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A Hückel study of the effect of a molecular resonance cavity on the quantum conductance of an alkene wire

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Abstract

We use Hückel theory to examine interference effects on conductance of a wire when a 'lollypop' side-chain is bonded to it, acting as a *resonance cavity*. A clear signature of interference is found at these ballistic conducting systems, stronger in small systems. Gating effects are enhanced by the presence of the loop, where the electronic wavefunctions can experience large changes in phase. Using an 'interference index', $I = \mathrm{mod}(S, 2) + \mathrm{mod}(L, 4)$, where S, L are stick and loop lengths, respectively, we conclude that interference is constructive (destructive) and conductance high (low) when $I = 0, 4 (I = 2)$.
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1. Introduction

As electronic components are getting smaller, the prospect of individual devices based on single molecules is approaching realization. Following experimental developments [1–3], theory can play a role in understanding and suggesting approaches for new mechanisms of conductance [4–7].

One possibility that theory suggests is the use of interference. Interference is very intriguing since it gives a handle with which control can be achieved. Qualitatively, there are two reasons why a molecular device can be made to have low conductance. One is that due to high barriers or large band gaps, there is tunneling. In that case it would be difficult to reach high conductance from such a device unless a high voltage-bias or gate is used. But an alternate reason for low conductance would be due to interference, a situation in which orbitals at the Fermi energy have a node in one or the other leads. Such a case allows sensitive control of conductance, by simply changing the phase in the orbitals thereby causing the node at the leads to move. Such a phase change would be feasible with a gating voltage, for example.

Sautet and Joachim [8] were the first to study interference of electrons passing through a benzene embedded in a polyacetylene chain. They concluded that interferences significantly alter the electronic transmission through the benzene in the meta and ortho cases. In a series of papers [9–12] we recently suggested the use of interference for controlling the conductance of simple molecular devices such as polyacetylene loops of various lengths, or a series of differently positioned polycyclic aromatic rings.

In this work, we extend the study of interference effects to a set of systems which have obvious engineering analogues, 'lollypop' type systems in which a molecule connected to a wire acts as a *resonance cavity*. Such cavities are known in optics as filtering and amplifying transmission, for example, the Mach–Zhender device. This effect was recently used to create Aharonov Bohm oscillations in carbon nanotubes [13] and are known also in mesoscopic systems [14]. It is thus interesting to explore the molecular analog of such a concept.

We study the systems by a very simple Hückel Hamiltonian. The method is necessarily qualitative, but

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it does predict trends which can be verified by more elaborate methodologies. For example, in a recent study of polycyclic aromatic molecules we verified that the Hückel results predicted the qualitative interference patterns [12]. Various Hückel or tight-binding analogues has been used by several researchers [15,16] for studying molecular conduction and electron transfer.

2. Methodology

The basic system is depicted in Fig. 1, where a long alkene molecular wire is bonded to a side ring (loop) by a short alkene chain (stick). The system is simulated using a simple Hückel model in which only π-electrons are considered and assumed non-interacting. For calculating conductance, the Landauer formula [17] is used

$$I(V) = \frac{2e}{h} \int T(E)[f(E - \mu_L) - f(E - \mu_R)]dE, \qquad (2.1)$$

where we introduced the voltage-dependent left and right lead potentials

$$\mu_L = \mu + \frac{V}{2} \mu_R = \mu - \frac{V}{2}. \qquad (2.2)$$

Here μ is the half-filling chemical potential for the alkene (-6.6 eV). In experiment, a gold metal is typically used as a lead with a higher chemical potential; still, the qualitative effects should still be conserved. f is the Fermi-Dirac function for room temperature. $T(E)$ is the transmission probability which for non-interacting electrons under zero bias is given by a simple Flux–Flux type formula [18], recently discussed by Baer and Neuhauser [19] in the context of molecular conductance.

$$T(E) = 4\text{Tr}\left(V_{IL} \frac{1}{E - H + iV_I} V_{IR} \frac{1}{E - H - iV_I} \right),$$

where H is the Hückel–Hamiltonian, in which each site (the location of a carbon containing a P_z orbital) carries a diagonal potential of -6.6 eV; nearby sites have a coupling of -2.7 eV. The coupling is uniform, so that we do not consider the effects of Peierls distortion. Such effects would change the conductance at low voltages (below about 0.2 V) but would not change the main conclusions for slightly larger bias.

V_{IL} and V_{IR} (the sum of which is V_I) are absorbing potentials are added to the ends of the left and right leads to simulate the outgoing-wave boundary condi-
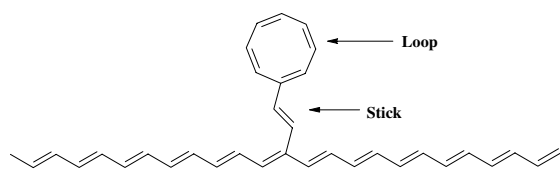

Fig. 1. The molecular 'Lollypop' resonator: a benzene molecule connected to a molecular wire.

tions. The length of the wires in the simulation has to be long enough so that the results converge as a function of absorbing potential. In our studies the absorbing potential had a length of up to 10 carbon bonds, and its maximum strength was varied around 2–3 eV.

3. Results

The effect of the lollypop on conductance may best be characterized by the loop circumference and the stick length. Both are measured in terms of the number of atoms.

3.1. Effect of the loop size

Initially, we study the effects on conductance of varying loop size. Fig. 2 shows the current vs. voltage characteristics for different loop sizes and stick lengths of 2, 3, 11 carbon atoms. The first thing to note is that there is an approximate periodicity of 4 in the number of atoms in the loop. This periodicity is due to the fact that the system is at half-filling, so that the phase of the wave function alternates its sign every two sites and repeats after four sites.

Next, note that there is considerable difference between two groups of results: one group would be loops of lengths 6 or 10, and the other loops of lengths 8 or 12. For each stick length, one group would show a linear current–voltage relation at low voltages, associated with a high conductance or more specifically a $T(E)$ which is close to 1 at the Fermi energy; the other group has a low conductance near zero voltages, associated with a gap in the conductance. The gap is created due to the interference of the wave inside the loop; heuristically, a wave entering the loop and a wave leaving the loop would have a different phase. More precisely, we verified that what happens is that the resonances in the transmission probability shift with E.

In a sense, these results are surprising, since classically the conductance should be influenced primarily by what happens along the wire which conducts the electrons. The key here however is that the system is completely coherent, so that the nodal structure is influenced by whatever happens to the molecule, even in an extended region like the 'lollypop', i.e., the side ring.

3.2. Stick size

Next wet studied the effect of the stick size on the $I-V$ relation for a constant number of atoms in the loop. Fig. 3a shows that the results are periodic, and depend on whether an even or odd of atoms is in the stick; the effects are most pronounced for a few number of atoms where the distinction between even and odd is strong. Fig. 3b shows that for more atoms in the stick the results
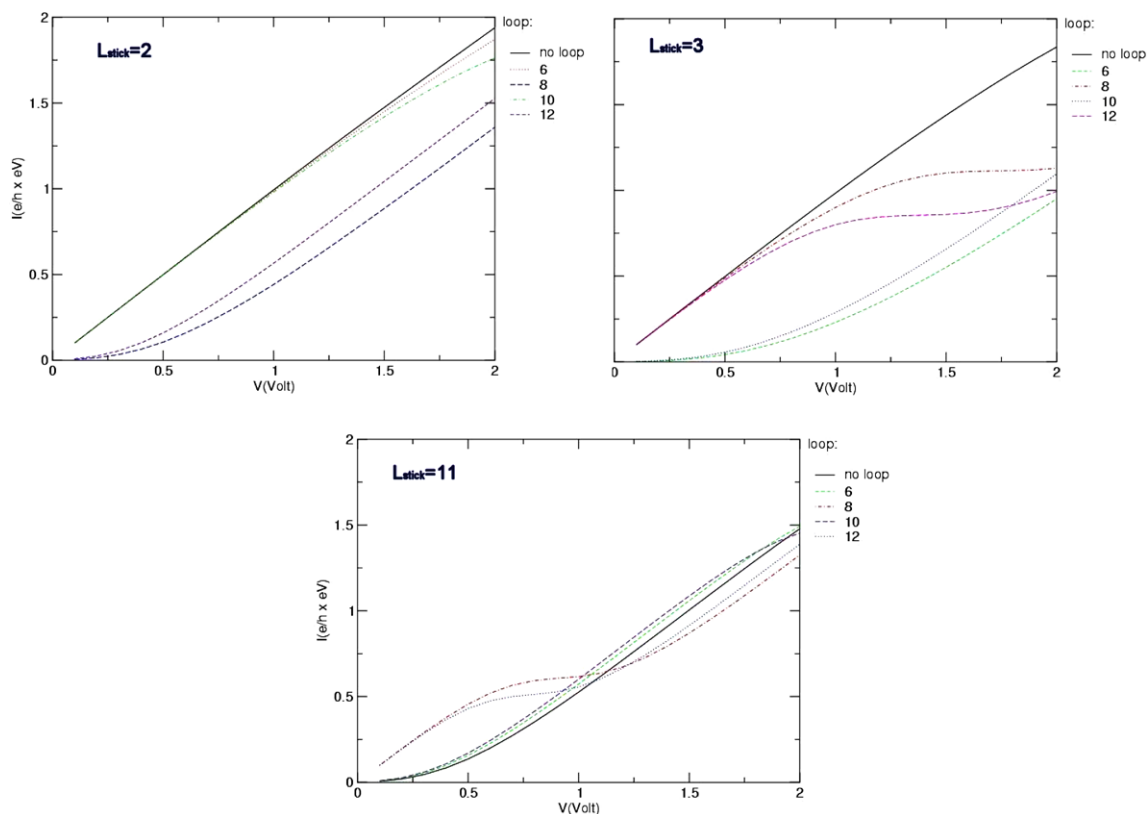
Fig. 2. *I–V* relation as a function of loop size for loops of 0, 6, 8, 10 and 12 atoms and varying 'stick' lengths (in number of C-atoms).

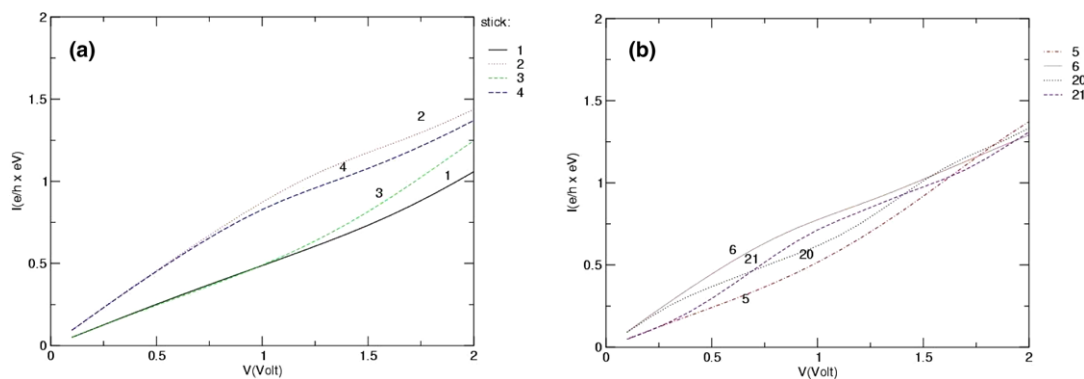

Fig. 3. *I–V* relation as a function of loop size for a 9 atoms loop system and stick sizes of: (a) 1, 2, 3 and 4 atoms; (b) 5, 6, 20 and 21 atoms.

are less pronounced. Again, the physical reason for the behavior is whether the $T(E)$ curve has a minimum or not at the Fermi energy. $T(E)$ has at a stick size of 1 at $E = -6.1$ eV causing a vanishing of $T(E)$ near the Fermi energy (not shown here). This effective band-gap is a simple consequence of interference.

Specifically, for an odd number of atoms, we can semi-classically say that an electronic wave function has an interference between a wave passing through the wire and a wave which passes the side stick back and forth; each double passage of the wire results in a phase reversal (i.e., for a stick of length 1, 3, 5, etc., the accu-

mulated phase change after passing back and forth would be $\pi/2 \times (1, 3, 5, \cdot) \times 2 = \pi, 3\pi, 5\pi \cdots$

3.3. Purely sticks or loops

Since the effects on the *I–V* curve are greatest as one decreases the number of atoms in the stick and loop we also studied the limiting cases of having a purely stick system (i.e., not having a loop) and a purely loop system (without a stick) for different stick sizes.

For the purely stick system, we varied the stick size from having 1 atom to having 12 atoms. Fig. 4a shows
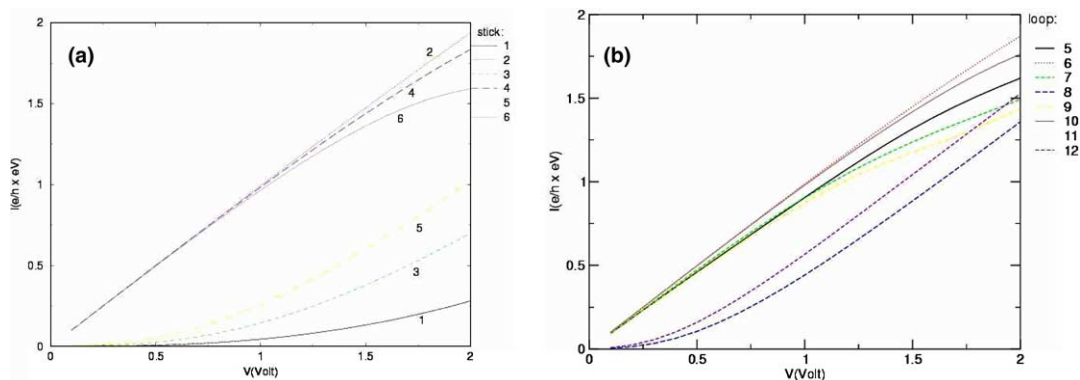
Fig. 4. (a) I–V relation as a function of: (a) stick size for a non-loop system and stick varying from having 1 to 6 atoms; (b) loop sizes for a non-stick system and loop varying from having 5 to 12 atoms.

the dramatic effect of the stick size and the odd-even dependence, coming, as explained before, from the fact that there is constructive interference for even stick lengths and destructive for odd stick lengths.

For a purely loop system the loop was varied from having 5 to 12 atoms. Fig. 4b shows that there is also a strong periodicity here. The periodicity of 4 with loop size is the same as found for a non-zero stick size, but is more pronounced here due to the fact that there is no stick.

In concluding, it is clear that the periodicity found can be schematically described by an index $I = \mod(S, 2) + \mod(L, 4)$, where S and L are the stick and length sizes; the different contribution to the periodicity arises since the wave passes through a stick twice and a loop once. If I is zero (or 4) then the interference pattern is purely constructive and the conductivity is high; if I is 2 then the interference is destructive. We also note that the interference behavior in purely-stick systems is reminiscent of some peaks found in dendrimeric systems
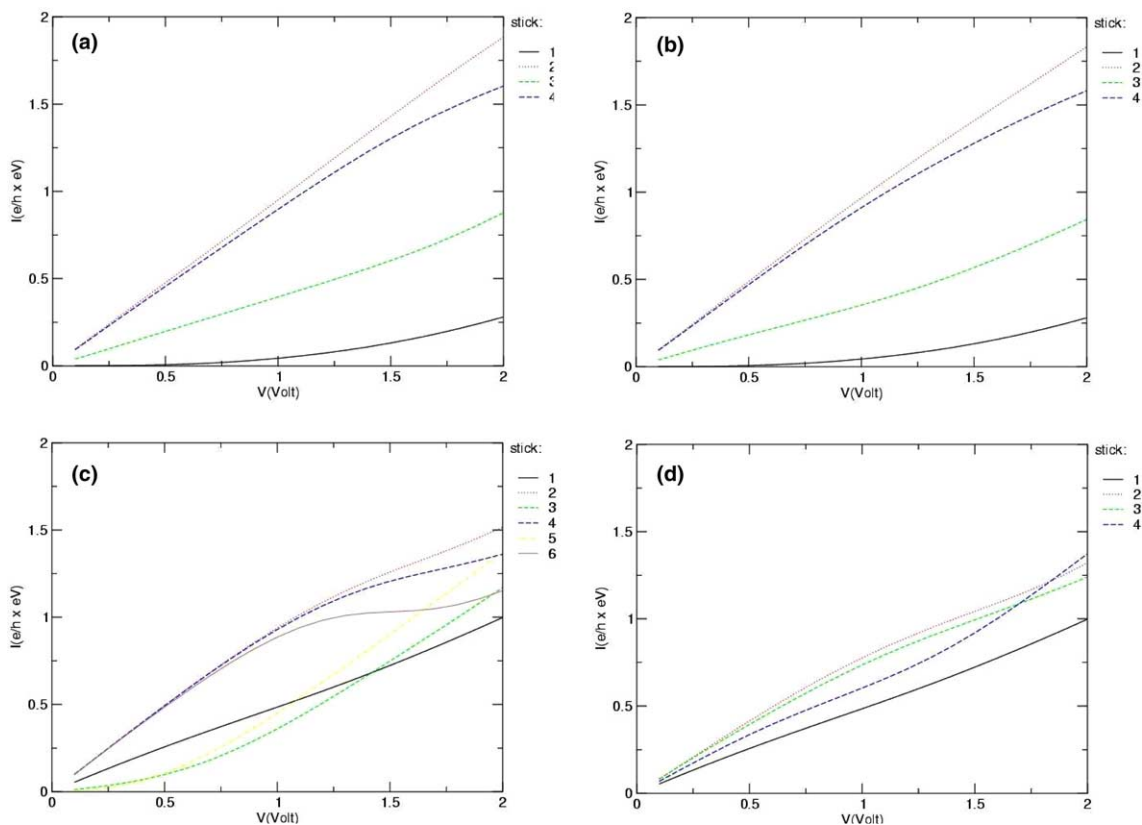

Fig. 5. I–V relation as a function of the stick size for a non-loop system with: (a) a voltage rise along the stick from 0 to 1 V; (b) a voltage drop along the stick from 0 to 1 V; (c) a voltage rise along the stick from 0 to 1 V and a voltage along the loop of 1 V; (d) a voltage drop along the stick from 0 to −1 V and a voltage along the loop of −1 V.

where there are often small branches – those branches effect the conductance in the same way that a stick here would [16].

3.4. Gating voltages

The most interesting aspect of the interference in these devices is whether it can result in an easy change of the current due to a gating voltage. For this we did several studies. First, we varied the voltage along the stick from 0 to 1 V linearly and from 0 to −1 V (where it is zero at the junction with the lead and 1 or −1 at the ends). In practice, of course, the voltage distribution along the stick need not be simply linear; however, the key is simply whether there could be a significant change of the phase that the electron experiences on the stick.

Fig. 5 shows that there is a significant effect of the gating voltages on the conductance. Even a 1 V voltage gating, which is quite reasonable, is sufficient for changing the voltage by orders of magnitudes.

Can the presence of the loop magnify the effects of the gating? To answer this question, we studied two systems. The systems had an identical stick; however, in one case there was a loop at the ends, and in the other there was no loop. The loop voltage was assumed to be the same as the gating voltage (i.e., 1 V when the voltage at the end of the stick was 1 V, etc.). As Fig. 5 shows the loop then magnifies the effects of the gating voltages. This is physically clear: since the electron passes through the loop, the effects of the gating voltages are amplified in the loop.

4. Conclusions

In conclusion, we found that there is a clear signature of interference in Hückel studies of 'lollypop'-like molecules. The existence of interference is due to the ballistic conductance of these systems and the fact that the voltage bias is not too large (less than about 1 eV); at higher voltages the summations in the transmission probability over energies mask the interference. The interference is strongest for small systems, as expected; further, we have shown that gating effects are enhanced by the presence of the loop, where the electronic wavefunctions can experience a large accumulated change in phase. The interference pattern can be summarized, for a lead with a stick-wire side group, as dependent on an interference index, $I = \mathrm{mod}(S, 2) + \mathrm{mod}(L, 4)$, defined in terms of the stick and loop lengths. If I is zero (or 4) then the interference pattern is purely constructive and the conductivity is high; if I is 2 then the interference is destructive.

An important issue is the role of electron correlation, which can be partially checked using density functional theory. A recent paper [12] discussing interference phenomena has shown, however, that the effect of inter-

ference remains strong even if electron correlation is included, at least at the level of density functional theory. Other shortcomings of the Huckel model, beyond correlations, include of-course the simplified nearest-neighbor treatment, which may be important in some systems [20]. In the present case, inclusion of a more realistic one-body Hamiltonian would only shift the resonances and not change the basic interference pattern, as the density-functional study, with its realistic one-body part shows [12]. The role of dynamic electron correlation is also unclear and future studies of this systems would use a more sophisticated electronic structure algorithm (such as using TDDFT [21,22]), which we expect to change the results mainly quantitatively. The most interesting aspect of using a more sophisticated algorithm is that the influence of gating would be assessed as it depends on the precise charge distribution induced by the gating.

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