Close relation between quantum interference in molecular conductance and diradical existence

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An empirical observation of a relationship between a striking feature of electronic transmission through a π-system, destructive quantum interference (QI), on one hand, and the stability of diradicals on the other, leads to the proof of a general theorem that relates the two. Subject to a number of simplifying assumptions, in a π-electron system, QI occurs when electrodes are attached to those positions of an N-carbon atom N-electron closed-shell hydrocarbon where the matrix elements of the Green's function vanish. These zeros come in two types, which are called easy and hard. Suppose an $N+2$ atom, $N+2$ electron hydrocarbon is formed by substituting 2 CH_2 groups at two atoms, where the electrodes were. Then, if a QI feature is associated with electrode attachment to the two atoms of the original N atom system, the resulting augmented $N+2$ molecule will be a diradical. If there is no QI feature, i.e., transmission of current is normal if electrodes are attached to the two atoms, the resulting hydrocarbon will not be a diradical but will have a classical closed-shell electronic structure. Moreover, where a diradical exists, the easy zero is associated with a nondisjoint diradical, and the hard zero is associated with a disjoint one. A related theorem is proven for deletion of two sites from a hydrocarbon.

molecular conductance | diradicals | quantum interference | determinants | nonbonding orbitals

Connections between concepts that at first sight seem unrelated are always intriguing, and hint at an underlying cause. We came across one such correspondence recently, between the existence of π-diradicals, on one hand, and quantum interference (QI) in the transmission of electrons across a π-system on the other.

We will say more about both diradicals and molecular transmission, but let us begin with the theoretical observation, and for that we need a simplified introduction to both phenomena.

The class of π-diradicals constitutes an important series of organic intermediates with two radical centers in their primary valence structure (1–3). Their Hückel matrix has two or more zero eigenvalues (in a choice of energy zero at the usual Coulomb integral $α$). Also, the molecules may exist in singlet and triplet states, competing in ways we understand reasonably well for being the ground state of the molecule. Trimethylenemethane (TMM), tetramethyleneethane (TME), and m-quinodimethane (each illustrated by one resonance structure in Fig. 1) are three simple examples.

The transmission of current across single molecules is an active theoretical and experimental field of contemporary chemical physics (4–9). Destructive QI describes a striking quantum effect in which transmission is much attenuated. For instance, QI occurs when electrodes are attached to 1,1 or 1,3 or 2,3 carbons in an ethylene (Fig. 2, *Left*) or a butadiene (Fig. 3, *Top*). There is normal transmission when the electrodes are attached 1,2 or 1,4; clearly, distance through space is not the determining factor in this phenomenon.

Consider the attachment of two electrodes 1,1 vs. 1,2 to an ethylene (substitution of two hydrogens by "linkers" to the electrodes, such as amines, thiols, and so on), vs. the substitution of two methylene (radical) units at these sites, generating a potential diradical. We indicate in Fig. 2 whether or not QI is observed in the

molecular transmission system, and whether the primary valence structure of the potential diradical is actually a diradical or not. The 1,2 substitution of two (*cis* or *trans*) hydrogens in ethylene yields not a 1,4-diradical but a closed-shell system, butadiene. The 1,4-diradical structure is a minor contributor to the valence bond (VB) description of butadiene, but the fully bonded structure dominates. Also, in the transmission system, the conductance 1,2 on ethylene is not accompanied by QI but is efficient and normal. On the other hand, 1,1 substitution yields a real diradical, trimethylenemethane, and a case of QI.

Fig. 3 shows the possible substitution patterns on a butadiene skeleton. There is a perfect correlation of diradical existence and QI in molecular transmission.

The correlation between diminished transmission and nonbonding molecular orbitals (NBMOs) was noticed by one of the authors in benzene (10) and naphthalene (11). This was partially explained by the orbital interaction between the parent molecule and the attached atoms. This correlation has also been noted by others in a variety of systems (12–18). The generality is intriguing and begs for an explanation. This we provide in this paper.

More on Transmission and Quantum Interference

The calculation of current through a molecule is most commonly approached through the nonequilibrium Green's function (NEGF) formalism (19). A conceptual model for the NEGF formalism is depicted in Fig. 4. According to the Landauer formula (20), the current can be calculated from

$$I = \frac{2e}{h} \int dE\, T(E) \left[f_L(E) - f_R(E) \right],$$ [1]

Significance

It might seem that the existence of a dramatic diminution in molecular conductance across a hydrocarbon (quantum interference, QI) would be unrelated to the existence of an important class of organic molecules with two electrons in two orbitals, diradicals. However, if you add two carbons to a planar π-electron hydrocarbon, you get a diradical if and only if there is a QI feature in conductance when two electrodes are attached to the molecule at the same sites. When you remove the two carbons where the electrodes are attached, you also generate a diradical. The connection, first empirically observed, is proven. Two kinds of diradicals, with different ground state spin consequences, are also easily distinguished by the relationship.
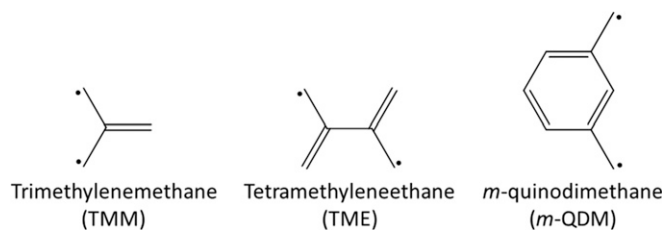
Fig. 1. Some typical diradicals (hydrogens omitted, one resonance structure).

Fig. 3. The arrows show attachment of electrodes in a molecular transmission experiment (*Top*). The primary contributor in a VB description of the corresponding potential diradical (*Bottom*).

where T is the transmission of electrons passing through a molecule and $f_{L(R)}$ is the Fermi distribution function for the left (right) electrode. T can be calculated from Eq. **2** (19),

$$T(E) = \text{Trace}\left[\Gamma_L \mathbf{G} \Gamma_R \mathbf{G}^\dagger\right], \qquad [2]$$

where $\mathbf{G}$ is the Green's function matrix and $\Gamma_{L(R)}$ is the broadening function matrix for the left (right) electrode, which describes the coupling between a molecule and electrodes.

Here we assume electron transmission through the chain is through the π-orbitals, and the Green's function can be approximated by the zeroth-order Green's function $\mathbf{G}^{(0)}$. Furthermore, we use, in the transmission calculations (such as the ones in *SI Appendix*), a Hückel model that has been described in detail elsewhere (21). In the limit of zero temperature and zero bias voltage, the conductance between the rth and sth atoms, g_{rs}, is then proportional to the square of the absolute value of the (r, s) entry of the zeroth-order Green's function matrix at the Fermi energy, $\mathbf{G}^{(0)}(E_F)$, as follows:

$$g_{rs} \approx \frac{2e^2}{h} \gamma_L \gamma_R \left| G(r,s) \right|^2. \qquad [3]$$

Here $2e^2/h$ is the quantum of conductance, $\gamma_{L(R)}$ is the nonzero element of the broadening function matrix, and $G(r,s)$ denotes the (r,s) entry of $\mathbf{G}^{(0)}$, which is approximated by the negative of the inverse of the Hückel–Hamiltonian matrix, $-\mathbf{H}^{-1}$.

When $G(r,s) = 0$, the conductance will be greatly diminished. This is QI. The conductance, of course, will not be vanishing even in the presence of QI, for the model we use neglects the σ-system of the molecule. However, from the experience of many calculations that include both σ- and π-electrons, when QI occurs, it lowers the calculated (or observed) conductance by an order of magnitude or more (22).

The condition for occurrence of QI in a one-dimensional (1D) chain has been mathematically derived elsewhere (21). When r and s have the same parity, i.e., they are both odd or both even, then
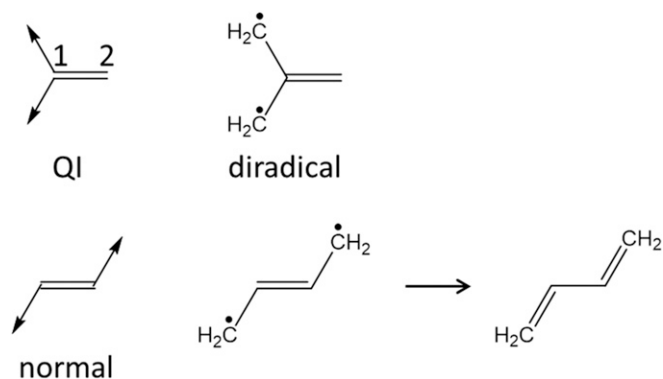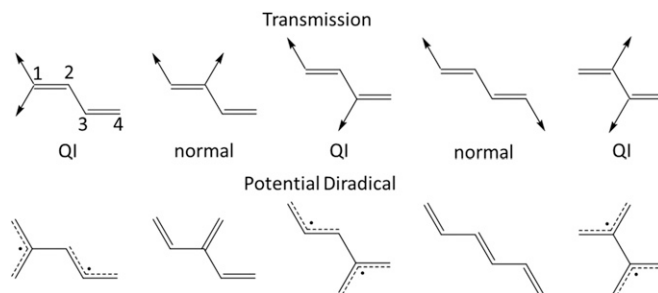
$G(r,s) = 0$. Or, when r is even and $s > r$ odd, then $G(r,s) = 0$. We call the former zero and the latter zero "easy zero" and "hard zero," respectively, because of the mathematical difficulty in evaluating the respective trigonometric sums (23). The two situations, two different kinds of zeros of the Green's function matrix, also have somewhat different physical consequences. The distinction has been investigated in detail by two of the authors and coworkers (24, 25). We will demonstrate another aspect of the difference between the two kinds of zeros in the context of the related diradicals.

The hard and easy zeros can be related to a classification of hydrocarbons rooted in the early days of Hückel theory (26). In a hydrocarbon, atoms are separated into starred and unstarred ones, every starred atom surrounded by unstarred ones. When this can be accomplished for all atoms in a molecule, it is said to be alternant. Obviously, hydrocarbons containing rings with an odd number of atoms are nonalternant. An assembly of beautiful theorems can be proved about the energies and wave function coefficients in alternant hydrocarbons. Also, the alternant character allows the easy proof of some regularities in transmission.

In the Hückel model for transmission across a π-system, the alternant nature of the hydrocarbon leads trivially to QI when r and s, the sites of electrode attachment, are both starred or both unstarred. These are precisely the easy zeros. On the other hand, when one of the rth and sth atoms is starred and the other is unstarred, $G(r,s)$ is not necessarily zero. However, there are some r and s in such cases where $G(r,s)$ is zero, and it is these we call hard zeros. This terminology is not limited to a 1D chain. A related

Fig. 2. The arrows show attachment of electrodes in a molecular transmission experiment (*Left*). The corresponding potential diradicals (*Right*).
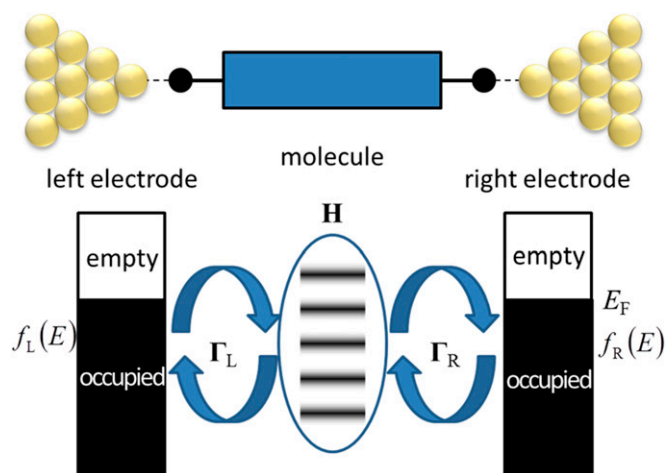

Fig. 4. Schematic descriptions of a molecule in contact with the left and right electrodes (*Top*) and the NEGF-based electron transport model, which allows us to model current flow through a molecule described by the Hamiltonian **H** (*Bottom*).

classification, used by two of us, is "odd class" and "even class" (25). It should be mentioned that although the Hückel model is very good at spotting the conditions for QI (6–10), it needs to be supplemented by detailed quantum mechanical transmission calculations for more detailed understanding of molecular transmission.

More on Diradicals

Two electrons in two (nearly) degenerate orbitals is the essence of diradicals. Diradicals are not only the π-electron systems we consider in this paper but also a wide variety of systems containing heteroatoms, such as aminoxyls or verdazyls (27). The natural concern in this class of molecules has been with the spin of the ground state of the system, a matter on which there is extensive literature (1–3). Diradicals of the π-type can be classified into two types, namely disjoint and nondisjoint. Disjoint diradicals have two NBMOs that can be chosen so that they share no common atoms, whereas nondisjoint diradicals have those that share common atoms (1). Fig. 5 gives an example of a disjoint and a nondisjoint diradical.

Borden and coworkers (28–30) showed that, in disjoint π-diradicals, the open-shell singlet and triplet states can generally be expected to be close in energy, but higher-order effects can often make the open-shell singlet state more stable than the triplet state [which, interestingly, is a violation of Hund's rule (31)]. On the other hand, nondisjoint diradicals generally have a triplet ground state. Borden and coworkers also provided a simple method to determine whether a diradical is disjoint or nondisjoint based on the starring procedure (28, 30). If, in a diradical, the number of starred carbons (N_S) is equal to that of unstarred carbons (N_U), then the NBMOs can be chosen to be disjoint, with one NBMO confined to the starred set of atoms and the other to the unstarred set. Otherwise, when $|N_S - N_U| = 2$, the NBMOs will be nondisjoint.

Using a VB formalism, Ovchinnikov (32) reasoned that the total spin quantum number S in an alternant hydrocarbon is equal to $|N_S - N_U|/2$. A "classical structure" (CS) is a Lewis or Kekulé structure with the maximum number of double bonds drawn; for a 2N atom, 2N electron molecule, that may be N or N−2 double bonds. Klein et al. (33) proved that the total spin quantum numbers S predicted by VB, CS, and MO theories are related by $S_{VB} \leq S_{CS} \leq S_{MO}$. Thus, there are situations when CS might point to a closed-shell ground state, but MO theory predicts a system with two NBMOs. No implication is drawn here as to whether such two-NBMO, two-electron systems are high spin or low spin; we call them both diradicals. We will encounter several such cases at the end of this paper. A detailed account of the singlet–triplet splitting in diradicals requires post-Hartree–Fock quantum mechanical computations and is beyond the scope of this work.

Why There Might Be a Relation Between Diradical Stability and Transmission

A single molecule can be not only a conductor of variable quality but also a spin > 0 "high" spin compound, a molecular magnet (a terminology we use loosely, fully aware that real magnetism is an emergent property of an extended system). These two properties, conductance and magnetism, are combined in the developing field of molecular spintronics (34–36).

A measure of electronic communication can be the electronic coupling matrix element (H_{AB}) (37), which describes the overlap of electronic wave functions between remote sites, in most cases donor and acceptor. On the other hand, a measure of magnetic interaction between localized unpaired spins typically is the exchange coupling constant (J), which appears in the Heisenberg-type Hamiltonian (38) and can be approximated by half of the splitting between the singlet and triplet states (39).

On the basis of foundational early work by Kramers (40), Anderson (41), and McConnell (42), important correlations between H_{AB} and J have been theoretically and experimentally discovered. Among the many systems investigated are dimers containing two weakly interacting metal centers (39, 43), dinu-
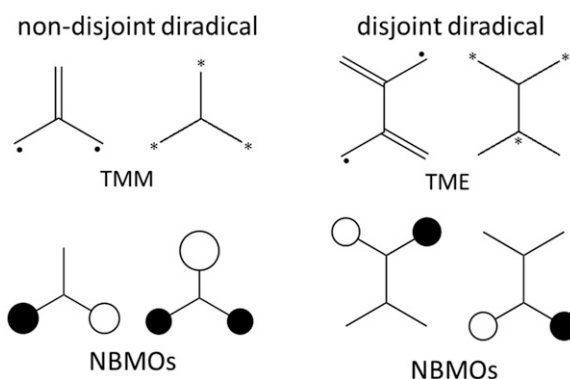

Fig. 5. An example of a nondisjoint diradical (TMM, *Left*) and a disjoint diradical (TME, *Right*). The hydrogens are omitted from the structures, and only the top lobe of the $2p_z$ orbitals is shown.

clear metal complexes with bridging π-conjugated ligands (44–46), and organic diradicals with two spins coupling via a π-stacking (47) or a π-conjugated bridge (48).

Owing to the above-mentioned correlation, it has been suggested by Ratner, Wasielewski, and coworkers (49) that both the amplitude of magnetic coupling and the rate constant of coherent electron transfer exhibit a similar exponentially decreasing trend with respect to the distance between two spins or two redox moieties. Furthermore, recent combined theoretical and experimental studies for donor-bridge-acceptor (D-B-A) diradical systems by Kirk, Shultz, and coworkers (12, 13) and for π-conjugated molecules bridged between two nitronyl nitroxide radicals by Matsuda and coworkers (14–16) have shown similar trends among magnetic coupling, electron transfer, and molecular conductance, with respect to the exponential attenuation as well as the dihedral-angle dependence. Herrmann and coworkers (17, 18) have explored the relationship between molecular conductance and magnetic coupling, but also its limit. Very recently, Klein and coworkers have found that a high-spin π-diradical can play an important role in molecular junctions as a spin filter (50).

In the molecular electronics community, QI has been appreciated as an important factor that significantly reduces molecular conductance, when it occurs. Various interpretations of QI exist, based on, for example, phase (5, 6), orbital (7), local current (8), and topology (9); they largely concur in associating QI with zero elements of a Green's function matrix, as we did (21). There are other ways to think about QI, so Kirk et al. relate QI to excited-state contributions to the ground-state singlet–triplet splitting in D-B-A diradicals (51).

We return now to the correlation we showed exists between transmission in a π-system when electrodes are attached to sites r and s of an alternant N atom, N electron hydrocarbon, and the electronic structure of the $N+2$ atom, $N+2$ electron molecule formed by replacing the electrode attachment sites by CH_2 units. It can be proven.

Proof of the Correlation Between Quantum Interference and a Good Diradical Valence Structure

After attaching two atoms numbered $N+1$ and $N+2$ to the rth and sth atoms of a parent molecule, which consists of N atoms (N is even), the new Hückel–Hamiltonian matrix H_{+rs} for the whole system, including the attached atoms, is given as an $(N+2) \times (N+2)$ block matrix,

$$H_{+rs} = \begin{bmatrix} H & B \\ B^T & 0 \end{bmatrix}, \qquad [4]$$

where H is the Hückel–Hamiltonian matrix for the parent molecule, dimension $N \times N$, and 0 is the zero matrix with the

dimension of 2×2. $\mathbf{B}$ is a matrix with the dimension of $N \times 2$. $B(r,1)$ and $B(s,2)$ describe the connections between the parent molecule and the attached atoms, being 1. The other entries of the matrix $\mathbf{B}$ are zero. $\mathbf{B}^T$ is the transposed matrix of $\mathbf{B}$.

To determine the existence/absence of a zero eigenvalue of the Hamiltonian matrix $\mathbf{H}_{+rs}$, we calculate its determinant. A method to calculate the determinant of a 2×2 block matrix is found in the mathematical literature (52, 53). We apply it to Eq. **4**, obtaining

$$\det(\mathbf{H}_{+rs}) = \det \begin{bmatrix} \mathbf{H} & \mathbf{B} \\ \mathbf{B}^T & \mathbf{0} \end{bmatrix} = \det(\mathbf{H})\det(-\mathbf{B}^T\mathbf{H}^{-1}\mathbf{B}). \quad [5]$$

Note that $\mathbf{H}$ is invertible as long as the parent molecule does not have any MO at $E = 0$, which is an NBMO. To put it another way, the parent molecule must be a closed-shell molecule.

Throughout this paper, we use the convention that the Hückel α is set equal to zero, and that the energy is measured in units of β, the Hückel resonance integral (which is also the transfer integral t of tight-binding theory). The determinants carry appropriate energy units, but these are not shown.

Because $-\mathbf{H}^{-1}$ is the zeroth Green's function at the Fermi level for the parent molecule, i.e., $\mathbf{G}^{(0)}$, Eq. **5** can be rewritten in the form

$$\det(\mathbf{H}_{+rs}) = \det(\mathbf{H})\det\left(\mathbf{B}^T\mathbf{G}^{(0)}\mathbf{B}\right). \quad [6]$$

Because $\mathbf{B}^T$ is a $2 \times N$ matrix, $\mathbf{G}^{(0)}$ is an $N \times N$ matrix, and $\mathbf{B}$ is an $N \times 2$ matrix, $\mathbf{B}^T \mathbf{G}^{(0)} \mathbf{B}$ is a 2×2 matrix, and can be written as follows:

$$\mathbf{B}^T\mathbf{G}^{(0)}\mathbf{B} = \begin{bmatrix} \sum_i^N \sum_j^N [\mathbf{B}^T]_{1i}[\mathbf{G}^{(0)}]_{ij}[\mathbf{B}]_{j1} & \sum_i^N \sum_j^N [\mathbf{B}^T]_{1i}[\mathbf{G}^{(0)}]_{ij}[\mathbf{B}]_{j2} \\ \sum_i^N \sum_j^N [\mathbf{B}^T]_{2i}[\mathbf{G}^{(0)}]_{ij}[\mathbf{B}]_{j1} & \sum_i^N \sum_j^N [\mathbf{B}^T]_{2i}[\mathbf{G}^{(0)}]_{ij}[\mathbf{B}]_{j2} \end{bmatrix}. \quad [7]$$

Note that only $[\mathbf{B}^T]_{1r}$, $[\mathbf{B}^T]_{2s}$, $[\mathbf{B}]_{r1}$, and $[\mathbf{B}]_{s2}$ entries are 1 and the others are 0 in the matrices $\mathbf{B}^T$ and $\mathbf{B}$. Therefore, Eq. **7** can be simplified as

$$\mathbf{B}^T\mathbf{G}^{(0)}\mathbf{B} = \begin{bmatrix} G(r,r) & G(r,s) \\ G(s,r) & G(s,s) \end{bmatrix}. \quad [8]$$

$G(r,r)$ and $G(s,s)$ are always 0, which holds true for all alternant hydrocarbons (22, 25). Further, it is evident that $G(r,s) = G(s,r)$. Hence, the determinant of $\mathbf{B}^T \mathbf{G}^{(0)}\mathbf{B}$ is $-[G(r,s)]^2$. Eventually, we arrive at the following equation:

$$\det(\mathbf{H}_{+rs}) = -\det(\mathbf{H})[G(r,s)]^2. \quad [9]$$

Eq. **9** is applicable to any π-system, as long as the parent molecule is an alternant hydrocarbon without any NBMO. Because the conductance between rth and sth atoms in the parent molecule is proportional to $|G(r,s)|^2$, Eq. **9** implies that the conductance should be proportional to $|\det(\mathbf{H}_{+rs})/\det(\mathbf{H})|$. Determinantal relations similar to those described here have recently been published by the Geerlings group (54). Another relationship holds for nonalternant systems (with odd-membered carbon rings); this is provided in *SI Appendix*.

The det($\mathbf{H}$) may, by a well-known theorem, be also represented by the product of the eigenvalues of $\mathbf{H}$. That product is a constant (in units of β^N) depending upon the parent molecule. For example, $\det(\mathbf{H}) = i^N$, where i denotes the imaginary unit, for linear chains consisting of even-numbered N atoms, and $\det(\mathbf{H}) = -4$ for cyclic $[4n + 2]$ π-systems, such as benzene (23).

Therefore, the site-specific conductance depends on $|\det(\mathbf{H}_{+rs})|$. This suggests the conductance is determined not only by the inverse of the Hamiltonian $\mathbf{H}$, or $\mathbf{G}^{(0)}$, but also by the determinant, or the product of the MO energies, of the "augmented Hamiltonian" $\mathbf{H}_{+rs}$. Experts in graph theory and linear algebra might find a still more fascinating translation of this equation.

The reason why we calculate the determinant is to make a bridge between the Green's function elements and diradical existence. According to Eq. **9**, when QI occurs in electron transport between the rth and sth atoms of the parent molecule, i.e., $G(r,s) = 0$, the molecule obtained by attaching two atoms to the rth and sth atoms, which hereafter we will call the "augmented molecule," will have at least one MO level at $E = 0$, or NBMO. However, the total number of the π-orbitals of the augmented molecule, i.e., $N+2$, is even, and the Coulson–Rushbrooke pairing theorem (55), which states that MO levels are symmetrically distributed with respect to $E = 0$, applies to the augmented system. Hence, there must be not one but at least two NBMOs. This also implies that the augmented molecule should be a diradical. On the other hand, when QI does not occur, i.e., $G(r,s) \neq 0$, the augmented molecule cannot have any MO at $E = 0$. Therefore, it must be a closed-shell molecule.

The Same Is True for Deleting Two Atoms

Consider a process complementary to the augmentation just discussed, now of deleting the rth and sth atoms from the parent molecule. We will call the molecule resulting from atom removal the "reduced molecule," and its Hamiltonian will be called $\mathbf{H}_{-rs}$. In *SI Appendix*, we prove the following equation:

$$\det(\mathbf{H}_{+rs}) = \det(\mathbf{H}_{-rs}). \quad [10]$$

Note that we assume $\beta = 1$; otherwise, this equation should read $\det(\mathbf{H}_{+rs}) = \beta^4\det(\mathbf{H}_{-rs})$. Eq. **10** suggests that if an augmented molecule, in which two atoms are attached to the rth and sth atoms, is a diradical, the reduced molecule, in which the rth and sth atoms are deleted, is also a diradical or can be divided into two monoradicals. If $r = s$, the reduced molecule consists of odd-numbered $N - 1$ atoms, resulting in a monoradical, where $\det(\mathbf{H}_{-rs}) = 0$. This is consistent with the fact that if $r = s$, the augmented molecule is always a diradical, where $\det(\mathbf{H}_{+rs}) = 0$.

Let us look at some examples. Fig. 6 shows processes of attaching two atoms to the rth and sth atoms, and, complementarily, deleting the rth and sth atoms in naphthalene. In the normal conductance cases (1,4; 1,5), atom addition leads to a closed-shell molecule, and so does atom removal, leading to a closed-shell molecule (1,5) or two closed-shell molecules (1,4). In the electrode attachment instances where transmission shows
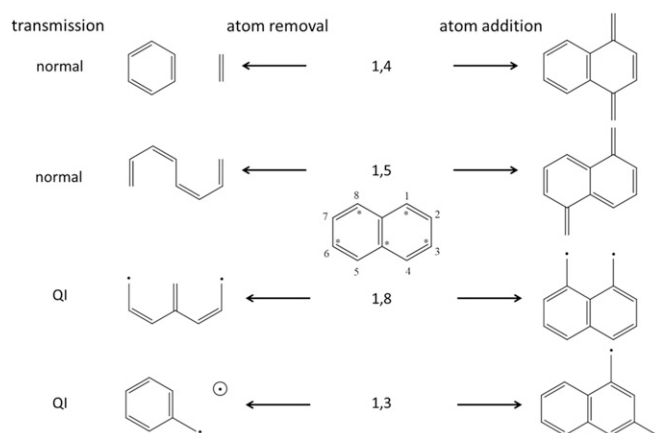

Fig. 6. Atom addition and atom removal for two sites in naphthalene.

Table 1. Summary of the derived relation between the QI and diradical existence

Attachment/removal sites (r,s)*	Green's function	Conductance	Augmented/reduced molecule[†]
(S,S)	$G(r,s) = 0$	QI (easy zero)	diradical (nondisjoint)
(U,U)	$G(r,s) = 0$	QI (easy zero)	diradical (nondisjoint)
(S,U) or (U,S)	$G(r,s) = 0$	QI (hard zero)	diradical (disjoint)
	$G(r,s) \neq 0$	conductive	closed shell

*S means a starred atom, and U means an unstarred atom.
[†]This holds true as long as $r \neq s$ and the reduced molecule is a single molecule (not divided into two).

a QI feature, atom addition leads to a diradical, and atom removal also leads to a diradical (1,8 case) or two monoradicals (1,3 case).

Another Way to Reach the Same Conclusion

In the heyday of Hückel theory and reactivity indices, in 1952, Dewar and Longuet-Higgins (56) derived a remarkable relation between the determinant of the Hückel matrix and the number of Kekulé structures (K). In 1958, Ham (57) showed how K and the Pauling bond order (58), the ratio of Kekulé structures for the molecule with two atoms deleted, K_{-rs}, to K, are connected. In 1972, this was further developed by Graovac et al. (59) on the basis of the Sachs graph. In 1976, Hosoya and Hosoi (60) derived a relation between the Pauling bond order and the determinant of the Hückel matrix. In 1980, Aono and Nishikawa (61) gave the connection between the determinant of Hückel matrix and the Green's function. In the 1970s, Caroli et al. (62) derived a relation between the Green's function and electron transport, which was further developed in the 1990s by many people, including Datta (19) and Ratner et al. (63). Recently, several groups have traced the consequences of the relation between the inverse of Hückel matrix and electron transport; references are given in ref. 21. Also, Stuyver et al. have recently pointed out a relation between molecular conductance and atom−atom polarizability (64).

Earlier this year, Stuyver et al. (65) summarized these diverse relations and derived the following equation:

$$g_{rs} \propto \left(\frac{K_{-rs}}{K}\right)^2, \qquad [11]$$

where K is the number of Kekulé structures for the parent molecule and K_{-rs} is the number of Kekulé structures when the rth and sth atoms are deleted from the parent molecule. We can derive an interesting determinant equation that relates Eq. **11** to *SI Appendix*, Eq. **S12**. Because we proved Eq. **10**, Eq. **11** can then be rewritten as follows:

$$g_{rs} \propto \left(\frac{K_{-rs}}{K}\right)^2 = \left(\frac{K_{+rs}}{K}\right)^2, \qquad [12]$$

where K_{+rs} is the number of Kekulé structures when two atoms are attached to the rth and sth atoms.

From Eq. **12**, we can derive the same conclusion as we reached earlier. If QI occurs between the rth and sth atoms in the parent molecule ($g_{rs} = 0$), the augmented molecule and reduced molecule are either a diradical or two monoradicals, for which no (full) Kekulé structure can be drawn, i.e., $K_{+rs} = K_{-rs} = 0$.

Correlation and, with It, a Bonus

The relation derived above between QI and diradical existence is summarized in Table 1. The bonus is the connection between easy and hard zeros and the nondisjoint or disjoint nature of the diradicals.

Because the parent molecule (the molecule before two CH_2 units are attached to it or two atoms are deleted) must be a closed-shell molecule ($S = 0$), $N_S = N_U$. Therefore, the number of stars on the two attached atoms or two deleted atoms determines whether the resulting diradical is disjoint or nondisjoint. Easy zero QI occurs when the rth and sth atoms are both starred or both unstarred. In this case, the attached two atoms are both unstarred or both starred, respectively. Therefore, in the resulting diradicals, $|N_S - N_U| = 2$, leading to a nondisjoint diradical. The same is true for the process of deleting two atoms. On the other hand, the hard zero QI occurs when one of the rth and sth atoms is starred and the other is unstarred. In the resulting diradical, $N_S = N_U$, leading to a disjoint diradical. The same is true for the process of deleting two atoms.

Figs. 2 and 3 summarize the correlation for $N = 2$ and $N = 4$ diradicals based on an ethylene or butadiene core. When both two-carbon atoms are attached to C1 atom of ethylene, a well-studied nondisjoint diradical, TMM (1,3), is generated. For $N = 4$, a butadiene framework, the 1,1 and 1,3 cases, which correspond to an easy zero case, provide a nondisjoint diradical, which can be viewed as a derivative of TMM. The 2,3 case, which corresponds to a hard zero case, provides a well-studied disjoint diradical, TME (1,3).

Further examples of the relationship we have proven, for linear chain skeletons with $N = 6$ and $N = 8$ are shown in *SI Appendix*, Figs. S1 and S2. Still other examples are shown in *SI Appendix*, Figs. S3, S13, and S16. Here we illustrate but two cases, each with its own special features.

First, consider an example of the consequence of the hard zero in a cyclic system, here derived from 1,4-paraquinodimethane (*p*-QDM), as shown in Fig. 7. Recently, the transmission properties
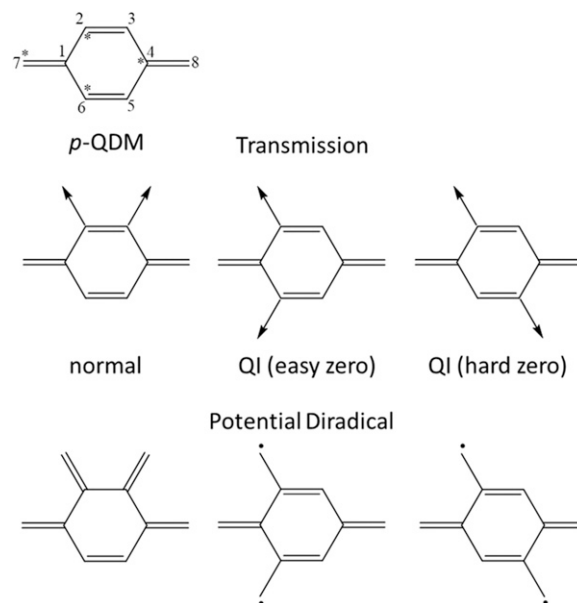
Fig. 7. The 1,4-paraquinodimethane molecule, with its numbering system (*Top*). The arrows show attachment of electrodes in a molecular transmission experiment (*Middle*). The primary contributor in a VB description of the corresponding potential diradical (*Bottom*).

through p-QDM have been reported by two of the authors and coworkers (25). It was shown that the 2,5 and 2,6 connections lead to QI; the QI features of the 2,5 and 2,6 connections are classified into hard zero and easy zero, respectively. From Fig. 7, we can see that the resulting augmented molecules of the 2,5 case (hard zero) and 2,6 case (easy zero) are a disjoint diradical and a nondisjoint diradical, respectively. They are called tetramethylenebenzenes (TMBs). The TMB resulting from 2,5 substitution has attracted interest in the diradical community (29), being predicted theoretically (66) and observed experimentally (67) to have a singlet ground state, a consequence of the disjoint nature of the NBMOs. On the other hand, the 2,3 case exhibits neither a QI feature nor a diradical structure (see *SI Appendix*, Fig. S11 for the transmission spectra).

Second, the Green's function allows one to identify diradicals that are less obvious. Consider benzocyclobutadiene **1** (see Fig. 8). Although this molecule is a highly reactive compound that readily undergoes dimerization, it has been actually isolated in an Ar matrix at very low temperature (68). The 3,6 connection of electrodes to this molecule exhibits QI (see *SI Appendix*, Fig. S12 and ref. 69), yet its augmented structure **2** seems to be described by an all-bonded Lewis or Kekulé resonance structure. However, things are not quite as they seem.

Parent molecule **1** itself is a closed-shell molecule with a highest occupied molecular orbital–lowest occupied molecular orbital gap of 0.53β at the Hückel level. Therefore, Eq. **9** is applicable to this system, and $G(3,6) = 0$, which is obtained from the calculation of the inverse of the Hamiltonian matrix for molecule **1**, leading to $\det(\mathbf{H}_{+rs}) = 0$. The existence of at least two NBMOs in molecule **2** is predicted. Also, remarkably, molecule **2** indeed has a pair of degenerate NBMOs, shown in Fig. 8. The NBMOs suggest that molecule **2** should be a disjoint diradical, which is consistent with the QI due to the hard zero.

Two smaller systems of this type are based on butalene **3** and dimethylenecyclobutene **4**. The 2,3 electrode attachment to the former and 5,6 electrode attachment to the latter lead to hardzero Green's function elements (Fig. 9), and to disjoint diradicals if methylenes are added at these sites. Incidentally, transition metal complexes of the 5,6 expanded hydrocarbons, aka divinylcyclobutadiene, are known (70).

Molecules **2**, **5**, and **6** belong to a rare class of hydrocarbons for which a classical, Lewis or Kekulé, structure is misleading—despite such a structure being readily drawn, the molecule is most certainly a diradical, in having two NBMOs and two elec-
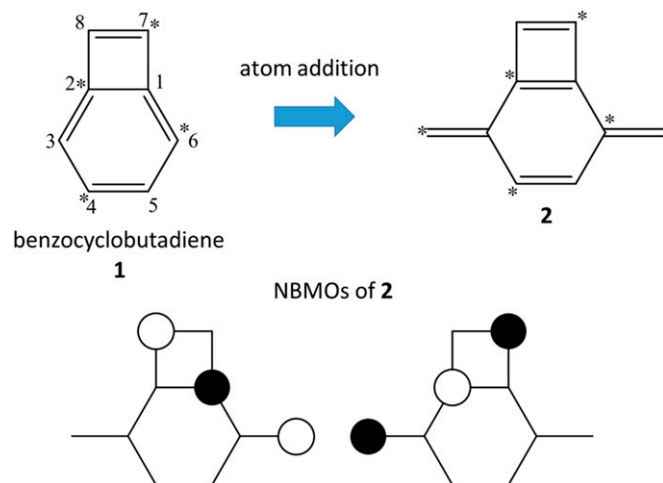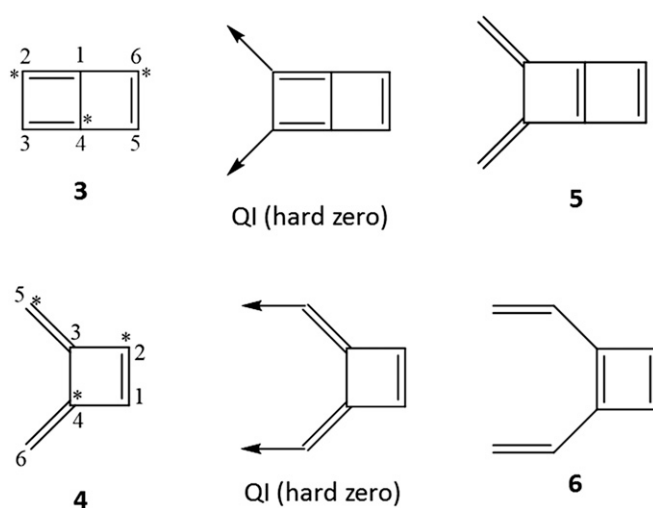
Fig. 9. The 2,3 and 5,6 expanded hydrocarbons for butalene **3** (*Top*) and dimethylenecyclobutene **4** (*Bottom*).

trons in them. Cyclobutadiene and planar cyclooctatetraene are the archetypes here. This kind of discrepancy between the presence of NBMOs and CS theory was recognized by Klein et al. (33). For it to manifest itself, one needs $4n$-membered rings. Such structures are troublesome in a number of ways, yielding abnormal Pauling bond orders, i.e., larger than unity or negative (60, 71). Whether the ground state of the molecule is a singlet or triplet requires further analysis; here the considerations of Ovchinnikov and of Klein et al. (33) are guides.

Conclusions

We have constructed a conceptual bridge between two concepts in different fields of chemistry, namely QI, in molecular conductance, and diradical existence. QI is characterized by zero elements in the matrix representation of the Green's function. We prove a theorem that relates such QI features to the determinant of the Hückel matrix of a molecule augmented by replacing the two electrode attachments with two radical sites or reduced by deleting the two atoms, to which electrodes are attached.

The existence of QI in transmission thus simultaneously implies the existence of a diradical, and vice versa. The relationship is a strong one for π-alternant systems, and can be used in either direction—relating the observation or calculation of QI to the existence of a diradical, or using diradical character to infer QI in transmission.

There is also further detail in the correspondence. Based on the starring procedure for alternant hydrocarbons, the two types of QI, termed by us hard zero and easy zero, find their counterparts in two types of diradicals of the augmented/reduced hydrocarbon, namely disjoint and nondisjoint. The validity of this remarkable relationship is checked not only for simple linear and cyclic π-systems, such as polyenes and benzene, but also for more complicated π-systems, such as p-QDM, benzeocyclobutadiene, butalene, and dimethylenecyclobutene. It may be—as some of the latter cases, which contain a $4n$-membered ring, show—that one can write a classical Lewis or Kekulé structure for a system, yet it still is a diradical, and the relationship between QI and diradical character holds.

Fig. 8. Schematic representation of attaching two atoms to the third and sixth atoms in benzocyclobutadiene (*Top*), and twofold degenerate NBMOs of the augmented molecule (**2**) (*Bottom*).

1. Borden WT (1982) *Diradicals* (Wiley-Interscience, New York).
2. Rajca A (1994) Organic diradicals and polyradicals: From spin coupling to magnetism? *Chem Rev* 94(4):871–893.
3. Abe M (2013) Diradicals. *Chem Rev* 113(9):7011–7088.
4. Lambert CJ (2015) Basic concepts of quantum interference and electron transport in single-molecule electronics. *Chem Soc Rev* 44(4):875–888.
5. Lee HW (1999) Generic transmission zeros and in-phase resonances in time-reversal symmetric single channel transport. *Phys Rev Lett* 82(11):2358–2361.
6. Solomon GC, et al. (2008) Understanding quantum interference in coherent molecular conduction. *J Chem Phys* 129(5):054701.
7. Tada T, Yoshizawa K (2002) Quantum transport effects in nanosized graphite sheets. *ChemPhysChem* 3(12):1035–1037.
8. Solomon GC, Herrmann C, Hansen T, Mujica V, Ratner MA (2010) Exploring local currents in molecular junctions. *Nat Chem* 2(3):223–228.
9. Markussen T, Stadler R, Thygesen KS (2010) The relation between structure and quantum interference in single molecule junctions. *Nano Lett* 10(10):4260–4265.
10. Tsuji Y, Staykov A, Yoshizawa K (2011) Orbital views of molecular conductance perturbed by anchor units. *J Am Chem Soc* 133(15):5955–5965.
11. Taniguchi M, et al. (2011) Dependence of single-molecule conductance on molecule junction symmetry. *J Am Chem Soc* 133(30):11426–11429.
12. Kirk ML, et al. (2013) Superexchange contributions to distance dependence of electron transfer/transport: Exchange and electronic coupling in oligo(para-phenylene)- and oligo(2,5-thiophene)-bridged donor-bridge-acceptor biradical complexes. *J Am Chem Soc* 135(45):17144–17154.
13. Stasiw DE, et al. (2015) Determining the conformational landscape of σ and π coupling using para-phenylene and "Aviram–Ratner" bridges. *J Am Chem Soc* 137(29):9222–9225.
14. Nishizawa S, Hasegawa J, Matsuda K (2013) Theoretical investigation of the β value of the π-conjugated molecular wires by evaluating exchange interaction between organic radicals. *J Phys Chem C* 117(49):26280–26286.
15. Shinomiya M, Higashiguchi K, Matsuda K (2013) Evaluation of the β value of the phenylene ethynylene unit by probing the exchange interaction between two nitronyl nitroxides. *J Org Chem* 78(18):9282–9290.
16. Nishizawa S, Hasegawa J, Matsuda K (2014) Theoretical investigation of the dependence of exchange interaction on dihedral angle between two aromatic rings in a wire unit. *Chem Lett* 43(4):530–532.
17. Herrmann C, Elmisz J (2013) Electronic communication through molecular bridges. *Chem Commun (Camb)* 49(89):10456–10458.
18. Proppe J, Herrmann C (2015) Communication through molecular bridges: Different bridge orbital trends result in common property trends. *J Comput Chem* 36(4):201–209.
19. Datta S (1995) *Electronic Transport in Mesoscopic Systems* (Cambridge Univ Press, Cambridge, UK).
20. Büttiker M, Imry Y, Landauer R, Pinhas S (1985) Generalized many-channel conductance formula with application to small rings. *Phys Rev B Condens Matter* 31(10):6207–6215.
21. Tsuji Y, Hoffmann R, Movassagh R, Datta S (2014) Quantum interference in polyenes. *J Chem Phys* 141(22):224311.
22. Solomon GC, et al. (2008) Quantum interference in acyclic systems: Conductance of cross-conjugated molecules. *J Am Chem Soc* 130(51):17301–17308.
23. Movassagh R, Strang G, Tsuji Y, Hoffmann R (2015) . The exact form of the green's function of the Hückel (tight binding) model. arXiv:1407.4780.
24. Solomon GC, Bergfield JP, Stafford CA, Ratner MA (2011) When "small" terms matter: Coupled interference features in the transport properties of cross-conjugated molecules. *Beilstein J Nanotechnol* 2(1):862–871.
25. Pedersen KGL, et al. (2014) Quantum interference in off-resonant transport through single molecules. *Phys Rev B* 90(12):125413.
26. Dewar MJS (1969) *The Molecular Orbital Theory of Organic Chemistry* (McGraw-Hill, New York).
27. Hicks RG, ed (2010) *Stable Radicals: Fundamentals and Applied Aspects of Odd-Electron Compounds* (Wiley, Chichester, UK).
28. Borden WT, Davidson ER (1977) Effects of electron repulsion in conjugated hydrocarbon diradicals. *J Am Chem Soc* 99(14):4587–4594.
29. Borden WT, Iwamura H, Berson JA (1994) Violations of Hund's rule in non-Kekulé hydrocarbons: Theoretical prediction and experimental verification. *Acc Chem Res* 27(4):109–116.
30. Lineberger WC, Borden WT (2011) The synergy between qualitative theory, quantitative calculations, and direct experiments in understanding, calculating, and measuring the energy differences between the lowest singlet and triplet states of organic diradicals. *Phys Chem Chem Phys* 13(25):11792–11813.
31. Hund F (1927) *Linienspektren und Periodisches System der Elemente* (Springer, Vienna).
32. Ovchinnikov AA (1978) Multiplicity of the ground state of large alternant organic molecules with conjugated bonds. *Theor Chim Acta* 47(4):297–304.
33. Klein DJ, Nelin CJ, Alexander S, Matsen FA (1982) High-spin hydrocarbons. *J Chem Phys* 77(6):3101–3108.
34. Shultz DA, Kirk ML (2014) Molecular spintronics: A web themed issue. *Chem Commun (Camb)* 50(56):7401–7402.
35. Li JJ, et al. (2015) Giant single-molecule anisotropic magnetoresistance at room temperature. *J Am Chem Soc* 137(18):5923–5929.
36. Castellanoa M, et al. (2015) Metallosupramolecular approach toward multifunctional magnetic devices for molecular spintronics. *Coord Chem Rev* 303:110–138.
37. Marcus RA, Sutin N (1985) Electron transfers in chemistry and biology. *Biochim Biophys Acta* 811(3):265–322.
38. Heisenberg W (1928) Zur theorie des ferromagnetismus. *Z Phys* 49(9-10):619–636.
39. Hay PJ, Thibeault JC, Hoffmann R (1975) Orbital interactions in metal dimer complexes. *J Am Chem Soc* 97(17):4884–4899.
40. Kramers HA (1934) L'interaction entre les atomes magnétogènes dans un cristal paramagnétique. *Physica* 1(1):182–192.
41. Anderson PW (1950) Antiferromagnetism. Theory of superexchange interaction. *Phys Rev* 79(2):350–356.
42. McConnell HM (1960) Theory of singlet-triplet splittings in large biradicals. *J Chem Phys* 33(1):115–121.
43. Brunold TC, Gamelin DR, Solomon EI (2000) Excited-state exchange coupling in bent Mn (III)-O-Mn (III) complexes: Dominance of the π/σ superexchange pathway and its possible contributions to the reactivities of binuclear metalloproteins. *J Am Chem Soc* 122(35):8511–8523.
44. Felthouse TR, Hendrickson DN (1978) Magnetic exchange interactions in binuclear transition-metal complexes. 17. Benzidine and p-phenylenediamine, extended aromatic diamine bridging ligands in binuclear copper (II) 2, 2', 2''-triaminotriethylamine and vanadyl bis (hexafluoroacetylacetonate) complexes. *Inorg Chem* 17(9):2636–2648.
45. Crutchley RJ (1994) Intervalence charge transfer and electron exchange studies of dinuclear ruthenium complexes. *Advances in Inorganic Chemistry*, ed Sykes AG (Elsevier, New York), Vol 41, pp 273–325.
46. Fabre M, Bonvoisin J (2007) Electronic and magnetic communication in mixed-valent and homovalent ruthenium complexes containing phenylcyanamide type bridging ligands. *J Am Chem Soc* 129(5):1434–1444.
47. Yoshizawa K, Hoffmann R (1995) The role of orbital interactions in determining ferromagnetic coupling in organic molecular assemblies. *J Am Chem Soc* 117(26):6921–6926.
48. Nelsen SF, Ismagilov RF, Teki Y (1998) Comparison of the singlet, triplet energy gap of a symmetrical diradical dication with ET parameters derived from its optical spectrum. *J Am Chem Soc* 120(9):2200–2201.
49. Weiss EA, et al. (2004) Making a molecular wire: Charge and spin transport through para-phenylene oligomers. *J Am Chem Soc* 126(17):5577–5584.
50. Shil S, Bhattacharya D, Misra A, Klein DJ (2015) A high-spin organic diradical as a spin filter. *Phys Chem Chem Phys* 17(36):23378–23383.
51. Kirk ML, et al. (2013) Electronic and exchange coupling in a cross-conjugated D-B-A biradical: Mechanistic implications for quantum interference effects. *J Am Chem Soc* 135(39):14713–14725.
52. Powell PD (2011) Calculating determinants of block matrices. arXiv:1112.4379.
53. Silverster JR (2000) Determinants of block matrices. *Math Gaz* 84(501):460–467.
54. Stuyver T, Fias S, De Proft F, Geerlings P (2015) Back of the envelope selection rule for molecular transmission: A curly arrow approach. *J Phys Chem C* 119(47):26390–26400.
55. Coulson C, Rushbrooke G (1940) Note on the method of molecular orbitals. *Proc Cambridge Philos Soc* 36(2):193–200.
56. Dewar MJS, Longuet-Higgins HC (1952) The correspondence between the resonance and molecular orbital theories. *Proc R Soc A Math Phys Sci* 214(1119):482–493.
57. Ham NS (1958) Mobile bond orders in the resonance and molecular orbital theories. *J Chem Phys* 29(6):1229–1231.
58. Pauling L, Brockway LO, Beach JY (1935) The dependence of interatomic distance on single bond-double bond resonance. *J Am Chem Soc* 57(12):2705–2709.
59. Graovac A, Gutman I, Trinajstić N, Živković T (1972) Graph theory and molecular orbitals application of Sachs theorem. *Theoret chim Acta (Berl)* 26(1):67–78.
60. Hosoya H, Hosoi K (1976) Topological index as applied to π-electronic systems. III. Mathematical relations among various bond orders. *J Chem Phys* 64(3):1065–1073.
61. Aono S, Nishikawa K (1980) Use of propagators in the Hückel model. *Bull Chem Soc Jpn* 53(12):3418–3423.
62. Caroli C, Combescot R, Nozieres P, Saint-james D (1971) Direct calculation of the tunneling current. *J Phys C Solid State Phys* 4(8):916–929.
63. Mujica V, Kemp M, Ratner MA (1994) Electron conduction in molecular wires. I. A scattering formalism. *J Chem Phys* 101(8):6849–6855.
64. Stuyver T, Fias S, De Proft F, Fowler PW, Geerlings P (2015) Conduction of molecular electronic devices: Qualitative insights through atom-atom polarizabilities. *J Chem Phys* 142(9):094103.
65. Stuyver T, Fias S, De Proft F, Geerlings P (2015) The relation between delocalization, long bond order structure count and transmission: An application to molecular wires. *Chem Phys Lett* 630:51–56.
66. Lahti PM, Rossi A, Berson JA (1985) Ab initio study of 1,2,4,5-tetramethylenebenzene: A disjoint non-Kekule molecule with a possible singlet ground state. *J Am Chem Soc* 107(14):4362–4363.
67. Reynolds JH, et al. (1992) A kinetically stable singlet state of 1,2,4,5-tetramethylenebenzene. *J Am Chem Soc* 114(2):763–764.
68. Chapman OL, Chang CC, Rosenquiste NR (1976) Benzocyclobutadiene. *J Am Chem Soc* 98(1):261–262.
69. Pedersen KGL, Borges A, Hedegård P, Solomon GC, Strange M (2015) Illusory connection between cross-conjugation and quantum interference. *J Phys Chem C* 119(48): 26919–26924.
70. Berens G, Kaplan F, Rimerman R, Roberts BW, Wissner A (1975) Synthesis of tricarbonyliron complexes of functional 1,2-disubstituted cyclobutadienes. *J Am Chem Soc* 97(24):7076–7085.
71. Herndon WC (1974) Resonance theory. VI. Bond orders. *J Am Chem Soc* 96(25):7605–7614.