Quantum Loop Current in a C_{60} Molecular Bridge

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The existence of a quantum loop current in a C_{60} molecular bridge is predicted using the Green's function method. The model for the molecular bridge consists of a C_{60} molecule attached to one-dimensional conductive electrodes. It is shown that the loop current is related to the degeneracy of the energy levels of the C_{60} molecule. Specific to this loop current is its magnitude which is much larger than that of the source-drain current. The associated magnetic moment also shows certain remarkable features such as its inversion with the energy across the molecular levels and the restriction of its direction onto a single plane.

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Molecular bridges are promising candidates for nanodevice elements since organic molecules are flexible and their doping can be efficiently controlled by organic synthesis techniques. An increasing number of papers have been devoted to materializing the age of molecular electronics (see review, Ref. [1]). In particular, gold-molecule-gold junctions with thiol chemical bonds have attracted much interest [2], and some promising applications have been reported such as parallel molecular bridges [3], negative differential resistance [4], and logic gates [5]. Among many types of molecules, the fullerene C_{60} is suitable for molecular bridge since its LUMO (lowest unoccupied molecular orbital) is situated at relatively lower energies compared to other organic materials. It is also mechanically stable and its electronic and mechanical properties have already been intensively studied [6]. In a benchmark experiment toward understanding the electron transmission through a C_{60} molecular bridge, its current-voltage characteristics were measured by deforming the C_{60} molecule with the tip of a scanning tunneling microscope [7]. The contact area between the C_{60} molecule and the tip was found to play an important role in the drastic increase of the conductance [8]. With this setup, an electrochemical amplifier was realized [9]. At the present stage, a theoretical effort should also be carried out in order to find and understand novel phenomena in molecule-based nanostructures which could serve as a basis for fabricating useful molecular devices.

While current research trends on molecular bridge structures have mainly been focused on its total conductance so far, we report in this Letter on the quantum internal current through the C_{60} molecular bridge. For certain electron energy regions, the internal current shows a large loop current which is induced by the source-drain current I_{SD}, and amounts to several tens of I_{SD}. This is related to the high symmetry of the C_{60} molecule entailing the degeneracy of molecular levels. Furthermore, the magnetic moment associated with this loop current exhibits remarkable properties. For instance, its direction changes if the electron energy is swept across the energy levels of the molecule. Moreover, under certain conditions, the induced magnetic moment is restricted to a single particular plane when the drain site is varied over any sites for a given fixed source position.

The model for the C_{60} molecular bridge is shown in Fig. 1. A tight-binding approach with one π-orbital per atom is used, and the source and drain electrodes are assumed to be one dimensional with a single channel. The resonance integral between nearest carbon sites is referred to as t and that between the molecule and the electrodes is denoted as t'. Between the nearest sites in the electrodes, the resonance integral is also set to t. Because we consider ballistic transmission, the bottleneck of the molecule-electrode contact should not be smaller than the order of the resonance integral t. Thus the value of t' is taken to be $t' = t/2$. This is legitimate because the essence of the results does not change with the detail value of t'. The site energy is set to a common value for all sites in the system and is chosen as the reference of the electron energy.

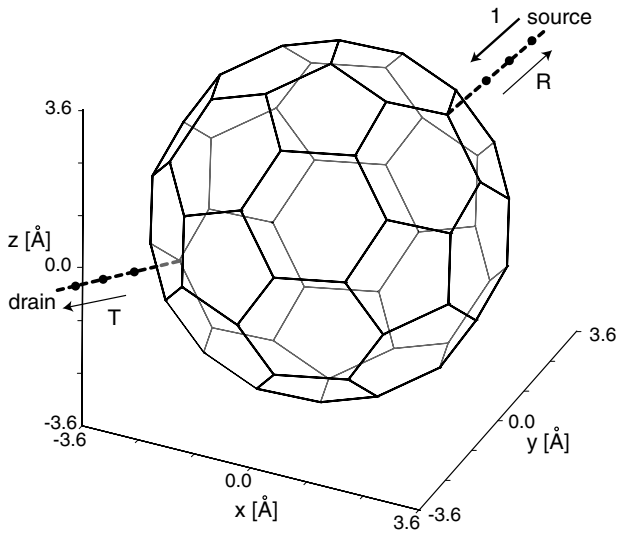

FIG. 1. The model for the C_{60} molecular bridge. One-dimensional electrodes are connected to the source and drain sites of C_{60}, respectively. The origin of the coordinate is the center of the C_{60} molecule.

It is worth noting that the C_{60} molecule has two different bonds (1.511 and 1.497 Å) [10]. In our calculation, this difference is ignored because the bond length difference amounts to less than 2% and the resonant integrals thus only differ by less than 2% [10,11]. In this paper, a simple one-electron description is used and many-body effects are neglected. We also restrict our investigation to infinitesimally small applied voltages (zero volt approximation).

The electron transmission through the system is calculated by the Landauer-Büttiker formula based on the Green's function method [12,13]. In the following, we discuss the energy density of the current and magnetic moment, but refer to it simply as current and magnetic moment, respectively, unless otherwise stated. The internal current from site j to i is calculated from the Green's function G^n, usually referred to as a correlation function [13]:

$$I_{ij} = \frac{4e}{\hbar}\,\mathrm{Im}[\psi_i^* H_{ij}\psi_j] = \frac{4e}{h}\,\mathrm{Im}[H_{ij}G_{ij}^n]. \qquad (1)$$

Here, H is the Hamiltonian and ψ_i, the amplitude of the total electron wave function at the site i. The correlation function G^n is defined as $G^n = G^R\Gamma_S G^A$ with $\Gamma_{S(D)} = i[\Sigma^R_{S(D)} - \Sigma^A_{S(D)}]$, where $G^{R(A)}$ is the retarded (advanced) Green's function and $\Sigma^{R(A)}_{S(D)}$ is the retarded (advanced) self-energy due to the connection to the source (drain) electrode. The correlation function is calculated by setting the occupation function of the source to unity and that of the drain to zero. The source-drain current $I_{SD} = \frac{2e}{h}T_{SD}$ is calculated from the transmission probability $T_{SD} = \mathrm{Tr}[\Gamma_S G^R \Gamma_D G^A]$.

The calculated transmission probability $T_{SD}(E)$ for the C_{60} bridge, where the source and the drain site are set as shown in Fig. 1, is shown in Fig. 2(a). T_{SD} has a large value near the molecular level of C_{60} and a dip just at the level because of the degeneracy. In the ballistic regime, a large transmission arises when the electron energy nearly coincides with the molecular levels since the electron resonantly transmits through the molecule. The dip appearing in $T_{SD}(E)$ is related to the vanishing elements of the Green's function connecting the source site to the drain site at the degenerate molecular levels [14].

Figure 3 illustrates the internal current distribution of the C_{60} molecular bridge for the electron energy $E = 0.134|t|$, slightly below the LUMO. A large loop current is induced in the C_{60} molecule which amounts to 24 times the source-drain current. The induced loop current distributes widely over the C_{60} molecule since it results from the interaction among the degenerate states at the LUMO. A large loop current is induced similarly around the energy regions close to any of the energy levels of C_{60}. To understand the behavior, the electron wave function of the open system can be expanded in terms of the molecular orbitals (MO) $\{\boldsymbol{\phi}_\mu\}$ at the C_{60} sites, i.e., $\boldsymbol{\psi} = \sum_\mu a_\mu \boldsymbol{\phi}^\mu$. The current from the jth to ith site is given by $I_{ij} = 4e\sum_{\mu,\nu} H_{ij}^{\mu\nu}|a_\mu||a_\nu|\sin(\theta_\nu - \theta_\mu)/\hbar$.

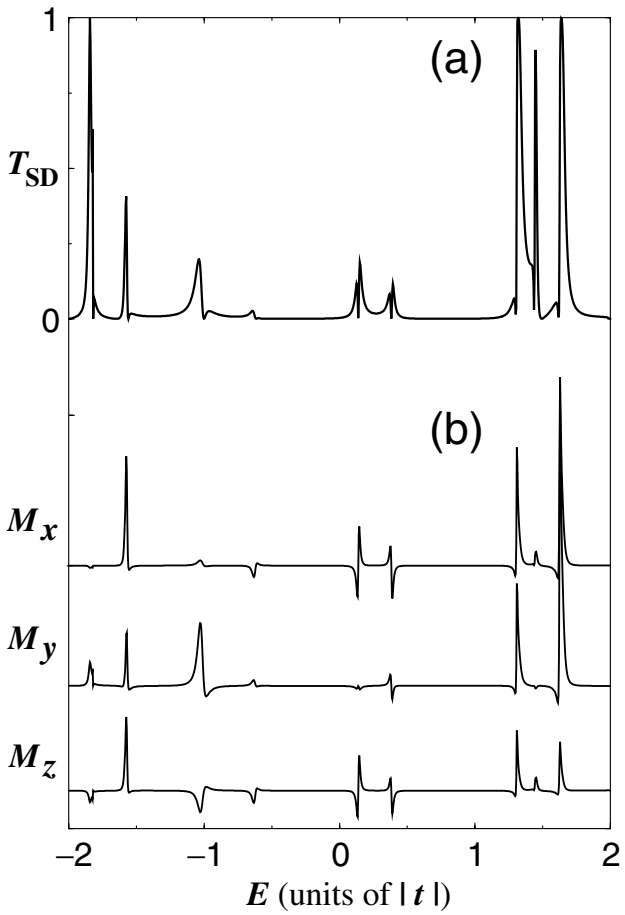

FIG. 2. (a) Transmission probability T_{SD} and (b) induced magnetic moment $\boldsymbol{M}$ of the molecular bridge. Each component of $\boldsymbol{M}$ is shown in arbitrary units. T_{SD} becomes large near the molecular levels, where a large loop current is induced in the C_{60} molecule. $\boldsymbol{M}$ also grows near the molecular levels and changes direction just on the level.

$H_{ij}^{\mu\nu}$ is the element of the Hamiltonian matrix in the site representation between the μth and νth component of MO. The phase of the coefficient a_μ is referred to as θ_μ. The coefficient a_μ has a non-negligible value only when the electron energy is in the vicinity of the molecular level μ. In other words, all molecular levels except the resonant levels located nearby the electron energy can be excluded from the summation. Therefore, a large resonant current is expected since both the amplitude $|a_\mu|$ and $|a_\nu|$ are resonantly enhanced around the common degenerate level and the phase difference $\theta_\nu - \theta_\mu$ is also enhanced near the level [15,16]. The phase difference reflects the asymmetry of the effective coupling between each molecular state and the electrodes.

It should be noted that the phase of the degenerate states is induced solely by the source-drain current, and the differences are appreciably enlarged just below and above the degenerate level. Thus the origin of the large current I_{ij} is a synergetic enhancement of the imaginary part of the current matrix element between the molecular states.

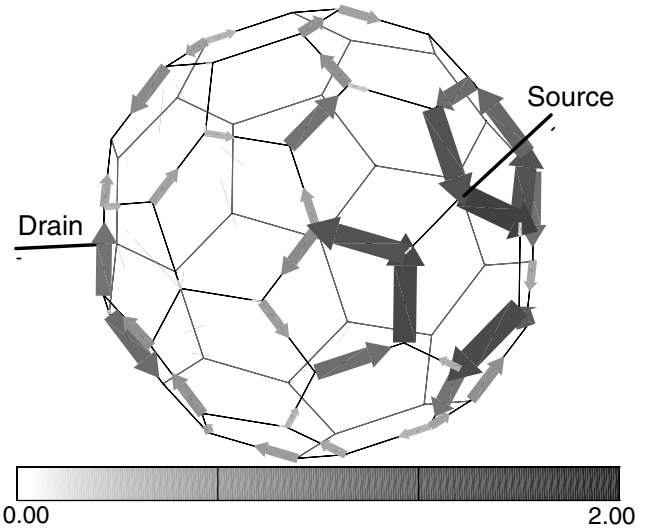

FIG. 3. Internal current distribution of the molecular bridge for the electron energy $E = 0.134|t|$ which is just below the LUMO of C_{60}. The source-drain current is $I_{SD} = 0.0663$. There is an induced loop current in the C_{60} molecule, whose magnitude amounts to $24I_{SD}$.

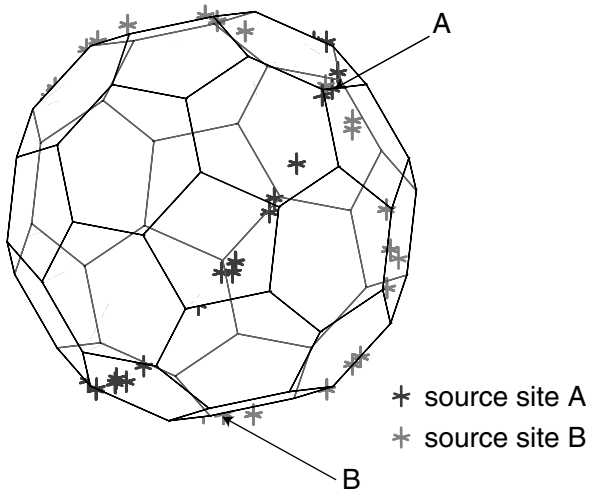

FIG. 4. Induced magnetic moment in the molecular bridge for the electron energy $E = 0.134|t|$. The source site s is fixed at A or B while the drain site d is varied over all other molecular sites. The magnetic moment is located on a single plane passing through the source site.

Because the electrode current is bounded to a single channel value $2e/h$ multiplied by bias voltage, the large segment current I_{ij} inevitably results in a large loop current in the molecule.

The magnetic moment arising as a result of the quantum loop current also has interesting properties. Recall that the induced magnetic moment is expressed as $\boldsymbol{M} = \sum_{(i,j)} I_{ij}(\boldsymbol{r}_i \times \boldsymbol{r}_j)/2$, where the summation is taken over each pair, ij, whose corresponding Hamiltonian matrix element is nonzero, and $\boldsymbol{r}_i$ indicates the coordinates of the site i. The components of the magnetic moment are shown in Fig. 2(b) as a function of the electron energy. The induced loop current and the corresponding magnetic moment become large near the molecular levels and change direction at the levels. This can be understood by examining the energy dependence of the phase θ_μ. The phase difference $\theta_\nu - \theta_\mu$ has a nonzero value in the vicinity of the correspondent energy level and changes the sign when the electron energy coincides with the level. This means that the direction of the induced magnetic moment could be reversed by sweeping the electron energy near a molecular level.

A second interesting feature is the drain site dependence of the magnetic moment. The magnetic moment $\boldsymbol{M}(s, d; E)$ is uniquely determined by designating the source site s, drain site d, and electron energy E. In Fig. 4, $\boldsymbol{M}$ is shown for two different source sites while the drain site d is widely changed. It is clear from Fig. 4 that the induced magnetic moment at this energy always lies on a plane in the (M_x, M_y, M_z) space when the source site is fixed.

The reason why the induced magnetic moment is confined to a single plane is as follows. The induced magnetic moment can be written in a bilinear form of the coefficients a_μ and the energy independent vector bases $\boldsymbol{m}(\mu, \nu)$,

$$\boldsymbol{M} = 2 \sum_{(\mu,\nu)} \mathrm{Im}[a_\mu^* a_\nu] \boldsymbol{m}(\mu, \nu), \tag{2a}$$

$$\boldsymbol{m}(\mu, \nu) = \frac{2e}{\hbar} \sum_{(i,j)} H_{ij} \begin{vmatrix} \phi_i^\mu & \phi_i^\nu \\ \phi_j^\mu & \phi_j^\nu \end{vmatrix} \frac{\boldsymbol{r}_i \times \boldsymbol{r}_j}{2}. \tag{2b}$$

The summation over the MO indices μ, ν is taken over only the resonant states closest to the relevant electron energy. By applying the Green's function method, the coefficients a_μ are obtained for any combination of states on the degenerate level. The vector bases of the magnetic moment $\boldsymbol{m}(\mu, \nu)$ are then chosen for any particular combination of resonant states. Here, for simplicity, we consider only the case where the electron energy is set near the tertiary degenerate molecular level. Let us assume that, by choosing a proper representation, we can make one of the coefficients $\mathrm{Im}[a_\mu^* a_\nu]$ zero for any arbitrary drain site d. Actually this is possible if the following condition is satisfied for an arbitrary d:

$$\mathrm{Im}[a_1^* a_2] = \frac{|t'|^2}{t}(E - E_r)^3(1 + t^2 - 2t\cos 2k) \times (s_1 d_2 - s_2 d_1) \sum_{\mu=1}^{3} s_\mu d_\mu \sin k = 0. \tag{3}$$

Here the value of the μth MO $\boldsymbol{\phi}_\mu(s)\,[\boldsymbol{\phi}_\mu(d)]$ at the source (drain) site is indicated by s_μ (d_μ), and k is the electron wave number which satisfies the dispersion relation $E = 2t\cos k$ at the source and drain electrodes. By choosing an appropriate combination of the molecular states at the degenerate level, it is always possible to satisfy the condition, $s_1 = s_2 = 0$. Then $\mathrm{Im}[a_1^* a_2] = 0$ for any of the drain sites. This means that the induced magnetic moment of the loop current for any choice of drain site is

a linear combination of $\boldsymbol{m}(2,3)$ and $\boldsymbol{m}(3,1)$, lying on the plane formed by these two base vectors. In other words, although there are three independent current channels inside C_{60} which are characterized by their respective magnetic moments, one of the current channels can be chosen so that it does not reach the source site.

In summary, we theoretically predict the existence of a quantum internal current through the C_{60} molecular bridge, which is an enhanced manifestation of the quantum electron transmission. This loop current emerges when the electron energy approaches the energy levels of the C_{60} molecule. The quantum loop current is induced by the source-drain current I_{SD} and amounts to several tens of I_{SD}. Moreover, interesting properties are also found in the magnetic moment associated with this loop current. For example, its direction is reversed if the electron energy is swept across the resonant levels. Furthermore, under certain conditions, the induced magnetic moment is restricted to a single particular plane regardless of the drain site for any fixed source position. These features could be applied, in principle, to quantum mechanical devices by using the quantum coupling to magnetic atoms. Since our results were obtained in the low-temperature and zero-bias limits, it is necessary to study the phenomenon under more accessible experimental conditions. However, note that the electron mean-free path inferred from a C_{60} (111) film at 180 °C [17] is larger than the scattering region, i.e., the C_{60} molecule and the nanocontacts. Therefore, it is not unreasonable to expect that the quantum loop current could be observed for some higher temperatures as well. We are currently investigating the effect of the finite voltage and the correlation between electrons.

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[1] C. Joachim, J. K. Gimzewski, and A. Aviram, Nature (London) **408**, 541 (2000).

[2] L. A. Bumm *et al.,* Science **271**, 1705 (1996); M. A. Reed *et al.,* Science **278**, 252 (1997); M. P. Samanta *et al.,* Phys. Rev. B **53**, R7626 (1996); S. Datta and W. Tian, Phys. Rev. B **55**, R1914 (1997); E. G. Emberly and G. Kirczenow, Phys. Rev. B **58**, 10 911 (1998); J. K. Gimzewski and C. Joachim, Science **283**, 1683 (1999); M. Magoga and C. Joachim, Phys. Rev. B **56**, 4722 (1997); C. Kergueris *et al.,* Phys. Rev. B **59**, 12 505 (1999); A. Onipko, Y. Klymenko, and L. Malysheva, Phys. Rev. B **62**, 10 480 (2000).

[3] M. Magoga and C. Joachim, Phys. Rev. B **59**, 16 011 (1999).

[4] J. Chen, M. A. Reed, A. M. Rawlett, and J. M. Tour, Science **286**, 1550 (1999).

[5] C. P. Collier *et al.,* Science **285**, 391 (1999).

[6] H. W. Kroto *et al.,* Nature (London) **318**, 162 (1985); A. D. J. Haymet, Chem. Phys. Lett. **122**, 421 (1985); M. Ozaki and A. Takahashi, Chem. Phys. Lett. **127**, 242 (1986); S. Saito and A. Oshiyama, Phys. Rev. Lett. **66**, 2637 (1991); K. Harigaya, Phys. Rev. B **45**, 13 676 (1992).

[7] C. Joachim, J. K. Gimzewski, R. R. Schlittler, and C. Chavy, Phys. Rev. Lett. **74**, 2102 (1995).

[8] M. Paulsson and S. Stafström, J. Phys. Condens. Matter **11**, 3555 (1999).

[9] C. Joachim and J. K. Gimzewski, Chem. Phys. Lett. **265**, 353 (1997).

[10] G. W. Hayden and E. J. Mele, Phys. Rev. B **36**, 5010 (1987).

[11] With the model which includes two types of bonds, we have confirmed that the shift in the energy spectrum is less than 2%. Also, there is no significant difference in the behavior and magnitude of both the quantum loop current and the induced magnetic moment.

[12] M. Büttiker, IBM J. Res. Dev. **32**, 63 (1988).

[13] S. Datta, *Electronic Transport in Mesoscopic Systems* (Cambridge University Press, Cambridge, 1995).

[14] S. Nakanishi, R. Tamura, and M. Tsukada, Jpn. J. Appl. Phys. **37**, 3805 (1998).

[15] S. Nakanishi and M. Tsukada, Surf. Sci. **438**, 305 (1999).

[16] M. Tsukada, N. Kobayashi, M. Brandbyge, and S. Nakanishi, Prog. Surf. Sci. **64**, 139 (2000).

[17] G. Gensterblum *et al.,* Phys. Rev. B **50**, 11 981 (1994).