Topological Phases in Graphitic Cones

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The electronic structure of graphitic cones exhibits distinctive topological features associated with the apical disclinations. Aharonov-Bohm magnetococonductance oscillations (period $\Phi_0$) are completely absent in rings fabricated from cones with a single pentagonal disclination. Close to the apex, the local density of states changes qualitatively, either developing a cusp which drops to zero at the Fermi energy, or forming a region of nonzero density across $E_F$, a local metalization of graphene.

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If one or more sectors are excised from a single layer of graphite (hereafter, graphene) as illustrated in Figure 1, and the remainder is joined seamlessly, a cone results. Researchers discovered how to produce such graphitic cones in 1997

We show that the topological nature of the apical defect profoundly modifies the low-energy electronic structure, with remarkable consequences for nonlocal transport properties in this new class of nanoscale carbon. Rings made from cones exhibit an anomalous Aharonov-Bohm effect. In some cones, the fundamental period is completely absent. Also, the Fermi-level density of states near the apex is enhanced and shows distinctive energy dependence.

We classify a cone by its opening angle, or equivalently the number $n_\alpha$ of sectors removed. All possible angles have been observed experimentally; we concentrate on $n_\alpha = 1$ and $n_\alpha = 2$, which reveal the essential physics. Since pentagonal defects are expected to predominate in real cones, $n_\alpha$ is also typically equal to the number of defects, which must be tightly clustered to produce a conical shape.

The gap of a semiconducting tube arises from frustration in the phase of the graphitic Fermi-level states as they pass around the tube circumference. In this sense, the semiconducting nanotube is a translational phase defect. A cone forms a rotational defect which also frustrates electronic phase. In nanotubes, the frustration affects states at the two graphene Fermi points in precisely the same way. In contrast, the topological phase in a cone of odd $n_\alpha$ entwines the two Fermi points. Although most of a large cone is just a gently curved graphene surface, the global electronic properties are significantly disturbed.

Before presenting the new results, we briefly recall the continuum theory of graphene, as it forms the framework for this understanding. We require a flexible real-space continuum formulation to handle structures which are locally graphitic but contain non-contractible closed loops, i.e., those surrounding the waist of a nanotube or the apex of a cone. We think of the entire cone as having a perfect graphene-like structure locally, by considering a pentagonal defect not as a five-membered ring, but as a hole in a graphene structure. In the continuum picture this makes sense and the hole can be shrunk to a point. We can then represent defects as pure gauge fields. Our continuum description is ideally suited to bringing out topological aspects, so long as one exercises care in handling phenomena on atomic length scales.

Graphene’s Fermi surface comprises only two points. Figure 1 depicts the Fermi point states in a tight-binding picture. The states are labelled by the direction of a wave-vector $\mathbf{K}$ and a sublattice index $A$ or $B$. The figure illustrates $|\mathbf{K}A\rangle$ and $|\mathbf{K}B\rangle$, where $\mathbf{K}$ points up the page. The Fermi level space is four-dimensional, and we choose $|\mathbf{K}_+A\rangle$ and $|\mathbf{K}_+B\rangle$ as our basis, with $\mathbf{K}_- = -\mathbf{K}_+$. Under rotation counterclockwise about any hexagon center by $120^\circ$, implemented by $R_0^2$, these states pick up simple phases: $R_0^2|\mathbf{K}A\rangle = \eta|\mathbf{K}A\rangle$, and $R_0^2|\mathbf{K}B\rangle = \overline{\eta}|\mathbf{K}B\rangle$, where $\eta = \exp(2\pi i/3)$.
the wavefunction simultaneously transformed by multi-

FIG. 2: Tight-binding wavefunctions of graphene Fermi-

level states. Pick a direction $\mathbf{K}$ pointing from the center of a
hexagon to the middle of one side, and assign amplitudes
as shown, where $\eta = \exp(2\pi i/3)$. If the nonzero amplitudes
are on the right-hand atoms of bonds cut by $\mathbf{K}$, as in (a),
the state is $|\mathbf{K}A\rangle$, if on the left-hand atoms, as in (b), $|\mathbf{K}B\rangle$.
There are only two distinct $\mathbf{K}$.

We avoid momentum space notions because they are not
available in systems such as cones, which lack trans-
lational invariance. $\mathbf{K}$ is only a label for the orienta-
tion of the pattern of amplitudes. However, whether in
a flat graphene sheet, a nanotube, a cone, or any other
nontrivial surfaces such as cones. If the coordinate frame
is 'up,' $\mathbf{K}$ 's are Pauli spin matrices operating in the
$\sigma$'s are Pauli spin matrices operating in the $A/B$
indices; $A$ is 'up,' $B$ is 'down,' and the $x$ axis is along
$\mathbf{K}_+$. For the $\mathbf{K}_-$ components of the wavefunction, the
appropriate frame ($x$ and $y$ axes) is rotated through 180°
relative to that for $\mathbf{K}_+$. However, by an appropriate
change of phases ($\pm \pi/2$), the $\mathbf{K}_-$ frame may be used for
all components. The frame need not be locked to the un-
derlying lattice, however, a fact which is very useful on
nontrivial surfaces such as cones. If the coordinate frame
$\{\hat{e}_x, \hat{e}_y\}$ in Eq. (A) is rotated by $\theta$ counterclockwise,
and the wavefunction simultaneously transformed by multi-
plication by $\exp(i\theta \sigma_3/2)$, the form of the Hamiltonian is
preserved. This invariance is made local, by introducing
a gauge field, replacing $\mathbf{\theta}$ by $\mathbf{\theta} - i\alpha$, where $\alpha = -\sigma_3 \mathbf{\theta}/2$.

We imagine taking the sheet in Fig. [4] with wedge $\beta \alpha \gamma$
missing and wrapping it up to form a cone. The edge
$\alpha \gamma$ is then labelled by azimuthal angle $\phi = 0$ and $\alpha \beta$ by
$\phi = 2\pi$. What are the appropriate boundary conditions?
Using the four Fermi point patterns described above, one
can see that, up to phases, $|\mathbf{K}_+ A; \phi = 0\rangle$ is the same
thing as $|\mathbf{K}_- A; \phi = 2\pi\rangle$, and $|\mathbf{K}_- B; \phi = 0\rangle$ the same as
$|\mathbf{K}_+ B; \phi = 2\pi\rangle$. There is no globally coherent distinction
between $\mathbf{K}_+$ and $\mathbf{K}_-$, a remarkable conclusion. In a
sense, just as a M"obius strip has only one side, cones
with odd $n_\alpha$ have only one Fermi point!

Before dealing with the awkward boundary conditions,
notice that the local frames $\{\hat{e}_x, \hat{e}_y\}$ are discontinuous
across the seam. Using the local rotation invariance men-
tioned earlier, we orient our frames so that $\hat{e}_x = \hat{e}_\phi$
points tangentially, and $\hat{e}_y = -\hat{e}_\phi$ toward the apex. This
change introduces a gauge field (now for general $n_\alpha$)
\[
\alpha = \frac{2\pi \hat{e}_\phi}{\ell} \left( \frac{1 - n_\alpha}{12} \right) \sigma_3,
\]
where $\ell = [1 - n_\alpha/6]2\pi r$ is the circumference of the cone
at distance $r$ from the apex. The adjustment of the
frames makes an additional contribution to the bound-
dary conditions. The various ingredients combine to give
\[
\Psi(\phi = 2\pi) = T(n_\alpha)\Psi(\phi = 0),
\]
where the operator $T$ (a holonomy) is
\[
T(n_\alpha = -1) = (-1)^{n_\alpha} \left[ \frac{2\pi n_\alpha}{4} \right] \tau_2.
\]
$\tau_2$ is the standard $(2 \leftrightarrow y)$ Pauli matrix acting on the
Fermi point indices $\pm$. For odd $n_\alpha$, the exponential factor is
eliminated by a singular gauge transformation, $\mathbf{\theta} \mapsto
\mathbf{\theta} - i\alpha \mapsto \mathbf{\theta} - i\alpha - i\beta$ with
\[
\beta = \frac{2\pi \hat{e}_\phi n_\alpha}{\ell} \tau_2.
\]
Recall that in solving the ordinary Schrödinger equation
on a flux-threaded ring, the vector potential can be elimi-
nated by imposing a discontinuous boundary condition
$\psi(\theta = 2\pi) = \exp[i \oint A \cdot dl] \psi(0)$. Here we perform es-
tenially the reverse procedure, but our gauge field is
proportional to a Pauli matrix. For even $n_\alpha$, the two
Fermi points are not mixed and the exponential factor is
just $-1$. So the gauge transformation need not involve
$\tau$-matrices, but merely introduces half a flux quantum of
fake magnetic flux. We deal with the first factor of $-1$
in Eq. (B) by using anti-periodic boundary conditions.

With the rotational symmetry more manifest, we can now
make a partial-wave decomposition of a general spinor as
\[
\Psi(r, \phi) = \sum_j \chi^{(j)}(r)e^{ij\phi},
\]
and a similar decomposition of the Hamiltonian as $H =
\sum_j h^{(j)}$. The total angular momentum takes on all half-
integer values, $j = \ldots, -3/2, -1/2, 1/2, \ldots$. We work
with a finite cone, so that the radial wavefunction \( \chi^{(j)} \) is in the Hilbert space of functions on \((0, R)\) which are square integrable with respect to \( r \, dr \), and the radial Hamiltonian \( h^{(j)} \) is of the form

\[
h^{(j)} = v_F \left( 0 - \frac{1}{2} \frac{\partial_r}{r} + \left( \nu + \frac{1}{2} \right) \frac{1}{r} \right).
\]

(5)

The value of \( \nu \) depends on \( j \) and the type of cone involved:

\[
\nu = \begin{cases} 
\frac{j}{2} \left( j + \frac{1}{2} \right), & n_\alpha = 0; \\
\frac{j}{2} \left( j + \frac{3}{2} \right), & n_\alpha = 1; \\
\frac{j}{2} \left( j - \frac{1}{2} + \frac{3}{2} \right), & n_\alpha = 2.
\end{cases}
\]

(6)

We include the flat sheet (\( n_\alpha = 0 \), no disclination) as a ‘control,’ and also introduce a magnetic flux \( \Phi \) through the disclination in order to study magnetoconductance (\( \Phi_0 = h/e \) is the normal flux quantum). Notice \( \tau_2 \) in the \( n_\alpha = 1 \) expression — energy eigenstates are superpositions of the two \( K \).

Comparing the eigenvalue equation for \( h^{(j)} \) to standard recursion relations for cylinder functions reveals the solutions to be ordinary Bessel functions:

\[
\chi^{\pm}_{\nu,1}(r) = \left( J_{\nu - \frac{1}{2}}(kr) \right), \quad \nu \geq 0
\]

and

\[
\chi^{\pm}_{\nu,2}(r) = \left( J_{\nu + \frac{1}{2}}(kr) \right), \quad \nu \leq 0.
\]

(8)

Thus,

\[
h^{(j)}\chi^{\pm}_{\nu,i}(r) = (\pm v_F k)\chi^{\pm}_{\nu,i}(r), \quad i = 1, 2.
\]

The indicated restrictions on \( \nu \) involve a subtlety. It is insufficient simply to ask that \( \chi \) and \( h^{(j)}\chi \) be square integrable. That requirement says that \( \chi_{\nu,1} \) is acceptable for \(-1/2 \leq \nu \) and \( \chi_{\nu,2} \) for \( \nu \leq 1/2 \). Also requiring that the radial Hamiltonian \( h^{(j)} \) be self-adjoint, as it must, forbids both \( \chi_{\nu,1} \) and \( \chi_{\nu,2} \) in the domain of \( h^{(j)} \) at the same time, except for the special case \( \nu = 0 \).

Now we turn to observable consequences. The energy density of states near the apex of a cone shows a remarkable dependence on the opening angle of the cone. In fact, the strictly local density of states diverges as \( r \to 0 \) for most cones, so we investigate instead the total density of states on a patch \( 0 < r \leq \delta \) for small \( \delta \). This quantity is more relevant anyway for comparison to both experiments and tight-binding computations. The result is

\[
D(E, \delta) \propto \begin{cases} 
E^2, & n_\alpha = 0; \\
E^{3/5} \delta^{8/5}, & n_\alpha = 1; \\
\delta, & n_\alpha = 2.
\end{cases}
\]

(9)

FIG. 3: Schematic densities of states for a small patch near the apex of a cone, according to Eq. (6).

as illustrated schematically in figure 3.

Eq. (6) is derived as follows. From the large-\( x \) asymptotic formula \( J_n(x) \sim (2/\pi x)^{1/2} \cos \left[ x - \left( n + \frac{1}{2} \right) \frac{\pi}{2} \right] \), we deduce a normalization factor of \( c = (\pi k/2R)^{1/2} \) for our \( \chi^{\pm}_{\nu,j} \) functions. The only values of \( j \) which contribute significantly to the density of states near \( r = 0 \) are \( j = \pm 1/2 \) for \( n_\alpha = 0,1 \) and \( j = 1/2 \) for \( n_\alpha = 2 \), and the leading order behavior of \( J_n \) is used to integrate over a small disk. Finally, the spacing of \( k \) values is \( \Delta k = \pi/R (2\pi/R \) for \( j = 1/2 \) and \( n_\alpha = 2 \)). Thus, the total density of states in the \( \delta \)-disk contributed by states associated with Bessel function order \( n \) is

\[
D(k, \delta, n) \sim c^2 |k|^{2n} \delta^2 \propto |E|^{2n+1} \delta^{2(n+1)}.
\]

Inserting appropriate values for \( n \), we get Eq. (6).

Strikingly, the low-energy density of states for the \( n_\alpha = 1 \) cone has a cusp at \( E_F \), and the cone with two sectors missing has a non-zero density of states near the Fermi level. An actual cone with the \( n_\alpha = 2 \) opening angle probably actually has a pair of \( n_\alpha = 1 \) defects. However, if the two pentagons are very near each other, we expect this conclusion to remain valid. These remarkable results should be observable in STM spectroscopy, so long as they are distinguished from the local effect of bond strain in the pentagonal defects(s).

Although the continuum description lacks atomistic detail, the qualitative conclusions agree well with an earlier atomistic computation of (apical) local densities of states using a one-orbital tight-binding model for similar structures. Direct comparison with our Eq. (6) can be made, bearing in mind the low-energy restriction on our calculations. In references [14], it was suggested that the states contributing to the non-zero density of states at \( E_F \) for \( n_\alpha = 2 \) are (power-law) localized. Our calculations show that they are extended states which are enhanced in the vicinity of the apex.

A mesoscopic normal metal ring in a perpendicular magnetic field exhibits oscillations as the flux through the ring is varied [14]. The longest period of oscillation is one normal flux quantum \( \Phi_0 = h/e \), corresponding essentially to the Aharonov-Bohm effect, and first observed in this context in the mid-1980’s[15]. Manufacturing such a ring from a graphitic cone seems possible. The apex could be etched away with acid, or cut off with an STM. Such
manipulation does not change $n_\alpha$, because it measures a topological property — the number of missing sectors, or equivalently, the opening angle.

The magnetoconductance of such conical rings also shows profound sensitivity to the opening angle. Although we could argue directly from the holonomies, it is perhaps simpler to appeal to Eq. (2). These expressions are still valid for a ring, even though the subsequent analysis was specific to a cone with only the apical point removed. For $n_\alpha = 0$ and $n_\beta = 2$, the Hamiltonian is $SU(2)_K$ invariant (the $SU(2)$ group acts on the $K^\pm$ indices), so that the two Fermi points produce two independent branches of excitations which respond identically to a magnetic flux. Each branch exhibits its own magnetoconductance, which has period $\Phi_0$, just as in an ordinary metal, and the phases are identical. The total response therefore also has fundamental period $\Phi_0$.

In an $n_\alpha = 1$ ring, on the other hand, the $\Phi_0$ component of the oscillations is extinguished. From Eq. (4), we see that the $\tau_2 = +1$ ($\tau_2 = -1$) branch behaves as though it were subjected to a flux of $\Phi = \Phi_0/4$ ($\Phi = -\Phi_0/4$). This relative shift of the magnetoconductance curves causes cancellation of the $\Phi_0$ periodic component. Cones with intact apices will also show novel magnetic phenomena, including the prospect for field-tuneable radial charge density waves.

Our neglect of disorder and inelastic scattering in this discussion should be permissible up to the micron length scale. The elastic scattering length, $\ell_p$, in single-wall nanotubes is believed to range up to many microns and there is direct evidence that the phase coherence length ($\ell_\phi$) at room temperature is also that long. A graphitic ring would be expected to have a somewhat reduced $\ell_p$, due to rough edges, but $\ell_\phi$ is likely comparable to that in the tube.

In conclusion, we demonstrate that graphene cones, which have been experimentally produced, but not yet adequately studied, comprise a new class of nanoscale carbon wherein phase frustration induces profound modulations of the low-energy electronic properties. These rotational phase defects (induced by topological lattice defects) leave distinctive and non-trivial local and global imprints on the electronic structure of graphitic cones. We predict two specific phenomena flowing from this observation: apical enhancement of density of states and an anomalous magnetoconductance.

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