Non-Condon theory of nonadiabatic electron transfer reactions in V-shaped donor–bridge–acceptor complexes

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The rate of nonadiabatic long-distance electron transfer (ET) is derived for the direct and superexchange electronic coupling between the donor and acceptor. The model takes into account a non-Condon thermal modulation of the electronic coupling through the interaction of the system transition dipoles with the polarization fluctuations of the solvent. Going from a linear donor–bridge–acceptor complexes to a bent, V-shaped geometry lowers the system symmetry resulting in several novel properties of the ET matrix element based on the fact that permanent and transition dipoles in the system are not polarized along the direction of ET. The effective ET matrix element $H_{ET}$ gains two zeros as a function of the donor–acceptor vertical energy gap. The positions of zeros of $H_{ET}$ depend on the sign relations between the donor–bridge and bridge–acceptor electronic couplings and corresponding transition dipoles. The ET matrix element becomes dependent on solvent through the solvent refractive index and the inhomogeneous width of the donor–acceptor optical transition. The former factor is mainly responsible for the temperature slope of $|H_{ET}|$. The derivative $d|H_{ET}|/dT$ switches its sign at the zero points of $H_{ET}$. The distance decay parameter of the donor–acceptor coupling is shown to vary linearly with the inhomogeneous width of the optical transition between the donor and acceptor. © 2003 American Institute of Physics.

[I. INTRODUCTION]

The rate of nonadiabatic (NA) electron transfer (ET) is derived as the product of the ET matrix element, $H_{ET}$, and the Franck–Condon weighted density of states (FCWDS), $k^{NA} \propto |H_{ET}|^2$ FCWDS.

The FCWDS factor represents the statistical distribution of donor–acceptor (DA) energy gaps arising from thermal excitations of quantum vibrations and classical nuclear motions. The transferred electron interacts with a large number of nuclear motions via the long-range Coulomb interaction potential. Electronic energy fluctuations arising from classical nuclear motions are therefore described as collective modes with essentially Gaussian statistics. The FCWDS factor is then well represented by a convolution of a Gaussian distribution of energy gaps coupled to classical nuclear modes with a Poisson distribution of intensities of quantum vibrational excitations. This nonspecific form of the FCWDS factor leaves very little room for fine-tuning of ET complexes, which is needed in design of molecular-based systems with specified characteristics. A considerable attention has therefore been given to the ET matrix element with the goal to formulate general principles of chemical control of ET rates.

Mulliken and Hush proposed a connection between the ET matrix element and the adiabatic transition dipole $m_{12}$. For two-site (donor D, and acceptor A), two-level system, the Mulliken–Hush (MH) relation reads

$$H_{ET} = \frac{m_{12}^\|}{\Delta m_{da}} \Delta E_{12}. \tag{2}$$

Equation (2) incorporates two modifications of the original MH formulation. First, according to Creutz, Sutin, and Newton, the diabatic energy gap $\varepsilon$ in the original MH formula is replaced by the adiabatic splitting $\Delta E_{12}$ referring to the ET system in the gas phase. Second, Eq. (2) emphasizes that only the longitudinal projection $m_{12}^\|=m_{12} \cdot \mathbf{u}^\|$ on the direction $\mathbf{u}^\|=\Delta m_{da}/\Delta m_{da}$ of the diabatic differential dipole $\Delta m_{da}$ is significant for $H_{ET}$. The theory of nonadiabatic, long-range ET is traditionally formulated in terms of diabatic, site-localized electronic wave functions. The adiabatic transition dipole can be expressed through diabatic matrix elements of the dipole moment and Hamiltonian operators in terms of a unitary transformation connecting the diabatic and adiabatic basis sets.

$$m_{12} = m_{da} \frac{\varepsilon}{\Delta E_{12}} - \Delta m_{da} \frac{H_{da}}{\Delta E_{12}}, \tag{3}$$

where $m_{da}$ is the diabatic transition dipole. Based on the assumption $m_{da}=0$, the effective ET matrix element $H_{ET}$ entering the NA rate constant is often replaced by the direct off-diagonal coupling between the diabatic D and A states, $H_{da}$. The condition $m_{12}^\|=\mathbf{m} \cdot \mathbf{u}^\|=0$ defines the generalized MH (GMH) diabatic basis proposed by Cave and Newton. Based on the Condon derivation of the NA rate constant, the condition $m_{da}=0$ has long been considered to be an approximation of the MH treatment. It turns out, however, that the MH formula, as given by Eqs. (2) and (3), is

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exact if the non-Condon modulation of the electron tunneling probability by the solvent polarization is included in the calculation of the NA rate (see below).

The direct DA coupling $H_{da}$ arises from the overlap of the diabatic D and A states, which decays exponentially with the DA separation $R_{DA}$,

$$H_{da} \propto e^{-\beta_{DA}R_{DA}}.$$  

Although system specific, the decay parameter $\beta_{DA}$ does not change dramatically among a wide variety of ET systems, hence offering little opportunity for specific tuning of ET rates. An alternative design based on superexchange mechanism of electronic coupling through a bridge (B) moiety in a donor–bridge–acceptor (DBA) complex has become a major motive in studies of long-range ET. Although the superexchange coupling also decays exponentially with the DA separation, the existence of a manifold of B states offers substantial flexibility for chemical design. A wide variety of bridging media including hydrocarbons, DNA, and polynyes has been considered for linear or bent DBA complexes. In some cases, a substantial modulation of the DA electronic coupling was achieved either by conformational changes of the DBA molecule for superexchange through B covalently attached to D and A or by changing the solvent for through-solvent superexchange. In the latter case a highly curved DBA geometry drives the electronic coupling pathway through the intervening solvent molecules instead of the molecular backbone of the DBA complex.

The present study explores possibilities for an effective alteration of the ET matrix element in bent DBA molecules. The basic idea of the present model follows from the notion that only the longitudinal projection of the adiabatic transition moment is effective in ET coupling [Eq. (2)]. Molecular configurations allowing rotations of the adiabatic transition dipole out of the longitudinal alignment should therefore generate substantial changes in the DA electronic coupling. A bent DBA molecule (Fig. 1) with a B unit placed off the DA line is considered to model such a situation. The diabatic transition dipoles aligned along the DB and BA bonds (double arrows in Fig. 1) create an adiabatic transition dipole with orientation sensitive to the DB and DA energy gaps.

We start our discussion in Sec. II with the classical case of a two-state DA complex to show how the non-Condon coupling of the ET matrix element to the solvent polarization leads to the MH relation. The MH formula is used for a three-level configuration of the DBA complex in Sec. III. In particular, we show that $H_{ET}$ switches its sign twice as a function of the vertical DA energy gap. A direct application of the MH formula to multilevel systems does not specify magnitudes of the energies in the Hamiltonian matrix. These energies are, in fact, determined by the condition of degeneracy between the D and A states required by the golden rule formula. In order to resolve this problem, we provide in Sec. IV a direct derivation of the NA rate constant for superexchange ET. It turns out that the MH formula does not directly extend to superexchange ET, although some qualitative features of the MH solution are reproduced by the golden rule derivation, e.g., the ET matrix element still has two zeros as a function of the vertical DA energy gap. The bent geometry of the DBA molecule brings about temperature dependence of $H_{ET}$. An extension of the three-state configuration to the McConnell model of n equivalent B sites makes the distance decay parameter $\beta_{DA}$ [Eq. (4)] temperature dependent with a negative temperature slope. The results of the study are discussed in Sec. V.

II. TWO-STATE DONOR–ACCEPTOR COMPLEX

An ET system is considered to consist of a D (subscript "d"), A (subscript "a"), and B (subscript "b") units connected into a single DBA complex. Correspondingly, the manifold of electronic states is limited to three single-electron states: D, B, and A. The electronic energies on D ($I_d$), B ($I_b$), and A ($I_a$) are generated by a vacuum basis set $|\Psi_d\rangle$ as diagonal elements of the vacuum Hamiltonian $H_0$, $I_a = \langle \Psi_a | H_0 | \Psi_a \rangle$. Off-diagonal matrix elements $\langle \Psi_a | H_0 | \Psi_b \rangle$ are nonzero for a diabatic basis set $|\Psi_a\rangle$; when $\langle \Psi_a | H_0 | \Psi_b \rangle = \delta_{ab}$, $|\Psi_a\rangle$ form an adiabatic basis set. For this special latter case, the Roman indexes $i = 1, 2, 3$ are used, while the Greek indexes $\alpha = d, b, a$ are reserved for the nonadiabatic basis. The basis functions $|\Psi_\alpha\rangle$ refer to "vertical" vacuum states corresponding to the equilibrium nuclear geometry (shown by an effective nuclear coordinate $Q$ in Fig. 2) of the DBA complex in its initial electronic state. The energy gap $\varepsilon = I_a - I_d$ then refers to the D–A vertical excitation energy (Fig. 2). The D–B vertical energy gap is $\varepsilon_b = I_b - I_d$. The vertical energies are different for the forward and backward reactions. For brevity, we drop any indexes specifying the direction of the process and assume that $\varepsilon$ and $\varepsilon_b$ stand for the vertical energy gaps in the vacuum for the corresponding transition.

When the DBA molecule is placed in a condensed medium (solvent), its (partial) charges polarize the surrounding molecules resulting in a reaction electric field acting back on the charges of the DBA complex. In the point dipole approximation, the interaction Hamiltonian becomes
where $m$ is the dipole moment operator. The solvent reaction field includes a fast (quantum) electronic component, $R_e$, and a slow (classical) nuclear component, $R_p$. The electronic polarization adiabatically solvates the transferred electron and fluctuations of the nuclear polarization create configurations with the DA resonance. Only these two, D and A states, are included in the two-state description of ET covered in this section. The energetic fluctuations of the electron “dressed” by the adiabatic potential of the solvent electrons is then described by a 2×2 matrix with the diagonal and off-diagonal matrix elements obtained by averaging the system density matrix over the fast electronic subsystem.\(^{37}\) The D and A energies, $E_d$ and $E_a$, are given as follows

$$E_a = I_a + F_a - m \cdot R_e,$$  \hspace{1cm} (6)

where $\alpha = a, d$. The off-diagonal matrix element becomes\(^ {15, 48}\)

$$E_{da} = H_{da} - 2a_1 (m_{da} \cdot m) - m_{da} \cdot R_p,$$  \hspace{1cm} (7)

In Eqs. (6) and (7), $F_a = -a_1 m^2$ is the free energy of dipole polarization by the electronic solvent polarization, with $a_1$ standing for the corresponding response function; $\bar{m} = (m_a + m_d)/2$, $m_{da} = \langle \Psi_d | m | \Psi_a \rangle$, $m_a = \langle \Psi_a | m | \Psi_a \rangle$, and $H_{da} = \langle \Psi_d | H_0 | \Psi_a \rangle$.

Equations (6) and (7) are the starting point of our derivation of the NA rate constant. The diagonal energies are linearly coupled to the Gaussian polarization field.\(^ {1}\) The off-diagonal term [Eq. (7)] is shifted from the vacuum coupling $H_{ab}$ by two effects: the equilibrium solvation of the DA transition dipole by the electronic polarization (second summand) and by a linear coupling to the nuclear reaction field (third summand). The last term is responsible for the non-Condon modulation\(^ {28-32, 36, 49-51}\) of $E_{da}$ by the solvent. Formally, this dependence is similar to the linear modulation of the BB coupling suggested by Medvedev and Stuchlbrukhov (MS)\(^ {32}\) to account for passing of the instantaneous DA coupling through zero in molecular dynamics (MD) simulations.\(^ {29}\) The MS model considers inelastic scattering of the tunneling electron by B vibrations decoupled from polarization fluctuations considered in the present model.

The off-diagonal matrix element $E_{da}$ mixes electronic D and A states resulting in electronic transitions between them. In the limit of weak perturbation, the golden rule formula predicts for the rate constant of NA ET,

$$k_{a}^{NA} = \frac{2 \pi}{\hbar} \langle |E_{da}|^2 \delta(E_a - E_d) \rangle_a.$$  \hspace{1cm} (8)

The average $\langle \cdots \rangle_a$ stands for an ensemble average in equilibrium with the DBA complex in the initial, $\alpha = d$, or final, $\alpha = a$, states. Because of thermal modulation by the solvent polarization\(^ {15, 48, 52}\) the off-diagonal coupling comes under the ensemble average together with the delta-function setting the DA resonance.

$$Q_a = \int \exp[-\beta E_a - \beta R_p^2/2a_p] dR_p.$$  \hspace{1cm} (9)

In Eqs. (9) and (10), $a_p$ is the response function of the nuclear polarization such that the chemical potential of nuclear solvation of the dipole $m_a = \mu_p = -a_p m_a^2$.

The integrals over the three-dimensional nuclear polarization field in Eq. (8) can be calculated exactly for an arbitrary orientations of the transition dipole $m_{da}$ and the dipole moments $m_a$ in the initial and final ET states. In order to reduce the number of independent parameters, collinear dipoles $m_a$ and $m_{da}$ are considered here. Equation (8) can then be brought to the standard form of the NA rate constant\(^ {1, 4}\)

$$k_{a}^{NA} = A (\pi \beta / h^2 \lambda_p)^{1/2} e^{-\beta \mu_a^{\text{act}}}.$$  \hspace{1cm} (11)

Here, $\lambda_p = a_p \Delta m_d^2$ is the solvent reorganization energy ($\Delta m_{da} = m_a - m_d$) and the pre-exponential factor $A$ is given by the expression\(^ {15, 54}\)

$$A = B_{ET}^2 + 2B_{ET} \frac{m_{da}^4}{\Delta m_{da}} \left[ \frac{\pi \lambda_p}{\beta} + \frac{4 \lambda_p}{\beta} \frac{m_{da}^4}{\Delta m_{da}} \right].$$  \hspace{1cm} (12)

The pre-exponential factor in Eq. (12) is a generalization of the standard golden rule equation for NA ET accounting for the coupling between the transverse projection of the di-
The vacuum gaps \( m_{\text{da}} \) (Fig. 3) to the nuclear solvent polarization. Here, \( \mathbf{u} \) specifies a unit vector perpendicular to \( \mathbf{u} \) and lying in the plane of the DBA molecule. The adiabatic energy gap in the equation for the ET matrix element [Eq. (2)] is given in terms of the diabatic parameters as follows

\[
\Delta E_{12} = \left[ \varepsilon^2 + 4|H_{\text{da}}|^2 \right]^{1/2}.
\]

(13)

Finally, the free energy of activation \( F_{\text{act}}^\text{a} \) in Eq. (11) is given by the Marcus formula

\[
F_{\text{act}}^\text{a} = \frac{(\Delta F)^2}{4\lambda_p},
\]

(14)

where

\[
\Delta F = \varepsilon + \Delta F^e - 2a_p(\Delta \mathbf{m}_{\text{da}} \cdot \mathbf{m}_a)
\]

is the DA vertical free energy gap (optical transition energy) of the DBA molecule in the solvent; \( \Delta F^e = F^e_D - F^e_A \).

The use of the “vertical” basis set is not very common in the theory of NA ET. A more traditional formulation is based on the basis \( \Psi_i^{(0)} \) defined at equilibrium nuclear configurations of D and A (Fig. 2). The change of the basis breaks the MH connection between the ET matrix element and spectroscopic observables. The derivation of Eqs. (11) and (12) can be repeated with the dipole matrix elements now evaluated on the basis \( \Psi_i^{(0)} \) and the ET matrix element \( H_{\text{ET}} \) changing to

\[
H_{\text{ET}}^{(0)} = \frac{(m_{12}^{(0)})}{(m_{\text{da}}^{(0)})} \frac{\Delta E_{12}^{(0)}}{(M_{ij})},
\]

(16)

where

\[
\Delta E_{12}^{(0)} = \left[ (\varepsilon^{(0)})^2 + 4|H_{\text{da}}^{(0)}|^2 \right]^{1/2}.
\]

(17)

The vacuum gaps \( \varepsilon \) and \( \varepsilon^{(0)} \) are related through the vibrational reorganization energy: \( \varepsilon = \varepsilon^{(0)} + \lambda_p \). The adiabatic transition dipole \( m_{12}^{(0)} \) couples equilibrium nuclear configurations (Fig. 2) and is not any more related to the vertical transition intensity. The implication of this result to the analysis of experimental data is that there is generally no reason to equate \( \Delta \mathbf{m}_{\text{da}} / \varepsilon \) to the distance between the centers of equilibrium electron localization, \( \varepsilon = r_{\text{da}} \), in particular in systems with large intramolecular reorganization energy. For self-exchange ET, \( 2m_{12}^{(0)} = \Delta m_{\text{da}}^{(0)} \) and Eq. (16) reduces to \( H_{\text{ET}} = H_{\text{ET}}^{(0)} \).

The non-Condon pre-exponential factor \( A \) in the NA rate constant points to some interesting implications absent in the Condon approximation. First, the MH connection between \( H_{\text{ET}} \) and the adiabatic transition dipole [Eq. (2)] turns out to be exact provided the longitudinal projection of \( \mathbf{m}_{12} \) on the direction of \( \Delta \mathbf{m}_{\text{da}} \) is taken. We stress that \( H_{\text{ET}} \) refers to the “longitudinal” electronic DA coupling in the activated state of the DBA molecule with degenerate D and A energies, whereas \( m_{12}^{(0)} \) is defined on the vacuum states at the equilibrium geometry of the DBA molecule in its initial electronic state. The electronic solvation term in Eq. (7) cancels with the equal contribution from \( \Delta F^e \) in the vertical gap \( \Delta F_A \) [Eq. (15)], and only the vacuum diabatic energy gap \( \varepsilon \) enters \( m_{12} \) as given by Eq. (3). Second, the coupling of the transverse transition dipole \( m_{\text{da}}^{(0)} \) (Fig. 3) to the solvent polarization fluctuations leads to a temperature dependence of \( A \), which becomes \( A \propto k_B T \) at \( H_{\text{ET}} = 0 \).

Equation (12) indicates that \( m_{\text{da}}^{(0)} = 0 \) is necessary to reduce Eqs. (11) and (12) to the standard form

\[
k_{\text{act}} = \frac{|H_{\text{ET}}|^2}{\hbar} \left( \frac{\pi \beta}{\lambda_p} \right)^{1/2} e^{-\beta m_{\text{da}}^{(0)}},
\]

(18)

The condition \( m_{\text{da}}^{(0)} = 0 \), employed in the GMH theory, is not necessary for deriving the MH relation as the latter is valid for any value of \( m_{\text{da}}^{(0)} \) within the non-Condon treatment of the NA reaction rate. However, the GMH choice of the diabatic basis is valuable in many respects. First, the off-diagonal matrix element of the Hamiltonian \( H_{\text{da}} \), instead of a more general construction

\[
H_{\text{ET}} = (m_{\text{da}}^{(0)} / m_{\text{da}}^{(0)}) (H_{\text{da}}) \varepsilon - H_{\text{da}},
\]

(19)

comes directly to the rate constant pre-exponent. Second, the GMH basis eliminates the solvent dependence of the electronic coupling. The solvent effect is most transparent for charge-separation (CS) reactions with \( m_{\text{da}}^{(0)} = 0 \): the electronic coupling is \( H_{\text{da}} = 2a_p (m_{\text{da}}^{(0)} - \mathbf{m}) \) at the equilibrium solvent configuration, becoming equal to \( H_{\text{ET}} \) [Eq. (19)] in the activated state with \( E_A = E_A^{(0)} \). The solvent dependence is eliminated at \( m_{\text{da}} = 0 \) and \( H_{\text{da}} \) replaces \( H_{\text{ET}} \) in Eq. (18). Note, however, that nullifying the two components of a vector cannot generally be achieved by a single unitary transformation of a two-state adiabatic basis. Real calculations must involve some sort of a trade-off minimizing each component of \( m_{\text{da}}^{(0)} \) unless one of them is identically zero by symmetry requirements.

The transverse component of the direct DA transition moment is identically zero for linear DA molecules due to molecular symmetry. The additional requirement \( m_{\text{da}}^{(0)} = 0 \) then generates the GMH diabatic basis set. A multisite generalization of this procedure to DBA molecules with a manifold of B states requires the diagonalization of the longitudinal adiabatic matrix \( \mathbf{M}^l \) \( [M_{ij}^{l} = m_{ij}^{l}] \) in the diabatic representation. Bending the DBA molecule (Fig. 1) lowers its symmetry leading to a generally nonzero transverse, adiabatic matrix \( \mathbf{M}^t \) \( [M_{ij}^{t} = m_{ij}^{t}] \). The two matrices, \( \mathbf{M}^l \) and \( \mathbf{M}^t \), do not diagonalize by a single unitary transformation of the adiabatic basis set. The desire to preserve the standard form for the NA reaction rate [Eq. (18)] then suggests to choose a diabatic basis set diagonalizing the transverse matrix \( \mathbf{M}^t \). This is the diabatic basis we adopt for the discussion of the three-level, nonlinear DBA complex in the next section. We will also neglect the transverse component of the diabatic dipole in the D state, \( m_{ij}^{d} = 0 \), which leads to \( m_{\text{da}}^{(0)} = 0 \) according to the definition of the longitudinal direction.

**III. THREE-STATE DONOR–BRIDGE–ACCEPTOR COMPLEX**

In this section, we consider a three-level DBA molecule with no direct DA electronic coupling (\( H_{\text{da}} = 0 \)). The superexchange mechanism assumes that any mixing to intermediate states that splits adiabatic energies of terminate groups can be assigned to an effective electronic coupling between
them. From this viewpoint, the MH formulation in terms of adiabatic transition dipoles is a convenient starting point to include mixing of D and A to B states. A nonzero $m_{12}$ in a multilevel description then signals about the presence of superexchange coupling and the effective matrix element can be evaluated from matrix algebra on the manifold of intermediate states. We first proceed from this standpoint and present a direct evaluation of the NA rate constant in the next section.

In order to reduce the number of independent parameters, we confine ourselves to a CS reaction starting from a nonpolar state with $m_d=0$ and ending up in a final state with $m_a=\Delta m_{da} \neq 0$. The diabatic dipole matrix has the longitudinal, $m^\parallel$, and transverse, $m^\perp$, components,

$$m^\parallel = \begin{pmatrix} 0 & p_d \gamma & 0 \\ p_d \gamma & m_b & p_a \gamma \\ 0 & p_a \gamma & m_a \end{pmatrix},$$

$$m^\perp = \begin{pmatrix} 0 & 0 & 0 \\ 0 & m_b & 0 \\ 0 & 0 & 0 \end{pmatrix},$$

where $m_b = \langle \Psi_b \mid m \Psi_b \rangle$, $p_d = \langle \Psi_d \mid m \Psi_b \rangle$, and $p_a = \langle \Psi_b \mid m \Psi_a \rangle$. The vacuum Hamiltonian matrix in the diabatic basis $\{ \Psi_i \}$ is

$$H_0 = \begin{pmatrix} 0 & \beta_d & 0 \\ \beta_d & \varepsilon_b & \beta_a \\ 0 & \beta_a & \varepsilon \end{pmatrix},$$

where $\beta_d = \langle \Psi_d \mid H_0 \mid \Psi_b \rangle$, $\beta_a = \langle \Psi_b \mid H_0 \mid \Psi_a \rangle$ and the off-diagonal matrix elements are assumed real.

The calculation of the MH matrix element requires the longitudinal adiabatic transition dipole $m_{12}$ to be taken on the states diagonalizing the Hamiltonian matrix $H_0$,

$$\langle \Psi_i \rangle = A_i^{-1/2} \left[ \frac{\beta_d}{\lambda_i} \langle \Psi_d \rangle + \langle \Psi_b \rangle - \frac{\beta_a}{\varepsilon - \lambda_i} \langle \Psi_a \rangle \right],$$

where

$$A_i = \left( 1 + \frac{\beta_d^2}{\lambda_i} + \frac{\beta_a^2}{(\varepsilon - \lambda_i)^2} \right)^{1/2}.$$

In Eqs. (22) and (23), $\lambda_i$, $i=1,2,3$ refer to the eigenvalues of the matrix $H_0$. The MH matrix element then becomes

$$|H_{ET}| = \frac{m_{12}^\parallel}{\Delta m_{da}} |\lambda_2 - \lambda_1|,$$

where $\lambda_1$ and $\lambda_2$ refer to the adiabatic energies obtained from the diabatic D and A states by mixing them with the B state.

In the weak perturbation limit, when DB and BA coupling constants are small compared to corresponding energy gaps

$$|\beta_d / \varepsilon_b| \ll 1, \quad |\beta_a / (\varepsilon_b - \varepsilon)| \ll 1,$$

the second-order Rayleigh–Schro¨dinger perturbation theory (RSPT) yields

$$m_{12} = \frac{\beta_d}{\varepsilon_b} p_a + \frac{\beta_a}{(\varepsilon_b - \varepsilon)} m_b - \frac{\beta_d}{\varepsilon_b} p_d,$$

and

$$|\lambda_2 - \lambda_1| = |\varepsilon|.$$

At $p_d = p_a = 0$, Eqs. (24), (26), and (27) reduce to the relation given by Newton

$$H_{ET} = \frac{\beta_d p_a}{\varepsilon_{eff}},$$

where

$$\frac{1}{\varepsilon_{eff}} = \frac{m_{12}^\|}{\Delta m_{da}(\varepsilon_b - \varepsilon)} + \frac{m_b - m_a}{\Delta m_{da} \varepsilon_b}.$$
in the effective DA coupling [Eq. (7)] with the equal component in the vertical DA energy gap [Eq. (15)]. In the next section, we show that this cancellation does not occur for superexchange coupling in a three-state molecule. (2) It remains to be proved that the golden rule rate constant in the multisite formulation leads to the MH relation between the ET matrix element and the transition dipole m_{12}. The derivation presented in the next section in fact shows that the MH relation does not extend to the three-level system, although some qualitative features of the analysis given here are paralleled by the golden rule solution of the three-state model.

IV. NONADIABATIC RATE CONSTANT FOR SUPEREXCHANGE ET

The three-state formulation of the NA reaction rate starts with the 3 × 3 matrix of instantaneous energies E_{ab} incorporating the effect of equilibrium solvation by the solvent electronic subsystem,

\[ \mathbf{E} = \begin{pmatrix} E_d & E_{db} & 0 \\ E_{db} & E_b & E_{ba} \\ 0 & E_{ba} & E_a \end{pmatrix}. \] (30)

The energies E_d and E_a in Eq. (30) are given by Eq. (6) and the other components are written similarly as

\[ E_{db}(R^1, R^2) = \beta_d - a_d(p_d \cdot m_b) - p_d \cdot \mathbf{R}_p, \]
\[ E_{ba}(R^1, R^2) = \beta_a - a_e(m_b + m_a) - p_a \cdot \mathbf{R}_p, \]
\[ E_a(R^1, R^2) = \epsilon_a - a_m m_b^2 - m_b \cdot \mathbf{R}_p. \] (31)

The diagonal and off-diagonal energies are functions of the longitudinal, R^l = \mathbf{R}_p, \mathbf{u}^l, and transverse, R^t = \mathbf{R}_p, \mathbf{u}^t, projections of the reaction field.\(^{57,59,65,66}\) This approach gives the effective D and A energies

\[ \bar{E}_d = E_d + \frac{E_{db}^2}{\lambda - E_b}, \]
\[ \bar{E}_a = E_a + \frac{E_{ba}^2}{\lambda - E_b}, \] (32)

where \( \lambda \) is an eigenvalue of the matrix E. The off-diagonal matrix element of the 2 × 2 matrix is

\[ \bar{E}_{da} = \frac{E_{db}E_{ba}}{\lambda - E_b}. \] (33)

Based on the effective two-state description, the golden rule rate constant is

\[ k_a^{\text{NA}} = \frac{2\pi}{\hbar} \langle |\bar{E}_{da}|^2 \delta(\bar{E}_a - \bar{E}_d) \rangle_a. \] (34)

The calculation of the exact analytical average in Eq. (34) encounters significant technical difficulties, although the rate constant can be calculated numerically. In order to address questions (1) and (2) posed above, we obtain here a solution for \( k_a^{\text{NA}} \) in the weak perturbation limit of Eq. (25). The resonance between the energies \( \bar{E}_d \) and \( \bar{E}_a \) can then be replaced by the resonance between \( E_d \) and \( E_a \), which is achieved at the resonant longitudinal field

\[ R_0^l = (\epsilon + \Delta E^c)/\Delta m_{da}. \] (35)

After substituting the longitudinal reaction field, the ensemble average reduces to a one-dimensional integral over the transverse field \( R^t = \mathbf{R}_p \cdot \mathbf{u}^t \). For the diabatic dipole matrix given by Eq. (20), only the transverse component of the B dipole moment, \( m_b^t \), couples to the transverse reaction field. For linear molecules, \( m_b^t = 0 \) and one gets

\[ H_{\text{ET}} = \langle E_{da} | R_0^t, R^t = 0 \rangle. \] (36)

The second order RSPT in the smallness parameters of ratios of DB and BA couplings to corresponding energy gaps [Eq. (25)] transforms Eq. (36) into Eq. (37).

\[ H_{\text{ET}} = \frac{1}{\epsilon_b} \left[ \beta_d \beta_a e^{-p_a^t p_d^t} m_a \right] m_a \] (37)

where

\[ e' = \epsilon + a_m m_b, \]
\[ e'' = \epsilon - a_m m_a - m_b, \]
\[ \tilde{e}_b = \epsilon - (m_b^t/m_a) e''. \] (38)

Equation (37) has two important implications. First, when the diabatic basis of a linear molecule is chosen to ensure zero diabatic transition dipoles, \( p_d^t = p_a^t = 0 \), Eq. (37) reduces to McConnell’s result for the B energy shifted from its vacuum value \( \epsilon_b \) by the electronic reaction field to \( e_b = \epsilon - a_m m_b^t \) and by the combined effect of the electronic and nuclear reaction fields to \( \tilde{e}_b \) (Fig. 5). The ET matrix element in the resonance is \( H_{\text{ET}} = \beta_d \beta_a \tilde{e}_b \). Second, when \( p_d^t \neq 0 \) and/or \( p_a^t \neq 0 \), Eq. (37) does not coincide with the ET matrix element obtained from the MH formula [Eqs. (24) and (26)]. For instance, at \( e = 0 \) the MH relation gives \( H_{\text{ET}} = \beta_d \beta_a e_b \) at any values of \( p_d^t \) and \( p_a^t \). The observation that the ET matrix elements obtained from the MH formula and from the golden rule solution do not coincide in the weak-perturbation limit allows us to conclude that the two-state MH formula cannot be carried over to the case of superexchange coupling.

For bent geometries of the DBA complex, \( m_b^t \neq 0 \) and the NA rate constant is given by the integral over the transverse reaction field

\[ k_a^{\text{NA}} = \frac{\beta}{2 \hbar a_p^{1/2}} \left( \frac{\pi \beta^2}{\lambda_p^2} \right)^{1/2} e^{-\beta R^t_{\text{act}}} \int_0^\infty dR^l | \bar{E}_{da}(R_0^l, R^t)|^2 e^{-\beta (R^t_{\text{act}})^2 / 4 a_p}. \] (39)

The integral can be evaluated in the limit \( 4k_BT \hbar (m_b^t)^2 / \epsilon_b^2 \ll 1 \), when it gives the standard NA rate constant [Eq. (18)] with
The effective ET matrix element for superexchange DBA is given by the relation

\[ |H_{ET}| = \frac{|E_{db}(1)E_{ba}(1)|}{e_b^{(1)}}. \]  

(40)

Here, the effective gap to the bridge state is

\[ e_b^{(1)} = e_b^{1/2} \left( e_b^{1/2} - 2(m_b/m_a)^{1/2} \sqrt{\pi k_B T \alpha_p} \right) \]  

(41)

and the DB and BA electronic coupling constants are

\[ E_{db}^{(1)} = E_{db}(R_{01}^1,0) = \beta_d - (p_d^1/m_a)e^\sigma, \]  

\[ E_{ba}^{(1)} = E_{ba}(R_{01}^1,0) = \beta_a - (p_a^1/m_a)e^\tau. \]  

(42)

The B energy \( e_b \) for a V-shaped DBA complex is

\[ e_b = e_b^{1/2} - (m_b/m_a)e^\sigma + (m_a m_b^2/m^3_a - m_b^2). \]  

(43)

The superscript “1” in Eqs. (40)–(42) refers to a single bridge state characteristic of the three-state model (see below).

Equation (40) is the principal result of this study. It gives the effective ET matrix element for superexchange DBA coupling. Some qualitative trends in the \( H_{ET} \) given by Eq. (40) are paralleled by the extended MH formalism presented in Sec. III. Most significantly, \( H_{ET} \) in Eq. (40) has two zeros (Fig. 6) similarly to the ET matrix element generated from the MH equations (24), (26), and (27) (Fig. 4). In Fig. 6, \( |H_{ET}| \) is plotted against \( e \) at various orientations of the B dipole. The zeros of \( H_{ET} \) are obtained when either \( E_{db}^{(1)} = 0 \) or \( E_{ba}^{(1)} = 0 \). The latter two conditions are satisfied at two values of the vertical energy gap

\[ \varepsilon_1 = \frac{\beta_d(m_a/p_d^1) - a_e m_b^2}{m_a}, \]  

\[ \varepsilon_2 = \frac{\beta_d(m_a/p_d^1) + a_e m_b(m_a - m_b^2)}{m_a}. \]  

(44)

The off-diagonal matrix elements \( \beta_{d,a} \) and \( p_{d,a}^1 \) enter Eq. (44) as ratios, which insures the invariance of the energies \( \varepsilon_{1,2} \) in respect to the sign switch of a basis wave function. The latter condition should certainly be fulfilled for any observable quantity. On the other hand, the signs of ratios \( \beta_d/p_d^1 \) and \( \beta_a/p_a^1 \) depend on phases of the basis wave functions and may be either positive or negative. The coupling constants \( \beta_{d,a} \) are commonly taken negative in Hückel-type models. The signs of \( p_{d,a}^1 \) depend on system-specific orientations of transition dipoles relative to the direction of ET. These considerations, and the magnitude of the response function \( a_e \), reflecting solvation by the solvent electronic subsystem, will ultimately determine the magnitudes of \( \varepsilon_{1,2} \).

Apart from nonzero diabatic transition dipoles \( p_{d,a}^1 \), bent geometry of the DBA molecule brings about a dependence of \( H_{ET} \) on temperature. The explicit dependence of the effective B energy on \( T \) in Eq. (40) arises from the coupling of the transverse component of the B dipole to the fluctuations of the transverse reaction field. This explicit temperature dependence yields \( d|H_{ET}|/dT \) versus \( e \) (Fig. 6) essentially replicating \( |H_{ET}| \) versus \( e \) (Fig. 6). The explicit dependence on \( T \) in \( e^{(1)} \) is not the only source of the overall temperature variation of \( |H_{ET}| \). The response coefficient \( a_e \) includes the solvent refractive index \( n(T) \) which depends on \( T \) through the solvent thermal expansivity. In the Onsager spherical–cavity model of dipole solvation, \( a_e \) is given by the relation

\[ a_e = \frac{1}{R_{eff}^3} \frac{n^2(T) - 1}{2n^2(T) + 1}, \]  

(45)

where \( R_{eff} \) is an effective radius of the DBA molecule. The temperature variation of the refractive index is the main source of the temperature variation of \( |H_{ET}| \), qualitatively altering the form of the \( d|H_{ET}|/dT \) versus \( e \) function. The derivative \( d|H_{ET}|/dT \) is positive for all values of \( e \) and is about an order of magnitude higher than the value obtained with the explicit temperature dependence only. However, because \( H_{ET} \) changes sign at \( \varepsilon_1 \) and \( \varepsilon_2 \), the derivative \( d|H_{ET}|/dT \) becomes discontinuous at these points switching.
from positive values for $\varepsilon$ outside the interval between zero points to negative values inside the interval (Fig. 7).

For parameter values considered here, the signs of the zero points $\varepsilon_1$ and $\varepsilon_2$ are determined by the signs of the ratios $\beta_a/p_a$ and $\beta_d/p_d$, respectively. One of the observable consequences of this is that the sign of the temperature derivative $dH_{ET}/dT$ may be strongly system specific. Figure 7 shows $dH_{ET}/dT$ for negative $\beta_d/p_d$ and $\beta_d/p_d$ and Fig. 8 shows $dH_{ET}/dT$ for positive ratios. In case of opposite signs of $\beta_d/p_d$ and $\beta_d/p_d$, negative temperature derivatives cover a broad range between negative and positive zero points of the electronic coupling. The sign switch of the temperature derivative of the ET matrix element allows one to measure the sign of the $\beta_d/a/p_d/a$ ratios from experiment. This sensitivity of observable quantities to the sign of the off-diagonal matrix elements of the Hamiltonian bears a close analogy to the dependence of the spectral shift of dimers of excitons to the sign of the interaction energy of their transition dipoles ($J$-aggregates versus $H$ aggregates).68,69

The ET matrix element in Eq. (40) is a perturbation result obtained by truncating the perturbation expansion after the second-order terms in off-diagonal matrix elements. This implies $\lambda=0$ in Eqs. (32) and (33). The latter, under the condition of degeneracy between $E_d$ and $E_a$, is given as

$$\lambda = E_p/2 - \sqrt{E_p^2/4 + E_{db}^2 + E_{ba}^2}. \quad (46)$$

The perturbation solution of Eq. (40) suggests a nonperturbative generalization

$$\left| H_{ET} \right| = \frac{2 |E_{db}(1) E_{ba}(1)|}{E_b(1) + \sqrt{(E_b(1))^2 + 4(E_{db}(1))^2 + 4(E_{ba}(1))^2}}. \quad (47)$$

Another generalization of the perturbation solution for the three-level system is to the McConnell model of $n$ B sites with equal energies $E_b$ coupled by off-diagonal matrix elements $\beta_b$.20 Off-diagonal coupling is assumed here to be independent of the solvent configuration. The application of the Lippman–Schwinger equation9 in the golden rule formalism then leads to the following ET matrix element

$$\left| H_{ET}^{(n)} \right| = \frac{|E_{db}(1)^n E_{ba}(1)^n|}{E_b(n) - \beta_b}, \quad (48)$$

where

$$E_b(n) = E_b - \left( \frac{n m_b}{m_a} \right) \sqrt{\pi k_B T \lambda_p} / \varepsilon_b. \quad (49)$$

Equations (48) and (49) are derived for the case when $n$ is not too high so that $2n(m_b/m_a) \sqrt{\pi k_B T \lambda_p} / E_b \ll 1$. The matrix element $H_{ET}^{(n)}$ retains two zeros in its dependence on the vertical energy gap $\varepsilon$ and a positive temperature slope $dH_{ET}^{(n)}/dT>0$ with the switch in the sign of $d|H_{ET}^{(n)}/dT$ between the zeros. The temperature derivative scales as $\propto n$ with the number of B units. From Eq. (48), the distance decay parameter of $H_{ET}^{(n)}$ [cf. to Eq. (4)] also gains a temperature dependence

$$\beta_{DA} = \beta_0 - \frac{n m_b}{2 m_a} \frac{\sqrt{\pi k_B T \lambda_p}}{\varepsilon_b^2}. \quad (50)$$

where $\beta_0 = \ln(\varepsilon_b/\beta_b)/a$ and $a$ is the size of a single B unit. The parameter $\beta_{DA}$ also decays with increasing solvent reorganization energy and its overall dependence on the solvent.
and temperature can be recast as a linear trend with the classical inhomogeneous width $\sigma(T)$ of the optical CS transition

$$\beta_{DA} = \beta_0 - \text{const} \times \sigma(T)/\bar{E}_b.$$  \hfill (51)

**V. RESULTS AND DISCUSSION**

The present formalism is based on the Marcus picture\(^1\) of ET activation: a linear electrostatic coupling of the transferred electron to the macroscopic solvent polarization driving D and A energy levels into the resonance. The standard model on NA transitions is modified by including the coupling of the solute transition dipole to the solvent polarization field in the off-diagonal system Hamiltonian:

$$H_{da} = m_{da} \cdot \mathbf{R}.$$  \hfill (52)

The polarization reaction filed $\mathbf{R}$ is very strong in the activated state where the ET matrix element is calculated: $\approx 10^5$ V/cm at the typical values of $\Delta F_a \approx 2$ eV and $m_a \approx 10$ D. The shift of the ET coupling then amounts to 160 cm$^{-1}$ at $m_{da} \approx 0.1$ D. The solvent polarization is the major driving mode of ET in its normal region for medium-size DBA molecules dissolved in polar solvents.\(^1\) Quantum skeletal vibrations become important in the inverted region. The present formulation can be generalized to this situation within well-developed formalisms of treating the vibronic effects.\(^2,3\) For large molecules of the size of bioproteins the polarization solvent field is less significant, and polarization and conformational flexibility of the protein matrix gain importance. The present model can be extended to such situations provided the couplings and force constants of Gaussian nuclear modulations are available. There is currently no generally accepted procedure of calculating these parameters, and our formulation is limited to systems where solvent polarization is the main classical nuclear mode coupled to ET.

The rate of NA ET is calculated as a first-order perturbation in the off-diagonal Hamiltonian given by Eq. (52). ET tunneling at the resonance of D and A diabatic states fixes the longitudinal polarization field $R_0$ [Eq. (35)]. With the account for equilibrium solvation by the solvent electronic subsystem the resonant coupling becomes

$$H_{da} = -e \frac{m_{da}^1}{\Delta m_{da}} - m_{da}^\dagger [e(m_d^1 + m_a^1) + R^\dagger].$$  \hfill (53)

The off-diagonal matrix element given by Eq. (53) generally contains three off-diagonal components: $H_{da}$ and two projections of $m_{da}^1$: $m_{da}^\dagger$ and $m_{da}$. A special choice of the basis set can eliminate some of these matrix elements. The GMH approach\(^16\) simplifies the above expression in a basis giving $m_{da}^1 = 0$. For linear molecules, the symmetry requires $m_{da}^\dagger = 0$ and the GMH basis leads to $H_{da}$ for the off-diagonal DA coupling. Lowering the symmetry in the case of nonlinear molecules leaves $m_{da}$ generally nonzero (Fig. 3). The rate constant preexponent then attains a temperature-dependent component arising from the coupling of $m_{da}^\dagger$ to the stochastic transverse solvent field $R^\dagger$ [Eq. (12)].

An alternative approach, going back to the static coupling theory of radiationless transitions,\(^70-72\) adopts the crude adiabatic\(^75\) vacuum basis in which $H_{da} = 0.5474$. The matrix element $m_{da} = m_{12}$ is then well defined as the “vertical” transition dipole in the vacuum, an experimentally measurable quantity. The effective ET coupling entering the rate constant is then fully defined in terms of experimentally accessible parameters as

$$H_{ET} = \frac{m_{12}^2}{\Delta m_{12}} h\nu_{max}.$$  \hfill (54)

where $h\nu_{max}$ is the frequency of absorption transition in vacuum; $h\nu_{max} = \lambda_v$ for self-exchange transitions. In this definition, the non-Condon modulation of the off-diagonal Hamiltonian matrix element [second term in Eq. (52)] causes ET transitions. When $m_{12}$ is large this effect leads to an observable difference in the widths of absorption and emission lines.\(^74\) Note that $m_{12}^2 \Delta E_{12} = M_{12}^2 h\nu_{max}$ in the two-state description, where $M_{12}$ and $h\nu_{max}$ are the adiabatic transition dipole and transition energy in the solvent. This relation allows one to use Eq. (54) with spectral parameters measured in solution.

The superexchange coupling of the McConnell model depends on the tunneling energy at the DA resonance through the DB energy gap. The coupling is strongly modulated by the nuclear subsystem (non-Condon effect) when the DB gap does not exceed the inhomogeneous width, $\sigma(T) = \sqrt{2k_B T\Lambda_T}$, of the DA gap fluctuations.\(^30,31,50\) The resonance energy may fluctuate due to conformational flexibility of the DBA molecule and, indeed, substantial thermal modulation of the superexchange coupling is observed in MD simulations of proteins,\(^28,29,31\) and DNAs.\(^26\) The coupling may pass through zero changing its sign along a nuclear coordinate as a result of destructive interference of tunneling pathways.\(^28,29,34\)

The present model adds to the traditional mechanism of non-Condon modulation the notion that coupling of the DB and BA transition dipoles to the polarization field modulates the corresponding matrix elements. This modulation is relatively independent of the DB gap and thus should be active both in the region when non-Condon effects are traditionally considered \[ e_b < \sigma(T) \] and in the region of large DB gaps when these effects are commonly neglected. In our derivation, the superexchange matrix element is included into the golden rule rate with the result represented in the form of an effective ET coupling [Eq. (40)]. The linear shift of the DA and BA matrix elements by the resonance longitudinal field $R_0$ leads to two zeros of the effective matrix element as a function of the DA vacuum energy gap $\varepsilon$ (or as a function of the ET driving force).

The superexchange state $D^+B^-A$ possesses a substantial dipole moment $m_1$. Its magnitude is approximately half of the charge-separated dipole if a bridge is placed half-way between D and A. If the DBA molecule has a bent geometry, $m_1$ has both longitudinal and transverse components (Fig. 1). The longitudinal component $m_1^0$ couples to the longitudinal resonance field $R_0$, shifting the bridge energy from the vacuum energy $\varepsilon_b$, to the resonance energy $\tilde{\varepsilon}_b$ [Fig. 5, Eq. (43)]. With a positive $m_1^0$, the second term in Eq. (43) lowers the effective bridge energy for reactions with $\varepsilon > 0$ and increases the bridge energy for reactions with $\varepsilon < 0$. ET systems should therefore demonstrate a hysteresis of $|H_{ET}|$ and
For a linear DBA molecule with p a Creutz superexchange in ruthenium binuclear complexes listed by these two approaches in application to electron metal–metal « effective B energy: m b energies, eV. 

change model, 20 the coupling of the bridge to the solvent regression line is about 1.7 indicating that Eqs. derived from the three-level extension of the MH model, coupling becomes can often be measured separately. 14,75,76 In this case, the B Figure 9 compares H ET and from Eq. (56) (x axis) for 9 DBA mixed-valence cation radicals studied by Rosokha et al. (Ref. 76) The dashed line is a linear regression with the slope 1.7.

\[ \beta_{DA} \] between CS and charge-recombination (CR) reactions. There is also a possibility of switch between electron and hole superexchange depending on the direction of the transition. 44 The shift due to electronic solvation [the last term in Eq. (43)] increases the bridge energy. This component is less significant than the second term: with the Onsager response function [Eq. (45)] and \( R_{eff} = 6 \text{ Å} \), \( m_a = 30 \text{ D} \), \( m_b = 13 \text{ D} \) and \( m_b = 7.5 \text{ D} \) (\( \theta = \pi/6 \)) one gets a shift of 0.2 eV.

In mixed-valence complexes, the optical DA transition energies, \( \Delta F_d \), and DB energies, \( \Delta F_{db} = e_b - a m_b \) (Fig. 5), can often be measured separately. 14,75,76 In this case, the B energy \( e_b \) is directly related to the optical transition energies:

\[ \bar{e}_b = \Delta F_{db} - (m_b/a) \Delta F_d. \]  

(55)

For a linear DBA molecule with \( p^b = p^d = m_b = 0 \) the ET coupling becomes

\[ H_{ET} = \frac{\beta_d \beta_a}{\Delta F_{db} - (m_b/a) \Delta F_d}. \]  

(56)

Figure 9 compares \( H_{ET} \) calculated according to Eqs. (28)–(29) and from (56) with \( m_b/a = 0.5 \) from the data on the hole superexchange in a series of organic mixed-valence cation radicals reported by Rosokha et al. 76 The slope of the regression line is about 1.7 indicating that Eqs. (28)–(29), derived from the three-level extension of the MH model, tend to give higher estimate for \( H_{ET} \) compared to Eq. (56). The same qualitative result follows from the comparison of these two approaches in application to electron metal–metal superexchange in ruthenium binuclear complexes listed by Creutz et al.14 Experiment, however, does not provide sufficient accuracy to distinguish between these two routes to \( H_{ET} \).

The transverse component of the reaction field does not affect the DA energy gap. It couples, however, to the transverse B dipole \( m_b \) producing an additional change in the effective B energy: \( e_b^{(1)} \) in Eq. (41) is shifted down by the width of the thermal fluctuations of B energy amounting approximately \( m_b^2/m_a \) fraction of the classical fluctuation width of the DA energy gap \( \sigma(T) \). Within the McConnell superexchange model, 20 the coupling of the bridge to the solvent fluctuations is projected into the distance decay parameter \( \beta_{DA} \) decreasing linearly with \( \sigma(T) \). Eqs. (50) and (51). Both \( H_{ET} \) and \( \beta_{DA} \) thus depend on solvent in the non-Condon picture.

The present calculations show that the temperature variation of the electronic response function in molecular liquid solvents is by far more significant for the overall temperature dependence of the electronic coupling than fluctuations of the bridge level. The temperature derivative \( d[H_{ET}]/dT \) switches its sign at zero points of \( H_{ET} \). A switch in sign of \( d[H_{ET}]/dT \) due to changing the solvent has been recently reported by Zimm et al. 25 In terms of the present model, this effect may be explained by the shift of one of zero points due to a change in the geometry of the DBA complex or/a change in the electronic response function.

Molecular complexes synthesized to convert the energy of light into chemical potential energy often mimic the basic design of natural photosynthetic centers. 77,78 D, or a complex of D and a light harvesting antenna, is photoexcited by visible light. The photoexcitation is quenched by destructive depopulation pathways and by constructive CS to A. In order for the constructive pathway to compete with destructive pathways, an efficient DA electronic coupling through a B unit is necessary. The redox potential of A can be tuned to ensure essentially activationless CS. However, if the electronic coupling between the excited D and A is close to that between the ground state D and A, the backward CR reaction may significantly lower the efficiency of the light energy conversion. 78 The present model suggests possible approaches to an efficient design of artificial photosynthetic systems. It predicts a substantial dependence of the electronic coupling on the vertical energy gap with two closely lying zeros in the region of negative vertical gaps (Fig. 5, \( \beta_a/p_a < 0, \beta_a/p_a < 0 \)). This region actually corresponds to the common deactivation pathway from the charge-separated state to the ground state D. If the excitation wavelength and the redox potential of A are tuned to ensure that the vertical energy gap of the backward reaction falls in the region of zeros of the electronic coupling, the efficiency of light energy conversion can be substantially enhanced. A similar set of ideas may be used to explain the extremely high efficiency of CS in the natural photosynthetic system. 79

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