Phase Coherent Electronics: A Molecular Switch Based on Quantum Interference

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Some tasks performed by solid-state electronic devices can also be carried out by single organic molecules. This was Aviram and Ratner's[1] avant-garde claim in 1974 when they described the first single molecule electronic device—the molecular rectifier. Recently, synthetic and analytic methods have progressed sufficiently to make possible the construction and characterization of single-molecule devices.[2-7]

Why are single-molecule devices important? Certainly, the most emphasized point is the reduction in size, envisioning an orders-of-magnitude increase in the density of electronic components. We draw the readers' attention to a different, quite exciting direction: the fact that electron transport in single molecules is quantum phase-coherent. This adds a new dimension to electronics: *coherent electronic circuitry*.

Several studies that consider quantum effects in molecular wires have been published recently, studies which examine tunneling transport[8-12] and interference effects[13,14] as well as progress toward construction of a molecular transistor.[15] In this communication we consider the basic quantum effect of interference in molecular wires and discuss a potential application as a molecular switch.

Our model system is a long alkene molecular wire, two points of which are cross-linked by a shorter alkene wire. This is a simple model with which to exhibit the effect we discuss. We depict in Figure 1 the considered systems. The molecular wire is considerably longer than shown in the figure, while the cross-linker is of constant length, which we chose for demonstration purposes to contain 11 carbon atoms.

To discuss the system quantitatively, yet in simple terms, we model the relevant electronic structure of the chain by a Huckel π-electron Hamiltonian. We take the usual parameters: the energy of each atomic carbon p orbital is $a = -6.6$ eV and only nearest neighbor carbon p orbitals are coupled, with coupling strength $\beta = -2.7$ eV.[16] This model predicts alkene to be metallic. In reality, a long molecular wire is not a metal because of a spontaneous Peierls distortion.[17] In the present model we take this into account by alternating the β parameter between two values[18] of $\beta_1 = -2.7$ eV and $\beta_2 = -2.7$ eV, creating a small energetic gap of ∼0.6 eV between the highest occupied and lowest unoccupied electronic levels of the wire.

To calculate the electric current as a function of the terminal voltages, we use the Landauer coherent transport[19] equation: $I(V) = eh^{-1}\int_{-\infty}^{\infty} T(E)\{f_{\mu+v}(E) - f_{\mu}(E)\}dE$ (eq 1) where μ is the electronic chemical potential in the metallic ele. The multi-channel microcanonical transmittance $T(E)$ is calculated by the Seideman—Miller[20] formula, giving for any pair of terminals a and
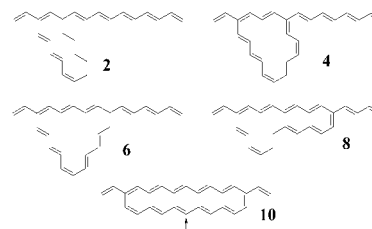

Figure 1. Cross-linked molecular wire configurations, indexed by the number of carbon bonds between the cross-linked points. The cross linker is a suitable combination of an 11-carbon cis—trans alkene.

b the transmittance: $T_{ab}(E) = 4tr\{G^{\ddagger}(E)W_a G(E)W_b\}$ (eq 2) where W_x is a negative imaginary potential located in asymptotic channel $x = a, b$ and $G(E) = (E - H + iW)^{-1}$ is the total Green's function for this system. Note that W is the total imaginary potential in all asymptotes. This theory is very flexible and easy to implement in many types of electronic structure calculations. It is based on two powerful methods of quantum reactive scattering theory, flux—flux correlation function[21] and channel decoupling methods.[22,23]

The imaginary potentials act to impose the correct outgoing boundary conditions on the terminal edges. In the present calculation, the length of the alkene wire is taken to be 50 carbon—hydrogen (CH) units. The imaginary potential is stretched linearly across 15 sites at both ends of the wire. For example, the leftmost carbon of the wire is assigned an imaginary potential $W_a = -iW_{max}$; with $W_{max} = 3$eV the next 15 consecutive sites feel a parabolically decreasing potential with the 15th site having zero imaginary potential. A similar construction applies for the opposite (rightmost) end of the wire. The imposed potential difference between the two ends of the wire is assumed to spread linearly across the entire wire. Other choices of the voltage distribution have only a small effect.

In Figure 2, the $I-V$ curves of the crossed-linked alkene molecular wires are shown, revealing dramatic differences in conduction properties, depending upon the configuration considered. Configurations, **2**, **6**, and **10** exhibit high resistance with respect to the bare wire (configuration **0**), while **4** and **8** display considerably higher conductance. Conductivity is determined primarily by the dynamics of electrons at the Fermi level where their wavelength is 4 multiples of a CC bond length (4 CCLs). This explains why configurations with cross-linked distance equal to 4 CCLs show similar behavior.

In Figure 3, the transmission probability functions of the six configurations are shown, displaying considerable variations. Especially impressive is the substantial flattening of the transmittance for configuration **10**. The surprising fact is that the decay of transmission, caused presumably by destructive interference, is observed over a wide energy range.

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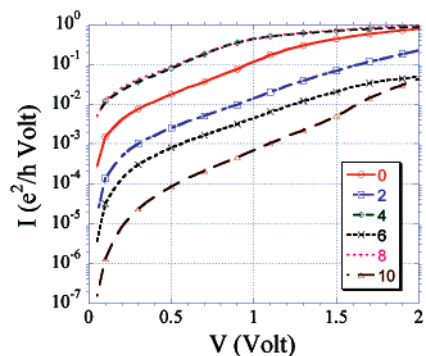† The Hebrew University of Jerusalem.
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Figure 2. The $I-V$ characteristic of an alkene wire cross-linked at two points by an alkene loop of length 11 carbon atoms. Characteristics are shown, as a function of the loop configuration (see Figure 1).
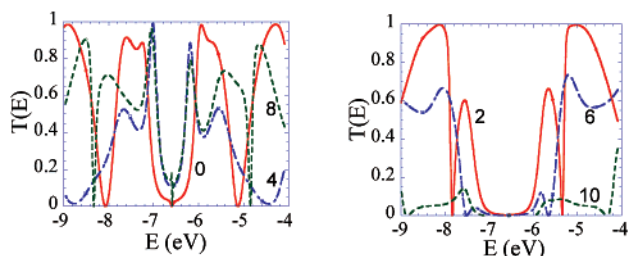

Figure 3. The transmission probability of an electron through the wire as a function of energy E for configurations: 0, 4, 8 (left panel) and 2, 6, 10 (right panel). Notice the huge effects on transmission. All plots refer to the same potential difference of 1 V.
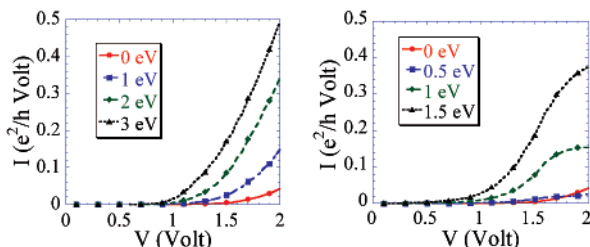

Figure 4. The $I-V$ functions of the wire in configuration **10**, where the potential energy of the site designated by an arrow in Figure 1 is increased by $\sigma\alpha$ (left plot) or the coupling strength connecting the cross link to the wire is decreased by $\delta\beta$ (right plot).

The quantum effect of destructive interference may be used within the molecular device to switch its conductance on and off. If the transmission in the cross-linker is hampered, the destructive interference disappears and conductance resumes. This can be seen in Figure 4, where the mere raising of the potential energy of one of the CH sites in the cross-linker or the change in the coupling strength of one bond strongly affects the conductance of the molecular wire.

How general are these results? While destructive interference is a general phenomenon in quantum mechanics, it must not be forgotten that in the present system the gap is small so that the conductance is mostly ballistic even at low voltages. Previous work showed electron transport via tunneling exhibiting only constructive interference.[14] We partially confirm this result; by artificially exaggerating the Peierls distortion we formed a large gap in the alkene wire and found destructive interference missing for low voltages, except for configuration **2** of Figure 1. Tunneling prevents the development of *phase differences* unless the two paths include ballistic parts. The Huckel treatment is first in a series of approximations. Future improvements are self-consistent Fock operator within a detailed basis and inclusion of electron correlation effects. These
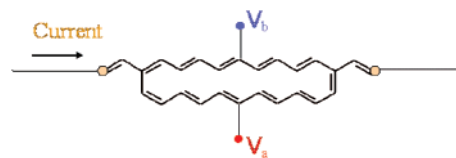

Figure 5. XOR switch based on quantum interference. The current through the wire is blocked only when $V_a = V_b$.

improvements will not prevent interference, unless ballistic conduction is destroyed by developing a larger gap, a problem which can be reduced or eliminated by periodically duplicating the system and using a proper electrode.

With these characteristics of the system, one can construct an XOR-type of gate where the input is voltage signals V_a and V_b as depicted in Figure 5 and the current is the output. It is clear immediately from Figures 4 and 5 that by changing the voltage of one site (e.g., by 1 V) the molecule acts as a switch, and is turned from "off" (low conductance) to "on" (high conductance). XOR behavior is explored in upcoming work. Molecules of high ionization (or affinity) potential can serve as gate voltages V_a and V_b.

In conclusion, we have shown that exploiting interchangeably ballistic phase coherence and tunneling within a single molecule is a promising direction for the construction of novel devices. We have discussed in this paper primarily the quantum effects of ballistic conduction, but other effects can be treated and will be studied in the future. This direction will gain in importance as new synthetic methods are bringing single-molecule devices closer to reality.

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