

# Reorganization Parameters of Electronic Transitions in Electronically Delocalized Systems.

## 1. Charge Transfer Reactions

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This paper addresses the problem of calculating the free energy surfaces of charge transfer (CT) reactions in electronically delocalized systems involving direct electronic overlap of the donor and acceptor units. The model includes two electronic states of the solute linearly coupled to a linearly responding solvent in both the diagonal and off-diagonal terms of the Hamiltonian matrix. The exact solution for the adiabatic free energy surfaces along the CT reaction coordinate is derived as a function of the reorganization parameters invariant to the extent of electron delocalization and the parameter of electron delocalization. For dipolar solutes, the latter is defined through adiabatic differential and transition dipoles measured by optical spectroscopy. The invariant reorganization energy is the real, observable reorganization energy determining the vertical transition energy, bandwidth, and the activation energy of self-exchange transitions. The Golden Rule expression for the ET rate constant is obtained in the adiabatic electronic basis of the solute by treating the non-Condon off-diagonal coupling to the solvent as a perturbation. The ET matrix element entering the rate constant is fully determined in terms of the adiabatic vacuum splitting of the electronic levels and the delocalization parameter. The CT energy gap law is very asymmetric with a shallow branch in the inverted region due to the dependence of the delocalization parameter on the CT driving force.

### 1. Introduction

Localization is a central concept in understanding and describing electron transfer (ET) reactions. The very definition of ET assumes the existence of two or more localized states separated by a potential barrier. Occupation of empty states occurs as underbarrier tunneling when the localized state energies equalize by absorption of energy from a thermal bath or radiation. The electron density can never be fully transferred unless the donor and acceptor electronic states do not overlap after the reaction. A direct electronic overlap of the donor and acceptor moieties should thus result in a partial charge transfer (CT) characteristic of electronic transitions in coupled donor/acceptor pairs (intramolecular transitions).<sup>1</sup>

The importance of partial CT was recognized already in the classical Marcus–Hush theory.<sup>2,3</sup> It was suggested that delocalization of the electron between the donor and acceptor states affects the solute field acting on the solvent,<sup>4–6</sup> so that the solvent reorganization energy of a delocalized CT complex,  $\lambda_s^{\text{ad}}$ , scales quadratically with the amount of charge  $\Delta z$  actually transferred

$$\lambda_s^{\text{ad}} = (\Delta z)^2 \lambda_s^{\text{d}} \quad (1)$$

Here,  $\lambda_s^{\text{d}}$  is the reorganization energy of any diabatic (super-script “d”) solute configuration assuming complete localization of the transferred electron. A delocalized solute configuration involving redistribution of the charge density between the donor and acceptor is referred to as the adiabatic configuration (superscript “ad”). Throughout this paper, the electronic basis diagonalizing the solute vacuum Hamiltonian is set as the adiabatic representation.

Hush defined electronic delocalization through the CT band intensity<sup>3a</sup> so that the Marcus–Hush delocalization parameter  $\Delta z$  can be assessed via the relation<sup>3–5</sup>

$$\Delta z^2 = 1 - 4\alpha^2, \quad \alpha = H_{\text{ab}}/h\nu_{\text{max}} \quad (2)$$

where  $H_{\text{ab}}$  is the off-diagonal matrix element of the diabatic Hamiltonian matrix (ET matrix element) and  $\nu_{\text{max}}$  stands for the frequency of the intervalence transition. Spectroscopic techniques characterize intensity of the donor–acceptor overlap in terms of the transition dipole of the optical transition. The delocalization parameter then becomes<sup>7–9c</sup>

$$\Delta z = \left[ 1 + \frac{4(m_{12}^{\text{max}})^2}{(\Delta m_{12}^{\text{max}})^2} \right]^{-1/2} \quad (3)$$

Here  $m_{12}^{\text{max}}$  is the adiabatic transition dipole and  $\Delta m_{12}^{\text{max}}$  is the adiabatic ground-excited state dipole-moment difference (differential dipole). Both parameters refer to the equilibrium configuration of the solvent probed by absorption (“max” = “abs”) or emission (“max” = “em”) transitions. The transition dipole is commonly extracted from integrated absorption/emission intensities or from the rate of spontaneous radiation.<sup>10,11</sup> The differential dipole can be measured by Stark spectroscopy,<sup>7–9,12</sup> time-resolved microwave<sup>13a,b</sup> and pulsed dc<sup>13c,d</sup> conductivity, and microwave absorption.<sup>13e</sup>

As defined by eqs 2 and 3,  $\Delta z$  is a complex function of the solute energetics and the solvent effect (it is also different for absorption and emission transitions). This results in a few major difficulties in constructing theoretical treatments of reaction kinetics and optical spectra in electronically delocalized systems: (i) the solvent effect enters the observables in a very complicated fashion, (ii) vacuum quantum calculations of the electronic parameters of the donor–acceptor complexes cannot

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be applied to estimating  $\Delta z$  and less reliable models involving solvent field should be used, and (iii) a connection between the adiabatic reorganization energy given by eq 1 and optical observables (optical width, Stokes shift, etc.) is not specified. Furthermore, the CT activation energy includes, apart from  $\lambda_s^{\text{ad}}$ , the equilibrium free energy gap  $\Delta F_0^{\text{ad}}$ . The Marcus–Hush formulation<sup>2,3</sup> does not address the question of scaling of  $\Delta F_0^{\text{ad}}$  with the extent of electron delocalization<sup>14</sup> thus leaving open the question of a general scaling law of the CT activation barrier.

In view of the mentioned difficulties of incorporating  $\Delta z$  into the CT theory, our present formulation is based on the delocalization parameter defined solely in terms of the vacuum solute dipoles

$$\Delta e = \left[ 1 + \frac{4m_{12}^2}{\Delta m_{12}^2} \right]^{-1/2} \quad (4)$$

where  $m_{12}$  is the vacuum, adiabatic transition dipole and  $\Delta m_{12} = m_2 - m_1$  is the vacuum, adiabatic differential dipole. The obvious advantage of  $\Delta e$  over  $\Delta z$  is that it does not depend on the solvent and can be obtained from vacuum quantum calculations or gas–phase measurements. In fact the transition dipole  $m_{12}$  can also be extracted from condensed phase measurements when the vacuum transition frequency  $\nu_0$  is known, since  $m_{12} = \nu_{\text{max}} m_{12}^{\text{max}} / \nu_0$  in the two-state model (see below for details). In view of its experimental, and potentially theoretical, availability, the parameter  $\Delta e$  can now be directly incorporated into the description of radiationless and optical electronic transitions.

The motivation of this and companion<sup>15</sup> studies is to develop a theory of thermally activated and optical electronic transitions in terms of the delocalization parameter  $\Delta e$  instead of  $\Delta z$ . The formulation involves two steps. The first step (the present paper) aims at constructing the free energy surfaces of partial CT along the reaction coordinate reflecting the strength of coupling of the two-state solute to a classical, linearly responding solvent. As the second step (the companion paper),<sup>15</sup> the Franck–Condon envelope<sup>16</sup> of electronic and vibrational excitations in electronically delocalized CT complexes is constructed to connect the theory parameters to optical observables.

The adiabatic free energy surfaces obtained in the present paper reflect charge delocalization through the vacuum transition dipole and the vacuum energy gap between the adiabatic states. The free energy surfaces are functions of the reorganization parameters invariant in respect to the unitary transformations of the solute basis (thus equal in the adiabatic and diabatic representations) and the delocalization parameter  $\Delta e$  (section 3.1). The non-Condon coupling of the solute transition dipole to the solvent field is considered as a perturbation in the Golden Rule calculation of the reaction rate (section 3.3). The ET matrix element entering the rate preexponent is fully defined in terms of adiabatic parameters and is connected to the absorption band intensity (section 4). The dependence of the extent of electron delocalization on the energy gap results in a nonparabolic energy gap law with a shallow branch in the inverted ET region (section 3.4). The results of the current model are compared to traditional treatments of ET in section 5, with conclusions drawn in section 6.

## 2. CT Free Energy Surfaces

**2.1. Model.** Here we calculate the CT free energy surfaces along the reaction coordinate reflecting the strength of coupling of the difference of the solute electric fields in the initial and

final adiabatic states,  $\Delta \mathcal{E}_{12}$ , to the nuclear electric polarization of the solvent  $\mathcal{P}_n$ <sup>17</sup>

$$X = \Delta \mathcal{E}_{12} \cdot \mathcal{P}_n \quad (5)$$

The scalar product of two calligraphic letters throughout below denotes the integral of the two fields depending on the position in the solvent  $\mathbf{r}$  over the solvent volume  $V$

$$\Delta \mathcal{E}_{12} \cdot \mathcal{P}_n = \int_V \Delta \mathcal{E}_{12}(\mathbf{r}) \cdot \mathcal{P}_n[\mathbf{r}, \{\mathbf{r}_j\}] d\mathbf{r} \quad (6)$$

This form does not assume a macroscopic solvent polarization that, in microscopic terms, is given by the density of permanent dipoles in the solvent

$$\mathcal{P}_n[\mathbf{r}, \{\mathbf{r}_j\}] = \sum_j \mathbf{m}_j \delta(\mathbf{r} - \mathbf{r}_j) \quad (7)$$

where the sum runs over all molecules in the solvent with coordinates  $\mathbf{r}_j$  and the dipole moments  $\mathbf{m}_j$ . The microscopic definition of the solvent polarization in eq 7 allows an extension of the present analytical theory to computer experiment with the microscopic field  $\mathcal{P}_n[\mathbf{r}, \{\mathbf{r}_j\}]$  generated by condensed phase simulations.

The CT free energy  $F(X)$  along the reaction coordinate  $X$  is given by the constrained trace of the system density matrix

$$\exp[-\beta F(X)] = (\beta Q_B)^{-1} \text{Tr}(\delta(X - \Delta \mathcal{E}_{12} \cdot \mathcal{P}_n) \exp[-\beta H]) \quad (8)$$

where  $H$  is the system Hamiltonian,  $\beta = 1/k_B T$ , and the trace runs over the nuclear and electronic degrees of freedom of the solvent and the electronic populations of the two CT states (Appendix A). The latter feature generates delocalization of the electronic density between the two CT states at each nonequilibrium configuration of the solvent characterized by the reaction coordinate  $X$ . The system Hamiltonian includes the vacuum part  $H_0$ , the solute–solvent interaction  $H_{0B}$ , and the Hamiltonian of the solvent thermal bath  $H_B$ :

$$H = H_0 + H_{0B} + H_B \quad (9)$$

In eq 8,

$$Q_B = \text{Tr}(\exp[-\beta H_B]) \quad (10)$$

is the partition function of the pure solvent.

For the quantum part of the Hamiltonian, one needs to define the basis set of electronic wave functions. Two adiabatic states,  $\{\Psi_1, \Psi_2\}$ , diagonalizing the two-state vacuum Hamiltonian  $H_0$ , are considered here

$$H_0 = \sum_{i=1,2} E_i a_i^+ a_i, \quad H_0 \Psi_i = E_i \Psi_i \quad (11)$$

In eq 11,  $a_i^+$  and  $a_i$  are the Fermionic operators of creation and annihilation of the electron in the  $i$ th adiabatic state. The adiabatic basis set is used in favor to traditionally employed diabatic, localized states  $\{\Psi_a, \Psi_b\}$  for two reasons: (i) the basis  $\{\Psi_1, \Psi_2\}$  takes into account directly the delocalization of the electronic density between the donor and acceptor for intramolecular ET and (ii) the matrix elements of the operators entering  $H$  can be given by quantum mechanical algorithms operating in terms of adiabatic states. The energies  $E_i$  are, therefore, the true electronic energies of the CT system in a vacuum that are split by the gap

$$\Delta E = E_2 - E_1 \quad (12)$$

This gap is nonzero even for self-exchange transitions due to the symmetry-breaking donor–acceptor overlap. The energies  $E_i$  do not include the solvent effect. They are the Born–Oppenheimer (BO) electronic terms depending on the intramolecular nuclear modes of the solute. Since the consideration of vibrational excitations of the solute is postponed to the companion paper,<sup>15</sup> each energy  $E_i$  refers to the electronic state in equilibrium with the nuclear coordinates. It means that the vacuum gap  $\Delta E$  corresponds to the 0–0 transition energy in the gas phase that can be measured by means of optical spectroscopy. The energies of CT absorption and emission in a vacuum are given as  $h\nu_{\text{abs,em}}^{(0)} = \Delta E \pm \lambda_v$ , where “+” and “–” refer to absorption and emission, respectively, and  $\lambda_v$  is the intramolecular, vibrational reorganization energy. The parameter  $\Delta E$  entering our equations below is thus  $\Delta E = h(\nu_{\text{abs}}^{(0)} + \nu_{\text{em}}^{(0)})/2$ .

The diabatic basis set is commonly used as a starting point in describing the solvent effect on ET. The ET reaction coordinate is then defined through the *diabatic* differential field of the solute,  $\Delta \mathcal{E}_{\text{ab}} = \mathcal{E}_{\text{b}} - \mathcal{E}_{\text{a}}$

$$Y = \Delta \mathcal{E}_{\text{ab}} \cdot \mathcal{P}_{\text{n}} \quad (13)$$

in place of the *adiabatic* field in eq 5. The two approaches are compared in section 5.1. The adiabatic and diabatic basis sets are connected by the unitary transformation

$$\Psi_{\text{a}} = \sqrt{1-f}\Psi_1 + \sqrt{f}\Psi_2 \quad (14)$$

$$\Psi_{\text{b}} = -\sqrt{f}\Psi_1 + \sqrt{1-f}\Psi_2 \quad (15)$$

Three theorems important for the following discussion can be derived from eqs 14 and 15. First, if an operator  $\hat{A}$  that generally does not commute with  $H_0$  is diagonal in the basis  $\{\Psi_{\text{a}}, \Psi_{\text{b}}\}$ , the off-diagonal elements of  $\hat{A}$  and  $H_0$  are connected by the relation

$$|A_{12}|/\Delta A_{\text{ab}} = |H_{\text{ab}}|/\Delta E, \quad \Delta E = E_2 - E_1 \quad (16)$$

where  $A_{jk} = \langle \Psi_j | \hat{A} | \Psi_k \rangle$ ,  $\Delta A_{jk} = A_k - A_j$ ;  $j, k = 1, 2$  or  $j, k = \text{a, b}$ , and  $H_{\text{ab}} = \langle \Psi_{\text{a}} | H_0 | \Psi_{\text{b}} \rangle$ . Here and below, for simplicity,  $A_j = A_{jj}$ . Equation 16 is used to construct the generalized Mulliken–Hush (GMH) basis<sup>18</sup> that diagonalizes the matrix of the solute dipole operator ( $\hat{A} = \hat{m}$ ) and allows an exact connection between the adiabatic transition dipole moment and the diabatic matrix element  $H_{\text{ab}}$ .<sup>18</sup> Second, any unitary transformation connecting  $\{\Psi_1, \Psi_2\}$  and  $\{\Psi_{\text{a}}, \Psi_{\text{b}}\}$  generates two invariants<sup>5</sup>

$$\Delta A_{12}^2 + 4A_{12}^2 = \Delta A_{\text{ab}}^2 + 4A_{\text{ab}}^2 \quad (17)$$

and

$$A_1 + A_2 = A_{\text{a}} + A_{\text{b}} \quad (18)$$

Third, there are two relations significant for self-exchange transitions. If  $H_{\text{a}} = H_{\text{b}}$ , one obtains

$$\Delta A_{12} = 2A_{\text{ab}}, \quad 2A_{12} = \Delta A_{\text{ab}} \quad (19)$$

The adiabatic energy gap  $\Delta E$  (eq 12) is related to the diabatic energy parameters as

$$\Delta E = [(H_{\text{b}} - H_{\text{a}})^2 + 4|H_{\text{ab}}|^2]^{1/2} \quad (20)$$

and is invariant in respect to the unitary basis transformations according to eq 17. For self-exchange transitions with  $H_{\text{a}} = H_{\text{b}}$ ,

$$\Delta E = 2|H_{\text{ab}}| \quad (21)$$

In the present approach, both the adiabatic and diabatic basis sets refer to a solute in the vacuum. An alternative approach would be to use the condensed phase electronic states of the solute in equilibrium with the solvent, the approach employed in the polaron problem.<sup>19</sup> In this way, however, all matrix elements entering the formulation (e.g., dipole moments) gain solvent dependence. One then loses the advantage of employing vacuum quantum calculations and gas-phase measurements to define the system parameters and linear response for the solvent effect.

The solute–solvent interaction Hamiltonian is the scalar product of the electric field operator of the solute and the solvent polarization integrated over the solvent volume

$$H_{\text{OB}} = -\hat{\mathcal{E}} \cdot \mathcal{P} \quad (22)$$

The adiabatic basis  $\{\Psi_1, \Psi_2\}$  consequently generates the Hamiltonian matrix including coupling to the solvent polarization in both the diagonal (the first summand in eq 23) and the off-diagonal (the second summand in eq 23) terms

$$H_{\text{OB}} = - \sum_{i=1,2} \mathcal{E}_i \cdot \mathcal{P} a_i^+ a_i - \mathcal{E}_{12} \cdot \mathcal{P} (a_1^+ a_2 + a_2^+ a_1) \quad (23)$$

The off-diagonal coupling is responsible for the solvent-induced, non-Condon mixing of the vacuum adiabatic states.<sup>20–22</sup> Note that the non-Condon mixing considered here differs from the non-Condon effect often considered for vibronic transitions where it is caused by the dependence of the transition dipole of the *solute* on its nuclear coordinates.<sup>23</sup> Here, we do not include such effects considering the off-diagonal coupling to the collective solvent mode of the nuclear polarization.

The nuclear polarization is a part of the overall solvent polarization  $\mathcal{P}$  that, additionally, includes the electronic  $\mathcal{P}_{\text{e}}$  component

$$\mathcal{P} = \mathcal{P}_{\text{n}} + \mathcal{P}_{\text{e}} \quad (24)$$

The bath Hamiltonian is assumed to be a bilinear form in  $\mathcal{P}_{\text{n}}$  and  $\mathcal{P}_{\text{e}}$

$$H_{\text{B}} = H_{\text{B}}[\mathcal{P}_{\text{n}}] + H_{\text{B}}[\mathcal{P}_{\text{e}}] = \frac{1}{2} \mathcal{P}_{\text{n}} \cdot \chi_{\text{n}}^{-1} \cdot \mathcal{P}_{\text{n}} + \frac{1}{2} (\omega_{\text{e}}^{-2} \mathcal{P}_{\text{e}} \cdot \mathcal{P}_{\text{e}} + \mathcal{P}_{\text{e}} \cdot \chi_{\text{e}}^{-1} \cdot \mathcal{P}_{\text{e}}) \quad (25)$$

In eq 25, the kinetic energy of the classical nuclear polarization is omitted (the BO approximation) and is retained only for the electronic polarization treated as a quantum field with the characteristic frequency  $\omega_{\text{e}}$ .<sup>20d</sup> The response functions  $\chi_{\text{e}}$  and  $\chi_{\text{n}}$  of the pure liquid can be defined through corresponding correlators of the polarization fluctuations.<sup>24</sup>

To simplify the consideration below and reduce the number of independent parameters, the off-diagonal, adiabatic matrix element of the solute field operator and the differential, adiabatic field of the solute are assumed to be linearly connected

$$\mathcal{E}_{12} = \alpha_{12} \Delta \mathcal{E}_{12} \quad (26)$$

Such a linear relation holds exactly when the solute field is approximated by that of a point dipole yielding

$$\alpha_{12} = \frac{m_{12}}{\Delta m_{12}} \quad (27)$$

Basilevsky et al.<sup>25</sup> used two separate reaction coordinates for the diagonal and off-diagonal couplings to the solvent polarization. Our approach thus produces a one-dimensional cross section of their two-dimensional CT surfaces along the line defined by eq 26.

**2.2. Free Energies.** The Hamiltonian  $H$ , as defined by eqs 11, 23, and 25, is a bilinear form in the quantum and classical coordinates of the solute and the solvent. The trace in eq 8 thus can be taken exactly under the following conditions of separation of the characteristic time scales: (i) the solvent electronic polarization is the fastest system mode with  $\hbar\omega_e \gg \Delta E$ <sup>26</sup> and (ii) the nuclear polarization is the classical mode with the characteristic frequency  $\nu_n$  such that  $\nu_n \ll \nu_{\max}$ . The condition (i) allows adiabatic elimination of the quantum electronic polarization of the solvent. The trace over  $\mathcal{P}_e$  retains the two-state form of the system Hamiltonian with the diagonal and off-diagonal matrix elements renormalized due to solvation by the solvent electronic polarization (eqs A6 and A7).<sup>20</sup> Then, the trace over the nuclear polarization generates the free energy composed of the ground (“−”) and excited (“+”) CT surfaces (Appendix A)

$$F(X) = -\beta^{-1} \ln[e^{-\beta F_-(X)} + e^{-\beta F_+(X)}] \quad (28)$$

Here,<sup>27</sup>

$$F_{\pm}(X) = \frac{X^2}{4\lambda_s^{\text{ad}}} \pm \frac{\Delta E(X)}{2} + C \quad (29)$$

$$\Delta E = [(\Delta F_0^{\text{ad}} - X)^2 + 4\alpha_{12}^2(\Delta F_s^{\text{ad}} - X)^2]^{1/2} \quad (30)$$

and

$$C = \frac{F_{01}^{\text{ad}} + F_{02}^{\text{ad}}}{2} + \frac{\lambda_s^{\text{ad}}}{4} \quad (31)$$

The adiabatic solvent reorganization energy in eqs 29 and 31 is

$$\lambda_s^{\text{ad}} = \frac{1}{2} \Delta \mathcal{E}_{12} \cdot \chi_n \cdot \Delta \mathcal{E}_{12} \quad (32)$$

The free energy gap

$$\Delta F_0^{\text{ad}} = F_{02}^{\text{ad}} - F_{01}^{\text{ad}} = \Delta E + \Delta F_s^{\text{ad}} \quad (33)$$

is composed of the adiabatic vacuum splitting  $\Delta E = E_2 - E_1$  and the solvation free energy

$$\Delta F_s^{\text{ad}} = -\mathcal{E}_{\text{av}} \cdot \chi \cdot \Delta \mathcal{E}_{12} \quad (34)$$

Here,  $E_{\text{av}} = (E_1 + E_2)/2$  and  $\chi = \chi_e + \chi_n$  is the total response function of the solvent.

### 3. CT Rates

**3.1. Reorganization Parameters.** Equations 28–34 define the CT free energy surfaces in terms of adiabatic parameters depending on the donor–acceptor electronic overlap. The theory can, however, be reformulated in terms of the reorganization parameters independent of delocalization, and invariant in respect to the unitary basis transformations, and the delocalization parameter

$$\Delta e = [1 + 4\alpha_{12}^2]^{-1/2} \quad (35)$$

Specifically, one obtains

$$F_{\pm}(X) = \frac{X^2}{4\Delta e^2 \lambda_s^{\text{I}}} \pm \frac{1}{2} \Delta E(X) + C \quad (36)$$

with

$$\Delta E(X) = [\Delta E^2 + 2\Delta E(\Delta e \Delta F_s^{\text{I}} - X) + (\Delta F_s^{\text{I}} - X/\Delta e)^2]^{1/2} \quad (37)$$

The invariant solvent reorganization energy is<sup>28</sup>

$$\lambda_s^{\text{I}} = \frac{1}{2} (\Delta \mathcal{E}_{12}^2 + 4\mathcal{E}_{12}^2)^{1/2} \cdot \chi_n \cdot (\Delta \mathcal{E}_{12}^2 + 4\mathcal{E}_{12}^2)^{1/2} \quad (38)$$

and the invariant solvent component of the free energy gap is given by

$$\Delta F_s^{\text{I}} = -\frac{1}{2} (\Delta \mathcal{E}_{12}^2 + 4\mathcal{E}_{12}^2)^{1/2} \cdot \chi \cdot (\mathcal{E}_1 + \mathcal{E}_2) \quad (39)$$

The invariance of  $\lambda_s^{\text{I}}$  and  $\Delta F_s^{\text{I}}$  in respect to the unitary transformations of the solute basis follows from eqs 17 and 18. For  $\alpha_{12}$  given by eq 27 the delocalization parameter  $\Delta e$  in eq 35 is equivalent to that in eq 4. At  $\Delta e = 1$ , eq 36 reduces to two diabatic parabolas

$$F_i(X) = F_{0i}^{\text{d}} + \frac{(X \pm \lambda_s^{\text{I}})^2}{4\lambda_s^{\text{I}}} \quad (40)$$

Here and throughout below the upper and lower signs in “±” refer to  $i = 1$  and to  $i = 2$ , respectively;  $F_{0i}^{\text{d}} = F_{0i}^{\text{ad}}(\Delta e = 1)$  is the diabatic free energy of the  $i$ th state referring to zero donor–acceptor overlap.

The comparison of eqs 32–34 with eqs 38–39 yields the scaling laws for the reorganization parameters with  $\Delta e$ . The adiabatic reorganization energy is a quadratic function of the delocalization parameter

$$\lambda_s^{\text{ad}} = (\Delta e)^2 \lambda_s^{\text{I}} \quad (41)$$

The solvent component of the equilibrium, adiabatic free energy gap scales linearly with  $\Delta e$

$$\Delta F_s^{\text{ad}} = \Delta e \Delta F_s^{\text{I}} \quad (42)$$

Equation 36 and the above scaling relations are exact and are limited only to the model of a two-state solute in a linearly responding solvent.

Comparison of eq 40 to standard expressions for the diabatic ET activation barrier suggests that the invariant reorganization energy  $\lambda_s^{\text{I}}$  should be considered as an analogue of the diabatic reorganization energy  $\lambda_s^{\text{d}}$  of the diabatic ET theories<sup>2,3</sup>

$$\lambda_s^{\text{d}} = \frac{1}{2} \Delta \mathcal{E}_{\text{ab}} \cdot \chi_n \cdot \Delta \mathcal{E}_{\text{ab}} \quad (43)$$

Indeed, the Marcus–Hush formulation assumes that the off-diagonal matrix element of the solute field  $\mathcal{E}_{\text{ab}}$  does not affect the barrier thermodynamics, and according to eqs 17 and 38,

$$\lambda_s^{\text{I}} \simeq \frac{1}{2} \Delta \mathcal{E}_{\text{ab}} \cdot \chi_n \cdot \Delta \mathcal{E}_{\text{ab}} \quad (44)$$

The above approximation may well fulfill for unsymmetrical CT systems, but becomes questionable for self-exchange reactions defined by the condition  $\Delta I_{ab} = H_b - H_a = 0$ . In this case, from eq 19,

$$\bar{\mathcal{E}}_{ab} = \Delta \mathcal{E}_{12}/2 \quad (45)$$

and neglect of the off-diagonal diabatic matrix element of the solute field operator is hardly justified. We, however, will assume  $\lambda_s^d \approx \lambda_s^1$  in the numerical illustrations below as this is the only way to compare the predictions of the present model to diabatic theories.

Figure 1 shows the lower and upper adiabatic free energy surfaces for a CT reaction with  $\Delta F_s^1 = 0$ . The positions of two minima at  $X_1^-$  and  $X_2^-$  indicate the initial and final equilibrium states. They are strongly affected by both the vacuum adiabatic splitting  $\Delta E$  and the delocalization parameter  $\Delta e$ . When  $\Delta E/\lambda_s^1 \rightarrow 0$ , the common picture of diabatic free energy surfaces with equal energies of the initial and final states<sup>2</sup> is recovered (Figure 1, upper part). The energies of the lower surface minima split with increasing  $\Delta E$  (Figure 1, lower part) and the positions of the minima shift linearly with  $\Delta e$  at  $\Delta E/\lambda_s^1 \ll 1$

$$X_i^- \approx \mp \Delta e \lambda_s^1 \quad (46)$$

Therefore, even for self-exchange CT, the adiabatic representation predicts a nonzero energy gap equal to  $\Delta e \Delta E$  at  $\Delta E/\lambda_s^1 \ll 1$  (see discussion in section 5.1 below). The barriers of the forward ( $i = 1$ , “+”) and backward ( $i = 2$ , “-”) reactions then differ

$$F_i^{\text{act}} \approx \frac{h\nu_{\text{abs}}^{(i)}}{4} \pm \frac{\Delta e}{4} \Delta E - \frac{\Delta E}{2} \sqrt{1 - \Delta e^2} \quad (47)$$

Here, because of a nonzero driving force, two absorption transitions are present (Figure 1, lower part)<sup>15</sup>

$$h\nu_{\text{abs}}^{(i)} = \lambda_s^1 \pm \Delta e \Delta E \quad (48)$$

**3.2. Delocalization Parameters.** The free energy surfaces in eq 36 can be used to calculate the Marcus–Hush delocalization parameter  $\Delta z$  as the difference in the equilibrium occupation numbers in the final and initial electronic states. The occupation number of the  $i$ th adiabatic state at a particular value of the reaction coordinate  $X$  is defined as

$$\begin{aligned} n_i(X) &= \partial F(X)/\partial E_i \\ &= n^{\mp}(X) \bar{n}_F(\Delta E(X)) + n^{\pm}(X) [1 - \bar{n}_F(\Delta E(X))] \end{aligned} \quad (49)$$

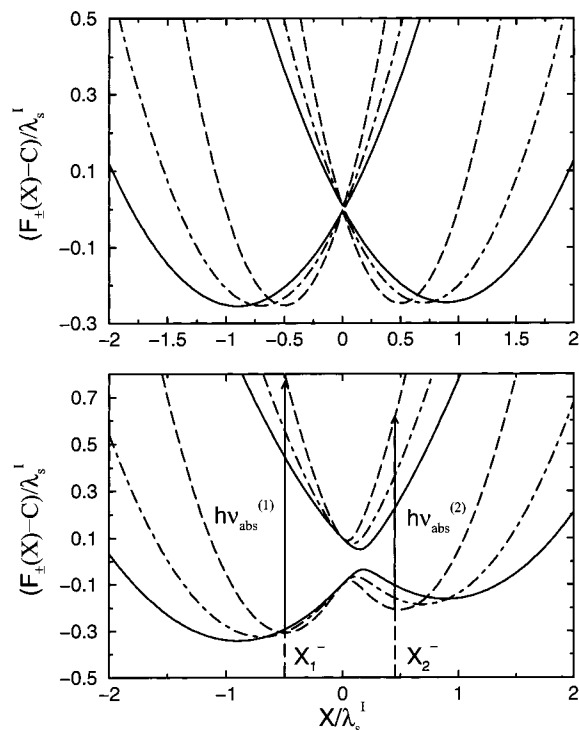
Here,

$$\bar{n}_F(\Delta E(X)) = [1 + e^{\beta \Delta E(X)}]^{-1} \quad (50)$$

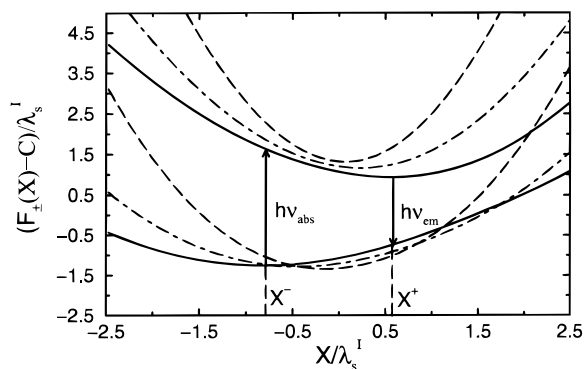
is the Fermi–Dirac thermal occupation number and

$$n^{\pm}(X) = \frac{1}{2} \pm \frac{\Delta E + \Delta e \Delta F_s^1 - X}{2 \Delta E(X)} \quad (51)$$

are the occupation numbers of the lower and upper ET surfaces without thermal excitations between them. The lower CT surface has two minima,  $X_1^-$  and  $X_2^-$ , in the normal CT region (Figure 1). The Marcus–Hush delocalization parameter  $\Delta z$  is then the difference in the occupation numbers  $n_i(X)$  taken at corresponding minima. Since the impact of thermal excitations on the



**Figure 1.** The upper,  $F_+(X)$ , and lower,  $F_-(X)$ , free energy surfaces for a CT reaction with  $\Delta F_s^1 = 0$  at three values of the delocalization parameter  $\Delta e$ : 0.5 (dashed lines), 0.7 (dot-dashed lines), 0.9 (solid lines). The upper and lower parts correspond to  $\Delta E/\lambda_s^1$  equal to 0.02 and 0.2, respectively;  $\lambda_s^1 = 1$  eV. In the lower panel,  $h\nu_{\text{abs}}^{(1)}$  and  $h\nu_{\text{abs}}^{(2)}$  indicate two absorption transitions;  $X_{1,2}^-$  are the positions of the minima of the lower ET surface.



**Figure 2.** CT free energy surfaces for the inverted CT region at  $\Delta e = 0.9$  (solid lines),  $\Delta e = 0.7$  (dot-dashed lines), and  $\Delta e = 0.5$  (dashed lines);  $\Delta E = 3.0$  eV,  $\Delta F_s^1 = 1.0$  eV,  $\lambda_s^1 = 1.0$  eV.  $X^-$  and  $X^+$  indicate the minima of the lower and upper surfaces, respectively.

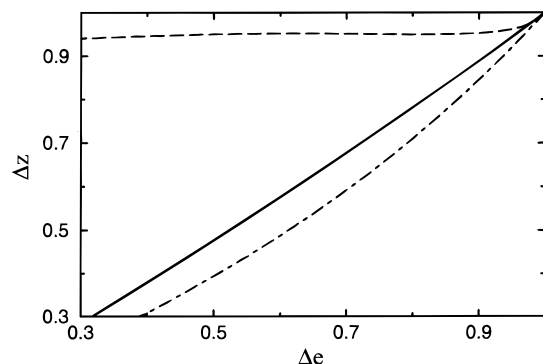
occupation numbers is negligible at  $\beta \Delta E(X_i^-) \gg 1$ ,  $\Delta z$  is given by the relation

$$\Delta z = |n^-(X_1^-) - n^-(X_2^-)| \quad (52)$$

For CT in the inverted region (Figure 2), the lower and the upper surface has only one minimum each,  $X^-$  and  $X^+$ . Hence,  $\Delta z$  is obtained from the occupation numbers taken at the upper and lower minima

$$\Delta z = |n^-(X^-) - n^+(X^+)| \quad (53)$$

Figure 3 illustrates the dissimilarity in the dependence of the transferred charge on the delocalization parameter  $\Delta e$  in the normal and inverted CT regions. For small ratios  $|\Delta E +$



**Figure 3.** Dependence of the charge  $\Delta z$  transferred in a CT reaction on the delocalization parameter  $\Delta e$  at  $\Delta E/\lambda_s^1 = 0.2$ ,  $\Delta F_s^1 = 0$  (solid line),  $\Delta E/\lambda_s^1 = 0.5$ ,  $\Delta F_s^1 = 0$  (dot-dashed line),  $\Delta E/\lambda_s^1 = 3.0$ ,  $\Delta F_s^1 = -1.0$  (dashed line).

$\Delta e \Delta F_s^1 / \lambda_s^1 < 1$  in the normal CT region, the parameters  $\Delta z$  and  $\Delta e$  are close to each other (solid and dot-dashed lines in Figure 3). The equilibrium charge is localized on the lower CT surface for the inverted CT configuration (dashed line in Figure 3). A CT reaction from an excited CT state in the inverted region hence results in a practically full transfer of the electron density. This shows that delocalization and the difference in equilibrium occupation numbers should not be equated to each other. A high magnitude of the transition dipole implying strong coupling between the CT states for vertical electronic transitions may exist along with a large energy gap resulting in a nearly complete CT between the equilibrium electronic configurations.

**3.3. Golden Rule Reaction Rate.** The adiabatic surfaces  $F_{\pm}(X)$  are eigenstates of the two-state matrix

$$\begin{pmatrix} V_1(X) + X/2 & \alpha_{12}(\Delta e \Delta F_s^1 - X) \\ \alpha_{12}(\Delta e \Delta F_s^1 - X) & V_2(X) - X/2 \end{pmatrix} \quad (54)$$

with

$$V_i(X) = F_{0i}^{\text{ad}} + \frac{X^2}{4\Delta e^2 \lambda_s^1} + \frac{\Delta e^2 \lambda_s^1}{4} \quad (55)$$

If  $\Delta e$  is close to unity ( $\alpha_{12} \ll 1$ ), the off-diagonal terms can be treated as a perturbation leading to transitions between the diagonal energy levels.<sup>29</sup> The standard Golden Rule procedure then applies resulting in the following equation for the rate constant

$$k_{\text{ET}}^{(i)} = \hbar^{-1} |H_{\text{ET}}|^2 \text{FC}_{\text{ad}}^{(i)} \quad (56)$$

with the Franck-Condon factor

$$\text{FC}_{\text{ad}}^{(i)} = \left( \frac{\pi\beta}{\Delta e^2 \lambda_s^1} \right)^{1/2} \exp \left[ -\beta \frac{(\Delta F_0^{\text{ad}} \pm \Delta e^2 \lambda_s^1)^2}{4\Delta e^2 \lambda_s^1} \right] \quad (57)$$

In eq 56, the ET matrix element

$$|H_{\text{ET}}| = \frac{\sqrt{1 - \Delta e^2}}{2\Delta e} \Delta E = \frac{m_{12}}{\Delta m_{12}} \Delta E \quad (58)$$

is fully defined in terms of adiabatic vacuum parameters: the energy gap and the differential and transition dipoles. The quantity  $2|H_{\text{ET}}|$  is, however, larger than the minimum splitting  $E_{\text{min}}$  between the adiabatic ET surfaces

$$E_{\text{min}} = \Delta E \sqrt{1 - \Delta e^2} = 2|H_{\text{ab}}^{\text{GMH}}| \quad (59)$$

commonly associated with the ET matrix element. The difference between the minimum splitting and the ET matrix element entering the rate constant arises due to the dependence of the off-diagonal matrix element on the reaction coordinate  $X$ . The diagonal matrix elements in the two-state Hamiltonian matrix (eq 54) equalize at the transition point

$$X^{\ddagger} = \Delta F_0^{\text{ad}} \quad (60)$$

This point does not coincide with the coordinate of the minimum splitting of the lower and upper ET surfaces

$$X_{\text{min}} = \Delta F_0^{\text{ad}} - \Delta E(1 - \Delta e^2), \quad \Delta e \leq 1 \quad (61)$$

resulting in a difference between  $2|H_{\text{ET}}|$  and  $E_{\text{min}}$  (Figure 4).

The minimum splitting  $E_{\text{min}}$  is equal to  $2|H_{\text{ab}}^{\text{GMH}}|$  calculated in the GMH basis proposed by Cave and Newton.<sup>18</sup> The GMH basis is constructed to diagonalize the matrix of the solute dipole operator with  $f$  in eqs 14 and 15 obeying the relation

$$\Delta e = 1 - 2f = \Delta J_{\text{ab}}^{\text{GMH}} / \Delta E \quad (62)$$

where

$$\Delta J_{\text{ab}}^{\text{GMH}} = H_{\text{b}}^{\text{GMH}} - H_{\text{a}}^{\text{GMH}} \quad (63)$$

is the diabatic vacuum energy gap<sup>30</sup> such that

$$\Delta E^2 = (\Delta J_{\text{ab}}^{\text{GMH}})^2 + 4|H_{\text{ab}}^{\text{GMH}}|^2 \quad (64)$$

The ET matrix element in the GMH basis is connected to that entering the adiabatic Golden Rule rate constant through the delocalization parameter (see also eq 50 in ref 20d)

$$|H_{\text{ab}}^{\text{GMH}}| = \Delta e |H_{\text{ET}}| \quad (65)$$

Equation 62 is a specific case of the general rule:  $\Delta e$  is equal to the difference in the occupation numbers of the two vacuum adiabatic states in respect to the basis diagonalizing the matrix of the solute field operator. Only in that basis is the delocalization parameter directly related to the system energetics. For any other basis set related to the adiabatic basis by a unitary transformation (eqs 14 and 15) the delocalization parameter defined through the adiabatic transition and differential dipoles cannot be directly related to the diabatic energetic parameters.

The Golden Rule approximation is more traditionally used within the diabatic representation. With the non-Condon coupling to the solvent retained in the Hamiltonian, the perturbation expansion is performed over the solvent-dependent ET matrix element

$$H_{\text{ab}}[\mathcal{P}] = H_{\text{ab}} - \mathcal{E}_{\text{ab}} \cdot \mathcal{P} \quad (66)$$

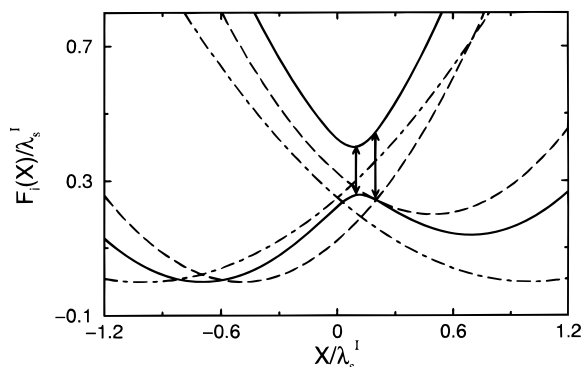
The transition point is then located at

$$Y^{\ddagger} = \Delta F_0^{\text{d}} = F_{02}^{\text{d}} - F_{01}^{\text{d}} \quad (67)$$

and the rate constant is<sup>20d</sup>

$$k_{\text{ET}}^{(i)} = \hbar^{-1} |H_{\text{ab}}^{\text{MH}}|^2 \text{FC}_{\text{d}}^{(i)} \quad (68)$$

Here,



**Figure 4.** Adiabatic free energies (solid lines, eq 36), diagonal energies in the two-state matrix in eq 54 (long-dashed lines), and diabatic free energy surfaces (dash-dotted lines, eq 40) for self-exchange CT at  $\Delta F_s^1 = \Delta F_s^d = 0$ ,  $\Delta E/\lambda_s^1 = 0.2$ , and  $\Delta e = 0.7$ . The two vertical arrows indicate: the point of intersection of the diagonal energies at which the splitting of adiabatic surfaces is  $2|H_{ET}|$  (longer arrow) and the position of minimum splitting  $E_{\min} = 2|H_{ab}^{GMH}|$  (shorter arrow). All curves are vertically shifted to pass through zero at the left minimum.

$$FC_d^{(i)} = \left(\frac{\pi\beta}{\lambda_s^d}\right)^{1/2} \exp\left[-\beta \frac{(\Delta I_{ab} + \Delta F_s^d \pm \lambda_s^d)^2}{4\lambda_s^d}\right] \quad (69)$$

is the diabatic Franck–Condon factor and

$$H_{ab}^{MH} = H_{ab} - \alpha_{ab}\Delta I_{ab} \quad (70)$$

is the Mulliken–Hush (MH) ET matrix element;  $\alpha_{ab} = \mathcal{E}_{ab}/\Delta\mathcal{E}_{ab}$ . In the dipolar approximation for the solute field, one obtains

$$H_{ab}^{MH} = \frac{m_{12}}{\Delta m_{ab}}\Delta E \quad (71)$$

Equations 68 and 69 make a considerable improvement compared to traditional theories of nonadiabatic (NA) ET<sup>3c</sup> considering transitions between diabatic states  $\{\Psi_a, \Psi_b\}$  induced by the ET matrix element  $|H_{ab}|$  independent of the solvent. The NA rate constant is then

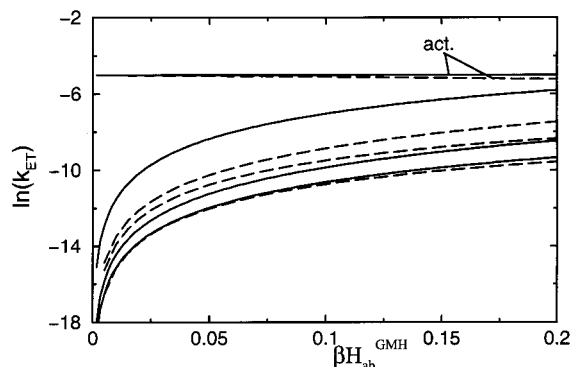
$$k_{ET}^{(i)} = \hbar^{-1}|H_{ab}|^2 FC_d^{(i)} \quad (72)$$

Equations 68 and 72 coincide for self-exchange ET when  $\Delta I_{ab} = 0$ . In this case also, from eq 19,  $\Delta m_{12} = 2m_{ab}$  and  $2m_{12} = \Delta m_{ab}$ .

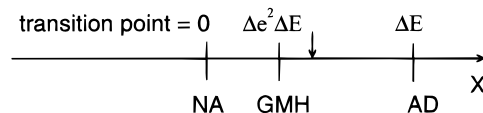
Figure 5 compares three Golden Rule solutions: the adiabatic (AD, eq 56), the diabatic with the GMH basis (GMH, eq 68), and the nonadiabatic (NA, eq 72). The AD and GMH solutions are directly comparable as the GMH basis generates invariant solvation free energies: the solvent reorganization energy and the solvent component of the equilibrium energy gap

$$\lambda_s^{GMH} = \lambda_s^1, \quad \Delta F_s^{GMH} = \Delta F_s^1 \quad (73)$$

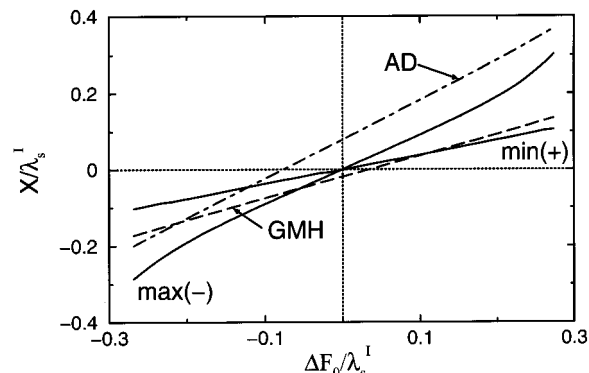
The AD and CMH rate constants are generated in Figure 5 by varying  $H_{ab}^{GMH}$  at  $\Delta e = \text{const}$ <sup>31</sup> and using eqs 62–65. The NA rate results from eq 72 with  $|H_{ab}| = \Delta E/2$  and  $\lambda_s^d = \lambda_s^1$ . All three approximations give different results, with the AD solution predicting the highest rate. The difference results from different placement of the transition state in each approximation. For self-exchange transitions, the transition states are  $X^\ddagger = 0$ ,  $X^\ddagger = \Delta e^2\Delta E$ , and  $X^\ddagger = \Delta E$  for the NA, GMH, and AD solutions, respectively. For self-exchange reactions, the GMH approxima-



**Figure 5.** Golden Rule rate constant calculated in the adiabatic (eq 72, upper curves), GMH (eqs 68–71, middle curves), and nonadiabatic (eq 72, lower curves) approximations for  $\Delta e = 0.7$  (solid lines) and  $\Delta e = 0.9$  (dashed lines). The curves marked “act.” refer to the activation barrier  $-\beta F_1^{\text{act}}$  determined as the difference in free energies of the lower-surface maximum and the first minimum  $X_1^-$ . A CT reaction with  $\lambda_s^1 = 0.5$  eV and  $\Delta F_s^1 = 0$  is considered. For the nonadiabatic approximation,  $\Delta I_{ab} = 0$  and  $|H_{ab}| = \Delta E/2$ .



**Figure 6.** Position of the CT transition state in the NA ( $X^\ddagger = 0$ , NA, eq 72), GMH ( $X^\ddagger = X_{\min}$ , eq 68), and AD ( $X^\ddagger = \Delta E$ , AD, eq 56) representations for self-exchange CT with  $\Delta F_s^1 = \Delta I_{ab} = 0$  and  $\Delta F_{ab}^{GMH} = \Delta e\Delta E$ . The arrow indicates the transition state associated with the maximum of the lower free energy surface.



**Figure 7.** Dependence of the maximum of the lower free energy surface (“max(–)”) and the minimum of the upper free energy surface (“min(+)”) on the gap  $\Delta F_0 = F_-(X_2^-) - F_-(X_1^-)$  in the normal CT region (Figure 1). AD and GMH indicate the transition points of the Golden Rule rates in the adiabatic and diabatic GMH representations, respectively;  $\Delta F_s^1 = -1.0$  eV,  $\lambda_s^1 = 0.5$  eV,  $H_{ab}^{GMH} = 0.1$  eV.

tion gives the best solution for the transition state among the three approximations (Figure 6). Although the GMH approximation gives the exact value of the minimum splitting between the upper and lower free energy surfaces, this point does not coincide with the maximum of the lower surface. This happens because the maximum of the lower and the minimum of the upper surface are generally shifted relative to each other coinciding only when  $F_-(X_1^-) = F_-(X_2^-)$  (Figure 7). The distinction between the maximum of the lower surface and the transition points in the AD and GMH perturbation schemes changes with the reaction exothermicity. Figure 7 shows the dependence of the maximum position and the transition points on the free energy gap between the  $X_2^-$  and  $X_1^-$  minima of the lower surface in the normal CT region.

Nonperturbative solutions for the two-state dynamics<sup>32</sup> are required to test the accuracy of each perturbation scheme. A qualitative estimate of the validity range of the Golden Rule solution can be gained from the Landau–Zener (LZ) adiabaticity parameter,  $\gamma_{LZ}$ .<sup>33</sup> The first-order perturbation expansion holds when  $\gamma_{LZ} < 1$ . The solution of the classical LZ problem<sup>33</sup> with the two-state matrix given by eq 54 leads to the following expression:<sup>34</sup>

$$\gamma_{LZ} = \frac{2\pi}{\hbar|\dot{X}|} |H_{ab}^{GMH}|^2 \quad (74)$$

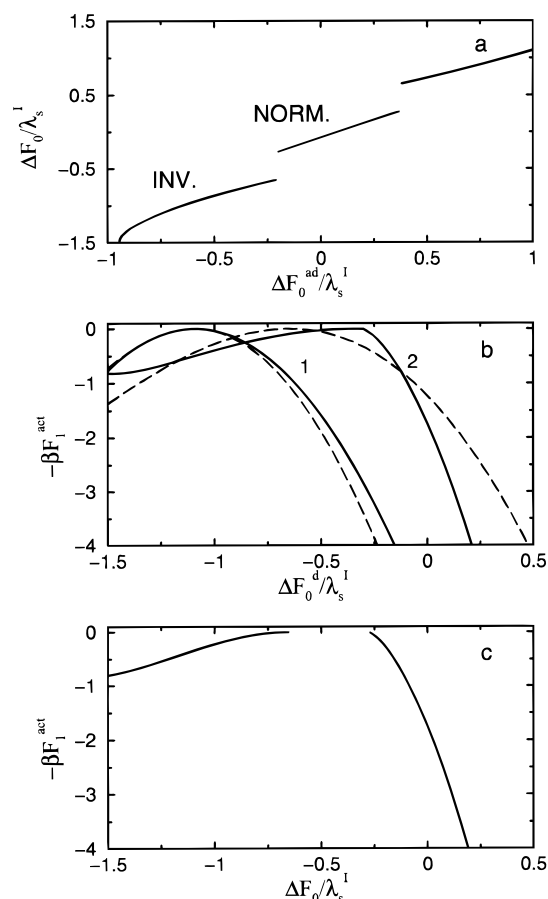
The LZ parameter is determined by the minimum splitting of the adiabatic surfaces and not by the ET matrix element  $|H_{ET}|$ . The non-Condon mixing thus enhances the range of applicability of the Golden Rule approximation for the ET rates by the factor  $\Delta e^{-2}$  (eq 65).

**3.4. Energy Gap Law.** Theories descending from the Marcus picture of ET<sup>2</sup> predict a bell-shaped, parabolic dependence of the ET rate constant on the diabatic driving force  $\Delta F_0^d$  for a reaction driven by classical solvent modes. This prediction is modified by the inclusion of the solute intramolecular vibrations that conserve the bell-shaped form of the energy gap law, but make the energy gap dependence shallower in the inverted ET region.<sup>16</sup> This generic behavior has indeed been documented for charge shift,<sup>35</sup> charge separation,<sup>36</sup> and charge recombination<sup>37</sup> reactions in organic CT complexes.

Experimental studies of the energy gap law of CT reactions<sup>35–37</sup> are commonly performed by chemical modification of the donor and/or acceptor moieties. The usual assumption is that such a modification keeps the solvation parameters of the CT complex reasonably constant, changing considerably only the diabatic vacuum splitting  $\Delta I_{ab}$  by varying the ionization potential and/or electron affinity of the donor and acceptor units. In modeling the energy gap law, we accept the same picture assuming the reorganization energy  $\lambda_s^1$  and the solvation stabilization  $\Delta F_s^1$  to be constant when varying  $\Delta I_{ab}$ . An important factor that needs inclusion is the dependence of the delocalization parameter on the diabatic energy gap. Since such a connection is available only in the GMH basis, we will vary  $\Delta I_{ab}^{GMH}$  and use eq 62 to calculate  $\Delta e$ . In doing this we will also assume that the GMH matrix element  $H_{ab}^{GMH}$  does not change with  $\Delta I_{ab}^{GMH}$ .

Transitions in the normal CT region occur between the two wells of the lower adiabatic surface  $F_-(X)$  with the transmission coefficient  $1 - \exp(-\gamma_{LZ})$  close to unity at  $\gamma_{LZ} \gg 1$  (adiabatic limit). The activation free energy is then defined as a barrier from a lower surface minimum to the maximum point. The dependence of this barrier on the diabatic splitting (b) and the free energy gap (c) are given by the right branches of the energy gap laws shown in Figure 8.

The adiabatic splitting between the CT surfaces leads to a fundamental distinction between reactions in the normal and inverted CT regions. Transitions in the inverted region proceed between different adiabatic surfaces, each having only one minimum, with the transmission coefficient  $\exp(-\gamma_{LZ})$  tending to zero at  $\gamma_{LZ} \gg 1$ . There is, therefore, no classical transition point and the splitting is overcome by quantum tunneling mechanisms. Solvent quantum modes<sup>38</sup> or intramolecular quantum skeletal excitations<sup>16</sup> can participate in this process. The transition is possible when  $m$  quanta of, for example, intramolecular vibrational excitation with the frequency  $\nu_v$  have enough energy to overcome the minimum adiabatic splitting,  $m h \nu_v \geq E_{min}$ . The Golden Rule Franck–Condon factor for such transitions is easy to calculate,<sup>15</sup> but an infinite order summation of the perturbation terms is necessary for large ET couplings.<sup>39</sup> In



**Figure 8.** Plot of the activation energy of forward CT 1→2 on the (b) equilibrium diabatic gap and the (c) equilibrium free energy gap at  $H_{ab}^{GMH} = 0.1$  eV. Also shown (a) is the dependence of the free energy gap  $\Delta F_0$  calculated as the difference in the free energies of the surface minima vs  $\Delta F_0^{ad}$ . In (b), 1 indicates the diabatic free energy surfaces (eq 40) and 2 indicates the adiabatic free energy surfaces (eq 36). The dashed lines show the results of calculations with constant delocalization parameter  $\Delta e = 0.9$ . Other parameters are  $\Delta F_s^1 = -1.0$  eV and  $\lambda_s^1 = 0.5$  eV.

the absence of such a solution we confine ourselves to a qualitative modeling of the energy gap law in the inverted ET region emphasizing the importance of the dependence of the delocalization parameter on the energy gap. Only the energy invested to achieve the crossing point  $X^\ddagger$  of the diagonal terms in eq 54 is considered to generate the left branches of the energy gap in Figure 8. At this point, the occupation numbers  $n^\pm(X^\ddagger)$  of the lower and upper CT surfaces (eq 51) are both equal to  $1/2$ .

The outcome for the energy gap law depends on the parameter experimentally accepted as a probe of the equilibrium energy gap. The most fundamental approach is to define the equilibrium reaction gap as the difference in the free energies at the minima of the CT free energy curve

$$\Delta F_0 = F_-(X_2^-) - F_-(X_1^-) \quad (75)$$

in the ET normal region (Figure 1) and

$$\Delta F_0 = F_-(X^-) - F_+(X^+) \quad (76)$$

in the inverted region (Figure 2). This equilibrium energy gap is in fact measured by the ratio of the forward and backward reaction rates.<sup>36b</sup> An alternative approach commonly used in experimental setup is to measure the equilibrium energy gap as



a difference in redox potentials of the separate donor and acceptor units. This energy gap is not affected by the donor–acceptor overlap and is reflected by the diabatic equilibrium free energy gap  $\Delta F_0^d$ . In view of these two approaches used in experimental studies, we plotted in Figure 8 the energy gap curve against  $\Delta F_0^d$  (b) and against  $\Delta F_0$  (c). Both curves, although bell-shaped, are very asymmetric with a much steeper dependence in the CT normal region, as it is usually observed in experiment.<sup>35–37</sup> The dotted line in Figure 8b shows the same results obtained with the fixed delocalization parameter  $\Delta e = 0.9$ . The curve is much more symmetric indicating that the dependence of the delocalization parameter on the diabatic energy gap is the crucial source of the curve asymmetry.

The discontinuity between the normal and inverted branches of  $F_1^{\text{act}}(\Delta F_0)$  is due to the switch from the inverted to the normal CT regions resulting in a gap in the  $\Delta F_0$  values of about  $2|H_{\text{ET}}|$  (Figure 8a). It arises due to adiabatic splitting of the lower and upper CT surfaces (Figures 1 and 2). Figure 8a shows that the free energy difference  $\Delta F_0^{\text{ad}}$  entering the free energy surfaces  $F_{\pm}(X)$  is not the real equilibrium gap measured by the ratio of the rate constants. The actual gap  $\Delta F_0$  is a discontinuous function of  $\Delta F_0^{\text{ad}}$  that should be determined according to eqs 75 and 76 from the free energy surfaces.

#### 4. Absorption Intensity

The ET matrix element, entering the Golden Rule reaction rate, is usually measured from absorption intensities<sup>5</sup> or rates of spontaneous radiation.<sup>10</sup> The equation for the extinction coefficient of CT absorption following from the present model is derived here. Optical absorption results from electronic transitions between the lower adiabatic surface  $F_-(X)$  and the upper adiabatic surface  $F_+(X)$ . Transitions are driven by the interaction of the solute electronic density with the electric field of the radiation. In the dipolar approximation, the interaction Hamiltonian reads

$$-f(n_{\text{D}})\hat{\mathbf{m}}\cdot\mathbf{E}_0 \quad (77)$$

where  $\hat{\mathbf{m}}$  is the solute dipole operator. The parameter  $f(n_{\text{D}})$  accounts for the deviation of the local field acting on the solute dipole from the external field  $\mathbf{E}_0$ ;  $n_{\text{D}}$  is the solvent refractive index. Dielectric theories<sup>40</sup> predict for spherical cavities

$$f(n_{\text{D}}) = \frac{3n_{\text{D}}^2}{2n_{\text{D}}^2 + 1} \quad (78)$$

The first order perturbation theory over the solute–radiation interaction is commonly applied to derive the one-photon transition probability and absorption intensity.<sup>41</sup> As the transitions occur between the adiabatic free energy surfaces  $F_{\pm}(X)$ , the unperturbed basis set is built on the wave functions  $\{\tilde{\Psi}_1(X), \tilde{\Psi}_2(X)\}$  diagonalizing the two-state Hamiltonian matrix in eq 54. The standard perturbation theory then yields for the extinction coefficient  $\epsilon(\nu)$  ( $\text{cm}^{-1} \text{M}^{-1}$ )

$$\frac{\epsilon(\nu)}{\nu} = A \frac{f^2(n_{\text{D}})}{n_{\text{D}}} \langle |\tilde{m}_{12}(X)|^2 \delta(\Delta E(X) - h\nu) \rangle_- \quad (79)$$

where  $\tilde{m}_{12}(X) = \langle \tilde{\Psi}_1(X) | \hat{\mathbf{m}} | \tilde{\Psi}_2(X) \rangle$  and

$$A = \frac{8\pi^3 N_{\text{A}}}{3000 \ln(10)c} \quad (80)$$

In eq 80,  $N_{\text{A}}$  is the Avogadro number and  $c$  is the velocity of light in a vacuum. The average in eq 79 is given by

$$\langle \dots \rangle_- = \int \dots e^{-\beta F_-(X)} dX / \int e^{-\beta F_-(X)} dX \quad (81)$$

and the transition moment is

$$|\tilde{m}_{12}(X)| = |m_{12}| \frac{\Delta E}{\Delta E(X)} \quad (82)$$

There is some confusion in the literature concerning the dependence of the extinction coefficient on the solvent refractive index.<sup>10,42</sup> The correct equation for the absorption intensity (eq 79) was given by Lax<sup>17a</sup> in the classical representation of the radiation field that is also reproduced in the formalism of quantum electrodynamics.<sup>41</sup>

Integration over the absorption band in eq 79 gives for the adiabatic transition dipole (in debye)

$$|m_{12}| = 9.585 \times 10^{-2} \frac{\sqrt{n_{\text{D}}}}{\bar{\nu}_0 f(n_{\text{D}})} \left[ \int \bar{\nu} \epsilon(\bar{\nu}) d\bar{\nu} \right]^{1/2} \quad (83)$$

where  $\bar{\nu}$  is the wavenumber ( $\text{cm}^{-1}$ ) and  $\bar{\nu}_0$  is the wavenumber of the 0–0 transition in a vacuum,  $\Delta E = hc\bar{\nu}_0$ . A relation similar to eq 83 was derived previously<sup>10</sup> by employing the first-order quantum mechanical perturbation theory limited to small delocalization (class II Robin–Day complexes<sup>43</sup>). The present treatment is exact for a two-state solute indicating that eq 83 is in fact valid for an arbitrary electronic delocalization including fully delocalized CT systems (Robin–Day class III<sup>43</sup>).

Equation 83 gives the *vacuum* transition dipole through the integrated absorption intensity. In contrast to this, the transition dipole at an equilibrium solvent configuration

$$m_{12}^{\text{max}} = m_{12} \bar{\nu}_0 / \bar{\nu}_{\text{max}} \quad (84)$$

is often considered in applications.<sup>5,7–9c,11,42</sup> It is this transition dipole that is used in eq 3 for the delocalization parameter  $\Delta z$ . The condensed phase transition dipole  $m_{12}^{\text{max}}$  may significantly differ from the vacuum dipole  $m_{12}$ , especially for self-exchange CT when  $\bar{\nu}_0 / \bar{\nu}_{\text{max}} \approx 2|H_{\text{ab}}|/\lambda_{\text{s}}^1 \ll 1$ . However, due to the invariance of the product  $m_{12}^{\text{max}} \bar{\nu}_{\text{max}}$ , the magnitude of the ET matrix element extracted from the integrated absorption intensity is not affected by this distinction. A somewhat corrected MH relation then follows from eqs 58 and 83

$$|H_{\text{ET}}| = 9.585 \times 10^{-2} \frac{\sqrt{n_{\text{D}}}}{\Delta m_{12} f(n_{\text{D}})} \left[ \int \bar{\nu} \epsilon(\bar{\nu}) d\bar{\nu} \right]^{1/2} \quad (85)$$

where  $|H_{\text{ET}}|$  is in  $\text{cm}^{-1}$  and  $\Delta m_{12}$  in debye. Here, the product  $f(n_{\text{D}})\Delta m_{12}$  is directly measured by means of Stark spectroscopy in nonpolar liquids with  $\epsilon_{\text{s}} = n_{\text{D}}^2$ .<sup>12</sup> Defining the adiabatic separation between the centers of charge localization as ( $e$  is the elementary charge)

$$r_{12} = \Delta m_{12}/e \quad (86)$$

one gets for a Gaussian absorption band

$$|H_{\text{ET}}| = 2.06 \times 10^{-2} \frac{\sqrt{n_{\text{D}}}}{r_{12} f(n_{\text{D}})} [\bar{\nu}_{\text{abs}}^{(1)} \epsilon_{\text{abs}}^{(1)} \Delta \bar{\nu}_{1/2}^{(1)}]^{1/2} \quad (87)$$

In eq 87,  $\bar{\nu}_{\text{abs}}^{(1)}$  ( $\text{cm}^{-1}$ ) and  $\Delta \bar{\nu}_{1/2}^{(1)}$  ( $\text{cm}^{-1}$ ) are the maximum and half-intensity width of the “reduced” spectrum  $\bar{\nu} \epsilon(\bar{\nu})$ ;  $\epsilon_{\text{abs}}^{(1)}$  is the

extinction coefficient ( $\text{cm}^{-1} \text{M}^{-1}$ ) at the maximum of  $\bar{\nu}\epsilon(\bar{\nu})$ . The effective adiabatic separation  $r_{12}$  is in Ångströms and  $|H_{\text{ET}}|$  is in  $\text{cm}^{-1}$ . Equation 87 assumes a Gaussian band shape. The electronic overlap of the donor and acceptor states results in two absorption transitions for self-exchange CT (Figure 1). When the higher-energy state has a nonvanishing population, the absorption line gains asymmetry<sup>15</sup> and the sum

$$(1 + \xi)^{-1} (\bar{\nu}_{\text{abs}}^{(1)} \epsilon_{\text{abs}}^{(1)} \Delta \bar{\nu}_{1/2}^{(1)} + \xi \bar{\nu}_{\text{abs}}^{(2)} \epsilon_{\text{abs}}^{(2)} \Delta \bar{\nu}_{1/2}^{(2)}) \quad (88)$$

should be used in the square root in eq 87;  $\xi$  is the ratio of populations of the minima at  $X_1^-$  and  $X_2^-$  (Figure 1).

## 5. Discussion

Traditional formulations of the ET theory invoke diabatic electronic states of the donor and acceptor defined as distinct electronic states corresponding to complete redistribution of the electronic density with the electronic transition. The diabatic states are naturally determined for *intermolecular* ET when the reactants and the products are separated before and after the reaction or internal rotation eliminates the electronic overlap. The definition of diabatic states becomes, however, obscure for *intramolecular* transitions with substantial mixing of the donor and acceptor wave functions both before and after the reaction. In view of the absence of a generally accepted definition, various diabatic basis sets are used for computing the diabatic activation parameters.<sup>18,44</sup> All definitions of diabatic states have the common feature that the diabatic wave functions are connected by a unitary transformation to the adiabatic wave functions diagonalizing the vacuum Hamiltonian. In this sense, the present theory unifies different approaches to describe localized and delocalized electronic transitions. The free energy surfaces of partial CT (eq 36) are given in terms of the energetic parameters (the vacuum splitting, the solvent reorganization energy, and the equilibrium free energy gap) that are *invariant* in respect to a unitary basis transformation. Therefore, they have the same magnitudes in the adiabatic basis and any diabatic basis constructed from the adiabatic wave functions. Note that the traditional definition of the solvent reorganization energy<sup>2</sup>  $\lambda_s^{\text{d}} \propto \Delta \mathcal{E}_{\text{ab}} \cdot \Delta \mathcal{E}_{\text{ab}}$  (eq 43) allows its dependence on a basis transformation thus rendering this important parameter rather poorly defined.

Another parameter of the theory is the extent of electron delocalization  $\Delta e$ . This parameter is given in terms of the diagonal and off-diagonal vacuum, adiabatic matrix elements of the solute field operator. When the solute field is approximated by that of a point dipole,  $\Delta e$  is expressed through the differential and transition adiabatic dipole moments (eq 4) and thus is amenable to experimental determination by spectroscopic techniques. In the basis diagonalizing the matrix of the solute field,  $\Delta e$  is the difference in the occupation numbers of the two adiabatic states and is represented through the diagonal and off-diagonal matrix elements of the Hamiltonian operator (eqs 62 and 64). In view of the substantial effect of the delocalization parameter on the ET free energy surfaces (Figures 1 and 2), all major results of the ET theory and optical spectroscopy<sup>15</sup> need revision and extension to the case of  $\Delta e < 1$ .

**5.1. Free Energy Surfaces.** The standard approach to construct the CT adiabatic free energies starts with the diabatic vacuum states  $\{\Psi_a, \Psi_b\}$ . Linear coupling of these localized states to a linearly responding solvent results in the diabatic free energy surfaces

$$F_i(Y) = F_{0i}^{\text{d}} + \frac{(Y \pm \lambda_s^{\text{d}})^2}{4\lambda_s^{\text{d}}} \quad (89)$$

with  $i = \text{a}$  (“+”) and  $\text{b}$  (“−”) and  $Y$  denoting the ET reaction coordinate defined through the diabatic solute field difference (eq 13). The two diabatic surfaces are then assumed to be coupled by the ET matrix element  $H_{\text{ab}}$  independent of the solvent configuration. This latter assumption simplifies the two-state Hamiltonian matrix that becomes

$$\begin{pmatrix} F_{\text{a}}(Y) & H_{\text{ab}} \\ H_{\text{ab}} & F_{\text{b}}(Y) \end{pmatrix} \quad (90)$$

A linear combination of the diabatic states

$$\Psi_{1,2}(Y) = c_{\text{a}}(Y)\Psi_{\text{a}} \pm c_{\text{b}}(Y)\Psi_{\text{b}} \quad (91)$$

diagonalizing the above matrix forms the condensed phase adiabatic states. The corresponding adiabatic energies are then<sup>3c-f,6</sup>

$$F_{\pm}(Y) = \frac{Y^2}{4\lambda_s^{\text{d}}} \pm \frac{1}{2} \Delta E^{\text{d}}(Y) + C^{\text{d}} \quad (92)$$

with

$$\Delta E^{\text{d}}(Y) = [\Delta E^2 + 2\Delta I_{\text{ab}}(\Delta F_{\text{s}}^{\text{d}} - Y) + (\Delta F_{\text{s}}^{\text{d}} - Y)^2]^{1/2} \quad (93)$$

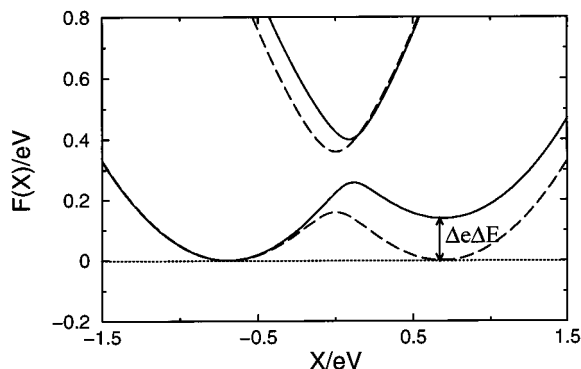
and

$$C^{\text{d}} = \frac{F_{01}^{\text{d}} + F_{02}^{\text{d}}}{2} + \frac{\lambda_s^{\text{d}}}{4} \quad (94)$$

The above free energy surfaces are defined by four parameters  $H_{\text{ab}}$ ,  $\Delta I_{\text{ab}}$ ,  $\Delta F_{\text{s}}^{\text{d}}$ , and  $\lambda_s^{\text{d}}$ .

A different approach is accepted here. The derivation starts from the adiabatic vacuum basis diagonalizing the vacuum Hamiltonian. The total two-state matrix including the solute–solvent coupling in its off-diagonal term (eq 23) is used to construct the free energy surfaces which are exact solutions in the framework of the present model based on the following assumptions: (i) a two-state solute, (ii) linear coupling of the solute electronic states to a linearly responding solvent bath, and (iii) adiabatic elimination of the fast subsystem of the solvent electrons.<sup>20,26</sup> We also use the one-electron approximation and issues involved in this approach are discussed in ref 45. The present solution is more general than that given by eqs 92 and 93 as it involves the non-Condon solute–solvent coupling in the Hamiltonian off-diagonal term. However, the solution is still determined by four parameters:  $\Delta E$ ,  $\Delta F_{\text{s}}^{\text{d}}$ ,  $\lambda_s^{\text{d}}$ , and  $\Delta e$ . The equal number of model parameters is achieved due to the simplification of the Hamiltonian in the Marcus–Hush description. The same form of  $F_{\pm}(X)$  as in eqs 36–39 follows from a diabatic basis with the solvent-dependent ET matrix element (eq 66). The diabatic formulation then defines the solution in terms of five model parameters:  $\Delta I_{\text{ab}}$ ,  $H_{\text{ab}}$ ,  $\lambda_s^{\text{d}}$ ,  $\Delta F_{\text{s}}^{\text{d}}$ , and  $\alpha_{\text{ab}} = \mathcal{E}_{\text{ab}}/\Delta \mathcal{E}_{\text{ab}}$ .

The different number of parameters in the diabatic and adiabatic representations makes it fundamentally difficult to compare them. The GMH basis<sup>18</sup> resolves this problem by defining the diabatic states to obey the condition  $\mathcal{E}_{\text{ab}} = 0$ . In this case,  $X = \Delta e Y$ ,  $\lambda_s^{\text{d}} = \lambda_s^{\text{d}}$ ,  $\Delta F_{\text{s}}^{\text{d}} = \Delta F_{\text{s}}^{\text{d}}$  and the diabatic and adiabatic representations can be compared to each other. The same condition is in fact *assumed*<sup>18a</sup> in the standard Marcus–



**Figure 9.** Adiabatic free energy surfaces  $F_{\pm}(X)$  in the present model (solid lines, eqs 36 and 37) and in the Marcus–Hush formulation (long-dashed lines, eqs 92 and 93) for self-exchange CT with  $\Delta F_s^f = \Delta F_s^d = 0$ ,  $\lambda_s^f = \lambda_s^d = 1$  eV,  $\Delta E = 0.2$  eV, and  $\Delta e = 0.7$ . All free energy surfaces are vertically shifted to have zero value (dotted line) at the position of the left minimum.

Hush formulation. Although this assumption makes the two models inequivalent, we compare here the solution given by eqs 36–39 to the solution given by eqs 92–93 in order to demonstrate the new features arising in the present model.

Figure 9 compares the free energy surfaces given by eqs 36–37 to those from eqs 92–93 for self-exchange CT ( $\Delta I_{ab} = 0$ ,  $\Delta F_s^d = \Delta F_s^f = 0$ ). Several important distinctions between the two adiabatic formulations can be emphasized. (1) The positions of transition points do not coincide. The maximum of  $F_-(X)$  in the present formulation deviates from the position of resonance of the diagonal elements of the two-state Hamiltonian matrix,  $X^\ddagger = 0$ , and is approximately equal to  $X^\ddagger = (\Delta e)^2 \Delta E$  when  $\Delta E/\lambda_s^f \ll 1$  and  $\Delta F_s^f = 0$  (Figures 6 and 7). (2) The splitting of the lower and upper adiabatic surfaces is larger in the Marcus–Hush formulation (eqs 93 and 93) than in the present model. For self-exchange CT, the splitting is  $2|H_{ab}| = \Delta E$  in the former case and  $\Delta E\sqrt{1-\Delta e^2}$  in the latter case. (3) The Marcus–Hush formula involves the diabatic equilibrium free energies  $F_{0i}^d$  without donor–acceptor overlap. The gap  $\Delta F_0^d$  is therefore zero for self-exchange reactions. The adiabatic representation considered here includes explicitly the donor–acceptor overlap that results in a symmetry-breaking splitting of the vacuum electronic states to the energy  $\Delta E$ . Electronic transition in a vacuum thus proceed from the lower state  $E_1$  to the upper state  $E_2$ . In condensed phases, these states are of course “dressed” by a solvating environment, but at  $\Delta F_s^f = 0$  one gets a nonzero equilibrium driving force approximately equal to  $\Delta e \Delta E = \Delta I_{ab}^{\text{GMH}} \neq 0$  when  $\Delta E/\lambda_s^f \ll 1$  (Figure 9). The origin of the factor  $\Delta e$  in the free energy driving force can be understood from eq 49. The free energy represents the work done to transfer the charge  $\Delta e$  over the energy barrier  $\Delta E$  that results in  $\Delta e \Delta E$  for small splittings  $\Delta E$ .

**5.2. Delocalization Parameters.** The Marcus–Hush formulation invokes the effect of partial electron delocalization on the reorganization energy through the magnitude of charge actually transferred in the reaction  $\Delta z$ .<sup>2,3</sup> This parameter can be defined as the difference in the occupation numbers of the two condensed-phase adiabatic states  $\Psi_{1,2}$  (eq 91) corresponding to the initial and final equilibrium states. This yields in the normal ET region

$$\Delta z = |c_a(Y_1^-)^2 - c_b(Y_2^-)^2| \quad (95)$$

In view of the recent advances of Stark spectroscopy applications to CT complexes,<sup>7–9</sup> the delocalization parameter

is often described in terms of the equilibrium differential  $\Delta m_{12}^{\text{max}}$  and transition  $m_{12}^{\text{max}}$  adiabatic dipoles of the solute at the equilibrium solvent configuration. Here, “max” refers to the equilibrium configurations in the initial states. In the normal CT region, these correspond to two absorption transitions (Figure 1). In the inverted CT region, “max” refers to absorption (“abs”) and emission (“em”). If the diabatic transition dipole is zero,  $m_{ab} = 0$ , the delocalization parameter becomes

$$\Delta z = \frac{1}{2} \left[ \frac{\Delta m_{12}^{\text{abs}}}{M^{\text{abs}}} + \frac{\Delta m_{12}^{\text{em}}}{M^{\text{em}}} \right] \quad (96)$$

with

$$M^{\text{max}} = [(\Delta m_{12}^{\text{max}})^2 + 4(m_{12}^{\text{max}})^2]^{1/2} \quad (97)$$

If the dipole moments for absorption and emission are close to each other, eq 96 transforms to eq 3. For self-exchange transitions, however,  $m_{ab} = \Delta m_{12}/2$  ( $\Delta I_{ab} = 0$ , eq 19) and the above representation of the delocalization parameter in terms of the dipole moments is inaccurate. It is expected to give an estimate of  $\Delta z$  for unsymmetrical CT complexes only (Table 1).

The  $\Delta z$  parameter, whatever way defined, does not enter the adiabatic free energy surfaces in the Marcus–Hush formulation (eqs 92 and 93). The present model is more general as it includes the non-Condon coupling to the solvent. As a result, the adiabatic free energy surfaces depend on the vacuum delocalization parameter  $\Delta e$  and, through it, on the transition dipole (eq 4). The electronic overlap of the donor and acceptor thus affects the free energy surfaces in two ways: through the vacuum energy gap and through the vacuum transition dipole. The first parameter defines the energetic splitting of the energy levels due to electronic overlap for self-exchange CT. The second parameter controls the off-diagonal coupling to the external field of the solvent or radiation. In view of the strong effect of  $\Delta e$  on activated transitions and optical spectra,<sup>15</sup> estimates of  $\Delta e$  magnitudes characteristic of CT complexes are pertinent here. These are listed in Table 1. The transition dipoles  $m_{12}$  are obtained from  $m_{12}^{\text{max}}$  according to eq 84. The requirement to know the vacuum frequency  $\nu_0$  considerably narrows the list of chromophores for which  $\Delta e$  can be evaluated and Table 1 includes those unsymmetrical CT systems for which this correction is possible.

The parameter  $\Delta e$  can be rewritten in an alternative way for self-exchange transitions. In this case,  $2m_{12} = \Delta m_{ab}$  and one obtains

$$\Delta e = \left[ 1 + \frac{r_{ab}^2}{r_{12}^2} \right]^{-1/2} \quad (98)$$

If the overlap of the diabatic donor and acceptor states results in a binding MO state, one can expect  $r_{12} < r_{ab}$ , where  $r_{ab} = \Delta m_{ab}/e$  is the distance between the centers of localization of the diabatic states. The upper limit for  $\Delta e$  is then (also see Table 1 in the companion paper<sup>15</sup>)

$$\Delta e \leq 1/\sqrt{2} \quad (99)$$

As mentioned above, eqs 3 and 96 are not very dependable for self-exchange CT due to the assumption  $m_{ab} = 0$  involved. This is illustrated by the last entry in Table 1. Equation 3 results in  $\Delta z = 0.98$ , whereas eq 98 yields  $\Delta e = 0.55$  with  $r_{ab} = 7.0$  Å estimated as twice the metal–ligand separation measured by

**TABLE 1: Delocalization Parameters  $\Delta e$  and  $\Delta z$** 

compound	$\bar{\nu}_0^a$	$\bar{\nu}_{\max}^a$	$(m_{12})^b$	$(m_{12}^{\max})^b$	$(\Delta m_{12})^{b,c}$	$\Delta e^d$	$\Delta z^e$
Ru <sup>2+</sup> (NH <sub>3</sub> ) <sub>5</sub> -py	38.0 <sup>f</sup>	24.5 <sup>f</sup>	2.48	3.84 <sup>g</sup>	3.36 <sup>g</sup>	0.56	0.40
Ru <sup>2+</sup> (NH <sub>3</sub> ) <sub>5</sub> -pz	32.6 <sup>f</sup>	21.2 <sup>f</sup>	3.09	4.80 <sup>g</sup>	3.36 <sup>g</sup>	0.47	0.36
coumarin-153	25.4 <sup>h</sup>	21.7 <sup>i</sup>	4.94	5.79 <sup>j</sup>	7.8 <sup>h</sup>	0.62	0.56
Ru <sup>2+</sup> (NH <sub>3</sub> ) <sub>5</sub> (4,4'-bpy)Ru <sup>3+</sup> (NH <sub>3</sub> ) <sub>5</sub> <sup>5+</sup>				2.4	21.4	0.55 <sup>j</sup>	0.98

<sup>a</sup> In 10<sup>3</sup> cm<sup>-1</sup>. <sup>b</sup> In debye. <sup>c</sup> Measurements of differential dipoles are commonly performed in low-polarity media and the measured differential dipole is assumed to be close to its vacuum value. <sup>d</sup> From eq 84. <sup>e</sup> From eq 3. <sup>f</sup> From ref 7b. <sup>g</sup> From ref 8b. <sup>h</sup> From Mühlpfordt, A. et al. *Phys. Chem. Chem. Phys.* **1999**, *1*, 3209. <sup>i</sup> Emission in c-hexane, from ref 32b. <sup>j</sup> Calculated from eq 98 with  $r_{\text{ab}} = 7.0$  Å.

metal–ligand absorption spectra.<sup>8a</sup> This discrepancy seems to contradict to Figure 3 predicting close magnitudes of  $\Delta z$  and  $\Delta e$  for self-exchange reactions. The latter prediction can be tested for the case of Ru<sup>2+</sup>(NH<sub>3</sub>)<sub>5</sub>(4,4'-bpy)Ru<sup>3+</sup>(NH<sub>3</sub>)<sub>5</sub><sup>5+</sup> by using eq 52 with the parameters  $\Delta F_s^1 = 0$ ,  $\Delta E = 2|H_{\text{ab}}| = 0.22$  eV,<sup>8b</sup> and  $\lambda_s^1 = 0.95$  eV. The solvent reorganization energy follows from  $h\nu_{\text{abs}} = 1.21$  eV,  $\lambda_v = 0.18$  eV,<sup>8b</sup> and the relation  $h\nu_{\text{abs}} = \lambda_v + \lambda_s^1 + \Delta e \Delta E$  (eq 48). From these parameters one obtains  $\Delta z = 0.52$  from eq 52 with  $\Delta e = 0.55$  in support of the conjecture that dipole moments measured at an equilibrium solvent configuration do not provide an accurate estimate of equilibrium delocalization for self-exchange reactions in terms of eq 3.

**5.3. ET Matrix Element.** The fundamental MH<sup>46</sup> relation establishes a connection between the ET matrix element and spectroscopic parameters of electronic transitions

$$|H_{\text{ab}}^{\text{MH}}| = \frac{m_{12}}{\Delta m_{\text{ab}}} \Delta E \quad (100)$$

Equation 100 is exact for a two-state solute<sup>5,18c</sup> with collinear  $\mathbf{m}_{12}$  and  $\Delta \mathbf{m}_{12}$ .<sup>20d</sup> The MH ET matrix element enters the Golden Rule rate of ET when the non-Condon coupling to the solvent is included in the diabatic Hamiltonian (eqs 66 and 68). The electronic coupling  $H_{\text{ab}}^{\text{MH}}$  derives from the integrated spectral intensity according to eq 87 with  $r_{12}$  replaced by  $r_{\text{ab}} = \Delta m_{\text{ab}}/e$ .<sup>3,5</sup> The latter is usually unknown and is estimated in practical calculations through the distance of donor–acceptor separation.

This complication is eliminated in the GMH<sup>18</sup> or adiabatic representations. The former defines the diabatic differential dipole in eq 100 as  $\Delta m_{\text{ab}} = [\Delta m_{12}^2 + 4m_{12}^2]^{1/2}$ . The later replaces  $\Delta m_{\text{ab}}$  in eq 100 with  $\Delta m_{12}$ . Both matrix elements are defined solely in terms of adiabatic vacuum parameters. The diabatic GMH and adiabatic representations provide two alternative routes to calculate the Golden Rule rate constant resulting in, respectively,  $H_{\text{ab}}^{\text{GMH}}$  and  $H_{\text{ET}}$  matrix elements in the rate preexponent. The former gives the activation barrier independent of delocalization, whereas the latter generates the barrier decreasing with delocalization. This difference leads to the predictions for the reaction rates diverging with increasing ET coupling (Figure 5). Among various choices of the diabatic basis set preference should be given to the GMH basis. It generates the invariant reorganization parameters  $\lambda_s^1$  and  $\Delta F_s^1$  in the activation barrier (eq 73), correctly positions the transition state for self-exchange transitions (Figure 6), and provides a simple connection between the MH and adiabatic ET matrix elements (eq 65). Both matrix elements enter rate constant preexponents in corresponding perturbation schemes only if the non-Condon coupling to the solvent is retained in the Hamiltonian.

**5.4. Reorganization Energy.** The present solution for the adiabatic free energy surfaces of partial CT provides two important insights concerning methods of calculation of the solvent effect on the reorganization parameters. First, the

Marcus–Hush relation (eq 1) in combination with eq 2 or eq 3 suggests that the solvent effect enters the reorganization energy in a rather complicated way: through the delocalization parameter and through the diabatic reorganization energy. On the contrary, the present formulation reestablishes the “diabatic paradigm”: the solvent effect enters the adiabatic reorganization energy only linearly through the linear response function  $\chi_n$  (eqs 32 and 38). Second, the establishment of the invariant reorganization energy  $\lambda_s^1$  allows to use electrostatic models for the reorganization energy based on solvation of fixed charges located at molecular sites<sup>47</sup> instead of using a more complicated algorithm through the delocalized electronic density.<sup>25</sup>

The invariant reorganization energy sets up the characteristic length between centers of charge localization to be used in electrostatic models of solvent reorganization<sup>18</sup>

$$r_{\text{CT}} = e^{-1} [\Delta m_{12}^2 + 4m_{12}^2]^{1/2} \quad (101)$$

For self-exchange transitions it becomes (eq 45)<sup>48</sup>

$$r_{\text{CT}} = [r_{12}^2 + r_{\text{ab}}^2]^{1/2} \quad (102)$$

For instance, for the CT complex Ru<sup>2+</sup>(NH<sub>3</sub>)<sub>5</sub>(4,4'-bpy)Ru<sup>3+</sup>(NH<sub>3</sub>)<sub>5</sub><sup>5+</sup> (Table 1), one obtains  $r_{\text{CT}} = 8.3$  Å with  $r_{\text{ab}} = 7$  Å. With this estimate and the radii of the donor and acceptor units  $r_a = r_d = 4.0$  Å,<sup>5b</sup> the two-sphere dielectric-continuum formula<sup>3d,e</sup> yields a reasonable estimate for the reorganization energy  $\lambda_s^1 \approx 0.98$  eV in water (experimentally, 0.95 eV). Note that both molecular solvation<sup>49a</sup> and quantum-SCRF<sup>49b</sup> calculations give the results close to the continuum model for this solute configuration.

In diabatic theories of ET,<sup>2,3</sup> the diabatic solvent reorganization energy is the universal parameter determining the activation barrier, absorption energy, and spectral width for self-exchange ET<sup>3d,e</sup>

$$\lambda_s^d = \lambda_s^\Delta = \lambda_{\text{abs}}^w = h\nu_{\text{abs}} \quad (103)$$

Here,  $\lambda_s^\Delta = |X_2^- - X_1^-|/2$  is half the distance between the coordinates of the minima of the diabatic free energy surfaces, and  $\lambda_{\text{abs}}^w$  is the reorganization energy extracted from the Gaussian width of absorption spectra  $\sigma_{\text{abs}}$ , via the relation  $\lambda_{\text{abs}}^w = \beta \sigma_{\text{abs}}^2/2$ . In the above relation, the vertical energy gap  $h\nu_{\text{abs}}$  and the spectral width  $\lambda_{\text{abs}}^w$  are experimental observables that may serve to determine the reorganization energy. Furthermore,  $2\lambda_s^\Delta$  is identically the Stokes shift in the inverted ET region and thus gives an alternative definition of the reorganization energy in that case. For partial CT in electronically delocalized systems, the Marcus–Hush theory suggests quadratic scaling of the reorganization energy with  $\Delta z$ , eq 1. In view of eq 103, a quadratic scaling law may be expected to apply equally to the activation and optical parameters of self-exchange CT. This does not, however, happen for the optical and activation observables.

The Marcus–Hush theory and the present model can be compared for self-exchange CT with  $\Delta E < \lambda_s^1$  as  $\Delta z \approx \Delta e$  in this case (Figure 3). The two wells of the lower ET surface have indeed the curvatures that scale quadratically with  $\Delta e$ . This quadratic scaling is, however, accompanied by a linear scaling of  $\lambda_s^\Delta$  (Figure 1, eq 46). The resulting activation energy  $\approx \lambda_s^1/4$  (eqs 47 and 48) is given in terms of the reorganization energy  $\lambda_s^1$  invariant in respect to the unitary basis transformations. The activation barrier is thus essentially independent of  $\Delta e$  and  $\Delta z$ . The same is true for the absorption width that is invariant in  $\Delta e$ .<sup>15</sup> Consequently, instead of equality 103, the following inequality holds

$$\lambda_s^{\text{ad}} \leq \lambda_s^\Delta \leq \lambda_{\text{abs}}^{\text{w}} \leq h\nu_{\text{abs}}^{(1)} \quad (104)$$

which transforms to equality only at  $\Delta e = 1$ . The last inequality is due to the shift of the energy of the light-induced donor-to-acceptor transition (eq 48)

$$h\nu_{\text{abs}}^{(1)} = \lambda_s^1 + \Delta e \Delta E \quad (105)$$

by the solvent-independent contribution  $\Delta e \Delta E$ . The fact that the absorption energy is essentially independent of the extent of electron delocalization has been noticed previously.<sup>5</sup> The vacuum term  $\Delta e \Delta E$  has not been, however, included in the previous studies. Despite the correction terms, it is the invariant reorganization energy  $\lambda_s^1$  that is primarily probed by the absorption energy, spectral width, and the activation barrier for self-exchange CT. Therefore,  $\lambda_s^1$ , and not  $\lambda_s^{\text{d}}$  or  $\lambda_s^{\text{ad}}$ , is the *real, observable reorganization energy* for both localized (ET) and delocalized (CT) transitions.

**5.5. Approximations and Extensions.** The basic assumption of this study is that the BO approximation is globally valid for the nuclear, solute and solvent, subsystems. This implies that the energies  $E_i = E_i(Q_j)$  (eq 11) are vacuum BO electronic terms depending on intramolecular solute modes  $Q_j$ . By using the harmonic approximation for a single effective mode  $Q$ , we build in the following paper<sup>15</sup> the Franck–Condon envelope on the basis of the vibrational overlap integrals<sup>16,17a</sup>

$$\langle \tilde{\Psi}_i(X) \chi_k | \hat{m} | \tilde{\Psi}_j(X) \chi_m \rangle \approx \langle \tilde{\Psi}_i(X) | \hat{m} | \tilde{\Psi}_j(X) \rangle \langle \chi_k | \chi_m \rangle, \quad i, j = 1, 2 \quad (106)$$

where  $\chi_m$  are the harmonic wave functions of the nuclear mode  $Q$ . As is seen, this equation involves the Condon principle for the intramolecular modes<sup>23</sup> and a non-Condon transition dipole for the solvent nuclear modes (eq 79). To summarize, our model involves the BO approximation for the solvent nuclear modes and the BO–Condon approximation for the solute intramolecular vibrations.

The BO and harmonic approximations are known to break down for some mixed-valence compounds resulting in a vibrational coupling of the electronic terms.<sup>50,51</sup> Although there are no exact criteria of such breakdown, the physical consequence of the BO approximation is to overestimate the tunneling splitting between the adiabatic surfaces.<sup>51d</sup> The error is, however, small if the ratio of the vibrational reorganization energy  $\lambda_v$  to the characteristic vibrational energy  $h\nu_v$  is large.<sup>51d</sup> This is in fact the common situation especially for organic optical chromophores for which the vibrational reorganization is distributed over many vibrational modes.<sup>52</sup> The present model is thus limited to such systems. In fact the vibronic analysis employed in the companion paper<sup>15</sup> has been successfully used for many mixed-valence compounds as well<sup>53</sup> and the limits of the BO approximation for such systems are not well established. When

the BO approximation fails, the crude adiabatic approximation<sup>23</sup> is used for the basis set with subsequent numerical diagonalization of the vibronic matrix.<sup>50,51</sup> Despite quite different physics, there is an interesting *mathematical* analogy between the present model and the methods used in solving the vibronic problem for mixed-valence CT.<sup>50,51</sup> The crude adiabatic approximation generates the delocalized diabatic basis<sup>51a,b</sup> diagonalizing the Hamiltonian matrix at zero nuclear displacements of the ligands. Similarly, our vacuum adiabatic basis corresponds to zero solvent polarization. The two-state Hamiltonian matrices are also very similar in the two problems: they are linear in the nuclear displacements (polarization) in the off-diagonal positions and bilinear in the nuclear displacements (polarization) in the diagonal positions.<sup>51c,d</sup> This close mathematical analogy suggests a numerical extension of the model to the case when the BO approximation fails and the vibrational wave functions become anharmonic. Such extension would also enable to relax the Condon approximation for the intramolecular solute modes.<sup>50</sup>

## 6. Conclusions

An exact solution for the adiabatic free energy surfaces of CT is derived. The free energies are represented as functions of reorganization parameters invariant in respect to electronic delocalization and the delocalization parameter. Electronic delocalization thus affects the solution through two parameters: the vacuum, adiabatic energy gap and the vacuum, adiabatic transition dipole. The invariant reorganization energy entering the free energy surfaces is the true, observable reorganization energy for both localized and delocalized reactions as it determines the vertical transition energy, bandwidth, and the activation barrier for self-exchange transitions. The equilibrium energy gap between the initial and final states is a discontinuous function of the adiabatic free energy difference showing a jump in its magnitude when going from the normal to inverted CT region. The adiabatic free energy surfaces of partial CT deviate considerably from those used in the Marcus–Hush adiabatic formulation showing a much weaker dependence of the activation barrier on delocalization. The inclusion of the non-Condon coupling to the solvent is the necessary condition for obtaining the Golden Rule reaction rate (GMH or adiabatic) with the preexponent connected to the integrated absorption intensity.

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## A. Appendix

The trace in eq 8 is carried out by functional integration over the solvent fields  $\mathcal{P}_n$  and  $\mathcal{P}_e$  as well as over the quantum operators of the solute electronic states

$$\text{Tr}(\dots e^{-\beta H}) = \frac{\partial}{\partial z_e} \int \dots \exp[-\hbar^{-1}(S_{0B} + S_B)] \mathcal{D}M \mathcal{D}\mathcal{P}_e(\mathbf{r}, \tau) \mathcal{D}\mathcal{P}_n(\mathbf{r}) |_{z_e=0} \quad (A1)$$

Here,

$$S_B = \beta \hbar H_B[\mathcal{P}_n(\mathbf{r})] + \int_0^{\beta \hbar} H_B[\mathcal{P}_e(\mathbf{r}, \tau)] d\tau \quad (A2)$$

is the Euclidian action of the solvent bath. The action  $S_{0B}$  is

built on the vacuum solute and solute–solvent Hamiltonians

$$S_{0B}[a_i^*, a_i, \rho_e, \rho_n] = \int_0^{\beta\hbar} [\hbar \sum_i a_i^* \partial_\tau a_i + \sum_i (\mu_e - E_i) a_i^* a_i - H_{0B}] d\tau \quad (\text{A3})$$

The trace over the quantum electronic states of the solute electrons in eq (A1) is performed in the holomorphic representation in which the Fermionic operators are replaced by  $c$ -numbers obeying the rules of the Grassmann algebra.<sup>54</sup> The integral measure  $\mathcal{DM}$  in eq A1 denotes integration over the Grassmann fields. It reads

$$\mathcal{DM} = \prod_{i=1,2} \prod_{0 \leq \tau \leq \beta\hbar} \frac{da_i^*(\tau) da_i(\tau)}{2\pi i} \quad (\text{A4})$$

with the Fermionic boundary conditions  $a_i(0) = -a_i(\beta\hbar)$ .

The direct integration in the holomorphic representation produces the grand partition function as the number of electrons in the system is not fixed. To obtain the canonical partition function, differentiation over the fugacity  $z_e = \exp(\beta\mu_e)$  is performed in eq A1. The chemical potential  $\mu_e$  of the two-state system ensures correct Fermi statistics of the electronic subsystem at finite temperatures. The value of  $\mu_e$  is derived from the condition that only one electron occupies the two levels of the solute:<sup>20c</sup>  $\langle \hat{N} \rangle = 1$ ,  $\hat{N} = a_1^+ a_1 + a_2^+ a_2$ . This condition determines the magnitude of the integration constant  $C$  in eq 31. The formalism used here can be directly extended on electrochemical discharge<sup>55</sup> and many-electron ET.

The derivation of the ET free energy surfaces assumes the electronic polarization to be the fastest mode in the system. In this case, the memory effects of solvation by the electronic polarization disappear and the Euclidian Green's function of the electronic polarization can be represented by a  $\delta$ -correlation on the Euclidian time  $\tau$  ( $\omega_m = 2\pi m/\beta\hbar$ )<sup>20c</sup>

$$G_e(\tau - \tau') = \sum_m \frac{\omega_e^2}{\omega_m^2 + \chi_e^{-1} \omega_e^2} e^{i\omega_m(\tau - \tau')} \cong \beta\hbar \chi_e \delta(\tau - \tau') \quad (\text{A5})$$

This assumption, corresponding to the Pekar adiabatic elimination of the electronic polarization modes,<sup>19a,20</sup> greatly simplifies the calculation of the trace over  $\rho_e$ . The bilinear form of the Hamiltonian  $H_{\text{int}}$  is conserved after taking the trace over  $\rho_e$ . The vacuum energies  $E_i$  renormalize to the energies  $\tilde{E}_i$  due to equilibrium solvation of the CT electronic states by the solvent electronic polarization<sup>20</sup>

$$\tilde{E}_i = E_i - \tilde{E}_i \cdot \rho_n - \frac{1}{2} (\tilde{E}_i \cdot \chi_e \cdot \tilde{E}_i + \tilde{E}_{12} \cdot \chi_e \cdot \tilde{E}_{12}) \quad (\text{A6})$$

The off-diagonal element in  $H_{\text{int}}$  transforms to

$$\tilde{H}_{12} = -\tilde{E}_{12} \cdot \rho_n - \tilde{E}_{\text{av}} \cdot \chi_e \cdot \tilde{E}_{12} \quad (\text{A7})$$

With the effective diagonal and off-diagonal matrix elements of the two-state matrix given by eqs A6 and A7, the Gaussian Euclidean integral over the Grassmann fields  $a_i^*(\tau)$ ,  $a_i(\tau)$  is easy to calculate. It generates the partition function of the spin-boson system<sup>56</sup> depending on the nuclear solvent polarization<sup>20c</sup>

$$Z_{\text{SB}}[\rho_n] = 2 \exp \left[ -\beta \frac{\tilde{E}_1 + \tilde{E}_2}{2} \right] \cosh \left( \frac{\beta \Delta \tilde{E}_{12}}{2} \right) \quad (\text{A8})$$

with

$$\Delta \tilde{E}_{12} = [(\Delta \tilde{E})^2 + 4(\tilde{H}_{12})^2]^{1/2} \quad (\text{A9})$$

and  $\Delta \tilde{E} = \tilde{E}_2 - \tilde{E}_1$ . The calculation of the ET free energy surfaces therefore reduces to the functional integral over the classical field  $\rho_n(\mathbf{r})$

$$e^{-\beta F(X)} = \int \delta(X - \Delta \tilde{E}_{12} \cdot \rho_n) Z_{\text{SB}}[\rho_n] e^{-\beta H_{\text{B}}[\rho_n]} \mathcal{D}\rho_n(\mathbf{r}) \quad (\text{A10})$$

This, with the linear connection between the diagonal and off-diagonal matrix elements of the solute field (eq 26), transforms to eqs 28–31.

## References and Notes

- (1) Throughout this paper, ET refers to a complete transfer of the electron and CT refers to a partial transfer of the electronic density. This distinction should, of course, be understood only in qualitative terms to help in distinguishing between the two limits of a continuous transition between the localized and delocalized regimes.
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