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This article presents the development of a new method for solving the so-called trivial crossing problem in simulations of adiabatic dynamics and an application of this method to a model of exciton dynamics on long chain conjugated polymer systems.

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Solving the Trivial Crossing Problem While Preserving the Nodal Symmetry of the Wavefunction

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In adiabatic mixed quantum-classical simulation, the avoided crossing of weakly coupled eigenstates can lead to unphysical discontinuities in wavefunction dynamics, otherwise known as the trivial crossing problem. A standard solution to the trivial crossing problem eliminates spatial discontinuities in wavefunction dynamics by imposing changes in the eigenstate of the wavefunction. In this paper, we show that this solution has the side-effect of introducing transient discontinuities in the nodal symmetry of the wavefunction. We present an alternative solution to the trivial crossing problem that preserves both the spatial and nodal structure of the adiabatic wavefunction. By considering a model of exciton dynamics on conjugated polymer systems, we show that failure to preserve wavefunction symmetry yields exciton dynamics that depend unphysically on polymer system size. We demonstrate that our symmetry preserving solution to the trivial crossing problem yields more realistic dynamics, and can thus improve the accuracy of simulations of larger systems that are prone to the trivial crossing problem.

Keywords: mixed quantum-classical dynamics, adiabatic dynamics, trivial unavoidable crossing, molecular semiconductor, exciton

I. INTRODUCTION

Many approaches to mixed quantum-classical simulation are based on the use of adiabatic dynamics, whereby the classical degrees of freedom (e.g., the nuclei) evolve according to the potential energy surface of a single specific eigenstate of the quantum subsystem. If the quantum subsystem has multiple eigenstates, then the dynamics of the classical subsystem can lead to variations in eigenstate energies and the emergence of avoided crossings, as illustrated in Fig. 1a. As a system moves along a single eigenstate through a typical avoided crossing, the adiabatic wavefunction transforms gradually from one eigenstate to the other in a manner that can be expressed as a linear combination of the two corresponding diabatic states, as shown in Fig. 1c. However, in the limit that the diabatic states are uncoupled, the quantum subsystem will exhibit a near-discontinuous transition at the crossing point, where the eigenstates are essentially degenerate in energy, as depicted in Fig. 1b. This abrupt unphysical change in the characteristics of the adiabatic wavefunction due to the crossing of eigenstates, as illustrated in Fig. 1d, is known as the trivial crossing problem (TCP).

A common solution to the TCP is to force the quantum subsystem to change eigenstates at the crossing point in order to maintain the continuity of the adiabatic wavefunction. However, this type of approach necessarily introduces a discontinuous transition in the number of nodes in the adiabatic wavefunction. In systems that require long time dynamics, or that feature multiple trivial crossings, this change in nodal symmetry can lead to inaccurate and inconsistent electronic dynamics. In this article, we present a solution to the TCP that preserves the symmetry of the adiabatic wavefunction. We demonstrate our approach and highlight its utility by applying it to model the dynamics of electronically excited conjugated polymer systems.

The TCP represents a breakdown in the adiabatic approximation. In the adiabatic limit, where classical degrees of freedom evolve infinitely slowly, the wavefunction of the quantum subsystem can instantaneously adjust to the motion of classical degrees of freedom and can thus access arbitrarily large changes in electronic state through arbitrarily small electronic couplings. Away from this limit, however, nonadiabatic effects are required to accurately represent the state of the system as it travels through and exits a trivial crossing. Nonadiabatic effects enable a wavefunction to transform in response to variations in the electronic energy levels and couplings by spreading across different eigenstates of the quantum subsystem. In the case of a trivial crossing, this transformation could prevent the occurrence of unphysical discontinuities and thus effectively preserve the diabatic characteristics of the wavefunction.

In simulations of adiabatic dynamics (i.e., where the wavefunction of the quantum subsystem is at all times represented by a single eigenstate), it has been proposed that these nonadiabatic effects can be effectively captured by imposing an appropriate change of eigenstate for the wavefunction as it passes through a trivial crossing. This approach to preventing the trivial crossing problem has been widely adopted because it provides an efficient solution without the need to perform com-
II. MODIFYING THE HAMILTONIAN TO ELIMINATE TRIVIAL CROSSINGS

A. General theoretical framework for two-state systems

Our solution to the trivial crossing problem is to modify the system Hamiltonian so that purely adiabatic dynamics are free from the occurrence of trivial crossings. In this section, we present a general theoretical formalism for constructing such a modified Hamiltonian. We begin by considering a system comprised of a quantum subsystem and a classical subsystem that are coupled and subject to the Born-Oppenheimer approximation. That is, we assume that the quantum subsystem is defined by the Hamiltonian \( \hat{H}(x(t)) \), where \( x(t) \) denotes the time-dependent configuration of the classical subsystem. An adiabatic state of the quantum subsystem, denoted by \( |\Psi_i \rangle \), and its associated energy level, denoted by \( \lambda_i \), are given by the solution to the time-independent Schrödinger equation,

\[
\hat{H}|\Psi_i \rangle = \lambda_i|\Psi_i \rangle,
\]

for \( i = 1, 2, \ldots \). Adiabatic states are generally indexed in order of increasing \( \lambda \), i.e., with \( |\Psi_1 \rangle \) representing the eigenstate with the lowest eigenvalue.

We assume that the classical subsystem evolves under the combined influence of a potential energy surface, such as a molecular mechanics force-field, which only depends on \( x(t) \), and the forces from the quantum subsystem, which are given by the Hellmann-Feynman formula,

\[
F^{(k)} = -\langle \Psi_k | \partial \hat{H} / \partial x_\alpha | \Psi_k \rangle,
\]

where \( x_\alpha \) denotes the position of the \( \alpha \)th classical degree of freedom. Notably, this expression describes the specific contribution of the \( k \)th adiabatic state to the overall nuclear forces. The formalism we present below is designed specifically for systems that are initialized with the quantum subsystem in the \( k = 1 \) state; however, the

Having one node, and so on. In simulations of adiabatic dynamics, a change in nodal structure can lead to impulsive and physically unwarranted changes in the interactions between the classical and quantum subsystems.

In this article, we present a solution to the trivial crossing problem that eliminates the need to change eigenstate index of the adiabatic wavefunction through dynamically inert modifications of the Hamiltonian of the quantum subsystem. Section II introduces the general theoretical framework for this method. Sections III and IV present the application of this method in simulating exciton dynamics on extended conjugated polymer chains. Section V highlights on the importance on preserving the nodal symmetry of wavefunction. Finally, we summarize and discuss implications of our method for large-scale adiabatic simulations.
In these equations, the system can therefore be written as,

\[ \hat{V}[x(t)] = \hat{H}_a[x(t)] + \hat{H}_b[x(t)] + \hat{V}[x(t)], \]

where

\[ \hat{H}_a[x(t)] = E_a[x(t)]|\phi_a\rangle\langle \phi_a|, \]
\[ \hat{H}_b[x(t)] = E_b[x(t)]|\phi_b\rangle\langle \phi_b|, \]

and

\[ \hat{V}[x(t)] = V_{ab}[x(t)]|\phi_a\rangle\langle \phi_b| + V_{ba}[x(t)]|\phi_b\rangle\langle \phi_a|. \]

In these equations, \( E_a \) and \( E_b \) are energies of respective diabatic states, and \( V_{ab} \) is the coupling magnitude between the diabats.

Under the Born-Oppenheimer approximation, the eigenstates and eigenvalues of the quantum subsystem can be solved by diagonalizing the full Hamiltonian. The coupling strength is related to the adiabatic energy gap via the equation,

\[ \lambda_2 - \lambda_1 = \frac{\sqrt{(E_a - E_b)^2 + 4V_{ab}^2 + 4f(S)}}{1 - S^2}, \]

where \( S = \langle \phi_a|\phi_b \rangle = \int \phi_a(\mathbf{r})^*\phi_b(\mathbf{r})d\mathbf{r} \) for \( \mathbf{r} \in \mathbb{R}^3 \) and \( f(S) \equiv S^2E_aE_b - SV_{ab}(E_a + E_b) \). In order for the diabatic coupling to be physically meaningful, the diabatic states must be orthonormal. Hence, we will focus on cases with orthonormal diabatic states, where \( S = 0 \) and thus Eq. 7 simplifies to,

\[ \lambda_2 - \lambda_1 = \sqrt{(E_a - E_b)^2 + 4V_{ab}^2}. \]

At a crossing point (i.e., \( E_a = E_b \)), the left-hand side of Eq. 8 is minimized and the intrinsic value of \( V_{ab} \) can be determined. However, since the quantities in Eq. 8 generally depend on \( x(t) \), a minimum in \( \lambda_2 - \lambda_1 \) does not necessarily correspond to a crossing point. We thus base our identification of crossing points on the diabatic composition of the adiabatic wavefunction. Specifically, the eigenstates of the full Hamiltonian in Eq. 9 have the general form,

\[ |\Psi_1(t)\rangle = c_a(1)(t)|\phi_a\rangle + c_b(1)(t)|\phi_b\rangle, \]
\[ |\Psi_2(t)\rangle = c_a(2)(t)|\phi_a\rangle + c_b(2)(t)|\phi_b\rangle, \]

where \( |c_a(\alpha)(t)|^2 + |c_b(\alpha)(t)|^2 = 1 \). The coefficients in the above equations can be determined through a unitary transformation of \( \hat{H} \) (see the Supporting Information for more details) and expressed as simple functions of the mixing angle,

\[ \theta[x(t)] = \arctan \frac{2V_{ab}[x(t)]}{E_a[x(t)] - E_b[x(t)]}. \]

Notably, at a crossing point \( \theta = \pm \pi/2 \), corresponding to the case where each adiabatic state contains an equal mixture of \( |\phi_a\rangle \) and \( |\phi_b\rangle \).

We distinguish between avoided and trivial crossings based on the strength of the intrinsic coupling, \( V_{ab} \), evaluated at the crossing point. We identify a crossing point based on the diabatic composition of the adiabatic wavefunctions. Specifically, we evaluate the joint probability density between eigenstates 1 and 2,

\[ P_{1,2}[x(t)] = \int \rho_1(\mathbf{r}; x(t))\rho_2(\mathbf{r}; x(t))d\mathbf{r}, \]

where \( \rho_1(\mathbf{r}) = |\Psi_1(\mathbf{r})|^2 \), and the integral is carried out over all space. The quantity \( P_{1,2} \) depends on the configuration of the classical subsystem and thus varies in time along a trajectory. As a system enters a crossing and the eigenstates adopt complimentary superposition states, the value of \( P_{1,2} \) will increase and eventually reach a local maximum when \( \theta \approx \pm \pi/2 \), i.e., the eigenstates are maximally overlapping. We assume that this local maximum corresponds to the crossing point and thus defines the crossing time, \( t_c \), as the point in time where \( P_{1,2} \) is at a local maximum. Likewise, \( P_{1,2} \) will go through another local maximum if the two states recross. We thus denote the time point of recrossing as \( t_r \). At the crossing point, we compute \( V_{ab} \) using Eqs. 9 and then categorize the point as an avoided crossing, if \( |V_{ab}| \geq V_c \), or a trivial crossing, if \( |V_{ab}| < V_c \). The value of \( V_c \) can be determined based on theoretical models, such as the Landau-Zener formula, or fit to match experimental data, as we describe in more detail in Sec. 11 and 15 below.

Once a trivial crossing is identified, we correct the TCP by temporarily modifying the Hamiltonian so as to effectively eliminate the higher energy (crossing) diabatic state. There are numerous ways to perform such a modi-
The diabatic wavefunctions and their coupling term do not change significantly between the trivial crossing and trivial recrossing points. If diabatic states do undergo significant changes during the trivial crossing interval (i.e., \( t_c < t < t_r \)), then it must be verified that the coupling (e.g., \( V_{ab} \)) remains below the threshold during the entire time interval. If this is not the case, then purely adiabatic dynamics are probably inappropriate for describing the evolution of the quantum subsystem. For multi-state systems, this approach can be applied recursively to address trivial crossings that occur within the dynamics of the modified Hamiltonian. In such a case, the modified Hamiltonian can itself be modified, as shown in the Supporting Information (SI).

### B. Eigenstate shifting in tight-binding models

The tight-binding model offers a convenient and flexible framework for studying the dynamics of multi-state quantum subsystems. In this model, the quantum subsystem is expressed using a Hamiltonian of the form,

\[
\hat{H}[\mathbf{x}(t)] = \sum_n \varepsilon_n[\mathbf{x}(t)] |n\rangle\langle n| + \sum_{n \neq m} J_{nm}[\mathbf{x}(t)] |n\rangle\langle m|,
\]

where \( |n\rangle \) represents a member of an orthonormal time-independent basis, \( \varepsilon_n \) is the energy of the system in basis state \( |n\rangle \), and \( J_{nm} \) is the coupling between basis states \( |n\rangle \) and \( |m\rangle \). As the notation indicates, in a mixed quantum-classical simulation both \( \varepsilon_n \) and \( J_{nm} \) generally depend on the state of the classical subsystem. For quantum subsystems that adopt this common form, it is convenient to define diabatic states in the same basis as the original Hamiltonian, i.e.,

\[
|\phi_a\rangle = \sum_n c_n^{(a)}|n\rangle,
\]

\[
|\phi_b\rangle = \sum_n c_n^{(b)}|n\rangle,
\]

where the coefficients define the subset of basis states that make up the diabat, and \( c_n^{(b)} = 0 \) if \( c_n^{(a)} \neq 0 \) and vice versa. Likewise, the diabatic Hamiltonian can be defined as

\[
\hat{H}_a = \sum_{n \in a} \varepsilon_n |n\rangle\langle n| + \sum_{(n \neq m) \in a} J_{nm} |n\rangle\langle m|,
\]

where the summations only include those basis states with a non-zero values of \( c_n^{(a)} \). An analogous diabatic Hamiltonian can be generated for \( \hat{H}_b \), so that the coupling operator takes the form,

\[
V_{ab} = \sum_{n \in a} \sum_{m \in b} (J_{nm} |n\rangle\langle m| + J_{mn} |m\rangle\langle n|).
\]

With this formulation, the full Hamiltonian can be expressed in terms of the two lowest energy diabatic Hamiltonians, \( \hat{H}_a \) and \( \hat{H}_b \), their coupling operator, \( V_{ab} \), and a
third effective diabatic state, $c$, representing the remainder of the quantum subsystem, i.e.,

$$\hat{H} = \hat{H}_a + \hat{H}_b + \hat{V}_{ab} + (\hat{H}_c + \hat{V}_{ac} + \hat{V}_{bc}), \quad (20)$$

where the basis states associated with diabat $c$ are all of those not included in either diabat $a$ or $b$. In this notation, the effective diabat $c$ may contain multiple eigenstates of the original Hamiltonian, while diabats $a$ and $b$ each correspond to a single eigenstate. By construction, these diabatic states are non-overlapping and the Hamiltonian decomposition in Eq. (20) can be expressed in matrix form,

$$\begin{bmatrix}
H_a & V_{ac} & V_{ab} \\
V_{ac} & H_c & V_{bc} \\
V_{ab} & V_{bc} & H_b
\end{bmatrix}.$$ \quad (21)

The relationship between the diabatic and adiabatic representations is illustrated in Fig. 2a-b.

An alternate strategy for modifying the Hamiltonian is to artificially shift the energy level of the crossing diabatic state, as illustrated in Fig. 2d. This strategy is convenient to implement in diabatic simulations because the size of the quantum subsystem is preserved upon switching between the standard and modified Hamiltonians. Formally, the modified Hamiltonian for this approach is given by the form,

$$\hat{H}_{\text{mod}} = \hat{H} + \sum_{n \in b} \Delta_b |n\rangle \langle n|,$$ \quad (22)

where $\Delta_b$ is a constant that is large enough eliminate the crossing of diabats $a$ and $b$ along the entire time interval $t_c \leq t \leq t_t$.

### III. APPLICATION: EXCITON DYNAMICS ON EXTENDED CONJUGATED POLYMER SYSTEMS

The energy transport properties of electronically excited conjugated polymers contribute significantly to determining the performance of organic electronic applications, such as organic photovoltaic and light-emitting devices.\textsuperscript{13,20} One of the challenges in modeling excited state properties is that these systems tend to exhibit frequent trivial crossings, as first discovered by Fernandez-Alberti et al. for phenylene ethynylene oligomer chains.\textsuperscript{21} Furthermore, the frequency of trivial crossings in these systems increases with polymer chain length, making it difficult to simulate anything but short (e.g., $\sim 10$ monomer units) isolated oligomers. A robust and accurate solution to the TCP is therefore essential to enabling the simulation of experimentally relevant time and length scales.

The tendency of these systems to exhibit TCPs arises because these systems possess a manifold of low-lying electronic excited states that are easily localized to nanometer length scales in the presence of room temperature thermal disorder. When these states are spatially separated, they exhibit weak coupling and can thus contribute to TCPs. For extended conjugated polymers on their ground-state potential energy surface, the low-lying excited states occupy the same crowded band of energies. This band includes numerous avoided and trivial crossings. By contrast, when the system is on an excited-state potential energy surface, the active eigenstate can be preferentially stabilized via polaronic interactions between the classical and quantum subsystems. These interactions contribute to reducing the energy of the active state and reducing state crossings.

Polaronic effects in neutral conjugated polymer systems arise due to the interaction of an electronic excitation, also known as an exciton, with the nuclear degrees of freedom. These interactions favor the planarization of the monomer-monomer torsional landscape.\textsuperscript{21} This planarization results in a higher degree of $\pi$-conjugation and thus a lowering of the excited state energy level.\textsuperscript{22} Since these planarizing forces are co-localized with the position of the exciton, only a limited region of the polymer chain is influenced, resulting in a phenomena known as exciton self-trapping.\textsuperscript{23} The dynamics of self-trapped excitons are thus naturally described in diabatic states that are spatially localized over several monomer units.

#### A. Model Description

The dynamics of an electronically excited conjugated polymer system can be efficiently modeled using a mixed quantum/classical approach in which the quantum subsystem is described by a Frenkel exciton Hamiltonian.\textsuperscript{26} In the Frenkel exciton Hamiltonian, the excited states of a polymer with $N$ monomers are expressed in an orthonormal basis of single monomer excitations, with a Hamiltonian of the form,

$$\hat{H}_\text{Frenkel} = \sum_i \varepsilon_i \hat{c}_i \hat{c}_i^\dagger + \sum_{i \neq j} J_{ij} \hat{c}_i \hat{c}_j^\dagger,$$ \quad (23)

where $|i\rangle$ represents the state in which only the $i$th monomer is excited (all other monomers are assumed to be in the ground state), $\varepsilon_i$ is the associated monomer excitation energy, and $J_{ij}$ is the electronic coupling between states $|i\rangle$ and $|j\rangle$. In the results presented below, we adopt a variation of this model that is specific to the physics of conjugated polymer systems and similar to that developed by Tozer and Barford to model poly(para-phenylene) chains.\textsuperscript{5} In this variation, the monomer excitation energies are all assumed to be identical, given by the parameter $\varepsilon_0$, and the coupling $J_{ij}$ is assumed to be the sum of a through-bond and a through-space contribution. The Hamiltonian of our
model is given by
\[ \hat{H}_{\text{poly}} = \sum_i N \epsilon_0 |i \rangle \langle i | + \sum_{i \neq j} J^{(\text{dip})}_{ij} |i \rangle \langle j | + \sum_{i} J^{(\text{bond})}_{i} (|i i+1 \rangle + |i+1 i \rangle), \] (24)
where \(J^{(\text{dip})}_{ij}\) describes the through-space dipolar coupling of states \(|i \rangle\) and \(|j \rangle\), and \(J^{(\text{bond})}_{i}\) describes the through-bond coupling of adjacent monomers. Specifically, the through-space coupling is given by
\[ J^{(\text{dip})}_{ij} = \frac{\kappa_{ij} \mu_0^2}{4\pi\epsilon_r \epsilon_0 R^{3}_{ij}}, \] (25)
where \(\mu_0\) is the strength of the transition dipole of state \(|i \rangle\), \(\epsilon_r\) and \(\epsilon_0\) denote the dielectric constant and the vacuum permittivity, respectively, \(R_{ij} = |R_{ij}|\) is the separation between monomer units \(i\) and \(j\), and \(\kappa_{ij} = \mu_i \cdot \mu_j - 3(R_{ij} \cdot \mu_i)(R_{ij} \cdot \mu_j)/R^{2}_{ij}\), is the dipole orientation factor, where \(\mu_i\) is the unit dipole vector for the transition dipole of state \(|i \rangle\). The through-bond coupling is given by
\[ J^{(\text{bond})}_{i} = J_{\text{SE}} \cos^2(\theta_i), \] (26)
where \(J_{\text{SE}}\) is a constant determined by the electronic exchange coupling between bonded monomers, and \(\theta_i\) is the torsional angle between monomers \(i\) and \((i + 1)\).

For the classical subsystem, we utilize a coarse grained model of a polymer that only includes the degrees of freedom that have dependencies in the quantum Hamiltonian of Eq. [23]. Namely, this includes the relative positions of monomers and the set of monomer-monomer torsional angles. In this coarse grained model, we describe the dynamics of the torsional landscape via a Langevin equation,
\[ I \frac{d^2 \theta_i}{dt^2} = -\eta \frac{d\theta_i}{dt} - \frac{dU_g(\theta_i)}{d\theta_i} + F^{(n)}_{\text{ex}}(\theta_i) + \xi_i(t), \] (27)
where \(I\) is the moment of inertia of a monomer ring about a rotational axis parallel to the polymer backbone, \(\eta\) is the friction coefficient for a given solvent, \(U_g(\theta)\) is the monomer state torsional potential energy function, \(F^{(n)}_{\text{ex}}\) is the torque exerted on monomer rings by \(n\)-th exciton state, and \(\xi\) is the stochastic torque on monomers due to the random fluctuations in the solvent. We model these random fluctuations as white noise with a correlation function, \(\langle \xi_i(t) \xi_j(t + \delta t) \rangle = 2\eta k_B T \delta_{ij} \delta(t)\), where \(k_B T\) is the Boltzmann’s constant times temperature. In this work, the ground state potential energy function, \(U_g(\theta)\), was numerically tabulated based on the analysis of molecular dynamics simulation data, as described in more detail in the following subsection.

We determine the excited state forces from the Hellmann-Feynman theorem,
\[ F^{(n)}_{\text{ex}}(\theta_i) = -\langle \Psi_n | \frac{\partial \hat{H}_{\text{ex}}}{\partial \theta_i} | \Psi_n \rangle = 2J_{\text{SE}} \sin(2\theta_i) b_i^{(n)} b_{i+1}^{(n)\dagger}, \] (28)
where \(b_i^{(n)} = \langle i | \Psi_n \rangle\). Notably, this expression for the excited state force vanishes in regions of the polymer that are far from the position of the localized exciton. We assume that there is a separation of timescales between the lifetime of an exciton and the changes in spatial configuration of the polymer. Thus, we treat the relative monomer positions as static. In this work, we assume the polymer is in an idealized extended linear configuration unless described otherwise.

**B. Model Parameterization**

We parameterize our model to correspond to simulation results generated for polythiophene in nonpolar solvent at \(T = 300\ K\). The parameters of the quantum Hamiltonian are assigned based on mixed QM/MM excited-state all-atom Molecular Dynamics (MD) simulations. These simulations utilize a QCFF/PI approach similar to one originally developed by Warshel and Karplus. In this approach, the electronic structure is only explicitly evaluated for the \(\pi\)-electrons, which are treated using a semiempirical Pariser–Parr–Pople (PPP) type Hamiltonian. All other electronic degrees of freedom are treated implicitly in the parameterization of the molecular mechanics force field. Excited state properties are computed using configuration interaction with single excitations (i.e., CIS).

Following the specific approach of Refs. 33 and 34, we generate multiple independent trajectories of a 30-mer thiophene at \(T = 300\ K\) in the first electronically excited state. This method is described in more detail in the SI. Shorter tetraphiophene are simulated in the ground state to compute the ground state torsional potential energy, \(U_g(\theta)\), used in Eq. [27]. \(U_g(\theta)\) is tabulated to reproduce the potential of mean force for ring-ring torsional angles computed from atomistic quaterthiophene simulations, and the resulting potential is plotted in Fig. S2 in the SI. This ground state torsional potential is bimodal with a local minimum at 35° (cis-configuration) and a global minimum at 143° (trans-configuration) that are separated by a barrier of approximately 12 meV. We assume that torsional angles are independent, which is supported by correlation analysis of the MD simulations. We neglect the subtle differences in \(U_g(\theta)\) that emerge at the chain ends. Further details about the MD simulations can be found in the SI.

Table I lists the parameters we derive based on the results of these simulations. These values are used to simulate the motion of exciton in a polythiophene chain in nonpolar solvent at room temperature (\(T = 300\ K\)).
TABLE I. Parameters of the exciton model of conjugated polymers

|          | $\epsilon_a$ (eV) | $J_{2E}$ (eV) | $\epsilon_r$ | $\mu_0$ (D) |
|----------|------------------|---------------|--------------|--------------|
| Quantum  | 5.0              | -0.5          | 2.7          | 9.0          |
| Classical| 3.0              | 0.0035        |              |              |

C. Model Implementation

Using our coarse grained model, we consider the time evolution of the exciton wavefunction starting in the lowest energy excited state. Before initializing our exciton dynamics, we prepare a polythiophene chain with N-monomers whose centroid positions are uniformly spaced by 3.88 Å along the x-axis. The initial torsional angles and their velocities are randomly drawn from a uniform distribution between -180 and 180 degrees and from the Maxwell-Boltzmann distribution at $T = 300$ K, respectively. We first equilibrate the ground state torsional angle configuration for 10 ps. The system is then evolved along the potential energy surface of the lowest eigenstate via Eq. 27 and $n = 1$. We numerically integrate Eq. 24 using the method developed by Vanden-Eijnden and Ciccotti with a timestep of $\delta t = 1$ fs. All results presented in this paper have been insensitive to the integration timestep as long as $\delta t \leq 1$ fs.

During adiabatic dynamics we identify crossing points by evaluating the joint probability density, $P_{1,2}$, as described in Sec. II A. We assume that at a crossing point, $|\Psi_1\rangle$ and $|\Psi_2\rangle$ represent spatially symmetric and antisymmetric linear combinations of diabatic states $|\phi_a\rangle$ and $|\phi_b\rangle$ (see Eqs. 9 and 10). We diabatize the quantum subsystem based on this assumption by locating the node in $|\Psi_2\rangle$ and then constructing two orthonormal diabatic states that are constrained to lie on opposite sides of the node. We set $|\phi_a\rangle$ (or $|\phi_b\rangle$) to be the diabatic wavefunctions with bigger (or smaller) overlap with the active state prior to the crossing point, $|\Psi_1(t - \delta t)\rangle$. The resulting diabats can thus be represented in a block matrix form similar to that of Eq. 21.

We compute the electronic coupling between the diabatic states under a line dipole approximation in Eq. 29.

$$V_{ab} = \langle \phi_a|\hat{V}_{ab}|\phi_b\rangle = \frac{\mu^2}{4\pi \epsilon_r \epsilon_0} \sum_i \sum_j \kappa_{ij} c^{(a)}_i c^{(b)}_j,$$  

(29)

where $c^{(a)}_i = \langle i|\phi_a\rangle$ and $c^{(b)}_j = \langle j|\phi_b\rangle$. We perform adiabatic dynamics along the lowest energy eigenstate and use the joint probability density and the switching function approach described in Sec. II for identifying and preventing trivial crossings. The algorithm we employ in these simulations is illustrated in the form of a flow chart in Fig. 3.

In Fig. 4a, we illustrate the outcome of our diabatization scheme for two eigenstates, $\Psi_1$ and $\Psi_2$, at their crossing point. The figure also contrasts the cases of strongly and weakly coupled states. Figure 4b contains a plot of the average coupling between crossing diabatic states as a function of the distance between the diabats, $d_{ab} = |\langle \phi_a|\hat{x}|\phi_b\rangle| - |\langle \phi_b|\hat{x}|\phi_a\rangle|$.  

(30)

The coupling strength versus distance converges to a point dipole scaling, i.e. $V \propto 1/r^3$, for $d > 200 \AA$, corresponding to 50 or more monomer units. The variation in computed coupling strength, as indicated in shaded areas, stems from variations in the state of the classical subsystem (i.e. the ring-ring torsional landscape) within our sampled ensemble of crossing points.

D. Selecting the Coupling Cutoff, $V_c$.

We categorize crossing points as trivial or not based on the computed value of the diabatic coupling, $|V_{ab}|$. Specifically, we identify a trivial crossing as having a value of $|V_{ab}| < V_c$ and standard avoided crossing as having a value of $|V_{ab}| \geq V_c$. Standard Born-Oppenheimer adiabatic dynamics correspond to the case...
which specifies the non-adiabatic transition probability for a two-state system. In Fig. 4, we plot a histogram of the values of $P_{LZ}$ and the corresponding values of $|V_{ab}|$ as computed from an equilibrium ensemble of configurations from our model. We observe significant scatter in the data but identify the expected trend that $P_{LZ}$ increases with decreasing $|V_{ab}|$. This trend suggests the tendency of the system to exhibit nonadiabatic effects in response to a weakly coupled state crossing. We utilize this trend to assign a value of $V_c$. In particular, we choose $V_c = 5$ meV, corresponding to the coupling value that has a Landau-Zener transition probability of about 95%. We find that the qualitative results of our findings presented in the rest of the paper do not depend on $V_c$ as long as it is chosen such that $P_{LZ} > 0.7$.

IV. DEMONSTRATING THE PERFORMANCE OF OUR APPROACH

In this section, we consider the dynamics of an excited state conjugated polymer system and show that our solution to the TCP yields physically reasonable adiabatic dynamics while preserving the nodeless symmetry of the excitonic wavefunction. Specifically, we compare adiabatic trajectories of the lowest exciton state of a thiophene 200-mer initiated in identical initial states, but with different values of $V_c$. In one trajectory, we set $V_c = 0$, corresponding to the traditional uncorrected Born-Oppenheimer-type adiabatic dynamics, and in the other we set $V_c = 5$ meV. The results of these two trajectories are plotted in Fig. 5.

We observe impulsive long-range exciton hopping in the $V_c = 0$ case (marked by dashed lines in Figs. 5a and 5b) that are not present in the case where $V_c = 5$ meV. These long range hopping events correspond to trivial crossings and are thus eliminated by our method when $V_c = 5$ meV. In the latter case, the lowest exciton state appears spatially unimodal unless its coupling goes through an avoided crossing (marked by solid vertical lines Figs. 5b and 5d). Notably, the two systems behave identically until the point of the first trivial crossing (i.e., $t \approx 0.4$ ps), at which point they evolve along different adiabatic potential energy surfaces and thus begin to diverge. The plots in Figs. 5b and 5d also highlight that our method can effectively handle multiple recursive trivial crossings separated in time.

V. THE EFFECT OF NODAL SYMMETRY PRESERVATION ON EXCITON TRANSPORT PROPERTIES

We now apply our method for simulating wavefunction symmetry preserving dynamics to study the migration of the lowest exciton state in long chain polythiophenes. We also demonstrate that failure to preserve the nodal symmetry of the adiabatic wavefunction can lead
FIG. 5. Comparing dynamics of our symmetry preserving method with $V_c = 0$ and $V_c = 5$ meV for a trajectory initialized from identical configurations. (a) Shading indicates local exciton density at the lowest (active) adiabatic state, i.e., \( \rho = |\Psi|^2 \) with $V_c = 0$. Dashed vertical lines mark discontinuities in exciton position. (b) Same as panel (a) but with $V_c = 5$ meV. Solid vertical lines marks the time points that the Hamiltonian is modified in response to a trivial crossing. Dashed lines indicate the point when the trivial crossing problem vanishes and the Hamiltonian is restored to its original unmodified form. (c) Time dependence of the excited state energy levels of the lowest eigenstates, computed for $V_c = 0$. The red curve indicates the active (lowest) eigenstate, which determines the excited state potential energy surface. (d) Same as panel (c), but with $V_c = 5$ meV.

to unphysical exciton dynamics. We first compare dynamics generated with our symmetry preserving method to the dynamics generated with a non symmetry preserving method of solving the TCP. We characterize the dynamical properties of excitons in terms of their diffusion coefficients, which we quantify by computing exciton mean-squared-displacements (MSD), and their sizes. For a sample of $M$ independent exciton trajectories, MSD is defined as

$$\text{MSD}(t) = \frac{1}{M} \sum_{m} |x_m(t) - x_m(0)|^2,$$

where $x_m(t) = \langle \Psi^{(m)}(t)|\hat{x}|\Psi^{(m)}(t)\rangle$ is the centroid position of exciton wavefunction at time $t$ for $m$-th trajectory. Exciton sizes are quantified in terms of the inverse participation ratio (IPR),

$$\text{IPR} = \frac{1}{\sum_{i}^N (i|\Psi|^2)^4},$$

which roughly corresponds to the number of basis states (i.e., excited monomers) that participate in a given excited state.

One contributing factor to differences between symmetry preserving and non symmetry preserving dynamics is that the size of an adiabatic wavefunction generally increases with the number of wavefunction nodes. As such, the hopping between adiabatic states to prevent the TCP can lead to unintended increases in wavefunction size. To illustrate this, we have computed the probability distribution of IPR values, $P(\text{IPR})$, for each of the five lowest eigenstates of an ensemble of ground state torsional configurations of a thiophene 100-mer. The results, plotted in Fig. 6, illustrate that both the mean and the width of $P(\text{IPR})$ increase with state index. In particular, the $n > 1$ state features exaggerated high-IPR tails (Fig. 6b) that reflect a greatly increased prevalence of highly delocalized states.

Preventing the TCP by artificially populating more delocalized $n > 1$ states can facilitate longer range coupling and thus more rapid diffusion. To illustrate consequences of this effect, we compare the MSD of excitons generated using our symmetry preserving approach to that generated with a common non symmetry preserving state hopping approach also known as the overlap method. Specifically, in the overlap method the active adiabatic state for any given time step is selected to be that which yields maximal wavefunction overlap with the active state of the previous timestep. In this case, overlap between states $i$ and $j$ at adjacent timesteps is given...
Notably, the short time diffusivity of the non symmetry preserving method yields larger values of the diffusion constant. We find that $D$ in the denominator accounts for diffusion in one dimension and account for approximately 15% (for $N = 50$) to 50% (for $N = 100$) of overall trajectories with an average quenching time of $t_{\text{quench}} \approx 5$ ps with $V_c = 5$ meV.

The results plotted in Figs. 7a and 7b show that the early time exciton diffusivity differs significantly between these two approaches to solving the TCP. The early time exciton diffusivity is given by the quantity $D_{\text{short}} = \text{MSD}(t = 1 \text{ ps})/[2 \cdot 1 \text{ ps}]$ where the factor 2 in the denominator accounts for diffusion in one dimension. We find that $D_{\text{short}}$ for the non symmetry preserving method yields larger values of the diffusion constant. Notably, the short time diffusivity of the non symmetry preserving approach grows with the length of the polymer chain. This length dependence is unexpected for chains with monomer numbers of $N \gtrsim \langle \text{IPR} \rangle + \langle d \rangle/l_0 \approx 40$, where $\langle \text{IPR} \rangle$ is the average size of the diabat ($\langle \text{IPR} \rangle \approx 8$); $\langle d \rangle$ is the average distance between diabats undergoing avoided crossings ($\langle d \rangle = 150 \text{ Å}$ for $P_{LZ} \approx 0.99$); and $l_0$ is the distance between two thiophene rings ($l_0 = 3.88 \text{ Å}$). The plateau in the MSD at longer times for the non symmetry preserving method represents a finite size effect.

Figure 7b highlights that our symmetry preserving approach delivers the desired physical behavior that exciton diffusivity is independent of chain length for sufficiently long polymer chains. For shorter chains ($N < 200$), the plateau in the MSD at longer times is due to a finite size effect. Based on the MSD data that are plotted in Fig. 7b, we find that the diffusivity at short times ($t < 500$ fs) is generally faster than at longer times. We attribute this difference to changes in the classical degrees of freedom, particularly the torsional landscape, that occur upon excitation. These changes result in self-trapping, which reduces the mobility of the exciton. Further evidence for self-trapping can be found by computing the time dependent average of the exciton IPR. As plotted in Fig. 8, we find a rapid decrease in exciton size during the first $\sim 100$ fs immediately following excitation.
At longer times \( i.e., t \gtrsim 5 \text{ ps} \), we observe a significant difference between the IPR computed with the symmetry preserving and non-symmetry preserving methods. Specifically, the non-symmetry preserving method leads to excitons that are more delocalized than with the symmetry preserving method. We observe that the IPR for unmodified purely diabatic dynamics \( i.e., V_c = 0 \) is essentially the same as with the symmetry preserving method, indicating that the symmetry preserving method effectively populates nodeless and torsionally relaxed adiabatic states. On the other hand, the tendency for the non-symmetry preserving approach to populate higher level \( (n > 1) \) states, which are inherently more delocalized (see Fig. [6]), leads to a small but unintended increase in mean exciton size.

The two dominant modes of exciton mobility in long chain conjugated polymers are the diffusion of the active diabat along the length of the polymer chain, as mediated by torsional fluctuations in the tails of the active diabatic state, and hopping through avoided crossings. Since \( V_c \) controls the threshold for this hopping mobility, it thus also contributes significantly to the determination of exciton diffusivity. This can be seen in Fig. [7], which contains a plot of the steady-state diffusivity as a function of \( V_c \). We find that \( D \) ranges between values of 0.005 and 0.04 cm\(^2\)/s, depending on the choice of \( V_c \).

Our simulated values of diffusivity are larger than estimated value of \( D \approx 0.001 \pm 0.0004 \text{ cm}^2\text{/s} \) based on fluorescence quenching experiments by Healy \textit{et al.}\cite{37} We attribute this difference to the lack of disorder in monomer excitation energy and in our assumption that the polymer chain is in an ideal extended linear configuration. For instance, in the presence of configurational disorder, diffusivity computed from our model is about 0.001 \pm 0.0002 cm\(^2\)/s at \( V_c = 10 \text{ meV} \), which is about 20\% smaller than that of linear configurations, and is also in good agreement with experimental measurement by Healy \textit{et al.} We have simulated disordered polythiophene backbone configurations using the coarse grained poly(3-hexylthiophene) model by Schwarz \textit{et al.}\cite{38} Details on simulations with disordered polymer configurations are described in the SI.

The large difference in steady-state diffusivity between our symmetry preserving method and the overlap-based non-symmetry preserving method is not entirely due to differences in exciton size. The analysis of trajectories generated on long chains indicate that when the nodal structure of the wavefunction is not preserved, the dynamics feature frequent long range hops. These long range hops, illustrated in Fig. [7], serve to artificially enhance exciton diffusivity. The frequency of these hops increases with increasing chain length even when the chain is much larger than the exciton size. This finding highlights that the effect is highly non-local and thus inconsistent with physical expectations for these dynamics.

The origin of this non-local hopping behavior is the use of wavefunction overlap as an identifier of trivial crossings. Specifically, with the overlap method, the signature of a trivial crossing is when \( S_{k,n} > S_{k,k} \) where \( k \) is the active state index, and \( n \neq k \). In practice, we have determined that this method is only reliable for detecting trivial crossings when the diabatic coupling is very small, \textit{i.e.}, \(|V_{ab}| < 0.1 \text{ meV} \), corresponding to states that are separated by more than 80 monomer units (See Fig. S1)\cite{24,25} These results thus suggest that in certain cases, such as we have presented here, the wavefunction overlap method for identifying trivial crossings can be prone to false positives and thus produce unphysical dynamics.

### VI. CONCLUSION AND OUTLOOK

In summary, we have presented a theoretical framework for solving the TCP that preserves the nodal symmetry of the adiabatic wavefunction. We have shown how changes in this symmetry can lead to artificial delocalization of the wavefunction as well as false positives in the identification of trivial crossings. When our symmetry preserving method is applied to simulations of exciton dynamics on long chain conjugated polymer systems, the TCP is effectively eliminated and exciton properties are free from unphysical polymer chain length dependent artifacts.

The results presented here highlight the importance of considering the nodal structure of the adiabatic wavefunction when implementing dynamics that include changes in eigenstate. This includes nonadiabatic methods based on surface hopping, which rely on gathering statistics of many adiabatic trajectories.\cite{16,10,19} In such approaches, artificially imposing hopping between eigen-
states to prevent trivial crossings may introduce uncontrolled sources of error. As we have highlighted, avoiding discontinuities in wavefunction nodal symmetry during simulations of adiabatic dynamics is especially important in large-scale systems with many diabatic states whose energy surfaces can potentially cross. Our method for solving the TCP ensures more reliable simulations for experimentally relevant system sizes.

SUPPLEMENTARY MATERIAL

See supplementary material (link) for multi-state symmetry preserving scheme, details on the polymer model parameterization, and comparisons of trivial crossing detection methods.

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Supplementary Information for
“Changes in wavefunction symmetry through a trivial crossing create unphysical adiabatic dynamics”

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S.1. MULTI-STATE SYMMETRY PRESERVING METHOD FOR NESTED TRIVIAL CROSSINGS

In a multi-state system, there is a possibility of additional trivial crossings during a given trivial crossing period, which we refer to as nested trivial crossings. We use the convention, $t_1^{(1)} < t_1^{(2)} < \cdots < t_1^{(n)} < t_2^{(n)} < \cdots < t_2^{(2)} < t_2^{(1)}$, to define $n$-number of nested trivial crossing periods. For example, consider a three-level system described as

$$\hat{H} = \hat{H}_a + \hat{H}_b + \hat{V}_{ab} + \hat{H}_c + \hat{V}_{ac} + \hat{V}_{bc}. \quad (S.1)$$
If there is a trivial crossing occurring first between states $| \phi_a \rangle$ and $| \phi_b \rangle$, we eliminate $| \phi_b \rangle$ by applying a switching function as follows:

$$\hat{H}^{(1)}_{\text{mod}}(t) = \hat{H}_a + f_b^{(1)}(t)[\hat{H}_b + \hat{V}_{ab} + \hat{V}_{bc}] + \hat{H}_c + \hat{V}_{ac},$$  \hspace{1cm} (S.2)

where

$$f_b^{(1)}(t) = \begin{cases} 
0 & \text{if } |V_{ab}| \leq V_c \text{ and } t_c^{(1)} \leq t \leq t_r^{(1)}, \\
1 & \text{otherwise}. 
\end{cases} \hspace{1cm} (S.3)$$

If there is another trivial crossing between the states $a$ and $c$ within the modified Hamiltonian $\hat{H}^{(1)}_{\text{mod}}$, we apply an additional switching function for state $c$ to eliminate both states $b$ and $c$ from the original Hamiltonian $\hat{H}$, i.e.,

$$\hat{H}^{(2)}_{\text{mod}}(t) = \hat{H}_a + f_b^{(1)}(t)[\hat{H}_b + \hat{V}_{ab} + \hat{V}_{bc}] + f_c^{(2)}(t)[\hat{H}_c + \hat{V}_{ac}],$$  \hspace{1cm} (S.4)

where

$$f_c^{(2)}(t) = \begin{cases} 
0 & \text{if } |V_{ac}| \leq V_c \text{ and } t_c^{(2)} \leq t \leq t_r^{(2)}, \\
1 & \text{otherwise}. 
\end{cases} \hspace{1cm} (S.5)$$

Let $| \Psi^{(\text{mod},k)}_1 \rangle$ be the lowest eigenstate of the modified Hamiltonian $\hat{H}^{(k)}_{\text{mod}}$ where $k = 0$ is the full Hamiltonian case ($\hat{H}^{(0)}_{\text{mod}} \equiv \hat{H}$). The modified Hamiltonian has the property that $\langle \Psi^{(\text{mod},k)}_1(t) | \Psi^{(\text{mod},k-1)}_1(t) \rangle^2 \approx 0.5$ at $t = t_c^{(k)}$ and $\langle \Psi^{(\text{mod},k)}_1(t) | \Psi^{(\text{mod},k-1)}_1(t) \rangle^2 \approx 1$ at $t = t_r^{(k)}$.

Our multi-state symmetry preserving method is summarized in Figure 3 (main text).

**S.2. COMPARISON OF TRIVIAL CROSSING DETECTION SCHEMES**

Figure S.1 compares the two trivial crossing detection schemes: the joint probability density and the overlap integral. While the overlap method is able to detect trivial crossing for small diabatic coupling (e.g., $|V_{ab}| < 0.5$ meV), it fails to detect crossing points with $|V_{ab}| \geq 0.5$ meV, whereas the joint probability density method succeeds in all cases.
FIG. S.1. Case studies of crossing points with varying coupling strength between two diabatic states for a 100-mer linear organic conjugated polymer model. From left to right column, the coupling strength, $|V_{ab}|$, is increasing. Each row plots properties of the two lowest adiabatic states: (a) eigenvalues of states 1 and 2, $E_i$, (b) the monomer site index with maximum exciton density, $n_{\text{max}}$, (c) joint exciton density of states 1 and 2, $P_{1,2}$, and (d) absolute value of the overlap integral between states $i$ and $j$, i.e., $S_{i,j} = |\langle \psi_i(t) | \psi_j(t + \delta t) \rangle|$ with $\delta t = 1$ fs. In all plots, the time origin is defined to be the crossing point, $t_c$. 
S.3. PARAMETERIZATION OF EXCITON DYNAMICS MODEL OF CONJUGATED ORGANIC POLYMERS

A. Benchmark method: all-atom QCFF/PI

Coarse-grained exciton transport model of conjugated organic polymer has been parameterized based on the QCFF/PI method, which has been used to study excited state dynamics of thiophene 30-mers in earlier work. In QCFF/PI, the molecular system is partitioned into two subsystems, one containing explicit quantum mechanical detail and the other in which such details are accounted for implicitly. In our case, the quantum subsystem contains only the π-electrons, which are described using a semi-empirical Pariser-Parr-Pople (PPP) Hamiltonian. All remaining degrees of freedom (nuclear as well as the core and sigma electrons) belong to the classical subsystem, which is modeled as a positively charged nuclear scaffold that evolves via a molecular mechanics force field. All calculations of electrostatic interactions here include the a uniform dielectric screening to approximately mimic the influence of a non-polar organic solvent. The particular value of the dielectric constant used in this study is $\varepsilon_r = 2.7$.

Following the notation of Warshel and Karplus, the molecular mechanics forcefield is given by

$$V_\sigma(r) = V_\sigma(r)_{\text{conj}} + V_\sigma(r)_{\text{sat-conj}}, \tag{S.6}$$

where the subscript $\text{conj}$ refers to the collection of atoms participating in the conjugated π-electron system, and the subject subscript $\text{sat-conj}$ refers to the interaction between the collections of saturated atoms (in this case, only hydrogen atoms) and conjugated atoms. The first term in the above equation is given by

$$V_\sigma(r)_{\text{conj}} = \sum_i D_b \left( e^{2-\alpha(b_i-b_0)} - 2e^{2-\alpha(b_i-b_0)} \right) + \frac{1}{2} \sum_i \left[ K_\theta(\theta_i - \theta_0)^2 + F(q_i - q_0)^2 \right]$$

$$+ \frac{1}{2} \sum_i \left[ K_\phi^{(1)} \cos \phi_i + K_\phi^{(2)} \cos 2\phi_i \right] + \sum_i K_{\theta\theta'}(\theta_i - \theta_0)(\theta'_i - \theta_0) \cos \phi_i$$

$$+ \sum_{ij} \left( A e^{-\mu r_{ij}} - B r_{ij}^{-6} \right), \tag{S.7}$$

non-bonded pairs
where $b_i$, $\theta_i$, and $\phi_i$ represent the bond lengths, bond angles, and torsional angles, respectively; $\theta_i$ and $\theta'_i$ are two bond angles, XAB and ABY of a bond AB; $q_i$ is the distance between the first and the third of three consecutively bonded atoms; and $r_{ij}$ is the distance between atoms $i$ and $j$. The second term in Eq. S.6 is given by

$$V(r)_{\text{sat-conj}} = \frac{1}{2} \sum_i [K_b(b_i - b_0)^2 + 2D_b] + \frac{1}{2} \sum_i [K_\theta(\theta_i - \theta_0)^2 + F(q_i - q_0)^2]$$

$$+ \frac{1}{2} \sum_i \left( K_{\phi}^{(2)} \cos 2\phi_i \right) + \sum_{ij} \left( Ae^{-\mu r_{ij}} - Br_{ij}^{-6} \right). \quad (S.8)$$

The values of forcefield used in this study are included in Table I.

Following the notation by Lobaugh and Rossky,$^6,^7$ the electronic energy portion of the potential is given by the PPP method and is expressed as

$$V_\pi = \frac{1}{2} \sum_{\mu\nu} P_{\mu\nu}(H_{\mu\nu} + F_{\mu\nu}), \quad (S.9)$$

where the summation is over the atomic sites that contribute to the $\pi$-system (i.e., Carbon and Sulfur). The terms $P_{\mu\nu}$, $F_{\mu\nu}$, and $H_{\mu\nu}$ are the bond-order, Fock, and one-electron core matrix elements, respectively. The bond-order matrix elements are given by

$$P_{\mu\nu} = 2 \sum_i c_\mu^i c_\nu^i, \quad (S.10)$$

where the product of molecular orbital coefficients $c_\mu^i$ and $c_\nu^i$ at site $\mu$ and $\nu$ is summed over occupied molecular orbitals ($n = 3N$ for $N$-mer polythiophene). The Fock matrix elements are

$$F_{\mu\nu} = H_{\mu\nu} - \frac{1}{2} P_{\mu\nu} \gamma_{\mu\nu} \text{ if } \mu \neq \nu$$

$$F_{\mu\mu} = H_{\mu\mu} + \frac{1}{2} P_{\mu\mu} \gamma_{\mu\mu} + \sum_{\rho \neq \mu} P_{\rho\rho} \gamma_{\rho\mu}. \quad (S.11)$$

$\gamma_{\mu\nu}$ are the two-electron repulsion matrix elements, which are in turn defined as

$$\gamma_{\mu\nu} = \frac{e^2}{R_{\mu\nu} + a_{\mu\nu}}, \quad (S.12)$$

where

$$a_{\mu\nu} = \frac{2e^2}{\gamma_{\mu\mu} + \gamma_{\nu\nu}}. \quad (S.13)$$
![Table I. Molecular Mechanics Forcefield Parameters](image-url)

\[
\begin{array}{|c|c|c|c|c|}
\hline
\text{Bond} & D_b \text{ (kcal mol}^{-1}\text{)} & K_b/2 \text{ (kcal mol}^{-1}\text{ \AA}^{-2}\text{)} & \alpha \text{ (\AA}^{-1}\text{)} & b_0 \text{ (\AA)} \\
\hline
\text{C-C} & 87.94 & - & 1.786 & 1.46 \\
\text{C-S} & 65.00 & - & 1.700 & 1.78 \\
\text{C-H} & 103.10 & 339.00 & 1.080 & - \\
\hline
\text{Bond Angle} & K_{\theta}/2 \text{ (kcal mol}^{-1}\text{ rad}^{-2}\text{)} & \theta_0 \text{ (rad)} & F/2 \text{ (kcal mol}^{-1}\text{ \AA}^{-2}\text{)} & q_0 \text{ (\AA)} \\
\hline
\text{C-C-C} & 52.8 & 2.094 & 32.05 & 2.56 \\
\text{C-C-S} & 50.0 & 2.094 & 30.40 & 2.90 \\
\text{C-S-C} & 50.0 & 2.094 & 30.40 & 2.50 \\
\text{C-C-H} & 24.0 & 2.094 & 29.535 & 2.178 \\
\text{S-C-H} & 15.0 & 2.094 & 26.50 & 2.18 \\
\hline
\text{Torsional Angle} & K_{\phi}^{(1)}/2 \text{ (kcal mol}^{-1}\text{)} & K_{\phi}^{(2)}/2 \text{ (kcal mol}^{-1}\text{)} & K_{\theta\theta} \text{ (kcal mol}^{-1}\text{ rad}^{-2}\text{)} \\
\hline
\text{X-C-C-X} & 2.3 & 2.54 & -6.0 & \\
\text{X-C-S-X} & 2.3 & 4.5 & -10.0 & \\
\text{X-C-H-X} & - & 0.8 & - & \\
\hline
\text{Non-bonded} & A \text{ (kcal mol}^{-1}\text{)} & B \text{ (kcal mol}^{-1}\text{)} & \mu \text{ (\AA}^{-1}\text{)} \\
\hline
\text{C···C} & 11392.84 & 560.44 & 3.0115 \\
\text{S···S} & 30923.41 & 1521.19 & 3.0115 \\
\text{H···H} & 4882.64 & 26.59 & 4.3458 \\
\text{C···S} & 18769.80 & 923.33 & 3.0115 \\
\text{C···H} & 7458.36 & 134.97 & 3.5577 \\
\text{S···H} & 12287.72 & 222.36 & 3.5577 \\
\hline
\end{array}
\]

\(e\) is the magnitude of the electron charge, \(R_{\mu\nu}\) is the distance between atoms \(\mu\) and \(\nu\), and \(\gamma_{\mu\nu}\) is the one-center repulsion parameter. The diagonal elements of the one-electron core matrix are

\[
H_{\mu\mu} = \alpha_{\mu} - \sum_{\rho \neq \mu} Z_{\rho} \gamma_{\mu\rho},
\]

where \(\alpha_{\mu}\) is the energy of the orbital \(\mu\). The second term is the interaction of the electron (at site \(\mu\)) with the nuclear core (at site \(\rho\)), which has formal charge \(Z_{\rho}\) (equal to the number of 2p electrons the atom donates to the \(\pi\)-system). The off-diagonal elements of the
TABLE II. PPP Hamiltonian Parameters

| Site | $\gamma_{\mu\mu}$ (hartree) | $\alpha_{\mu\nu}$ (hartree) |
|------|----------------------------|-----------------------------|
| C    | 0.3895                     | -0.42078                    |
| S    | 0.3598                     | -0.734986                   |

| Bond | $\mu_{\mu\nu}$ (bohr$^{-1}$) | $\beta_{1}^{\mu\nu}$ (hartree) | $\beta_{2}^{\mu\nu}$ (hartree bohr$^{-1}$) | $R_{\mu\nu}^{\text{eq}}$ (bohr) |
|------|-------------------------------|-------------------------------|---------------------------------|---------------------------------|
| C-C  | 0.73868                       | -0.089586                     | -0.019198                       | 2.639948                        |
| C-S  | 0.81325                       | -0.078013                     | 0.025506                        | 2.66941                         |

The parameters for the PPP Hamiltonian that are used in this study are given in Table II.

Excited electronic states are computed using configuration interaction with single excitations (CIS).

B. Ground state coarse grained model parameterization

Ground state torsional dihedral angle potential energy, $U_g$, for thiophene rings has been parameterized from ground state QCFF/PI simulations of quaterthiophene at $T = 300$ K. The ground state potential energy is calculated from the potential of mean force (PMF) of torsional angles, i.e., $\text{PMF} = -k_B T \ln P(\theta)$. $P(\theta)$ is the probability distribution of torsional angles based on the statistics of the middle bond torsional angle of each ground-state quaterthiophene at $T = 300$ K with a sample size of 100 equilibrated configurations. We fit the PMF to a fourier series of the form,

$$U_g(\theta) = \sum_{i=1}^{3} a_i \sin (b_i \theta + c_i),$$

where the coefficients $a_i$, $b_i$, and $c_i$ are tabulated in Table III. The resulting ground state torsional potential energy function is shown in Figure S.2.
FIG. S.2. Parameterization of ground state torsional potential energy. Potential of mean force computed from the QCFF/PI method is plotted in shown in gray curve. The ground state torsional potential energy, $U_g$, of the coarse-grained exciton model is plotted in red curve. Torsional angle, $\theta$, is defined to be zero at the cis-configuration of two sulfur atoms in adjacent monomers as shown in the top schematics.

TABLE III. Ground state torsional potential coefficients

| i | $a_i$ (eV) | $b_i$ (eV/deg) | $c_i$ (rad) |
|---|---|---|---|
| 1 | 0.02831 | 0.00465 | 1.571 |
| 2 | 0.01993 | 0.03616 | -1.571 |
| 3 | 0.01626 | 0.06993 | 1.571 |

To analyze dynamical properties of torsional modes, we compute the ring-ring planarity time correlation function,

$$C(t) = \frac{\langle \delta A(t) \delta A(0) \rangle}{\langle \delta A(0)^2 \rangle},$$  \hspace{1cm} (S.18)

$$\delta A(t) = | \cos \theta(t) | - | \cos \theta |_{avg};$$  \hspace{1cm} (S.19)

where $| \cos \theta |_{avg}$ is the average value of $\cos \theta$ of a given trajectory. The pair of angle brackets in Eq. S.18 represents an ensemble average over all 100 trajectories. We have generated a hundred 10 ps-long equilibrated trajectories of quaterthiophene.
The moment of inertia ($I$) and frictional damping coefficient ($\eta$) of torsional modes in the coarse grained Langevin model are chosen by fitting $C(t)$ generated by the coarse grained method to those of the QCFF/PI method. The results from the coarse grained Langevin model have been averaged over 1000 trajectories of linear quarterthiophene. The QCFF/PI data and the final fitting results are shown in Figure S.3. The resulting best fit parameters are $I = 3.0$ eV fs$^2$ deg$^{-2}$ and $\eta = 0.0035$ eV fs deg$^{-2}$.

FIG. S.3. Comparisons of the ground state time correlation function (a) and its fourier transform (b) generated from two different methods: the atomistic QCFF/PI method (gray lines) and the coarse-grained Langevin model (red lines). QCFF/PI results have been averaged over 100 trajectories of quarterthiophene, each 10 ps long. The coarse grained model parameters are $U_g(\theta)$ (plotted in Figure S.2), $I = 3.0$ eV fs$^2$ deg$^{-2}$, $\eta = 0.0035$ eV fs deg$^{-2}$, and $T = 300$ K.

C. Frenkel exciton Hamiltonian parameterization

Excited state parameters in the Frenkel exciton Hamiltonian are determined based on the excited state QCFF/PI simulations of 30-mer polythiophene at $T = 300$ K. Starting from a linear polythiophene chain, we equilibrate its structure in the electronic ground state for 100 ps. We then turn on the excited state force in the lowest excited state to sample 100 configurations of 3 ps-long excited state dynamics.

To compute the through-bond coupling term $J_{SE}$, we project the excited state force acting on each atoms to the ring-ring torsional coordinate to compute $F_{ex}(\theta_i)$, which is the torque acting on the $i$-th ring junction. We also compute the exciton density across each ring junction, $\rho_i$, by taking the overlap of electron and hole wavefunctions of all atoms in each
ring connected to the $i$-th junction. The average value of $F_{ex}(\theta_i)/\rho_i$ computed from the QCFF/PI method is shown in Figure S.4a. We fit the average force from the QCFF/PI method to an analytical expression of the excited state force that we have derived based on the Frenkel exciton Hamiltonian model,

$$F_{ex}(\theta_i) = 2J_{SE} \sin(2\theta_i)\rho_i,$$  \hspace{1cm} (S.20)

in which the only free-parameter during the fitting procedure is $J_{SE}$. From this approach, we obtain $J_{SE} = -0.5$ eV. The resulting fit is also depicted as a red curve in Figure S.4a.

We estimate the transition dipole coupling magnitude, $\mu_0$, by performing the coarse grained model simulations of 30-mer polythiophene in a linear configuration with varying values of $\mu_0$. We compare the distribution of inverse participation ratio (IPR) of the lowest exciton state calculated from the coarse grained model to that of the QCFF/PI method. We find that $\mu_0 = 9.0$ D best reproduces the distribution obtained from QCFF/PI method (see Figure S.4b).

**FIG. S.4.** Benchmarking excited state properties to the atomistic QCFF/PI simulations. Panel (a) shows the excited state torque acting on ring junctions, normalized by the exciton density across those ring junctions. The red curve in panel (a) is the best fit result to the QCFF/PI data using Eq. S.20. Panel (b) plots the probability distribution of exciton sizes, quantified by the inverse participation ratio (IPR). The coarse grained model data are computed over 100 equilibrium torsional configurations of a 30-mer thiophene in the ground electronic state at $T = 300$ K.
S.4. SIMULATION OF CONJUGATED ORGANIC POLYMERS WITH CONFORMATIONAL DISORDER

The solution phase structure of 110-mer polythiophene is simulated using molecular dynamics of a coarse-grained polymer model of poly(3-hexylthiophene) (P3HT) developed by D. Huang et al.\textsuperscript{8} Simulations have been carried out at constant volume and temperature using Langevin dynamics, starting from an initial configuration of randomly placed and oriented chain with intermonomer dihedral angles selected from a Boltzmann distribution of the intermonomer torsional potential. The temperature and friction coefficient are set to $T = 300$ K and $\gamma = (180 \text{ fs})^{-1}$, respectively. We have generated 300 disordered backbone conformations, each resulting from a 50 ns-long equilibration run. The average radius of gyration of these polymers is $R_g = 6.4 \pm 2.4$ nm.

To compute exciton diffusion coefficient, we have sampled 200 independent trajectories per backbone conformation, resulting in 60,000 trajectories in total. We follow the same procedure of equilibrating the ground state torsional configurations as in the linear chain conformation. We then run excited state dynamics in the lowest exciton state for 10 ps with $V_c = 10 \text{ meV}$ and the quenching boundary conditions. We find that the average exciton diffusion coefficient for disordered backbone conformations is $D = 0.001 \pm 0.0002 \text{ cm}^2/\text{s}$.

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