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The explicit form of the zeroth Green's function in the Hückel model, approximated by the negative of the inverse of the Hückel matrix, has direct quantum interference consequences for molecular conductance. We derive a set of rules for transmission between two electrodes attached to a polyene, when the molecule is extended by an even number of carbons at either end (transmission unchanged) or by an odd number of carbons at both ends (transmission turned on or annihilated). These prescriptions for the occurrence of quantum interference lead to an unexpected consequence for switches which realize such extension through electrocyclic reactions: for some specific attachment modes the chemically closed ring will be the ON position of the switch. Normally the signs of the entries of the Green's function matrix are assumed to have no physical significance; however, we show that the signs may have observable consequences. In particular, in the case of multiple probe attachments – if coherence in probe connections can be arranged – in some cases new destructive interference results, while in others one may have constructive interference. One such case may already exist in the literature. © *2014 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4903043]

INTRODUCTION

Understanding and predicting the flow of electrons through molecules is a persistent challenge for molecular electronics. Organic π-electron systems, whose electrons are known to be mobile in other circumstances, are a clear focus for experimental and theoretical exploration, with potential applications as the functional building blocks in nanoelectronic devices.[1]

Transmission of electrons through a π system is affected not only by mode of electrode attachment[2] and electron-transport distance[3] but also by molecular conformation[4] and the underlying σ-electron framework.[5] The quantum interference (QI) effects in a π system are, however, the most striking, for they are a purely a consequence of quantum mechanical aspect of electron transport. QI features are seen theoretically in many molecular systems, such as cross-conjugated molecules[6,7] and *meta*-linked aromatic systems.[8,9] And they control site-dependent electron transport in polycyclic aromatic hydrocarbons[10,11] even in a large annulene.[12]

Quantum interference has been demonstrated experimentally, for instance through atomic force microscopy (AFM), comparing the current through self-assembled monolayers of a cross-conjugated anthraquinone derivative and an anthracene derivative.[13] Mechanically controllable break junctions (MCBJ) are another way to observe site-specific conductance, as demonstrated by Taniguchi *et al.* for four different naphthalenedithiol derivatives.[14] The conductance

difference in benzene derivatives between *meta* and *para* linkages have also been studied experimentally by the Kiguchi group[15] using a scanning tunneling microscope (STM), the Venkataraman group[16] using a conductive AFM, and the van der Zant group[17] using an MCBJ.

Theoretically, QI manifests itself as an anti-resonance around the Fermi energy in transmission spectra. It can also occur in other energy ranges.[18] The effects have fascinated theoreticians, and theoretical chemists in particular, who are familiar with the governing role of another pure quantum phenomenon, orbital phases, for chemical structure and reactivity. As the community has struggled for understanding, a number of interpretations have emerged, which we describe briefly.

Fundamental phase relationships are clearly important in QI; this is evident in the fundamental work of Lee,[19] and of Ratner, Solomon, and co-workers.[20] The latter group made a thorough study of QI in cross-conjugated systems, explaining it in terms of local atom to atom transmission.[6,21] Yoshizawa, Tada, and their co-workers have provided a method for predicting the presence/absence of the QI effects in polycyclic π systems based on simple Hückel molecular orbital (HMO) theory.[10,22] Markussen, Stadler, and Thygesen have proposed a simple and useful graphical scheme that provides a direct link between QI and the topology of various alternant π systems, including *meta*-linked benzene derivatives, anthraquinone derivatives, and cross-conjugated molecules.[23] They have also looked at how QI in a polyene is modified by chain extension or substitution.[24] Nozaki and his co-workers have developed a simple graphical scheme, a parabolic diagram approach, which allows one to visualize the conditions for the appearance of QI in a molecular junction with

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a side group (T-shaped molecular junction) based on a few electronic parameters.[25] Kalyanaraman and Evans have investigated the effect of side chains on interference in electron transfer through linear chains, focusing on dendritic wires.[26] Baer and his co-workers have examined the interference effects of a side chain with a loop on conductance of a linear chain.[27] Ernzerhof *et al.* have investigated conductance through a linear chain with a side group and demonstrated the relationship between the eigenvalues of the Hamiltonian of the side chain and zero transmission probabilities.[28] And Fowler and co-workers have constructed an explicit connection between QI and the graph-theoretical properties of a molecule and its subgraphs.[29]

The idea of constructive (and destructive) interference in molecular conduction through two parallel backbones has been explored previously, both theoretically and experimentally, by Magoga and Joachim,[30] and more recently by Vazquez *et al.*,[31] and by Lambert, who provides an excellent tutorial on quantum interference.[32]

In this paper, we begin by investigating systematically the effects of QI in linear polyene chains, based on the Green's function method,[33] in conjunction with HMO. The exact form of the Green's function for open and cyclic boundary conditions have been analytically derived.[34] These Green's functions can be derived from previous expressions in the literature,[23] but here are given in explicit matrix form. From the general form of the Green's function for a polyene we deduce a set of rules for the effect of adding atoms to the chain on the conductance between attached electrodes. We apply the rules deduced to molecular switches[35] using electrocyclic reaction, confirming a previous result, and suggesting new, realistic chemical examples which would show normal, and untypical, switching behavior. In the second part of this paper we consider the consequences of the sign of the matrix elements of the Green's function, which cannot be observed in conventional two-probe devices, but, as we will show, may have observable effects in coherent multi-probe devices. Several systems for realizing amplification and interference are suggested.

GENERAL FORM OF THE ZEROTH ORDER GREEN'S FUNCTION FOR LINEAR POLYENES

When electrodes, typically a gold contact, are connected at sites r and s of a molecule, the simplest model for conductance (one that in some way sweeps under the rug the problem of the microscopic nature of the contacts[36]) expresses the conductance as proportional to the square of the absolute value of the entries of the Green's function matrix at the Fermi energy, $G_{rs}(E_F)$.[33]

In this paper we specifically consider molecules weakly coupled to the contacts, such that the conduction properties are well approximated by the zeroth order Green's function, in which the self-energies describing the connection to the macroscopic contacts are omitted. The relation between the zeroth order Green's function and the transmission probability is clarified in Sec. S2 in the supplementary material.[37] For the sake of concreteness, in this section we summarize the exact results pertaining to the exact form of the Green's function

previously proved.[34] The zeroth order Green's function may be expanded in a set of delocalized molecular orbitals and then takes on the following form:[38]

$$G_{rs}^{(0)}(E_F) = \sum_k \frac{C_{rk} C_{sk}^*}{E_F - \epsilon_k + i\eta}, \qquad (1)$$

where C_{rk} is the coefficient of the rth atomic orbital (AO) in the kth molecular orbital (MO) in an orthogonal basis, ϵ_k is the kth MO energy, and η is an infinitesimal positive number. Let us assume in the following qualitative argument that η is negligible unless E_F coincides with ε_k; this is the condition of derivation of the exact form we will use.[34,35] In our actual numerical calculations of the transmission, the assumption that η is negligible is not made and we use the non-equilibrium Green's function (NEGF) instead of the zeroth order Green's function.

Green's functions as such not only arise in the analysis of molecular conductance but also are widespread in theoretical chemistry and physics. So they are used for the analysis of spin-spin repulsion in conjugated systems,[39] chemical reactivity,[40] and communicability of a complex network.[41]

Let us further restrict our system to a linear polyene chain having an even number of carbon atoms and assume transmission is primarily through the π orbitals and electrons of the polyene. We then apply for that π system the Hückel model, a ubiquitous and tremendously useful model of quantum chemistry (and in its incarnation as tight binding, of solid state physics[42]).

A word is in place here about our restriction to even-number carbon chains. If a one-dimensional (1D) chain has an odd number of sites, soliton formation can take place and new states, which dramatically modify the density of states and conductivities of a molecular junction, can be created in the band gap. In the case that the energy of the new state coincides with the Fermi energy, the zeroth order Green's function without η provably diverges for an odd-C-number polyenyl system. Conduction in the presence of a soliton can be understood in terms of a first-order perturbation expansion of the Green's function.[43] In a future paper we will explore charged and neutral odd-carbon-number linear and cyclic polyenyls. Here we confine our discussion to even-numbered neutral polyenes.

The Hückel Hamiltonian matrix emerges from the application of the variational method to a trial function (a molecular orbital, MO ψ_k, k is the label of the MO) that is a linear combination of atomic orbitals χ_r,

$$\psi_k = \sum_r C_{rk} \chi_r. \qquad (2)$$

The matrix is characterized by diagonal matrix elements α (Coulomb integrals) and off-diagonal elements β (resonance integrals, t in the language of tight binding), where two atoms are neighbors. All other interactions (e.g., non-nearest neighbor ones) are set equal to zero in the Hückel model, as are all overlaps. The Coulomb integral α is in this model the energy of each carbon p_π orbital (electron) before interaction (approximately -11.4 eV[44]) and is also the midpoint in energy between the energy of the highest occupied molecular orbital (HOMO) and that of the lowest unoccupied molecu-

lar orbital (LUMO) of isolated π-conjugated molecules. It is reasonable to assume that the Fermi energy lies between the HOMO and LUMO, unless there is significant charge transfer between electrode and molecule.[10,22,35,45] It is for this reason that in our work both the Fermi energy and α are set to be the energy zero.

The resonance integral β measures the interaction energy between two adjacent p_π orbitals and is negative. We use energy units of β, in which case the nonvanishing elements of the Hückel matrix, the nearest neighbor interactions, can be replaced by unity, 1. All other (non-nearest neighbor) interactions are set equals to 0. The Hückel Hamiltonian matrix for a linear polyene then takes on the form of a bordered matrix,

$$\mathbf{H} = \begin{bmatrix} 0 & 1 & & & & \\ 1 & 0 & 1 & & & \\ & 1 & 0 & \ddots & & \\ & & \ddots & \ddots & 1 & \\ & & & 1 & 0 & 1 \\ & & & & 1 & 0 \end{bmatrix}. \quad (3)$$

It is also, by construction, the adjacency matrix of the molecular graph,[46] and this is the basis of an important link between graph theory and quantum chemistry. The general solutions for the eigenvalues (energy levels) and eigenfunctions (molecular orbitals, the AO coefficients) of this Hamiltonian are available.[47] Specifically, the energy levels ε_k are (in units of β, so a positive value of ε_k corresponds to a negative energy, bonding MO)

$$\varepsilon_k = 2\cos(k\omega), \quad (4)$$

where $\omega = \pi/(N+1)$ and k runs from 1 to N. The orbital coefficient for the rth AO in the kth MO ψ_k (in Eq. (2)) is given by

$$C_{rk} = \left(\frac{2}{N+1}\right)^{1/2} \sin(rk\omega). \quad (5)$$

When Eqs. (4) and (5) are substituted in Eq. (1) (under the assumption of $\eta \to 0$) we obtain the trigonometric form of the zeroth order Green's function for a linear polyene in units of β^{-1} as follows:

$$G_{rs}^{(0)} = -\frac{1}{N+1}\sum_{k=1}^{N} \frac{\sin(rk\omega)\sin(sk\omega)}{\cos(k\omega)}. \quad (6)$$

This relation was discussed by McLennan *et al.* in the context of quantum transport using the NEGF method.[48] It is easy to see that the right hand side of Eq. (6) is minus the (r, s) entry of inverse of $\mathbf{H}$.[34]

Some elements of $G_{rs}^{(0)}$ (below, for simplicity, we denote $G(r, s) = G_{rs}^{(0)}$) are easy to obtain from ideas already known to chemists in the context of alternant hydrocarbons. Thus when r and s have the same parity, i.e., are both odd or both even, then $G(r, s) = 0$. Alternant hydrocarbons are molecules in which the carbon atoms can be divided into two groups, *starred* and *unstarred*, in such a way that no two atoms of the same group are directly linked.[47,49] In al-

ternant hydrocarbons the energy levels are paired, positive and negative, and the r, s site coefficients in paired MOs are pairwise identical. The resulting QI features are experimentally observed when the electrode attachment is made to two starred or to two unstarred atoms.[6,22] However, regardless of the electrode-attachment site, clear QI features at the Fermi energy are not observed in nonalternant hydrocarbons, such as dithienylethene[35] and azulene.[50]

The other elements of the symmetric $\mathbf{G}^{(0)}$ matrix are less obvious, even as they may be obtained from the inverse of the Hückel matrix.[51] In Ref. 34, we prove the following theorem. For $r \geq s$:

$$G(r, s) = \frac{(-1)^{\left(\frac{r+s-1}{2}\right)}}{4}[1 + (-1)^{s-1}][1 - (-1)^{r+1}]. \quad (7)$$

It is evident that $G(r, s) = G(s, r)$. In matrix representation,

$$\mathbf{G}^{(0)} \equiv -\mathbf{H}^{-1} = \begin{bmatrix} 0 & -1 & 0 & +1 & 0 & -1 & \cdots \\ -1 & 0 & 0 & 0 & 0 & 0 & \\ 0 & 0 & 0 & -1 & 0 & +1 & \\ +1 & 0 & -1 & 0 & 0 & 0 & \cdots \\ 0 & 0 & 0 & 0 & 0 & -1 & \\ -1 & 0 & +1 & 0 & -1 & 0 & \\ \vdots & & & \vdots & & & \ddots \end{bmatrix}. \quad (8)$$

Evidently, the entries of the zeroth order Green's function matrix are only 0, +1, or −1. Zero entries correspond to destructive QI, while ±1 entries correspond to good transmission. The difference between +1 and −1 is not immediately evident, but emerges in the last part of this paper.

When r is odd and $s \leq r$ is even, then $G(r, s) = 0$; similarly for r even and $s > r$ odd. These zeroes are not predictable from the simple alternant properties of a polyene. However, the graphical scheme of Markussen *et al.*,[23] which also emerges from considerations of the inverse of the Hamiltonian, predicts these zeroes correctly. We will see that the two kinds of zeroes, call them "easy" (for the ones arising from the alternant character of the wave function), and "hard" (the others) have somewhat different physical consequences when interactions beyond nearest neighbors, be they small, are introduced.

The inverse of the Hückel matrix, the negative of the Green's function above, plays an important (if neglected[52]) role in theoretical chemistry. As Heilbronner showed,[53] following an important paper by Günthard and Primas,[54] the inverse allows a connection between the molecular orbital energy levels of an organic π system and the valence bond resonance structures for a molecule, with graph theory shaping that bridge. We will explore in a subsequent paper this connection, relating quantum interference in molecular conductance to the stability of diradicals.

ADDING ATOMS TO A CHAIN

Quantum interference operates in intriguing ways that are not (yet) chemically transparent. We would like to build a set of rules for the way transmission is affected by substitution

SCHEME 1. Schematic representations of the three cases of adding atoms to a chain. Before adding atoms the left and right electrodes are attached to the sites r and s (> r), respectively. After adding atoms the attachment sites r and s change to the sites r' and s', respectively.

and molecular elaboration, rules that work in a way like synthetic construction of a molecule. We are not the only ones who have had this goal; others, as mentioned, have looked at regularities in quantum interference as a molecule's topology is built up.[21,23,26–28]

With this aim in mind, and still remaining within the linear polyene class, the explicit matrix form of the polyene Green's function, (7), provides a way in to one set of chemical elaborations that might be useful. Effectively, the polyene Green's function allows us to deduce a set of rules to determine how adding atoms to a chain affects its conductance. The idea is to keep the attachment points of hypothetical electrodes fixed, but add carbon atoms at the end. The process is very constrained, branched polyenes are not created by it. These, as well as structures in which a loop is attached, will be discussed in future work.

Given the constraint that the total number of atoms should be even, the following cases are possible: (a) adding an even number of atoms to one end of a polyene, (b) adding an even number of atoms to both ends, and (c) adding an odd number of atoms to both ends. Adding an odd number of atoms to only one side leads to an odd-carbon-number polyene and a noninvertible Hückel matrix, so we will omit this possibility. The three situations examined are shown in Scheme 1, exemplified by adding one center as a prototype odd number, two for an even number.

Let us first consider cases (a) and (b). Since the parities of r and s are left unchanged by adding an even number of atoms, the value of the zeroth order Green's function is also left unchanged. Therefore, in cases (a) and (b) conductance is preserved.

Consider next case (c). When the parities of r and s are the same, both change on adding an odd number of atoms (odd to even, or even to odd). The matrix elements, zero to begin with, remain zero. When the parities of r and s are opposite (one odd, the other even), those parities after adding an odd number of atoms at the ends are interchanged. Hence the values of the zeroth order Green's function before and after adding an odd number of atoms are different. They may change from zero to ± 1 or vice versa.

To summarize: To maintain invertability of **H**, we can only in total add an even number of atoms to the chain. This could result from adding an even number (including zero) to each side or an odd number to both sides. Adding an even number of carbons in a polyene to either its left or right end, or to both ends of the molecule, will not change the transmission at the connected sites. But adding an odd number of carbons to both ends has a drastic effect on the transmission, sometimes "turning it on," sometimes "killing" it. The utilization of this QI phenomenon to design a molecular switch is obvious; we discuss a realization in the "Application to electrocyclic switches" section.

APPLICATION TO ELECTROCYCLIC SWITCHES

An electrocyclic reaction (Scheme 2) involves the conversion of a linear system containing N π electrons to a cyclic system with $(N-2)$ π electrons by σ bond formation between the termini or the reverse.[55] Since the cyclic system can also be viewed as a linear system with a reduced $(N-2)$ number of π electrons, the electrocyclic reaction corresponds to case (c) of the "Adding atoms to a chain" section – relative to the cyclic form, the π system is augmented by one C at each end. Clearly, as the "Adding atoms to a chain" section implies, there is an opportunity for a quantum interference switch here.

Scheme 3 shows two prototype electrocyclic reactions, the classical ones of the intercoversion of butadiene (BD)-cyclobutene (CB) and of hexatriene (HT)-cyclohexadiene (CH). *Note the numbering of carbons changes between the closed and open molecules, so as to maintain a connection to the transmission discussion above.* Thus carbon 2 of butadiene is carbon 1 of cyclobutene, etc.

Let us limit the attachment of electrodes to carbons that are part of a conjugated system – 1 to 4 in butadiene, 1 to 2 in cyclobutene. Thus in the BD-CB interconversion, only a 1-2 positioning of connecting electrodes in CB, which corresponds to 2-3 connection in BD, is considered. From the arguments of the "Adding atoms to a chain" section (or the general expression for the Green's function) we expect high
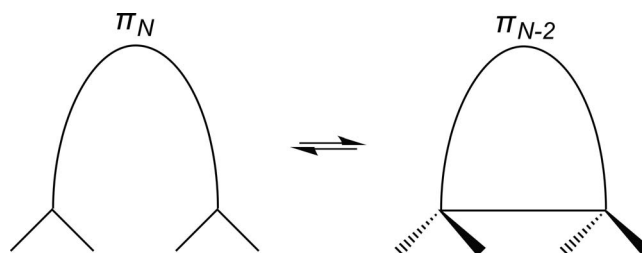
SCHEME 2. Schematic representation of an electrocyclic reaction.
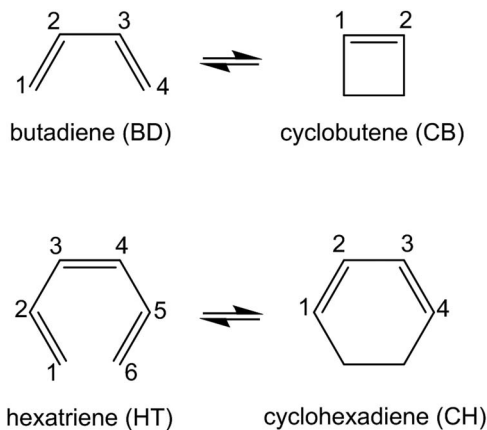
SCHEME 3. Two prototype electrocyclic reactions, the butadiene (BD)-cyclobutene (CB) interconversion and the hexatriene (HT)-cyclohexadiene (CH) interconversion.

transmission for the ring CB (ON) and low for the same positioning of the electrodes in the chain BD (OFF).

Computed transmission spectra for 1-2 connection in CB and 2-3 connection in BD are shown in Figure 1 as a function of the electrode potential in units of β (see Sec. S1 in the supplementary material[37] for the way the transmission probabilities are calculated). The sharp positive peaks come from resonance tunneling at the location of MO energy levels. Since the HOMO-LUMO gap in BD is smaller than that in CB, the resonance peaks of BD are closer to the Fermi level than those of CB. However, it is clear that the same (2-3) connection in BD has a much lower transmission probability around the Fermi level than in CB (where it is 1-2) due to the quantum interference.

The low transmission through a 2-3 connection in BD has already been pointed out by Solomon and her co-workers.[20, 21] They have analyzed the system based on the phase of the transmission function and also estimated the influence of the
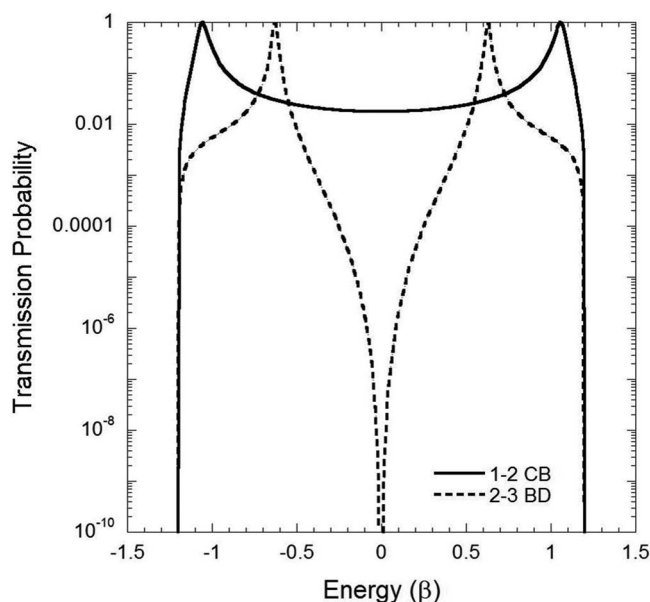
through-space coupling and many-body charge-charge correlations on the QI feature.

As Figure 1 implies, the ON/OFF ratios computed for this model are very high, near 2×10^7 for a bias voltage of 0.1 V (the ON/OFF ratio of the BD-CB system as a function of bias voltage is shown in Sec. S8 in the supplementary material[37]). However, even if one stays in the Hückel model, we will soon see that inclusion of non-nearest neighbor interactions, small as they are, lowers the ON/OFF ratio to a maximal 10^3. This is still large enough for an effective switch.

In the same way, we are able to predict which connections should show a high ON/OFF ratio in the other electrocyclic system studied here in detail: hexatriene, HT – cyclohexadiene, CH. The 1-3 connection of electrodes in CH (2-4 in HT) is not a good candidate for a switch, as inherent transmissions are expected to be low (between same parity sites). We are left with 1-2, 2-3, and 1-4 possibilities in CH, which transform into 2-3, 3-4, and 2-5 in HT. We certainly appreciate the experimental difficulty of achieving some of these, but let us examine the possibilities. From the general form of the Green's function (Eq. (8)), we expect that 1-2 and 1-4 connections in the closed polyene form of CH should be ON, 2-3 OFF. In the open polyene HT form, these become 2-3 (OFF), 2-5 (OFF), and 3-4 (ON), respectively.

Thus all attachments show switching potential. The really interesting ones are 1-2 CH/2-3 HT and 1-4 CH/2-5 HT, for these two positionings of electrodes lead to a switch that is ON in the chemically *closed* ring form, OFF in the *open* extended chain, the seemingly more conjugated HT. The ON isomer changes in dramatic fashion, depending on the position of the electrodes; sometimes it is the chemically ring-closed form, sometimes the open chain.

As shown in Figure 2, our qualitative predictions are in good agreement with transmission spectra. The computed

FIG. 1. Computed transmission spectra for 1-2 connection in CB and 2-3 connection in BD. The ON and OFF states are indicated by the solid and dotted lines, respectively. The legend numbers refer to the site of electrode attachment.
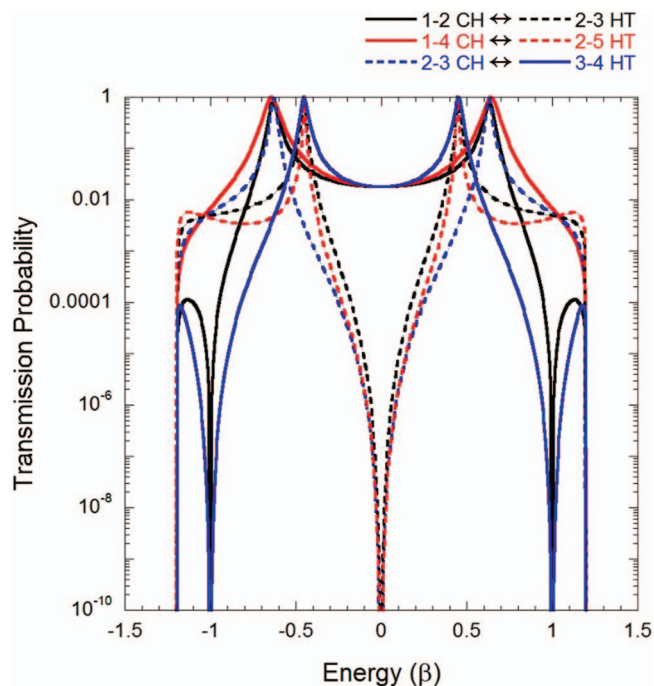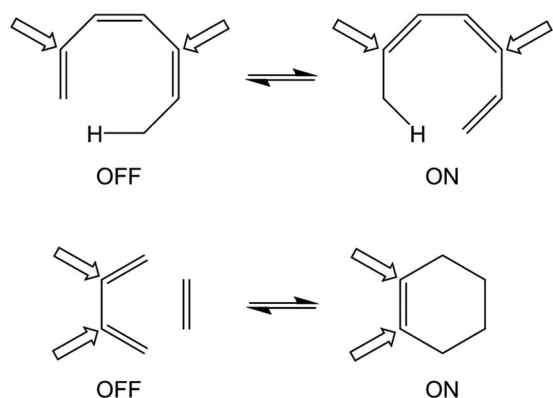
FIG. 2. Computed transmission spectra for 1-2, 1-4, and 2-3 connections in CH and 2-3, 2-5, and 3-4 connections in HT. The ON and OFF states are indicated by the solid and dotted lines, respectively.

SCHEME 4. Examples of switches based on a sigmatropic reaction (top) and cycloaddtion (bottom). Arrows denote probe attachment sites.

ON/OFF ratios (see Sec. S8 in the supplementary material[37]) are all high; they will be less so when non-nearest-neighbor interactions are included, as we discuss below.

The extension to higher polyenes is straightforward. With nanoelectronics in mind, many researchers have explored molecules whose conductivity can be reversibly turned on and off by external stimuli such as light and heat.[56] Photochromic molecules, for example, dihydropyrene[57] and dithienylethene, often make use of an electrocyclic reaction, specifically one or another variant of the HT-CH pair.[58,59] The molecular conductance change in photochromic systems has been measured at the single-molecule level.[60] Quantum interference, where it occurs (nonalternants perturb the situation greatly) is a dominant factor in setting the OFF position of the switch. The regularities we deduce will help in the molecular design of new optically or thermally controllable molecular switches based on a variety of electrocyclic reactions.

AND SIGMATROPIC REACTIONS AND CYCLOADDITIONS

Electrocyclic reactions are, of course, only one type of cycloaddition.[55] So the possibility occurs of constructing other switches, based on sigmatropic reactions and cycloadditions. Two examples are shown in Scheme 4. Transmission calculations (details are not given here) confirm this idea.

THE HARD ZEROES ARE DIFFERENT

In the Hückel model, quantum interference occurs for the zeroes of the Green's function matrix representation, expressed in Eq. (8). It has become clear with time that in more detailed calculation, transmission through the σ system provides a reasonably constant and definitely non-zero transmission near the Fermi level.[5,6] Moreover, every all electron calculation, whether at the Hartree-Fock level or beyond, shows that even in the π system alone (neglecting the σ transmission) the QI antiresonance of some connections, for instance 2-3 of butadiene, splits into two. Perhaps the first demonstration of this is in the work of Solomon and Ratner.[21]

The effect may be traced back to inclusion of non-nearest neighbor interactions, even if these are small. In Figure 3 we contrast the 2-3 transmission in the simplest Hückel model (already given in Figure 2) with that for an "extended Hückel" model, where we include H_{13} (H_{31}), H_{24} (H_{42}), and H_{14} (H_{41}) for butadiene. The actual matrix used, with Hamiltonian matrix elements given in units of β, is also shown for both an s-trans and an s-cis butadiene, with no bond alternation. The H_{ij} fall off exponentially with distance, scaling as the corresponding overlaps. Details of their computation are given in Sec. S5 in the supplementary material.[37]

Including non-nearest neighbor interactions converts every transmission antiresonance for a "hard" zero into a twin resonance, or, alternatively and simultaneously, diminishes the "sharpness" and depth of the QI feature. The situation is actually complex – as the discussion in Sec. S6 in the supplementary material[37] shows, including 1,3 interactions (we use a notation of i-j for electrode connections, r,s for interactions) produces splitting of a QI antiresonance, but 1,4 interactions diminishes them. The distant interactions, overlap-dependent as they are, fall off exponentially with distance. So effectively
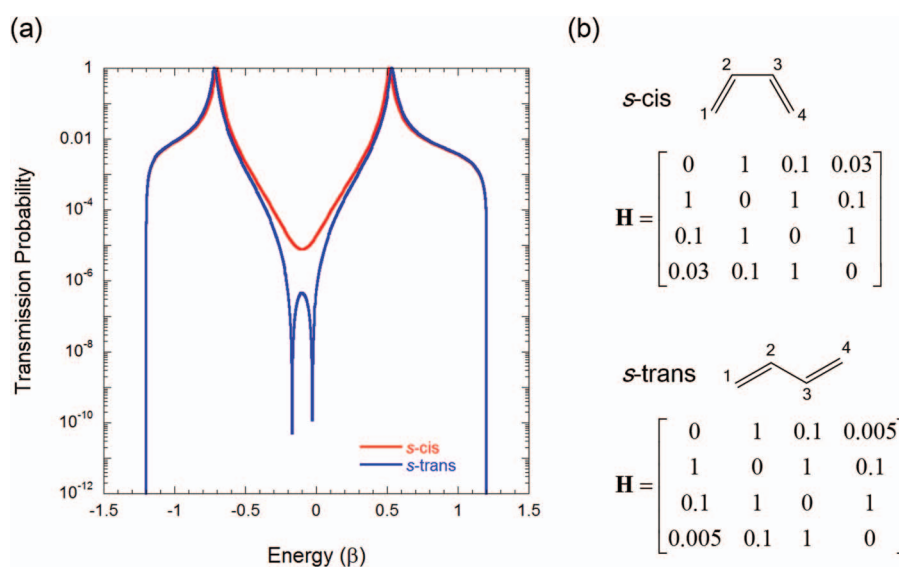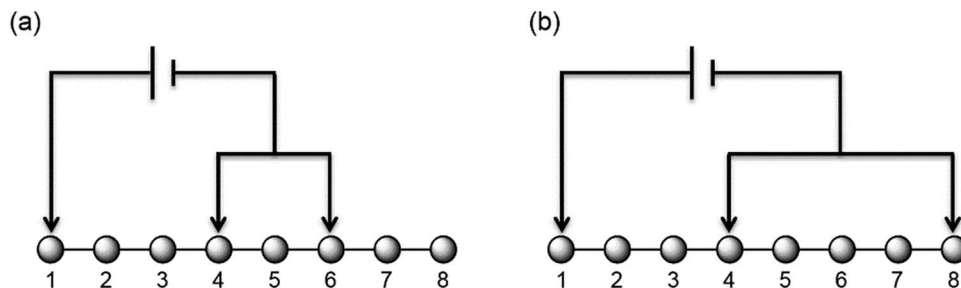

FIG. 3. (a) Computed transmission spectra for the 2-3 connection in s-cis (indicated by red) and s-trans (indicated by blue) butadienes. (b) The structures and Hamiltonian matrices for s-cis and s-trans butadienes.

only perturbations due to 1,3 interaction matter. Note also the slight shift of all resonance features to higher energy.

The splitting of a QI feature into two or the diminution of the sharpness and depth of a QI feature occurs for 2-3 in BD, or CH, or HT; also for 2-5 in HT (see Sec. S6 in the supplementary material[37] for detailed calculations). Does this have consequences for the capability of such electrode attachment configurations to transmit current? In every instance we have seen, in our work, and in that of others,[61] in the hard zero cases the transmission at the Fermi level is increased by the antiresonance splitting, but remains substantially lower than the transmission for "good" (non-zero Green's function matrix element) connections. It is as if the split antiresonances "remember" the zero of the Green's function for the simplest Hückel model. Thus the ON/OFF ratios in reality will be smaller than those shown above in Figs. 1 and 2 (see Sec. S8 in the supplementary material[37] for a calculation; we already mentioned the extent of reduction for the 2-3 butadiene connection above), but still substantial.

BOND ALTERNATION AND ITS CONSEQUENCES

Up to now we have considered the polyene chain as consisting of uniformly spaced carbons, i.e., all β or t in the Hückel model equal. Of course, real polyenes, e.g., butadiene or hexatrienes, show CC bond alternation, CC bonds typically tending to ~1.34 and 1.47 Å. This alternation persists to the infinite chain, polyacetylene, a classic manifestation of a Peierls distortion.[62,63]

To take into account the effect of bond alternation one can modify the Hückel Hamiltonian matrix as follows:

$$\mathbf{H} = \begin{bmatrix} 0 & \beta & & & & & \\ \beta & 0 & \beta' & & & & \\ & \beta' & 0 & \ddots & & & \\ & & \ddots & \ddots & \beta' & & \\ & & & \beta' & 0 & \beta \\ & & & & \beta & 0 \end{bmatrix}, \qquad (9)$$

where $\beta > \beta'$. The ratio of the resonance/transfer integrals β'/β can be estimated from the relevant $2p_z$-$2p_z$ overlap integrals. In a separate contribution, we will trace the consequences of such alternation. What will be seen there is the zeroes of the Green's function remain, but the magnitude of the nonzero elements is not 1, but goes down as

$(\beta)^{-1}(\beta'/\beta)^{(|r-s|-1)/2}$ with increase of a bond (not spatial) distance between r and s.[64] This will furnish (in work to be published) a physical basis for an exponential formula[65] for the fall-off of through-bond transmission.

The switching characteristics of the electrocyclic switches discussed above are not significantly affected by bond alternation. A comparison of transmission between the systems with and without bond alternation is shown in Sec. S5 in the supplementary material.[37]

SIGNIFICANCE OF THE SIGN OF THE GREEN'S FUNCTION

The Green's function for the polyene in the HMO model without bond alternation, (7), has +1 or −1 entries. Since the transmission is related to the absolute value squared of the Green's function, it would appear that the sign of a $G(r, s)$ element would have no significance. This is not so.

Consider a two-terminal, three-probe model shown in Scheme 5(a), where the left terminal (electrode) is connected to the site r and the right electrode is split between the sites s and s' ($r < s < s'$). Note that the Green's function $G(r, s)$ represents the response of the wavefunction at atom r due to an incoming electron from atom s. A measurement that extracts/inserts the electron coherently from/into atoms s and s' should yield a conductance that is expected to be proportional to $|G(r, s) + G(r, s')|^2$. If $G(r, s)$ and $G(r, s')$ have nonzero values but have the opposite sign, the transmission probability at the Fermi level will vanish. *Multiprobe attachment thus allows one to probe the sign of $G(r, s)$, normally not accessible experimentally.*

Let us consider for example a polyene chain with $N = 8$ shown in Scheme 6. For the moment let us assume that there is no bond alternation; the consequences of such alternation will be discussed below. The left electrode is connected to the beginning of the chain (site 1). The first row of the zeroth order Green's function matrix for the eight-site chain is [0, −1, 0, +1, 0, −1, 0, +1]. The Green's function matrix elements are in units of $1/\beta$ as usual, and β is negative. There should be no transmission if the right electrode is connected to both carbons 4 and 6 (Scheme 6(a)) because $G(1, 4) = +1$ and $G(1, 6) = -1$. There may be a transmission if the right electrode is connected to both carbons 4 and 8 (Scheme 6(b)) because $G(1, 4) = +1$ and $G(1, 8) = +1$.

Detailed transmission calculations probe this supposition (see Sec. S3 in the supplementary material[37] for the way the transmission probabilities for the multiprobe attachment are calculated). Figure 4(b) shows the normal transmission

SCHEME 5. Schematic representations of (a) a three-probe model, where the left electrode is connected to the site r and the right electrode is split between the sites s and s' (r < s < s') and (b) a conventional two-probe model, where the left and right electrodes are connected to the sites r and s (> r), respectively.

(a)   (b)

SCHEME 6. Schematic representation of three-probe molecular junctions composed of linearly chained 8 carbon atoms. The left electrode is connected to the site 1 and the right electrode is split between the sites (a) 4 and 6 and (b) 4 and 8.

spectra for connections 1 to 4, 1 to 6, and 1 to 8; all have a transmission probability of 1.76×10^{-2} at the Fermi level. In contrast, as shown in Figure 4(a), there is a transmission dip at the Fermi level in the case that the right electrode is connected to both 4 and 6, whereas there is no transmission dip at the Fermi level for the case that the right electrode is connected to both 4 and 8. This computational result is fully consistent with the qualitative prediction based on the zeroth order Green's function.

When the right electrode is connected to both 4 and 8 (see Figure 4(a)), the transmission probability at the Fermi level is 6.86×10^{-2}, which is nearly 4 times as large as in the case that the right electrode is connected to only one atom. The conductance depends on the square of the zeroth order Green's function; we have quantum reinforcement, indeed amplification in this coherent electrode attachment.

We have already mentioned the preceding theoretical and experimental study of constructive and destructive interference in a parallel molecular system by Magoga and Joachim,[30] by Vazquez *et al.*,[31] and by Lambert.[32] In the constructive mode, they also find a characteristic conductance that is more than twice that of a molecule with a single backbone.

QI features in two-probe systems rely on zero elements of $G(r, s)$, which remain unaffected by bond alternation. On the other hand, those in two-terminal three-probe systems rely on nonzero elements of $G(r, s)$ cancelling or reinforcing. The $G(r, s)$ magnitudes involved depend on bond separation, so that the interference between $G(1, 4)$ and $G(1, 6)$ cannot be as perfect as shown in Figure 4(a).

Consider a polyene chain with $N = 8$, which is connected to the electrodes in the same way as shown in Scheme 6. A reasonable degree of bond alternation leads to that $\beta = 1.1$ and $\beta' = 0.9$ (predicated on the values estimated for a bond-alternated butadiene, see Sec. S5 in the supplementary material[37]). The first row of the zeroth order Green's function matrix is then [0, −0.91, 0, +0.74, 0, −0.61, 0, +0.50] in units of $1/\beta$. It follows that there should not be zero but low transmission if the right electrode is connected to both 4 and 6 (Scheme 6(a)) due to partial, not complete, interference between $G(1, 4) = +0.74$ and $G(1, 6) = −0.61$. The consequence of reinforcement when, instead, the right electrode is connected to both 4 and 8 (Scheme 6(b)), will also be different.

Detailed transmission calculations support the qualitative expectation, even when bond alternation occurs. As shown in

(a)   (b)
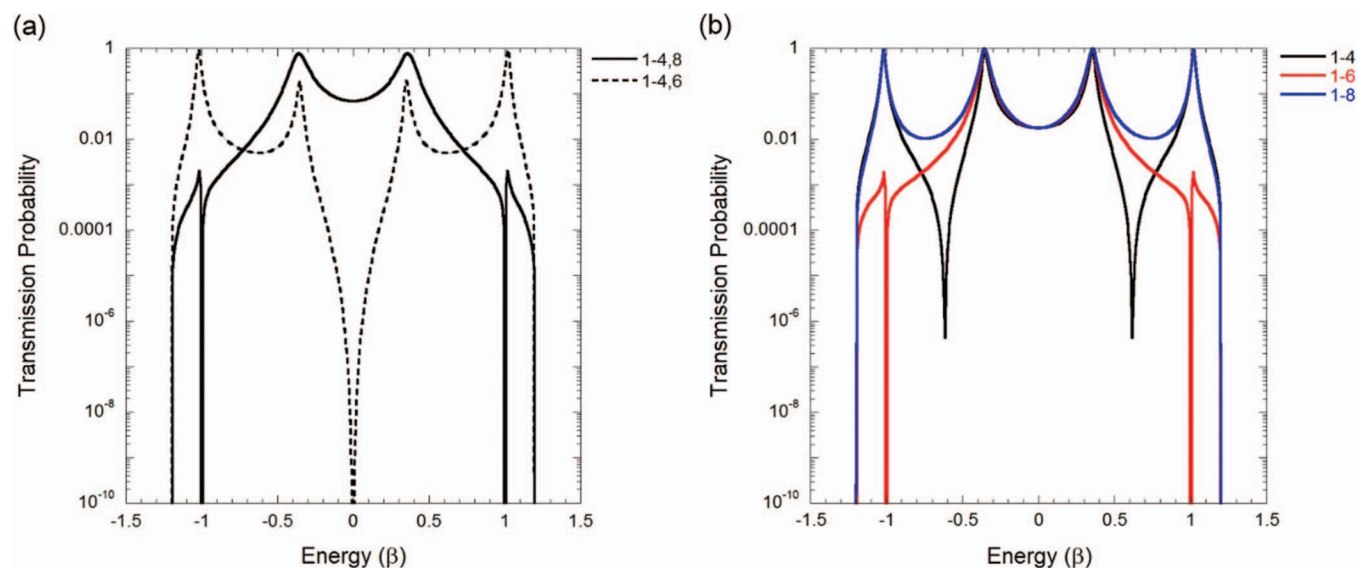
FIG. 4. (a) Computed transmission spectra for the three-probe molecular junctions composed of a uniform linear chain of 8 carbon atoms, where the left electrode is connected to the site 1 and the right electrode is split between the sites 4 and 6 (indicated by the dotted line), and 4 and 8 (indicated by the solid line). (b) Computed transmission spectra for the individual two-probe molecular junctions, where the left and right electrodes are connected to only one site, respectively.
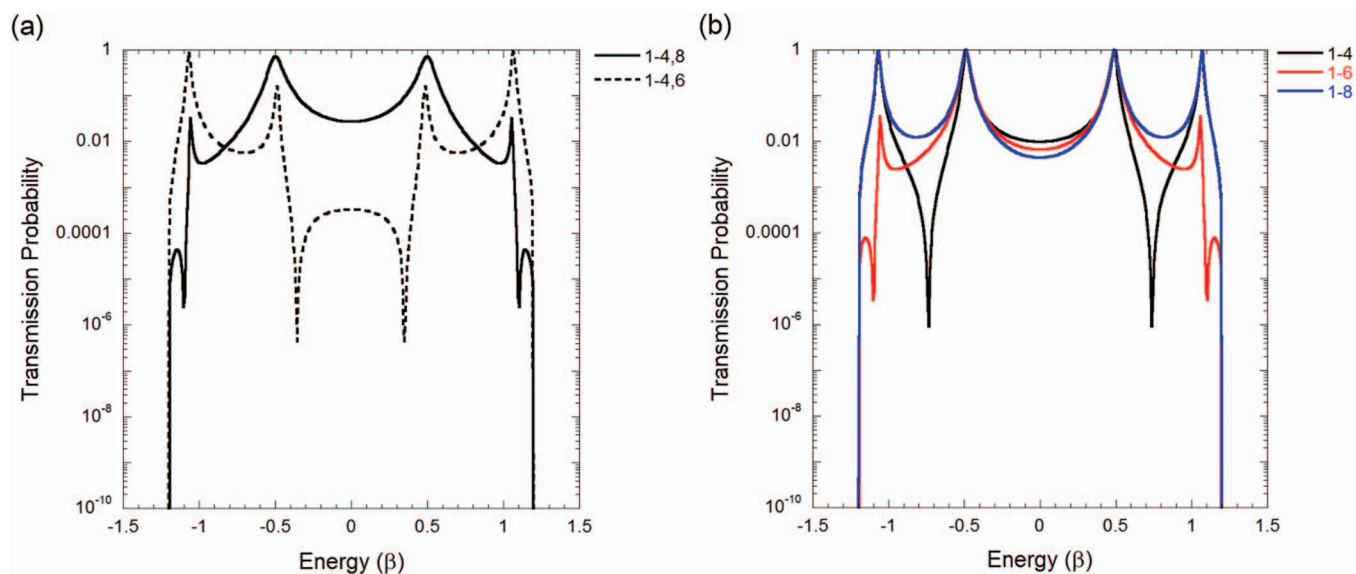
FIG. 5. (a) Computed transmission spectra for the three-probe molecular junctions in a bond-alternated linear chain of 8 carbon atoms, where the left electrode is connected to the site 1 and the right electrode is split between the sites 4 and 6 (indicated by the dotted line) and 4 and 8 (indicated by the solid line). (b) Computed transmission spectra for the individual two-probe molecular junctions, where the left and right electrodes are connected to only one site, respectively.

Figure 5(a), in the case that the right electrode is connected to both 4 and 6, the transmission probability at the Fermi level is lower by two orders of magnitude than the case that the right electrode is connected to both 4 and 8. Interestingly, the deep QI-induced anti-resonance peak in the non-bond-alternated system splits into two shallow anti-resonance peaks in the bond-alternated system. Adding in non-nearest neighbor interactions (see Sec. S9 in the supplementary material[37]) changes the picture little, but shifts the spectrum to higher energy.

Figure 5(b) shows the individual transmission spectra for the connections 1 to 4, 1 to 6, and 1 to 8 in the bond-alternated polyene. In contrast to Figure 4(b) the attenuation of conductance with respect to increase of a distance between connection sites is observed in the bond-alternated polyene. We will fit the attenuation to an exponential formula for the fall-off of conductance and estimate.

Transmission through π-electron systems coupled in parallel (e.g., one electrode coherently connected to position 1 of a diene and an ethylene, the other electrode connected to position 4 of a diene and 2 of an ethylene) provide further examples of new destructive interference. Constructive interference in parallel systems has been already discussed in the literature.[30–32]

COHERENCE

There is an assumption we have made in the analysis of multiprobe attachment. This is complete phase coherence between the two probes attached to one terminal, e.g., of 4 and 6 in the 1 to 4 and 6 thought experiment. In calculation (see Sec. S3 in the supplementary material[37]) we assure this by connecting the polyene to the same gold atoms of the electrode. In reality it is difficult to engineer complete coherence – the molecular connectors (amines, thiols) may attach themselves to widely separated (on an atomic scale) areas of the gold electrode surface.

The difference between decoherent attachment, transmission proportional to $|G(r, s)|^2 + |G(r, s')|^2$ and coherent attachment, $|G(r, s) + G(r, s')|^2$ is large. We think one needs to consider both possibilities and vary experimentally the electrode attachment configuration to try to realize both eventualities.

CYCLIC POLYENES AND A POTENTIAL EXPERIMENTAL REALIZATION OF MULTIPLE PROBE ATTACHMENT

Let us now consider, for reasons that will become apparent, transmission through cyclic polyenes. For cyclic polyenes containing $4n + 2$ carbon atoms, Hückel systems, Longuet-Higgins and Salem found that if n is less than 8 the symmetrical structure should be preferred, but that for greater values of n bond alternation should set in Ref. 66. Experimentally, bond alternation sets in around $n = 4$.[67] Realistic examples so far involve benzene, $n = 1$, so we will not be concerned with bond alternation.

Though we have not discussed in detail the orbitals and Green's functions of a cyclic (as opposed to a linear) polyene, they are easily obtained from the inverse of the corresponding Hückel matrix.[34] When $N = 4n$, where n is a positive integer, the Hückel matrix is not invertible and therefore the zeroth order Green's function matrix cannot be defined.[34, 68] In the work cited, we derive, we believe for the first time, the explicit form of the Green's function for the cyclic case – the resulting matrices have entries always 0 or $\pm 1/2$, and are constant along diagonals (i.e., they are symmetric Toeplitz matrices).[34]

For the specific case of $N = 6$ (benzene), the Hamiltonian matrix and zeroth order Green's function matrix for benzene

are

$$\mathbf{H} = \begin{bmatrix} 0 & 1 & 0 & 0 & 0 & 1 \\ 1 & 0 & 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 & 0 & 1 \\ 1 & 0 & 0 & 0 & 1 & 0 \end{bmatrix} \qquad (10)$$

and

$$\mathbf{G}^{(0)} = \frac{1}{2} \begin{bmatrix} 0 & -1 & 0 & +1 & 0 & -1 \\ -1 & 0 & -1 & 0 & +1 & 0 \\ 0 & -1 & 0 & -1 & 0 & +1 \\ +1 & 0 & -1 & 0 & -1 & 0 \\ 0 & +1 & 0 & -1 & 0 & -1 \\ -1 & 0 & +1 & 0 & -1 & 0 \end{bmatrix}, \qquad (11)$$

respectively. The nonzero elements of the zeroth order Green's function matrix for benzene are not ± 1 but $\pm 1/2$; there is a good topological reason for this fraction, as explained to us by Estrada.[69]

Consider now the first electrode connected to site 1. There should be no transmission if the second electrode is connected to both 2 and 4 (see Scheme 7(a)), because $G(1, 2) = -1/2$ and $G(1, 4) = +1/2$. There will be transmission if the second electrode is connected to both 2 and 6 (see Scheme 7(b)), because $G(1, 2) = -1/2$ and $G(1, 6) = -1/2$.

Detailed calculations, support this qualitative conclusion – as shown in Figure 6(a), there is a transmission dip at the Fermi level in the case that the second electrode is connected to both 2 and 4, whereas there is no transmission dip at the Fermi level in the case that the second electrode is connected to both 2 and 6, confirming the simple argument.

For comparison we show the transmission spectra for connections 1 to 2 (1 to 6) and 1 to 4 in Figure 6(b). All con-
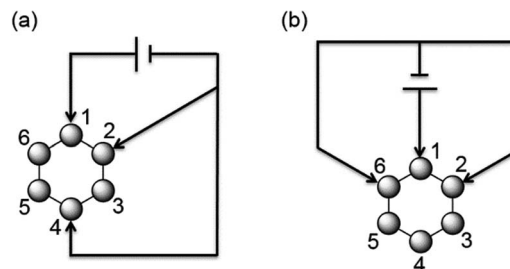
SCHEME 7. Schematic representation of three-probe molecular junctions composed of cyclic 6 carbon atoms. The first electrode is connected to the site 1 and the second electrode is split between the sites (a) 2 and 4 and (b) 2 and 6.

nections have the transmission probability of 4.43×10^{-3} at the Fermi level. When the second electrode is connected to both 2 and 6 (see Figure 6(a)), the transmission probability at the Fermi level is 1.76×10^{-2}, which is nearly 4 times as large as the case that the second electrode is connected to only one atom. Once again we see quantum interference and amplification as a consequence of specific multiple electrode attachment.

There is a good reason why we turned to benzene – remarkably this multiprobe attachment system has been studied experimentally! Kiguchi and his co-workers[70] measured the conductance of a single-molecule junction with multipodal anchoring units, where multiple equivalent conduction pathways between two electrodes are formed. They synthesized 1,2,4,5-tetrakis (2-mercaptothienylethynyl) benzene derivative 4-TEB (see Scheme 8(a)) and its bidirectional counterpart 2-TEB (see Scheme 8(b)) and performed conductance measurements using the STM break junction technique. As shown in Scheme 8(a), 4-TEB is assumed to be connected to electrodes by two anchor groups on each side. This system can be viewed as a multiple-probe system, consisting of two terminals (electrodes) each having two connection points. The conductances of 4-TEB and 2-TEB were determined to be
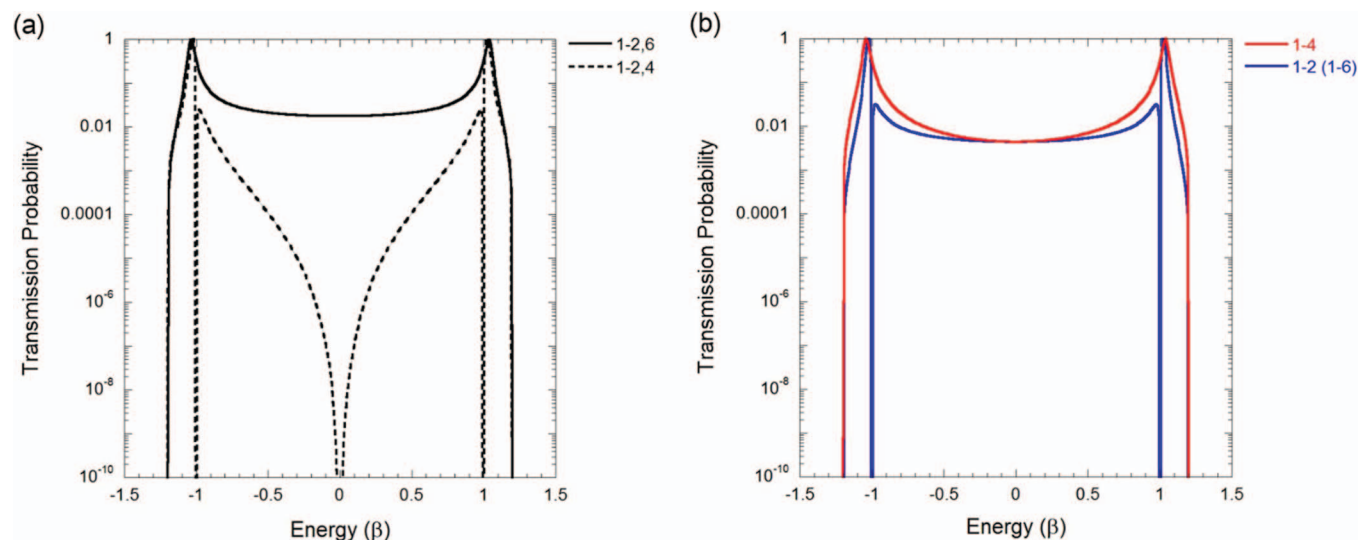
FIG. 6. (a) Computed transmission spectra for the three-terminal molecular junctions in a cyclic 6 carbon atom system, where the first electrode is connected to the site 1 and the second electrode is split between the sites 2 and 4 (indicated by the dotted line) and 2 and 6 (indicated by the solid line). (b) Computed transmission spectra for the individual two-terminal molecular junctions, where the first and second electrodes are connected to only one site, respectively.
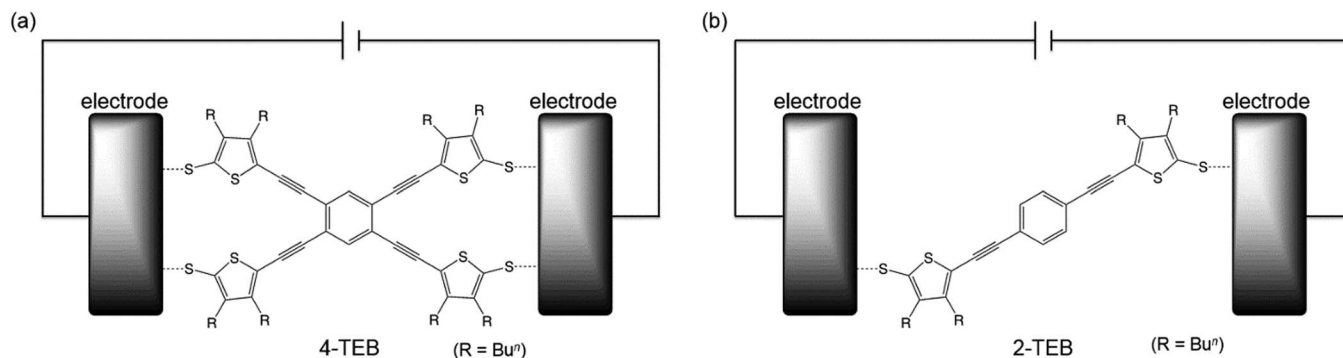
SCHEME 8. Schematic representations of single-molecule junctions of (a) 4-TEB and (b) 2-TEB in the work of Kiguchi *et al.*

$2.7 \times 10^{-4} \ G_0$ and $5.0 \times 10^{-5} \ G_0$, respectively, where G_0 is the quantum of conductance ($2e^2/h$). The conductance of 4-TEB is about 5 times as large as that of 2-TEB. To analyze their result, Kiguchi *et al.* performed detailed electronic transport calculations, which showed that there is an overlap resonance effect involving the HOMO conducting orbital in the 4-TEB molecule junction.

Our qualitative considerations lead to an understanding of the observed and calculated conductance. The molecular junctions of 4-TEB and 2-TEB shown in Schemes 8(a) and 8(b) can be simplistically (we hope not overly so) reduced to circuits including a 6-membered ring, as shown in Schemes 9(a) and 9(b), respectively. In the case of the four-probe system (two electrodes, each having two connection points to the molecule) the conductance should be proportional to $|G(1, 4) + G(1, 5) + G(2, 4) + G(2, 5)|^2 = |0.5 + 0 + 0 + 0.5|^2 = 1$ while in the case of the two-probe system the conductance should be proportional to $|G(1, 4)|^2 = |0.5|^2 = 0.25$ assuming perfect coherence. Therefore the conductance of the four-probe system can be expected to be 4 times as large as that of the two-probe system. This ratio is not far from the experimental ratio of 5, but the assumption of perfect coherence needs careful scrutiny.

QUESTIONS OF COHERENCE AGAIN

We have to pick our way carefully through what happens in the system just discussed, or for that matter in any multiple electrode system. In the actual molecular junction, built on benzene, the connection sites 1 and 2 (and also 4 and 5) are microscopically apart from the electrode surface, connected to it through thienylethynyl linkers. It is possible that there is little phase coherence between electrons traveling through the

different linkers. If so, the conductance would be expected to be proportional to $|G(1, 4)|^2 + |G(1, 5)|^2 + |G(2, 4)|^2 + |G(2, 5)|^2$ rather than $|G(1, 4) + G(1, 5) + G(2, 4) + G(2, 5)|^2$. The conductance then is no longer sensitive to the sign of the Green's function. Since $|G(1, 4)|^2 + |G(1, 5)|^2 + |G(2, 4)|^2 + |G(2, 5)|^2 = 0.5$ and $|G(1, 4)|^2 = 0.25$ in the incoherent case, the conductance of the four-probe system would be expected to be two times as large as that of the two-probe system.

In Figure 7 we show the calculated transmission spectra for electron transmission through a 6-membered ring with both coherent and incoherent multiprobe attachments, from 1 and 2 to 4 and 5, compared to that for the simpler system, 1 to 4. In the coherent case, the transmission spectrum for the four-probe system is unsymmetric with respect to the energy zero, whereas that for the incoherent case and the two-probe case are symmetric with respect to the energy zero. The peaks around 1.1β and -1.05β can be attributed to the HOMO- and LUMO-resonance peaks, respectively. Although the HOMO-resonance peaks of the incoherent four-probe and two-probe systems are closer to the Fermi level than that of the coherent four-probe system, the coherent four-probe system has a larger transmission probability around the Fermi level than the two-probe one, due to the long tail of the HOMO-resonance peak.

In Figure 7 the transmission probabilities at the Fermi level for the coherent four-probe, incoherent four-probe, and two-probe systems are 1.75×10^{-2}, 8.85×10^{-3}, and 4.43×10^{-3}, respectively. The transmission probabilities for the coherent and incoherent four-probe systems are 4 and 2 times as large as that for the two-probe system, respectively. This is consistent with the above qualitative discussion. Although the coherent case gives better agreement with the experimental results obtained by Kiguchi and his co-workers than the
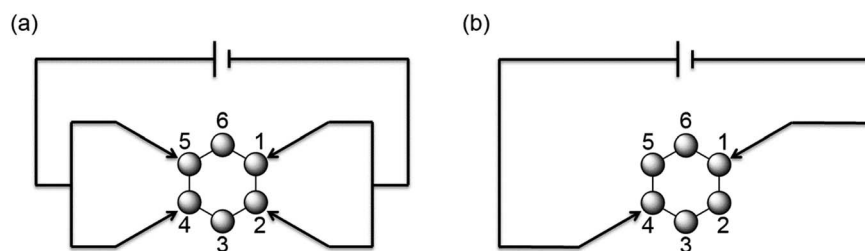
SCHEME 9. Schematic representations of (a) a four-probe and (b) two-probe molecular junctions composed of cyclic 6 carbon atoms.
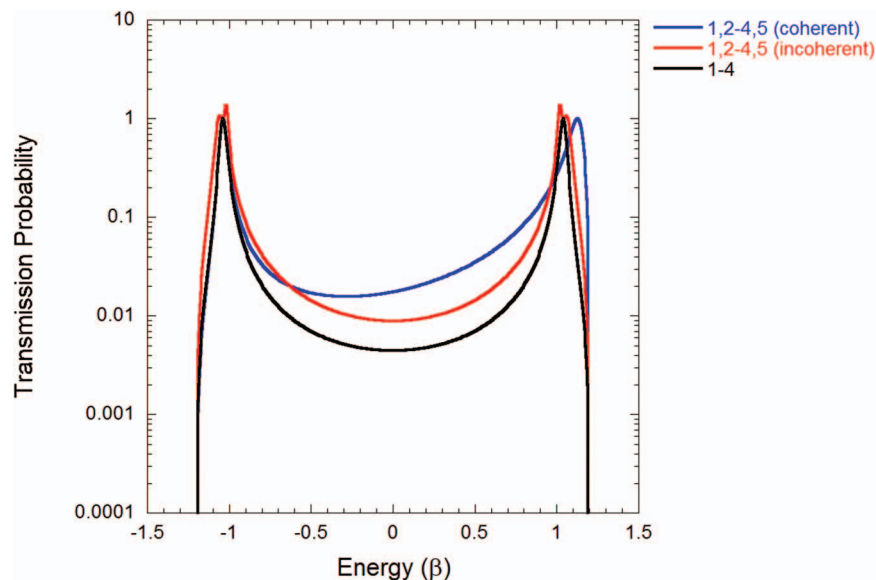
FIG. 7. Computed transmission spectra for the coherent four-probe (indicated by blue line), incoherent four-probe (indicated by red line), and two-probe (indicated by black line) molecular junctions composed of cyclic 6 carbon atoms.

incoherent case, whether the coherence of the electrons is maintained even after traveling through the different linkers remains an open question.

In Sec. S10 in the supplementary material,[37] we compare in detail our model transmissions (Fig. 7) with the DFT transmission calculations of Kiguchi *et al.*[70] There is rough agreement, but a direct comparison cannot be made as the two calculations use different anchoring groups to the electrodes.

Aside from making sense of these clever experiments, our simple theory shows clearly that the signs of the Green's function matrix elements can actually be made use of, resulting in unexpected, new quantum interference patterns, and in amplification of a signal due to quantum superposition. Bond alternation may modify these results in a small way, and coherence in large ones.

SUMMARY

For a specific model, an even-carbon-number polyene without bond alternation in a Hückel model, the explicit expression for the elements of the zeroth order Green's function matrix, approximated by the inverse of the Hückel matrix, leads to some simple rules for the effect on the transmission between specific sites of electrode attachment of adding carbons to the chain at left or right. These rules in turn lead to the prediction of interesting switching behavior in a simple electrocyclic reaction, actually a commonly used switching device. In some cases seemingly counterintuitive behavior is predicted, with the chemically closed organic cycle actually being the more conducting one. These findings hold true even for polyenes with bond alternation, and can be extended to other cycloadditions.

Curiosity about the positive and negative signs of Green's function matrix elements led us to think about ways in which these could have physical consequences. Multiprobe attachment allows one to explore the significance of these signs,

leading to either new quantum interference (where none would occur for simple pair electrode attachment), or reinforcement, indeed amplification. Remarkably, a relevant system has recently been studied experimentally by Kiguchi *et al.*; under the assumption of constructive quantum interference their observation of amplification can be understood. Whether the experimental structure actually exhibits the requisite coherence needs further consideration. In general, we have to pay careful attention to the attenuation of the nonzero elements of the Green's function due to bond alternation and the coherence of electrons passing through different transmission pathways.

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