Conceptual molecular quantum phase transistor based on first-principles quantum transport calculations

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A conceptual molecular phase-coherent transistor is proposed based on first-principles quantum transport calculations. The device is formed by two molecules connected via a one-dimensional wire and it is operated by gating the interconnect between the molecules and exploiting quantum-mechanical interference. The transistor thus works by controlling the electron phase instead of the position of the molecular energy levels, and it paves the way for phase-controllable electronic circuits.

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Molecular electronics is among the most promising proposed solutions for tackling the limitation of Si microelectronic device miniaturization, and therefore it is a potential technology at the end of the Si road map. The idea is that of using molecules as active components of a device, allowing high integration density and enhanced circuit performances.[1,2] At present, most of the experimental studies are focused on the measurement of the conductance of individual molecules. These have demonstrated the applicable foreground of molecular electronics.[3–9]

However, great challenges remain in the assembly of single-molecule devices to form complex circuits. In particular one needs to construct interconnects whose size is comparable to that of the molecules to be measured, since bulk contacts can only be used as electron source and sink. Some success in this direction has been achieved with carbon nanotubes[10,11] and with alternatives suggested by several theoretical works.[12,13] Importantly, when the size of the interconnects between molecules is comparable to the phase relaxation length,[14] standard Kirchhoff's laws break down and the whole circuit becomes a phase-coherent object. This opens the possibility of using quantum-mechanical interference instead of the electrostatics for operating the device. Here we demonstrate such a possibility by accurate *ab initio* transport calculations for two-terminal devices containing multiple molecular components.

A widely used theoretical approach for calculating electronic transport in real systems[15,16] combines the nonequilibrium Green's-function (NEGF) formalism with density-functional theory (DFT).[17–20] Typically a phase-coherent circuit is modeled by performing a self-consistent calculation for the whole device, i.e., by including in the simulation cell both the molecules and the interconnects. In this approach however only the transport properties of the entire device are evaluated and information on the individual phase relations between the different components is lost. For this reason, in order to interpret our results better, we also adopt a second strategy by using a divide and conquer technique combined with the scattering matrix formalism (S matrix). We first divide the device into sections [see Fig. 1(a)], then we calculate the S matrix of each section (with NEGF+DFT),[21] and finally we combine them in writing the S matrix of the entire circuit.[14] From the total S matrix the conductance is evaluated with the Landauer-Büttiker formula[22] $T = \Sigma_{\alpha\beta} |t_{\alpha\beta}|^2 (v_\alpha^{\text{out}} / v_\beta^{\text{in}})$. Here t is the transmission matrix, v^{out} and v^{in} are the velocities of the transmitted and the incident waves, respectively, and the subscript runs over the different channels in the electrodes.[22] In this approach the computational costs are kept at the level of those necessary to calculate a single element of the circuit and the phase relations between the different circuit components are explicitly taken into account. The method assumes that the devices in the circuit can be considered as independent, i.e., that the existence of one device does not affect the Hamiltonian and the charge distribution of the other. This is a good assumption when the actual device components are rather extended molecular objects so that their electron screening is effective [see Figs. 1(b) and 1(c)]. In this work for instance we consider as a single-molecule component a device made by the

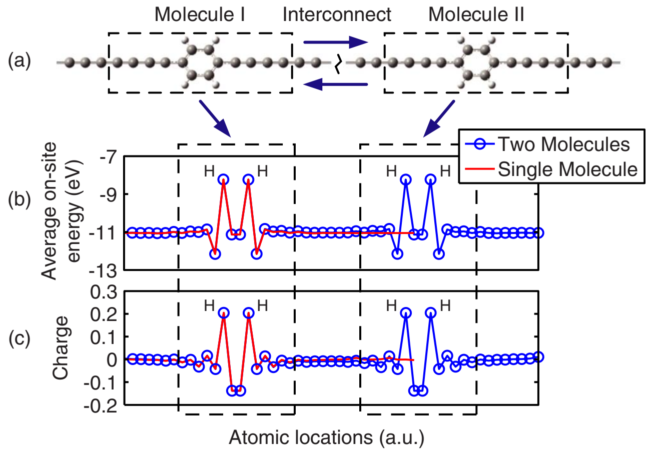

FIG. 1. (Color online) (a) Schematic diagram of a circuit obtained by connecting in series two single-molecule devices. Note that both the transmitted and the reflected waves travel in the interconnect, generating quantum interference. The average on-site energy (b) and the excess charge on atoms (c) of a single-benzene device are compared with those of the corresponding part in a two-benzene device using 16 carbon atoms as the interconnect after the fully self-consistent calculations are completed, which demonstrates the validity of the independent-device assumption. The circles labeled H represent the hydrogen atoms in benzene, while the other circles represent the carbon atoms in benzene and the interconnect.

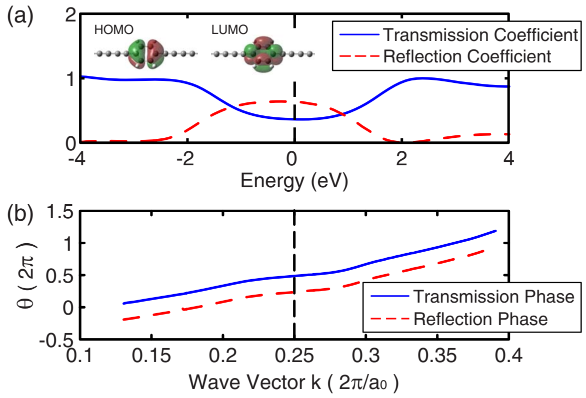

FIG. 2. (Color online) (a) Transmission and reflection coefficient and (b) transmission and reflection phases of the single-molecule device consisting of a benzene molecule sandwiched between C monatomic chains. The inset pictures the HOMO and LUMO states of benzene, which make the most of the contribution to the transmission near the E_F. Note that E_F is shifted to zero and the Fermi wave vector of the carbon monatomic chain is $k_F=\pi/2a_0$, where $a_0=1.29$ Å is the C–C bond length.

benzene and several carbon atoms of the interconnect. In addition, the electrodes connecting different devices are taken to be long enough to be treated electronically as infinite periodic systems.

We start our analysis with a simple single-molecule device formed from a benzene molecule connected to C monatomic chain electrodes. Monatomic C chains have already been reported to be one-dimensional molecular wires with promising use in molecular circuitry.[12,23] Due to the conjugation between the benzene and the C chain, this single-molecule device has a high conductance near the Fermi energy E_F, with a transport channel mainly formed from the highest occupied molecule orbital (HOMO) and the lowest unoccupied molecule orbital (LUMO) of the benzene. The HOMO and LUMO are delocalized π orbitals which also possess a large amplitude over the two C atoms connecting the benzene to the electrodes [see inset of Fig. 2(a)]. In the case of only one transport channel in the electrodes, both the transmission and the reflection matrices reduce to two complex numbers, with their absolute values squared corresponding respectively to the transmission and reflection coefficients [Fig. 2(a)]. Their complex arguments, the transmission phase θ_t and the reflection phase θ_r, account for the phase shifts of an electron when either transmitted or reflected by the molecule [see Fig. 2(b)]. Although the phases are usually ignored in most of two-terminal transport calculations, they are important in a multimolecule coherent circuit, as we will demonstrate in the following discussion. As we can see from Fig. 2(b), both θ_t and θ_r show an approximate linear behavior with the wave vector k of the incident channel. The fitted slope for the two phases, in units of the C-C distance $a_0=1.29$ Å, is found to be around $N_0=4.13$. Note that, similar to the transmission coefficients, the phases are also determined by the molecule and the portion of the electrodes adjacent to the molecule where the potential is not that of bulk. Therefore part of the electrodes is always included in the self-consistent calculation of the transport coefficients.[16]

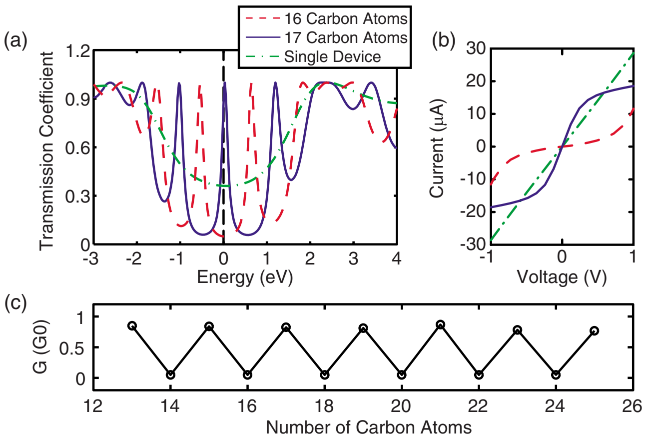

FIG. 3. (Color online) (a) Transmission coefficients of the two-molecule devices using 16- (red) and 17-carbon-atom (blue) interconnects. The transmission coefficient of the single-molecule device (green) is also given for comparison. E_F is taken to be zero. (b) Current-voltage characteristics of these two-molecule devices, compared with that of the single-molecule one. (c) Conductance at a small bias of 0.1 V as a function of the number of carbon atoms in the interconnect.

We now proceed at connecting two identical molecules together via a C monatomic chain [see Fig. 1(a)]. Figure 3(a) shows the calculated transmission coefficients for two interconnects of different lengths in comparison with that of a single-molecule junction. The calculations in this case have been performed with the fully self-consistent algorithm[16] and further interpreted by using the divide and conquer scheme. As expected from quantum interference, for the double-molecule junctions these are found to be an oscillating function of the energy of the incident electron and they are rather sensitive to the actual interconnect length. For instance, there is a half-period shift near E_F when the length of the interconnect increases from 16 to 17 carbon atoms. The oscillations of $T(E_F)$ can then be understood directly from the S matrix of the whole device expressed in terms of the S matrices of the individual molecules (identical in this case). For electrodes with only one scattering channel, the transmission coefficient of the two-molecule device follows the equation $T_2=|T_1/[1-R_1\exp(2i\theta_r+2ika_0N)]|^2$, where T_1 and R_1 are the transmission and reflection coefficients of the single-molecule device [Fig. 2(a)] and N denotes the number of unit cells in the interconnect. The oscillations of this phase-coherent system are determined by the exponent with the period mainly given by the band energy and the length of the interconnect: $\Delta E=\Delta k(\Delta E/\Delta k)\simeq\frac{\pi}{(N+N_0)a_0}\frac{\partial E}{\partial k}$. Here we have assumed a linear relation between θ_r and the wave vector $\theta_r=ka_0N_0+\mathrm{C}$ as suggested in Fig. 2(b). Note that when one adds one cell to the interconnect, i.e., when its length goes from N to $N+1$ carbon atoms, the phase increases by $2k_Fa_0\Delta N=\pi$ at E_F, since the C monatomic chain has a half-filled band with the Fermi wave vector $k_F=\pi/2a_0$. Thus, the transmission coefficient displays a half-period shift near E_F when the length of the interconnect increases from 16 carbon atoms to 17 carbon atoms. As a result of the oscillatory transmission coefficient, steplike current-voltage (I-V) curves are obtained for these two-molecule circuits [see Fig. 3(b)].

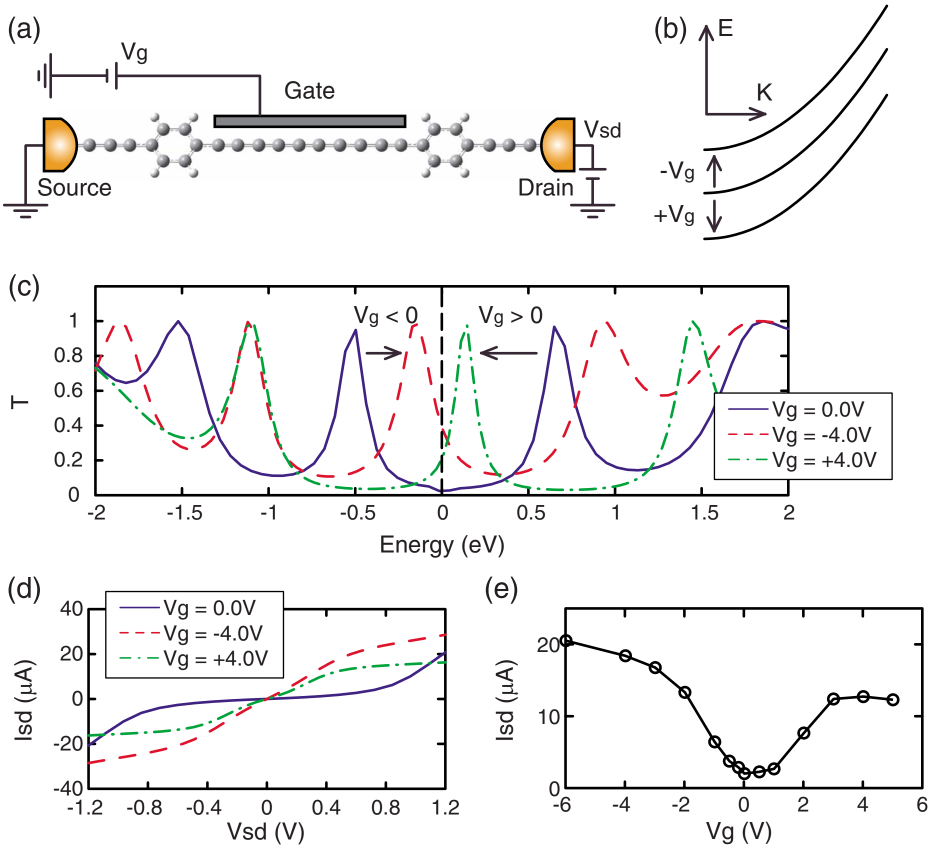

FIG. 4. (Color online) (a) Schematic diagram of a FET-like circuit and (b) the shift of the energy band as a function of the applied gate voltage. (c) Transmission coefficients of the two-molecule circuit with 16 carbon atoms used as the interconnect at the gate voltages of 0.0 (blue), −4.0 (red), and +4.0 V (green). A clear shift of the transmission coefficient can be seen. (d) Source-drain current (I_{sd}) versus the bias voltage (V_{sd}) at different gate voltages. (e) Source-drain current (I_{sd}) versus the gate voltage (V_g) for this two-molecule circuit at V_{sd} =0.5 V.

These are sensitive to the interconnect length. For instance, if we look at the conductance calculated at 0.1 V, we find a clear oscillating behavior as a function of the interconnect length [see Fig. 3(c)], with conductances larger for odd-numbered interconnects than for even-numbered ones. This phenomenon is similar to that of carbon monatomic chains sandwiched between two metal contacts as reported previously.[23]

It is important to note that the oscillation in the transmission coefficient and thus the steplike *I*-*V* curves are universal properties of multimolecule coherent devices. This provides a method for tuning the circuit performance by controlling the electron phase in the interconnect, instead of controlling the position of the energy levels of the molecules. Although in the two-molecule device discussed before the phase was controlled by the length of the interconnect [Fig. 3(c)], the same phase shift can be achieved by other means. This represents a powerful concept for designing high-sensitivity devices and sensors. For instance, the adsorption of a certain molecule may induce the desired phase shift in the interconnect leading to large changes in the measured *I*-*V* curve. The device thus can be used as a chemical sensor. Another possible application is that of using this structure as a tunable spin injector or spin detector when ferromagnetic interconnects are employed. In this case the different electronic structures of the two different spin subbands leads to different interference patterns and, hence, to a potentially tunable spin polarization of the device.

Here we demonstrate another possibility, namely, the use of an electric field to control the interconnect electron phase; i.e., we explore the viability of phase-driven field-effect transistors (FETs). The setup is that of Fig. 4(a) with a 16-C-atom monatomic chain used as interconnect, and a constant voltage simulating the gate electrode is added to these 16 carbon atoms. Since the interconnect in this situation can no longer be treated as an infinite periodic system due to the applied voltage, we have to perform a fully self-consistent calculation including both the two molecules and the interconnect in the simulation cell.[16] The results for the transmission coefficient are given in Fig. 4(c). When a positive gate voltage is applied, the peaks in the transmission coefficient shift to lower energies as the voltage increases, leading to an increase in the conductance at E_F. Similarly, the peaks in $T(E)$ shift to higher energies for negative voltages, also resulting in a higher zero-bias conductance. This result can be easily understood by looking at the shift of the energy band of the C monatomic chain as a function of the gate voltage [see Fig. 4(b)]. A positive gate voltage shifts the energy band downward in energy. Thus, the energy corresponding to any interference-enhancing wave vector *k* will shift downward. In contrast, a negative gate voltage pushes the energy band upward in energy, causing any coherent-enhancing energy to shift upward. Such an energy shift generates the peak shift in the transmission coefficient and thus modifies the zero-bias conductance. Note also that the modulation of $T(E)$ with the gate voltage saturates at large voltages. This is a consequence of the local charge neutrality violation as the result of the shift of the energy band. Such violation counterbalances the effects of the local gate voltage leading to a saturation of the band-shift as the voltage increases and thus to a saturation in the $T(E)$ modulation [Fig. 4(e)].

We finally want to spend a few words in discussing the experimental feasibility of our concept device. First we wish to note that a modulation of the low-bias conductivity with gate voltage as a result of quantum interference has already been demonstrated experimentally in carbon nanotubes.[24] In that case the level spacing is small as compared with the broadening due to the coupling to the leads. As a consequence the conductance modulation is only fractional around its mean value of $\sim 3.1G_0$ and an off state is never achieved. Our proposal to realize this concept at the molecular level bypasses this complexity and Fig. 4 clearly demonstrates the realization of an operational transistor.

Certainly the making of complex molecular devices with monatomic interconnects is experimentally rather challenging. We believe that a more promising materials system is that of semiconductor nanowires with reconstructed surfaces functionalized by organic molecules. Surface states can be used as phase-coherent transport channels (interconnects) as recently demonstrated,[25] and molecules can be placed in forming the multidevice architecture. Crucially the gating of such wires has already been demonstrated,[26] suggesting that all the components needed by our concept device can be, in principle, implemented in nanowires.

In conclusion, we have theoretically studied the performance of phase-coherent circuits consisting of multiple benzene molecular devices. Oscillations in the transmission coefficient originating from the electron interference in the interconnect have been found. Since those are a universal feature of multimolecule coherent devices and significantly depend on the properties of the interconnect, one may envision of tuning the circuit performance by controlling the electron phase in the interconnect instead of controlling the energy levels of the molecules. Here we have explored one of these concept devices, showing that gating the interconnect can effectively control the *I-V* curve of a two-molecule circuit, providing a structure for FET-like devices. The performances of these tiny circuits are very sensitive to the interconnect length, requiring an atomic-scale control of their geometry.

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