Intramolecular Vibrations in Excitation Energy Transfer: Insights from Real-Time Path Integral Calculations

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Abstract

Excitation energy transfer (EET) is fundamental to many processes in chemical and biological systems and carries significant implications for the design of materials suitable for efficient solar energy harvest and transport. This review discusses the role of intramolecular vibrations on the dynamics of EET in non-bonded molecular aggregates of bacteriochlorophyll, a perylene bisimide, and a model system, based on insights obtained from fully quantum mechanical real-time path integral results for a Frenkel exciton Hamiltonian that includes all vibrational modes of each molecular unit at finite temperature. Generic trends, as well as features specific to the vibrational characteristics of the molecules, are identified. Weak electronic-vibrational (EV) interaction leads to compact, near-Gaussian densities on each electronic state, whose peak follows primarily a classical trajectory on a torus, while non-compact densities and nonlinear peak evolution are observed with strong EV coupling. Interaction with many intramolecular modes and increasing aggregate size smear, shift and damp these dynamical features.

1. Introduction

A great deal of theoretical and experimental effort continues to be devoted to the understanding of excitation energy transfer (EET) in molecular aggregates. Energy transfer is fundamental to all of chemistry and biology. Apart from the desire to understand energy transfer processes for the sake of advancing knowledge, intense investigations of EET are motivated by the quest for materials suitable for efficient solar energy harvest and transport.

Except for special regimes where weak coupling assumptions, mode separability or statistical descriptions are applicable, the dynamics of energy transfer in molecular systems is highly complex. The difficulty in understanding the rate and mechanistic details of such processes lies in the strongly quantum mechanical nature of the systems themselves. Each polyatomic molecule involved comprises several electronic states which couple to tens or hundreds of vibrational modes, and multiple such molecules interact. Further, the thermal energy at physiological temperatures, the electronic coupling between molecular units, the frequencies of several important vibrational modes and the total nuclear reorganization energy characterizing EET in molecular aggregates often fall within a rather narrow energy range, and their interplay leads to very rich behaviors. The intermediate value of electronic couplings commonly found in such systems often leads to pronounced quantum mechanical effects that may include coherent dynamics, while analytical or numerical approximations are unsuitable. However, without simplifications, the intricate dynamics of EET is beyond the reach of accurate quantum mechanical calculations.

This review discusses recent progress in understanding the EET dynamics of non-covalently interacting molecular aggregates in which the electronic couplings have the Frenkel exciton form (1; 2). The ground and excited electronic states in each molecular unit are coupled to all intramolecular vibrations, which are described within the normal mode approximation. Even with these simplifications, the ensuing dynamics is highly complex and displays a plethora of dynamical behaviors, which share some common trends but also exhibit unique features that are specific to each system. In spite of the very large Hilbert space resulting from two electronic states per molecule and several hundred thermally excited vibrational degrees of freedom, the nonadiabatic dynamics of EET in long molecular aggregates can be treated without approximation using fully quantum mechanical methods based on the path integral formulation of time-dependent quantum mechanics (3; 4), which provide a wealth of information and novel physical insights.

We begin with some simple and general theoretical considerations regarding the dynamics of molecular dimers, which illustrate some of the key elements underlying the mechanism of EET. We also review a transformation that maps the Hamiltonian of a homodimer to the familiar spin-boson problem, where the two sets of intramolecular vibrations are mapped on a single set of common modes. Next, we use fully quantum mechanical results to investigate the electronic-vibrational (EV) dynamics of the dimer by alternating between this common mode representation and the full intramolecular mode picture. Even with only one or two normal modes in each molecule, the overall EV evolution of the dimer is rather nontrivial and offers several key elements for the interpretation of multimode EET dynamics. We discuss these effects, as well as the role of all other molecular vibrations, on the time evolution of electronic populations and EV densities, analyzing observables that probe the correlated dynamics of the electronic system and the vibrational modes. We then move to long aggregates (chains and rings of up to 25 molecular units) and observe the dynamics of energy transfer to nearby as well as distant molecular units. The discussion focuses on symmetric aggregates, whose eigenstates are delocalized, thus maximizing quantum coherence possibilities. At the same time, the increased system size and larger number of vibrational modes contribute to more effective damping.

We illustrate the basic trends of EET using three sets of intramolecular vibrational parameters:

(i) A smooth, continuous spectral density of the Ohmic form (5), $J(\omega)=\gamma\omega\, e^{-\omega/\omega_c}$, which is commonly employed for studying the effects of model dissipative environments (6). The dynamics of a two-level system coupled to an Ohmic bath is characterized by very rich dynamical behaviors (7), which have been the subject of countless investigations. We choose a coupling strength γ of moderate magnitude, motivated by the parameters of molecular EET calculations that follow.

(ii) The set of 28 discrete modes of a bay-substituted perylene bisimide molecule (8) (PBI-1, see Fig. 3c) that have been determined to couple significantly to its electronic states. PBI dyes and their derivatives are attractive candidates for their stacking, self-assembly and photophysical properties, and have been thoroughly investigated (9). The J-aggregates of PBI-1 are of particular interest because of their high fluorescence quantum yield (10-12). The monomers in these aggregates interact strongly with a calculated exciton coupling value $J=-514\,\mathrm{cm}^{-1}$ (13). Further, the normal modes of the PBI-1 molecule (13) are unevenly distributed and some of these are strongly coupled to the electronic states, making this molecule an interesting case study for EET. The zero-temperature dynamics of small PBI-1 aggregates with 5-10 vibrational modes per monomer have been studied by various methods, and some finite-temperature calculations have been reported using a truncated set of excited vibrational states for each mode (13-15).

(iii) The set of 50 vibrational modes of the bacteriochlorophyll (BChl) molecule with nonzero Huang-Rhys factors, available from spectroscopic data (16). The intriguing dynamics of BChl aggregates, such as the LH2 (Fig. 6b, left panel) and FMO complexes found in the light harvesting systems of photosynthetic bacteria and plants (17) have been the subject of intense experimental and theoretical investigations; for example see (18-24). The exciton coupling in the B850 ring of the LH2 complex has been determined to have the value $J=363\,\mathrm{cm}^{-1}$ (25). In sharp contrast to PBI-1, the vibrational modes of the BChl molecule are more uniformly distributed over the entire frequency range and no mode is characterized by a particularly large coupling strength.

These three examples exhibit rich dynamical behaviors that are representative of diverse regimes encountered in EET of molecular aggregates.

Even though the normal mode (or dissipative bath) coordinates included in the calculations are not explicitly coupled to each other in the EET Hamiltonian, we observe signatures of indirect interaction between modes in the ensuing dynamics. This is the result of effective coupling through the electronic degree of freedom. Further, even though the diabatic surfaces are quadratic functions, the nonadiabatic coupling introduces an implicit anharmonicity which leads to nonlinear effects in the EV dynamics. The discussion in sections 5 and 6 further elaborates on these observations.

2. Preliminaries

We begin by describing the EV Hamiltonian for an aggregate, where the two electronic states that are relevant to EET in each molecular unit are coupled to all the vibrational modes of the molecule. In this review we focus on the effects of intramolecular vibrations and do not consider external environments that can further modulate the EET dynamics.

2.1 Exciton-vibration Hamiltonian

Consider an aggregate of n identical molecular units, labeled by the index $\alpha = \mathrm{A,B,C},\ldots$, in a single-file arrangement. Each molecular unit has two relevant electronic states: the ground state $|0_\alpha\rangle$ with eigenvalue ε_α^0 and the excited state $|1_\alpha\rangle$ with eigenvalue ε_α^1. The Hamiltonian of monomer α is thus given by

$$\hat{H}_\alpha = \left(\varepsilon_\alpha^0 + \hat{h}_\alpha^0\right)|0_\alpha\rangle\langle 0_\alpha| + \left(\varepsilon_\alpha^1 + \hat{h}_\alpha^1\right)|1_\alpha\rangle\langle 1_\alpha| \tag{2.1}$$

where h_α^0 and h_α^1 describe the nuclear degrees of freedom on each electronic state.

Throughout this review we focus on the dynamics of energy transfer within the singly excited electronic subspace of the aggregate. We use the abbreviated notation $|\alpha\rangle$ to denote the state of the aggregate in which monomer α is excited, and $|0\rangle$ for the ground state:

$$|0\rangle \equiv |0_\mathrm{A} 0_\mathrm{B} 0_\mathrm{C} \cdots\rangle,\; |\mathrm{A}\rangle \equiv |1_\mathrm{A} 0_\mathrm{B} 0_\mathrm{C} \cdots\rangle,\; |\mathrm{B}\rangle \equiv |0_\mathrm{A} 1_\mathrm{B} 0_\mathrm{C} \cdots\rangle,\; \ldots \tag{2.2}$$

The interaction between the monomers is described by Frenkel exciton (1; 2; 26) terms and the full aggregate Hamiltonian is

$$\hat{H}_\mathrm{full} = \hat{H}_\mathrm{A} + \hat{H}_\mathrm{B} + \cdots + J_\mathrm{AB}\left(|\mathrm{A}\rangle\langle\mathrm{B}| + |\mathrm{B}\rangle\langle\mathrm{A}|\right) + J_\mathrm{BC}\left(|\mathrm{B}\rangle\langle\mathrm{C}| + |\mathrm{C}\rangle\langle\mathrm{B}|\right) + \cdots \tag{2.3}$$

where J_AB etc. are the electronic coupling parameters, which allow the transfer of excitation energy. Further, the single-excitation block of the aggregate Hamiltonian can be partitioned into an electronic part and a sum of uncoupled EV components, $\hat{H}_\mathrm{single} = \hat{H}_\mathrm{e} + \hat{H}_\mathrm{ev}$, where

$$\hat{H}_\mathrm{e} = E_\mathrm{A}|\mathrm{A}\rangle\langle\mathrm{A}| + J_\mathrm{AB}\left(|\mathrm{A}\rangle\langle\mathrm{B}| + |\mathrm{B}\rangle\langle\mathrm{A}|\right) + E_\mathrm{B}|\mathrm{B}\rangle\langle\mathrm{B}| + J_\mathrm{BC}\left(|\mathrm{B}\rangle\langle\mathrm{C}| + |\mathrm{C}\rangle\langle\mathrm{B}|\right) + \cdots \tag{2.4}$$

Eq. (2.4) involves only singly excited states of the aggregate (i.e. it does not include the ground electronic state), and $E_\mathrm{A} = \varepsilon_\mathrm{A}^1 + \varepsilon_\mathrm{B}^0 + \cdots$, $E_\mathrm{B} = \varepsilon_\mathrm{A}^0 + \varepsilon_\mathrm{B}^1 + \cdots$. The EV interaction is given by

$$\hat{H}_\mathrm{ev} = \left(\hat{h}_\mathrm{A}^1 + \hat{h}_\mathrm{B}^0 + \cdots\right)|\mathrm{A}\rangle\langle\mathrm{A}| + \left(\hat{h}_\mathrm{A}^0 + \hat{h}_\mathrm{B}^1 + \cdots\right)|\mathrm{B}\rangle\langle\mathrm{B}| + \cdots \tag{2.5}$$

In the case of linear aggregates with nearest neighbor interactions, Eq. (2.4) is the simple tridiagonal Hückel matrix, whose eigenvalues and eigenvectors are well known. Aggregates with a circular topology also include a term that couples the first and last unit. In most situations and also in J aggregates, $J < 0$, while H aggregates are characterized by $J > 0$ (12; 26).

The potential energy surface of each electronic state is a function of the nuclear coordinates. Within the normal mode approximation and assuming that the ground and excited states have the same normal mode coordinates, the two vibrational Hamiltonians form a pair of multidimensional parabolas,

$$\hat{h}_\alpha^0 = \sum_{i=1}^{\nu_\alpha}\left(\frac{\hat{p}_{i\alpha}^2}{2m} + \frac{1}{2}m\omega_i^2\hat{q}_{i\alpha}^2\right), \quad \hat{h}_\alpha^1 = \sum_{i=1}^{\nu_\alpha}\left(\frac{\hat{p}_{i\alpha}^2}{2m} + \frac{1}{2}m\omega_{i\alpha}^2\left(\hat{q}_{i\alpha} - \frac{c_{i\alpha}s_1}{m\omega_i^2}\right)^2\right), \tag{2.6}$$

where $q_{i\alpha}$ and $p_{i\alpha}$ are the mass-weighted ($m = 1$) coordinates and momenta, $\omega_{i\alpha}$ and $c_{i\alpha}$ denote the respective vibrational frequencies and exciton-vibration coupling parameters, and the parameter s_1 has dimensions of length. The displacement $q_{i\alpha}^{\min} = c_{i\alpha} s_1 / m\omega_{i\alpha}^2$ characterizes the distance between the minima of the two potential energy surfaces along mode *i.* The displacement of the excited state potential minimum can be expressed in terms of the Huang-Rhys factor (27) $S_{i\alpha}$ through the relation $c_{i\alpha} = \sqrt{2m\omega_{i\alpha}^3 \hbar S_{i\alpha} / s_1^2}$. Only the ν_α normal modes with nonzero Huang-Rhys factors contribute to the EET dynamics and are included in the all-mode calculations presented in sections 5 and 6.

2.2 Vibrational modes, initial conditions and dynamical observables

The EV interaction can be quantified through the individual Huang-Rhys factors of the various modes or in terms of the spectral density function (5; 7),

$$\mathcal{J}_\alpha(\omega) = \frac{\pi}{2} \sum_i \frac{c_{i\alpha}^2}{m\omega_{i\alpha}} \delta(\omega - \omega_{i\alpha}) \tag{2.7}$$

When only intramolecular vibrations are considered the spectral density consists of discrete lines. On the other hand, if the number of nuclear degrees of freedom is very large, as in the case of a chromophore embedded in a biological environment, the spectral density is practically a continuous function.

The two molecular examples that we study include only intramolecular modes. In both cases the coupling of vibrations is of moderate strength and gives rise to underdamped population dynamics in the dimer. However, the spectral densities of the two molecules (shown in Figures 3 and 5) differ in significant ways. The 50 coupled BChl modes are distributed over the entire frequency range, with none of the coupling parameters (obtained from spectroscopic Huang-Rhys factors) sufficiently large to generate new vibronic peaks in the electronic populations. On the other hand, the spectral density of PBI-1, obtained through DFT calculations (13), has sizable gaps and includes a few strongly coupled high-frequency modes. In particular, the intramolecular mode q_{25} (which is associated with the breathing motion of the perylene core (13)) displays distinct vibronic dynamics, and mode q_{27} also contributes to such features. We choose the coupling parameter of the continuous model spectral density to have a moderate value in order to also produce quenched oscillations in the populations.

The studies we report in this review correspond to a localized excitation on a single monomer. This initial condition is most relevant for understanding transport properties related to the evolution of the excitation energy. The character of the state produced through photoexcitation depends on the specifics of its preparation. While the absorption of monochromatic light would result in a dipole-allowed eigenstate, which in the case of a symmetric aggregate is delocalized, excitation by ultrafast lasers produces superpositions that tend to resemble localized states. Further, localized excitations may arise from symmetry breaking which leads to eigenstates that span only one or a few monomers. Static disorder owing to external (e.g. biological) environments can create asymmetry in the site energies. Such disorder, if sufficiently strong, would also lead to the localization of excitation energy upon photoexcitation.

We assume that at $t = 0$ a particular monomer, for example unit A, undergoes a "vertical" Franck-Condon (FC) electronic excitation, which leaves the intramolecular vibrations of all molecules unchanged, i.e. equilibrated to their respective ground electronic states. The initial density matrix is given by

$$\hat{\rho}(0) = \hat{\rho}_{\mathrm{e}}(0)\hat{\rho}_{\mathrm{v}}(0), \quad \hat{\rho}_{\mathrm{e}}(0) = |\mathrm{A}\rangle\langle\mathrm{A}|, \quad \hat{\rho}_{\mathrm{v}}(0) = \frac{e^{-\beta\hat{h}_{\mathrm{A}}^{0}}}{\mathrm{Tr}\, e^{-\beta\hat{h}_{\mathrm{A}}^{0}}} \frac{e^{-\beta\hat{h}_{\mathrm{B}}^{0}}}{\mathrm{Tr}\, e^{-\beta\hat{h}_{\mathrm{B}}^{0}}} \cdots \tag{2.8}$$

where $\beta = 1/k_{\mathrm{B}}T$ is the reciprocal temperature in units of Boltzmann's constant.

For the purpose of understanding some of the effects described below, it is useful to decompose the initial density in terms of Boltzmann-weighted harmonic oscillator eigenfunctions. In the absence of electronic coupling between the two surfaces, each of these components is a displaced harmonic oscillator wavefunction in the quadratic Hamiltonian of monomer A, and thus its evolution is simply the generalization of Gaussian wavepacket dynamics (28), i.e. the wavefunction retains its original width while its center follows a classical trajectory (which is the same for all eigenstate components). As a result, the entire density evolves as a rigid Gaussian that follows classical dynamics for $J = 0$. However, the leakage of density to other electronic states enabled by the exciton coupling leads to complex behaviors. Some basic theoretical considerations that govern the ensuing dynamics are discussed in section 2.4 in the context of a homodimer.

2.3 Populations and densities

The simplest way of quantifying the dynamics of EET is through the elements of the reduced density matrix (RDM), which is defined as

$$\rho_{\alpha'\alpha'';\beta'\beta''}^{(N0)} = \mathrm{Tr}_{\mathrm{vib}} \langle\alpha'| e^{-i\hat{H}N\Delta t/\hbar} |\beta'\rangle \hat{\rho}_{\mathrm{v}}(0) \langle\beta''| e^{i\hat{H}N\Delta t/\hbar} |\alpha''\rangle \tag{2.9}$$

Here the superscript indicates the final and initial time values ($N\Delta t$ and 0), and the subscripts β', β'' and α', α'' denote the initial and final states, respectively. The diagonal elements (with respect to the final states, i.e. with $\alpha' = \alpha'' \equiv \alpha$) of the RDM are the populations of singly excited states. When the initial states are specified, we express the populations with the compact notation $P_\alpha(t) \equiv \rho_{\alpha\alpha;\beta'\beta''}^{(N0)}$. Off-diagonal elements of the RDM are commonly referred to as "coherences".

To understand the mechanistic details of the EV dynamics, we investigate the time evolution of electronic-vibrational densities (EVD) along select vibrational modes or pairs of modes. Useful insights are obtained from the two-mode EVDs of a dimer (29), where we track a single vibrational mode i in each monomer or two modes in one of the monomers:

$$D_{i\alpha,j\beta}^{\alpha}\left(q_{i\alpha}, q_{j\beta}; t\right) = \left\langle \alpha; q_{i\alpha} q_{j\beta} \right| e^{-i\hat{H}_{\mathrm{dimer}}t/\hbar} \hat{\rho}(0) e^{i\hat{H}_{\mathrm{dimer}}t/\hbar} \left| \alpha; q_{i\alpha} q_{j\beta} \right\rangle . \tag{2.10}$$

In the common mode representation (see section 3.2) the single-mode EVD is given by

$$D_{i}^{\alpha}\left(Q_i; t\right) = \left\langle \alpha; Q_i \right| e^{-i\hat{H}_{\mathrm{dimer}}t/\hbar} \hat{\rho}(0) e^{i\hat{H}_{\mathrm{dimer}}t/\hbar} \left| \alpha; Q_i \right\rangle . \tag{2.11}$$

The effects of the remaining molecular vibrations are quantified through two-mode projections of the all-mode EVD, which are obtained from the dynamics of the full Hamiltonian (including all v normal modes) by tracing with respect to all other modes,

$$\tilde{D}_{i\alpha,j\beta}^{\alpha}\left(q_{i\alpha}, q_{j\beta}; t\right) = \mathrm{Tr}_{\mathrm{vib} \neq i\alpha, j\beta} \left\langle \alpha; q_{i\alpha} q_{j\beta} \right| e^{-i\hat{H}_{\mathrm{dimer}}t/\hbar} \hat{\rho}(0) e^{i\hat{H}_{\mathrm{dimer}}t/\hbar} \left| \alpha; q_{i\alpha} q_{j\beta} \right\rangle . \tag{2.12}$$

3. The dimer

Many insights are derived from the EV dynamics of a dimer. In this case the Hamiltonian of the singly excited states is a 2×2 matrix,

$$\hat{H}_{\text{dimer}} = \begin{pmatrix} \varepsilon_{\text{A}}^{1} + \hat{h}_{\text{A}}^{1} + \varepsilon_{\text{B}}^{0} + \hat{h}_{\text{B}}^{0} & J \\ J & \varepsilon_{\text{A}}^{0} + \hat{h}_{\text{A}}^{0} + \varepsilon_{\text{B}}^{1} + \hat{h}_{\text{B}}^{1} \end{pmatrix} \tag{3.1}$$

where $J = J_{\text{AB}}$. In the case of a homodimer, the excited state energies are equal, i.e. $\varepsilon_{\text{A}}^{1} + \varepsilon_{\text{B}}^{0} = \varepsilon_{\text{A}}^{0} + \varepsilon_{\text{B}}^{1}$, thus these constants may be dropped, and in the absence of EV coupling the electronic population is given by $\cos(J\,t/\hbar)$.

3.1 Topology and symmetries

We begin with a pictorial discussion (30) of EV dynamics for the simplest case of a single vibrational mode in each of the two molecules, $q_{i\text{A}}$ and $q_{j\text{B}}$, with frequencies $\omega_{i\text{A}}$ and $\omega_{j\text{B}}$. Figure 1a shows an illustration of the potential energy surfaces for the two excited states, which are two-dimensional parabolas that interact through the Frenkel coupling term. In the $|\text{A}\rangle$ excited state the potential is displaced only along the $q_{i\text{A}}$ vibrational coordinate, thus its minimum lies at $\left(q_{i\text{A}}^{\min}, 0\right)$, while the potential minimum of the excited state $|\text{B}\rangle$ lies at $\left(0, q_{j\text{B}}^{\min}\right)$. The potential surface of the ground electronic state is not displaced, thus the vibrational density created on state $|\text{A}\rangle$ through a FC excitation is (at any temperature) a Gaussian centered about $(0,0)$. Since this density is displaced with respect to the excited state, it begins to evolve along $q_{i\text{A}}$ toward the potential minimum. As discussed earlier, with $J = 0$ the density follows classical motion on this potential surface, where its center executes fixed-amplitude oscillations between the turning points located at $q_{i\text{A}} = 0$ and $2q_{i\text{A}}^{\min}$. However, in the presence of electronic coupling, density simultaneously transfers to state $|\text{B}\rangle$. The amount and location of emerging density in this state depends on Landau-Zener arguments (31-33) (local potential slopes, strength of coupling and wavepacket velocity), the density distribution on the “donor” state A, as well as the relative magnitudes of J and ω. The nonadiabatic density transfer creates displacements along both vibrational coordinates, leading to intricate two-dimensional EV motion that creates various dynamical patterns in the populations of the two states.

An analogous picture applies to the case of two distinct normal modes *i* and *j* of the same molecule. Both vibrations are now simultaneously excited and de-excited by EET. The potential energy surfaces are shown in Figure 1b for two modes in the initially excited monomer. With $J = 0$, the motion of the Gaussian density now occurs along both coordinates, where its center undergoes Lissajous rotations (34) within a rectangular area bound by the respective positions of the minima.

It can be shown using the quantum-classical path integral formulation (35-37) of nonadiabatic dynamics that the electronic dynamics of energy transfer is modified along each Feynman path by a vibrational phase that depends on the integrated difference between the two diabatic potential values. Figures 1a and 1b also show the seam (i.e. the tangent of the potential contours at the point of intersection with the line that connects the two potential minima) for the two cases discussed above. Motion parallel to this direction does not modify the vibrational phase, thus does not contribute to EV mixing.

3.2 Spin-boson mapping

In the case of the exciton dimer AB, the single-excitation electronic subspace of the Frenkel Hamiltonian is a two-level system (TLS) while the vibrational modes constitute a coupled vibrational bath. The picture simplifies considerably in the case of a homodimer. The frequency degeneracy of each pair of identical modes $q_{i\mathrm{A}}$ and $q_{j\mathrm{B}}$ implies that the potential surface is separable along any linear combination of the two monomer coordinates. Earlier work (38; 39) has shown that only the difference linear combination $Q_i = \left(q_{i\mathrm{A}} - q_{i\mathrm{B}}\right)/\sqrt{2}$ (the antisymmetric, anticorrelated common mode of the dimer (40)) couples to the electronic states, while the sum coordinate combination (the symmetric, correlated mode) is uncoupled and thus does not alter the EET dynamics, even though the EV density in full space moves along this coordinate as well. The coupled antisymmetric mode combination Q_i coincides with the line that connects the potential minima, while the sum coordinate is parallel to the seam line (see Fig. 1c).

Using the common mode representation, the dimer EET Hamiltonian can be mapped on the familiar TLS-bath or spin-boson model (7),

$$\hat{H}_{\mathrm{dimer}} = J\hat{\sigma}_x + \sum_{j=1}^{\nu}\left(\tfrac{1}{2}\hat{P}_j^2 + \tfrac{1}{2}m\omega_j^2\hat{Q}_j^2 - C_j\hat{Q}_j\hat{\sigma}_z\right), \tag{3.2}$$

where σ_x, σ_z are the Pauli spin matrices and (in order to account for the length rescaling dictated by Eq. (3.2), where the distance between potential minima is 2 length units) the coupling coefficients are given by the relation $C_i = c_i s_1/\sqrt{2}$. Figure 1d shows potential energy surfaces along the common (correlated) spin boson mode for the exciton dimer.

4. Methods

Dynamical calculations of EET in a dimer with one or two vibrational modes in each monomer are easily performed using standard basis set methods, using either the separate or the common bath form. The required computational effort increases rapidly as the number of vibrational modes grows. On the other hand, accurate calculations with many modes at finite temperature present a challenge to wavefunction-based methods. The high cost of such calculations is primarily a consequence of the rapid increase of Hilbert space size. In addition to the large basis sets required to propagate a wavefuction, thermal averaging involves a very large number of microcanonical calculations. Low-frequency vibrational modes present a particularly serious problem in this regard, as many vibrational states can be populated at room temperature. The situation becomes even more difficult in aggregates with more than two units, as the number of system states as well as the total number of vibrational modes is proportional to aggregate length.

As discussed in the Introduction, path integral methods offer several advantages for Hamiltonians of the system-bath form. One of the most significant advantages of the path integral is the ability to account for harmonic degrees of freedom analytically (41), at zero or finite temperature, although this gain introduces other difficulties. In this section we give an overview of real-time path integral methods suitable for numerically exact treatment of EET dynamics in dimers and in long molecular aggregates. This section does not intend to provide a comprehensive description of these methods, and the reader is referred to the original papers for additional details.

The first step in the discretized path integral formulation of time-dependent quantum mechanics (4; 42) is to express the time evolution operator at the time t as a product of N short-time operators over the time step $\Delta t = t/N$. Inserting the resolution of identity in the chosen basis between each pair of short-time evolution operators expresses the propagator as an $(N-1)$-dimensional sum of a product of short-time propagators. Each term in this sum is the quantum mechanical amplitude along a "path" formed by the particular realization of basis states, and the sum with respect to all such paths gives the total amplitude, i.e. the quantum mechanical propagator (3; 4). Approximate expressions for the short-time propagators are obtained with the symmetric Trotter splitting (43) of the Hamiltonian into kinetic and potential energy terms, which leads to error that scales as Δt^3 for the evolution operator. (Note, however, that the error scaling is less favorable for the propagator (44).) Quadratic degrees of freedom appear as Gaussian functions in the path integral expression and thus can be integrated out analytically, giving rise to an influence functional (41).

Application of the path integral idea to the Boltzmann operator involves precisely the same steps in imaginary time (45). In this case the basis is the continuous Cartesian coordinate for each particle, and the integrals are evaluated by Monte Carlo (46) (or molecular dynamics) methods. The path integral Monte Carlo (PIMC) method (47; 48) is widely used for calculating equilibrium properties of many-body quantum mechanical spinless or bosonic systems at finite temperature. Further, it has been shown (49) that the path integral representation of the quantum mechanical partition function for a single particle is isomorphic to the expression for the classical partition function of N particles forming a "necklace". The quantum-classical isomorphism invites the use of classical trajectory methods for evaluating the integrals and leads to the path integral molecular dynamics (PIMD) methods (50-52), which offer an attractive alternative to PIMC for molecular systems. The imaginary-time path integral formulation also forms the starting point for centroid (53) (CMD) and ring-polymer molecular dynamics (54) (RPMD) methods, which extract approximate real-time information from the equilibrium formulation.

Early attempts to apply similar ideas to the real-time path integral formulation were met with limited success (55; 56). The main problem stems from the nature of the real-time propagator: the quantum mechanical amplitude is a highly oscillatory pure phase (i.e. the exponential of an imaginary function), whose magnitude is the same for all paths, leading to an integrand that is completely delocalized over the entire space and which has a large variance. Stochastic sampling is extremely inefficient in such cases, thus Monte Carlo-based methods fail to converge (except for special cases and/or short-time calculations where the number of integration variables is small).

The methods described briefly in this section employ discrete basis (e.g. grid) representations and quadrature-based integral evaluation (or, in some cases, combine quadrature and Monte Carlo techniques). The discrete state, minimal-sized basis formulation of the path integral (57; 58) for a system of continuous coordinates allows elimination of the rapidly oscillatory phase and leads to a localized integrand, thus greatly improving stability. Still, the mildly oscillatory amplitude that remains is problematic for long-time calculations, suggesting that full quadrature-based evaluation of the multidimensional integral may provide the only stable option. This is achieved through various decompositions of the path integral, which are described in the next four subsections.

The first two methods (sections 4.1 and 4.2) were originally developed for the generic system-bath (or generalized spin-boson) Hamiltonian,

$$\hat{H}_{\text{system-bath}} = \hat{H}_{\text{system}} + \sum_{j=1}^{\nu} \left(\tfrac{1}{2} \hat{p}_j^2 + \tfrac{1}{2} m \omega_j^2 \hat{Q}_j^2 - C_j \hat{s} \hat{Q}_j \right) \tag{4.1}$$

where $\hat{H}_{\text{system}}$ is the Hamiltonian for a discrete system of *n* basis states and the coordinate operator $\hat{s}$ is diagonal in this basis. The discretized quantum paths are represented by sequences of these states, and the influence functional involves the coordinates of these paths, which take on *n* values at each time point.

However, the single-excitation EET Hamiltonian, Eq. (2.4), has the form of a discrete system of $\alpha = 1,\ldots,n$ states, where each state is coupled to its own vibrational harmonic bath. While it is clear that the influence functional from a separable bath factorizes (59), writing its precise form is not obvious, since each bath is attached to a single state of the system (and thus it appears that there is a single possible value for the system coordinate). A simple procedure for dealing with separate baths is obtained by thinking in terms of the Hamiltonian in the augmented space that includes the ground electronic state of all monomers. If the system path at a particular time is in the state α, this implies that monomer α is in the displaced potential whose minimum along mode *i* is at $c_{i\alpha} s_1 / m\omega_i^2$, while all other monomers are in the unshifted ground state. Upon writing down the amplitude for each path in terms of electronic and vibrational components, one immediately notices that the overall influence functional can now be decomposed into a product of two-state influence functional factors for each two-state monomer. This implicit two-state representation allows us to obtain the influence functional from the standard form, even though the overall ground electronic state of the aggregate does not appear in the single-excitation system-bath Hamiltonian.

4.1 Quasi-adiabatic propagator path integral (QuAPI)

The QuAPI methodology was developed in the 1990s for simulating the dynamics of system-bath Hamiltonians. The path integral variables for the system coordinate are discrete states obtained from a discrete variable representation (58) (DVR). The quasi-adiabatic propagator partitioning of the time evolution operator (57) is physically motivated and is designed to minimize the Trotter error (43) for this Hamiltonian. The harmonic bath degrees of freedom enter as a discretized Gaussian influence functional, with coefficients obtained from integrals of the spectral density function (60) (which, if desired, may be discretized (61)) or, alternatively, from bath correlation functions (62). The QuAPI expression for the RDM has the form (60; 63)

$$\tilde{\rho}^{(N0)}_{i_N^\pm i_0^\pm} = \sum_{i_{N-1}^\pm} \cdots \sum_{i_1^\pm} K_{i_N^\pm, i_{N-1}^\pm} \cdots K_{i_1^\pm, i_0^\pm} F_{i_N^\pm, i_{N-1}^\pm, \ldots, i_0^\pm} \tag{4.2}$$

where the path integral variables $i_k^\pm$ label the auxiliary states of the *n*-state Frenkel Hamiltonian, which define the paths in the space of electronic states, $K_{i_k^\pm, i_{k-1}^\pm}$ are short-time forward-backward propagators for H_{e}, and

$$F_{i_N^\pm, i_{N-1}^\pm, \ldots, i_0^\pm} = \prod_{k'=0}^{N} \prod_{k''=0}^{k'} F^{(k'k'')}_{i_{k'}^\pm i_{k''}^\pm} \tag{4.3}$$

is the QuAPI-discretized influence functional, which captures in an exact fashion the effects of the vibrational degrees of freedom on the electronic subsystem at the specified temperature. The influence functional contains nonlocal interactions that couple the path integral variables at different times. This temporal nonlocality, which is the path integral analogue of memory in the generalized Langevin equation

(64), prevents the evaluation of Eq. (4.2) by the standard, step-by-step iterative methods designed for propagation in full space (65-67).

Nevertheless, progress can be made if the influence functional arises from a condensed phase environment, because the memory length is then finite. If the memory induced by the bath spans $\Delta k_{\max}$ path integral time steps, evaluation of the RDM can be performed through the iterative QuAPI algorithm (68; 69), which leads to linear scaling with propagation time. Once converged with respect to the time step and the memory length included, the QuAPI propagation yields the full quantum mechanical result for the RDM of the system-bath Hamiltonian. For each single-state initial condition, the QuAPI algorithm generally requires the storage of a tensor of $n^{2\Delta k_{\max}}$ path amplitudes and involves $n^{2\Delta k_{\max}+2}$ operations for each iteration. In many situations, the number of paths that must be stored can be dramatically reduced through filtering techniques (70-74), coarse graining (75-77), or singular value decomposition (78).

Further, the blip decomposition (79; 80) reduces the QuAPI array size from $n^{2\Delta k_{\max}}$ to $(n^2-n+1)^{\Delta k_{\max}}$, i.e. that the configurations where the coordinates of the forward and backward paths differ, leading to exponential storage reduction even in the absence of filtering. Moreover, the path segments between blips can be summed using iterative small matrix multiplications, leading to similar acceleration. Under incoherent conditions (high temperature and/or strong dissipation) the blip decomposition also offer a powerful and systematic filtering approach, as forward-backward paths with multiple blips make exponentially small contributions and thus may be dropped.

4.2 Small matrix decomposition of the path integral (SMatPI)

A further decomposition of the QuAPI algorithm is possible, which eliminates the need for storing large arrays of paths that span the influence functional memory. Even though the path integral variables are fully entangled within the memory length, it has been shown (81; 82) that it is possible to disentangle these variables sequentially, decomposing the RDM into a sum of products that involve small, $n^2 \times n^2$ matrices $\mathbf{M}^{(Nm)}$, as well as a residual:

$$\tilde{\boldsymbol{\rho}}^{(N0)} = \sum_{r=1}^{N-1} \mathbf{M}^{(N,N-r)} \cdot \tilde{\boldsymbol{\rho}}^{(N-r,0)} + \mathbf{M}^{(N0)}, \quad N = 2,\ldots \tag{4.4}$$

Each of these matrices is the residual of the previous step in this process, and is fully accounted for at the next step. The matrices capture the entanglement of the path integral variables and decrease in magnitude. Eventually, when a particular entanglement length of $r_{\max}$ time steps is reached, the residual becomes small and can be dropped, yielding a numerically exact decomposition through the expression

$$\mathbf{U}^{(N0)} = \sum_{r=1}^{r_{\max}} \mathbf{M}^{(N,N-r)} \cdot \mathbf{U}^{(N-r,0)}, \quad N = r_{\max}+1,\ldots \tag{4.5}$$

It has been shown (82) that the entanglement length is practically equal to the memory span, i.e. $r_{\max} = \Delta k_{\max}$, so the path integral time step and the memory remain the two convergence parameters. The SMatPI elimination of large tensor storage allows the inclusion of much longer memory, as well as the treatment of multistate systems.

4.3 Quantum-classical path integral (QCPI)

The rigorous and consistent quantum-classical formulation of nonadiabatic dynamics for systems interacting with general, anharmonic environments results has been derived by evaluating the stationary phase, semiclassical limit of the path integral expression with respect to the coordinates of the nuclei (35; 36). This procedure avoids approximations associated with Ehrenfest-based approaches (83; 84) and leads to the QCPI expression (35-37) in which the effects of the nuclear are captured through classical trajectories. The RDM has the form

$$\tilde{\rho}^{(N0)}_{i_N^\pm i_0^\pm} = \int d\mathbf{x}_0 \int d\mathbf{p}_0 W\left(\mathbf{x}_0,\mathbf{p}_0\right) \sum_{i_{N-1}^\pm=1}^{n} \cdots \sum_{i_1^\pm=1}^{n} \; G_{i_N^\pm i_{N-1}^\pm} \cdots G_{i_1^\pm i_0^\pm} e^{\frac{i}{\hbar}\Delta\Phi\left(\mathbf{x}_0,\mathbf{p}_0;i_N^\pm,i_{N-1}^\pm,\ldots,i_0^\pm\right)} \tag{4.6}$$

where $\mathbf{x}_0,\mathbf{p}_0$ denote the coordinates and momenta of the nuclei, which serve as initial conditions of classical trajectories, $W\left(\mathbf{x}_0,\mathbf{p}_0\right)$ is the Wigner phase space distribution (85), $G_{i_k^\pm i_{k-1}^\pm}$ is the short-time propagator for a time-dependent Hamiltonian that involves the system augmented by the system-environment interaction along a chosen reference trajectory (86), and $\Delta\Phi$ is the difference of action integrals along the forward and backward system paths. This phase contains all dynamical effects due to the interaction of the system with its environment, which are responsible for quantum interference as well as decoherence (87). In the special case of a harmonic bath, stationary phase procedures are exact (88) and thus the QCPI expression reproduces the full quantum mechanical result for the RDM (37).

A classical trajectory in the QCPI expression is governed by the sequence of forces exerted by the system along each discrete path. This dependence leads to an exponential proliferation of classical trajectories with the number of path integral time steps, which can be considered the quantum-classical manifestation of nonlocality. Again, the memory-quenching effects of the environment may be exploited to obtain an iterative decomposition of the QCPI expression that maintains a constant number of trajectories (36). The incorporation of the action along reference trajectories in the system propagator (86) automatically captures the entire real part of the influence functional (which corresponds to the "classical" memory (87)) and beyond, while the action phase $\Delta\Phi$ supplies the "quantum" memory, which is necessary to correctly account for detailed balance (87) but is often considerably shorter than the classical memory. In the case of a harmonic bath, this phase can be included via the QuAPI influence functional coefficients, leading to a method that involves a single, analytically available classical trajectory from each initial condition (89; 90) The QCPI expression requires evaluation of the phase space integral by Monte Carlo or molecular dynamics methods but converges with larger time steps and shorter memory than the QuAPI and SMatPI methods. Thus, while applicable to general, anharmonic environments, the QCPI formulation also provides an efficient, numerically exact alternative approach to system-bath dynamics and the EET Hamiltonian.

4.4 Modular path integral (MPI)

Unlike the previous three methods, the MPI algorithm uses the full aggregate Hamiltonian given in Eq. (2.3) and is ideally suited to extended systems with local couplings. Propagation is performed through the sequential linking of the quantum paths of each monomer to those of the neighboring unit (91; 92), where the amplitudes of each monomer are augmented by influence functional factors arising from the molecular vibrations at the given temperature (93). Once this linking is complete, the paths of the treated monomer are discarded and the process is repeated with the next pair of molecular units. The sequential nature of the MPI algorithm leads to linear scaling with aggregate size. In the case of the Frenkel exciton Hamiltonian, the basic structural element involves a pair of adjacent monomers (94). A factorization of the MPI linking procedure (95) leads to efficiency comparable to that achieved by the fast Fourier transform algorithm. A SMatPI-based iterative decomposition of MPI has recently been described (96), which exploits a small matrix factorization of path amplitudes (97) to bypass the path storage requirements of the original algorithm and to allow iterative propagation, extending calculations to long times.

5. EET dynamics in molecular dimers

The frequency distribution of normal mode vibrations, along with the geometrical arrangement of the ground and excited state potential minima which determine the Huang-Rhys factors, are unique to each molecule. Since these parameters govern the EV dynamics, the specifics of EET can present a diverse spectrum of behaviors. In this section we describe some generic effects associated with the EV dynamics of vibrational modes in molecular homodimers, along with their signatures in the dynamics of the PBI-1 dimer. We integrate the simple description offered by minimal-dimension common anticorrelated modes with the molecular picture in terms of the vibrations of the individual monomers by considering both (common and separate) mode representations.

5.1 Weak EV coupling: near-Gaussian, classical-like density evolution on each state

We first consider the simplest case of a single vibrational mode of frequency ω in each monomer, which is weakly coupled to the electronic states, at a low temperature with respect to the mode frequency. As described in section 3.2, in this case the dimer Hamiltonian can be transformed to a pair of electronic states coupled to a common vibration (the difference linear combination of the molecular modes). Under weak EV coupling, the displacement of the monomer excited states (thus also the distance between the two potential minima) is small and the density remains in the curve crossing region throughout its evolution, as seen in Fig. 2c. As a result, the electronic population retains its oscillatory cosine-like shape (Fig. 2a, top panel). The EV dynamics is rather simple in this regime: the probability densities on the two excited states remain compact and largely Gaussian-like, and one may accurately interpret the normalized coordinate expectation value of the mode (Fig. 2a, middle panel) as the EVD peak position. The density oscillates between the classical turning points of each quadratic diabatic potential in a classical-like fashion, retaining its shape while transferring back and forth between the two states. Spike-like features develop in regions of low state populations, as depletion of the Gaussian density through nonadiabatic transfer shifts the EVD peak away from the crossing region, beyond the outer turning point (98). With a single vibrational mode the EVD oscillations on the two electronic states are out of phase.

As is well known from spin-boson studies, coupling of the two-state electronic system to a weakly dissipative bath introduces quenching effects that lead to underdamped oscillatory population dynamics. The motion of the EVD becomes even simpler in this case: since the dissipative effects eliminate very small population values, no spikes are seen in the average mode coordinate. Although not directly coupled, the vibrational mode slowly exchanges energy with the dissipative bath through the electronic degree of freedom. As a result, the average mode coordinate in Fig. 2a (bottom panel) loses amplitude at a very slow rate and the EVD oscillations persist for times that are extremely long compared to the time for redistribution and equilibration of the excitation energy. Further, the dissipative environment synchronizes the EVD oscillations on the two diabatic potentials.

The EET dynamics of the BChl dimer is discussed in the next section, where population evolution is investigated as a function of aggregate length. In this case the normal mode frequencies are distributed throughout the frequency range and none have particularly strong couplings. As a result, the population dynamics (shown in Figures 6d and 6e) is qualitatively similar to that of Fig. 2a, with smooth underdamped oscillations.

While the common antisymmetric mode combination provides an exact description of the EET dynamics with a pair of identical modes on the two monomers, exploring the EVD motion in the two-dimensional space of the molecular vibrations is important for arriving at a complete physical picture in terms of the individual molecular modes. In Figure 3d we illustrate the full dynamics of the two q_{23} modes in the PBI-1 dimer (30). This mode is weakly coupled to the electronic states (see Fig. 3a). In close analogy to our observations with the model bath, the two-dimensional EVD retains its near-Gaussian shape with its peak following a classical trajectory. On short-to-intermediate time scales the influence of all other normal modes of the two PBI molecules is similar to that of a dissipative bath in some respects (Fig. 3b), leading to a substantial reduction of oscillation amplitude and a smearing of the electronic populations. However, the all-mode EET dynamics of the PBI dimer is dominated by other more strongly coupled modes, which introduce additional dynamical features. We thus defer the discussion of the resulting dynamics to section 5.2 which deals with strongly coupled vibrations.

Last, we examine the dynamics of two modes of different frequencies on the EET dynamics of a dimer using the model spectral density. Since visualization is not feasible in the space of four coordinates, we return to the common mode representation. Fig. 2d shows the two-mode trajectories of the EVD peak (on one of the diabatic potentials) for two parameter sets. Apart from some loops extending beyond the classically allowed area, which originate from nonadiabatic depletion of low-population regions and are therefore analogous to the spikes observed in the single-mode results, the two-mode trajectories now trace out classical Lissajous patterns, whose precise shape is dictated by the relation of the two vibrational frequencies (98). This behavior indicates that the motion of the EVD peak follows classical dynamics characteristic of the "regular" regime, where trajectories lie on a two-dimensional torus (34) (Fig. 2e). As is well-known, frequency ratios closer to irrational numbers give rise to rectangular-like shapes, while ratios that correspond to low-order resonances produce twisted shapes.

The coupling of the two-state system to a dissipative bath simplifies and softens these features, even eliminating the differences in the shapes of two-mode EVD trajectories (Fig. 2f). Over short times, the resulting Lissajous trajectories of the EVD peak appear confined within a rectangular boundary. However, in close analogy to the single-mode dynamics, the peak trajectory loses amplitude here as well, leading to a slowly shrinking boundary (98).

5.2 Moderately strong EV coupling: complex evolution, density retention, vibronic peaks

We now discuss the effects of vibrational modes with substantial EV coupling on the EET dynamics of the dimer. Even with a single coupled mode, significant changes are seen in the populations, whose specifics depend on the relation between electronic coupling and mode frequency as well as the EV coupling value. The main effects identified in Figures 4 and 5 are a lengthening of the EET transfer time, a significant suppression of electronic population recurrences, and the appearance of new features such as shoulders and minor peaks (29; 99). The first two of these effects are observed with both (model and molecular) vibrational parameter sets, while the emergence of new population features is present only in the case of the strongly coupled vibronic mode of the PBI-1 dimer. Strong EV coupling leads to a large displacement of the potential minima (Fig. 5c), such that the initial density which is centered at the curve crossing point has a sizable amount of potential energy, overlapping with many vibrational eigenstates which interfere to significantly alter the RDM dynamics. As the EVD moves rapidly toward the outer turning point, the depletion of the crossing region leads to density retention, thus preventing the population of the initially excited state from falling to zero (30) (Fig. 5d, top panel, and to a smaller degree Fig. 4a). Similar retention effects on the other electronic state contribute to the suppression of population recurrences. By preventing the complete transfer of population out of either electronic state, density retention also softens the spikes of coordinate expectation values (Fig. 4a, middle panel) observed with weak EV coupling. At the same time, the pattern of the averaged coordinate oscillations becomes more erratic, as deviations from Gaussian-like densities become more prominent with increasing EV coupling and/or temperature (Fig. 4c). Eventually, when non-compact EVD shapes become dominant, mode coordinate averages no longer accurately represent the density peak. In addition, the partial depletion of the crossing region while the density is located closer to the distant turning point prevents the effective transfer of population, leading to a lengthening of the EET time (juxtapose Fig. 5d against Fig. 3b). This phenomenon is similar to the renormalization of tunneling splittings by high-frequency bath modes (100).

With strong EV coupling, the different time scales of electronic and vibrational dynamics manifest themselves in the emergence of vibronic population peaks and shoulders. These features are the consequence of nonadiabatic back-transfer from state B when the main density on state A is near the outer turning point of that surface, which causes the formation of a new, disconnected density peak (the "island" in Fig. 5e). These features lead to split, non-Gaussian densities, which become more complex with stronger EV coupling and (through the involvement of more excited vibronic states) increasing temperature. The intricate EVD shapes (crescents and densities with internal holes) observed in the PBI-1 dimer with the strongly coupled mode q_{25} in each monomer or with two different modes (q_{25} and q_{27}) illustrate the complexity and nonlinear character of EET (Figures 5a and 5b) with moderate-to-strong EV coupling parameters that often characterize vibronic molecular modes (30). The nonlinear character of the motion is also conveyed very clearly in the two-common-mode average coordinate trajectories displayed in Fig. 4d. In contrast to the weak coupling case, the Lissajous patterns are now significantly perturbed and the distinct shapes associated with particular frequency relations are wiped out (98). In classical mechanics such effects are characteristic of nonlinear motion, where trajectories are not confined on a two-dimensional torus and are able to explore a larger portion of the energetically allowed phase space (101).

Again, coupling of the electronic two-state system to a dissipative bath further quenches the recurrence features of the population dynamics and synchronizes the EVD oscillations (see Fig. 4e). Interestingly however, we now observe a much faster decay of the mode amplitude compared to the weak coupling case (Fig. 4b). This is a consequence of the faster exchange of energy between the vibrational mode and the bath through coupling to the electronic degree of freedom. Similar smearing effects are observed in the dynamics of the vibronic PBI-1 mode (Fig. 5d), where the remaining vibrations do not couple as strongly to the electronic dynamics. However, due to the sparseness of the discrete spectral density, the blurring effect of the molecular vibrations is less pronounced than that of the continuous bath. The vibronic peaks in the populations are preserved, and because of the high frequency of mode q_{25} which is primarily responsible for these features, these peaks show no temperature dependence. This is in contrast to the pronounced temperature variation of other population features, which arise from the combined effect of intramolecular modes over the entire frequency range.

6. EET in large molecular aggregates

As the number of molecular units increases, the process of EET becomes more complex. The n eigenstates of the electronic Frenkel Hamiltonian are clustered within a band of maximum (for $n \to \infty$) width $4J$, with a distribution of level spacings that introduces multiple time scales (Fig. 6a, left panel). The resulting dynamics is characterized by the sequential population of units away from the initially excited molecule, with peaks of slowly varying width as well as recurrence features that are minor at early times but become very prominent when the excitonic wavefunction reflects off an edge and interferes (Fig. 6a, right panel). Further, important features of the dynamics depend on the location of the initial excitation. Faster EET is observed when an interior molecule is excited, as the excitation can then travel along two different directions, compared to the dynamics resulting from excitation of an edge unit.

With coupling to intramolecular vibrations, the intricate interplay of a host of electronic and vibrational time scales leads to very rich dynamics and distinct patterns compared to those observed in the case of a dimer. Figures 6d and 6e display the electronic populations in linear BChl aggregates of 2, 5, 9 and 19 units (which include up to 950 intramolecular modes), as well as the 18-unit B850 ring of the LH2 complex (Fig. 6b, left panel), following excitation of the central chromophore. As discussed earlier, the EV coupling in BChl molecules is of weak to intermediate strength (Fig. 6b, right panel), the mode frequencies are distributed throughout the frequency range, and no single vibration has a much larger Huang-Rhys factor compared to those of the remaining modes. These vibrational features lead to mostly uniform amplitude quenching (Figures 6d and 6e) of electronic recurrence peaks (102). The excitation energy oscillations in the BChl dimer are underdamped and have a simpler, smoother appearance (39), in contrast to the populations of the PBI-1 dimer shown in Fig. 3. The damping effects from the molecular vibrations become much more pronounced with increasing aggregate length, as electronic recurrences occur at longer times, allowing a larger range of vibrational timescales to smear them.

From the perspective of coherence, long BChl chains and the B850 ring of LH2 seem to be in the borderline regime between damped oscillatory and overdamped dynamics. This behavior enables a rapid spreading of excitation energy along the ring and may be optimal for inter-ring energy transfer. The extent of coherence is quantified through the time evolution of RDM off-diagonal elements. Fig. 6c shows that the coherences span a few BChl units at physiological temperatures. We emphasize that these results represent only the effect of intramolecular vibrations. If embedded in the dissipative environment of its protein scaffold, the coherence of the BChl aggregates will be further reduced. Such effects have been thoroughly investigated in the FMO complex using QuAPI with spectral densities obtained from simple models and molecular dynamics simulations (103; 104).

Last, we investigate the EET in J-aggregates of PBI-1 composed of 25 molecular units and a total of 700 vibrational modes. As observed in the case of BChl aggregates, EV interaction again causes smearing of oscillatory features as well as delayed recurrences of electronic populations. However, there are two major differences in the dynamics of these two systems. First, as discussed in the context of the dimer, the sparsity of normal modes in the case of PBI-1 aggregates leaves the dynamics somewhat underdamped, leading to larger remnants of electronic recurrences that survive in the overall EET dynamics (Fig. 7a, both panels). Second, in contrast to BChl, the presence of strongly coupled vibronic and nearly vibronic modes in PBI-1 is felt in the long chain populations as well; most of the early monomer populations (neighboring the initial excitation) show the vibronic feature that was identified in the dimer EET (Fig. 5d), which arises from the back-transfer of EVD through crossing regions in multidimensional space, owing to large displacements between potential energy surfaces. However, as the excitation spreads along the aggregate with time, lower frequency vibrations that operate on a longer time scale become more relevant, reducing the impact of this vibronic effect in subsequent monomers before eventually washing it away completely in the populations of distant monomers.

To further clarify the role of intramolecular vibrations in the EET dynamics for long chains, as mentioned above, we compare the distributions of monomer populations at three instants (20, 40 and 60 fs) with and without coupling to intramolecular vibrations (Fig. 7b). In the purely electronic dynamics, a rapid wave-like spreading of the excitation along the aggregate is observed, which exhibits nodes and oscillatory patterns resulting from quantum interference of a pure state. The distribution of energy is tremendously modified by vibrations, which lead to a slower and smoother spread of the excitation, washing away nodes and other oscillatory progressions (29).

The path integral calculations also make it possible to separate the effects of different frequency vibrations on the EET dynamics. Figure 7c shows the survival probability of the initial excitation and the probability of a distant transfer as a function of time, when each monomer is coupled to the high-, mid-range and low-frequency modes. At very short times the most prominent vibrational effects (including the population shoulder) are due to high-frequency vibrations. As time progresses, the low frequency and mid-range vibrations start impacting the dynamics by exchanging energy with the electronic degree of freedom. As expected, EET to distant monomers is seen to be affected by all three ranges of frequencies (29).

7. Concluding Remarks

Intramolecular vibrational modes have a profound effect on the dynamics of EET in molecular aggregates. In this review we examined the dynamical behaviors induced by EV coupling to one, two, or many vibrational modes, with a simple continuous spectral density and also with parameters that describe the EET in aggregates of BChl and PBI-1, at finite temperatures. Through these three different systems we identified generic effects as well as specific behaviors resulting from the characteristic spectral features of two molecules. We analyzed the physics of EV dynamics in the relatively simple case of a homodimer, but also the different behaviors that emerge with increasing aggregate size.

All results presented in this review were obtained from fully quantum mechanical calculations using numerically exact methods. We studied the EET dynamics in systems as large as a PBI-1 aggregate of 25 molecular units with a total of 700 vibrations and BChl aggregates of up to 19 monomers and 950 vibrational modes, over a range of temperatures. In addition to population dynamics, we presented the time evolution of EV densities of one or two modes in the presence of the remaining vibrations and of mode expectation values. These calculations became possible using real-time path integral methods which are ideally suited to this task, as they can account for any number of quadratic degrees of freedom, at zero or finite temperature, without approximation.

In the case of weak EV coupling to one or two vibrational modes, the dynamics is dominated by Gaussian-like densities on each electronic state, whose peaks follow (with the exception of regions of near-zero state population) classical-like evolution characterized by Lissajous patterns. Coupling to a continuous bath is seen to regularize the dynamics and introduces smearing effects that lead to damped oscillatory dynamics.

Moderate to strong exciton-vibration coupling creates nontrivial deviations from the above behaviors. The probability densities no longer remain Gaussian, especially at higher temperatures, and two-mode trajectories explore larger areas of the available phase space, creating patterns reminiscent of chaotic classical dynamics. EVD snapshots obtained for strongly coupled PBI-1 modes assume non-compact shapes. The large excursion of the density far from the curve crossing region leads to population retention that leads to a delay of electronic recurrences and generally slows down EET. In parallel, the addition of density within the crossing region through untimely back-transfers introduces additional vibronic peaks to the electronic populations.

In larger aggregates, additional time scales are introduced through the eigenvalues of the electronic Hamiltonian. Electronic recurrences are shifted to longer times with increasing aggregate length and vibrational modes lead to more effective damping. With the parameters of BChl and PBI-1 vibrations, only minor oscillatory features are seen in the electronic populations of long aggregates. The damping is more uniform in the case of BChl, effectively spreading the excitation energy throughout the aggregate, whereas the sparsity of the PBI-1 density allows the preservation and creation of small oscillatory structures during short to intermediate times.

It is rather fascinating that the seemingly simple Frenkel exciton Hamiltonian with the normal mode description of intramolecular vibrations can lead to such diverse and complex behaviors. Even though the present discussion focused on this particular type of electronic coupling, the path integral methods described in section 4 can also account for charge transfer exciton states, which are important to EET in some systems. Further, potential anharmonicity beyond the normal mode picture can alter the dynamics of molecular systems, and thus may play a significant role in EET. Future work will address such effects.

Disclosure statement

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