Controlling quantum transport through a single molecule

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We investigate multi-terminal quantum transport through single monocyclic aromatic annulene molecules, and their derivatives, using the nonequilibrium Green function approach in the self-consistent Hartree-Fock approximation. A new device concept, the Quantum Interference Effect Transistor (QuIET) is proposed, exploiting perfect destructive interference stemming from molecular symmetry, and controlling current flow by introducing decoherence and/or elastic scattering that break the symmetry. This approach overcomes the fundamental problems of power dissipation and environmental sensitivity that beset many nanoscale device proposals.

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From the vacuum tube to the modern CMOS transistor, devices which control the flow of electrical current by modulating an electron energy barrier are ubiquitous in electronics. In this paradigm, a minimum energy of $k_B T$ must be dissipated to switch the current “on” and “off,” necessitating incredible power dissipation at device densities approaching the atomic limit [1]. A possible alternative is to control electron flow using quantum interference [2, 3, 4, 5]. In mesoscopic devices, quantum interference is typically tuned via the Aharonov-Bohm effect [6]; however, in nanoscale conductors such as single molecules, this is impractical due to the enormous magnetic fields required to produce a phase shift of order one radian. Similarly, a device based on an electrostatic phase shift [3, 4] would, in small molecules, require voltages incompatible with structural stability. We propose a solution exploiting perfect destructive interference stemming from molecular symmetry, and controlling quantum transport by introducing decoherence or scattering from a third lead.

As daunting as the fundamental problem of the switching mechanism, is the practical problem of nanofabrication [1]. In this respect, single molecules have a distinct advantage over other types of nanostructures, in that large numbers of identical devices can be readily synthesized. Single-molecule devices with two leads have been fabricated by a number of techniques [7]. Our transistor requires a third terminal coupled locally to the molecule, capacitively or via tunneling (see Fig. 1). To date, only global gating of single-molecule devices has been achieved [5]; recently, however, there has been significant progress toward a locally coupled third terminal [8].

This Letter reports the results of our recent theoretical investigations into the use of interference effects to create molecular transistors, leading to a new device concept, which we call the Quantum Interference Effect Transistor (QuIET). We demonstrate that for all monocyclic aromatic annulenes, particular two-terminal configurations exist in which destructive interference blocks current flow, and that transistor behavior can be achieved by supplying tunable decoherence or scattering at a third site. We also propose a realistic model for introducing scattering in a controllable way, using an alkene chain of arbitrary length (cf. Fig. 1). Finally, we present nonequilibrium Green function (NEGF) calculations within the self-consistent Hartree-Fock approximation, indicating that the QuIET functions at room temperature with a current-voltage characteristic strikingly similar to macroscale transistors.

The Hamiltonian of the system can be written as the sum of three terms: $H = H_{mol} + H_l + H_{tun}$. The first is the $\pi$-electron molecular Hamiltonian

$$H_{mol} = \sum_{n\sigma} \varepsilon_n d_{n\sigma}^\dagger d_{n\sigma} - \sum_{\langle nm \rangle\sigma} (t_{nm} d_{n\sigma}^\dagger d_{m\sigma} + H.c.) + \sum_{nm} U_{nm} Q_n Q_m, \quad (1)$$

where $d_{n\sigma}^\dagger$ creates an electron of spin $\sigma$ in the $\pi$-orbital of the $n$th carbon atom, $\varepsilon_n$ are the orbital energies, and $\langle \rangle$ indicates a sum over nearest neighbors. The tight-
binding hopping matrix elements \( t_{nm} = 2.2eV, 2.6eV, \) or \( 2.4eV \) for orbitals connected by a single bond, double bond, or within an aromatic ring, respectively. The final term of Eq. (1) contains intra- and intersite Coulomb interactions, as well as the electrostatic effects of the leads. The interaction energies are given by the Ohno parameterization \[ U_{nm} = \frac{11.13eV}{\sqrt{1 + .6117 \left( R_{nm}/\text{Å} \right)^2}}, \] (2)

where \( R_{nm} \) is the distance between orbitals \( n \) and \( m \). \( Q_n = \sum_{\alpha} \epsilon_k \tilde{c}_{k\sigma}^{\dagger} c_{k\sigma} \) is an effective charge operator \[ \delta \] for orbital \( n \), where the second term represents a polarization charge. Here \( C_{n\alpha} \) is the capacitance between orbital \( n \) and lead \( \alpha \), chosen consistent with the self-consistent Hartree-Fock method \[ \delta \]. \( \Sigma \) is the retarded self-energy induced by lead \( 3 \). The real part is replaced by the corresponding mean-field Hamiltonian \( H_{mol}^{HF} \), which is quadratic in electron creation and annihilation operators, and contains long-range hopping. Within mean-field theory, the retarded self-energy due to the leads is

\[ \Sigma_{n\sigma,m\sigma'}(E) = -\frac{i}{2} \delta_{nm} \delta_{\sigma\sigma'} \sum_{\langle \alpha \rangle} \Gamma_{\alpha}(E) \delta_{n\alpha}, \] (6)

where \( \Gamma_{\alpha}(E) = 2\pi \sum_{k<\alpha} |V_{nk}|^2 \delta (E - \epsilon_k) \) is the Fermi’s Golden Rule tunneling width. As a result, the molecular density of states changes from a discrete spectrum of delta functions to a continuous, width-broadened distribution. We take the broad-band limit \[ \delta \], treating \( \Gamma_{\alpha} \) as constants characterizing the coupling of the leads to the molecule. Typical estimates \[ \delta \] using the method of Ref. \[ \delta \] yield \( \Gamma_{\alpha} \approx 0.5eV \), but values as large as 1eV have been suggested \[ \delta \].

The effective hopping and orbital energies in \( H_{mol}^{HF} \) depend on the equal-time correlation functions, which are found in the NEGF approach to be

\[ \langle d_{n\sigma}^{\dagger} d_{m\sigma'} \rangle = \frac{\Gamma_{\alpha}}{2\pi} \int_{-\infty}^{\infty} dE \left[ G_{n\sigma,m\sigma}(E) G_{n\sigma,m\sigma}^{*}(E) f_{\alpha}(E) \right], \] (7)

where \( f_{\alpha}(E) = \{ 1 + \exp((E - \mu_{\alpha})/k_B T) \}^{-1} \) is the Fermi function for lead \( \alpha \). Finally, the Green function is determined by iterating the self-consistent loop, Eqs. (4)–(6).

The current in lead \( \alpha \) is given by the multi-terminal current formula \[ \delta \] from lead \( \alpha \) to lead \( \beta \), and \( a (b) \) is the orbital coupled to lead \( \alpha (\beta) \). The QuIET exploits quantum interference stemming from the symmetry of monocylic aromatic annulenes, such as benzene. Quantum transport through single benzenic molecules with two metallic leads connected in the para orientation has been the subject of extensive experimental and theoretical investigation \[ \delta \]; however, a
The third lead introduces decoherence\cite{20} and additional paths that are not cancelled, thus allowing current to flow, as shown in Fig. 3b. As a proof of principle, a QuIET could be constructed using a scanning tunneling microscope tip as the third lead, with tunneling coupling $\Gamma_3(x)$ to the appropriate $\pi$-orbital of the benzene ring, the control variable $x$ being the piezo-voltage controlling the tip-molecule distance.

By contrast, a real self-energy $\Sigma_3$ introduces elastic scattering, which can also break the molecular symmetry. This can be achieved by attaching a second molecule to the benzene ring, for example an alkene chain (cf. Fig. 1). The retarded self-energy due to the presence of a second molecule is

$$\Sigma_3(E) = \sum_\nu \frac{|t_\nu|^2}{E - \epsilon_\nu + i0^+}, \quad (10)$$

where $\epsilon_\nu$ is the energy of the $\nu$th molecular orbital of the second molecule, and $t_\nu$ is the hopping integral coupling this orbital with the indicated site of benzene. The sidegroup introduces Fano antiresonances\cite{21}, which block current through one arm of the annulene, thus lifting the destructive interference. Put another way, the second molecule’s orbitals hybridize with those of the annulene, and a state that connects leads 1 and 2 is created in the gap (see Fig. 3c). Shifting $\epsilon_\nu$ by gating the sidegroup then yields transistor action.

Tunable current suppression occurs over a broad energy range, as shown in Fig. 3b; the QuIET functions with any metallic leads whose work function lies within the annulene gap. Fortunately, this is the case for many bulk metals, among them palladium, iridium, platinum, and gold\cite{10}. Appropriately doped semiconductor electrodes\cite{8} could also be used.

In Fig. 4 the $I$-$V$ characteristic of a QuIET based on sulfonated vinyl benzene is shown, whose molecular structure is given in Fig. 1. The three metallic electrodes were taken as bulk gold, with $\Gamma_1 = \Gamma_2 = 1\text{eV}$, while $\Gamma_3 = .0024\text{eV}$, so that the coupling of the third electrode to the alkene sidegroup is primarily electrostatic. The device characteristic resembles that of a macroscopic transistor. As the voltage on lead 3 is increased, the antibonding orbital of the alkene sidegroup comes into resonance with the Fermi energies of leads 1 and 2, leading to a broad peak in the current. For $\Gamma_{1,2} \gg \Gamma_3 \neq 0$, the device amplifies the current in the third lead (dotted curve), emulating a bipolar junction transistor. For $\Gamma_3 = 0$, the calculated current $I_1$ is almost identical to that shown in Fig. 4 and the device acts like a field effect transistor.
Alkene chains containing 4 and 6 carbon atoms were also studied, yielding devices with characteristics similar to that shown in Fig. 4, with the maximum current $I_1$ shifting to smaller values of $V_{32}$ with increasing chain length. As evidence that the transistor behavior shown in Fig. 4 is due to the tunable interference mechanism discussed above, we point out that if hopping between the benzene ring and the alkene sidegroup is set to zero, so that the coupling of the sidegroup to benzene is purely electrostatic, almost no current flows between leads 1 and 2.

Operation of the QuIET does not depend sensitively on the magnitude of the lead-molecule coupling $\bar{\Gamma} = \Gamma_1 = \Gamma_2 = 1$ eV. $\Gamma_3$ is taken as 0.0024 eV, which allows a small current in the third lead, so that the device amplifies current. A field-effect device with almost identical $I-V$ can be achieved by taking $\Gamma_3 = 0$. The curve for $I_3$ is for the case of 1.00 V bias voltage; $I_3$ for other biases look similar.

The QuIET mechanism applies to any monocylic aromatic annulene with leads 1 and 2 positioned so the two most direct paths have a phase difference of $\pi$. Furthermore, larger molecules have other possible lead configurations, based on phase differences of $3\pi$, $5\pi$, etc. Figure 5 shows the lead configurations for a QuIET based on [18]-annulene. The bold lines represent the positioning of the two leads. Each of the four arrangements has a different phase difference associated with it: (a) $\pi$; (b) $3\pi$; (c) $5\pi$; and (d) $7\pi$.

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FIG. 4: $I-V$ characteristic of the QuIET shown in Fig. 1 at room temperature. The current in lead 1 is shown, where $V_{12} = V_{23} = V_{31}$. Here, $\Gamma_1 = \Gamma_2 = 1$ eV. $\Gamma_3$ is taken as 0.0024 eV, which allows a small current in the third lead, so that the device amplifies current. A field-effect device with almost identical $I-V$ can be achieved by taking $\Gamma_3 = 0$. The curve for $I_3$ is for the case of 1.00 V bias voltage; $I_3$ for other biases look similar.

FIG. 5: Source-drain lead configurations possible in a QuIET based on [18]-annulene. The bold lines represent the positioning of the two leads. Each of the four arrangements has a different phase difference associated with it: (a) $\pi$; (b) $3\pi$; (c) $5\pi$; and (d) $7\pi$.

[1] International technology roadmap for semiconductors: 2004 update, http://public.itrs.net.
[2] P. Sautet and C. Joachim, Chem. Phys. Lett. 153, 511 (1988).
[3] F. Sols, M. Macucci, U. Ravaioli, and K. Hess, Appl. Phys. Lett. 54, 350 (1989).
[4] R. Baer and D. Neuhauser, J. Am. Chem. Soc. 124, 4200 (2002).
[5] R. Stadler, M. Forshaw, and C. Joachim, Nanotechnology 14, 138 (2003).
[6] S. Washburn and R. A. Webb, Adv. Phys. 35, 375 (1986).
[7] A. Nitzan and M. A. Ratner, Science 300, 1384 (2003), and references therein.
[8] P. G. Piva et al., Nature 435, 658 (2005).
[9] K. Ohno, Theor. Chim. Acta 2, 219 (1964).
[10] M. Chandross, S. Mazumdar, M. Liess, P. A. Lane, Z. V. Vardeny, M. Hamaguchi, and K. Yoshino, Phys. Rev. B 55, 1486 (1997).
[11] C. A. Stafford, R. Kotlyar, and S. Das Sarma, Phys. Rev. B 58, 7091 (1998).
[12] W. Tian et al., J. Chem. Phys. 109, 2874 (1998).
[13] A. Nitzan, Annu. Rev. Phys. Chem. 52, 681 (2001).
[14] A.-P. Jauho, N. S. Wingreen, and Y. Meir, Phys. Rev. B 50, 5528 (1994).
[15] S. Datta, Electronic Transport in Mesoscopic Systems (Cambridge University Press, Cambridge, UK, 1995).
[16] M. P. Marder, Condensed Matter Physics (John Wiley & Sons, Inc., New York, 2000).
[17] V. Mujica, M. Kemp, and M. A. Ratner, J. Chem. Phys. 101, 6849 (1994).
[18] M. Büttiker, Phys. Rev. Lett. 57, 1761 (1986).
[19] J. M. Luttinger, Phys. Rev. 119, 1153 (1960).
[20] M. Büttiker, IBM J. Res. Dev. 32, 63 (1988).
[21] A. A. Clerk, X. Waintal, and P. W. Brouwer, Phys. Rev. Lett. 86, 4636 (2001).