Solvent Reorganization in Long-Range Electron Transfer: Density Matrix Approach

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The dynamics of charge transfer from a photoexcited donor to an acceptor coupled through a bridge is investigated by using a correlation-function approach in Liouville space that takes into account solvent dynamics with an arbitrary distribution of time scales. The time- and frequency-resolved fluorescence spectrum from the acceptor is used to probe the scaling of the ET rate with bridge size. The crossover between the coherent tunneling (transfer) and the incoherent sequential (transport) regimes and its implications on the nature of ET processes in DNA are discussed.

I. Introduction

Many important chemical and biological processes involve long-range transfer of energy or charge carriers (electrons and holes). Intense experimental and theoretical effort has been devoted to exploring how the transfer rate depends on the nature of the bridge connecting the donor and the acceptor.1–6 Several recent experiments have focused on electron transfer (ET) in DNA,7–13 which is involved in DNA damage and repair mechanisms.14 Electron and energy transport through DNA is used in sequence-specific DNA probes currently being developed.15 It has long been recognized that charge transfer in a donor/bridge/acceptor system may proceed in two distinct mechanisms. When the bridge energy is much higher than the donor/bridge/acceptor and bridge energies are closer than kT, the bridge acts as a quantum wire and the electron hops through the bridge. This sequential electron transport mechanism has been studied extensively in, for example, doped polymers.17 The value of the exponent β for ET in DNA is controversial, with experimental estimates varying between 0.2 Å−17,8 and 0.9 Å−19,10,13 ET rate of 1.6 × 106 s−1 has been reported for an eight-base-pair bridge with donor–acceptor separation of 21 Å.13 A 2.5 × 109 s−1 rate was found in a different system (six base pairs, 17-Å separation).9,10 These relatively slow rates suggest an exponent β ~ 1.2–1.6 Å−1, similar to that found in proteins. Recent calculations of VDA for ET in DNA using the semiempirical complete neglect of differential overlap (CNDO) method18 and neglecting dynamical effects of nuclear degrees of freedom are consistent with these observations. In contrast, the unusually rapid ET rate 3.0 × 109 s−1 (40 Å, 15 base pairs) reported in ref 7 suggests a much smaller value of β (0.2 Å−1). This has been attributed to sequential hopping (transport), where the DNA molecule may act as a quantum wire,8,19 since the sequential mechanism results in a much weaker distance dependence of the rate.

Hu and Mukamel have shown that by formulating the problem of long-range electron transfer using the density matrix, it is possible to incorporate both mechanisms into a single unified theoretical framework.20 The process may then be analyzed using Liouville space pathways. The superexchange (sequential) mechanism proceeds through off-diagonal (diagonal) density matrix elements in the site representation. The competition between the two mechanisms drew much attention in the context of the primary charge separation in the photosynthetic reaction center,25,26 where a single chlorophyll molecule serves as a bridge between the special pair and the bacteriopheophytin.

Using the site representation for the electronic states and assuming that each molecule (donor, acceptor, and bridge) interacts independently with the solvent, it is possible to calculate the electron-transfer rate perturbatively in the intermolecular hopping integral. Coupling with the solvent can then be incorporated rigorously and nonperturbatively. The problem with this approach is that the number of necessary Liouville space pathways increases very rapidly with the bridge size. Higher order contributions in electronic couplings among sites are required to calculate the superexchange transfer from the donor to the acceptor in these theories. For example, for a system whose electronic structure can be modeled by an N-site one-dimensional tight binding Hamiltonian (the end sites are the donor and the acceptor), the superexchange ET rate is represented by the 2(N − 1)th order term in the electronic couplings between sites. For long bridges, higher order terms must be included, resulting in a large number of Liouville space pathways. Because of this difficulty, numerical calculations based on this expansion were limited to a three-site system. The competition between the two mechanisms was discussed for systems with more than three sites,24 by neglecting nuclear degrees of freedom, using projection operator techniques. The density matrix approach has been recently applied to calculate the time evolution of ET in DNA including nuclear dynamics by applying the Redfield equations of motion.19 The Redfield
superoperator was calculated perturbatively in the coupling with the solvent. Consequently, this approach does not incorporate the solvent reorganization energies, which are required for a complete theoretical description of electron transport. In particular it does not reduce to the Marcus theory in the proper way.

In this paper we extend the density matrix theory of photoinduced charge transfer in a donor/bridge/acceptor system to incorporate the reorganization energy, taking into account a realistic model for nuclear dynamics with an arbitrary distribution of time scales. The nuclear degrees of freedom are modeled as a continuous distribution of harmonic oscillators. All nuclear properties that affect the electronic degrees of freedom are contained in the spectral densities which describe the coupling of nuclear degrees of freedom to electronic populations in the site (real space) representation. By using the delocalized molecular orbital basis set, the number of Liouville space paths is greatly reduced. The present theory is nonperturbative in the electronic couplings among sites and in the coupling to solvent and applies even when the donor or the acceptor is strongly coupled to the bridge. It thus reproduces all the known limiting cases for the rate, including the Marcus theory.

We found that ET is governed by the superexchange mechanism for shorter bridges and by the sequential mechanism for longer bridges. The effects of the bridge size, the energy gap between the donor/acceptor and the bridge, the reorganization energies, and the temperature on the competition between these two mechanisms are investigated. Time-resolved and frequency-resolved fluorescence from the acceptor following an optical excitation of the donor are calculated. Both excitation and emission processes are treated microscopically without invoking the standard assumption that the excited donor state is equilibrated initially. The signal has two contributions: a short-time coherent process, representing a direct excitation of the acceptor by the radiation field, and a long-time, incoherent process. Only the latter can be described by a simple rate equation. The short-time component may be neglected when nuclear relaxation is fast compared with the ET rate. This corresponds to an assumption that the nuclei are equilibrated with the initial distribution of electronic states. Although this assumption is used in the present numerical calculations, the formulation applies to slow nuclear relaxation as well.

The plan of this paper is as follows: The Hamiltonian for the donor/bridge/acceptor ET system is presented in section II. In section III we calculate the time- and frequency-resolved fluorescence signal from the acceptor following excitation of the donor. Simplified expressions for measurements conducted with a short (impulsive) pulse are derived in section IV. The spectral-diffusion limit is considered in section V. The numerical studies presented in section VI demonstrate the competition between the tunneling and the sequential mechanisms. These calculations use typical parameters employed in current experiments on DNA charge transfer. Finally our results are summarized in section VII.

II. Hamiltonian and Nuclear Spectral Densities

We consider a system consisting of a donor and an acceptor coupled though a bridge (Figure 1a). We denote the state where the transferring electron is on the nth molecule by |n⟩ and its energy $E_n$ (I) and |N⟩ represent an electronically excited state of the donor and acceptor, respectively and |n⟩ (n = 2, 3, ..., N−1) are bridge states. The donor and the acceptor ground states will be denoted by |D⟩ and |A⟩, respectively. The hopping integral between the mth and nth molecules is $V_{mn}$. We assume that each molecule is coupled to its own harmonic bath, and the molecular Hamiltonian is

$$H = \sum_{n=1}^{N} E_n |n\rangle \langle n| + \sum_{m \neq n} V_{mn} |m\rangle \langle n| +$$

$$\sum_{n=1}^{N} \left( \sum_{m,j} p_{jm}^2 + \frac{m_j \omega_j^2 q_{jm}^2}{2m_j} - m_j \omega_j^2 d_{jm} q_{jm} |n\rangle \langle n| \right) +$$

$$E_D|D\rangle \langle D| + \sum_{j} m_j \omega_j^2 d_{jm} q_{jm} |D\rangle \langle D| + E_A|A\rangle \langle A| -$$

$$\sum_{j} m_j \omega_j^2 d_{jm} q_{jm} |A\rangle \langle A|$$

(2.1)

where $p_{jm}$, $q_{jm}$, $m_j$, and $d_{jm}$ are the momentum operator, the coordinate, the mass, the frequency, and the displacement of the jth oscillator coupled to the nth molecule.

The total Hamiltonian representing the system interacting with the radiation field $\epsilon(t)$ is

$$H_T(t) = H - \epsilon(t) P$$

(2.2)

We assume that only the donor and the acceptor are coupled to the radiation field, and the polarization (dipole) operator is given by

$$P \equiv P_D + P_A$$

(2.3)

$$P_D \equiv \mu_D (|D\rangle \langle 1| + |1\rangle \langle D|)$$

(2.4)

$$P_A \equiv \mu_A (|A\rangle \langle N| + |N\rangle \langle A|)$$

(2.5)

Initially the system is in its ground state |D⟩, which is therefore denoted |0⟩. To decouple the bath in the initial (ground) state, we apply a transformation $q_{j1} \equiv q_{j1} - d_{jm}$ and recast the Hamiltonian in the form.
C_n defined by eq 2.8 are described by the spectral densities $C_{n}$, where we introduced operators $H_{n})\) and the collective coordinates $q^{(c)}$ are defined by

$$q_{n}^{(c)} = \sum_{j} m_{j} \alpha_{j}^{m} d_{j} q_{j}$$

$$q_{D}^{(c)} = \sum_{j} m_{j} \alpha_{j}^{m} d_{j} r_{j}$$

$$q_{A}^{(c)} = \sum_{j} m_{j} \alpha_{j}^{m} d_{j} q_{j}$$

(2.8)

In eq 2.6 we have set the ground-state energy of the system $E_{D} - \sum_{j}(m_{j} \alpha_{j}^{m} d_{j})^{2} / 2$ to zero. The collective coordinates defined by eq 2.8 are described by the spectral densities $C_{n}(\omega)$, $n = 1, \ldots, N$, $C_{D}(\omega)$, $C_{A}(\omega)$, $C_{1D}(\omega)$, and $C_{NA}(\omega)$,

$$C_{n}(\omega) = \sum_{j} \frac{m_{j} \alpha_{j}^{m}}{4} d_{j}^{2} 2\pi [\delta(\omega - \omega_{j}) - \delta(\omega + \omega_{j})]$$

$$C_{D}(\omega) = \sum_{j} \frac{m_{j} \alpha_{j}^{m}}{4} d_{j}^{2} 2\pi [\delta(\omega - \omega_{j}) - \delta(\omega + \omega_{j})]$$

$$C_{A}(\omega) = \sum_{j} \frac{m_{j} \alpha_{j}^{m}}{4} d_{j}^{2} 2\pi [\delta(\omega - \omega_{j}) - \delta(\omega + \omega_{j})]$$

$$C_{1D}(\omega) = \sum_{j} \frac{m_{j} \alpha_{j}^{m}}{4} d_{j} 2\pi [\delta(\omega - \omega_{j}) - \delta(\omega + \omega_{j})]$$

$$C_{NA}(\omega) = \sum_{j} \frac{m_{j} \alpha_{j}^{m}}{4} d_{j} 2\pi [\delta(\omega - \omega_{j}) - \delta(\omega + \omega_{j})]$$

For $n = 1, 2, \ldots, N$ (2.9)

(2.10)

(2.11)

(2.12)

(2.13)

Using this notation, the donor and acceptor dipole operators assume the form

$$P_{D} = \mu_{D}(B_{1}^{1} + B_{1})$$

$$P_{A} = \mu_{A}(Y^{1} B_{N} + B_{N}^{1} Y)$$

(2.14)

(2.15)

We next switch to the delocalized molecular orbital representation (see Figure 1b). To that end we consider the electronic Hamiltonian $V^{(e)}$ consisting of first two terms in eq 2.27. $[H^{(e)}]_{mm} = \delta_{mm} \Omega_{m}^{*} + (1 - \delta_{mm}) V_{mm}$. We denote its normalized eigenfunctions $\psi_{j}(n)$ with energies $\Omega_{j}$ and introduce the exciton creation operators $B_{k}^{1}$. The Hamiltonian is recast in a form

$$H = H_{0} + H_{1}$$

(2.17)

with

$$H_{0} = \sum_{k} \Omega_{k} B_{k}^{1} B_{k} - \sum_{k} q_{k}^{(c)} B_{k}^{1} B_{k} - q_{k}^{(c)} Y^{1} Y + H_{ph}$$

(2.18)

$$H_{1} = -\sum_{k k'} \delta_{k k'} B_{k}^{1} B_{k}$$

(2.19)

In eqs 2.18–2.26, $k'$ label exciton states. The collective coordinates $q_{j}^{(c)}$, $q_{k}^{(c)}$, and $q_{kk}^{(c)}$ in the exciton representation are defined by

$$q_{j}^{(c)} = \delta_{j}^{(*)} - \delta_{j}^{(*)}$$

$$q_{k}^{(c)} = \delta_{k}^{(*)} - \delta_{k}^{(*)}$$

$$q_{kk}^{(c)} = \delta_{kk}^{(*)} - \delta_{kk}^{(*)}$$

(2.20)

(2.21)

and $q_{kk}^{(c)} = q_{kk}^{(c)}$. The corresponding spectral densities are given by

$$C_{kk}^{* q q}(\omega) = \sum_{mm} \psi_{j}^{*}(m) \psi_{j}^{*}(m) \psi_{j}(n) \psi_{j}(n) [\delta_{mm} C_{m}(\omega) + C_{D}(\omega) - \delta_{nn} C_{1D}(\omega) - \delta_{nn} C_{1D}(\omega)]$$

(2.22)

$$C_{kk}^{* q q}(\omega) = \sum_{mn} \psi_{j}^{*}(m) \psi_{j}(n) [C_{D}(\omega) - \delta_{nn} C_{1D}(\omega) + \delta_{nn} C_{NA}(\omega)]$$

(2.23)

$$C_{kk}^{* q q}(\omega) = C_{D}(\omega) + C_{A}(\omega)$$

(2.24)

The dipole operators adopt the form

$$P_{D} = \mu_{D}(B_{1}^{1} + B_{1})$$

$$P_{A} = \mu_{A}(Y^{1} B_{N} + B_{N}^{1} Y)$$

(2.25)

(2.26)

with the dipole matrix elements

$$\mu_{D} = \sum_{k} \mu_{D} \psi_{j}(1)$$

$$\mu_{A} = \sum_{k} \mu_{A} \psi_{j}(N)$$

(2.27)

(2.28)

This Hamiltonian will be used in the coming sections.

III. Time- and Frequency-Resolved Fluorescence Signal

The Hamiltonian (eqs 2.17–2.26) is formally identical to that derived in ref 30 for molecular aggregates, where $B_{j}^{1}$ denoted one-exciton creation operators, whereas $Y^{1}$ were creation operators for two-exciton states. In our case the $Y^{1}$ operator moves an electron from the ground state of the donor to the ground state of the acceptor. However, the two Hamiltonians are formally identical, and all the results of ref 30 can be applied to the present problem.

The time- and frequency-resolved signal $S(t, \omega)$ can be represented in a form...
where the free molecular Hamiltonian correlation functions of the dipole operators, $G_{kk}$ representing the detection process.

$S(t, \omega_o) = \int_{-\infty}^{\infty} dt e^{i\omega_o t} \tilde{S}(t, \tau)$ (3.1)

with

$\tilde{S}(t, \tau) \equiv \langle \hat{P}_A(t + \tau) \hat{P}_A(t) \rangle$ (3.2)

where for any operator $B$ we define the Heisenberg operator $B(t)$ whose evolution is determined by the total Hamiltonian $H_t$. The simpler time-resolved signal $I(t)$ is given by

$I(t) \equiv \int d\omega_I S(t, \omega_o) = \langle \hat{P}_A(t + \tau) \hat{P}_A(t) \rangle$ (3.3)

Expanding the expectation value in the rhs of eq 3.1 to second order in the driving field $\epsilon(t)$ and invoking the rotating wave approximation, $\tilde{S}(t, \tau)$ is expressed in terms of four-point correlation functions of the dipole operators,

$\tilde{S}(t, \tau) \equiv \int_{-\infty}^{\prime} dt' \int_{-\infty}^{\prime+\tau} dt'' P_A(t') P_A(t + \tau) \times
\frac{e(t')}{h} \frac{e(t'')}{h}$ (3.4)

In contrast to eq 3.2, the time evolution is now determined by the free molecular Hamiltonian $H$ (without the radiation field),

$P(t) \equiv \exp\left[\frac{i}{\hbar} Ht\right] P \exp\left(-\frac{i}{\hbar} Ht\right)$ (3.5)

Making use of eqs 2.25 and 2.26, we obtain

$\tilde{S}(t, \tau) \equiv \int_{-\infty}^{\prime} dt' \int_{-\infty}^{\prime+\tau} dt'' F^\dagger_{\tau}(t', t + \tau, t) \frac{e(t')}{h} \frac{e(t'')}{h}$ (3.6)

where

$F^\dagger_{\tau}(t', t + \tau, t) \equiv \sum_{kk'qq'} \mu_{kk'} \mu_{kk'} \mu_{qq} \mu_{qq'} B_{k1}(t_1) B_{k1}(t_2) Y(t_3) Y(t_4) B_{q2}(t_3) B_{q2}(t_4)$ (3.7)

The correlation function in the rhs of eq 3.7 has been calculated in ref 30 using a perturbative expansion in $H_1$. Substituting the result of ref 30 into eq 3.7, we obtain

$\tilde{S}(t, \tau) \equiv \theta(\tau) \int_{-\infty}^{\prime} dt' \int_{-\infty}^{\prime+\tau} dt'' W^\dagger_{\tau}(t) G_{kk}(t - \tau') \times
\frac{e(t')}{h} \frac{e(t'')}{h} + \theta(-\tau) \int_{-\infty}^{\prime} dt' \int_{-\infty}^{\prime+\tau} dt'' \times
\frac{e(t')}{h} \frac{e(t'')}{h}$

$W_{\tau}^k(t) G_{kk}(t + \tau - \tau') D_k(t' - \tau') \frac{e(t')}{h} \frac{e(t'')}{h} + \tilde{S}^{(a)}(t, \tau)$ (3.8)

where

$D_k(t) \equiv D_k^\dagger(t) + D_k^\dagger(-t)$ (3.9)

$D_k^\dagger$ is the doorway function representing the density matrix created upon optical excitation. $W^k$ is a window function representing the detection process. $G_{kk}$ is the Green function representing polaron population relaxation, and $\tilde{S}^{(a)}$ is the short-time component of the signal. These quantities can be expressed in terms of line-shape functions $g_{\mu\nu}(\tau)$, $\mu = k', \nu = k$. $Y$ related to spectral densities $C_{\mu\nu}(\omega)$.

$$g_{\mu\nu}(\tau) \equiv \int_{-\infty}^{\infty} d\omega \frac{C_{\mu\nu}(\omega)}{\hbar \omega^2} \left[ (1 - \cos(\omega \tau)) \coth \left( \frac{\hbar \omega}{2k_B T} \right) + i \sin(\omega \tau) \right]$$ (3.10)

All quantities are given in Appendix A.

The Green function $G_{kk}(\tau)$ can be calculated by solving the master equation

$$\frac{d}{d\tau} G_{kk}(\tau) = \sum_q K_{kk} G_{kk}(\tau)$$ (3.11)

with $G_{kk}(0) = \delta_{kk'}$, and the kernel

$$K_{kk} \equiv \int_{-\infty}^{\infty} d\tau K_{kk}^\dagger(\tau) \quad \text{for} \quad q \neq q'$$ (3.12)

$$K_{kk} \equiv \sum_q K_{kk} q' q$$ (3.13)

$K_{kk}^\dagger(\tau)$ has the form

$$K_{kk}^\dagger(\tau) = K_{kk}(\tau) \left[ \bar{g}_{kk' q' q}(\tau) - \left[ \bar{g}_{kk' q' q}(\tau) - \bar{g}_{kk' q' q}(\tau) + \frac{2i}{\hbar} \left( \bar{g}_{kk' q' q}(\tau) + \bar{g}_{kk' q' q}(\tau) \right) \right] \right] \left( 3.14 \right)$$

with

$$K_{kk}(\tau) \equiv \exp\left[ -\frac{i}{\hbar} (\Omega_q - \Omega_{q'}) \tau - \bar{f}_{kk}(\tau) \right]$$ (3.15)

and

$$\bar{f}_{kk}(\tau) \equiv g_{qq' q' q}(\tau) + g_{qq' q' q}(\tau) - g_{qq' q' q}(\tau) + g_{qq' q' q}(\tau) + \frac{2i}{\hbar} (\lambda_{q' q' q'} - \lambda_{q' q' q'}) \tau$$ (3.16)

Equations 3.1 and 3.8–3.16 provide a closed expression for the time- and frequency-resolved fluorescence signal.

In concluding this section we present the expression for the simpler, time-resolved, signal (integrated over frequency) defined by eq 3.3. Using eqs 3.3, 3.8, and A3, it can be represented in the doorway/window form:

$$I(t) = \sum_{kk} \mu_{kk}^2 \int_{-\infty}^{\prime} dt' \int_{-\infty}^{\prime+\tau} dt'' G_{kk}(t - \tau') \times
\frac{e(t')}{h} \frac{e(t'')}{h} + I^{(a)}(t)$$ (3.17)

with the short-time component

$I^{(a)}(t) = \int_{-\infty}^{\prime} dt' \int_{-\infty}^{\prime+\tau} dt'' F_2(t', t + \tau, t) \frac{e(t')}{h} \frac{e(t'')}{h}$

$$\sum_{kk} \mu_{kk}^2 \int_{-\infty}^{\prime} dt' \int_{-\infty}^{\prime+\tau} dt'' D_k(t' - \tau') \frac{e(t')}{h} \frac{e(t'')}{h}$$ (3.18)

IV. Impulsive Signals Obtained with Short Excitation Pulses

The expressions for the signals derived in section III can be simplified considerably when the excitation pulse is short. We represent the driving electric field $\epsilon(t)$ in the form

$\epsilon(t) = E(t) e^{-i\omega t} + E^*(t) e^{i\omega t}$ (4.1)
where \( \omega_0 \) is the carrier frequency of the exciting pulse and \( E(\tau) \) is the envelope, which is slow compared to the carrier frequency \( \omega_0 \); \( t_0 \gg \omega_0^{-1} \), where \( t_0 \) is the pulse duration. We also assume that \( t_0 \ll t_p \), where \( t_p \) is the time scale of population relaxation defined by the lowest nonzero mode of the master equation. The other two important time scales characterizing the system are the dephasing time \( t_d \), determined by the time scale of \( D(t) \) and \( W(t) \), and the nuclear relaxation time scale \( t_n \). We assume \( t_d, t_n \ll t_p \), where the ratio of \( t_d \) and \( t_n \) may be arbitrary. The limits \( t_d \ll t_n \) and \( t_n \ll t_0 \) are known as spectral diffusion and homogeneous limits respectively.\(^{27}\)

We first consider the snapshot limit when \( t_d \ll t_0 \ll t_p \). The expressions for the time- and frequency-resolved signal

\[
S(t, \omega) = \sum_{kk} W_k(\omega) G_{kk}(t) \sum_{\omega_0} d_{kk}(\omega) \int_{-\infty}^{\infty} d\tau \left( E(\tau) e^{i\omega_0 \tau} \right)^2
\]


The time-resolved signal is similarly given by

\[
I(t) = \sum_{kk} \left| \mu_{kk} \right|^2 G_{kk}(t) D_k(\omega_0) \int_{-\infty}^{\infty} d\tau \left( E(\tau) e^{i\omega_0 \tau} \right)^2 + I^{(0)}(t)
\]

The expressions for the short-time components can be simplified further in the spectral diffusion limit \( t_d \ll t_n \) and for snapshot excitation: \( t_d \ll t_0 \ll t_p \) where they assume the form

\[
I^{(s)}(t) = \int_{-\infty}^{\infty} d\tau' F_s(0, t, \tau') e^{i\omega_0 \tau'} - \sum_k \left| \mu_{kk} \right|^2 D_k(\omega_0) \int_{-\infty}^{\infty} d\tau'' \left( E(\tau'') e^{i\omega_0 \tau''} \right)^2
\]

\[
S^{(s)}(\omega, t) = \int_{-\infty}^{\infty} d\tau' \int_{-\infty}^{\infty} d\tau'' F_s(0, t, \tau, \tau') e^{i\omega_0 \tau'' + i\omega_0 \tau'} - \sum_k W_k(\omega) D_k(\omega_0) \int_{-\infty}^{\infty} d\tau' \left( E(\tau') e^{i\omega_0 \tau'} \right)^2
\]

V. Spectral Diffusion Limit

In this section, using the overdamped Brownian oscillator model for the spectral density,\(^{27}\) we derive closed expressions for the DW function, \( D_k(\omega) \), \( W_k(\omega) \), and the kernel \( K_{qq}^{\sigma} \). We assume that all collective bath coordinates have the same relaxation rate \( \Lambda \),

\[
C_n(\omega) = \frac{\lambda_n}{k} C(\omega) \quad \text{for} \quad n = 1, 2, ..., N
\]

\[
C_p(\omega) = \frac{\lambda_D}{k} C(\omega)
\]

\[
C_A(\omega) = \frac{\lambda_A}{k} C(\omega)
\]

where

\[
\lambda_n = \sum_j m_j \omega_j^2 d_{j}^2 / 2
\]

\[
\lambda_D = \sum_j m_j \omega_j^2 d_{j}^2 / 2
\]

\[
\lambda_A = \sum_j m_j \omega_j^2 d_{j}^2 / 2
\]

\[
\lambda \equiv \sum_{N=1}^{N} \lambda_n
\]

\[
C(\omega) = \frac{\lambda_0 \Lambda}{\omega^2 + \Lambda^2}
\]

with \( d_{jj} = \sqrt{\lambda_D \lambda_A} d_j \) and \( d_{jj} = \sqrt{\lambda_D \lambda_A} d_j \). For simplicity we assume that the reorganization energies are uncorrelated (i.e., each site has its own bath). This assumption may be relaxed without a major complication. All \( g_{n,n}(t) \) are now expressed using a single function \( g(t) \) as

\[
g_{n,n}(t) = \frac{\lambda_{jj} \tau}{\Lambda} g(t)
\]

The expression for \( \lambda_{ij} \) is given by

\[
g(t) \equiv \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \frac{C(\omega)}{\omega^2} \left( 1 - \cos(\omega t) \right) \cot\left( \frac{\hbar \omega}{2k_B T} \right) + i(\sin(\omega t) - \omega t)
\]

\[
\lambda_{ij}^{\sigma,qq} \equiv \sum_{m,n} \psi_i^*(m) \psi_j^*(n) \psi_i(n) \psi_j(m) \delta_{mn} \lambda_\sigma + \lambda_D - i(\sin(\omega t) - \omega t)
\]

In the high-temperature limit, \( k_B T \gg \hbar \Lambda \), using eqs 5.8 and 5.10 we have

\[
g(t) \equiv z e^{-\lambda_\sigma t} - 1 \quad \text{for} \quad t \geq 0
\]

\[
g(-t) = g^*(t)
\]

where

\[
z = \frac{2\lambda_\sigma k_B T}{\hbar^2 \Lambda^2 - i \hbar \Lambda}
\]
In the static limit, $2\lambda B T \gg (\hbar \Lambda)^2$, using eqs 3.12–3.16 and 5.11–5.16, we obtain

$$K_{qq} = F_{qq} \left( \frac{\pi \hbar^2}{\lambda_{qq} \kappa_B T} \right)^{1/2} \exp \left[ -\frac{(\Omega_q - \Omega_q' + \lambda_{qq}')^2}{4 \lambda_{qq} \kappa_B T} \right] \quad (5.17)$$

where

$$F_{qq} \equiv \frac{1}{K^2} \left[ (\Omega_q - \Omega_q') (\lambda_{qq,qq} - \lambda_{qq,qq}') - \lambda_{qq} (\lambda_{qq,qq} + \lambda_{qq,qq}') \right] + \frac{2 \kappa_B T}{\hbar^2} \left( \frac{\lambda_{qq,qq} - \lambda_{qq,qq}'}{\lambda_{qq'}} \right)^2 \quad (5.18)$$

with

$$\Omega_q \equiv \Omega_q - \lambda_{qq,qq}$$

$$\lambda_{qq} \equiv \lambda_{qq,qq} + \lambda_{qq,qq} - \lambda_{qq,qq}'$$

Equations 5.17–5.18 satisfy the detailed balance condition, $K_{qq}/K_{q'q} = \exp[-(\Omega_q - \Omega_q)/k_B T]$. In the same manner we obtain

$$D_\sigma(\omega) = \mu_\sigma^2 \left( \frac{\pi \hbar^2}{\lambda_{kk} \kappa_B T} \right)^{1/2} \exp \left[ -\frac{(\Omega_k - \hbar \omega)^2}{4 \lambda_{kk} \kappa_B T} \right] \quad (5.21)$$

$$W_\sigma(\omega) = \mu_\sigma^2 \left( \frac{\pi \hbar^2}{\lambda_{kk} \kappa_B T} \right)^{1/2} \exp \left[ -\frac{(\Omega_k - \Omega_k' + \lambda_{kk}') - \hbar \omega)^2}{4 \lambda_{kk} \kappa_B T} \right] \quad (5.22)$$

with

$$\lambda_{kk} \equiv \lambda_{kk,kk}$$

$$\lambda_{kk} \equiv \lambda_{kk,kk} + \lambda_{kk,kk} - \lambda_{kk,kk}'$$

$$\Omega_k = \Omega_k - \lambda_{kk,Y}$$

The complete expression for the rate matrix $K_{qq}$ for the overdamped Brownian oscillator spectral density, which is not limited to the static limit, is given in Appendices B and C.

VI. Interplay or Tunneling and Sequential Transfer

The calculations presented in this section illustrate the range of parameters and time scales whereby the ET process can be considered either direct (tunneling) or hopping type. We have used typical parameters for DNA charge transfer and varied them over a broad range. These results show under what conditions a DNA bridge acts as a quantum wire. For the electronic parameters we used $E_D = 1.25$ eV, $E_A = -2.29$ eV, $E_N = -0.29$ eV, $E_n = 0.0$ eV for $n = 2, 3, ..., N - 1$, and $V_m = 0.025$ eV for $m = n - 1$ or $m = n + 1$; otherwise $V_m = 0$. The carrier frequency of the exciting pulse $\omega_0$ is $\omega_0 \approx 1.059$ eV. The population of the acceptor (eq 6.1) is plotted as well. Solid line: Time-resolved fluorescence $I(t)$. Dashed line: eq 6.1.

$$\int_{-\infty}^{\infty} \text{d}t' |E(t')|^2 \hbar^2$$

are normalized to 1. Since typical nuclear relaxation time scales (~1 ps) are much shorter than the ET time scale ($\approx 1$ ns) in DNA, we neglect the short-time component which decays to zero on the nuclear relaxation time scale. The lowest eigenvalue of the matrix $K$ (whose elements are $K_{qq}$) is zero and gives the thermal equilibrium distribution. The second eigenvalue $K$ dominates the relaxation to equilibrium at long times. In Figure 2 the scaled time $Kt$ is used as an abscissa. Since for these parameters population of the bridge is negligible compared with the donor and acceptor, we expect the population of the acceptor $P_N(t)$ to be close to

$$p_N(t) = p_N(\infty) (1 - e^{-Kt}) \quad (6.1)$$

with

![Figure 2](image-url)

Figure 2. Time-resolved fluorescence $I(t)$ (which is proportional to the population of the acceptor) vs the scaled time $Kt$ for different values of the number of sites $N$, as indicated. Temperature is 300 K. Reorganization energies are $\lambda_n = 0.1$ eV ($n = 1, 2, ..., N$), $\lambda_0 = 0.05$ eV, and $\lambda_a = 0.05$ eV. Nuclear relaxation rate $\Lambda$ is 1 ps$^{-1}$. Electronic structure is as follows: $E_D = -1.25$ eV, $E_A = -2.29$ eV, $E_N = -0.29$ eV, $E_n = 0.0$ eV, for $n = 2, 3, ..., N - 1$, and $V_m = 0.025$ eV for $m = n - 1$ or $m = n + 1$; otherwise $V_m = 0$. The carrier frequency of the exciting pulse $\omega_0$ is $\Omega_1 = 1.059$ eV. The population of the acceptor (eq 6.1) is plotted as well. Solid line: Time-resolved fluorescence $I(t)$. Dashed line: eq 6.1.

![Figure 3](image-url)

Figure 3. ET rate $\log_{10} K$ (in ps$^{-1}$) vs the number of sites $N$ (the distance between the donor and the acceptor). Parameters are the same as Figure 2. Solid line: $\log_{10} K$. Dashed line: $\log_{10} K^{\text{opt}}$. Short dashed line: $\log_{10} K^{\text{nm}}$. Dotted line: $\log_{10} K^{\text{eq}}$. Dash–dotted line: $\log_{10} K^{\text{opt}}$. $$\int_{-\infty}^{\infty} \text{d}t' |E(t')|^2 \hbar^2$$

are normalized to 1. Since typical nuclear relaxation time scales (~1 ps) are much shorter than the ET time scale ($\approx 1$ ns) in DNA, we neglect the short-time component which decays to zero on the nuclear relaxation time scale. The lowest eigenvalue of the matrix $K$ (whose elements are $K_{qq}$) is zero and gives the thermal equilibrium distribution. The second eigenvalue $K$ dominates the relaxation to equilibrium at long times. In Figure 2 the scaled time $Kt$ is used as an abscissa. Since for these parameters population of the bridge is negligible compared with the donor and acceptor, we expect the population of the acceptor $P_N(t)$ to be close to

$$p_N(t) = p_N(\infty) (1 - e^{-Kt}) \quad (6.1)$$

with
Here the delocalized state that goes to $k$th site state in the limit of $V_{nn} = 0$ is denoted by $q_k$. Figure 2 shows that eq 6.1 indeed represents very well the fluorescence decay curves. $K$ can thus be interpreted as a sum of the forward and backward ET rates. All time-resolved fluorescence curves are similar except for the variation of the forward and backward ET rates. All time-resolved fluorescence curves are similar except for the difference between the donor and the acceptor, for varying values of the energy gap $\Delta E$, as indicated. Other parameters are the same as in Figure 2.

We further introduce the sequential rate matrix $K^{(seq)}$.

$$K^{(seq)}_{qq'} = \begin{cases} 0 & \text{for } (q, q') = (q_1, q_N) \text{ or } (q, q') = (q_N, q_1) \\ K_{qq'}^{(seq)} & \text{for } q \neq q', (q, q') \neq (q_N, q_1), \\
\sum_{q' \neq q} K_{qq'}^{(seq)} & \text{for } q = q' \end{cases}$$  

For $N = 2$ we define $K^{(sup)} = K^{(seq)}$. We define the superexchange and sequential ET rates, $K^{(sup)}$ and $K^{(seq)}$, as the second lowest eigenvalues of $K^{(sup)}$ and $K^{(seq)}$, respectively. These quantities are plotted in Figure 3 as well. We see that for smaller $N$ the superexchange transfer dominates, and for larger $N$ the sequential transfer takes over.

To investigate the competition between the two mechanisms, we calculated the ET rate as a function of $N$, varying the energy gap between the donor site and the first bridge site, $\Delta E \equiv E_2 - E_1$. We kept all bridge energies to be the same, $E_n = 0.0$ eV for $n = 2, 3, ..., N - 1$, and the difference between the donor and the acceptor energies is the same as in Figure 2, setting $E_1 = -\Delta E$ and $E_N = -\Delta E - 0.04$ eV. Figure 4 shows that as the energy gap $\Delta E$ is increased, the superexchange rate curve becomes steeper, and the sequential transfer rate slows down. The reorganization energy $\lambda$ and temperature $T$ are also varied (Figures 5 and 6). Figure 7 displays the variation of the rate with bridge size on a logarithmic scale. The rate varies as $N^{-\alpha}$ for large $N$, where the exponent $\alpha$ is not universal and depends on the parameters.

We next investigate the effect of energetic disorder of the bridge sites. $E_n$ for $n = 3, ..., N - 1$ are modeled as independent random Gaussian variables whose average value is zero and variance $\sigma = 2.5 \times 10^{-3}$ eV$^2$. This static disorder is sufficient to localize the excitation state within $\sim$2 sites. Other parameters are identical to Figure 2.

At this point we would like to compare the present rates with those calculated perturbatively in the electronic coupling $V_{nn}$. The perturbative $2 \times 2$ superexchange rate matrix is $K^{(sup)}$ with matrix elements

\begin{equation}
K^{(sup)}_{ij} = \frac{\exp(-\Omega_{ij}^{-1})}{\exp(-\Omega_{ij}^{-1}) + \exp(-\Omega_{ij}^{-1})^{(6.2)}}
\end{equation}
Assuming that Nth electronic state is well-localized on the acceptor, time- and frequency-resolved fluorescence $S(t, \omega_s)$ can be approximated as,

$$S(t, \omega_s) = I(t) W(\omega_s)$$  \hspace{1cm} (6.17)

where $W(\omega_s)$ is fluorescence from an isolated acceptor.

Figure 5. Same as Figure 4, except that the reorganization energy $\lambda$ is varied, as indicated where $\lambda_n = \lambda (n = 1, 2, ..., N)$, $\lambda_D = \lambda/2$, and $\lambda_A = \lambda/2$.

Figure 6. Same as Figure 4, except that the temperature $T$ is varied, as indicated.

Figure 7. Same as Figure 4, but abscissa in logarithmic scale $N$. Solid line: $\log_{10} K$. Dashed line: $-\alpha \log_{10} N$. The exponents $\alpha$ are listed in this figure.

Assuming that Nth electronic state is well-localized on the acceptor, time- and frequency-resolved fluorescence $S(t, \omega_s)$ can be approximated as,

$$S(t, \omega_s) = I(t) W(\omega_s)$$  \hspace{1cm} (6.17)

where $W(\omega_s)$ is fluorescence from an isolated acceptor.

Figure 8. Same as Figure 2, but disorder is included in the bridge site energies. Each $E_n$ for $n = 2, 3, ..., N - 1$ has Gaussian distribution with average 0.0 and variance 0.05 eV.

Figure 9. Time- and frequency-resolved fluorescence $S(t, \omega_s)$. The parameters are the same as in Figure 2, but the number of sites $N$ is 10. The abscissa is $\log_{10} K$. Dashed line: $-\alpha \log_{10} K$. The exponents $\alpha$ are listed in this figure.

$$W(\omega_s) = \left( \frac{\pi \hbar^2}{\lambda_{AN} k_B T} \right)^{1/2} \exp \left[ -\frac{(\hbar \omega_{AN} - \hbar \omega_s)^2}{4 \lambda_{AN} k_B T} \right]$$  \hspace{1cm} (6.18)

with $\lambda_{AN} = \lambda_A + \lambda_N - 2 \sqrt{\lambda_A \lambda_N}$ and $\hbar \omega_{AN} = (\Omega_A - \lambda_A) - (\Omega_N - \lambda_N) + \lambda_{AN}$. In general, the fluorescence line shape varies with time and may not be factorized in the form of eq 6.17.

VII. Discussion

In the present theory the ET system is modeled by a Hamiltonian describing localized electronic states in the site representation, coupled to each other and to harmonic nuclear degrees freedom. To include higher order contributions in the electronic couplings among sites, the eigenstates of the electronic part of Hamiltonian are used as a basis set. In this representation the nuclei couple to diagonal as well as off-diagonal elements of the electronic Hamiltonian. Only the latter couplings are treated perturbatively. This treatment of nuclear modes incorporates the reorganization energy as well as memory effects of nuclear modes. The photoexcitation of the donor and the resulting fluorescence are formulated microscopically, without
invoking the common assumption that the excited donor state is equilibrated initially. Using the present theory, the effects of the bridge size, the energy gap between the donor/acceptor and the bridge, the reorganization energies, and the temperature on the competition between the superexchange and sequential transfer were investigated, and the time- and frequency-resolved fluorescence was calculated.

Effects of solvation on long-range ET in DNA have been studied recently in ref 19 using the density matrix approach. A single high-frequency vibrational oscillator was coupled to the electronic states of the donor/bridge/acceptor systems. The oscillator and the electronic states were then coupled to other nuclear bath modes. Eliminating these external degrees of freedom and applying the Redfield equation of motion, the time evolution of ET in DNA including nuclear dynamics was calculated. The Redfield equation retains terms only up to second order in the system–bath coupling, and the bath time scale is assumed to be much shorter than the ET process. Consequently, the reorganization energy (which originates from slow nuclear modes) and the finite time scale of the nuclear modes except for the high-frequency mode were not included.

Finally, we comment on the relation between the present calculations which use the delocalized electronic basis set and the direct perturbative calculation of the rate in intermolecular electronic coupling. We expect the two to be similar if the coupling is weak, |Ωs' - Ωd'p| >> Vnn'. Expanding the transfer rate between the qth and q′th excitons in Vnn', we obtain

\[ K_{qq'} = \left(1 + \frac{\lambda_{n'} - \lambda_n}{E_{n'} - E_n} \right)^2 K_{nn'} \]  

where

\[ K_{nn'} = \left( \frac{V_{nn'}}{\hbar} \right)^2 \frac{\exp\left[ \frac{-\Omega_s(t)}{\hbar} \right]}{\left( \lambda_n + \lambda_{n'} \right) k_B T} \times \frac{1}{4(\lambda_n + \lambda_{n'}) k_B T} \]  

is the Marcus rate between the nth and n′th states. The qth and q′th states go to the nth and n′th states, respectively, in the Vnn' = 0 limit. Here

\[ \lambda_{qq,qq} = \lambda_n \]  
\[ \lambda_{qq',qq'} = \lambda_n' \]  
\[ \lambda_{q'q,q'} = \left( \frac{V_{nn'}}{E_{n'} - E_n} \right)^2 (\lambda_n + \lambda_{n'}) \]  
\[ \lambda_{qq',q'q} = \frac{V_{nn'}}{E_{n'} - E_n} \lambda_n \]  
\[ \lambda_{q'q,qq'} = \frac{V_{nn'}}{E_{n'} - E_n} \lambda_n' \]  
\[ \lambda_{qq',q'q} = \lambda_n + \lambda_{n'} \]  

When Vnn' is weak, the two perturbation theories give similar expressions for the rate except for different prefactors. The two expressions coincide when |E_{n'} - E_n| >> |\lambda_{n'} - \lambda_n|.

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**Appendix A: Quantities Appearing in Eq 3.8**

The auxiliary functions appearing in eq 3.8 are given by

\[ D'_s(t) = \mu_{kd}^2 \exp\left[ -\frac{i}{\hbar} \Omega_s t - g_{kk,dd}(t) \right] \] \hspace{1cm} (A1)
\[ W'_{s}(t) = \mu_{kd}^2 \exp\left[ -\frac{i}{\hbar} (\Omega_s - \Omega_p) t + 2\frac{j}{\hbar} (\lambda_{kk,dd} - \lambda_{kk,dd})(t) - g_{kk,dd}(t) \right] \] \hspace{1cm} (A2)
\[ S^{(n)}(t, \tau) = \int_{-\infty}^{\tau} dt' \int_{-\infty}^{\tau+\tau} dt'' F_{n}(t', t + \tau, t') \frac{\exp(i\tau')}{\h} \frac{\exp(i\tau'')}{\h} \] \hspace{1cm} (A3)

where the correlation function \( F_{n} \) defined by eq 3.7 is calculated under the assumption that \( H_1 = 0 \) and has the form \( \lambda_{s,p} = -\hbar \lim_{\tau \to \infty} \frac{\Im\left[ d\theta_{n,p}(t) / dt \right]}{\h} \) \hspace{1cm} (A5)

The function \( f^{(2)} \) in eq A4 is given by

\[ f^{(2)}_{kk,dd}(t_4, t_3, t_2, t_1) = g_{kk,dd}(t_2 - t_1) - g_{kk,dd}(t_2 - t_1) \] \hspace{1cm} (A6)

**Appendix B: ET Rates for a Finite Solvent Time Scale**

In this Appendix we present expressions for doorway/window functions and the kernel \( K_{qq} \) for the overdamped Brownian oscillator model for the spectral density, which do not assume the static limit. A confluent hypergeometric function is used to derive the expressions.

For \( \tau \geq 0 \) we have
\[ D^2_k(\tau) = \frac{\mu_{Dk}}{2} \exp \left[ -i\omega_{Dk} \tau - \frac{\tilde{\lambda}_{Dk}}{\lambda} q(\tau) \right] \] (B1)

\[ W^2_k(\tau) = \frac{\mu_{Ak}}{2} \exp \left[ -i\omega_{Ak} \tau - \frac{\tilde{\lambda}_{Ak}}{\lambda} q(\tau) \right] \] (B2)

\[ K^k_{qq}(\tau) = (A_{qq}e^{-2\lambda\tau} + B_{qq}e^{-\lambda\tau} + C_{qq}) \times \exp \left[ -i\omega_{qq} \tau - \frac{\tilde{\lambda}_{qq}}{\lambda} q(\tau) \right] \] (B3)

where

\[ \tilde{\omega}_{Dk} \equiv \frac{\Omega_k}{\hbar} \] (B4)

\[ \tilde{\lambda}_{Dk} \equiv \lambda_{kk, kk} \] (B5)

\[ \tilde{\omega}_{Ak} \equiv \frac{1}{\hbar} (\Omega_A - \Omega_k - \frac{2}{\hbar} \lambda_{kk, Y} - \lambda_{kk, kk}) \] (B6)

\[ \tilde{\lambda}_{Ak} \equiv \lambda_{kk, Y} + 2\lambda_{kk, Y} \] (B7)

\[ \tilde{\omega}_{qq} \equiv \frac{1}{\hbar} (\Omega_q - \Omega_q) + \frac{2}{\hbar} (\lambda_{q,q', q} - \lambda_{q,q', q}) \] (B8)

\[ \tilde{\lambda}_{qq} \equiv \lambda_{q,q,q} + \lambda_{q,q,q} - \lambda_{q,q', q} \] (B9)

\[ A_{qq} \equiv -\frac{z^2}{\lambda^2} \Lambda^2 (\lambda_{q,q,q,q} - \lambda_{q,q,q,q}) (\lambda_{q,q,q,q} - \lambda_{q,q,q,q}) \] (B10)

\[ B_{qq} \equiv \frac{z^2}{\lambda^2} \Lambda^2 (\lambda_{q,q,q,q} - \lambda_{q,q,q,q}) \times \] (B11)

\[ C_{qq} \equiv \left[ \frac{z^2}{\lambda^2} \Lambda (\lambda_{q,q,q,q} - \lambda_{q,q,q,q}) + \frac{1}{2} \Lambda (\lambda_{q,q,q,q} - \lambda_{q,q,q,q}) \times \right] \] (B12)

Using eqs B1–B12, we obtain\textsuperscript{27,31}

\[ D_1(\omega) = \] (B13)

\[ \frac{2\Re \mu_{Dk}^2}{\lambda_{Dk}^2 - i(\omega - \tilde{\omega}_{Dk})} \sum_{m=0}^{\infty} \frac{\left( \frac{\tilde{\lambda}_{Dk}}{\lambda} \right)^m}{(\frac{\tilde{\lambda}_{Dk}}{\lambda} z - i(\omega - \tilde{\omega}_{Dk})/\Lambda + 1)_m} \]

\[ W_1(\omega) = \] (B14)

\[ \frac{2\Re \mu_{Ak}^2}{\lambda_{Ak}^2 - i(\omega - \tilde{\omega}_{Ak})} \sum_{m=0}^{\infty} \frac{\left( \frac{\tilde{\lambda}_{Ak}}{\lambda} \right)^m}{(\frac{\tilde{\lambda}_{Ak}}{\lambda} z - i(\omega - \tilde{\omega}_{Ak})/\Lambda + 1)_m} \]
Using eqs B10–B12 and C1–C12, we obtain

\[ D_q(\omega) = -2Re \mu_D e^{-\nu q} \sum_{n=0}^{\infty} \frac{b^{n}_{Dk}}{n!} \frac{1}{a_{Dk} - n\lambda + i\nu} \]

(13)

\[ W_q(\omega) = -2Re \mu_k e^{-\nu q} \sum_{n=0}^{\infty} \frac{b^{n}_{Dk}}{n!} \frac{1}{a_{Dk} - n\lambda + i\nu} \]

(14)

\[ K_{qq'} = -2Re e^{-\nu q} \sum_{n=0}^{\infty} \frac{b^{n}_{qq'}}{n!} \left( A_{qq'} \frac{1}{a_{qq'} - (n+2)\lambda} + B_{qq'} \frac{1}{a_{qq'} - (n+1)\lambda} + C_{qq'} \frac{1}{a_{qq'} - n\lambda} \right) \]

for \( q \neq q' \) (15)

**References and Notes**


