt{\omega^*} \\
0 & 0 & \sqrt{\omega} & 0 \\
\sqrt{\omega} & 0 & 0 & 0
\end{pmatrix}.
\]

A straightforward calculation shows that this matrix satisfies the following relations:
\[
\Omega^2 = 1,
\]
\[
\Omega H \Omega^{-1} = H,
\]
\[
\Omega T_{\pi/3} \Omega^{-1} = T_{\pi/3},
\]
and
\[
\Omega P \Omega^{-1} = -P.
\]

These equations (B2) and (B3) show that when \( \Omega \) is multiplied a wave function with parity \( p \) is transformed into one with parity \(-p\) and the same energy, where \( p \) is an eigen value of \( \Pi \) and \( p = \pm 1 \) because of \( \Pi^2 = 1 \). As discussed in Appendix A, a state with \( \sigma = 3 \) (and also \( \sigma = 0 \)) can be chosen as an eigenstate of the mirror reflection because \( \Pi \) commutes with the \( \pi/3 \) rotation in this case. The presence of \( \Omega \) shows that a pair of states with parity \( p = \pm 1 \) are always degenerate for \( \sigma = 3 \) (and also \( \sigma = 0 \)).

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**Table 1** The cap-state energies in the absence of a magnetic flux for a pencil \((q = 6)\) and bowl \((q = 5)\) caps obtained in the effective-mass approximation and in a tight-binding model \((L = 30\sqrt{3}a\) and \(L = 25\sqrt{3}a\) for a pencil and bowl cap, respectively).

| \(\sigma\) | \(\varepsilon(2\pi\gamma/L)^{-1}\) |
|---|---|
| \(q = 6\) | \(\pm 1.75\) | \(\pm 2.81\) | 0 | \(\pm 1.81\) |
| \(q = 5\) | \(\pm 1.82\) | \(\pm 2.91\) | 0.14 | \(+ 1.90\) |

**Table 1**

| \(\sigma\) | \(\varepsilon(2\pi\gamma/L)^{-1}\) |
|---|---|
| \(q = 6\) | \(-1.64\) | \(+ 2.84\) | -2.55 |
| \(q = 5\) | \(-2.67\) |

**Figure Captions**

Fig. 1 The lattice structure of a 2D graphite. A unit cell contains two carbon atoms denoted by A and B
and two primitive translation vectors are denoted by $a$ and $b$. The $y$ axis is along the tube axis and the $x$ axis is along the circumference, while $x'$ and $y'$ axis are fixed on the graphite sheet. The chiral vector corresponding to a circumference of the tube is denoted by $L$ and the chiral angle $\eta$ is the direction of $L$ measured from the $x'$ axis.

**Fig. 2** The projection mapping of a (a) pencil and (b) bowl cap consisting of 6 and 5 regular triangles. The origin $r=0$ is chosen at the tip of the cap.

**Fig. 3** A schematic illustration of a pencil cap with a magnetic flux $\phi$ passing through the cap center.

**Fig. 4** Angular momentum $\mu_{\pm}$ as a function of $\sigma_{\phi}$ near lower bounds. Only the region $0 \leq \sigma_{\phi} \leq 3$ is shown because of the symmetry between positive and negative $\sigma_{\phi}$. The integrability of the wave function leads to $\mu_{\pm} > -1$. The condition that the Hamiltonian should be Hermitian excludes $\mu_{\pm}$ denoted by the dotted lines. A discrete jump occurs in $\mu_{\pm}^{\text{min}}$ at $\sigma_{\phi} = 3/2$.

**Fig. 5** Energy-band edges $\pm \gamma |\kappa(j)| = \pm \gamma |6j+\sigma_{\phi}|$ around $j \sim n$ with integer $n$. Two cutoffs $\epsilon_{c1}(j)$ and $\epsilon_{c2}(j)$ are shown by dotted lines.

**Fig. 6** (a) Calculated energy levels of the localized cap states lying in the band gap $|\epsilon| < 2\pi \gamma \sigma_{\phi}/L$. The solid lines represent the results obtained in the effective-mass approximation with cutoff $\epsilon_{c1}(j)$ and $\epsilon_{c2}(j)$ with $j = 8$. The dotted lines represent the results obtained in a tight-binding model.\(^{29}\) In the gray region there remains some uncertainty in the choice of the cutoff. In the absence of a magnetic flux, localized cap states with the angular momentum $\sigma$ on the pencil ($q = 6$) and the bowl ($q = 5$) cap are shown by arrows with $(q, \sigma)$. Two new states appear from the top of the valence band and the bottom of the conduction band near $\sigma_{\phi} = 3$.

(b) A blowup of (a) in the range $2.85 \leq \sigma_{\phi} \leq 3$ and $2.6 \leq \epsilon(2\pi \gamma/L)^{-1} \leq 3.1$.

**Fig. 7** The dependence of $\Delta$ and energy levels on the number of the modes ($N = N_1 + N_2 + 1$) for $\epsilon = 0$ with $\sigma_{\phi} = 1$ and for $\epsilon(2\pi \gamma/L)^{-1} \sim 2$ with $\sigma_{\phi} = 2$.

**Fig. 8** The average amplitude of the wave function in the cap region as a function of $y$. The solid and dotted lines represents the wave function ($j = 8$) in the effective-mass approximation (EMA) and triangle or plus marks that in a tight-binding (TB) model. (a) $\sigma_{\phi} = 0.5, 1.0, \text{and } 1.4$. (b) $\sigma_{\phi} = 1.6, 2.0, \text{and } 2.5$.

**Fig. 9** Calculated energy levels for $\epsilon_{c} = \epsilon_{c1}$ (upper panel) and $\epsilon_{c2}$ (lower panel). The band gap is represented by dashed lines. The solid lines represent the energy levels with converging $\Delta$ and the dotted lines spurious states with nonconverging $\Delta$.

**Fig. 10** The dependence of $\Delta$ and energy levels for spurious solutions with $\epsilon = 0$ at $\sigma = 2$ and $\epsilon(2\pi \gamma/L)^{-1} \approx 1.16$. The wave-function matching is not achieved because $\Delta$ does not converge to 0.
Localized Eigenstates in Carbon Nanotube Caps

Fig. 1

Fig. 2 (a) Fig. 2 (b)

Fig. 3
Localized Eigenstates in Carbon Nanotube Caps

Fig. 7

Fig. 8 (a)

Fig. 8 (b)

Fig. 9
Fig. 10