A Nonadiabatic Theory for Ultrafast Catalytic Electron Transfer: A Model for the Photosynthetic Reaction Center

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Abstract. A non-adiabatic theory of Electron Transfer (ET), which improves the standard theory near the inversion point and becomes equivalent to it far from the inversion point, is presented. The complex amplitudes of the electronic wavefunctions at different sites are used as Kramers variables for describing the quantum tunneling of the electron in the deformable potential generated by its environment (nonadiabaticity) which is modeled as a harmonic classical thermal bath. After exact elimination of the bath, the effective electron dynamics is described by a discrete nonlinear Schrödinger equation with norm preserving dissipative terms and a Langevin random force, with a frequency cut-off, due to the thermalized phonons.

This theory reveals the existence of a specially interesting marginal case when the linear and nonlinear coefficients of a two electronic states system are appropriately tuned for forming a Coherent Electron-Phonon Oscillator (CEPO). An electron injected on one of the electronic states of a CEPO generates large amplitude charge oscillations (even at zero temperature) associated with coherent phonon oscillations and electronic level oscillations. This fluctuating electronic level may resonate with a third site which captures the electron so that Ultrafast Electron Transfer (UFET) becomes possible. Numerical results are shown where two weakly interacting sites, a donor and a catalyst, form a CEPO that triggers an UFET to an acceptor. Without a catalytic site, a very large energy barrier prevents any direct ET. This UFET is shown to have many qualitative features similar to those observed in the primary charge separation in photosynthetic reaction centers. We suggest that more generally, CEPO could be a paradigm for understanding many selective chemical reactions involving electron transfer in biosystems.

Key words: electron transfer, ultrafast electron transfer, catalysis, photosynthetic reaction center, coherent oscillations, nonlinear phenomena

1. Introduction

Ultrafast electron transfers (UFETs) in biological systems have been intensively studied during the last two decades with a variety of sophisticated optical spectroscopic techniques. In particular, ultrafast visible and near-IR time-resolved pump-probe experiments have been used to study Electron Transfer (ET) in proteins that exhibit ET between their cofactors [1–7]. In these systems, the reaction energies

involved in ET are small and range in the scale of phonon energies. The time scale for ET becomes of the order of a picosecond (ps), which is the order of phonon relaxation times. Many experiments reveal new features such as coherent phonon oscillations which are difficult to interpret. Clearly, the standard adiabatic approximation which was valid and successful in describing ordinary ET reaction breaks down in these situations. A correct description of UFET phenomena requires an intrinsically nonadiabatic theory. The purpose of this paper is to present such a theory and show that even within simple models, it captures the main features experimentally observed in these UFET processes.

1.1. THE PHOTOSYNTHETIC REACTION CENTER

We first describe the well-studied example of UFET in the Photosynthetic Reaction Center (PRC) and focus on some important features. Photosynthetic bacteria collect the energy of light with pigments inserted in membranes and forming a kind of antenna surrounding the PRC. This pigment can be a (bacterio)chlorophyll, carotenoid or bilin (open chain tetrapyrrole), depending on the type of organism. The excitons which are created by the absorption of photons, funnel systematically within a few ps to the PRC where a highly efficient primary charge separation occurs. The high speed of the charge separation excludes any charge recombination or any other competing transfer, which is much slower. Speed is thus essential for favoring a high efficiency. The PRC is a membrane-bound protein which forms a scaffolding on which cofactors are arranged. Figure 1 represents a scheme of the arrangement of the cofactors in the PRC involved in ET. This PRC consists of two almost symmetric branches denoted *A* and *B*. An exciton created by a

Figure 1. Scheme of the organization of cofactors in the Reaction Center in the membrane and path followed by the electron.

photon absorption in the pigments surrounding the PRC, funnels to the special pair **P** of bacteriochlorophylls $D_M - D_L$ which is raised to its excited state **P**^{*}. Then UFET occurs within 3 ps to the bacteriopheophytin **H**_A which is at a distance of approximately 2 nm (10^{-9} m). The role of the ancillary bacterioclorophyll **B**_A has been proved to be essential but is still controversial. In this work we propose an interpretation of its role.

Next, much slower ETs occur which may not require nonadiabatic theory. The electron on **H**_A is transferred to the menaquinone **Q**_A within 200 ps and then to ubiquinone **Q**_B through a Fe^{++} ion bridge within 10 μ s. Further ETs through electron carriers (cytochrome) follow in the cytoplasm, which we do not discuss.

We focus on understanding the UFET between **P**^{*} and **H**_A including the ancillary molecule **B**_A. The high speed of this ET prevents the exciton from decaying and, thus, makes the efficiency of this UFET close to 100%. Unlike ordinary ETs which are thermally activated, it is important to note that this ET becomes even faster at cryogenic temperatures, where it occurs within 1 ps. We also note that UFET systematically selects the A branch although the second branch B is almost equivalent. However, this UFET is highly sensitive to certain mutations of the cofactors [9] and also to a macroscopic electric field [10] even though it may induce only small relative changes in electronic energy levels. Another important feature is that vibrational coherence [6] is observed in the stimulated emission prior to UFET. This phenomenon may be a common feature for many UFET [11] and could be related to the existence of Coherent Electron-Phonon Oscillators (CEPO) described here.

1.2. THE SIMPLEST THEORY FOR ELECTRON TRANSFER

The standard theory for ET was pioneered by Marcus in the 60's and is successful in describing ordinary ETs which occur over a wide range of time scales, usually much longer than nanoseconds (see [12] for a review). It is based on the adiabatic (Born-Oppenheimer) approximation which assumes that the quantum states of the electron on the donor and on the acceptor are always (or at least most of the time) in adiabatic equilibrium with the configuration of their environment. When the thermal fluctuations of this environment induce a resonance between two electronic levels, occupied and unoccupied, ET may take place.

More precisely, the free energy of the system depends on the coordinates of the nuclei describing the configuration of the system (reaction coordinates) including the whole environment (e.g. solvent) [12] and on the state of the electron in adiabatic equilibrium with its environment. Consequently, there are two free energy surfaces, the first one corresponding to the electron on the donor (called reactant state **R**) and the second one corresponding to the electron on the acceptor (called product state **P**).

The scheme of Figure 2 represents the free energy of the system with the electron on the donor (surface **R**) and with the electron on the acceptor (surface **P**). There are generally many reaction coordinates, so the abscissa in Figure 2 represents a very

Figure 2. Profile of potential energy surfaces versus reaction coordinates for reactants+environment (curve **R**) and products+environment (curve **P**) in the normal regime, the inverted regime and at the inversion point (thin line).

large dimension space. Because the electron strongly interacts with its environment, ET involves an important reorganization of this environment and thus the minima of these two surfaces are reached at different reaction coordinates. ΔG_0 appearing in Figure 2 is the reaction energy which is the difference of energy between the reactant and the product states. ΔG^* at the intersection of the two free energy surfaces **R** and **P** is the energy barrier between the reactant and the product states. Δ_{el} is the energy which has to be provided to the electron in the initial state to be transferred at fixed reaction coordinates (i.e., without reorganization of the environment), which is nothing but the difference between the electronic energy levels on donor and acceptor.

Considering that the system is initially in the reactant state **R**, the thermal fluctuations of the nuclei move randomly the system on the free energy surfaces **R**. When the energy difference between **R** and the free energy surface **P** becomes zero, the electronic levels in the reactant and product states are equal at fixed reaction coordinate and the electron may tunnel. This situation occurs with the maximum probability at the lowest intersection point which corresponds to the transition state. Within the standard theory, ET is essentially a slow thermally activated process. Its reaction rate is found to be [12]

$$k = A \exp \left[\frac{-\Delta G^*}{k_B T} \right] \quad (1)$$

where A is a prefactor depending on the tunneling probability at resonance. For ordinary ET, this energy barrier is not small and the characteristic time required to reach the transition state is much longer than the tunneling time, which can thus be neglected. However, the coefficient A depends on the small interaction which

couples the two states **R** and **P**. When this coupling is relatively strong (strong reactants) at the scale of phonon energies, the adiabatic approximation is still valid at this point and the tunneling probability is 1. Otherwise, at weak coupling (weak reactants), this tunneling is not adiabatic. This diabatic correction may be estimated using Landau-Zener formula [13, 11]. Such an empirical calculation turns out to be sufficient.

An important success of this theory, besides its simplicity, is that it predicts the existence of two regimes for ET which can be experimentally distinguished, namely the normal and the inverted regime. In the normal regime, the direct electronic transition from the donor to the acceptor at fixed reaction coordinates (i.e., at fixed nuclear coordinates and environment) requires a positive energy Δ_{el} while in the inverted regime, this energy Δ_{el} is negative. In the normal regime, electron has to overcome an energy barrier, so ET must be induced by thermal fluctuations or photon absorption. In the inverted regime, ET could be achieved directly by photon emission at frequency (energy) $\hbar\omega_{el} = \Delta_{el}$ (photoluminescent chemical reaction [12]). Actually, this process is possible but it is slow and operates only at low temperature. At higher temperatures, the activation process above the energy barrier ΔG^* becomes prevalent.

Consequently, when varying the redox potential ΔG_0 , the rate of ET given by Eq. (1) becomes maximum when $\Delta G^* = 0$ or equivalently $\Delta_{el} = 0$, i.e., at the inversion point where there is no energy barrier for ET. Then, no thermal fluctuations are required and at low temperature ET is essentially reduced to a direct quantum tunneling (followed by a relaxation of the environment once the electron is on the acceptor). The inversion point is where ET is expected to become the fastest and most efficient. In this case, according to the standard theory, the absence of energy barrier allows ET to persist at zero temperature.

At or near the inversion point, the standard theory has to be improved because the characteristic time for ET is essentially the time of the tunneling process, which cannot be neglected. The energy difference between the electronic levels on donor and acceptor is small so that the adiabatic approximation breaks down. This regime should be described within a nonadiabatic model such as the one we present in what follows.

2. A Nonadiabatic Model for Electron Transfer

We propose a model for ET in the vicinity of the inversion point which may also reproduce the results of the standard theory away from this inversion point. This model has been already described in previous publications [14, 15]. We describe here its main features, emphasize its differences from earlier approaches and, in addition, we complete our discussion with new results. Up to now, we have investigated systematically ET at zero temperature only, with interesting nontrivial results.

2.1. BASIC ASSUMPTIONS OF THE MODEL

We consider a system with two quantum states (or, by extension, several quantum states) denoted by α which are coupled to a large collection of harmonic oscillators (phonon bath) that model the complex environment of the system.¹ Actually, in some systems, such as the PRC, we should consider more than two quantum states, i.e., other quantum states in the same energy range that could interact with the process of excitation transfer. In the simplest case, the system consists of a donor and an acceptor molecule (or the same molecule with two electronic sites). The quantum state $\alpha = \mathbf{D}$ corresponds to the single electron on the donor site (D) and the second quantum state $\alpha = \mathbf{A}$ to the electron on the acceptor site (A). The variables describing this system are:

- The complex components ψ_α of the system in the diabatic basis of quantum states α which fulfill the normalization condition

$$\sum_{\alpha} |\psi_{\alpha}|^2 = 1$$

Then, $|\psi_{\alpha}|^2$ is the probability to observe the system in the state α .

- The pairs of conjugate variables $(u_i, p_i = m_i \dot{u}_i)$ of oscillator i with mass m_i in the phonon bath which describes the reorganization of the environment during ET.

The Hamiltonian describing our system can be written with the form

$$\mathbf{H}(\{\psi_{\alpha}\}, \{u_i, p_i\}) = H_T(\{\psi_{\alpha}\}) + \sum_i \left(\frac{1}{2m_i} p_i^2 + \frac{1}{2} m_i \omega_i^2 \left(u_i - \sum_{\alpha} k_{i,\alpha} |\psi_{\alpha}|^2 \right)^2 \right) \quad (2)$$

Oscillator i has frequency ω_i and is linearly coupled to the charge densities $|\psi_{\alpha}|^2$ by the coupling constant $k_{i,\alpha}$. We have chosen for convenience the form of the electron-phonon coupling in order that

$$H_T(\{\psi_{\alpha}\}) = \min_{\{u_i, p_i\}} \mathbf{H}(\{\psi_{\alpha}\}, \{u_i, p_i\}) \quad (3)$$

The Hamiltonian H_T describes the system in the approximation opposite to the Born-Oppenheimer approximation, where one assumes that the dynamics of the electron is much slower than that of the phonons. We can describe this situation as anti-adiabatic. Actually, we do not make this crude approximation but mostly focus on the intermediate regime between adiabatic and anti-adiabatic.

At this stage, despite the different notation, our formalism is equivalent to the standard one (e.g. in [11]). We obtain the diabatic energy surface for the reactant shown in Figure 2 as a function of the reaction coordinates $\{u_i\}$ by fixing $(\psi_D = 1, \psi_A = 0, p_i = 0)$ in (2) and the diabatic energy surface for the products by fixing $(\psi_D = 0, \psi_A = 1, p_i = 0)$.

Note that, as in most ET theories, we neglect the possible energy radiation of photons induced by the dynamics of the electron charge during ET. We justify this approximation by the fact that the contribution of the coupling with the transverse electromagnetic field [16] which may induce transitions between electronic states, is rather weak compared to the electron-phonon coupling. The usual characteristic time for a photon emission would generally be larger than ns, which is much longer than the time for UFET we consider here. However, we do take into account the electrostatic contribution of the charge distribution to the energy of our system which may be important.

Many theories improving the standard theory (e.g. [11]) consider the phonons as quantum and treat the electron-phonon coupling as a small perturbation. These theories yield a rate for electron transfer given by a golden rule type expression. The transfer rate calculation is similar to that for the transition between two electronic quantum states coupled to the electromagnetic field [16]. However, note that the coupling with the electromagnetic field is small and thus must be considered as quantum. Then, perturbation theory at the lowest order correctly yields the Fermi golden rule. We must emphasize that the situation is very different when considering the coupling of the electron with the phonon bath because this coupling generally induces a large reorganization of the environment during ET and cannot be considered as small. In other words, the displacements of the nuclei in the close environment of the electron are much larger than their quantum zero point motion. The average number of phonons involved in the coherent state corresponding to the reorganization of the environment, is large. Clearly, a Fermi-like golden rule obtained within the lowest order perturbation theory, cannot be valid. A correct perturbative quantum treatment would require to consider the electron-phonon coupling up to very high orders, thus involving complex diagrams with many quantum phonons. However, a text-book result in quantum mechanics is that when many phonons (or quanta) are involved in physical processes, the classical limit should be recovered. Thus, we believe that a classical approximation on the phonons becomes a good approximation and, moreover, it is much simpler than high order quantum calculations.

2.2. EQUATIONS FOR COHERENT DYNAMICS OF ET

With the classical approximation for the phonons, the dynamics of the whole system is described by the standard Hamilton equations

$$i\hbar\dot{\psi}_\alpha = \frac{\partial \mathbf{H}}{\partial \psi_\alpha^*} = \frac{\partial H_T}{\partial \psi_\alpha^*} - \left(\sum_i k_{i,\alpha} m_i \omega_i^2 \left(u_i - \sum_\beta k_{i,\beta} |\psi_\beta|^2 \right) \right) \psi_\alpha \quad (4)$$

$$\ddot{u}_i + \omega_i^2 \left(u_i - \sum_\alpha k_{i,\alpha} |\psi_\alpha|^2 \right) = 0 \quad (5)$$

which combines a quantum equation for the electron and classical equations for the phonons.

The linear Eq. (5) has a general solution of the form $u_i = u_i^{(n)} + u_i^{(0)}$ where

$$u_i^{(0)}(t) = \sum_{\beta} k_{i,\beta} \left(|\psi_{\beta}(t)|^2 - \int_{-\infty}^t \cos \omega_i(t - \tau) \frac{d|\psi_{\beta}(\tau)|^2}{d\tau} d\tau \right) \quad (6)$$

and $u_i^{(n)} = a_i \cos(\omega_i t - \phi_i)$ is a solution with arbitrary amplitude a_i and phase ϕ_i of (5) without driving force (i.e., assuming $|\psi_{\alpha}|^2 = 0$). Substituting $u_i(t)$ as a function of $|\psi_{\alpha}|^2$ in Eq. (4) yields an effective equation which involves only the complex amplitudes ψ_{α}

$$i\hbar \dot{\psi}_{\alpha} = \frac{\partial H_T}{\partial \psi_{\alpha}^*} + \left(\int_{-\infty}^t \sum_{\beta} \Gamma_{\alpha,\beta}(t - \tau) \frac{d|\psi_{\beta}(\tau)|^2}{d\tau} d\tau + \zeta_{\alpha}(t) \right) \psi_{\alpha} \quad (7)$$

where

$$\Gamma_{\alpha,\beta}(t) = \sum_i k_{i,\alpha} k_{i,\beta} m_i \omega_i^2 \cos \omega_i t \quad (8)$$

will be assumed to be a smooth function because there are many modes i assumed to have a smooth frequency distribution and

$$\zeta_{\alpha}(t) = \sum_i k_{i,\alpha} m_i \omega_i^2 u_i^{(n)}(t) \quad (9)$$

is a colored random force. The time correlation function averaged over τ of oscillator i is

$$\langle u_i^{(n)}(t + \tau) u_j^{(n)}(\tau) \rangle_{\tau} = \delta_{i,j} \langle (u_i^{(n)})^2 \rangle \cos \omega_i t. \quad (10)$$

If we assume that the phonon bath is thermalized, we have $\langle (u_i^{(n)})^2 \rangle = k_B T / (m_i \omega_i^2)$ which yields the Langevin relation

$$\begin{aligned} \langle \zeta_{\alpha}(\tau) \zeta_{\beta}(t + \tau) \rangle_{\tau} &= \sum_i k_{i,\alpha} k_{i,\beta} m_i^2 \omega_i^4 \langle u_i^{(n)}(\tau) u_i^{(n)}(t + \tau) \rangle \\ &= k_B T \Gamma_{\alpha,\beta}(t). \end{aligned} \quad (11)$$

It can be verified that the total norm $\sum_{\alpha} |\psi_{\alpha}|^2 = 1$ is invariant by Eq. (7). The Fourier transform $\gamma_{\alpha,\beta}(\omega)$ of $\Gamma_{\alpha,\beta}(t)$ defined as

$$\Gamma_{\alpha,\beta}(t) = \frac{1}{\pi} \int_{-\infty}^{+\infty} \gamma_{\alpha,\beta}(\omega) e^{i\omega t} d\omega \quad (12)$$

which by Eq. (11) corresponds also to the Fourier transformed correlation function of the random force in the master Eq. (7), corresponds to the weighted phonon spectrum of the phonon bath

$$\gamma_{\alpha,\beta}(\omega) = \frac{\pi}{2} \sum_i k_{i,\alpha} k_{i,\beta} m_i \omega_i^2 (\delta(\omega - \omega_i) + \delta(\omega + \omega_i)). \quad (13)$$

It is also worthwhile to note that the reorganization energy can be calculated directly from the initial model Hamiltonian Eq. (2). Setting $u_i = p_i = 0$ (no reorganization), the energy of the system becomes $H_C = H_T + \sum_i \frac{1}{2} m_i \omega_i^2 (\sum_\alpha k_{i,\alpha} |\psi_\alpha|^2)^2$. Since H_T is the energy of the system after complete relaxation of the atoms, the reorganization energy is using definition (8)

$$H_{\text{reorg}} = H_T - H_C = -\frac{1}{2} \sum_{\alpha,\beta} \Gamma_{\alpha,\beta}(0) |\psi_\alpha|^2 |\psi_\beta|^2. \quad (14)$$

Note that even though the global Schrödinger equation describing the whole quantum system of the electron coupled with the electromagnetic and phonon fields was initially *linear*, the effective equation describing the electron dynamics becomes *nonlinear* after the elimination of the classically approximated electrostatic field (included in H_T) and phonon field.

At zero temperature (zero random force) it can be proved [14] that the effect of the term with kernel $\Gamma_{\alpha,\beta}$ is that the time average (over a sufficiently long time) of the energy $H_T\{\psi_\alpha\}$ always decays. Thus, the role of the phonon bath is clearly essential for ensuring the dissipation of the chemical reaction energy (when ET occurs). At finite temperature, the additional Langevin random force ensures the thermal equilibrium of the system and will thus generate ET since the initial state is out of equilibrium.

If for simplicity, we assume $\Gamma_{\alpha,\beta}(t) = 2\gamma_{\alpha,\beta}\delta_{\alpha,\beta}\delta(t)$, i.e., $\gamma_{\alpha,\alpha}$ is independent of ω (no frequency cut-off) and $\gamma_{\alpha,\beta} = 0$ for $\alpha \neq \beta$ (this approximation corresponds to the white noise approximation for the random force ζ_α by Eq. (11)), we find that the time derivative of the energy $\dot{H}_T = -\sum_\alpha \gamma_{\alpha,\alpha} (\frac{d|\psi_\alpha|^2}{dt})^2 < 0$ is necessarily negative because $\gamma_{\alpha,\alpha}(\omega)$ is obviously positive from its definition (13).

Since our theory requires less hypotheses than the standard theory, the latter should be recoverable with extra assumptions. Actually, Eq. (13) implies the existence of a cut-off corresponding to the largest phonon frequency ω_c of the phonon bath, i.e., of the environment. Thus, the white noise approximation is not correct when the frequencies of the phonon spectrum are much smaller than the electronic frequencies ($\hbar\omega_c \ll \Delta E_{el}$). This is just the situation in the adiabatic regime. Then, the adiabatic approximation can be used on the slow varying random force and as was explained in details in [15], Eq. (7) yields the main results of the Marcus theory [12]. In the adiabatic regime, the electronic states follow adiabatically the fluctuations of the environment (phonon bath) without any damping. ET can only

Figure 3. Scheme of the fluctuations versus time of the electronic levels on Donor D and Acceptor A in the normal regime (left) and in the inverted regime (right). Within the standard Marcus theory, ET is obtained at resonance (with some probability).

be obtained when the electronic levels become approximately resonant under the effect of the slow varying random force $\zeta_\alpha(t)$ the amplitude of which depends on the temperature (see Figure 3). This is just another representation of the barrier scheme shown in Figure 2 since this random force is the consequence of the nuclei displacements. However, the standard theory treats empirically the tunneling process (usually with the Landau-Zener formula) while in principle, our theory describes precisely this tunneling in all cases, including the strong and weak reactant limits.

2.3. MAIN ENERGY CONTRIBUTIONS TO THE NONLINEAR HAMILTONIAN FOR ET

Although Eq. (7) formally describes the electron dynamics in the general case, practical applications require to know precisely the antiadiabatic Hamiltonian $H_T(\{\psi_\alpha\})$ as well as the damping functions $\Gamma_{\alpha,\beta}(t)$. These terms involve in principle *all interactions* in the system but their theoretical calculation would require for each specific example expensive *ab initio* numerical investigations.

However, we propose simple (although rough) approximations of these functions with only a few parameters characterizing our system. Considering that the molecules and the redox orbitals α of the different electronic states α are weakly interacting, the antiadiabatic Hamiltonian H_T can be written as a sum

$$H_T(\{\psi_\alpha\}) = \sum_{\alpha} H_{\alpha}(|\psi_{\alpha}|^2) + H_T^{\text{int}}(\{\psi_{\alpha}\}) \quad (15)$$

where $H_{\alpha}(|\psi_{\alpha}|^2)$ is the energy of the isolated molecule or site α , which is only a function of its electronic charge $I_{\alpha} = |\psi_{\alpha}|^2$, and $H_T^{\text{int}}(\{\psi_{\alpha}\})$ is the perturbation due to the interaction. We may choose for simplicity the simplest *nonlinear* form

$$H_{\alpha}(I_{\alpha}) = \mu_{\alpha} I_{\alpha} + \frac{1}{2} \chi_{\alpha} I_{\alpha}^2 \quad (16)$$

where μ_α is the electronic level of the unoccupied state (i.e., before reorganization of the environment). The coefficient $\chi_\alpha = \chi_\alpha^R + \chi_\alpha^C$ of the nonlinear term may be viewed as the sum of two terms, where $\chi_\alpha^R < 0$ takes into account the energy gain due to the reorganization of the nuclei in the environment and $\chi_\alpha^C > 0$ is the capacitive energy due to the electrostatic field which is modified (taking into account the local dielectric constant ε_∞).

Thus, χ_α may be negative when the reorganization energy is prevalent (*soft* electronic state) or positive when the capacitive energy is prevalent (*hard* electronic state).

We suggest that the capacitive energy might be prevalent for electronic states α which are not involved in chemical bonds (e.g. those corresponding to inner layers of metallic ions, but not only). They generate relatively small reorganization energy and then we could have $\chi_\alpha > 0$. When the reorganization energy of electronic states is important, e.g. when they are involved in covalent bonds, this energy is generally prevalent and $\chi_\alpha < 0$.

$H_T^{\text{int}}(\{\psi_\alpha\})$ in (15) is the small interaction energy between the different sites. It may contain cross-capacitive and reorganization energy terms which depend on the electronic densities. These terms may play an important role in case of fine tuning (see the CEPO) but, for simplicity, we do not include them here. The most important term in the interaction energy originates from the overlap of the redox orbitals and depends on phase differences of the complex amplitudes ψ_α . Their role is essential in allowing electron tunneling. We choose for simplicity, the form

$$H_T^{\text{int}}(\{\psi_\alpha\}) = \sum_{\beta \neq \gamma} \lambda_{\beta,\gamma} (\psi_\beta \psi_\gamma^* + \psi_\beta^* \psi_\gamma) \quad (17)$$

where $\lambda_{\beta,\gamma}$ are parameters independent of the electronic densities. We could also assume that the overlap integrals $\lambda_{\alpha,\beta}$ depend on the electronic densities through reorganization but this dependence has not any essential role in our theory and can be discarded.

Assuming that we are close to the inversion point, the differences between the electronic energy levels are comparable (and remain so while they vary) to the characteristic phonon energies, which means that the phonon bath remains always efficient for generating energy damping in the electron dynamics. Then, we may drop the details of the damping functions $\Gamma_{\alpha,\beta}(t)$ which again would affect quantitatively (but not qualitatively) the details of the dynamics of ET and the rate of ET. We also assume for simplicity that the non-essential off-diagonal terms $\Gamma_{\alpha,\beta}$ are zero for $\alpha \neq \beta$. Finally, we can set $\Gamma_{\alpha,\beta}(t) = 2\gamma_\alpha \delta(t) \delta_{\alpha,\beta}$ where $\gamma_{\alpha,\alpha} = \gamma_\alpha$ are constant.

Before ending this section, let us now make some rough estimate of the order of magnitude of the coefficients involved in our model that are physically reasonable. Electronic energy differences are usually measured in electron-volt (eV). However, close to the inversion point they should become much smaller and of the order of

the largest phonon energies, which are of the order of few 10^{-1} eV. Nevertheless, the reorganization and electrostatic energies can be counted in eV units which make realistic coefficients χ_α of the order of few units $\times \hbar$. The small coupling parameters $\lambda_{\alpha,\beta}$ should be of the order of $10^{-2} \times \hbar$ for reaching an absolute maximum speed for ET of a fraction of ps. Thus their energies lie in the range of thermal energies at room temperature T_R ($k_B T_R \approx 3 \cdot 10^{-2}$ eV). Concerning the damping coefficients, γ_α , it is worthwhile to remind that both the damping and the reorganization energy originate from the phonon bath and are related. Coefficient χ_α^R the reorganization energy is equal to $-\Gamma_{\alpha,\alpha}(0)$ because of Eq. (14). With the assumption, $\gamma_\alpha(\omega) = \gamma_{\alpha,\beta}(\omega)\delta_{\alpha,\beta}$, it can be also assumed for simplicity that $\gamma_\alpha(\omega)$ is constant with a cut-off at ω_c . Then, we get with Eq. (12), $\chi_\alpha^R = -\Gamma_{\alpha,\alpha}(0) = 2\omega_c\gamma_\alpha/\pi$. Thus the order of magnitude we could expect for γ_α could be $\approx -\pi\hbar\chi_\alpha^R/(2\hbar\omega_c)$. Considering a maximum for the phonon energy $\hbar\omega_c$ of the order of 10^{-2} eV as above, we find that reasonable values for γ_α could be of the order of several $10 \times \hbar$.

3. The Dimer Model at Zero Temperature

3.1. GENERAL CASE

We consider first the two state donor-acceptor system ($\alpha = D$ or A). With the above assumptions, the Hamiltonian H_T of this dimer takes the form

$$H_T(\psi_D, \psi_A) = \mu_D|\psi_D|^2 + \frac{1}{2}\chi_D|\psi_D|^4 + \mu_A|\psi_A|^2 + \frac{1}{2}\chi_A|\psi_A|^4 - \lambda(\psi_D^*\dot{\psi}_A + \psi_A^*\dot{\psi}_D) \quad (18)$$

where constant λ is supposed to be small, real (and positive for fixing the ideas).

Then, at zero temperature ($\zeta_\alpha = 0$) we obtain from Eq. (7) two coupled equations

$$i\hbar\dot{\psi}_\alpha = \left(\mu_\alpha + \chi_\alpha|\psi_\alpha|^2 + \gamma_\alpha \frac{d|\psi_\alpha|^2}{dt} \right) \psi_\alpha - \lambda\psi_\beta \quad (19)$$

where (α, β) denotes the pair (D, A) or (A, D) respectively. These two equations describe the quantum tunneling of the electron coupled with the phonon bath at zero temperature.

When the transfer integral is zero $\lambda = 0$, there is no coupling between the two units so that $|\psi_D|^2$ and $|\psi_A|^2$ are time constant. Then, $\psi_\alpha(t) = e^{-iE_\alpha t/\hbar}\psi_\alpha(0)$. The electronic energy level, E_α , at site α depends on the electron densities $|\psi_\alpha|^2$:

$$E_\alpha(I_\alpha) = \frac{dH_\alpha}{dI_\alpha} = \mu_\alpha + \chi_\alpha I_\alpha. \quad (20)$$

These energy levels are those of an electron which would tunnel very slowly (λ very small) while the nuclei reorganize adiabatically then following the electron

Figure 4. Energy profiles $\epsilon_T(I_A)$ versus electron transfer I_A (defined by Eq. (21)) for different values of μ_A when $\chi_D + \chi_A < 0$ (left) (soft anharmonicity) and when $\chi_D + \chi_A > 0$ (right) (hard anharmonicity).

density (inverse Born-Oppenheimer approximation). We call these energy levels *antiadiabatic*.

Neglecting the small interaction energy in (18), the main contribution to the energy variation $\epsilon_T(I_A) = H_D(1 - I_A) + H_A(I_A) - H_D(1) - H_A(0)$ of the system (18) is only a function of the electron density I_A on the acceptor (since $|\psi_D|^2 + |\psi_A|^2 = I_D + I_A = 1$)

$$\epsilon_T(I_A) = (\mu_A - \mu_D - \chi_D)I_A + \frac{1}{2}(\chi_A + \chi_D)I_A^2 \quad (21)$$

Figure 4 shows some possible profiles of $\epsilon_T(I_A)$. The derivative of this curve with respect to I_A is the difference $E_A(I_A) - E_D(1 - I_A)$ between the electronic energy level of A and D at charge transfer I_A . Consequently, there is electronic resonance $E_A(I_A) = E_D(1 - I_A)$ when this curve has an horizontal slope. At the Marcus inversion point this slope is zero at zero transfer ($E_A(0) = E_D(1)$), i.e., $\mu_A = \mu_D + \chi_D$.

There are two possible situations which are qualitatively different. Either the curve $\epsilon_T(I_A)$ has negative convexity, i.e., $\chi_A + \chi_D < 0$ (Figure 4 left) (soft dimer) or positive convexity when $\chi_A + \chi_D > 0$ (hard dimer).

- When the dimer is soft (Figure 4 left), which we believe to be physically the most common case, the reorganization energy of the system is prevalent, there is an energy barrier in the normal Marcus regime $\mu_A > \mu_D + \chi_D$ which disappears just at the inversion point $\mu_A = \mu_D + \chi_D$.³ Since the energy must decay because of the dissipation, ET will occur in principle as soon as the energy barrier disappears. Actually, ET is globally faster just at the inversion point because the initial resonance triggers ET. ET starts with a linear slope while beyond the inversion point it needs a small initial perturbation (next growing exponentially

Figure 5. Electron density I_D on the donor (full line) and I_A on the acceptor (dashed line) versus time for a soft dimer model at the inversion point and zero temperature where $\mu_D = 2$, $\chi_D = -1$, $\mu_A = 1$, $\chi_A = -0.75$, $\lambda_{AD} = 10^{-2}$, $\gamma_D = \gamma_A = 40$ (the time unit is 1 ps = 10^{-12} s for energy in units of eV).

(see Ref. [15] for details). The observed dynamics in Figure 5 confirms the existence of ET at the scale of picoseconds with physically reasonable parameters. The time scale of ET of course depends on the damping constants γ_D and γ_A . Without damping, no ET may occur because there is no energy dissipation. When the damping increases, the time scale decreases till it reaches an optimum which roughly corresponds to the cross-over between underdamped to overdamped. Next for very large damping the time scale for ET diverges again.

Beyond the inversion point $\mu_A < \mu_D + \chi_D$ in the inverted regime, there is no initial resonance and ET becomes slower for the reason we mentioned above. Moreover, when the difference $\mu_D + \chi_D - \mu_A$ becomes larger than the phonon energy cut-off $\hbar\omega_c$, the phonon energy damping vanishes so that at zero temperature, ET disappears. Actually, it may occur but very slowly by photon emission (not treated in the model) which yields a *chemiluminescent* ET reaction.

- When the dimer is hard (Figure 4 right), ET does not occur at zero temperature, neither in the normal regime nor at the inversion point, simply because the energy on the acceptor is larger than the energy on the donor. When μ_A is below $\mu_D + \chi_D$, $\epsilon_T(I_A)$ gets its energy minimum at $0 < I_A^m = (\mu_D + \chi_D - \mu_A)/(\chi_A + \chi_D) < 1$. Then ET occurs but is incomplete while the ground-state of the system is obtained at I_A^m . The physical reason is that when the electrostatic energy is prevalent, sharing the electron density on two sites may reduce the total energy. Since the transfer integral is small, there are two quantum states where ψ_D and ψ_A are in phase or out of phase which are close in energy, one of them being the ground-state.⁴ When $\mu_D > \chi_A + \mu_A$ ET becomes complete because the minimum of $\epsilon_T(I_A)$ reaches $I_A^m = 1$.

3.2. COHERENT ELECTRON-PHONON OSCILLATOR (CEPO)

The special case corresponding to $\chi_D + \chi_A = 0$ is especially interesting. In this situation, the reorganization energy and the electrostatic energy exactly balance each other. As a result, the energy of the system remains constant at any partial electron transfer. Thus, the derivative of the energy variation $\epsilon_T(I_A)$ with respect to I_A is zero, which implies that the electronic resonance between the electronic levels of the donor and of the acceptor persists at any transfer. In this case, the reaction energy is zero but despite ET being ultrafast, it is also reversible.

We could say *a priori* that this situation is identical to a standard linear tunneling of an electron between two degenerate electronic levels. However, there is an essential difference because the tunneling mode in our model is heavily coupled to its environment. Then, the large electron density oscillation is accompanied coherently by a large amplitude reorganization of the environment. Another essential consequence is that the degenerate electronic levels oscillate as well with large amplitudes, which could have important consequences in the system's reactivity as we shall see in the next section for trimer models. We call this new mode *Coherent Electron-Phonon Oscillator* (CEPO). Let us note that this electron oscillation between two nonlinear electronic states is analogous to the situation of Targeted Energy Transfer between two weakly coupled anharmonic oscillators described earlier [17, 18].

When $\epsilon_T(I_A) = 0$, the Hamiltonian of this CEPO is reduced to the small interaction term $H_T^{\text{int}}(\{\psi_\alpha\})$. Without damping, it describes a single nonlinear oscillator since this Hamiltonian is integrable because of energy and norm conservation. With the special form chosen in Eq. (18), $H_T^{\text{int}} = -\lambda(\psi_D^* \psi_A + \psi_A^* \psi_D)$, explicit calculations can be made which show unusual properties for this anharmonic oscillator. Actually, in this specific example, it looks like a harmonic oscillator but with a maximum amplitude which cannot be exceeded and a variable damping which may be positive or negative but systematically operates in order to bound the oscillation amplitude.

Considering the set of (real) conjugate action angle variables $(I_\alpha, \theta_\alpha)$ defined by $\psi_\alpha = \sqrt{I_\alpha} e^{-i\theta_\alpha}$, we define new conjugate variables by $(\theta = \theta_A - \theta_D, I = (I_A - I_D)/2)$ and $(\theta_0 = \theta_A + \theta_D, I_0 = (I_A + I_D)/2)$. Using the norm conservation $2I_0 = I_A + I_D = 1$, Eqs. (19) become

$$\hbar \dot{\theta} = \lambda \frac{4I}{\sqrt{1-4I^2}} \cos \theta + \gamma \dot{I} \quad (22)$$

$$\hbar \dot{I} = -\lambda \sqrt{1-4I^2} \sin \theta \quad (23)$$

where $\gamma = \gamma_A + \gamma_D$. These equations are those of a damped oscillator with Hamiltonian

$$H_T^{\text{int}} = -\lambda \sqrt{1-4I^2} \cos \theta \quad (24)$$

This model was exactly solved in the absence of damping in [17]. In our case, energy is not conserved but we have

$$H_T^{\text{int}} = -\gamma \dot{I}^2 < 0 \quad (25)$$

Then, Eqs. (24) and (23) yield

$$H_T^{\text{int}2} + \hbar^2 \dot{I}^2 = \hbar^2 \Omega^2 \left(\frac{1}{4} - I^2 \right) \quad (26)$$

with

$$\hbar \Omega = 2\lambda \quad (27)$$

and then $H_T^{\text{int}} = F(I, \dot{I}) = \pm \hbar \sqrt{\Omega^2(\frac{1}{4} - I^2) - \dot{I}^2}$ is only a function of I and $\dot{I}$. Actually, the sign of $F(I, \dot{I})$ is the one of the coupling energy H_T^{int} which is well defined because of Eq. (25). $F(I, \dot{I})$ is necessarily monotonically decreasing as a function of time. Thus, if the sign of $F(I, \dot{I})$ is initially negative it will remain negative at all times. If it is positive, it will decay until it vanishes and then continue to decay negative. Then, the time differentiation of Eq. (26) yields, using Eq. (25)

$$\ddot{I} - \frac{\gamma}{\hbar^2} F(I, \dot{I}) \dot{I} + \Omega^2 I = 0 \quad (28)$$

which is the equation of a harmonic oscillator at frequency Ω with a damping parameter $-\frac{\gamma}{\hbar^2} F(I, \dot{I})$ which depends on I and $\dot{I}$ and may be positive or negative. If the initial energy is positive (i.e., $\cos \theta < 0$ at time zero in Eq. (24)), the effective damping is negative which means the amplitude of the harmonic oscillation increases while the coupling energy H_T^{int} decreases. When it vanishes, the sign of the damping is reversed so that the amplitude of the oscillation decreases again till it reaches the energy minimum $-\lambda$ of $H_T^{\text{int}} = F(I, \dot{I})$ at $I = \dot{I} = 0$ (and $\cos \theta = 1$). Figure 6 shows the time evolution of a CEPO dimer with initial conditions at its maximum amplitude.

The time oscillations of I are accompanied by large amplitude oscillation of the degenerate electronic energy level on Donor and Acceptor since we have

$$E_D(t) = E_A(t) = \mu_D + \chi_D \left(\frac{1}{2} - I(t) \right) = \mu_A + \chi_A \left(\frac{1}{2} + I(t) \right). \quad (29)$$

Since the (underdamped) frequency Ω of this CEPO (27) is determined by the small coupling constant λ , it ranges in the phonon spectrum and could be experimentally confused with a pure phonon mode. However, this low frequency oscillator is associated with a *large amplitude* oscillation of the electronic density between

Figure 6. Electron density $I_D = 1/2 - I$ on the donor and $I_A = 1/2 + I$ on the acceptor when the dimer is a Coherent Electron-Phonon Oscillator (CEPO) ($\mu_D = 2$, $\chi_D = -1$, $\mu_A = 1$, $\chi_A = 1$, $\lambda = 10^{-2}$, $\gamma_D = \gamma_A = 1$).

two distant sites associated with a *large amplitude* reorganization of the environment. This coherent mode involves collectively the whole set of phonons without involving any specific phonon. It is not a normal mode. Otherwise, because of the charge oscillation, it is highly polar and should be quite visible in IR experiments. A CEPO is fragile because it requires a fine tuning of the donor-acceptor system. Thus, minor mutations which change the parameters beyond the energy scale determined by the small coupling energy λ , destroy the CEPO. Applied macroscopic electric fields could also change the fine tuning when they are sufficiently strong.

4. Catalytic ET at Zero Temperature with a CEPO

4.1. PRINCIPLE OF THE EFFECT

We now describe the catalytic effect of a CEPO on electronic reactivity. Let us consider an electron on a D state that cannot be transferred to an A state (e.g. large energy barrier). We show that in the presence of a third ‘catalyst’ state, C , which is tuned to D in order to form a CEPO, ET between D and A may become extremely efficient and ultrafast. Figure 7 shows a scheme of the system and of the transfer mechanism.

Let us assume that the donor state initially receives an electron, for example by photoexcitation which raises a lower energy electron up to this D state. Its electronic level varies as a function of its occupancy because of the reorganization of the environment and electrostatic energy. When it reaches full occupancy, the donor electronic level becomes resonant with the unoccupied electronic level of the catalyst. As explained above, the CEPO is then at maximum amplitude. Slow electronic level oscillations are generated on the donor-catalyst system. Then, if a

Figure 7. Principle of ET with a Coherent Electron-Phonon Oscillator: Two weakly coupled molecular units donor and catalyst generate a CEPO. This system is weakly coupled to a third unit, the acceptor (left scheme). An electron initially on the donor generates an oscillation of the electronic level of the CEPO. If the bare electronic level of a third molecular unit (acceptor) is included in the interval of variation, as soon as resonance between the CEPO and the acceptor is reached, ET is triggered irreversibly to the acceptor (right scheme).

third unoccupied electronic site with an electronic level in the interval of variation of the CEPO is present and weakly coupled with the donor-catalyst system, a resonance is shortly established during the first oscillation.

Then, assuming a small but nevertheless sufficiently large coupling, a substantial part of the electronic density flows to the acceptor. As a consequence, the electronic density on the CEPO is reduced, which immediately interrupts the oscillation because the resonance Donor-Catalyst is detuned. Since there has been already a substantial energy dissipation, the electron cannot return to its initial state. As a result, the electronic state is forced to flow to a final state which is a local minimum of the energy. If the nonlinear parameters of the acceptor are appropriately chosen, the only accessible minimum of energy could correspond to the whole electron density on the acceptor.

There are two stages in this catalytic ET process. First, the triggering of the resonance to the Acceptor is ultrafast because it occurs within less than half a period of oscillation of the CEPO. Second, ET to the acceptor continues, initially fast but then slowing down as a function of transfer because the electronic resonances disappear. However, energy dissipation makes the transfer to the acceptor irreversible and thus it is forced to terminate after some longer time.

4.2. ULTRAFAST ET ON A TRIMER MODEL

We illustrate these principles on the trimer model with Hamiltonian

$$H_T(\{\psi_\alpha\}) = \sum_{\alpha} \mu_{\alpha} |\psi_{\alpha}|^2 + \frac{1}{2} \chi_{\alpha} |\psi_{\alpha}|^4 - \sum_{\alpha \neq \beta} \lambda_{\alpha, \beta} \psi_{\alpha}^* \psi_{\beta} \quad (30)$$

where $\alpha = D, C$ or A . Using the action-angle coordinates defined as above $\psi_\alpha = \sqrt{I_\alpha} e^{-i\theta_\alpha}$, the dynamical Eqs. (7) of this system with damping at zero temperature and with the assumptions described in Section 2.3 become

$$\hbar \dot{I}_\alpha = -2 \sum_\beta \lambda_{\alpha,\beta} \sqrt{I_\alpha I_\beta} \sin(\theta_\alpha - \theta_\beta) \quad (31)$$

$$\hbar \dot{\theta}_\alpha = E_\alpha + \sum_\beta \lambda_{\alpha,\beta} \sqrt{\frac{I_\beta}{I_\alpha}} \cos(\theta_\alpha - \theta_\beta) + \gamma_\alpha \dot{I}_\alpha \quad (32)$$

where $E_\alpha = \mu_\alpha + \chi_\alpha I_\alpha$. We consider a situation where the energy of the electron on A is lower than on D and such that there is an energy barrier as shown in Figure 4. In this situation

$$\chi_A + \chi_D < 0 \quad (33)$$

$$\mu_A + \frac{1}{2}\chi_A < \mu_D + \frac{1}{2}\chi_D. \quad (34)$$

In the absence of Catalyst ($I_C = 0$ or $I_D + I_A = 1$), ET is not possible at zero temperature. We now show that the presence of a catalyst may induce ultrafast ET.

Neglecting the small coupling constants $\lambda_{\alpha,\beta}$, and using the CEPO conditions $\mu_C = \mu_D + \chi_D$, $\chi_D = -\chi_C$, the energy variation $\epsilon_T(I_D, I_A) = H_D(I_D) + H_C(I_C) + H_A(I_A) - H_D(1) - H_C(0) - H_A(0)$ is only a function of I_D and I_A , since $I_D + I_C + I_A = 1$

$$\epsilon_T(I_D, I_A) = (\mu_A - \mu_D)I_A - \chi_D I_A I_D + \frac{1}{2}(\chi_A - \chi_D)I_A^2 \quad (35)$$

where $0 \leq I_D \leq 1$, $0 \leq I_A \leq 1$ and $I_D + I_A \leq 1$. We have

$$\frac{\partial \epsilon_T}{\partial I_D}(I_D, I_A) = E_D(I_D) - E_C(1 - I_A - I_D) = -\chi_D I_A \quad (36)$$

$$\begin{aligned} \frac{\partial \epsilon_T}{\partial I_A}(I_D, I_A) &= E_A(I_A) - E_C(1 - I_A - I_D) \\ &= \mu_A - \mu_D - \chi_D I_D + (\chi_A - \chi_D)I_A. \end{aligned} \quad (37)$$

The extrema of this two variable function are obtained when the electronic energy levels of the three sites are equal. The first equation requires $I_A = 0$ and then, the second equation yields $\mu_A = \mu_D + \chi_D I_D$. This equation can be fulfilled only if μ_A belongs to the interval of frequency variation of the CEPO which yields

$$\mu_D + \chi_D \leq \mu_A \leq \mu_D \quad \text{if } \chi_D < 0 \quad \text{or} \quad (38)$$

$$\mu_D \leq \mu_A \leq \mu_D + \chi_D \quad \text{if } \chi_D > 0. \quad (39)$$

Figure 8. 3D plot of the energy surface $\epsilon_T(I_D, I_A)$ defined by (35) versus I_A and I_D and contour lines in projection for an example where conditions (33), (34) and (38) are fulfilled ($\mu_D = 2$, $\chi_D = -1$, $\mu_C = 1$, $\chi_C = 1$, $\mu_A = 1.5$, and $\chi_A = -0.75$). The triple resonance point S and the resonance lines D_{DC} , D_{DA} and D_{CA} are also shown (dashed lines). The electron path (real and averaged) is schematically represented.

When both conditions (33) and (34) and one of the conditions (38) and (39) are fulfilled, the energy surface (35) appears as shown in Figure 8.

There are three resonance lines:

- D_{DC} defined by $E_D = E_C$ which yields $I_A = 0$ from Eq. (36).
- D_{CA} defined by $E_c = E_A$ which yields $-\chi_D I_D + (\chi_A - \chi_D) I_A = \mu_D - \mu_A$ from Eq. (37).
- D_{DA} defined by $E_D = E_A$ which yields $-\chi_D I_D + \chi_A I_A = \mu_D - \mu_A$ from Eqs. (36) and (37).

D_{DC} , D_{CA} and D_{DA} intersect at the same point with coordinates $S = (I_D = I_S, I_A = 0)$ with $0 < I_S = (\mu_A - \mu_D)/\chi_D < 1$.

Moreover, $\epsilon_T(I_D, I_A)$ is constant and zero on the resonance line D_{DC} where $I_A = 0$ at the edge of the domain of definition. It is also constant and zero on the line (D_0) defined by $-\chi_D I_D + \frac{1}{2}(\chi_A - \chi_D) I_A = \mu_D - \mu_A$. The intersection point (S) is a saddle point of the surface. Along the other edge on the line $I_D + I_A = 1$ from (D) to (A), ϵ_T exhibits an energy barrier, increasing first from zero and then decreasing below zero with a maximum $\epsilon_T^m = -(\mu_D + \chi_D - \mu_A)^2 / (2(\chi_A + \chi_D)) > 0$ at $I_A = 1 - I_D = (\mu_D + \chi_D - \mu_A) / (\chi_A + \chi_D)$ while on the other border line $I_D = 0$, joining (C) to (A), ϵ_T is monotonically decreasing.

At zero damping, the trimer Hamiltonian (19), which has $3 + 3$ degrees of freedom, is not integrable because there are only two time invariants: only the total

energy and the total norm are conserved. However, it is trivially integrable at zero coupling. Then, in the weakly coupled system, most of the non resonant solutions are preserved as KAM tori. Narrow chaotic regions (Arnold webs) located close to the resonance points, appear but are generally confined and negligible. However, in our case and because the donor and catalyst form a CEPO, an extended Arnold web appears along the edge line D_{DC} where there is both resonance $E_D = E_C$ and constant energy. Indeed, as shown in Ref. [14], at zero damping, with an initial state where the electron is on the donor, the trimer system exhibits large amplitude chaotic trajectories mostly in the vicinity of the saddle point S unlike the isolated donor-catalyst dimer which is integrable. Obviously in this case, no complete and irreversible ET may occur at zero damping because the reaction energy cannot be dissipated.

When there is damping, this chaotic behavior persists transiently but tends to disappear in the limit of strong damping. This is the origin of the small random-looking oscillations which are visible on Figure 9.

Figure 9 shows an example of numerically calculated transfer of electron with Eqs. (19) extended for the trimer. Considering the electron initially on the donor, the CEPO oscillation is initiated and the electron density starts to flow toward the catalyst only and close to the edge line DC. Then, arriving in the close vicinity of the saddle point,⁵ the resonance with the acceptor becomes effective and the electron density starts to flow to the acceptor. Since some energy has already been dissipated, the electron cannot return to the edge line and has to move with its own dynamics to the unique minimum of the surface on the acceptor. The electron density on the catalyst reaches a maximum which does not correspond to a full occupation and decays to zero while simultaneously the electron density on the donor continues to decay to zero.

Figure 9. Electron density on donor (solid), acceptor (dashed), and catalyst (long dashed) versus time in the trimer for the example shown Figure 8 where $\lambda_{DA} = \lambda_{AC} = \lambda_{DC} = 10^{-2}$ and damping $\gamma_D = \gamma_C = \gamma_A = 10$.

In summary, the role of the CEPO formed by the weakly coupled donor-catalyst system is to trigger ET to the Acceptor even at zero temperature, while in the absence of the small perturbation induced by the catalyst, direct ET from donor to acceptor is impossible at low temperature because of the existence of a large energy barrier.

4.3. ANALYTIC CALCULATION OF CHARGE CURRENTS OUT OF RESONANCE

Neglecting the fast oscillations, we can derive an explicit, smooth equation for the average dynamics of the system which is valid at zero temperature and at small couplings $\lambda_{\alpha,\beta}$ assumed to be at the order of λ . This equation only concerns the charge current flows and does not involve the phases θ_α . It describes only the incoherent dynamics of the system out of resonance and thus is not valid in the vicinity of the resonance lines $D_{\alpha,\beta}$ where $E_\alpha = E_\beta$ for all pairs α, β . It is thus not valid at the first stage of the ultrafast ET described above, when ET dynamics is coherent, i.e., when the electronic charge is on Donor and Catalyst, but it is valid for the final stage of ET.

For that purpose, we define $\bar{I}_\alpha$ as

$$I_\alpha = \bar{I}_\alpha + \frac{2}{\hbar} \sum_{\beta} \lambda_{\alpha,\beta} \frac{\sqrt{I_\alpha I_\beta}}{\dot{\theta}_\alpha - \dot{\theta}_\beta} \cos(\theta_\alpha - \theta_\beta). \quad (40)$$

When there is no resonance $E_\alpha \neq E_\beta$ for $\alpha \neq \beta$, and since $\dot{\theta}_\alpha \approx E_\alpha/\hbar$, the fluctuations around $\bar{I}_\alpha$ in Eq. (40) are fast at frequency $(E_\alpha - E_\beta)/\hbar$. Their amplitude at coupling of order λ is bounded at any time and thus this term does not contribute in average to the large amplitude variation of I_α involved in ET which is essentially contained in $\bar{I}_\alpha$. Using Eq. (31), we have

$$\hbar \dot{\bar{I}}_\alpha = -2 \sum_{\beta} \lambda_{\alpha,\beta} \frac{d}{dt} \left(\frac{\sqrt{I_\alpha I_\beta}}{\dot{\theta}_\alpha - \dot{\theta}_\beta} \right) \cos(\theta_\alpha - \theta_\beta). \quad (41)$$

Eq. (32) yields the time derivatives $\dot{\theta}_\alpha$ and $\dot{\theta}_\beta$ as functions of $\{I_\alpha, \theta_\alpha\}$, as Eq. (31) for $\dot{I}_\alpha$. Then, it comes out after time derivation and substitution of the time derivatives $\dot{\theta}_\alpha$ and $\dot{I}_\alpha$ that $\dot{\bar{I}}_\alpha$ is a function of the set of variables $\{I_\alpha\}$ and $\{\theta_\alpha\}$ and is of order 2 in λ . We do not give the complete set of terms here (for the sake of brevity) which contains many sine products like $\lambda_{\alpha,\beta} \lambda_{\alpha,\gamma} \cos(\theta_\alpha - \theta_\beta) \cos(\theta_\alpha - \theta_\gamma)$ or $\lambda_{\alpha,\beta} \lambda_{\alpha,\gamma} \cos(\theta_\alpha - \theta_\beta) \sin(\theta_\alpha - \theta_\gamma)$. Since the set of $\{I_\alpha\}$ does not involve any resonance, most sine products time average to zero at leading order in λ , except for the terms which are sine squared, such as $\cos^2(\theta_\alpha - \theta_\beta)$, which average to 1/2. These terms are essentially provided by the damping coefficient γ_α . Then, keeping only those terms, it comes out that the average $\langle \dot{\bar{I}}_\alpha \rangle$ over time long at the scale of the fast fluctuations but short

at the order $1/\lambda^2$ becomes

$$\langle \dot{I}_\alpha \rangle \approx - \sum_{\beta} J_{\alpha,\beta} \quad (42)$$

where $J_{\alpha,\beta}$ is the charge current from α to β along the bond α, β

$$J_{\alpha,\beta} = -J_{\beta,\alpha} = \frac{2\lambda_{\alpha,\beta}^2}{\hbar^2} \frac{\gamma_\alpha + \gamma_\beta}{E_\alpha - E_\beta} I_\alpha I_\beta. \quad (43)$$

This formula describes the average current in the configuration space $\{I_\alpha\}$. It extends a formula which was established in Ref. [15] but only for the dimer model and by different means.⁶

We note first that the bond current along the bond α, β is zero in the absence of damping $\gamma_\alpha + \gamma_\beta = 0$ which should be expected because in the non-resonant case the dynamics of the trimer reduces to a KAM torus where I_α does not vary in average but only fluctuates.

Second, we note that the total derivative $\sum_\alpha \langle \dot{I}_\alpha \rangle = \sum_{\alpha,\beta} J_{\alpha,\beta}$ is zero, which is consistent with the total norm conservation.

Third, the current sign is to flow from the higher electronic energy level in the bond to the lower electronic energy level. It is larger when the energy level approaches resonance.

We also note that in case of resonance, some denominators $E_\alpha - E_\beta$ vanish. Then, the current diverges, but this is an artifact of our approximation of incoherent phase valid in the absence of resonance. Actually, the dynamics becomes coherent and faster at order $\lambda_{\alpha,\beta}$ instead of $\lambda_{\alpha,\beta}^2$.

It can be assumed within the same calculation that $\{\gamma_\alpha\}$ depend on the energy level difference $E_\alpha - E_\beta$ involved in the bond (α, β) . Then, we have

$$J_{\alpha,\beta} = -J_{\beta,\alpha} = \frac{2\lambda_{\alpha,\beta}^2}{\hbar^2} \frac{\gamma_\alpha(E_\alpha - E_\beta) + \gamma_\beta(E_\alpha - E_\beta)}{E_\alpha - E_\beta} I_\alpha I_\beta \quad (44)$$

This formula shows that when this energy level difference exceeds the phonon energy cut-off $\hbar w_c$, the current flow vanishes at zero temperature. Actually, ET is expected to continue slowly because of the interaction with the electromagnetic field and also small thermal fluctuations if the temperature is not zero.

A consequence of this calculation is that close to the Marcus inversion point and at low temperature, the rate of electron transfer cannot be constant as a function of time but depends on the electron transfer itself. Generally, it slows down as a function of time so that the density of electron transferred may look like a stretched exponential. Actually, this depends on the details of the damping function.

5. Discussion of ET in the PRC and Concluding Remarks

Subpicosecond oscillations in the PRC have been observed [2] and demonstrate the existence of a coupling between ET and coherent vibrational motions [19]. However, it is still unclear what the reason for these oscillations is or whether they are connected to ET. Quantum chemical methods have been used to calculate wave functions, energies and coupling parameters. It has been confirmed that there is indeed an increase of electron density on $\mathbf{B}_A$ during some time after excitation of $\mathbf{P}$ (see Refs. [20]). Recently more accurate quantum chemical calculations (see Refs. in [20]) of the PRC have been performed by solving the time-dependent and time-independent Schrödinger equation. It is shown that there is an important change of geometry of the special pair dimer from neutral $\mathbf{P}^*$ to ionized $\mathbf{P}^+$ while the reorganisation of $\mathbf{B}_A$ from neutral to ionized is small. Moreover, there are a number of low frequency normal modes of $\mathbf{P}$ which are clearly coupled to the primary charge separation. It is suggested that (mainly) the oscillating charge of the acetyl group modifies the relative energies of the local LUMOs. Otherwise, it is mentioned that there is experimental and theoretical evidence that the primary charge separation is activationless. It is also noted that the energy of $\mathbf{P}^+ - \mathbf{B}_A^-$ is strongly correlated to the rate of electron transfer. The maximum efficiency is obtained when this energy is slightly below the energy of $\mathbf{P}^* - \mathbf{B}_A$. These features seem to be qualitatively in quite good agreement with the predictions of our theory when assuming the system $\mathbf{P}^* - \mathbf{B}_A$ is a CEPO.

Actually, our approach starts from fundamental considerations about ET which are valid in general and are not specific to a particular physical system. It is based on the remark that in the vicinity of the Marcus inversion point (i.e., specifically in the region where ultrafast ET may occur), electron and phonon dynamics get comparable time scale. Thus, the standard theory which assumes the adiabatic approximation, cannot describe properly ET in this regime, not even with some perturbative corrections, because ultrafast ET is intrinsically a *nonadiabatic phenomenon*. Our theory uses basically the same general framework and the same hypothesis as the standard theory (classical harmonic phonons) *except that it discards the adiabatic approximation* by keeping the electronic variables independent of the atomic variables. Thus, our theory can fully describe the electron dynamics in all cases when it is almost adiabatic or when it becomes nonadiabatic and intricated with the phonon dynamics as well.

The classical harmonic phonon field is formally eliminated through exact transformations and then manifests itself through the nonlinearities, random forces, and memory kernels in an effective extended Schrödinger equation describing the electron dynamics. With some reasonable simplifications (considering the nonlinearities at lowest significant order and weak coupling), our model only involves few essential parameters which are physically significant. We consider these parameters given but they could be obtained from *ab initio* calculations or/and experimental data for each specific situation of ET.

Since the phase of the electronic wavefunction and of the phonon oscillations is intrinsically involved in electron dynamics, our theory can describe coherent ET (nonlinear tunnelling) which may occur at low temperature and incoherent ET when the temperature (and thus the random force) becomes large, as well as intermediate regimes.

Optimizing the rate of ET naturally leads us to consider the dimer model at zero temperature where reorganization energy and capacitive energy just balance in order to get faster ET, i.e., when there is no energy barrier *at all intermediate ET*. This situation requires more conditions than just being at the Marcus inversion point. Then, this optimized ET is precisely activationless and associated with large amplitude coherent phonon oscillations, but it is also reversible. Because of that, it is not physically efficient in itself but as we explained, electronic level oscillations are generated and may trigger ET to a third site, thus removing the large energy barrier for direct ET from the first site. This trimer model appears as the simplest possible device for obtaining both *ultrafast* and irreversible ET. More complex models could also be described with our approach but are left to further investigations (logical devices?).

The physical consequences of our theory are far from having been explored in detail. In particular, further investigations are required for understanding how the thermal fluctuations (represented by the random force $\zeta_\alpha(t)$ in Eq. (7)) smear out the zero temperature coherent phenomena and exactly how this theory connects to standard theory when temperature increases.

Nevertheless, at the present stage it is worthwhile to note that the observed features in the Photosynthetic Reaction Center (PRC) described in the introduction have strong qualitative similarities with our findings in the trimer model with CEPO.

The excited dimer of bacteriochlorophylls $\mathbf{P}^*$ and the ancillary bacteriochlorophyll $\mathbf{B}_A$ of the A branch form a well-tuned Coherent Electron Phonon Oscillator (CEPO). This seems to be supported by the findings of Ref. [20] mentioned above. The fine tuning of the CEPO requires conditions on both linear and nonlinear coefficients on $\mathbf{P}^*$ and $\mathbf{B}_A$. It suffices that the coefficients for $\mathbf{B}_B$ on the second branch B be slightly different (at the order of the small coupling parameter λ) in order to detune the possible CEPO on $\mathbf{P}^* - \mathbf{B}_B$ and make the B branch not involved in ET. We have confirmed this claim by numerical tests on slightly asymmetric two branch systems, where only the branch A with a well tuned CEPO is involved in ET. Branch B is not involved and the system may be reduced to the A branch only ($\mathbf{P}^* - \mathbf{B}_A - \mathbf{H}_A$) as a trimer model $D - C - A$ described above. Our theory yields some predictions *at zero temperature* in qualitative agreement with the observations. In the natural system, ET should be triggered to the acceptor (the nearest bacteriopheophytin $\mathbf{H}_A$) at the resonance of the CEPO with the acceptor, which occurs during the first half period of its oscillation. At this instant, we have triple resonance between the three electronic levels on $\mathbf{P}^*$, $\mathbf{B}_A$, and $\mathbf{H}_A$. Then, electron transfer to the catalytic site $\mathbf{B}_A$ is only partial. Next, it stops and is reversed. ET on the catalyst $\mathbf{B}_A$ should be observable partially and only during

a short transient time. During the second stage, ET occurs globally between the pair $\mathbf{P}^* - \mathbf{B}_A$ (donor-catalyst) and the acceptor $\mathbf{H}_A$ but then electronic resonances gradually disappear. ET slows down on the acceptor. The consequence is that ET versus time is non-exponential. If the acceptor is removed or if its electronic level is shifted out of the interval of energy where there are electronic level oscillations (which may occur in mutated PRC), the amplitude of coherent electron-phonon oscillation of the CEPO is magnified because it is not interrupted anymore at the triple resonance with the Acceptor. The CEPO oscillations should last longer with a larger amplitude than when ET occurs.

This UFET can be easily affected by small mutations which change the tuning of the CEPO. It is even possible to make mutations which produce slower ET along the B branch if the mutated A branch is blocked. Then, we should consider the role of temperature restoring some efficiency as a CEPO of the second pair $\mathbf{P}^* - \mathbf{B}_B$.

Although large macroscopic electric fields correspond microscopically to small relative energy shifts between electronic levels, these shifts may become of the order of the small coupling (transfer integral) of the CEPO and, depending on the sign, may block or slow down ET. This is also easily confirmed numerically within the simple model treated here.

Let us recall that our predictions are made for zero temperature. Although no systematic numerical investigations of the same model at finite temperature (with a nonzero random force) have been carried out, we suggest that the effect of the random force will be to reduce the phase coherence in the CEPO, generating stochastic large amplitude oscillations and retarding the occurrence of the triple resonance. The net consequence is that the rate of ET slows down when increasing the temperature.

On the other hand, if the CEPO is not well tuned, it should not exhibit any substantial charge oscillations at zero temperature. However, at relatively small temperature the fluctuations of the random force could restore intermittently the resonance (as in standard Marcus theory), thus inducing large charge fluctuations that trigger ET to the acceptor. Finally, we expect that well-tuned and slightly not-well-tuned CEPO become equivalent at sufficiently high temperature (of the order of the detuning energy).

A well-tuned CEPO may appear as physically exceptional in general because it requires specific parameter relations. Nevertheless, we think CEPOs could be very common in biosystems because of their ability to induce highly selective chemical reactions. It has been already noted that coherent phonon oscillations are often observed [11], although not well identified. CEPO could be found in single macromolecules (enzymes) or be formed by the association of two biomolecules in appropriate configuration by key-lock principle. One of their essential property is that they may be easily tuned or detuned by small perturbations of the environment which may change their parameters. As a consequence, their biochemical function could be inhibited or amplified, according to minor but specific changes of the environment, e.g., changes in the protein conformation, in pH or ion concentration, adsorption of extra molecules, etc.

Because of their ability to produce UFET, the concept of CEPOs could be an essential paradigm for understanding the physics of the complex machinery of living systems. Furthermore, they could be involved in networks of electronic states for forming complex logical devices, either natural or artificial.

Notes

1. Our theory is not valid for small molecules reacting in a vacuum. These small systems are highly anharmonic with few degrees of freedom which cannot be modeled as a phonon bath.
2. At the present stage, we did not find any advantage in describing ET within the density-density matrix representation which is more commonly used [11].
3. This energy barrier is identical to those shown in Figure 2 only when the capacitive terms χ_α^C vanish (see [15] for details).
4. This situation is quite different from the standard covalent bond in chemistry where the electronic density is shared between two sites because of quantum tunneling. Then, there is a bonding and an antibonding quantum state, these two separated by a large difference in energy (corresponding to twice the chemical bond energy).
5. In case the CEPO is overdamped, the trajectory might not reach the saddle point if $I_S < 1/2$ at strictly zero temperature. However, small thermal fluctuation would be enough to reach it.
6. Note a mistake in that paper where a factor 2 in formula (45) should be removed, thus requiring corrections in the subsequent formulas.

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