Chiral Control of Electron Transmission through Molecules

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Electron transmission through chiral molecules induced by circularly polarized light can be very different for mirror-image structures, a peculiar fact given that the electronic energy spectra of the systems are identical. We propose that this asymmetry—as large as 10% for resonant transport—arises from different dynamical responses of the mirrored structures to coherent excitation. This behavior is described in the context of a general novel phenomenon of *current transfer* (transfer of charge with its momentum information) and accounts for the observed asymmetry and its dependence on structure.

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Charge transfer between donor and acceptor species mediated by a molecular bridge is of intensive interest in chemistry, physics, biology, energy science, and nanoscience. Recent experiments report the control of molecular phenomena with polarization-shaped light pulses [1–3]. Indeed, theoretical studies suggest that circularly polarized light can induce molecular circular electronic currents that can be considerably larger than molecular ring currents induced by static magnetic fields [4,5]. Two of us and co-workers [6,7] have shown experimentally that the relative yield of electron transfer (ET) induced by circularly polarized light (CPL) through helical molecular bridges depends on the relative handedness of the bridge and the optical circular polarization, in spite of the indistinguishability of the underlying electronic energy spectra. Reversing the direction of the circular polarization, or of the molecular handedness, has similar effects, while the molecular handedness does not influence the transmission of electrons generated by unpolarized light.

In this Letter, we advance a simple tight-binding model that accounts for the yield asymmetries in the context of the more general phenomenon of *current transfer*. By current transfer, we refer to charge transfer in which the transferred charge carrier maintains at least some of its linear and/or angular momentum. A recent example of current transfer in photoemission appears in Ref. [8], where a biased linear momentum distribution created on a Cu (100) surface is observed in the angular distribution of the photoemitted current. Figure 1 shows several tight-binding models for current transfer. In all cases, at issue is the question of whether or not electron transfer between donor *D* and acceptor *A* is affected by, and/or carries information about, the initial electron momentum states in *D*. In Figs. 1(a) and 1(b), these states correspond to linear and circular currents, respectively. If some of the current directionality is preserved during transfer then, as

shown in Fig. 1(c), the indicated circular current in the donor would produce a helical current in the helical bridge, whose clockwise orientation implies motion towards the acceptor. An opposite donor circular current induces an anticlockwise bridge helical current that tends to move in the opposite direction, implying a lower probability to reach the acceptor. This intuitive picture is substantiated below, using the fact that the nearest-neighbor tight-binding model is equivalent to the linear model displayed in Fig. 1(d). Realization of such (partial) conservation of linear or angular momentum in the charge-transfer process and its reflection in the electron transmission probability would account for the observations of Refs. [6,7], if we assume that the circularly polarized light excites a superposition of donor states with a finite angular momentum, similar to the ring currents discussed in Refs. [4,5]. Our analysis provides a starting point for understanding how to
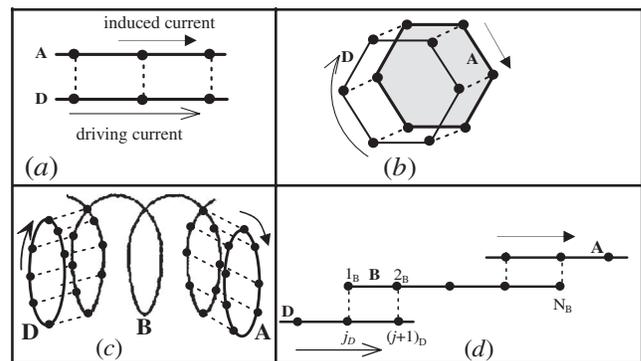
FIG. 1. Shown are specific examples of current transfer from donor to acceptor moieties [direct contact in (a), (b), transfer via intermediates in (c) and (d)]. In the case of long or cyclic chains, the wave function amplitudes of the building blocks have well-defined phase relationships that produce the effects described here.

control through-bridge electron transmission by manipulating the phase properties of the initial electronic state in conjunction with suitable bridge structures. As discussed below, it may also provide a tool for characterizing the observed transmission as a resonant or nonresonant process. Another source of yield asymmetry in transmission through helical bridges could be spin-orbit coupling involving spin-polarized photoelectrons. We believe that this effect is small in the molecular bridges of Refs. [6,7] because the spin-orbit coupling in these bridges is very weak.

Transport analysis.—We focus on the model of Fig. 1(d), which describes the donor, bridge, and acceptor species as tight-binding chains [9]. The corresponding Hamiltonian is $\hat{H} = \hat{H}_D + \hat{H}_A + \hat{H}_B + \hat{V}_{BA} + \hat{V}_{BD}$, where

$$\hat{H}_K = \sum_{j_K \in K} \varepsilon_{j_K}^{(K)} |j_K\rangle\langle j_K| + \sum_{j_K \in K} V_{j_K, j_K+1}^{(K)} |j_K\rangle\langle j_K + 1|;$$

$$K = D, A, B \tag{1}$$

and

$$\hat{V}_{KK'} = \sum_{j_K \in K} \sum_{j_{K'} \in K'} V_{j_K, j_{K'}}^{(K,K')} |j_K\rangle\langle j_{K'}|;$$

$$(K, K') = (D, B) \quad \text{or} \quad (B, A) \tag{2}$$

$\hat{H}_D$, $\hat{H}_B$, and $\hat{H}_A$ are the Hamiltonians of the D, B, and A moieties, respectively, while $\hat{V}_{BD}$ and $\hat{V}_{BA}$ are the D-B and B-A interactions. When the donor (say) is a cyclic molecule with N_D sites, as in Fig. 1(c), the periodicity is reflected by an additional cyclic boundary condition. A ring current in the donor is then represented by the complex quantum state

$$|M_D\rangle = \frac{1}{\sqrt{N_D}} \sum_{j_D=1}^{N_D} \exp\{i[2\pi M_D(j_D - 1)/N_D]\}|j_D\rangle. \tag{3}$$

In the equivalent model of Fig. 1(d), if coupling is assumed negligible among all but the nearest two sites of D and B, reversing the bridge handedness amounts to interchanging the coupling scheme from $j_D \leftrightarrow 1_B$ and $(j + 1)_D \leftrightarrow 2_B$, shown in Fig. 1(d), to $(j + 1)_D \leftrightarrow 1_B$ and $j_D \leftrightarrow 2_B$. Clearly, reversing the bridge handedness or the current direction ($M_D \rightarrow -M_D$) has the same effect on the electron dynamics. Indeed, this symmetry is observed in the ET yields reported in Refs. [6,7].

We next examine the effect of current transfer on electron-transfer yield following the initial excitation of donor states $|\phi_{in}\rangle = |M_D\rangle$ and $|\phi_{in}^*\rangle = |-M_D\rangle$. For definiteness, we assume that the excited donor state is characterized by a finite lifetime $\hbar/\gamma_D$ and that the electron-transfer signal is associated with the decay of the acceptor state with rate $\hbar/\gamma_A$ [10]. These population relaxations are described by replacing ε_{j_K} by $\varepsilon_{j_K} - i(1/2)\gamma_K$ in Eq. (1) for

the corresponding donor and acceptor sites, i.e., $\langle j_K|\hat{H}|j_K\rangle = \varepsilon_{j_K}^{(K)} - i(1/2)\gamma_K$, $K = D, A$.

Starting from states $|M_D\rangle$ and $|-M_D\rangle$, the yields for specific relaxation channels can then be calculated as follows. Starting from a given initial state $|\phi_{in}\rangle$, the probability that the acceptor state $|j_A\rangle$ is populated at time t, $P_{j_A, in}(t) = |\langle j_A|e^{-i\hat{H}t/\hbar}|\phi_{in}\rangle|^2$ [$\hat{H}$ is the (non-Hermitian) Hamiltonian of Eq. (1) with site energies $\varepsilon_j - i(1/2)\gamma_j$] can be computed in terms of the right and left eigenvectors, $|X_n^{(R)}\rangle$ and $\langle X_n^{(L)}|$ of $\hat{H}$, and the corresponding eigenvalues, $\varepsilon_n = E_n - i\Gamma_n/2$ ($\Gamma_n > 0$):

$$\langle j_A|e^{-i\hat{H}t/\hbar}|\phi_{in}\rangle = \sum_n R_{j_A, in}^{(n)} e^{-i\varepsilon_n t/\hbar};$$

$$R_{j_A, in}^{(n)} = \langle j_A|X_n^{(R)}\rangle\langle X_n^{(L)}|\phi_{in}\rangle. \tag{4}$$

The yield of the irreversible flux out of the acceptor is then

$$Y(in) = \gamma_A \int_0^\infty dt \sum_{j_A} P_{j_A, in}(t). \tag{5}$$

The asymmetry associated with the excitation circular polarization or, equivalently, with the molecular bridge handedness, may be quantified by the yields obtained from the initial states $|\phi_{in}\rangle = |M_D\rangle$ and $|\phi_{in}^*\rangle = |-M_D\rangle$

$$\mathcal{A} \equiv \frac{Y(M_D) - Y(-M_D)}{Y(M_D) + Y(-M_D)}. \tag{6}$$

Dephasing.—Current transfer, as described above, is a coherent phenomenon, sensitive to environmental dephasing interactions. To investigate this effect, we incorporate additional relaxation of coherences in the site representation of the Liouville equation for the system's density matrix $\tilde{\rho}$.

$$i\hbar \frac{d}{dt}\rho_{j,l}(t) = \sum_k [H_{j,k}\rho_{k,l}(t) - \rho_{j,k}(t)H_{kl}]$$
$$- [i(\gamma_j/2 + \gamma_l/2) + i\gamma_{jl}]\rho_{j,l}(t), \tag{7}$$

where, as above, the population relaxation rates γ_j are nonzero only for donor and acceptor states. The probability $P_{j_A, in}(t) = \rho_{j_A, j_A}(t)$ needed in Eq. (5) is obtained from Eq. (7) using the initial condition $\hat{\rho}(t = 0) = |\phi_{in}\rangle\langle\phi_{in}|$.

Model calculation.—We demonstrate the concept using the minimal model of Fig. 2: a bridge (sites 3 to $N - 1$) interacting with a donor (represented by two sites 1 and 2 and an acceptor site, N). All bridge site energies are taken equal ($\varepsilon_{j_B}^{(B)} = \varepsilon_{br}$), and similarly for the bridge nearest-neighbor couplings ($V_{j_B, j_B+1}^{(B,B)} = \beta_{br}$), and for the donor-bridge and acceptor-bridge couplings ($V_{1,3}^{(D,B)} = V_{2,4}^{(D,B)} = V_{N-1,N}^{(B,A)} = V$). The complex energies of the donor sites (1 and 2) and acceptor site (N) are taken to be $\varepsilon - i(1/2)\gamma_D$, ε, and $\varepsilon - i(1/2)\gamma_A$. The physics of the electron transmission asymmetry reported in Refs. [6,7] is captured by
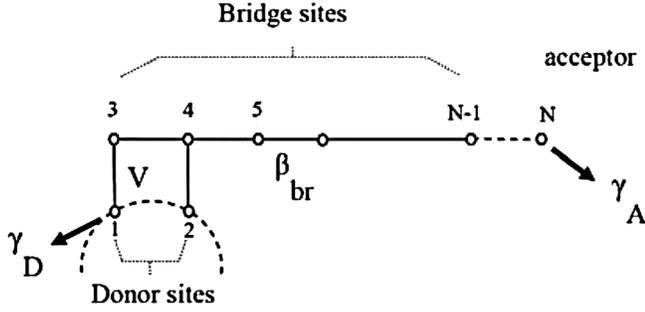
FIG. 2.   A minimal model demonstrating the effect of current transfer: The donor, containing sites 1 and 2, is coupled to the acceptor, site N, via the bridge, sites 3 to $N - 1$. The population relaxation rates of the donor and acceptor sites are indicated with arrows (rates γ_D and γ_A). The initial states, Eq. (8), represent the initial current on the donor.

this model, if we represent the opposite initial circular currents on the donor by

$$|\phi_{in}\rangle = \frac{1}{\sqrt{2}}(|1\rangle + e^{i\theta}|2\rangle); \quad |\phi_{in}^*\rangle = \frac{1}{\sqrt{2}}(|1\rangle + e^{-i\theta}|2\rangle),$$

(8)

and take for the acceptor state $|j_A\rangle = |N\rangle$. Using Eqs. (5) and (6), this leads to

$$\int_0^\infty dt P_{N,in}(t) = \hbar \sum_{n=1}^N \frac{|R_{N,in}^{(n)}|^2}{2\Gamma_n}$$
$$+ 2\hbar \sum_{n>m}^N \text{Im}\left\{\frac{R_{N,in}^{(n)}[R_{N,in}^{(m)}]^*}{(E_n - E_m) - i(\Gamma_n + \Gamma_m)}\right\},$$

(9)

where $\varepsilon_m = E_m - i\Gamma_m$ are the eigenenergies of the dissipative Hamiltonian, and $R_{N,in}^{(n)} = \langle N|X_n^{(R)}\rangle\langle X_n^{(L)}|\phi_{in}\rangle$. In the Liouville formalism, we solve Eq. (7) using $\hat{\rho}(t = 0) = |\phi_{in}\rangle\langle\phi_{in}|$ or $|\phi_{in}^*\rangle\langle\phi_{in}^*|$ with $\gamma_{D(A)}/2 > 0$. In either case, we use Eqs. (5) and (6) to calculate the yield asymmetry. Coherence relaxation on the donor is accounted for by taking $\gamma_{12} > 0$.

Results.—Figure 3 shows the asymmetry factor $\mathcal{A}$, Eq. (6), as a function of bridge length for resonant ($\varepsilon_{br} - \varepsilon = 0$) and nonresonant ($\varepsilon_{br} - \varepsilon = 3$ eV) bridges, for different donor and acceptor lifetimes and in the absence of dephasing. It should be emphasized that while the parameters used (donor and acceptor lifetimes in the range 3–30 fs and tight-binding couplings of order 1 eV) are reasonable for nonfluorescing excited electronic states with covalent intersite bonding, other values of lifetimes and couplings will yield such asymmetries. The yield asymmetry is found to become independent of length for long bridges and to be about an order of magnitude larger in the resonant case. Furthermore, in both resonant and nonresonant cases, $\mathcal{A}$ increases with decreasing donor and acceptor lifetimes, and more detailed studies show that the donor lifetime
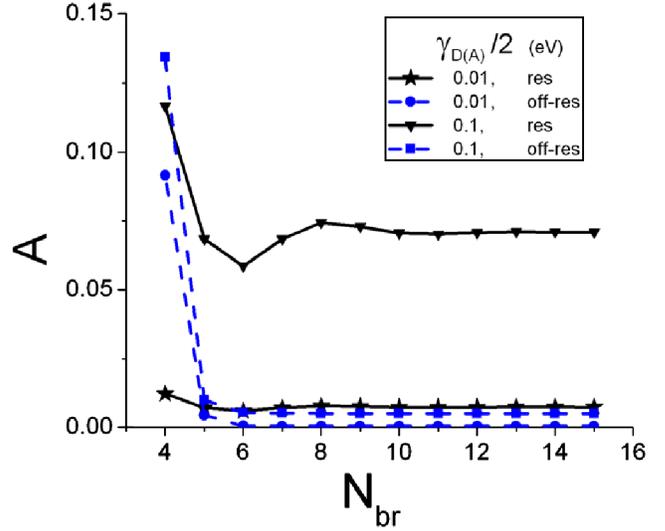
FIG. 3 (color online).   The yield asymmetry $\mathcal{A}$ as a function of bridge length $N_{br} = N - 3$, for the model of Fig. 2, for resonant ($\varepsilon_{br} - \varepsilon = 0$, solid lines), and off-resonant ($\varepsilon_{br} - \varepsilon = 3$ eV, dashed lines) bridges. The asymmetry is plotted for $\gamma_D = \gamma_A = 0.02$ eV, and $\gamma_D = \gamma_A = 0.2$ eV. Other parameters used are $\beta_{br} = 0.5$ eV, $V = 1.0$ eV, $\theta = \pi/4$, and $\gamma_{i,j} = 0$ for $i \neq j$.

effect is dominant in this regard. Finally, for parameters in the range of those used here, and for short enough donor lifetimes, we find effects of the order seen in the experiments of Refs. [6,7] (~10% for resonant bridge, <1% in the off-resonant case). For extremely short donor (acceptor) lifetimes, the asymmetry disappears.

Next, consider the effect of dynamic interactions with the thermal environment, in particular, nuclear motions. Such interactions give rise to decoherence as well as an inelastic component to the transmission. Here, we focus on the former, keeping in mind that inelastic effects on the overall transmission are usually small. The effect of donor decoherence is shown in Fig. 4, which plots $\mathcal{A}$ vs γ_{12} for resonant and nonresonant bridges of different lengths. A remarkable observation here is that although increasing decoherence eventually destroys the asymmetry, as expected, this happens only at unphysically large values of γ_{12}, in particular, in the resonant bridge case. Similar results are obtained in the presence of decoherence on the bridge.

While this simple model cannot be expected to reproduce the specific experimental results of Refs. [6,7], we have found three distinctive and robust features to characterize our model in a relatively large range of system parameters: (1) independence of bridge length for large molecular bridges, (2) asymmetry increases as donor lifetimes shorten (within physically reasonable values), and (3) asymmetry persists in the presence of decoherence. Furthermore, for a reasonable range of system parameters, the calculated asymmetry is of the same order as seen experimentally under reversed handedness of the circular
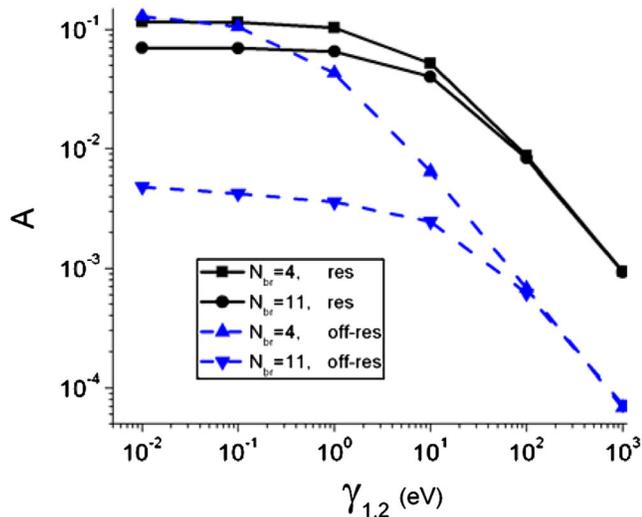
FIG. 4 (color online). The yield asymmetry $\mathcal{A}$ as a function of donor decoherence for the model of Fig. 2 for resonant and nonresonant bridges of different lengths. Parameters used (except γ_{12}) are the same as in Fig. 3 with $\gamma_D = \gamma_A = 0.2$ eV. The behavior of the asymmetry with respect to donor decoherence shown above is obtained for a wide range of values of $\gamma_{D(A)}$.

Two predictions highlighted in Figs. 3 and 4 may be of particular value in probing molecular ET mechanisms: (1) the stronger yield asymmetry in the resonant regime and (2) the peaking of the yield asymmetries at short distances. These effects suggest that ET yield asymmetries may be used to distinguish between resonant and super-exchange molecular charge-transfer mechanisms. Indeed, the transition between these regimes is of central interest in DNA electron transfer [12,13] and direct strategies for mechanistic interrogation have proven elusive. A key experiment in DNA ET, therefore, would be to measure ET yield asymmetries for photoinduced ET with an intercalated ET active species excited with CPL. This experiment would be particularly informative if performed over a range of transport distances.

polarization. Significantly, although this asymmetry is explained as a manifestation of a current transfer phenomenon resulting from coherent excitation, the resilience of this effect to decoherence rationalizes the observed behavior in condensed thermal environments. Preliminary analysis shows that the introduction of site-energy and nearest-neighbor coupling impurities in the Hamiltonian reduces the magnitude of the asymmetry for resonant transport. Indeed, the experiments of Ref. [6] find that the asymmetry disappears when, in a molecular layer of a given handedness, as few as 1% of the molecules are substituted by molecules of opposite handedness.

It is important to note that our model does not rely inherently on the bridge's chiral structure, but rather on the nature of the donor excitation and on proximity effects (that, we propose, result from the chiral geometry) that determine the nature of the donor-bridge coupling. Such proximity effects are expected to be apparent in chiral molecules and in nanostructures. Indeed, our results suggest that electron donor-bridge-acceptor molecular devices could be used to carry electron phase information by optically creating angular-momentum-polarized electron donor states and by manipulating the bridge's connectivity to donor and acceptor. Semiconductor nanoparticles connected by chiral (helical) bridge molecules are particularly promising candidates for such devices, in addition to monolayers of DNA, and to helical polypeptide molecules adsorbed on metal surfaces [11].

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