Control of Quantum Dynamics of Electron Transfer in Molecular Loop Structures: Spontaneous Breaking of Chiral Symmetry under Strong Decoherence

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Manipulation of quantum systems is the basis for many promising quantum technologies. However, how quantum mechanical principles can be used to manipulate the dynamics of quantum dissipative systems remains unanswered because of strong decoherence effects arising from interaction with the surrounding environment. In this work, we demonstrate that electron transfer dynamics in molecular loop structures can be manipulated with the use of Floquet engineering by applying an laser field. Despite strong dephasing, the system’s dynamics spontaneously breaks the chiral symmetry of the loop in a controllable fashion, followed by the generation of a steady-state electronic current. A novel exponential scaling law that relates the magnitude of the current to the system-environment coupling strength is revealed numerically. The breaking of chiral symmetry and the consequent controllable unidirectional flow of electrons could be employed to construct functional molecular electronic circuits.

\textbf{Introduction.} Quantum manipulation of different degrees of freedom in various types of physical systems has recently attracted growing attention as an indispensable ingredient at the heart of the quantum revolution. Examples include the manipulation of qubits for quantum computation \cite{11, 12}, ultracold atoms and molecules for quantum simulation \cite{13, 14}, and NV centers and exotic quantum states for quantum sensing and quantum metrology purposes \cite{15, 16}. As a tool of quantum manipulation, Floquet engineering has been employed to investigate various aspects of nonequilibrium dynamics in well-isolated quantum systems such as ultracold atoms \cite{17, 18}. In Floquet engineering, a system parameter is temporally modulated in a periodic manner. Floquet engineering has been employed to control the superfluid-Mott-insulator phase transition in an atomic cloud of \textsuperscript{87}Rb \cite{19}, to simulate frustrated classical magnetism in triangular optical lattices \cite{20}, to generate artificial magnetic fields for charge-neutral particles \cite{21, 22}, and to realize topologically nontrivial band structures \cite{23}. However, because quantum mechanical effects are often vulnerable to decoherence originating from interaction with the numerous dynamic degrees of freedom in the surrounding environment, it has been believed that nearly perfect isolation of the system from the environment, e.g., ultracold atomic gases, is a prerequisite for quantum manipulations such as Floquet engineering \cite{24}. Unlike well-isolated quantum systems, molecules in condensed phases are often embedded in a high density of environmental particles, leading to moderate-to-strong system-environment coupling. Consequently, the question of how quantum mechanical principles can be harnessed to manipulate the dynamics of condensed-phase molecular systems is nontrivial. Nevertheless, the present authors have recently demonstrated that Floquet engineering can significantly accelerate electronic excitation transfer between two molecules \cite{25}. The key is that time periodic modulation of the Franck-Condon transition energy of photoactive molecules leads to minimization of the decoherence effect in a similar manner to the decoherence-free subspace \cite{26}. In this work, we show that Floquet engineering can be employed to manipulate not only the amplitude but also the phase associated with inter-site coupling, namely the Peierls phase, which would dramatically influence electron transfer (ET) in molecular networks.

Investigations of quantum dynamics in various types of network structures \cite{27} are significant in understanding fundamental processes such as energy and charge transfers in chemical and biological systems \cite{28}, the physics of quantum-walk-related phenomena \cite{29}, and practical applications using artificial materials such as photovoltaics \cite{30, 31} and photonic circuits \cite{32, 33}. However, in the regime of moderate-to-strong system-environment coupling, quantum coherence between electronic states at different sites in a molecular network can be rapidly destroyed. Therefore, we need a new mechanism to protect the effect of quantum manipulation on the system under such strong decoherence, which is shown to be possible by exploiting the topological loop structure in molecular systems. In particular, we show that ET dynamics spontaneously break the chiral symmetry of the loop in a controllable fashion and in turn generate a robust steady-state electronic current that remains nonvanishing even when the system-environment interaction is stronger than the characteristic energy scale of the system. By numerically investigating the dependence of the magnitude of the current on the system-environment coupling strength, we derive a new exponential scaling law relating these two quantities.

\textit{ET in molecular networks.} To demonstrate the manipulation of ET dynamics in molecular networks using...
Floquet engineering, we consider ET in a triangular loop made of three sites as illustrated in Fig. 1. The molecular loop structure possesses a chiral symmetry, i.e., there is equality between transports in the clockwise and anticlockwise directions.

The Hamiltonian to describe ET dynamics in condensed phases can be expressed as $H = H^a + H^{env} + H^{int}$ with the Hamiltonian of the ET given by

$$H^a = \sum_{m=1}^{3} E_m |m\rangle\langle m| + \sum_{m,n=1}^{3} \hbar V_{mn} |n\rangle\langle m|.$$  \hspace{1cm} (1)

In the above, $|m\rangle$ denotes the state where only the $m$th molecule is reduced and negatively charged while the other molecules are in the electronically ground neutral states, i.e., an excess electron is located on the $m$th site. The energy of state $|m\rangle$ is given by $E_m$ when the energy of the “vacuum state” where all the molecules are in the electronically ground neutral states is set to be zero. The real number $\hbar V_{mn}$ denotes the inter-site coupling to drive ET reaction between the $m$th and $n$th molecules.

The Hamiltonian of the environment associated with the $m$th site is given by $H^{env} = \sum_\xi \hbar \omega_{m,\xi} b_{m,\xi}^\dagger b_{m,\xi}$, where $b_{m,\xi}$ denotes the annihilation operator of the $\xi$th mode of the environment with frequency $\omega_{m,\xi}$. The electronic energy at the $m$th site experiences fluctuations caused by the environmental dynamics as expressed by the interaction Hamiltonian $H^{int} = |m\rangle\langle m| \sum_\xi g_{m,\xi} (b_{m,\xi}^\dagger + b_{m,\xi})$, where $g_{m,\xi}$ denotes the coupling strength of the $\xi$th mode. This form of the interaction Hamiltonian induces environmental reorganization. The environmental reorganization and its timescale are characterized by the relaxation function $\Psi_m(t) = (2/\pi) \int_0^\infty d\omega J_m(\omega) \cos(\omega t)/\omega$, where $J_m(\omega)$ stands for the spectral density $J_m(\omega) = \sum_\xi g_{m,\xi}^2 \delta(\omega - \omega_{m,\xi})$ of the environment. Generally, the relaxation function may have a complex form involving various components. For the sake of simplicity, however, we model the function using an exponential form, $\Psi_m(t) = 2\lambda_m \exp(-t/\tau_m)$, where $\lambda_m$ is the environmental reorganization energy, which is usually employed to characterize the system-environment coupling strength, and $\tau_m$ is the characteristic timescale of the environmental relaxation or reorganization process.

In this work, we consider the case of independent environments associated with three sites. In general, there can be some correlation between fluctuations caused by environments associated with different sites in a molecular network as the change of configuration of the environment around one molecule as ET occurs can affect the configurations of environments of other molecules. As shown in the Supplementary Information (SI), however, the main results of this paper remain unchanged, at least qualitatively, for both cases of correlated and anticorrelated fluctuations. For the sake of simplicity, we set $\tau_m = \tau$, $\lambda_m = \lambda$, $\Omega^0_m = \Omega^3$, and $V_{mn} = V$ for $m, n = 1, 2, 3$.

Floquet engineering. In Floquet engineering, the Hamiltonian of the system is temporally modulated in a periodic manner by, for example, applying a laser pulse through the Stark effect. The time-dependent electronic energy at the $m$th site is expressed as $E_m(t) = E_m^0 + \hbar u_m(t)$, where the modulation $u_m(t)$ needs to satisfy $u_m(t) = u_m(t + T)$ and $\int_0^T dt u_m(t) = 0$ with $T$ being the modulation period. In the limit of high driving frequency, the system’s dynamics are characterized by an effective time-independent Hamiltonian $H^0$ obtained by taking the lowest-order terms in the high-frequency expansion. This has the same form as the original Hamiltonian in Eq. (1); however, the inter-site coupling $V_{mn}$ is replaced by $V^\text{eff}_{mn} = (V_{mn}/T) \int_0^T dt \exp \{i[\chi_m(t) - \chi_n(t)]\}$ with $\chi_m(t) = \int_0^t dt' u_m(t')$. In general, the effective inter-site coupling, $V^\text{eff}_{mn}$, is a complex number expressed as $V^\text{eff}_{mn} = |V^\text{eff}_{mn}| \exp(i\theta^\text{eff}_{mn})$, where $\theta^\text{eff}_{mn}$ is termed the effective Peierls phase. For a sinusoidal modulation, $V^\text{eff}_{mn}$ takes real values and thus $\theta^\text{eff}_{mn}$ takes only the value of 0 or $\pi$. However, it was shown that the effective inter-site coupling can take a complex value, provided that the time-periodic modulation breaks two special symmetries: reflection symmetry for a suitable time $\tau$, namely $u_m(t - \tau) = u_m(-t - \tau)$, and shift antisymmetry $u_m(t - T/2) = -u_m(t)$. For example, we can take a time-periodic modulation composed of two sinusoids, $u_m(t) = A_m \sin(\omega t) + B_m \sin(2\omega t)$, by applying a shaped laser pulse. Since the wavelength of the laser is typically much larger than the size of the molecular system, the electric field of the laser can be considered as homogeneous over the whole...
ET dynamics in the closed loop depends on the effective electron, and the distance between neighboring sites. The dependence of the electron as it travels in the clockwise direction. The emergent imbalance in the population distribution of the two sites are reversed when the driving amplitude varies from $A/\omega = 2$ to $A/\omega = 4$ with keeping $B$ constant, indicating that the emergent chirality of the system can be fully controlled by Floquet engineering. It should be noted that the direction of the emergent chirality changes by only varying the driving amplitude without any change of phase or direction or other parameters of the modulation, reflecting the fact that the chiral symmetry is spontaneously broken by the ET dynamics under Floquet engineering. The control of the emergent chirality can be understood through the sign of the effective total Peierls phase. Indeed, $\theta_{\text{eff}}^{\text{tot}}$ changes its sign from negative to positive when the driving frequency increases from $A/\omega = 2$ to $A/\omega = 4$ (see the SI for details).

The small zigzag pattern on top of the time evolution in Fig. 2 usually called micromotion, is a direct consequence of a time-periodic driving with finite frequency. It corresponds to higher-order terms in the high-frequency expansion; therefore, the higher the driving frequency, the smoother the time evolution. In the following sections, to remove the micromotion and in turn obtain smooth time evolution, we consider the high-driving-frequency limit in which ET dynamics are characterized by the effective inter-site coupling $V_{mn}^{\text{eff}}$. Experimentally the micromotion can be removed by filtering out high-frequency components from the measured signal.

Electronic current. It is not only the electronic population but also the electronic current flowing in the molecular loop that are substantially affected by Floquet engineering. The current is defined as $I_{mn}(t) = -e\text{Tr}[\hat{I}_{mn}\hat{\rho}(t)]$ ($m, n = 1, 2, 3$), where $-e$ is the unit charge of an electron and $I_{mn} = -i\langle V_{mn}|n\rangle\langle m| - V_{mn}^{\ast}|m\rangle\langle n|$ is the current operator defined in Ref. [42]. Technical details are given in Ref. [35].

Spontaneous breaking of chiral symmetry. We consider the case where the system-environment coupling strength is comparable to the characteristic energy scale of the system’s dynamics, $\lambda = V$, and the system is driven with the driving amplitudes $A/\omega = 2$ and $B/\omega = 6$. Time evolutions of the electronic populations at three sites are shown in Fig. 2. The populations rapidly equilibrate to the steady-state values $P_1(t \to \infty) = P_2(t \to \infty) = P_3(t \to \infty) = 1/3$, showing no noticeable signature of quantum interference due to the strong decoherence. Nevertheless, there is clearly a population imbalance between the second and the third sites, $P_2(t) < P_3(t)$, over a relatively long time period of approximately 2 ps. It should be noted that the three sites are identical, leading to a chiral symmetry between two possible ET pathways along the loop in the clockwise and anti-clockwise directions. Meanwhile, the AC driving also preserves this symmetry on time average, which is relevant to the high-driving-frequency limit under consideration. Therefore, the emergent imbalance in the population distribution of electron between the two sites implies that ET dynamics under Floquet engineering spontaneously breaks the chiral symmetry of the molecular loop structure.

Moreover, the direction of the emergent chirality can be manipulated by varying the driving amplitudes. It is evident from the inset of Fig. 2 that the relative electronic distributions at the two sites are reversed when the driving amplitude varies from $A/\omega = 2$ to $A/\omega = 4$ with keeping $B$ constant, indicating that the emergent chirality of the system can be fully controlled by Floquet engineering. It should be noted that the direction of the emergent chirality changes by only varying the driving amplitude without any change of phase or direction or other parameters of the modulation, reflecting the fact that the chiral symmetry is spontaneously broken by the ET dynamics under Floquet engineering. The controlling of the emergent chirality can be understood through the sign of the effective total Peierls phase. Indeed, $\theta_{\text{eff}}^{\text{tot}}$ changes its sign from negative to positive when the driving frequency increases from $A/\omega = 2$ to $A/\omega = 4$ (see the SI for details).

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describing the flow of electron from the $m$th to the $n$th sites. The time evolutions of the current $I_{32}(t)$ for the two different driving amplitudes $A/\omega = 2$ and $A/\omega = 4$ considered above are shown in Fig. 3 where $B$ is kept constant. It is evident that $I_{32}(t)$ makes a sharp rise to a positive (negative) value at early time, then undergoes a short damped oscillation before approaching the steady-state value which is positive (negative) for $A/\omega = 2$ ($A/\omega = 4$). The non-zero electronic current between the two molecules reflects the breaking of chiral symmetry while the dependence of the direction of current on the driving amplitude indicates again that the emergent chirality can be fully controlled under Floquet engineering. Since the electron’s populations $P_m(t)$ ($m = 1, 2, 3$) are time-independent in the steady state, it must be that $I_{13}(t \to \infty) = I_{32}(t \to \infty) = I_{21}(t \to \infty) \equiv I_{ss}$.

Despite the strong effect of decoherence, the steady-state electronic current is non-vanishing. To investigate the effect of decoherence on the steady-state current, we repeated the calculation of $I_{ss}$ for different values of the environmental reorganization energy $\lambda$ with the driving amplitudes fixed to be $A/\omega = 2$ and $B/\omega = 6$. The dependence of $I_{ss}$ on $\lambda$ is plotted in Fig. 4 with a logarithmic scale on the vertical axis. The clearly observed linear correlation in the figure indicates an exponential dependence $I_{ss} = I_0 e^{-\kappa(\lambda/V)}$ between the steady-state current and the system-environment coupling strength with the constants $I_0 \simeq 1.24$ nA and $\kappa \simeq 0.11$ obtained numerically by using a standard procedure of linear fitting. It should be noted that, while an exponential time decay of quantum coherence has often been derived in typical models of dephasing, here we found a different exponential scaling law for the effect of decoherence in terms of a steady-state current that persists as long as the modulation is applied.

It is understood from the small damping factor $\kappa \ll 1$ of the steady-state current that it remains non-vanishing even for a very strong system-environment coupling where the environmental reorganization energy is much larger than the characteristic energy scale of the system’s dynamics. This is unlike the normal situation in open quantum systems, where typical physical quantities often decay very quickly owing to the strong effect of decoherence. The robustness of the steady-state current even in the presence of very strong system-environment coupling can be attributed to a classical topological feature of the effect that drives the current. Indeed, the effect of a nonzero effective total Peierls phase in a molecular loop structure is equivalent to the effect of a magnetic field on a charged particle moving in closed loop as shown by the Aharonov-Bohm effect [43]. Since the effect of a magnetic field on a charged particle persists in the classical regime, it is reasonable to expect that the effect is robust against decoherence.

Conclusion. We have investigated how the quantum dynamics of ET in molecular loop structures can be manipulated using Floquet engineering. We found that, despite strong dephasing, ET dynamics can spontaneously break the chiral symmetry of the loop in a controllable fashion and in turn generate a robust steady-state electronic current that remains non-vanishing even in the strong system-environment-coupling limit. Employing this kind of topological loop structure in quantum manipulation for protection from environmental effects can serve as a useful guide for controlling dynamical processes in molecular systems. A new exponential scaling law that relates the magnitude of the steady-state current to the system-environment coupling strength was also revealed numerically.

The controllable unidirectional flow of electrons follow-
ing the breaking of chiral symmetry in molecular loop structures can find numerous applications in, for example, constructing functional molecular electronic circuits. The steady-state electronic current in molecular loop structures is closely related to the persistent current in mesoscopic normal metal rings observed at very low temperature ($\lesssim 1$ K) in the presence of an external magnetic field [44–46], although in which case the effect of decoherence is dominated by that of static disorders. It should be noted that a steady-state electronic current of the same order of magnitude as the persistent current in mesoscopic normal metal rings ($\sim 1$ nA) can be generated in nanoscale molecular loop structures at room temperature without an external voltage. Although this study focuses on the ET dynamics, similar results should be expected for other important dynamical processes such as electronic excitation transfer in condensed-phase molecular systems if we can make a site-dependent time-periodic modulation of the Franck-Condon transition energy in the molecular network.

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