

Understanding and Controlling Crosstalk between Parallel Molecular Wires

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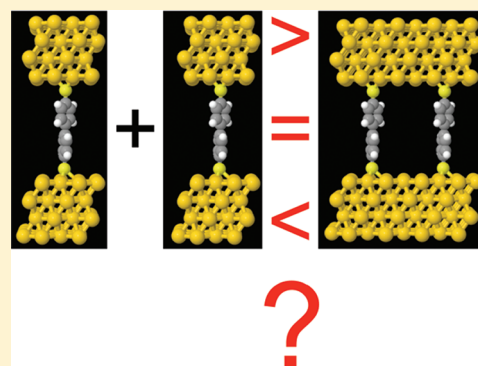
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ABSTRACT: Cooperative effects between molecular wires affect conduction through the wires, and studies have yet to clarify the conditions under which these effects enhance (diminish) conduction. Using a simple but general model, we attribute this crosstalk to the duality of energetic splitting and phase interference between the wires' conduction channels. In most cases, crosstalk increases (decreases) conductance when the Fermi level is far from (close to) an isolated wire's resonance. Finally, we discuss strategies for controlling crosstalk between parallel molecular wires.

SECTION: Electron Transport, Optical and Electronic Devices, Hard Matter



The flow of electric current through molecules and the transfer of charge between molecules and substrates are interesting problems for both their intrinsic conceptual challenges and their applications to solar cells, scanning probe microscopies, and molecular electronics.^{1–3} Although considerable progress has been achieved in describing electron transport through a single molecular wire,³ the scaling of these results to multiple wires in parallel remains nebulous.^{4–16} In many cases, the conductance per wire increases over that of a single wire;^{4–8,11,13} however, decreases have also been reported.^{6,8,10–12} Regardless, such a change in conductance per wire is a manifestation of crosstalk,^{17,18} a conventionally undesirable effect indicating insufficient insulation between the wires. Direct, interwire coupling (e.g., π – π interactions) and substrate-mediated coupling are both responsible for this crosstalk^{5–7} and are collectively termed “cooperative effects”.¹⁹ Despite understanding the consequences of direct or substrate-mediated coupling independently,^{4,14,15,20} the conditions under which cooperative effects increase (decrease) the conductance per wire have yet to be identified. Interactions between the two types of coupling, introducing the possibility of quantum interference effects, are likely to be key factors and need to be investigated. Unraveling the underlying physics of conduction through multiple molecular wires is imperative for the viability of molecular electronic devices that utilize molecular wires in parallel.

In this Letter, we explore the combined role of these two couplings on electron transport using a one-electron tight-binding model. Similar models have previously been employed to expose the fundamental physics of molecular conduction^{4,5,8,21,22} and have the advantage of producing exact, (semi)analytical results.

This benefit also applies to the present model. Specifically, we calculate the conduction channels^{23–25} formed by two parallel molecular wires within the Landauer–Imry (coherent scattering) formalism.²⁶ As we will show, direct and substrate-mediated couplings each split the conduction channels, and this splitting is the primary symptom of crosstalk between molecular wires. Having revealed the nature of crosstalk, we proceed to discuss criteria for crosstalk to increase the conductance per wire and mechanisms for controlling electron transport through parallel molecular wires.

We model each electrode by a semi-infinite cubic lattice of single-state sites, where each site has energy ε and couples to its nearest neighbors with element V_c .^{8,22,27,28} In what follows, we take $V_c = -0.82$ eV,²⁹ define ε as our energy origin (centering the band around $E = 0$), and denote the states at the electrode surface by $|m, n\rangle$, where m and n are integers describing the coordinates of a site on the electrode surface. Likewise, each molecular wire is represented by a single state, $|\varphi_i\rangle$, which is conceivably the highest-occupied or lowest-unoccupied molecular orbital. The wire Hamiltonian is

$$\mathbf{H}_{\text{wire}} = \alpha \sum_{j=1}^2 |\varphi_j\rangle\langle\varphi_j| + \beta |\varphi_1\rangle\langle\varphi_2| + \beta^* |\varphi_2\rangle\langle\varphi_1| \quad (1)$$

where α is the energy of each molecular state and β is the direct, interwire coupling (which depends on, and generally decays with, the

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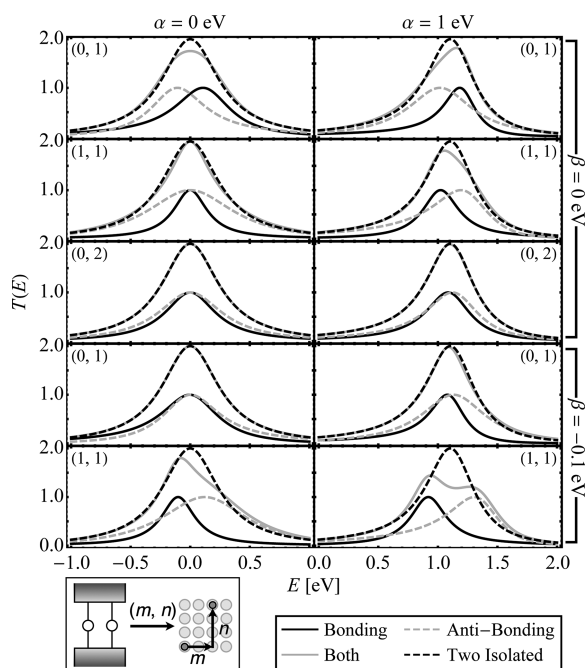


Figure 1. Transmission spectra for molecular wires in arrangement (m,n) (bottom-left schematic); the wire levels are at energy α . Nearby wires exhibit crosstalk (that is, their spectra differ from those of two isolated wires) in the absence of direct, interwire coupling ($\beta = 0$, top three rows). Crosstalk decreases as the molecules are moved farther apart. When direct coupling is added (bottom two rows), crosstalk is either reduced or enhanced. Decomposition into the “bonding” and “anti-bonding” conduction channels [$T_+(E)$ and $T_-(E)$ in eq 8, respectively] shows that β contributes to crosstalk and channel splitting. Tuning β can largely cancel the effects of crosstalk (fourth row); however, the proper β depends on the wires’ arrangement (fifth row).

interwire separation). For simplicity, we assume that the wires are identical, that β is real, and that $|\varphi_1\rangle$ and $|\varphi_2\rangle$ are orthonormalized. Furthermore, each wire sits atop a single electrode site; the electrode–wire coupling operator is

$$V = V|\varphi_1\rangle\langle 0,0| + V|\varphi_2\rangle\langle m,n| \quad (2)$$

where $V = -0.45$ eV.²⁹ We designate the wire arrangement described in eq 2 by (m,n) ; see Figure 1. Finally, if we assume that the wires couple identically to both electrodes (for simplicity), the total system Hamiltonian is

$$H = \begin{bmatrix} H_{\text{elec}} & V^\dagger & 0 \\ V & H_{\text{wire}} & V \\ 0 & V^\dagger & H_{\text{elec}} \end{bmatrix}$$

where H_{elec} is the Hamiltonian of either electrode.

Due to the vast (infinite) sizes of the electrodes and our focused interest in electron transport through the two wires, we write an effective Hamiltonian for the wires, $H_{\text{wire}} + 2\Sigma(E)$, where $\Sigma(E)$ is the self-energy of coupling the wires to an electrode¹ and the factor of 2 reflects identical coupling of the wires to both electrodes. Formally,¹ $\Sigma(E) = V G_{\text{elec}}(E) V^\dagger$, where $G_{\text{elec}}(E)$ is the (retarded) Green function³⁰ of an isolated electrode. The identical coupling between either electrode and both molecules also produces $\Sigma_{00}(E) = \langle \varphi_1 | \Sigma(E) | \varphi_1 \rangle = \langle \varphi_2 | \Sigma(E) | \varphi_2 \rangle$ and $\Sigma_{mn}(E) = \langle \varphi_1 | \Sigma(E) | \varphi_2 \rangle = \langle \varphi_2 | \Sigma(E) | \varphi_1 \rangle$. While the following derivations are general, our choice of electrodes facilitates this

analysis by providing semianalytical forms for the matrix elements of $G_{\text{elec}}(E)$ ²⁸

$$G_{|m-m'|, |n-n'|}(E) = \langle m', n' | G_{\text{elec}}(E) | m, n \rangle$$

$$= \frac{1}{2|V_e|\pi^2} \int_0^\pi d\theta_1 \cos(|m-m'|\theta_1) \int_0^\pi d\theta_2 \cos(|n-n'|\theta_2)$$

$$\times \Xi \left[\frac{E}{2|V_e|} + \cos(\theta_1) + \cos(\theta_2) \right] \quad (3)$$

where

$$\Xi(x) = 2x - 2 \operatorname{sign}(x+1) \sqrt{x^2 - 1}$$

Furthermore, eq 3 shows $G_{mn}(E) = G_{nm}(E)$, implying that arrangements (m,n) and (n,m) are the same (for our specific system). More complicated systems, such as those caused by using a less symmetric surface or different molecule–electrode binding configurations,²² are easily included in the following derivation through $\Sigma_{00}(E)$ and $\Sigma_{mn}(E)$.

Within a coherent scattering formalism,²⁶ the zero-bias conductance through the wires at zero temperature is

$$G(0) = \frac{2e^2}{h} T(E_F) \quad (4)$$

where E_F is the Fermi level, and, assuming identical coupling to both electrodes

$$T(E) = \operatorname{Tr}[\Gamma(E)G(E)\Gamma(E)G^\dagger(E)] \quad (5)$$

is the transmission through the wires. For use in eq 5, $\Gamma(E) = i[\Sigma(E) - \Sigma^\dagger(E)]$ and $G(E) = [E\mathbf{I} - H_{\text{wire}} - 2\Sigma(E)]^{-1}$.

We begin by examining the transmission through two isolated wires, that is, $\beta = 0$ and $m,n \rightarrow \infty$. In this case, the transmission is

$$T_{\text{iso}}(E) = \frac{8[\operatorname{Im} \Sigma_{00}(E)]^2}{|E - \alpha - 2\Sigma_{00}(E)|^2} \quad (6)$$

and is displayed in Figure 1. As is typical of conduction through single molecules,³ the transmission spectrum is roughly Lorentzian, where the sole maximum corresponds to the wire resonance. At this resonance, each conduction channel is completely open, and the transmission is equal to the number of conduction channels (here, two). Moreover, from eq 6, the resonance occurs at E_R^1 , given by

$$E_R^1 - \alpha - 2 \operatorname{Re} \Sigma_{00}(E_R^1) = 0 \quad (7)$$

Proceeding to two coupled wires, Figure 1 shows the transmission spectra for two wires in various arrangements. In the absence of direct coupling, nearby wires display crosstalk [i.e., different $T(E)$ from the isolated wires] both near and far from the isolated wire resonance. Crosstalk disappears as the wires move apart, consistent with our intuition from conventional electronics,^{17,18} because substrate–mediated coupling decays with distance.^{5,7,28} Finally, the addition of direct coupling increases crosstalk in the (1,1) arrangement, as expected; however, increasing $|\beta|$ in the (0,1) arrangement surprisingly cancels crosstalk.

That direct coupling between the wires can either amplify or reduce crosstalk is unintuitive. Clearly, each wire is no longer an independent conduction channel, and determination of the

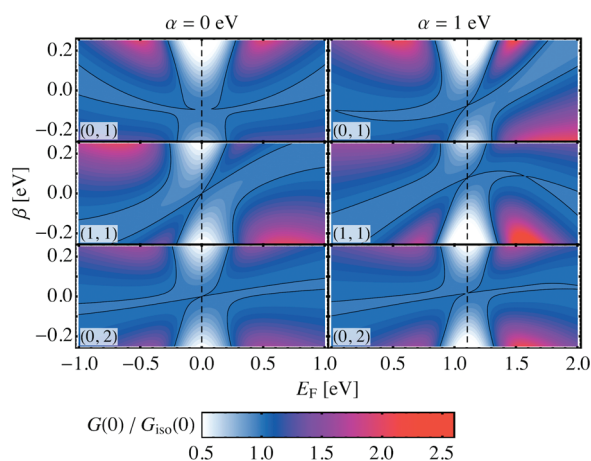


Figure 2. The conductance through two coupled wires relative to that through two isolated wires as a function of E_F , each wire's site energy (α), and the direct, interwire coupling (β). The solid black curves trace a ratio of one; crosstalk has no net effect in these cases. At the isolated wire's resonance (E_R^1 , dashed black lines), crosstalk never increases conductance over the isolated wires and only matches it at $\beta = -2\text{Re}\Sigma_{mn}(E_R^1)$. Off resonance, crosstalk tends to increase conductance by shifting the channels' resonances away from the isolated wire resonance (see Figure 1).

independent channels will help us understand the relationship between coupling and crosstalk. Using the transmission eigen-channel algorithm,²⁴ this system's channels are the bonding $[(|\varphi_1\rangle + |\varphi_2\rangle)/\sqrt{2}]$ and antibonding $[(|\varphi_1\rangle - |\varphi_2\rangle)/\sqrt{2}]$ channels, which have transmissions

$$T_{\pm}(E) = \frac{4[\text{Im}\Sigma_{00}(E) \pm \text{Im}\Sigma_{mn}(E)]^2}{|E - \alpha \mp \beta - 2[\Sigma_{00}(E) \pm \Sigma_{mn}(E)]|^2} \quad (8)$$

These transmissions are displayed in Figure 1, and $T_+(E)$ corresponds to the bonding channel. From eq 8, each channel resembles a single-wire channel with energy $\alpha \pm \beta$ that couples to surface sites $|0,0\rangle$ and $|m,n\rangle$.²²

Similar to an isolated wire, each channel's transmission spectrum is quasi-Lorentzian with a resonance at E_R^{\pm}

$$E_R^{\pm} - \alpha \mp \beta - 2\text{Re}[\Sigma_{00}(E_R^{\pm}) \pm \Sigma_{mn}(E_R^{\pm})] = 0 \quad (9)$$

Comparing eqs 7 and 9, E_R^{\pm} shifts from E_R^1 by $\mp[\beta + 2\text{Re}\Sigma_{mn}(E_R^1)]$, which is an effective splitting between the channels induced by both the direct (β) and substrate-mediated ($2\text{Re}\Sigma_{mn}$) couplings. This splitting can be removed by balancing the two couplings, $\beta = -2\text{Re}\Sigma_{mn}(E_R^1)$, in which case $E_R^{\pm} = E_R^1$. For example, wires in the (0,1) arrangement exhibit relatively strong substrate-mediated coupling, but an apt amount of direct coupling ($\beta \approx -0.1$ eV) significantly reduces crosstalk. Arrangements with more interwire distance have less substrate-mediated coupling and thus require smaller direct coupling for balance; larger $|\beta|$ will then intensify crosstalk.

Having identified the underlying physical manifestation of crosstalk between molecular wires—energetic splitting between the conduction channels—we turn to the relationship between crosstalk and conduction. Under what conditions does crosstalk increase (decrease) the zero-bias conductance per wire? To investigate, we plot the conductance ratio between coupled and isolated wires, $G(0)/G_{\text{iso}}(0)$, in Figure 2. At the

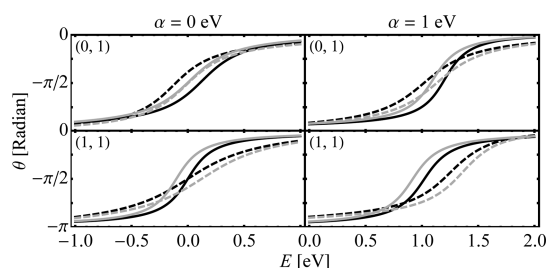


Figure 3. Phases of the bonding (solid lines) and antibonding (dashed lines) channels for various arrangements and couplings. The black lines correspond to only substrate-mediated coupling ($\beta = 0$), and the gray lines are $\beta = -0.1$ eV. Generally, these phases exhibit Breit–Wigner distributions and smoothly increase by π as the energy sweeps past a resonance.³⁸ Near the isolated wire resonance ($E \approx E_R^1$), channels for wires in the (0,1) arrangement are relatively out of phase in the absence of direct coupling, whereas $\beta = -0.1$ eV brings them into phase. Because substrate-mediated coupling decays with interwire distance, the addition of direct coupling in the (1,1) arrangement imbalances the couplings and takes the channels out of phase with each other. Comparing with Figures 1 and 2, crosstalk indicates that the channels are mutually out of phase.

isolated wire resonance ($E_F = E_R^1$), the isolated wire's channel is completely open, and crosstalk cannot improve the conductance. At best, crosstalk makes both channels resonant at E_R^1 , which, from eq 9, occurs when $\beta = -2\text{Re}\Sigma_{mn}(E_R^1)$.

Away from this resonance ($E_F \neq E_R^1$), however, crosstalk tends to increase conductance. For most β values, the bonding and antibonding channels are shifted away from E_R^1 in opposite directions, meaning that E_R^+ or E_R^- will most likely be closer to E_F than E_R^1 . Because transmission through each channel decays roughly as a Lorentzian away from its respective resonance, the closest resonance ought to produce the largest transmission. (The scant decrease in off-resonance conductance is caused by deviation from a pure Lorentzian line shape.)

Akin to inelastic effects,^{31,32} crosstalk tends to diminish conductance near resonance ($E_F \approx E_R^1$) while enhancing it off resonance ($E_F \neq E_R^1$). In this sense, molecular wires resemble conventional wires near resonance; crosstalk is undesirable and most readily removed by separating the wires (where both the direct and substrate-mediated couplings decay to 0). Off resonance, though, parallel molecular wires stray from conventional electronics; crosstalk is usually beneficial. For certain choices of the wire site level (α) and direct, interwire coupling (β), 2-fold (or more) increases in conductance are possible.

At first glance, designing molecular wires with these desirable values of α and β seems like an engineering problem; however, the relationship between α , β , and crosstalk subtly introduces novel opportunities for controlling conduction. First, the site energy α and direct coupling β are not static properties and can be manipulated in various ways.^{16,33–37} Such dynamic tuning of these parameters may lead to switches or memory elements that operate on molecular time and length scales. For example, the application of a gating voltage shifts α relative to the Fermi level. Furthermore, β is sensitive to the relative orientation (geometry) of the wires,¹⁶ and numerous mechanisms can change these geometries, including photoisomerization,^{33,34} current-induced dynamics,³⁵ and coherent control.^{36,37}

Second, the balance of direct and substrate-mediated couplings in the channel splitting suggests interference effects between the channels, which may be exploitable. Following ref

38, the phase of each channel is

$$\tan[\theta_{\pm}(E)] = \frac{2 \operatorname{Im}[\Sigma_{00}(E) \mp \Sigma_{mn}(E)]}{E - \alpha \pm \beta - 2 \operatorname{Re}[\Sigma_{00}(E) \mp \Sigma_{mn}(E)]} \quad (10)$$

and Figure 3 shows $\theta_{\pm}(E)$ for various arrangements and couplings. Crosstalk indicates that the channels are out of phase with each other (as seen by comparing Figure 3 with Figures 1 and 2) and that balancing the two couplings brings the channels into phase. In this sense, the channels' phase relationship is a dual to energetic splitting,³⁸ both indicate crosstalk. Moreover, this phase interpretation suggests a new application for coherent control schemes,^{39–41} which use phase relations to manipulate dynamics. A similar quantum-interference-based control strategy for conduction through two channels within a single molecule has been proposed and theoretically demonstrated.⁴²

In summary, we have presented a semianalytical formulation of electron transport through two parallel molecular wires. While our model neglects vibronic coupling and electron–electron interactions, both of which may be particularly important on resonance, these results reveal the fundamental and general nature of crosstalk between molecular wires. Direct, interwire coupling and substrate-mediated coupling each induce crosstalk by energetically splitting (or, alternatively, spoiling the phase relationship of) the conduction channels. As with conventional electronics, crosstalk can be removed by separating the wires; however, unlike conventional electronics, crosstalk can also be desirable in molecular wires. These results explain previous observations regarding the conductance of a collection of molecular wires as compared to that of a single wire.^{4–16} If the Fermi level is near an isolated wire's resonance, crosstalk almost invariably hurts conduction, whereas crosstalk usually increases conduction when E_F is away from such a resonance. Finally, understanding the underlying physical symptoms of crosstalk suggests mechanisms for controlling conduction through parallel molecular wires. Crosstalk can be enhanced or diminished by manipulating the relative geometry of the wires or, as we propose, by coherently controlling the phase relationship between the channels.

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