Sign reversal of Hall conductivity and quantum confinement in graphene ribbons

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Abstract

Characterized by zigzag and armchair boundaries, the narrow ribbons display the very different characteristics in Hall conductivities. It is shown that the multi-band-crossings occur in the energy spectrum for armchair ribbons, and the number of them depends on the width of ribbons. Theoretically, it is predicated that the conductivities exhibit drastic sign reversals for narrow ribbons as the Fermi energy sweep over the band-crossings. A new classification of armchair ribbons is suggested based on the emergence of a flat band in the energy spectrum only for odd armchair ribbons. The evolution of jumped Hall conductivities to step-like plateaus and the restore of density of states at the van Hove singularity in the limitation to graphene sheet have been analyzed.

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Experimentally, many novel properties have been observed in graphene systems, such as the electron-hole symmetry, the odd-integer quantum Hall effect, and the finite conductivity in dissipationless process. Among these the peculiar odd-integer Hall plateaus has been theoretically recognized in the frame of the Landau quantization of massless Dirac fermions. Considering the potential applications in future nanoelectronic devices, there is a steep rise recently in the interest in studying the various properties of graphene nanoribbons (GNRs). Borne on their honeycomb atomic structure, two kinds of ribbons, with zigzag edges (ZGNRs) and armchair edges (AGNRs) respectively, can be configured when graphene sheets are transversely cut. Actually, transversely reduced size of ribbons introduces important physical phenomena such as quantum confinement and edge effects, which have been revealed in the studying of electronic structure, unconventional transport, and optical excitations. The anisotropy in their electrical properties relies upon the structures of GNRs in the special set up. Therefore, of particular interest, it is desirable to know how the effects of the quantum confinement and the edge characteristics are reflected in the Hall-like conductivity in GNRs under a magnetic field.

In the present letter, we consider narrow ribbons subject to a perpendicular magnetic field for this purpose. We take some values of the strength of magnetic field so that Landau levels are not well developed in the comparison of the characteristic discretization of energy spectrum originated from the transversely confined sizes of ribbons. The magnetic field is, here, used to play only a role to achieve the electronic motion in longitudinal direction of GNRs. Hall-like conductivities can, then, be investigated. Because multi-band-crossings occur in the energy spectrum for AGNRs while only one at van Hove singularity for ZGNRs, the behaviors of electrical properties under the magnetic field are expected to be very different for ZGNRs and AGNRs when Fermi energy sweeps over the band-crossings. We show that, similar to the infinite graphene sheet, the Hall conductivities for ZGNRs undergo a sign-reversal jump merely at the van Hove singularities where the transition from the Dirac fermion to the ordinary fermion happens. But, the Hall conductivities for AGNRs exhibit extra drastic sign-reversal jumps as functions of Fermi energy. The number of sign reversals depends on the width of AGNRs. The regularity is not changed regardless of AGNRs being metal or semiconductor. This reflects the physical situation in which more than one meaningful classifications are involved to characterize the electronic structure for rib-
bons. These extra sign-reversal jumps in the Hall conductivity for AGNRs could be receded when the width of ribbons or the strength of magnetic field is increased. In the limitation of infinite graphene sheets, the oscillations would disappear except that one related to the van Hove singularity and the step-like plateaus are formed, which is consistent with observations for the infinite graphene sheet [17, 18].

We describe GNRs by a tight-binding Hamiltonian on two-dimensional (2D) honeycomb lattice

$$H = t \sum_{\langle ij \rangle} \exp (i \gamma_{ij}) c_i \dagger c_j,$$

where $\langle ij \rangle$ denotes the summation over the nearest neighbor sites, $t = 2.71 eV$ is the hopping integral for nearest neighbors, and $c_i \dagger (c_i)$ represents the creation (annihilation) operator of electrons on the site $i$ neglecting the spin degree of freedom. The magnetic field is applied perpendicularly to the sheet of the ribbon and is responsible for incorporating the Peierls phase $\gamma_{ij} = (2\pi/\phi_0) \int_i^j \mathbf{A} \cdot d\mathbf{l}$, with the vector potential $\mathbf{A}$ and the magnetic flux quantum $\phi_0 = hc/e$. ZGNRs and AGNRs are classified by their characteristics on edges, respectively [19]. The width $N$ of ZGNRs is defined by the number of longitudinal zigzag lines, while by dimer lines for AGNRs. In our calculations, we extend the coupled Harper equations to describe a ribbon in width $N$ with the boundary condition $\psi_0 = \psi_{N+1} = 0$. The corresponding Hamiltonian can, then, be written as a $2N \times 2N$ matrix [20]. For a ribbon along the $y$-direction longitudinally and its transversal section along the $x$-direction, the eigenfunction can be expressed in the form of

$$\psi_{kj} = \xi_j (k) \exp (iky),$$

where $k = k_y$ is the longitudinal wave vector while $j$ ($j = 1, 2, 3, \cdots 2N$) indicate the transversal channels on the transversal section, and $\xi_{kj}$ denotes the $j$-th eigenstate which satisfies equation $H \xi_{kj} = \epsilon_{kj} \xi_{kj}$. The energy eigenvalues $\epsilon_{kj}$ and the eigenvectors $\xi_{kj}$ can be obtained by a numerical diagonalization of the Hamiltonian. As a finite system, the energy levels are discretized.

To calculate the DC Hall conductivity at zero temperature we apply Kubo formula [21],

$$\sigma_{yx} = -(2\hbar/W) \sum_k \sum_{\epsilon_{kj} > \epsilon_{kj'} < \epsilon_{EF}} \text{Im} \left( J_{kj}^y J_{kj'}^x \right) / (\epsilon_{kj} - \epsilon_{kj'})^2,$$

where $W$ is the width of ribbons, $W = (3N/2 - 1)a$ for ZGNRs and $W = (\sqrt{3}a/2)(N - 1)$ for AGNRs with the c-c bond length $a = 0.142 nm$. The current operators $J_\alpha$ ($\alpha = x$ and $y$) are obtained by $J_\alpha = c(\partial H/\partial A_\alpha)$. In the Hilbert space of eigenvectors $\xi_j$, current operators can be represented in terms of a matrix with elements $J_{jj'}^y = \xi_j^\dagger J_\alpha \xi_{j'}$, where $\xi_j$ and $\epsilon_{kj}$ are the $j$-th eigenstate and eigenvalue. The summation in this formula denotes that $j$ always takes in the subbands above the Fermi energy while $j'$ always in the subbands below the Fermi energy. Thus, if these two subbands $j$ and $j'$ are crossed, the indices $j$ and $j'$ would undergo
FIG. 1: (a) The Hall conductivity versus the Fermi energy for ZGNRs at the zero temperature: widths $N = 10, 20, \text{and } 50$ are chosen. The magnetic flux through a plaquette in the unit of a quantum flux, $f = 1.0 \times 10^{-4}$; (b) The Hall conductivity in the strong field regime, where $N = 60$ and $f = 2.0 \times 10^{-2}$; (c) The energy spectrum for a ZGNR in width $N = 10$; and (d) The evolution of DOS with widening ribbons.

an exchange when the Fermi energy sweeps over the energy at the crossing point. The contributions to $\sigma_{yx}$ from the two crossing subbands becomes divergence if the Fermi energy comes close to the crossing point. Therefore, the exchange between crossing bands $j$ and $j'$ leads to a sign reversal and the drastic jump in the Hall-like conductivity.

Now we investigate the characteristics in Hall-like conductivities for ZGNRs and AGNRs, respectively. In our numerical calculations all energies are taken in the unit of hopping integral and the magnetic field is introduced by the magnetic flux through a plaquette in the unit of a quantum flux, $f \equiv \phi/\phi_0$. The strength of magnetic field is chosen not to destroy the band-crossings caused by transverse confinement. Therefore, the band-structure is dominated by its transverse confinement. Electrons move along longitudinal direction when a transverse electric field is applied. For the ZGNRs, the numerical calculation shows that band-crossings appear only at $E = \pm |t|$ [22, 23] (Fig.1(c)). Correspondingly, the Hall conductivity, $\sigma_{yx}$, exhibits the sign-reversal jumps at $E = \pm |t|$. In Fig.1(a) we have shown the Hall conductivities for ZGNRs in various widths under the magnetic flux $f = 1.0 \times 10^{-4}$ via the Fermi energy over the region $0 < E_F < 3|t|$. For $-3|t| < E_F < 0$ the behavior of $\sigma_{yx}$ is antisymmetric to that for $0 < E_F < 3|t|$ due to the electron-hole symmetry. Actually,
FIG. 2: Band structure $E(k)$ for AGNRs in widths $N = 3(a), 9(b), 17(c), 21(d), 4(e), 6(f), 14(g)$ and 18(h). The magnetic flux is taken as $f = 1.0 \times 10^{-4}$. The blue dash lines and the red circles indicate those crossing points which induce the sign reversals in Hall conductivities.

the appearance of jumps at $E = \pm |t|$ is robust and attributed to the van Hove singularity as happened for infinite graphene sheets $^{17, 18}$. Increasing the strength of magnetic field or widening the ribbons lead the Hall conductivity gradually to become quantized, as shown in Fig.1(b). The reason is that if the effect of magnetic field is strong enough, the Landau levels dominate the band structure. It, thus, leads to the quantized Hall conductivity, which is equivalent to increasing the width of ribbon at a fixed magnetic field. When width of ribbon is increased large enough, the discretization of bands is receded and Landau levels become dominative. The quantized plateaus in the Hall conductivity are achieved as experimental observation for infinite graphene sheets.

However, for AGNRs, besides the band-crossings near of $E = \pm |t|$ there might emerge some extra band-crossings. The number of crossing points depends on the width of ribbons.
In fact, the AGNRs can be divided into two classes, odd and even AGNRs, respecting to their widths \( N = 2n + 1 \) and \( N = 2n \). One of the different characteristics between them is that there presents a full flat band at \( E = \pm |t| \) only for odd AGNRs (Fig.2(a)-(d)). Such a flat band is absent if widths \( N = 2n \) (Fig.2(e)-(h)) due to reflection symmetry breaking with respect to the transversal direction. An immediate consequence of this classification is the density of states at \( E = \pm |t| \) to be different for two-class AGNRs. Hence, the conductivities display precisely very different when Fermi energy sweeps over \( E = \pm |t| \).

This characteristics implies that there is another index in classifying the AGNRs beyond the distinction between metallic and semiconductor by \( N = 3m - 1 \) or not, where \( m \) is an integer. In general, the \( k \)-independent flat bands at \( E = \pm |t| \) become \( k \)-dependent in the presence of magnetic field. Therefore, we have to investigate the Hall conductivities for odd and even AGNRs separately.

For \( N = 2n + 1 \), it is shown in Fig.3(a) that the flat band provides a sign-reversal jump in Hall conductivity. In addition, the energy spectrum shows that there exist \( n \) subbands above \( E = |t| \) and \( n \) subbands below \( E = |t| \) at \( k = 0 \) in the region \( 0 < E < 3|t| \). The two sets of \( n \) subbands belong to two different valleys. The phase shift between them is \( \pi \). The values of matrix elements \( J_y^{j,j'}, J_x^{j,j'} \) among inter-valley bands are small in the comparison of those among the intra-valley bands. Thus, the crossing points executed by the two bands belonged to different valleys contribute to the Hall conductivity weakly respect to those contribution from the intra-valley. At some special intra-valley crossing points the values of matrix elements \( J_y^{j,j'}, J_x^{j,j'} \) are significantly enhanced. We evidently affirm these intra-valley crossing points with dash lines and circles in Figs.2(a)-(d). If we sort those \( n \) bands with energies located above \( E = |t| \) at \( k = 0 \) in numbers \( j = 1, 2, 3, \ldots, n \), the crossing points formed between two neighbor subbands \( j = j' \pm 1 \) would lead the sign-reversal jumps in the Hall conductivity, while contributions from those band-crossings related two bands \( j' \) and \( j = j' \pm m \) with \( m \geq 2 \) are very small. Fig.3(a) shows that the sign-reversal jumps in conductivities occur when the Fermi energy takes the values of energies at special band-crossings. The number of crossing points caused by two neighbor subbands depends on the width of ribbons. For those narrow ribbons, the population of subbands is too sparse to form intra-valley crossings except the one on the flat band at \( E = |t| \). With increasing the width of ribbons, the band-crossing starts to appear. The number of crossing points is fixed for a certain range of ribbon widths, so does that of sign-reversal jumps in conductivities.
FIG. 3: The Hall conductivities at zero temperature versus the Fermi energy for AGNRs in various widths (a) \( N = 3, 9, 17, \) and 21) and (b) \( N = 4, 6, 14, \) and 18), with the magnetic flux \( f = 1.0 \times 10^{-4} \). The evolution of jumps in Hall conductivities for AGNRs with increasing the strength of magnetic field (c) \( f = 1.0 \times 10^{-4}, 5.0 \times 10^{-4}, \) and \( 1.0 \times 10^{-3} \), for a fixed width \( N = 21 \); and with increasing width (d) \( N = 24, 36, \) and 60, for a fixed magnetic flux \( f = 1.0 \times 10^{-4} \); (e) and (f) The DOS for odd and even AGNRs in various widths.

For example in the range \( N = 3 \) to \( N = 7 \), the band-crossing occurs only on the flat band. Correspondingly only one sign-reversal jump appears at \( E_F = |t| \). If the width is increased to \( N = 9 \), another intra-valley crossing point occurs at \( E = 0.52 \). A new sign-reversal jump appears in the Hall-like conductivity. In further, the second new intra-valley crossing point, satisfying rule of \( j = j' \pm 1 \), appears only when the ribbon is widened to \( N = 15 \) and the second sign-reversal jump is formed.

For AGNRs in width \( N = 2n \), there are also \( n \) subbands above \( E = |t| \) and \( n \) subbands below \( E = |t| \) at \( k = 0 \) as shown in Fig.2(e)-(h). However, different from the case of \( N = 2n + 1 \), there is no reflection symmetry in the transversal direction and the flat band at \( E = |t| \) is absent. The Hall conductivity would have no sign reversal when the Fermi energy is swept over \( E_F = |t| \). Fig.2(e)-(h) show the band-crossings below \( E = |t| \) for various
widths. Widening ribbon makes those band-crossings at high energies to inhabit near of \( E = |t| \) and be gathered exactly at \( E = |t| \) in the limitation of an infinite graphene sheet. As discussion above, the band-crossing between two neighbor subbands gives rise to a drastic change in the Hall-like conductivity. In Fig.3(b) we have shown the Hall conductivities for \( N = 2n \) AGNRs with several \( n \). The jumps are attributed to band-crossings indicated by dash lines and circles in Fig.3(c)-(h). It has been seen that, for the narrowest even AGNRs, \( N = 4 \), there is no intra-valley crossing point in the band spectrum and no any jump in the Hall-like conductivity, either. The conductivity is very small. When the ribbon is widened to \( N = 6 \), the first intra-valley crossing point is shaped and a sign reversal jump appears in the Hall-like conductivity. Widening the ribbons to \( N = 12 \) and \( 18 \), the two and three band-crossings caused by neighbor subbands are shaped below \( E = |t| \), respectively. Correspondingly, two and three sign-reversal jumps in the Hall conductivity are bound to be followed by the number of band-crossings. It is noticeable that, along with widening ribbons, the last sign reversal jump tends toward to \( E = |t| \).

It is worthwhile to point out that, although the ribbons in widths \( N = 3m - 1 \) (integer \( m \)) are metallic, the number of band-crossings does not change so long as the width is fixed in some regions. For example, between \( N = 9 \) and \( 15 \), AGNRs in width \( N = 11 \) becomes metallic, there is still only one band-crossing point below \( E = |t| \). The only difference from those semiconductor ribbons \((N = 9 \text{ and } 13)\) is that the Hall conductivity is nonzero for metallic ribbons at \( E_F = 0 \) \((N = 17 \text{ and } 14 \text{ have been shown in Figs.3(a) and (b)})\).

Although the Hall conductivities for ZGNRs and AGNRs of finite widths have been shown very different, they manifest themselves the same peculiar odd-integer Hall plateaus as the widths are widened to transversely infinite. We have seen in Figs.3(a) and (b) that increasing the width lifts those sign-reversal jumps in the low energy region. For the ribbons widened enough, the conductivities become positive for \( E_F < |t| \) while negative for \( E_F > |t| \). The only jump occurs at \( E_F = |t| \). As a demonstration, we show shrinking oscillations with increasing magnetic field in Fig.3(c) and with widening the ribbon in Fig.3(d). It is well known that both the band structure and density of states (DOS), \( D(E) \), of a material contain important information about transport properties. Our numerical calculation show that most of the physical features appearing in the DOS of the infinite system could be recovered if the width enlarges to \( N \approx 140 \) \((\text{Figs.1(d), 3(e), and 3(f)})\). The whole DOS profile evidently shows the Dirac fermion and the ordinary fermion to be separated at \( E = |t| \). For an infinite graphene
sheet the DOS tends to constant at $\Gamma$ point ($E = 3 |t|$) due to parabolic dispersion of ordinary fermions, while vanishes linearly around zero energy due to the relativistic dispersion of Dirac fermions. As shown in Fig.1(d), although edge states (Fig.1(c)) give rise to a DOS divergence at zero energy for ZGNRs, it is deduced as the width of ribbon increase so the edge effect is relieved. In the view of the restore of van Hove singularities for even AGNRs in the limitation to the graphene sheets, Fig.3(f) shows that increasing the width to a certain region, one can clearly see the emergence of important characteristics of the DOS of the infinite graphene sheet, namely, to buildup of the van Hove singularities. Therefore, although the flat band is absent for a narrow even AGNRs, it is found that the bands would gather at $E = |t|$ in infinite width, the flat band is built at $E = |t|$ and the DOS becomes singularity. However, the changes of the DOS for $N = 2n + 1$ (Fig.3(e)) and $N = 2n$ (Fig.3(f)) in increasing $N$ are not the complete same. On the one hand, the global feature of DOS tend to similar for both odd and even AGNRs. On the other hand, for the region near of $E = |t|$, they show very different behavior when the width of ribbons increase. Although those peaks in the regions near of $E = |t|$ are smoothed as the width of AGNRs increased, the amplitude of the main peak around $E = |t|$ deduces for odd AGNRs, while, on the contrary, a sharp peak at $E = |t|$ is developed for even AGNRs (as shown in the inset of Fig.3(f)). The emergence of a peak structure for both cases is expected to be consistent with the diverging DOS at van Hove singularity for the graphene sheet. Experimentally, it is expected to observe the sign-reversal jumps. For ribbons in certain widths, it is hopeful to build band-crossing at the Fermi energy not far from Dirac point. For example, for the ribbon in width $\sim 2.46 \text{nm}$ ($N = 21$), there is one band-crossing at the energy $0.8672 \text{eV}$ and, correspondingly, one jump appears. Therefore, the quantum confinement effect on electronic properties for narrow GNRs can be detected through measuring Hall-like conductivity. The above calculations are carried at zero-temperature, however, the fundamental characteristics in conductivities for ribbons does not changed at the finite temperature. It is found that the amplitudes of jumps are weakly reduced at the finite temperature.

In summary we have investigated the quantum confinement effect on the Hall conductivity for GNRs under a magnetic field. It is found that edge characteristics and quantum confinement of ribbons affect the electronic transport significantly. Different from sign reversal jump occurred only at $E_F = |t|$ in the Hall-like conductivities for ZGNRs, there are extra drastic jumps for AGNRs. The occurrence of jumps in conductivities is attributed to the
band-crossings in the band spectrum. The sign-reversal oscillations would be relieved partly when the width of ribbons or the strength of magnetic field is increased. The restore of Hall plateaus and van Hove singularity in the band structure has been discussed by analyzing the evolution of DOS with widening GNRs to the graphene sheets.

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