A Novel Viewpoint for Source-drain Driven Current inside Triangular Nanographene: Close Relationship with Magnetic Current

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By theoretical simulations the relationship between the quantum transport current and magnetic field induced current in triangular nanographene molecules is investigated. In both cases the time-reversal symmetry between the doubly degenerate states of the isolated molecule is broken, which results in incomplete cancellation of the two equivalent circulating current patterns with opposite flow directions. This shows that the source-drain driven current loop and the diamagnetic circulating current can be understood on the same theoretical footing.

Keywords: Models of non-equilibrium phenomena, Magnetic phenomena, Electrical transport, Nano-electronics and related devices, Graphite, Zigzag edge, Circulating current patterns

I. INTRODUCTION

Recently, quantum transport properties through single molecules have attracted much attention not only from their conductance but also from various novel functions. For example, they are expected to operate as the field effect transistor (FET)[1], switch [2–9], spin filter [10–12], solenoid [13], and so on. Furthermore, it has been theoretically predicted that as a consequence of quantum coherence, a circulating current much stronger than the source-drain current can be formed inside the molecule [14–16]. As an application of this quantum nature, the single molecular memory was proposed, in which the orientation of a local spin is controlled by the field generated by the circulating current [14]. However, neither the mechanism inducing the enhancement of the current inside the molecule nor the factors determining its spatial distribution have been fully clarified yet. One of its reasons is that comparatively small molecules have been treated in the previous works above mentioned. In those cases the transmission probability and the internal current distribution are sensitive to the positions of atomic sites to which the source and drain leads are connected [17–19], which might obscure the essential mechanism of the circulating current. On the other hand, under magnetic field, the diamagnetic circulating current has been known to appear inside the molecule. The relationship between such a usual molecular current and the source-drain driven circulating current has not been investigated.

Our purpose in this work is, therefore, to clarify these issues with theoretical analyses as well as numerical simulations on a specific model of large molecules. For the case study useful to illustrate very clearly the physical mechanism of the circulating current, we adopt the triangular nanographene molecules with well-defined boundaries formed by the zigzag edges. In the past, the zigzag and/or armchair edges have been studied from the viewpoint of their electronic/magnetic properties and the transport character of their junctions [20–29]. However, their transport properties have not been studied well in the context

![FIG. 1: Schematic illustration of triangular nanographene. The sites to which the source and drain leads are connected are labelled as s and d, respectively.](image-url)
of internal current. In this paper, we will concentrate on clarifying the two points, i.e., 1) the origin of the internal current loop which does not depend on the connecting sites of the leads, and 2) its relationship with the intramolecular current such as the diamagnetic current or the persistent current under a magnetic field.

II. MODEL AND METHOD

We consider the two terminal system in which the source and drain leads are connected to the triangular nanographene as illustrated in Fig. 1. Here, the protruded atoms along the topmost zigzag edge are numbered from 1 to \(N\). In total the number of atoms in the nanographene is \(N^2 + 4N + 1\). The small molecule with \(N = 2\) corresponds to the phenalenyl studied in the previous works [18, 19]. In this article, we will focus on the large system with \(N = 56\).

The source and drain leads are modeled by semi-infinitely long atomic chains, and are assumed to be connected to the sites labelled as \(s\) and \(d\), respectively. In particular, we choose a symmetric lead connection, i.e., \((s, d) = (N/4 + 1, 3N/4)\). The computational details have been published elsewhere [19]. Briefly speaking, the electronic states of the nanographene with the two leads are described by a single \(\pi\) orbital per atomic site. The hopping integral between the \(\pi\) orbitals on the nearest atomic sites are set to \(t\), except the interactions between the leads and the nanographene, which are assumed as 0.6t. The transmission probabilities between the two leads are calculated by the Landauer-Büttiker theory, using the Green’s functions method. The internal current distributions are calculated based on the electron correlation Green’s functions.

III. RESULTS AND DISCUSSION

A. Current patterns at resonant levels

First we will show the transmission spectrum. The red curve in Fig. 2 shows the spectrum in the energy range \([-0.2t, 0]\). As seen in the figure, it has three peaks at (a) \(E = -0.106\ t\), (b) \(E = -0.160\ t\), and (c) \(E = -0.165\ t\). These energy positions agree with the levels of the isolated nanographene shown by the blue curve, which plots the density of states (DOS) with a Lorentzian smearing of \(10^{-3}t\). Each of these levels has a two-fold degeneracy. Noticeably, the DOS has prominent peak at \(E = 0\) which is brought about by the \((N-1)\)-fold degeneracy of the edge states. On the contrary, the corresponding transmission spectrum shows a sharp dip at \(E = 0\), which indicates that the transmission is strongly prohibited at this level irrespective of the high density of states. This may be due to the non-bonding (localized) character of the edge state molecular orbitals [24].

At the incident energies near the three resonant peaks, the corresponding internal currents, i.e., the bond currents per energy, are illustrated in Fig. 3. The figures in the left column show the spatial distribution of the bond current \(J_{ji}(E)\) (from site \(i\) to \(j\)) with a linear color scale, so that the strongest one is expressed by the red color in each current pattern. The figures in the right column schematically illustrate the orientations of the current flow. It is found that the current distributions have
totally different patterns among these levels. Namely, (a) at \( E = -0.106 \) a current loop is formed around the gravity center of the nanographene. (b) At \( E = -0.160 \) the four current loops are formed so that the neighboring loops have opposite flow directions. (c) At \( E = -0.165 \), a current loop which winds inside the nanographene appears. However, in either case, the current distribution exhibits the three-fold symmetry, reflecting the triangular shape of the nanographene.

Here, it is very significant to point out that even when the source and drain sites are moved to different sites along the topmost side of the nanographene, almost the same current patterns are obtained at these energy levels. We have confirmed this by various simulations, though they are not shown in the figures. It suggests that the internal current distribution is determined from the nature of the nanographene itself, rather than it is accidentally induced by the current from the leads.

B. Origin of current patterns from ordinary viewpoint

Then, what is the origin of such a lead-independent current? In general, the wave function \( \Psi \) of the whole system is described as the summation of the wave functions of the nanographene and the leads. Using this wave function, the current per energy from site \( i \) to \( j \) is given by

\[
J_{ji}(E) = \frac{4e}{\hbar} \text{Im} \{ \Psi_j^\dagger \mathcal{H} \Psi_i \},
\]

where \( \Psi(E) \) is the wave function at energy \( E \), and \( \mathcal{H} \) is the Hamiltonian of the system. However, in our case, as discussed in the previous subsection, attaching the leads seems to give little effects on the spatial distribution of the internal current in the vicinity of the resonant levels \( E = E_r \). In addition, the resonant levels in consideration ( \( E_r = -1.06 \), \(-1.60\), \(-1.65 \)) are doubly degenerate, as previously denoted. Thus, as long as the current inside the nanographene at \( E \sim E_r \) is concerned, it is legitimate to approximate such that

\[
\Psi = c_1 \phi_1 + c_2 \phi_2,
\]

where \( c_n \)'s are c-numbers and \( \phi_n \)'s are the eigen wave functions of the isolated nanographene at \( E = E_r \). Note here that since the Hamiltonian of the isolated nanographene is a real Hermitian, \( \phi_n \)'s are real numbers. Therefore, the bond current at energy \( E \) can be written by

\[
J_{ji}(E) = \frac{4e}{\hbar} \text{Im} [c_1^* c_2 \{ \phi_{j1} \phi_{2i} - \phi_{2j} \phi_{1i} \} ] = f(\theta) I_{ji},
\]

where

\[
f(\theta) \equiv \frac{4e}{\hbar} |c_1|^2 |c_2| \sin \theta \quad I_{ji} \equiv \phi_{j1} \phi_{2i} - \phi_{2j} \phi_{1i}.
\]

Here \( \theta \) is a phase difference between the two c-numbers, \( c_1 \) and \( c_2 \). Note that while \( f(\theta) \) only describes a macroscopic phase which does not depend on the positions, \( I_{ji} \) gives the spatial distribution of the internal current. It should be remarked that the quantity \( I_{ji} \) is invariant against any real unitary transformation between the two degenerate states. The figures in the left column in Fig. 4 illustrate the spatial distributions of \( I_{ji} \) at the nanographene levels, \( (a) E = -1.06 \), \( (b) E = -1.60 \), and \( (c) E = -1.65 \), which show quite similar patterns to those observed in Fig. 3. It assures the validity of our analysis presented above.

C. Novel viewpoint: relation with magnetic current

In the above subsection we found that the phase difference between the two c-numbers describes the orientation of the internal current. However, its physical significance is not clear. Then, in this subsection, we will consider the internal current from a different viewpoint.

Let the \( \phi_L \) and \( \phi_R \) express the wave functions generated from the real wave functions \( \phi_1 \) and \( \phi_2 \) by a unitary transformation, i.e.,

\[
\begin{pmatrix}
\phi_L \\
\phi_R
\end{pmatrix} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & i \\ 1 & -i \end{pmatrix} \begin{pmatrix} \phi_1 \\
\phi_2
\end{pmatrix}
\]

In analogy with the optics, these new functions correspond to the left- and right-circularly polarized wave. Even if the multiple loops exist as in the case of Fig. 3(b), these two components have the same flow pattern except that the flow direction is reversed. In this representation,
Ψ can be approximated by

$$\Psi = c_L \phi_L + c_R \phi_R,$$

where $c_L$ and $c_R$ are c-numbers. The bond current is now written by

$$J_{ji}(E) = \frac{4et}{\hbar} \left\{ |c_L|^2 \text{Im}(\phi_{ij}^* \phi_{Lj}) + |c_R|^2 \text{Im}(\phi_{ij}^* \phi_{Rj}) \right\}$$

$$= g(E) I_{ji},$$

where

$$g(E) \equiv \frac{2et}{\hbar} (|c_L|^2 - |c_R|^2)$$

represents the difference in the occupation number of the left- and right-polarized states. In the isolated nanographene $|c_L(E_r)| = |c_R(E_r)|$ is satisfied, which ensures that no net current is generated in the molecule from this degenerate level. However, once the leads are attached to the molecule and the bias is applied between them, the equivalence between the two polarized states is broken, which brings about a difference between $|c_L|$ and $|c_R|$ in the vicinity of $E = E_r$. In that case the current can flow in either circulating direction.

A similar intra-molecular current is realized when a magnetic field is applied perpendicular to the isolated nanographene, by which the degeneracy of the two polarized states $\phi_L$ and $\phi_R$ is lift. Numerically the internal bond current is calculated by Eq. (1) where $\mathcal{H}$ is now the complex Hermitian, because the hopping integral includes a Peierls phase factor [30, 31]. The wave functions $\Psi$ are the eigen wave functions of this Hamiltonian matrix. The figures in the right column of Fig. 4 show the current distributions at the lower energy states ($E_{ji}^L$) split from the doubly degenerate levels, i.e., (a) $E = -1.06t$, (b) $E = -1.60t$, and (c) $E = -1.65t$. The upper energy states ($E_{ji}^R$) have the similar current patterns but with opposite flow directions. From the remarkable agreement of these patterns with the figures in the left column of Fig. 4, we consider that the energetically split two states ($E_{ji}^L$ and $E_{ji}^R$) are dominantly composed of the wave functions, $\phi_L$ or $\phi_R$. Roughly speaking, the diamagnetic current is generated by a slight difference between $|c_m(E_{ji}^L)|$ and $|c_m(E_{ji}^R)|$ ($\{m, n\} = \{L, R\}$). If the Fermi is located very close to the degenerate level, and the lift of the degenerated level is larger than the Zeeman splitting, we might expect a persistent current whose intra-molecular distribution is almost the same as the source-drain induced circulating current.

**D. Net current patterns observable in experiments**

It should be noted that the similarity of the internal current distributions between the source-drain driven current and diamagnetic current is not assured in the net current. In the former case, the net current is obtained by integrating the current between the bias window. In the latter case, it is obtained by summation of the current over all the occupied levels formed by $\pi$-electrons. For example, Figs. 5(a) and 5(b) show the current distribution at $V = 0.1t$ and $0.4t$, respectively, which are obtained by integrating the bond current $J_{ji}(E)$ evaluated at every energy point on the mesh in the bias window $[-V/2, V/2]$. (Note that the contribution from $E = E_r$ and $E = -E_r$ is equivalent.) In each map the current orientation is schematically illustrated in the right column. In the case of $V = 0.1t$, since no resonant level contributes to the current, the transport occurs in a tunneling regime. The current which enters from the source site tunnels into deep inside the nanographene and then exits from the drain site. The reason why the current detours the zigzag edge may be due to the non-bonding, i.e., strictly localized character of the edge states [24]. In the case of $V = 0.4t$, the net current has a clear three-fold symmetry, and the circulating currents are observed at many places, each of which encloses large area. This is basically understood by the superposition of the current patterns in Fig. 3 weighted by the corresponding transmission amplitudes. In contrast, Fig. 5(c) shows the net current in the isolated molecule under a weak magnetic field applied perpendicular to the molecular plane. The circulating current is found to flow strongest along the zigzag edges. Note that the contribution from the edge states at $E = 0$ are negligible, which indicates that the lower energy levels are relevant to such a circulating current.

Finally we comment on the advantage of adopting the triangular nanographene sheet bound with zigzag edges to experimental observation of the net circulating current patterns. In the nanographene sheet with other structures, such as the triangular nanographene bound with armchair edges or the hexagonal nanographene bound with zigzag edges, we found that not only doubly degen-
erate but also non-degenerate levels appear in the energy range \([-0.2f, 0]\). The internal currents originated from the latter energy levels spreads inside the molecule and do not bring about any circulating current patterns. However, their contribution to the net bond currents is large due to the high transmission peaks at these levels. As a result, in many cases, the circulating current patterns become obscure when the applied bias reaches \(V = 0.4f\). On the contrary, in the case of triangular nanographene with zigzag edges, only the doubly degenerate levels are aligned in the vicinity of the Fermi level, instead of forming multiply degenerate levels at \(E = 0\). Since there is no contribution from the non-degenerate levels, the nanographene studied in this paper would be promising for detecting the source-drain driven circulating current patterns inside the molecule. In addition, as the size of the nanographene becomes large through the number \(N\), the doubly degenerate levels relevant to the circulating patterns get closer to the Fermi level. This would make the experimental observation of the circulating current much easier by applying low bias voltages between the source and drain leads.

**IV. CONCLUSION**

In conclusion, we clarified the close relationship between the source-drain driven current and the magnetic field induced current, assuming a large triangular nanographene molecule bound with zigzag edges. In both cases the time-reversal symmetry between the doubly degenerate states of the isolated molecule is broken, by which the two large circulating current components with opposite chirality cancels each other incompletely. This is the origin of the appearance of the internal current flowing in either circulating direction. However, the experimentally observable is the integration of the current between the bias window, or the summation of the current over all the occupied levels. In order to confirm the close relationship denoted above, it would be necessary to detect somehow the derivative of the net current with respect to the energy at many places on the nanographene sheet.

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