A nonadiabatic theory for electron transfer and application to ultrafast catalytic reactions

2007 J. Phys.: Condens. Matter 19 255204

(http://iopscience.iop.org/0953-8984/19/25/255204)

IOP Publishing Journal of Physics: Condensed Matter

J. Phys.: Condens. Matter **19** (2007) 255204 (30pp) doi:10.1088/0953-8984/19/25/255204

A nonadiabatic theory for electron transfer and application to ultrafast catalytic reactions

S Aubry

Laboratoire Léon Brillouin, CEA Saclay, 91191-Gif-sur-Yvette, France

E-mail: saubry@idsm-mail.saclay.cea.fr

Received 14 September 2006, in final form 6 October 2006
Published 30 May 2007

Abstract

We propose a general formalism which extends those used for the standard theory of electron transfer (ET) in chemistry but also becomes equivalent to it far from the inversion point. Our model yields different results essentially in the vicinity of the inversion point when the energy barrier for ET is small. In that regime, the electronic frequencies become of the order of the phonon frequencies and the process of electron tunnelling is nonadiabatic because it is strongly coupled to the phonons. The consequence of nonadiabaticity is that the effective electron dynamics becomes nonlinear and that there is energy dissipation through the phonon bath. Thermal fluctuations appears as a random force in the effective equation.

We use this formalism for a careful investigation of the vicinity of the inversion point. We find that when the model parameters are finely tuned, ET between donor and acceptor becomes reversible. Then, large amplitude electronic oscillations, associated with large amplitude and collective phonon oscillations at the same frequency, are spontaneously generated. This system is a coherent electron–phonon oscillator (CEPO) which cannot be confused with a standard normal mode. The acceptor which does not capture the electron may play the role of a catalyst. Thus when the catalyst is finely tuned with the donor in order to form a CEPO, it may trigger an irreversible and ultrafast electron transfer at low temperature between the donor and an extra acceptor, while in the absence of a catalyst, ET cannot occur. Such a trimer system may be regulated by small perturbations and behaves as a molecular transistor. We illustrate this idea by explicit numerical simulations on trimer models of the type donor–catalyst–acceptor. We discuss the relevance of our approach for understanding the ultrafast electron transfer experimentally observed in biosystems such as the photosynthetic reaction centre.

(Some figures in this article are in colour only in the electronic version)

0953-8984/07/255204+30$30.00

1. Introduction

Standard chemical models describing electron transfer (ET) between a donor and an acceptor site (or molecule) consider that the local atomic reorganization around an electron is essential. A single electron in a molecule interacts by its charge and also by orbital overlaps with its local environment which induces a local reorganization of the nuclei. The consequence is that the electron self-traps as a *polaron* so that, for transferring an electron from its initial site (donor) to another site (acceptor), it is first necessary to extract the electron from the potential well around the donor site which has been generated self-consistently. Thus, there is an energy barrier which is generally relatively large for transferring the electron and is in the range of an eV. Thermal fluctuations are necessary to overcome this barrier and which make ET generally a slow thermally activated process which requires times much longer than a nanosecond.

Reorganization effects should be especially important in biosystems such as DNA or enzymes which are proteins. These proteins are polyelectrolytes with charged amino acids wrapped in a special conformation for reaching their functionality because of relatively small interactions (electrostatic, steric and van de Waals forces). Some functional parts are hydrophobic without water and ions which could screen the charges. Thus, an extra electron in those soft systems should strongly interact with the charged radicals of its environment, which moreover is highly deformable.

Biosystems exhibit many examples where ET becomes unusually ultrafast ET (at the scale of a ps) (UFET) and even faster at low temperature (for example the photosynthetic reaction centre (PRC)). In that case, there should clearly exist almost no energy barrier for transferring the electron despite the fact that the reorganization energy might be very important.

We propose here new theoretical investigations reviewing and continuing those published earlier [18, 9, 19]. This paper is organized as follows.

- We briefly recall the standard ET theory (section 2).
- We extend this standard theory of ET to the nonadiabatic case. For that purpose, we introduce new reaction coordinates which are the electronic complex amplitudes in order to describe the electron dynamics which thus is not necessarily slaved to those of the atoms. We obtain a new theory which in principle contains the former standard theory as a particular case but does not assume the adiabatic approximation since it describes the intrinsic dynamics of the electronic wavefunction coupled to its environment. The electron dynamics is described by an effective nonlinear Schrödinger equation with a memory kernel and a random force describing the effect of thermal fluctuations (sections 3 and 4).
- We apply this improved theory for understanding ET in the vicinity of the inversion point for a dimer model (donor–acceptor) at zero temperature. A special case yields the coherent electron–phonon oscillator (CEPO) which could induce important and novel physical phenomena. We show that while no direct ET between a donor and an acceptor is possible at zero temperature, the interaction of this system with an appropriately tuned catalyst which forms a CEPO with the donor could trigger ultrafast ET between donor and acceptor (section 5).
- We briefly describe experimentally observed phenomena in the photosynthetic reaction centre (PRC) [17] and emphasize their qualitatively agreement with the predictions of our theory (section 6).
- In appendix A, in the limit of small transfer integral and low temperature, we derive an effective approximate nonlinear Schrödinger equation for the electron dynamics without memory kernel which is formally simpler than our general equation. Appendix B derives

an approximate equation for the electron densities where the phases of the electronic amplitudes are eliminated, assuming there are no resonances between the electronic levels.

2. Basics of standard electron transfer theory

It is first necessary to recall the basic concept of the standard theory for ET in chemistry. We describe here the basic concepts of the standard theory of ET used in chemistry which was pioneered by Marcus [1] and later developed by many others (Levich, Dogonadze, Hush, Jortner *et al* [2–6]). Considering ET between two molecules (donor and acceptor) or two different sites of a molecule, it is assumed that the system has two electronic states. The first one corresponds to the initial state where the electron is on the donor molecule and the second one corresponds to the final state where the electron is on the acceptor molecule. The overlap between the redox orbitals associated with these two states is supposed to be small so that they can be considered as eigenstates (except at resonance when their two energy levels are equal). The free energy of the system depends on the many coordinates describing the displacements of nuclei of the molecules and the environment and also on the state of the electron. Thus, there are two free energy surfaces which take into account all contributions from the chemical, electrostatic, etc interactions. The first surface describes the reactants (that is, the state before the chemical reaction when the electron is on the donor molecule) and the second one describes the products (that is, the state after the chemical reaction when the electron is on the acceptor molecule). These surfaces are well defined within the standard adiabatic (or Born–Oppenheimer) approximation where the electronic energy is only a function of the coordinates of the nuclei. It is assumed that the transfer integral between the donor and the acceptor is small so that the eigenstates of the donor and acceptor practically do not hybridize (except near resonance).

For the same reaction coordinates, the reorganization energy is the same and thus the difference between the first and the second energy surface is nothing but the difference of the electronic levels on the donor and on the acceptor for the same environment.

The minimum versus the nuclear coordinates of these two energy surfaces with the electron either in the initial or the final electronic state determines the initial (reactant) and the final (product) average configurations respectively of the molecules. However, the environment is supposed to be at nonvanishing temperature; that is, the reaction coordinates fluctuate away from their local minima.

It is also assumed for simplicity that these surfaces are quadratic with the same curvature, which is equivalent to assuming that the phonons of these molecules are perfectly harmonic with frequencies independent of the electronic state. These surfaces can be determined in principle from the knowledge of the structures of the molecules and from their normal modes and frequencies [1]. Thus, these two quadratic surfaces are the same. except they are shifted.

ET may only occur by tunnelling (with some probability) when the electronic states on the donor and the acceptor become almost degenerate. The electronic eigenstate hybridizes the electronic states on the donor and the acceptor only in the near resonant situation. Then, the electron may be transferred from the donor to the acceptor by quantum tunnelling with some probability. This situation precisely occurs at the intersection of these two energy surfaces.

Thermal fluctuations are thus necessary for bringing the reaction coordinates from the initial energy minimum at this interaction. The point which may be reached with the largest probability corresponds to the saddle point which is the lowest point at the intersection between the two energy surfaces. This point determines the lowest energy barrier $\Delta G^{\star}$ for transferring the electron (see figure 1) (this situation is similar to those of the general theory of chemical reactions described from the pioneering ideas of Kramers [7]). Thus, it turns out that the

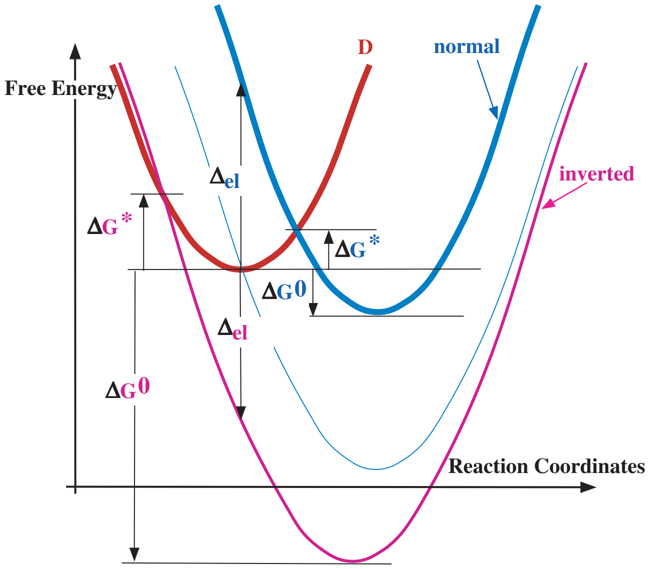

Figure 1. Energy versus reaction coordinates for the reactants (curve D) and the products for normal reaction (curve $A_{\rm n}$), inverted reaction (curve $A_{\rm i}$) and at the inversion curve (curve $A_{\rm c}$). The electron in the initial state requires a positive excitation energy $\Delta_{\rm el}^{\star}$ for the normal reaction, and a negative excitation energy $-\Delta_{\rm el}^{\star}$ for the inverted reaction (which could be directly emitted as light). There is a positive energy barrier $\Delta_{\rm n}$ or $\Delta_{\rm i}$ in both cases between the reactants and products which requires thermal activation for the reaction to occur. This energy barrier as well as the energy for a direct electron excitation vanishes for the inversion curve and then the electron transfer becomes ultrafast.

probability of ET per unit time depends on temperature T with the standard Arrhenius form $A(T)\,{\rm e}^{-\Delta G^{\star}/k_{\rm B}T}$.

The prefactor $A(T)$ is determined more or less empirically according to the tunnelling probability at electron resonance. Standard theory of tunnelling assumes that the double-well potential due to the environment of the electron is static during the time of tunnelling between the two wells. Actually, the local potential generated by the thermal fluctuations is not static but varies over the characteristic time of phonons. Because of that, the resonance between the two electronic levels may not persist long enough to allow electron tunnelling. This fact is taken into account by considering that tunnelling occurs only with a certain probability which can be estimated for example from Landau–Zeener models [8].

Two regimes can be defined regarding the tunnelling [8]. The adiabatic regime is obtained when the overlap between the redox orbitals (although supposed to be small) is nevertheless sufficiently large (strong reactants) in order that, when resonance occurs, electron tunnelling is fast at the scale of the phonon frequencies. Thus its probability to occur is almost 1. The diabatic regime is obtained at small overlap (weak reactants). Then, the tunnelling becomes slow at the scale of the phonon characteristic time and has a small probability to occur. In any case, the intrinsic time for tunnelling is usually much shorter than the characteristic time required for the thermal fluctuations to overcome an energy barrier supposed to be large compared to the thermal energy.

Despite the fact that the standard theory does not properly describe the electron tunnelling in a self-consistent deformable potential, it appears that nevertheless the essential contribution to the time required for ET is the time to reach the top of the energy barrier. When this energy barrier is large, the standard theory yields results which are in excellent agreement with the experimental observations.

The standard theory distinguishes two regimes shown by the scheme in figure 1. The normal regime is when the second energy surface with the electron on the acceptor at the initial configuration is above the first energy surface with the electron on the donor. Then, a direct transfer of the electron from donor to acceptor at fixed reaction coordinates would require a positive energy Δ_{el}.

The second regime, called inverted, is obtained when the second energy surface is below the first one for the initial configuration. Note that this inverted situation differs from the normal situation because there is a second pathway for the electron to reach the final state. The electron may also decay directly from its initial state to its final state which has a lower energy by the direct emission of a photon at fixed nuclei configuration. Actually, this process is generally very slow. Nevertheless it may manifest in this inverted regime as chemiluminescence which may be observed at low temperature when the first pathway requiring thermal fluctuations becomes inefficient enough [1].

The energy barrier for ET precisely vanishes at the Marcus inversion point when the initial electronic state and the final electronic state are degenerate at the initial atomic configuration (see figure 1). Since there is no need of thermal fluctuation for having resonance, the standard theory expects that ET becomes ultrafast in the close vicinity of this inversion point and is even more efficient at low temperature. In that case, the characteristic time for ET is essentially due to the prefactor $A(T)$ which has only been empirically estimated.

It is then clear that the standard ET theory which phenomenologically reduces tunnelling to a probability of transfer is clearly not sufficient for describing ET in the vicinity of the inversion point. This problem was explicitly mentioned in section 3.6 (Tunnel Times) of [8] as an unsolved problem although its relevance in the case of ultrafast ET was not recognized.

For improving the theory of ET in the vicinity of the inversion point, it is required to consider the intrinsic dynamics of the electron which should be considered as slaved adiabatically to the reaction coordinates.

3. Extended ET Theory

For improving the standard theory in the vicinity of the inversion point, the electronic variables should not be slaved to the reaction coordinates but should be considered as independent variables with their intrinsic dynamics coupled to those of the reaction coordinates. In other words, we should miss out the standard adiabatic approximation. This is essentially the extension we are presenting here. Thus, unlike the standard theory, we shall not consider tunnelling as a probabilistic event which is estimated empirically, but we shall consider the real dynamics of the quantum electron during tunnelling in its self-consistent deformable potential.

The hypotheses we use for constructing our model are included in the set of hypotheses used by the Marcus theory except for the adiabatic hypothesis.

- We consider a model with a single electron which may occupy two states, either on the donor molecule (D) or on the acceptor molecule (A) or two sites of the same molecule. Actually, we extend our model to more than two states but to a larger collection of electronic states α (redox orbitals).
- We assume that there is a small overlap between the orbitals of the different electronic states α.
- We neglect the possible energy radiation through the electromagnetic field induced by the variation of the spatial distribution of charges during ET.

- We consider the environment as a large collection of harmonic oscillators (corresponding to the normal modes of the molecules labelled by i)[1].
- We assume that the dynamics of the nuclei of the environment can be described classically. In other words, the displacements of the nuclei in the close environment of the electron are much larger than their quantum zero point motion[2].

We describe the wavefunction of the electron $\Psi(\mathbf{r})$ within a tight-binding representation as a linear combination of the (orthogonalized) orbitals

$$\Psi(\mathbf{r}) = \sum_\alpha \psi_\alpha \Psi_\alpha(\mathbf{r})$$

where $\Psi_\alpha(\mathbf{r})$ are the wavefunctions of the electron at the collection of sites α which might be involved during electron dynamics (for the two-site model, we only have $\alpha = D$ (donor) or $\alpha = A$ (acceptor)). The complex amplitudes ψ_α fulfil the normalization condition $\sum_\alpha |\psi_\alpha|^2 = 1$.

The total energy $\mathbf{H}$ of the system is a function of the electronic variables $\{\psi_\alpha\}$ and of the coordinates $\{u_i\}$ and their conjugate momenta $\{p_i = m_i \dot{u}_i\}$ of the normal modes labelled by i of the environment. With the standard assumption that the oscillators are harmonic and that the coupling with the electron densities $|\psi_\alpha|^2$ is linear, $\mathbf{H}$ has the general form

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

Each normal mode i is linearly coupled to the local density $|\psi_\alpha|^2$ of the electron at site α by the coupling constant $k_{i,\alpha}$. Thus, this collection of harmonic oscillators plays the role of a thermal bath.

$H_{\mathrm{T}}(\{\psi_\alpha\})$ is the rest of the energy which thus only depends on the complex amplitudes ψ_α. It can be defined as the minimum at fixed $\{\psi_\alpha\}$ of the total energy of the system with respect to all the nuclei coordinates and momenta

$$H_{\mathrm{T}}(\{\psi_\alpha\}) = \min_{\{u_i, p_i\}} \mathbf{H}(\{\psi_\alpha\}, \{u_i, p_i\}). \tag{2}$$

By definition, this energy H_{T} is the total energy of the system after complete relaxation of the environment at fixed $\{\psi_\alpha\}$. This energy includes in particular the variation of the atomic interactions due to their reorganization (elastic energies, chemical bond energies, etc) and the variations of electrostatic energies due to the charge redistribution. It is important to note from now on that this energy is not a *bilinear* function of $\{\psi_\alpha\}$ and $\{\psi_\alpha\}^\star$ as it would be for an electron in a rigid potential which does not involve any reorganization energy.

Actually, H_{T} is the (nonlinear) Hamiltonian which would describe the dynamics of the electron if the variations of electronic densities were very slow compared to the dynamics of the atoms. In principle, to be valid this approximation requires the transfer integrals between the different sites to be small compared with the characteristic phonon energies. This approximation is thus valid in the situation opposite to those where the standard adiabatic approximation is valid, that is when the electron dynamics is much faster than the atom dynamics. For that reason, H_{T} may be called the anti-adiabatic electronic Hamiltonian.

Thus near the anti-adiabatic limit, the electron dynamics may be described by an effective nonlinear Hamiltonian while the atomic motion is slaved to the electron dynamics. It is the

---

[1] Our theory is not valid for small molecules reacting in the vacuum. These small systems have only a few modes which cannot play the role of a thermal bath. In addition, in that situation, these modes should be considered as anharmonic.

[2] This approximation may be not valid when only very light nuclei (protons) are involved in the reorganization of the environment. We discard this possible situation.

opposite in the adiabatic case; then it is the dynamics of the atoms which may be described by an effective Hamiltonian (Born–Oppenheimer) while the electron dynamics is slaved to the atomic motions. Let us recall now that the theory we consider does not focus on a specific limit but treats all the intermediate situations between the adiabatic limit and the anti-adiabatic limit.

The energy surface considered in the Marcus theory (see figure 1) is defined for the donor by $H_\mathrm{D}(\{u_i\}) = \mathbf{H}(\{\psi_\alpha\}, \{u_i, p_i\})$ where ψ_α is fixed as $|\psi_\alpha|^2 = 1$ for $\alpha = \mathrm{D}$ and $\psi_\beta = 0$ for $\beta \neq \alpha$ (and $p_i = 0$). Its minimum is obtained for $\{u_i = k_{i,\mathrm{D}}\}$. The energy surface is obtained identically for the acceptor by fixing $|\psi_\alpha|^2 = 1$ for $\alpha = \mathrm{A}$. Its minimum is obtained for $\{u_i = k_{i,\mathrm{A}}\}$. Then all the quantities involved in the standard Marcus theory can be calculated [9] from (1).

$H_\mathrm{T}(\{\psi_\alpha\})$ is a real function which should be invariant on a global phase rotation of $\{\psi_\alpha\}$, that is by changing $\{\psi_\alpha\}$ into $\{\mathrm{e}^{\mathrm{i}\theta}\psi_\alpha\}$, where θ is arbitrary. It may be also considered as a function of the electron densities $\{I_\alpha = |\psi_\alpha|^2\}$ and the phases θ_α (defined by $\psi_\alpha = \sqrt{I\alpha}\mathrm{e}^{-\mathrm{i}\theta_\alpha}$). Since H_T is 2π periodic with respect to each phase, it may be expanded as a Fourier series of θ_α. Then H_T can be written as a sum

$$H_\mathrm{T}(\{\psi_\alpha\}) = \hat{H}_\mathrm{T}(\{|\psi_\alpha|^2\}) + H_\mathrm{T}^{\mathrm{int}}(\{\psi_\alpha\}) \tag{3}$$

where $\hat{H}_\mathrm{T}$ is the zero order component of this expansion which is independent of the phase of the complex amplitudes ψ_α (it can be defined by averaging H_T over the phases θ_α).

The rest of the energy $H_\mathrm{T}^{\mathrm{int}}$ in (3) depends on the phase θ_α of the complex amplitudes ψ_α. It originates physically from the overlap of the redox orbitals. We consider situations where this overlap is small (but however essential because this term is necessary for electron transfer). Thus, we may keep only the lowest order nonvanishing terms of the Fourier expansion $H_\mathrm{T}^{\mathrm{int}}$ which is second order because of the invariance of H_T under global phase rotation. We thus obtain the form

$$H_\mathrm{T}^{\mathrm{int}}(\{\psi_\alpha\}) = -\sum_{\beta\neq\gamma} \lambda_{\beta,\gamma}(\{|\psi_\alpha|^2\})\psi_\beta\psi_\gamma^\star \tag{4}$$

where $\lambda_{\beta,\gamma}(\{|\psi_\alpha|^2\}) = \lambda_{\gamma,\beta}(\{|\psi_\alpha|^2\})$ may be chosen real (in the absence of magnetic field).

4. Dynamical equation for electron transfer

We derive the effective equation which governs the ET after elimination of the thermal bath of phonons considered as classical. We show that its effect is to dissipate energy and, at finite temperature, to generate a random force as for the standard Langevin model. It is essential however to take into account that the Fourier spectrum of the random force has a cut-off at frequencies larger than the phonon frequencies for recovering the standard theory.

4.1. Hamilton equations

We write the standard Hamilton equations associated with (1),

$$\mathrm{i}\hbar\dot{\psi}_\alpha = \frac{\partial \mathbf{H}}{\partial \psi_\alpha^\star} = \frac{\partial H_\mathrm{T}}{\partial \psi_\alpha^\star} - \left(\sum_i k_{i,\alpha} m_i \omega_i^2 \left(u_i - \sum_\beta k_{i,\beta}|\psi_\beta|^2\right)\right)\psi_\alpha \tag{5}$$

$$0 = \ddot{u}_i + \omega_i^2\left(u_i - \sum_\alpha k_{i,\alpha}|\psi_\alpha|^2\right); \tag{6}$$

$u_i(t)$ can be made explicit from the second equation (6) which is linear with respect to u_i. The general solution has the form $u_i = u_i^{(n)} + u_i^{(0)}$, where

$$u_i^{(0)}(t) = \sum_\alpha k_{i,\alpha}\omega_i \left(\int_{-\infty}^{t} \sin \omega_i (t-\tau) |\psi_\alpha(\tau)|^2 \, \mathrm{d}\tau \right)$$
$$= \sum_\alpha k_{i,\alpha} \left(|\psi_\alpha(t)|^2 - \int_{-\infty}^{t} \cos \omega_i (t-\tau) \frac{\mathrm{d}|\psi_\alpha(\tau)|^2}{\mathrm{d}\tau} \, \mathrm{d}\tau \right) \tag{7}$$

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 (6) without force (i.e. assuming $|\psi_\alpha|^2 = 0$). Substituting $u_i(t)$ as a function of $|\psi_\alpha|^2$ in equation (5) yields the effective equation for the dynamics of the electron,

$$\mathrm{i}\hbar\dot{\psi}_\alpha = \frac{\partial H_\mathrm{T}}{\partial \psi_\alpha^\star} + \left(\int_{-\infty}^{t} \sum_\beta \Gamma_{\alpha,\beta}(t-\tau) \frac{\mathrm{d}|\psi_\beta(\tau)|^2}{\mathrm{d}\tau} \mathrm{d}\tau + \zeta_\alpha(t) \right) \psi_\alpha \tag{8}$$

where

$$\Gamma_{\alpha,\beta}(t) = \sum_i k_{i,\alpha} k_{i,\beta} m_i \omega_i^2 \cos \omega_i t \tag{9}$$

and

$$\zeta_\alpha(t) = -\sum_i k_{i,\alpha} m_i \omega_i^2 u_i^{(n)}(t). \tag{10}$$

We define $\gamma_{\alpha,\beta}(\omega)$ as

$$\gamma_{\alpha,\beta}(\omega) = \pi \sum_i k_{i,\alpha} k_{i,\beta} m_i \omega_i^2 \left(\delta(\omega - \omega_i) + \delta(\omega + \omega_i) \right). \tag{11}$$

If we assume that the environment plays the role of a thermal bath, that is the density of normal modes i at frequency ω_i in the interval $\mathrm{d}\omega$ is $N(\omega)\,\mathrm{d}\omega$, where $N(\omega)$ is a smooth integrable function of $\omega = \omega_i$, and that the coupling parameters $k_{i,\alpha}$ and $m_i\omega_i^2$ are also smooth integrable functions $k_\alpha(\omega)$ and $K(\omega)$, we obtain that

$$\gamma_{\alpha,\beta}(\omega) = \gamma_{\alpha,\beta}(-\omega) = \pi k_\alpha(\omega) k_\beta(\omega) \omega^2 N(\omega) \tag{12}$$

is a smooth function of ω. Its Fourier transform is the memory function

$$\Gamma_{\alpha,\beta}(t) = \frac{1}{\pi} \int_0^{+\infty} \gamma_{\alpha,\beta}(\omega) \cos(\omega t) \, \mathrm{d}\omega = \frac{1}{2\pi} \int_{-\infty}^{+\infty} \gamma_{\alpha,\beta}(\omega) \mathrm{e}^{\mathrm{i}\omega t} \, \mathrm{d}\omega \tag{13}$$

which may be assumed to be also a smooth function of time, which goes to zero at infinity.

Actually, it is important to note that, in physical systems, the phonon spectrum does not extend to infinity and has a cut-off at some frequency ω_c, that is $N(\omega) = 0$ for $|\omega| > \omega_\mathrm{c}$. In practice, $\hbar\omega_\mathrm{c}$ cannot exceed the largest known phonon quanta energies, around 0.3 eV.

It can be readily checked that the operator $\mathbf{g}(\omega)$ defined by the matrix element $\{\gamma_{\alpha,\beta}(\omega)\}$ is positive since $K(\omega)$ and $N(\omega)$ are positive functions.

Thermal fluctuations appear in equation (8) through the coloured random force (10). The time correlation function averaged over τ of oscillator i is

$$\langle u_i^{(n)}(t+\tau) u_j^{(n)}(\tau) \rangle_\tau = \delta_{i,j} \langle (u_i^{(n)})^2 \rangle \cos \omega_i t. \tag{14}$$

If we assume that the harmonic oscillators are thermalized at temperature T, we have $\langle (u_i^{(n)})^2 \rangle = k_\mathrm{B} T / (m_i \omega_i^2)$, which yields the Langevin relation

$$\langle \zeta_\alpha(\tau) \zeta_\beta(t+\tau) \rangle_\tau = \sum_i k_{i,\alpha} k_{i,\beta} m_i^2 \omega_i^4 \langle u_i^{(n)}(\tau) u_i^{(n)}(t+\tau) \rangle$$
$$= k_\mathrm{B} T \Gamma_{\alpha,\beta}(t). \tag{15}$$

4.2. Energy dissipation at zero temperature

At zero temperature, the random force $\zeta_\alpha(t)$ disappears $\zeta_\alpha(t) = 0$. Then, we have as a consequence of equation (8)

$$\begin{aligned}\dot{H}_\mathrm{T} &= \sum_\alpha \left(\frac{\partial H_\mathrm{T}}{\partial \psi_\alpha^\star} \dot{\psi}_\alpha^\star + \frac{\partial H_\mathrm{T}}{\partial \psi_\alpha} \dot{\psi}_\alpha \right) \\ &= \sum_\alpha \left(\mathrm{i}\hbar \dot{\psi}_\alpha - \psi_\alpha \int_{-\infty}^{t} \sum_\beta \Gamma_{\alpha,\beta}(t-\tau) \frac{\mathrm{d}|\psi_\beta(\tau)|^2}{\mathrm{d}\tau} \mathrm{d}\tau \right) \dot{\psi}_\alpha^\star + \mathrm{C.C.} \\ &= -\sum_{\alpha,\beta} \frac{\mathrm{d}|\psi_\alpha|^2}{\mathrm{d}t} \int_{-\infty}^{t} \Gamma_{\alpha,\beta}(t-\tau) \frac{\mathrm{d}|\psi_\beta(\tau)|^2}{\mathrm{d}\tau} \mathrm{d}\tau. \end{aligned} \tag{16}$$

The role of the thermal bath is essential for ensuring the dissipation of the energy released by ET if it occurs at zero temperature. We show then that the dynamical equation (8) always yields energy dissipation after a long time [9].

For simplicity, we may assume for example that $\Gamma_{\alpha,\beta}(t) = \gamma_\alpha \delta_{\alpha,\beta} \delta(t)$, that is $\gamma_{\alpha,\alpha}$ is independent of ω and $\gamma_{\alpha,\beta} = 0$ for $\alpha \neq \beta$. This approximation corresponds to the white noise approximation for ζ_α by equation (15). Then, we find $\dot{H}_\mathrm{T} = -\frac{1}{2} \sum_\alpha \gamma_{\alpha,\alpha} (\frac{\mathrm{d}|\psi_\alpha|^2}{\mathrm{d}t})^2 < 0$ is necessarily negative because $\gamma_{\alpha,\alpha}(\omega)$ is obviously positive from its definition (11). However, this white noise approximation is not correct physically.

Using the equation (A.2) and the approximation (A.11), we get a complex sum over four indices $\alpha, \beta, \gamma, \delta$ which involves time-dependent terms like $\mathrm{Im}(\psi_\alpha \psi_\beta^\star)\,\mathrm{Im}(\psi_\gamma \psi_\delta^\star)$ or $\mathrm{Im}(\psi_\alpha \psi_\beta^\star)\,\mathrm{Re}(\psi_\gamma \psi_\delta^\star)$ where $\psi_\alpha(t)\psi_\beta^\star(t) \approx \psi_\alpha(0)\psi_\beta^\star(0)\mathrm{e}^{\mathrm{i}(\Omega_\beta - \Omega_\alpha)t}$. Then, time averaging of $\mathrm{Im}(\psi_\alpha \psi_\beta^\star)\,\mathrm{Re}(\psi_\gamma \psi_\delta^\star)$ yields zero while the time averaging $\mathrm{Im}(\psi_\alpha \psi_\beta^\star)\,\mathrm{Im}(\psi_\gamma \psi_\delta^\star)$ is nonzero only if $\gamma = \alpha$ and $\delta = \beta$ (we assume the nonresonance condition; that is, we never have $\Omega_\beta - \Omega_\alpha \neq \Omega_\gamma - \Omega_\delta$ unless $\gamma = \alpha$ and $\delta = \beta$). Then averaging the fast time periodic oscillations to zero, we obtain

$$\dot{H}_\mathrm{T} \approx -\sum_{\alpha,\beta} \frac{\lambda_{\alpha,\beta}^2}{\hbar^2} (\gamma_{\alpha,\alpha} - \gamma_{\alpha,\beta}) |\psi_\alpha|^2 |\psi_\beta|^2 = -\frac{1}{2} \sum_{\alpha,\beta} \frac{\lambda_{\alpha,\beta}^2}{\hbar^2} (\gamma_{\alpha,\alpha} + \gamma_{\beta,\beta} - 2\gamma_{\alpha,\beta}) |\psi_\alpha|^2 |\psi_\beta|^2 \tag{17}$$

which is negative since the coefficient $(\gamma_{\alpha,\alpha} + \gamma_{\beta,\beta} - 2\gamma_{\alpha,\beta})$ calculated at frequency $\Omega_\alpha - \Omega_\beta$ is positive according to the positivity of matrix $\{\gamma_{\alpha,\beta}(\Omega)\}$ at any Ω. We note that the energy dissipation is the sum of the contributions at each bond (α, β) of the current density (note each bond appears twice in the sum (17) as α, β) and (β, α). Otherwise, we should remove the prefactor $\frac{1}{2}$). It is thus interesting to note for consistency that the same result (17) can be obtained from equation (B.6) since the contribution to the energy dissipation due to each bond (α, β) is the product of the average current $\bar{J}_{\alpha\to\beta}$ by the electronic energy level difference $-(E_\alpha - E_\beta)$ which yields $\dot{H}_\mathrm{T} \approx -\sum_{\langle\alpha,\beta\rangle} \bar{J}_{\alpha\to\beta}(E_\alpha - E_\beta)$ (each bond $\langle\alpha, \beta\rangle$ appears only once in this sum).

If all the electronic frequencies differences do not belong to the phonon spectrum, there is no energy dissipation calculated at the lowest order. However, calculation at higher order would involve integer combinations of the electronic frequencies $\sum_{\alpha,\beta} n_{\alpha,\beta}(\Omega_\alpha - \Omega_\beta)$ with $n_{\alpha,\beta}$ integer. When there are more than two electronic frequencies, these integer combinations yield a dense set of frequencies which necessarily overlap with the phonon spectrum (assuming incommensurability). Thus, there is necessarily some energy dissipation which could be found at some finite order expansion. However, this dissipation could become much smaller than other sources of dissipation, for example by photon emission. It could be neglected in the limit of small transfer integrals and when the temperature is nonvanishing. This is the case in the standard theory of ET.

4.3. Adiabatic limit

The adiabatic limit can be recovered by assuming that the cut-off frequency ω_c is very small at the scale of the electronic frequencies, that is $\gamma_{\alpha,\beta}(\omega) \approx \pi \Gamma_{\alpha,\beta}(0)\delta(\omega)$. Since the variations of $\frac{d|\psi_\beta(\tau)|^2}{d\tau}$ are very fast, $\Gamma(t) = \Gamma(0)$ may be assumed to be time constant in equation (8). Then, one readily obtains the adiabatic equation by explicit integration:

$$i\hbar\dot{\psi}_\alpha = \frac{\partial H_C}{\partial \psi_\alpha^\star} + \zeta_\alpha(t)\psi_\alpha \tag{18}$$

where

$$H_C = H_T + \tfrac{1}{2}\sum_{\alpha,\beta} \Gamma_{\alpha,\beta}(0)|\psi_\alpha|^2|\psi_\beta|^2. \tag{19}$$

It can readily be checked that $H_C(\{\psi_\alpha\})$ is equal to the initial Hamiltonian (1) where the atomic positions and momenta are fixed at $u_i = p_i = 0$. It is the electronic energy without atomic reorganization. It is important to note that due to the capacitive energies of the charge distribution, $H_C(\{\psi_\alpha\})$ is not necessarily a bilinear function of $\{\psi_\alpha\}$ and $\{\psi_\alpha^\star\}$. Thus the reorganization energy due to the electrostatic energy of the charge distribution is

$$H_{\mathrm{reorg}} = H_T - H_C = -\tfrac{1}{2}\sum_{\alpha,\beta} \Gamma_{\alpha,\beta}|\psi_\alpha|^2|\psi_\beta|^2. \tag{20}$$

We also note that generally the general equation (equation (8)) may be written again after part integration as

$$i\hbar\dot{\psi}_\alpha = \frac{\partial H_C}{\partial \psi_\alpha^\star} + \left(\int_{-\infty}^{t} \sum_\beta G_{\alpha,\beta}(t-\tau)|\psi_\beta(\tau)|^2 \,d\tau + \zeta_\alpha(t)\right)\psi_\alpha \tag{21}$$

where the memory function

$$G_{\alpha,\beta}(t) = \frac{d\Gamma}{dt} = -\sum_i k_{i,\alpha}k_{i,\beta}m_i\omega_i^3 \sin\omega_i t = -\int k_\alpha(\omega)k_\beta(\omega)\omega K(\omega)N(\omega)\sin\omega t \,d\omega$$

represents the effect of the correction to the adiabatic approximation.

4.4. Recovering the standard Marcus theory

When the electron dynamics is much faster than the phonon dynamics, that is the differences between the electronic frequencies are much larger than the phonon frequencies, the adiabatic approximation becomes valid and we should use equation (18). The electronic state remains at equilibrium with respect to its environment while it slowly varies. This feature is essential for recovering the standard Marcus theory from our approach [9].

Then, since the transfer integral is small (and while there is no electronic resonance) the electronic density remains peaked at $\alpha = $ D or A (for the two-site model), that is $|\psi_\alpha|^2 \approx 1$ and $|\psi_\beta|^2 \approx 0$ for $\beta \neq \alpha$. The total energy of the system evolves as a function of the thermal fluctuations characterized by the reaction coordinates $\{u_i\}$ on the surfaces $G_D(\{u_i\}) = \hat{H}_T(1,0) + \sum_i m_i\omega_i^2(u_i - k_{i,D})^2$ and $G_A(\{u_i\}) = \hat{H}_T(0,1) + \sum_i m_i\omega_i^2(u_i - k_{i,A})^2$ defined in the standard theory (see figure 1). This approximation is valid while the electronic energies do not approach resonances which would imply both that there are electronic frequencies entering the phonon spectrum and the failure of the adiabatic approximation.

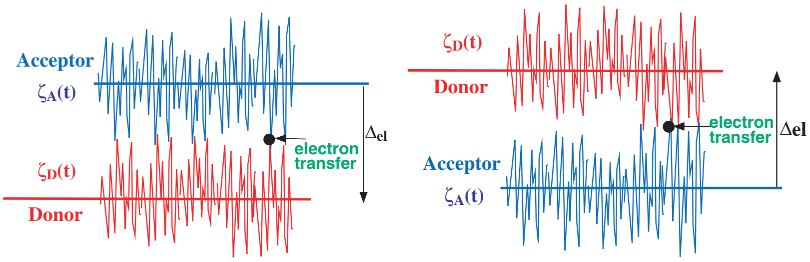

Figure 2. Time-dependent random fluctuations (induced by thermal lattice fluctuations) of the adiabatic electronic levels of the donor $E_{\rm D}^{\rm (ad)}(t)$ and acceptor $E_{\rm A}^{\rm (ad)}(t)$ in normal regime (a) and in the Marcus inverted regime (b). Within Marcus theory, ET occurs at time t where resonance $E_{\rm D}^{\rm (ad)}(t) = E_{\rm A}^{\rm (ad)}(t)$ occurs.

The adiabatic electronic frequencies $\Omega_\alpha^{\rm (ad)}$ can be obtained from Hamiltonian (1) as functions of the atomic coordinates $\{u_i\}$. They can be equivalently obtained from equation (18) at zero transfer integral

$$E_\alpha^{\rm (ad)} = \hbar\Omega_\alpha^{\rm (ad)} \approx \frac{\partial \hat{H}_{\rm C}}{\partial|\psi_\alpha|^2} + \zeta_\alpha(t) \tag{22}$$

where $|\psi_\alpha|^2 = 1$ and $|\psi_\beta|^2 = 0$ for $\beta \neq \alpha$ and $\hat{H}_{\rm C} = \hat{H}_{\rm T} - H_{\rm reorg}$ does not involve the reorganization energy due to the atomic motions (20). $\zeta_\alpha(t)$ is essentially the potential generated by the atomic displacements. Note that the adiabatic electronic levels $E_\alpha^{\rm (ad)}$ are different from and systematically larger than the anti-adiabatic energy levels E_α obtained with Hamiltonian $\hat{H}_{\rm T}$ in (22) instead of $H_{\rm C}$ which takes the lattice relaxation into account.

At nonvanishing temperature, these electronic frequencies $\Omega_{\rm D}^{\rm (ad)}$ and $\Omega_{\rm A}^{\rm (ad)}$ slowly vary as a function of time. When the random fluctuations make these adiabatic electronic levels equal, we have a dynamical resonance, that is when

$$\frac{\partial \hat{H}_{\rm C}}{\partial|\psi_\alpha|^2}(1,0) + \zeta_{\rm D}(t) = \frac{\partial \hat{H}_{\rm C}}{\partial|\psi_\alpha|^2}(1,0) + \zeta_{\rm A}(t), \tag{23}$$

which may trigger ET (see the scheme in figure 2). However, when resonance occurs, the adiabatic approximation ceases to be valid and electron tunnelling should be described with the original equation (8). Nevertheless, we obviously recover the two situations, predicted by the standard theory, called normal and inverted (see figure 2).

In the standard theory, electronic resonance should occur in the vicinity of the intersection of the two energy surfaces $G_{\rm D}(\{u_i\})$ and $G_{\rm A}(\{u_i\})$; however, there are subtle problems already discussed for the dimer model [9] because this electronic resonance does not necessarily occur at the intersection between these two energy surfaces $G_{\rm D}$ and $G_{\rm A}$. The intersection of the two energy surfaces is obtained when

$$\hat{H}_{\rm C}(1,0) + \zeta_{\rm D}(t) = \hat{H}_{\rm C}(0,1) + \zeta_{\rm A}(t) \tag{24}$$

which is a condition different from (23). *A priori*, these two conditions (23) and (24) are nonequivalent because $H_{\rm C}(\{\Psi_\alpha|^2)$ is the electronic energy without reorganization of the atoms of the environment. It should be generally a nonlinear function of the electronic densities because of the capacitive energies of the charge distribution (this is the energy of the local electrostatic field which depends on the dielectric constant ε_∞).

It was shown nevertheless in [9] that when the donor and the acceptor have the same capacitive coefficients (and *a fortiori* when $H_{\rm C}(\{\Psi_\alpha|^2)$ is a linear function of the electronic densities), electronic resonance precisely occurs at the intersection of the two energy surfaces $G_{\mathrm{D}}(\{u_i\})$ and $G_{\mathrm{A}}(\{u_i\})$. This assumption may not be physically unreasonable in many cases.

Let us emphasize now that our theory does not consider the electron tunnelling as a probabilistic process but intrinsically describes the quantum dynamics of the electron wavefunction interacting with a bath of classical phonons. It should reproduce all the predictions of the standard theory when they are valid and predict more where the standard theory fails, that is in the vicinity of the inversion point.

5. Analytical and numerical investigations of specific models

We now apply our formalism for studying simple models and propose a new mechanism for ultrafast catalytic electron transfer. First, we propose simple forms for the energies involved in our model.

5.1. Main energy contributions to the nonlinear Hamiltonian for ET

Although equation (8) formally describes the electron dynamics in the general case, practical applications require us to know precisely the anti-adiabatic Hamiltonian $H_{\mathrm{T}}(\{\psi_\alpha\})$ 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 and realistic example, expensive *ab initio* numerical investigations.

Up to now we have studied models with only a few parameters. This is sufficient to make clear the basic mechanisms for ultrafast electron transfer which could be extended to more complex models. Considering that the molecules and the redox orbitals α of the different electronic states α are weakly interacting, the anti-adiabatic Hamiltonian $\hat{H}_{\mathrm{T}}$ may be chosen as separable, with the form

$$\hat{H}_{\mathrm{T}}(\{|\psi_\alpha|^2\}) = \sum_\alpha H_\alpha(|\psi_\alpha|^2), \tag{25}$$

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 $I_\alpha = |\psi_\alpha|^2$ with the form

$$H_\alpha(I_\alpha) = \mu_\alpha I_\alpha + \tfrac{1}{2}\chi_\alpha I_\alpha^2, \tag{26}$$

where μ_α is the electronic level of the unoccupied state (i.e., before reorganization of the environment). The coefficient $\chi_\alpha = \chi_\alpha^{\mathrm{R}} + \chi_\alpha^{\mathrm{C}}$ of the nonlinear term may be viewed as the sum of two terms, where $\chi_\alpha^{\mathrm{R}} < 0$ is the coefficient of the reorganization energy (20) and $\chi_\alpha^{\mathrm{C}} > 0$ is the coefficient for the capacitive energy (which depends on 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). The capacitive energy ($\chi_\alpha > 0$) is obviously prevalent for electronic states α which involve only small reorganization energy of the environment (e.g. those corresponding to inner layers of metallic ions). When the reorganization energy of electronic states is important, e.g. when they are involved in covalent bonds, we generally have $\chi_\alpha < 0$.

We assume for simplicity that the transfer integrals $\lambda_{\alpha,\beta}$ in $H_{\mathrm{T}}^{\mathrm{int}}(\{\psi_\alpha\})$ (25) are small and independent of the electronic densities. This dependence is not essential in our theory and can be discarded.

Actually, a real system could involve cross capacitive and reorganization energy terms, which are important for fine tuning (see the CEPO), but for simplicity, we do not include them here.

Assuming that we are close to the inversion point, the differences between the electronic energy levels $\hbar\Omega_\alpha^{(\mathrm{ad})}$ are comparable (and remain so while they vary) to the characteristic phonon energies, which means that the phonon bath always remains 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 nonessential off-diagonal terms $\Gamma_{\alpha,\beta}$ are zero for $\alpha \neq \beta$. Finally, we can set $\Gamma_{\alpha,\alpha}(t) = 2\gamma_\alpha\delta(t)\delta_{\alpha,\beta}$, where $\gamma_{\alpha,\alpha} = \gamma_\alpha$ are constant.

Electronic energy differences are usually measured in electron-volts (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 a 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 a picosecond. Thus their energies lie in the range of thermal energies at room temperature T_R ($k_\mathrm{B}T_\mathrm{R} \approx 3\times 10^{-2}$ eV).

ET at zero temperature requires that there is energy dissipation of the reaction energy and thus the damping coefficients, γ_α, should not be negligible. However, both the damping and the reorganization energy originate from the phonon bath and are related. Coefficient χ_α^R for the reorganization energy is equal to $-\Gamma_{\alpha,\alpha}(0)$ because of equation (20). 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 equation (13), $\chi_\alpha^\mathrm{R} = -\Gamma_{\alpha,\alpha}(0) = 2\omega_\mathrm{c}\gamma_\alpha/\pi$. Thus the order of magnitude we could expect for γ_α could be $\approx -\pi\hbar\chi_\alpha^\mathrm{R}/(2\hbar\omega_\mathrm{c})$. Considering a maximum for the phonon energy $\hbar\omega_\mathrm{c}$ of the order of 10^{-2} eV as above, we find that reasonable values for γ_α could be of the order of several $10\times\hbar$, which turns out to be quite sufficient in our numerical simulations.

5.2. The dimer model at zero temperature

We consider first the two-state donor–acceptor system (α = D or A). This model discusses the situation where ET may occur at zero temperature between donor and acceptor because the reaction energy can be dissipated through the phonon bath. This situation requires the difference between the electronic levels on donor and acceptor remains within the phonon energies and thus is relatively small.

Similar situations were considered by Jortner [6]. He assumed that the phonons are quantum but also that the electron interaction with this quantum phonon bath is small so that it can be treated as a perturbation through the Fermi golden rule. Actually, this treatment is quite similar to those of the interaction of the electron with the quantum electromagnetic field which describe the electronic relaxation by emitting a quantum photon. Although this quantum treatment is justified for photon emission, we do not believe that a perturbative treatment of the interaction with quantum phonons is physically relevant in most cases. The reason is that the interaction of the electron with its environment generally generates an important reorganization involving atomic displacements much larger than the width of their quantum zero point motion. Thus, the interaction of the electron with the quantum phonon bath should be treated at very high order which becomes a considerably more difficult task. Moreover, one should then reasonably expect that the fully quantum calculation at strong interaction reproduces results which are practically identical to those obtained from a simpler classical treatment.

With the above assumptions, the Hamiltonian H_T of this dimer takes the form

$$H_\mathrm{T}(\psi_\mathrm{D},\psi_\mathrm{A}) = \mu_\mathrm{D}|\psi_\mathrm{D}|^2 + \tfrac{1}{2}\chi_\mathrm{D}|\psi_\mathrm{D}|^4 + \mu_\mathrm{A}|\psi_\mathrm{A}|^2 + \tfrac{1}{2}\chi_\mathrm{A}|\psi_\mathrm{A}|^4 - \lambda(\psi_\mathrm{D}^\star\psi_\mathrm{A} + \psi_\mathrm{A}^\star\psi_\mathrm{D}) \qquad (27)$$

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

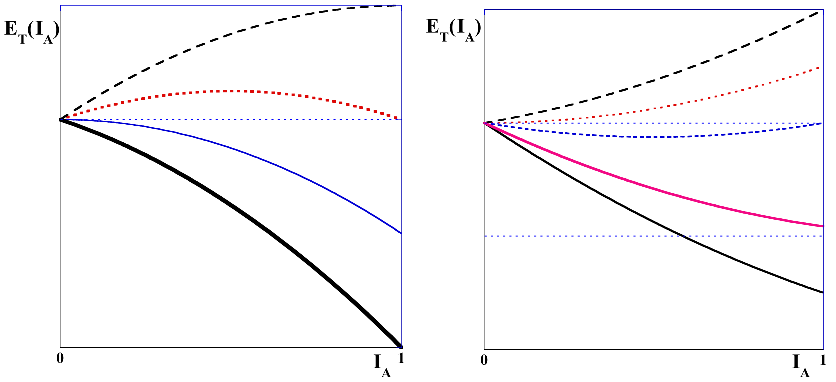

Figure 3. Energy profiles $\epsilon_{\rm T}(I_{\rm A})$ versus electron transfer $I_{\rm A}$ (defined by equation (30)) for different values of $\mu_{\rm A}$ when $\chi_{\rm D} + \chi_{\rm A} < 0$ (left) (soft anharmonicity) and when $\chi_{\rm D} + \chi_{\rm A} > 0$ (right) (hard anharmonicity).

Then, at zero temperature ($\zeta_\alpha = 0$) we obtain from equation (8) two coupled equations

$$i\hbar\dot{\psi}_\alpha = \left(\mu_\alpha + \chi_\alpha|\psi_\alpha|^2 + \gamma_\alpha\frac{{\rm d}|\psi_\alpha|^2}{{\rm d}t}\right)\psi_\alpha - \lambda\psi_\beta \tag{28}$$

where (α, β) denotes the pair (D, A) or (A, D), respectively. These two equations describe the quantum tunnelling 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 $|\psi_{\rm D}|^2$ and $|\psi_{\rm A}|^2$ are time constant. Then, $\psi_\alpha(t) = {\rm e}^{-{\rm i}E_\alpha t/\hbar}\psi_\alpha(0)$. The electronic energy level, E_α, at site α depends on the electron densities $|\psi_\alpha|^2$:

$$E_\alpha(I_\alpha) = \frac{{\rm d}H_\alpha}{{\rm d}I_\alpha} = \mu_\alpha + \chi_\alpha I_\alpha. \tag{29}$$

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 density (inverse Born–Oppenheimer approximation).

Neglecting the small interaction energy in (27), the main contribution to the energy variation $\epsilon_{\rm T}(I_{\rm A}) = H_{\rm D}(1 - I_{\rm A}) + H_{\rm A}(I_{\rm A}) - H_{\rm D}(1) - H_{\rm A}(0)$ of the system (27) is only a function of the electron density $I_{\rm A}$ on the acceptor (since $|\psi_{\rm D}|^2 + |\psi_{\rm A}|^2 = I_{\rm D} + I_{\rm A} = 1$)

$$\epsilon_{\rm T}(I_{\rm A}) = (\mu_{\rm A} - \mu_{\rm D} - \chi_{\rm D})I_{\rm A} + \tfrac{1}{2}(\chi_{\rm A} + \chi_{\rm D})I_{\rm A}^2. \tag{30}$$

Figure 3 shows some possible profiles of $\epsilon_{\rm T}(I_{\rm A})$. The derivative of this curve with respect to $I_{\rm A}$ is the difference $E_{\rm A}(I_{\rm A}) - E_{\rm D}(1 - I_{\rm A})$ between the electronic energy level of A and D at charge transfer $I_{\rm A}$. Consequently, there is electronic resonance $E_{\rm A}(I_{\rm A}) = E_{\rm D}(1-I_{\rm A})$ when this curve has a horizontal slope. At the Marcus inversion point this slope is zero at zero transfer ($E_{\rm A}(0) = E_{\rm D}(1)$), i.e., $\mu_{\rm A} = \mu_{\rm D} + \chi_{\rm D}$.

There are two possible situations which are qualitatively different. Either the curve $\epsilon_{\rm T}(I_{\rm A})$ has negative convexity, i.e., $\chi_{\rm A} + \chi_{\rm D} < 0$ (figure 3 left) (soft dimer) or positive convexity when $\chi_{\rm A} + \chi_{\rm D} > 0$ (hard dimer).

- When the dimer is soft (figure 3 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 $\mu_{\rm A} > \mu_{\rm D} + \chi_{\rm D}$ which disappears just at the inversion point $\mu_{\rm A} = \mu_{\rm D} + \chi_{\rm D}$.[3]

---

[3] This energy barrier is identical to those shown in figure 1 only when the capacitive terms $\chi_\alpha^{\rm C}$ vanish (see [9] for details).

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 (see [9] for details). The observed dynamics confirms the existence of ET at the scale of picosecond with physically reasonable parameters. The timescale 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 timescale decreases until it reaches an optimum which roughly corresponds to the cross-over between underdamped and overdamped. Next, for very large damping the timescale 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 3 right), ET does not occur at zero temperature, either in the normal regime or 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 $I_A^m = 1$. Figure 4 shows an electron transfer versus time at zero temperature in an example which is slightly beyond the inversion point. There is no energy barrier and the electronic levels remains sufficiently close to each other in order that energy dissipation can occur through the phonon bath. The electronic frequency $\Omega_D - \Omega_A$ is visible in the narrow oscillations which apparently broaden the curves.

5.3. Coherent electron–phonon oscillator (CEPO)

The special case where $\epsilon_T(I_A)$ is a constant is especially interesting. In this situation, the reorganization energy and the electrostatic energy exactly balance each other. Then, the derivative of the energy variation $\epsilon_T(I_A)$ with respect to I_A is zero, which implies that the electronic resonance $\Omega_D = \Omega_A$ between the electronic levels of the donor and of the acceptor persists all along the electron transfer. In this case, the reaction energy is zero but despite ET becoming ultrafast, it is also reversible.

We could say *a priori* that this situation is identical to a standard linear tunnelling of an electron between two degenerate electronic levels. However, there is an essential difference because the tunnelling 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

---

[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 tunnelling. Then, there is a bonding and an antibonding quantum state which are separated by a large difference in energy (corresponding to twice the chemical bond energy).

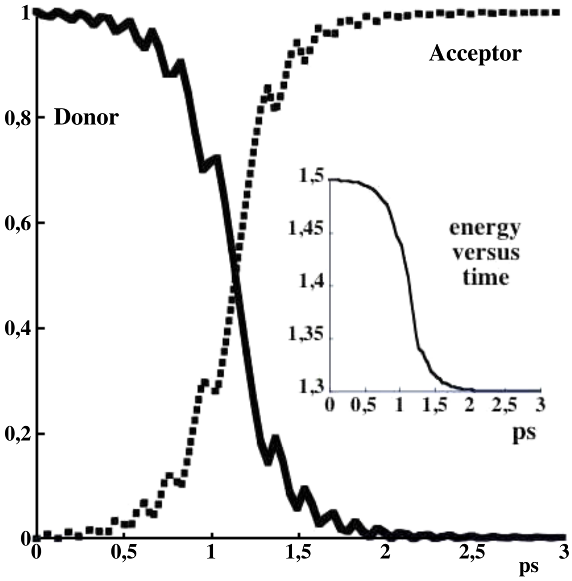

Figure 4. Electron density $I_D = 1/2 - I$ on the donor and $I_A = 1/2 + I$ on the acceptor for a dimer model beyond the inversion point in the marginal case between hard and soft ($\mu_D = 2$, $\chi_D = -1$, $\mu_A = 0.8$, $\chi_A = 1$, $\lambda = 10^{-2}$, $\gamma_D = \gamma_A = 10$).

system's reactivity, as we shall see in the next section for trimer models. We call this new mode a *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 [10, 11]. In that case, a numerical test has confirmed [12] that this classical concept of targeted transfer persists when these anharmonic oscillators are considered as quantum providing the energy transfer involving the creation and annihilation of many quantum phonons. This remark supports the idea that the classical treatment of the phonon bath is sufficient and physically correct in the case of a strong interaction of the electron with its phonon bath.

When $\epsilon_T(I_A) = 0$, the Hamiltonian of this CEPO is reduced to the small interaction term $H_T^{\mathrm{int}}(\{\psi_\alpha\})$. 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 equation (27), $H_T^{\mathrm{int}} = -\lambda(\psi_D^\star \psi_A + \psi_A^\star \psi_D)$, 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 $2I_0 = I_A + I_D = 1$, equation (28) becomes

$$\hbar\dot{\theta} = \lambda \frac{4I}{\sqrt{1-4I^2}} \cos\theta + \gamma \dot{I} \tag{31}$$

$$\hbar\dot{I} = -\lambda\sqrt{1-4I^2} \sin\theta \tag{32}$$

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

$$H_T^{\mathrm{int}} = -\lambda\sqrt{1-4I^2}\cos\theta. \tag{33}$$

This model was exactly solved in the absence of damping in [10]. In our case, energy is not conserved but we have

$$\dot{H}_T^{\mathrm{int}} = -\gamma\dot{I}^2 < 0. \tag{34}$$

Then, equations (33) and (32) yield

$$H_T^{\mathrm{int}\,2} + \hbar^2\dot{I}^2 = \hbar^2\Omega^2(\tfrac{1}{4} - I^2) \tag{35}$$

with

$$\hbar\Omega = 2\lambda \tag{36}$$

and then $H_T^{\mathrm{int}} = F(I,\dot{I}) = \pm\hbar\sqrt{\Omega^2(\frac{1}{4}-I^2)-\dot{I}^2}$ 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 equation (34). $F(I,\dot{I})$ 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 equation (35) yields, using equation (34),

$$\ddot{I} - \frac{\gamma}{\hbar^2}F(I,\dot{I})\dot{I} + \Omega^2 I = 0, \tag{37}$$

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 equation (33)), the effective damping is negative, which means that 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 until it reaches the energy minimum $-\lambda$ of $H_T^{\mathrm{int}} = F(I,\dot{I})$ at $I = \dot{I} = 0$ (and $\cos\theta = 1$). Figure 5 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

$$E_D(t) = E_A(t) = \mu_D + \chi_D(\tfrac{1}{2} - I(t)) = \mu_A + \chi_A(\tfrac{1}{2} + I(t)). \tag{38}$$

Since the (underdamped) frequency Ω of this CEPO (36) 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 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.

5.4. Catalytic ET at zero temperature with a CEPO

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

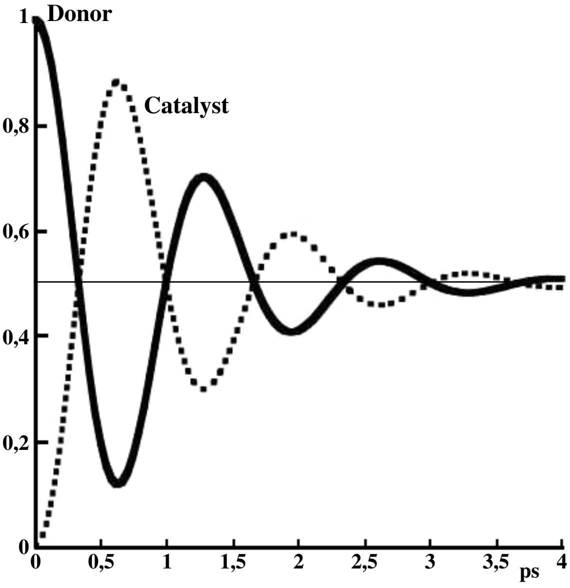

Figure 5. Electron density $I_D = 1/2 - I$ on the donor and $I_A = 1/2 + I$ on the acceptor when the dimer is a coherent electron–phonon oscillator (CEPO) ($\mu_D = 2$, $\chi_D = -1$, $\mu_A = 1$, $\chi_A = 1$, $\lambda = 10^{-2}$, $\gamma_D = \gamma_A = 1$).

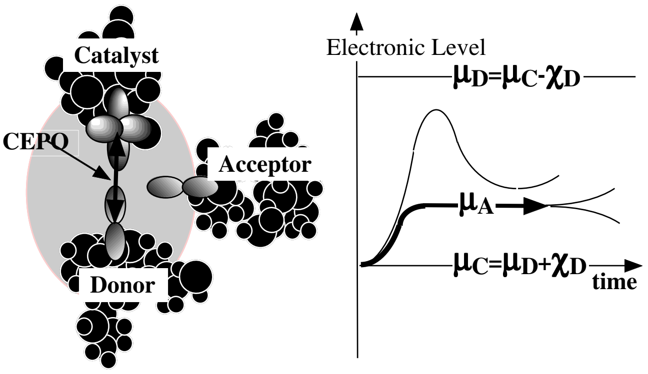

Figure 6. Principle of ET with a coherent electron–phonon oscillator: two weakly coupled molecular units (donor and catalyst) generate a CEPO. This system is weakly coupled to a third unit, the acceptor (left scheme). An electron initially on the donor generates an oscillation of the electronic level 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).

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 6 shows a scheme of the principle for catalytic electron transfer.

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 system donor–catalyst. Then, if a third unoccupied electronic site with an electronic level in the interval of variation of the CEPO is present and weakly coupled with the system donor–catalyst, 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 already been 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.

5.5. *Ultrafast ET on a trimer model*

We illustrate these principles on the trimer model with Hamiltonian

$$H_{\mathrm{T}}(\{\psi_\alpha\}) = \sum_{\alpha=\mathrm{D,C,A}} \mu_\alpha|\psi_\alpha|^2 + \tfrac{1}{2}\chi_\alpha|\psi_\alpha|^4 - \sum_{\alpha\neq\beta}\lambda_{\alpha\beta}\psi_\alpha^\star\psi_\beta. \tag{39}$$

Using the action angle coordinates defined as above, $\psi_\alpha = \sqrt{I_\alpha}\mathrm{e}^{-\mathrm{i}\theta_\alpha}$, the dynamical equations (8) of this system with damping at zero temperature and with the assumptions described in section 5.1 become

$$\hbar\dot{I}_\alpha = -2\sum_\beta \lambda_{\alpha,\beta}\sqrt{I_\alpha I_\beta}\sin(\theta_\alpha-\theta_\beta) \tag{40}$$

$$\hbar\dot{\theta}_\alpha = E_\alpha + \sum_\beta \lambda_{\alpha,\beta}\sqrt{\frac{I_\beta}{I_\alpha}}\cos(\theta_\alpha-\theta_\beta) + \gamma_\alpha\dot{I}_\alpha \tag{41}$$

where $E_\alpha = \hbar\Omega_\alpha = \mu_\alpha + \chi_\alpha I_\alpha$. 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 3. In this situation

$$\chi_\mathrm{A} + \chi_\mathrm{D} < 0 \tag{42}$$

$$mu_\mathrm{A} + \tfrac{1}{2}\chi_\mathrm{A} < \mu_\mathrm{D} + \tfrac{1}{2}\chi_\mathrm{D}. \tag{43}$$

In the absence of a catalyst, ($I_\mathrm{C} = 0$ or $I_\mathrm{D} + I_\mathrm{A} = 1$), 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 $\mu_\mathrm{C} = \mu_\mathrm{D} + \chi_\mathrm{D}$, $\chi_\mathrm{D} = -\chi_\mathrm{C}$, the energy variation $\epsilon_\mathrm{T}(I_\mathrm{D}, I_\mathrm{A}) = H_\mathrm{D}(I_\mathrm{D}) + H_\mathrm{C}(I_\mathrm{C}) + H_\mathrm{A}(I_\mathrm{A}) - H_\mathrm{D}(1) - H_\mathrm{C}(0) - H_\mathrm{A}(0)$ is only a function of I_D and I_A, since $I_\mathrm{D} + I_\mathrm{C} + I_\mathrm{A} = 1$

$$\epsilon_\mathrm{T}(I_\mathrm{D}, I_\mathrm{A}) = (\mu_\mathrm{A} - \mu_\mathrm{D})I_\mathrm{A} - \chi_\mathrm{D}I_\mathrm{A}I_\mathrm{D} + \tfrac{1}{2}(\chi_\mathrm{A} - \chi_\mathrm{D})I_\mathrm{A}^2 \tag{44}$$

where $0 \leqslant I_\mathrm{D} \leqslant 1$, $0 \leqslant I_\mathrm{A} \leqslant 1$ and $I_\mathrm{D} + I_\mathrm{A} \leqslant 1$. We have

$$\frac{\partial\epsilon_\mathrm{T}}{\partial I_\mathrm{D}}(I_\mathrm{D}, I_\mathrm{A}) = E_\mathrm{D}(I_\mathrm{D}) - E_\mathrm{C}(1 - I_\mathrm{A} - I_\mathrm{D}) = -\chi_\mathrm{D}I_\mathrm{A} \tag{45}$$

$$\frac{\partial\epsilon_\mathrm{T}}{\partial I_\mathrm{A}}(I_\mathrm{D}, I_\mathrm{A}) = E_\mathrm{A}(I_\mathrm{A}) - E_\mathrm{C}(1 - I_\mathrm{A} - I_\mathrm{D}) = \mu_\mathrm{A} - \mu_\mathrm{D} - \chi_\mathrm{D}I_\mathrm{D} + (\chi_\mathrm{A} - \chi_\mathrm{D})I_\mathrm{A}. \tag{46}$$

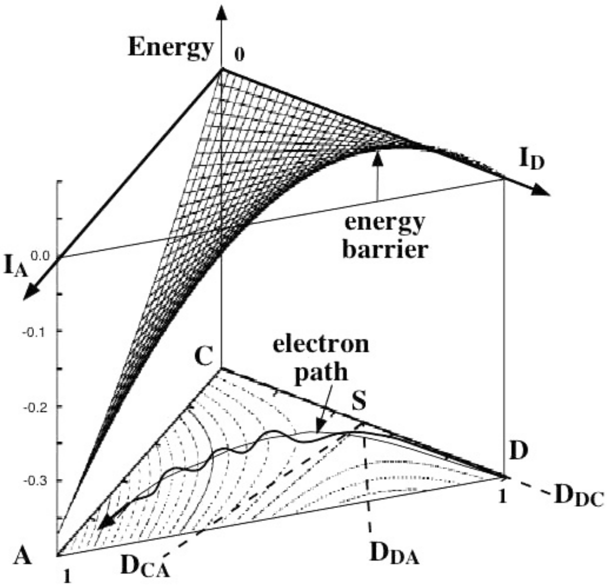

Figure 7. 3D plot of the energy surface $\epsilon_{\mathrm{T}}(I_{\mathrm{D}}, I_{\mathrm{A}})$ defined by (44) versus I_{A} and I_{D} and contour lines in projection for an example where conditions (42), (43) and (47) are fulfilled ($\mu_{\mathrm{D}} = 2$, $\chi_{\mathrm{D}} = -1$, $\mu_{\mathrm{C}} = 1$, $\chi_{\mathrm{C}} = 1$, $\mu_{\mathrm{A}} = 1.5$, and $\chi_{\mathrm{A}} = -0.75$). The triple resonance point S and the resonance lines $\mathrm{D_{DC}}$, $\mathrm{D_{DA}}$ and $\mathrm{D_{CA}}$ are also shown (dashed lines). The electron path (real and averaged) is schematically represented.

The extrema of this two-variable function are obtained when the electronic energy levels of the three sites are equal. The first equation requires $I_{\mathrm{A}} = 0$, and then the second equation yields $\mu_{\mathrm{A}} = \mu_{\mathrm{D}} + \chi_{\mathrm{D}} I_{\mathrm{D}}$. This equation can be fulfilled only if μ_{A} belongs to the interval of frequency variation of the CEPO which yields

$$\mu_{\mathrm{D}} + \chi_{\mathrm{D}} \leqslant \mu_{\mathrm{A}} \leqslant \mu_{\mathrm{D}} \qquad \text{if } \chi_{\mathrm{D}} < 0 \qquad \text{or} \tag{47}$$

$$\mu_{\mathrm{D}} \leqslant \mu_{\mathrm{A}} \leqslant \mu_{\mathrm{D}} + \chi_{\mathrm{D}} \qquad \text{if } \chi_{\mathrm{D}} > 0. \tag{48}$$

When both conditions (42) and (43) and one of the conditions (47) and (48) are fulfilled, the energy surface (44) appears as shown in figure 7.

There are three resonance lines:

- D_{DC} defined by $E_{\mathrm{D}} = E_{\mathrm{C}}$ which yields $I_{\mathrm{A}} = 0$ from equation (45);
- D_{CA} defined by $E_{\mathrm{C}} = E_{\mathrm{A}}$ which yields $-\chi_{\mathrm{D}} I_{\mathrm{D}} + (\chi_{\mathrm{A}} - \chi_{\mathrm{D}}) I_{\mathrm{A}} = \mu_{\mathrm{D}} - \mu_{\mathrm{A}}$ from equation (46);
- D_{DA} defined by $E_{\mathrm{D}} = E_{\mathrm{A}}$ which yields $-\chi_{\mathrm{D}} I_{\mathrm{D}} + \chi_{\mathrm{A}} I_{\mathrm{A}} = \mu_{\mathrm{D}} - \mu_{\mathrm{A}}$ from equations (45) and (46).

$\mathrm{D_{DC}}$, $\mathrm{D_{CA}}$ and $\mathrm{D_{DA}}$ intersect at the same point with coordinates $\mathrm{S} = (I_{\mathrm{D}} = I_{\mathrm{S}}, I_{\mathrm{A}} = 0)$ with $0 < I_{\mathrm{S}} = (\mu_{\mathrm{A}} - \mu_{\mathrm{D}})/\chi_{\mathrm{D}} < 1$.

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

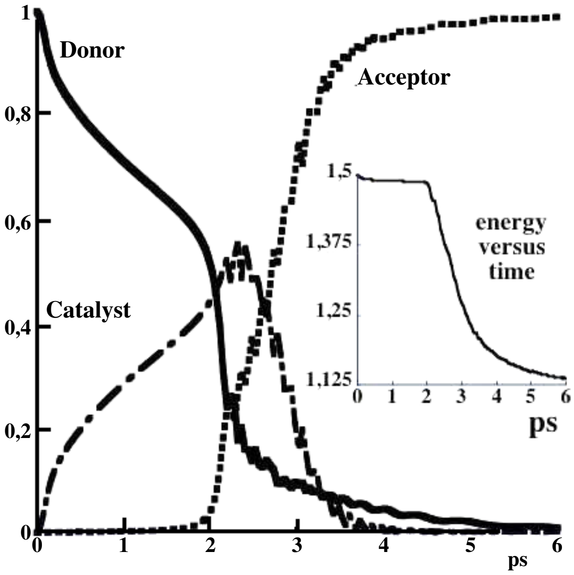

Figure 8. Electron density on donor (solid), acceptor (dashed), and catalyst (long dashed) versus time in the trimer model (39) where $\mu_D = 2$, $\chi_D = -1$, $\mu_C = 1$, $\chi_C = 1$, $\mu_A = 1.5$, $\chi_D = -0.75$, $\lambda_{DA} = \lambda_{AC} = \lambda_{DC} = 10^{-2}$ and $\gamma_D = \gamma_C = \gamma_A = 10$ (units are supposed to be eV).

At zero damping, the trimer Hamiltonian (28), 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 nonresonant solutions are preserved as Kolmogorov–Arnol'd–Moser (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 [18], 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 dimer donor–catalyst 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 behaviour 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 in figure 8.

Figure 8 shows an example of numerically calculated transfer of an electron with equation (28) 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

---

[5] In the case when 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.

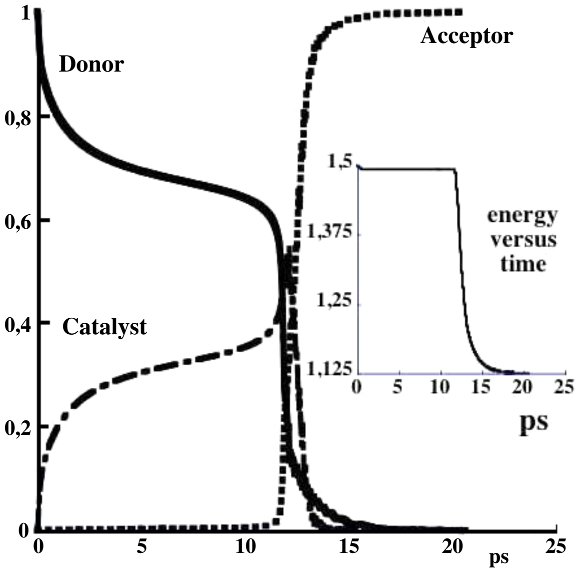

Figure 9. Electron density on donor (solid), acceptor (dashed), and catalyst (long dashed) versus time in the trimer model (39) at zero temperature, where the parameters are the same as in figure 7 except that $\mu_C = 1.0112$. The CEPO donor–catalyst has been slightly detuned and ET is retarded. For larger values of μ_C, the electron mostly remains on the donor and there is no ET.

to a full occupation and decays to zero while simultaneously the electron density on the donor continues to decay to zero.

The role of the CEPO formed by the weakly coupled donor–catalyst system is to trigger ET from that system 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.

Small perturbations which detune the CEPO have drastic consequences on ET. Actually, the trimer model may be viewed as a molecular transistor. For example, if the difference between the energy levels $\mu_C - \mu_D$ on the donor and the catalyst is increased from its optimal value by a small amount, the CEPO oscillation is sharply killed, which immediately blocks ET to the acceptor. The example of ET shown in figure 9 concerns the same model as figure 8, but μ_C has been increased to a value very close to the threshold where ET become blocked $\mu_C^{(c)} \approx 1.0115$. It is clearly visible that ET to the acceptor lasts much longer than ET at the optimum value of μ_C.

Actually, the effect of the local electric field variation is asymmetric. If, in contrast, $\mu_C - \mu_D$ is decreased, the CEPO system becomes a donor–acceptor system in the inverted regime, as for example the one shown in figure 4. The electron starts to transfer to C but more slowly than for the optimized CEPO and next to the final acceptor A. As a result ET is not blocked but is substantially slows down.

This local perturbation of the CEPO could be obtained by an electric field at the microscopic scale which may be either generated by minor permanent ‘mutations’ of the system (poison) or produced transiently by particular charged molecules which could be used for regulating the system by binding at specific sites during a certain time in a close vicinity of the CEPO, thus producing a local electric field. In conclusion, it appears that ultrafast catalytic ET could be controlled by weak external perturbations at the nanoscale level and thus could be used as part of logical devices in living cells.

6. Discussion of ET in the PRC

Subpicosecond oscillations in the PRC [17] have been observed [13], and they demonstrate the existence of a coupling between ET and coherent vibrational motions [14]. 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 wavefunctions, 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 the excitation of $\mathbf{P}$ (see references in [16]). Recently more accurate quantum chemical calculations [16] of the PRC have been performed by solving the time-dependent and time-independent Schrödinger equations. It is shown that there is an important change of geometry of the special pair dimer from neutral $\mathbf{P}^\star$ to ionized $\mathbf{P}^+$ while the reorganization 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 $\mathbf{P}^+ - \mathbf{B}_\mathbf{A}^-$ is strongly correlated to the rate of electron transfer. The maximum efficiency is obtained when this energy is slightly below the energy of $\mathbf{P}^\star - \mathbf{B_A}$. These features seem to be qualitatively in quite good agreement with the predictions of our theory when assuming the system $\mathbf{P}^\star - \mathbf{B_A}$ 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 have a comparable timescale. Thus, the standard theory, which assumes the adiabatic approximation, cannot properly describe 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 intricate 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 a 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 in 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 is 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 equation (8)) 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 noting that the observed features in the photosynthetic reaction centre (PRC) described in the introduction have strong qualitative similarities with our findings in the trimer model with CEPO.

The excited dimer of bacteriochlorophylls $\mathbf{P}^\star$ 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 [16] mentioned above. The fine tuning of the CEPO requires conditions on both linear and nonlinear coefficients on $\mathbf{P}^\star$ and $\mathbf{B_A}$. It suffices that the coefficients for $\mathbf{B_B}$ on the second branch B be slightly different (of the order of the small coupling parameter λ) in order to detune the possible CEPO on $\mathbf{P}^\star - \mathbf{B_B}$ 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 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 ($\mathbf{P}^\star - \mathbf{B_A} - \mathbf{H_A}$) 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 $\mathbf{P}^\star$, $\mathbf{B_A}$, 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 $\mathbf{P}^\star - \mathbf{B_A}$ (donor–catalyst) and the acceptor $\mathbf{B_A}$ but then electronic resonances gradually disappear. ET slows down on the acceptor. The consequence is that ET versus time is nonexponential. 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 any more 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 $\mathbf{P}^\star - \mathbf{B_B}$.

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.

In contrast, 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 the resonance intermittently (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 CEPOs 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 [15], although they are not well identified. CEPOs 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 properties 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.

7. Concluding remarks

We proposed here a nonadiabatic theory for ET which becomes useful in the vicinity of the Marcus inversion point where electron transfer is expected to become ultrafast.

Our approach initially consists of considering the complex amplitudes of the tight-binding electronic wavefunction as extra reaction coordinates. Thus the dynamics of the electron is not slaved by the adiabatic approximation to the dynamics of the environment. Then, we show after exact elimination of the atomic variables that the electron dynamics can be described by an effective equation which is a discrete nonlinear Schrödinger equation with extra dissipative terms and coloured Langevin forces describing the thermal fluctuations. The advantage of our approach is that the electron dynamics may involve coherent behaviour when some conditions are fulfilled and then its tunnelling should be described as a probabilistic process as assumed in early theories.

It is close to the inversion point where electron transfer is supposed to occur at zero temperature that our model reveals an important difference with the standard approach. We obtain in particular nonexponential transfer with long tails. The most interesting result is that our model naturally suggests the possible existence of coherent electron phonon oscillators (CEPOs).

A CEPO is a two-site system which is finely tuned in order the atomic reorganization energy and the electrostatic energy almost balance one with each other. Then, the energy barrier for electron transfer between the two sites is flattened. The result is that despite the electronic levels changing during ET, the electronic resonance persists at any transfer. Since ET is then obviously reversible, there is a coherent electronic oscillation similar to those between two resonant electronic levels. The important novelty of this oscillation is that it may become highly nonlinear when it involves both a collective motion of the atoms and a spatial oscillation of the electronic charge. Then, the electronic level of the electron on the CEPO oscillates at the same frequency.

The oscillations of the electronic level of a CEPO could be used for triggering ultrafast and catalytic electron transfer of the electron of the CEPO towards an acceptor by catching the resonance with its LUMO. This CEPO is formed by interaction of the donor site with a catalyst site. In the absence of a catalyst site, the CEPO does not exist and no ET could occur towards the acceptor (at low temperature). Such a chemical reaction may be easily controlled by small perturbations of the CEPO formed by the donor–catalyst system. It appears that this trimer model behaves like a transistor since small change in the electrostatic environment of the CEPO may block the electron transfer between the donor and the acceptor. Such small changes are physically rather easy to induce by mutations or transient binding of specific charged molecules, and also change in the local dielectric constant which may be induced by the solvent (pH, . . .) etc.

The concept of CEPOs was extended to multisite chains for inducing polaron mobility [20] as a model for signal transmission in enzymes. We used similar ideas in a very different context for improving bipolaron mobility by depressing its Peierls–Nabarro energy barrier due to the well-tuned competition between electron–phonon coupling and electron–electron repulsion by a Hubbard term [21].

This new theory needs more developments. First, only results valid at low temperature were presented. Although the thermal fluctuations were formally included in the effective dynamics of the electron as a random force their effect was not precisely studied. Further study will be necessary to investigate how thermal fluctuations affect and finally destroy the coherence effect allowing ultrafast ET and finally how the standard ET theory is recovered at high temperature. Second, the parameters for the example we treated were chosen empirically in a range which looks physically realistic. It might be possible to determine those parameters in specific example by *ab initio* numerical calculations and to check if, in some cases, their values could generate CEPOs. Otherwise, our theory predicts many qualitative consequences of the existence of CEPOs which could be experimentally checked in systems where they may be suspected to exist.

Appendix A. Approximate equation for the electron dynamics at small transfer integral and low temperature

We show that equation (8) may be approximated by a differential equation without retarded interaction. First, the last term of equation (8) can be expressed as a function of $\{\psi_\alpha\}$ which involves the currents without time derivatives. It readily turns out from equation (8) that

$$\frac{\mathrm{d}|\psi_\alpha|^2}{\mathrm{d}t} = \psi_\alpha^\star \dot{\psi}_\alpha + \psi_\alpha \dot{\psi}_\alpha^\star = \frac{\mathrm{i}}{\hbar}\left(\psi_\alpha \frac{\partial H_\mathrm{T}}{\partial \psi_\alpha} - \psi_\alpha^\star \frac{\partial H_\mathrm{T}}{\partial \psi_\alpha^\star}\right) \tag{A.1}$$

can be replaced by a function of $\{\psi_\alpha\}$ without time derivatives. Since we assumed in equation (3) that $H_\mathrm{T} = \hat{H}_\mathrm{T}(\{|\psi_\alpha|^2\}) - \sum_{\beta\neq\gamma} \lambda_{\beta,\gamma}(\{|\psi_\alpha|^2\})\psi_\beta\psi_\gamma^\star$, it turns out that the electron density variation at site α is equal to the sum of the entering density currents from the other sites β,

$$\frac{\mathrm{d}|\psi_\alpha|^2}{\mathrm{d}t} = \sum_\beta J_{\beta\to\alpha} = 2\sum_\beta \frac{\lambda_{\alpha,\beta}}{\hbar}\,\mathrm{Im}(\psi_\alpha\psi_\beta^\star) \tag{A.2}$$

where the density current from site β to site α is

$$J_{\beta\to\alpha} = \frac{\mathrm{i}}{\hbar}\lambda_{\alpha,\beta}(\{|\psi_\gamma|^2\})(\psi_\alpha^\star\psi_\beta - \psi_\alpha\psi_\beta^\star) = 2\frac{\lambda_{\alpha,\beta}}{\hbar}\,\mathrm{Im}(\psi_\alpha\psi_\beta^\star) = -J_{\alpha\to\beta}. \tag{A.3}$$

Since $\lambda_{\alpha,\beta}$ is supposed to be small, the variation of the electron density is slow and only varies over the timescale of $\hbar/\lambda_{\alpha,\beta}$. We also assume that the random force $\langle\zeta_\alpha(t)\rangle$ is small, of the order of or smaller than the transfer integral energies $\lambda_{\alpha,\beta}$, that is the temperature $k_B T\Gamma(t) < \approx\lambda^2_{\alpha,\beta}$ is small enough. Then, neglecting all the terms of order $\lambda_{\alpha,\beta}$ small in the second member of equation (8) yields the set of equations

$$\mathrm{i}\hbar\dot{\psi}_\alpha \approx \left(\frac{\partial \hat{H}_\mathrm{T}}{\partial|\psi_\alpha|^2}\right)\psi_\alpha \tag{A.4}$$

which yields the approximate solution $\psi_\alpha(t) = \psi_\alpha(0)\mathrm{e}^{-\mathrm{i}(\Omega_\alpha t)}$, where $|\psi_\alpha|^2$ is time constant and

$$\Omega_\alpha = \frac{1}{\hbar}\frac{\partial \hat{H}_\mathrm{T}}{\partial|\psi_\alpha|^2} \tag{A.5}$$

is a function of $\{|\psi_\alpha|^2\}$. Thus using equation (A.3), we have

$$\int_{-\infty}^{t}\Gamma_{\alpha,\beta}(t-\tau)\frac{\mathrm{d}|\psi_\beta(\tau)|^2}{\mathrm{d}\tau}\mathrm{d}\tau = 2\sum_\gamma\frac{\lambda_{\beta,\gamma}}{\hbar}\int_{-\infty}^{t}\Gamma_{\alpha,\beta}(t-\tau)\,\mathrm{Im}(\psi_\beta(\tau)\psi^\star_\gamma(\tau))\,\mathrm{d}\tau. \tag{A.6}$$

We have

$$\begin{aligned}\int_{-\infty}^{t}\Gamma_{\alpha,\beta}(t-\tau)\,\mathrm{Im}\left(\psi_\beta(\tau)\psi^\star_\gamma(\tau)\right)\,\mathrm{d}\tau &= \mathrm{Im}\left(\int_{-\infty}^{t}\Gamma_{\alpha,\beta}(t-\tau)\psi_\beta(\tau)\psi^\star_\gamma(\tau)\,\mathrm{d}\tau\right)\\ &\approx \mathrm{Im}\left(\psi_\beta(0)\psi^\star_\gamma(0)\int_{-\infty}^{t}\Gamma_{\alpha,\beta}(t-\tau)\mathrm{e}^{\mathrm{i}(\Omega_\gamma-\Omega_\beta)\tau}\,\mathrm{d}\tau\right)\\ &= \mathrm{Im}\left(\psi_\beta(t)\psi^\star_\gamma(t)\int_{0}^{\infty}\Gamma_{\alpha,\beta}(x)\mathrm{e}^{-\mathrm{i}(\Omega_\gamma-\Omega_\beta)x}\,\mathrm{d}x\right).\end{aligned} \tag{A.7}$$

We decompose

$$\int_0^\infty \Gamma_{\alpha,\beta}(x)\mathrm{e}^{-\mathrm{i}\Omega x}\,\mathrm{d}x = \tfrac{1}{2}(\gamma_{\alpha,\beta}(\Omega)+\mathrm{i}\sigma_{\alpha,\beta}(\Omega)) \tag{A.8}$$

into its real and imaginary parts, where $\gamma_{\alpha,\beta}(\Omega)$ is obtained from equation (13) and $\sigma_{\alpha,\beta}(\Omega)$ is related to $\gamma_{\alpha,\beta}(\Omega)$ through a standard Kramers–Kronig relation

$$\sigma_{\alpha,\beta}(\Omega) = \frac{1}{\pi}\int_{-\infty}^{+\infty}\frac{\gamma_{\alpha,\beta}(\Omega')}{\Omega'-\Omega}\,\mathrm{d}\Omega' = \lim_{\epsilon\to 0_+}\frac{1}{\pi}\int_{-\infty}^{+\infty}\gamma_{\alpha,\beta}(\Omega')\frac{\Omega'-\Omega}{\epsilon^2+(\Omega'-\Omega)^2}\,\mathrm{d}\Omega'. \tag{A.9}$$

Consequently, equations (A.7) and (A.8) yield

$$\begin{aligned}\int_{-\infty}^{t}\Gamma_{\alpha,\beta}(t-\tau)\,\mathrm{Im}\left(\psi_\beta(\tau)\psi^\star_\gamma(\tau)\right)\,\mathrm{d}\tau &\approx \tfrac{1}{2}\gamma_{\alpha,\beta}(\Omega_\gamma-\Omega_\beta)\,\mathrm{Im}\left(\psi_\beta(t)\psi^\star_\gamma(t)\right)\\ &\quad - \tfrac{1}{2}\sigma_{\alpha,\beta}(\Omega_\gamma-\Omega_\beta)\,\mathrm{Re}\left(\psi_\beta(t)\psi^\star_\gamma(t)\right)\end{aligned} \tag{A.10}$$

which yields with equation (A.6)

$$\begin{aligned}\int_{-\infty}^{t}\Gamma_{\alpha,\beta}(t-\tau)\frac{\mathrm{d}|\psi_\beta(\tau)|^2}{\mathrm{d}\tau}\,\mathrm{d}\tau &\approx 2\sum_\gamma\frac{\lambda_{\beta,\gamma}}{\hbar}\int_{-\infty}^{t}\Gamma_{\alpha,\beta}(t-\tau)\,\mathrm{Im}(\psi_\beta(\tau)\psi^\star_\gamma(\tau))\,\mathrm{d}\tau\\ &\approx \sum_\gamma\frac{\lambda_{\beta,\gamma}}{\hbar}\Big(\gamma_{\alpha,\beta}(\Omega_\gamma-\Omega_\beta)\,\mathrm{Im}\left(\psi_\beta(t)\psi^\star_\gamma(t)\right)\\ &\quad - \sigma_{\alpha,\beta}(\Omega_\gamma-\Omega_\beta)\,\mathrm{Re}\left(\psi_\beta(t)\psi^\star_\gamma(t)\right)\Big).\end{aligned} \tag{A.11}$$

Ω_α are functions of the electron densities $\{|\psi_\alpha|^2\}$ defined by equation (A.5). $\Gamma_{\alpha,\beta}(t)$ is supposed to be known with a frequency cut-off which defines functions $\gamma_{\alpha,\beta}(\Omega)$ and $\sigma_{\alpha,\beta}(\Omega)$. Thus by substitution of (A.11) in equation (8), this equation can be approximate at low temperature and $\lambda_{\alpha,\beta}$ small as a set of simple differential equations with the global form $\mathrm{i}\hbar\dot{\psi} = F(\psi, \psi^\star)$ without any retarded interaction. Despite the expanded form of this equation being tediously long, its advantage is in being much simpler for numerical integrations when the temperature is low.

Appendix B. Equation for the charge currents out of resonance at zero temperature

We go beyond the previous equation which involves both the amplitude and the phase of the electronic amplitudes. We derive an explicit, smooth equation for the dynamics of the electron densities (where the phases are eliminated by averaging the fast electronic oscillations) which as in the previous case is valid at zero temperature and at small couplings $\lambda_{\alpha,\beta}$ assumed to be of the order of λ. This equation describes the current flow when the dissipation of energy during electron transfer may occur by (classical) phonon emission, that is when on the one hand the differences between the electronic energy level do not exceed the phonon energies $\hbar\omega_c$, and on the other hand, these differences remains larger than the transfer integrals λ.

This equation only concerns the averaged 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 $\mathrm{D}_{\alpha,\beta}$, 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 the 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. Using equation (A.11), equation (8) yields for the action angle variables I_α and θ_α defined as $\Psi_\alpha = \sqrt{I_\alpha}\mathrm{e}^{-\mathrm{i}\theta_\alpha}$,

$$\hbar\dot{\theta}_\alpha = E_\alpha + \sum_{\beta,\gamma} \frac{\lambda_{\beta,\gamma}}{\hbar}\sqrt{I_\beta I_\gamma}\left(\gamma_{\alpha,\beta}\sin(\theta_\gamma - \theta_\beta) - \sigma_{\alpha,\beta}\cos(\theta_\gamma - \theta_\beta)\right) - \sum_\beta \lambda_{\alpha,\beta}\sqrt{\frac{I_\beta}{I_\alpha}}\cos(\theta_\alpha - \theta_\beta) \tag{B.1}$$

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

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

$$\bar{I}_\alpha = I_\alpha - \frac{2}{\hbar}\sum_\beta \lambda_{\alpha,\beta}\frac{\sqrt{I_\alpha I_\beta}}{\dot{\theta}_\alpha - \dot{\theta}_\beta}\cos(\theta_\alpha - \theta_\beta) \tag{B.3}$$

so that equation (B.2) yields

$$\hbar\dot{\bar{I}}_\alpha = -2\sum_\beta \lambda_{\alpha,\beta}\frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{\sqrt{I_\alpha I_\beta}}{\dot{\theta}_\alpha - \dot{\theta}_\beta}\right)\cos(\theta_\alpha - \theta_\beta). \tag{B.4}$$

When there is no resonance, that is $|E_\alpha - E_\beta|$ for $\alpha \neq \beta$ is much larger than the transfer integrals $|\lambda_{\gamma,\delta}|$, and since then $\dot{\theta}_\alpha \approx \Omega_\alpha = E_\alpha/\hbar$, the fluctuations around $\bar{I}_\alpha$ in equation (B.3) are fast at frequency $(E_\alpha - E_\beta)/\hbar$. Their amplitude at coupling of order λ is small at any time and thus this term does not contribute on average to the large amplitude variation of I_α involved in ET. Thus, the electron transfer is essentially described by $\bar{I}_\alpha$.

Equation (B.1) yields the time derivatives $\dot{\theta}_\alpha$ and $\dot{\theta}_\beta$ as functions of $\{I_\alpha, \theta_\alpha\}$, as well as equation (B.2) for $\dot{I}_\alpha$. Then, it turns 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. It is not necessary to calculate explicitely all the terms coming from the derivative in equation (B.4). It will contain essentially a combination of sine products like $\lambda_{\alpha,\beta}\lambda_{\alpha,\gamma}\cos(\theta_\alpha-\theta_\beta)\cos(\theta_\alpha-\theta_\gamma)$ or $\lambda_{\alpha,\beta}\lambda_{\alpha,\gamma}\cos(\theta_\alpha-\theta_\beta)\sin(\theta_\alpha-\theta_\gamma)$ with prefactors which are functions of $\{I_\alpha\}$ with slow time variations.

Since the set of electronic frequencies $\{\Omega_\alpha\}$ does not involve any resonance, most terms of this expansion have fast time periodic variations which average to zero. The only terms which do not average to zero have the form $\cos^2(\theta_\alpha-\theta_\beta)$, which average to $1/2$. These terms are essentially provided by those which depend on the damping parameters $\gamma_{\alpha,\beta}$ in the second time derivatives $\ddot{\theta}_\alpha$. Then, keeping only those terms, it turns out that the average $\langle\dot{\bar{I}}_\alpha\rangle$ over times long at the scale of the fast fluctuations but short at the order $1/\lambda^2$ becomes

$$\langle\dot{\bar{I}}_\alpha\rangle \approx -\sum_\beta \bar{J}_{\alpha\to\beta} \tag{B.5}$$

where $\bar{J}_{\alpha\to\beta}$ is the averaged charge current from α to β along the bond α,β. This formula is similar to equation (A.2) but it concerns the averaged current and densities. We have at leading order in λ

$$\bar{J}_{\alpha\to\beta} = -\bar{J}_{\beta\to\alpha} \approx \frac{\lambda_{\alpha,\beta}^2}{\hbar^2}\frac{\gamma_{\alpha,\alpha}+\gamma_{\beta,\beta}-2\gamma_{\alpha,\beta}}{E_\alpha-E_\beta}\bar{I}_\alpha\bar{I}_\beta. \tag{B.6}$$

These parameters $\gamma_{\alpha,\beta}$ are calculated at frequency $\Omega_\alpha-\Omega_\beta=(E_\alpha-E_\beta)/\hbar$. This sum $\gamma_{\alpha,\alpha}+\gamma_{\beta,\beta}-2\gamma_{\alpha,\beta}$ is necessarily positive because of the positivity of operator with matrix element $\gamma_{\alpha,\beta}(\Omega)$ at any Ω.

We note that the bond current along the bond α,β is zero when the damping coefficients are zero at the corresponding frequency. This result should be expected because formula (17) shows the absence of energy dissipation in the same conditions.

Moreover, at zero damping and zero transfer integral, the trimer model is integrable and all its orbits are quasiperiodic tori (or exceptionally periodic). When the transfer integrals are small but nonzero, the Kolmogorov–Arnol'd–Moser (KAM) theory predicts that the nonresonant quasiperiodic tori persist as quasiperiodic orbits (KAM tori) where I_α is a quasiperiodic function of time which cannot vary on average. In the absence of damping, perturbation calculations at lowest order essentially approximate these KAM tori.

The direction of the current in the bond α,β is to flow from the highest electronic energy level towards the lowest electronic energy level, which is reasonable because of the energy dissipation. The current density increases when the energy level approaches resonance. In the case of resonance, the current diverges at the resonant bonds $E_\alpha=E_\beta$, but this is an artefact of our approximation of incoherent phase which is only valid in the absence of resonance. In that case, the electron dynamics becomes coherent and faster at order $\lambda_{\alpha,\beta}$ instead of $\lambda_{\alpha,\beta}^2$.

This formula also shows that when this energy level difference exceeds the phonon energy cut-off $\hbar\omega_c$, the current flow vanishes at zero temperature. Actually, ET is expected to continue slowly because of higher order terms. There is also 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 the density of electron transferred may look like a stretched exponential. Actually, this depends on the details of the damping function.

References

[1] Marcus R A 1956 *J. Chem. Phys.* **24** 966
Marcus R A 1993 *Rev. Mod. Phys.* **65** 599–610 (review)
[2] Levich V G and Dogonadze R R 1959 *Dokl. Akad. Nauk SSSR* **124** 123–6
[3] Hush N S 1961 *Trans. Faraday Soc.* **57** 557
[4] Levich V G 1966 *Adv. Electrochem. Eng.* **4** 825
[5] Hush M S (ed) 1971 *Reactions of Molecules at Electrodes* (London: Wiley–Interscience)
[6] Jortner J 1976 *J. Chem. Phys.* **64** 4860–7
[7] Kramers H A 1940 *Physica* **7** 284
[8] Kuznetzov A M and Ulstrup J 1999 *Electron Transfer in Chemistry and Biology: An Introduction to the Theory* (*Wiley Series in Theoretical Chemistry*) (New York: Wiley)
[9] Aubry S 2004 *Nonlinear Waves: Classical and Quantum Aspects* (*NATO Science Series II Mathematics, Physics and Chemistry* vol 153) ed F Kh Abdullaev and V V Konotop (Dordrecht: Kluwer) pp 443–71
[10] Aubry S, Kopidakis G, Morgante A-M and Tsironis G 2001 *Physica* B **296** 222–36
[11] Kopidakis G, Aubry S and Tsironis G 2001 *Phys. Rev. Lett.* **87** 165501
[12] Maniadis P, Kopidakis G and Aubry S 2004 *Physica* D **188** 153–77
[13] Vos M H, Lambry J-C, Robles S J, Youvan D C, Breton J and Martin J-L 1991 *Proc. Natl Acad. Sci.* **88** 8885–9
[14] Vos M H, Rischel C, Jones M R and Martin J-L 2000 *Biochemistry* **39** 8353–61
[15] Wynne K and Hochstrasser R M 1999 Electron transfer: from isolated molecules to biomolecules, Part two *Adv. Chem. Phys.* **107** 263–390
[16] Ivashin N and Larsson S 2002 *J. Phys. Chem.* B 3996–4009
[17] Hu X, Damjanovic A, Ritz T and Schulten K 1998 *Proc. Natl Acad. Sci. USA* **95** 5935
[18] Aubry S and Kopidakis G 2003 *Int. J. Mod. Phys.* B **17** 3908–21
[19] Aubry S and Kopidakis G 2005 *J. Biol. Phys.* **31** 375–402
[20] Hervé G and Aubry S 2006 *Physica* D **216** 235–45
[21] Proville L and Aubry S 1998 *Physica* D **113** 307–17
Proville L and Aubry S 1999 *Eur. Phys. J.* B **11** 41–58
Proville L and Aubry S 2000 *Eur. J. Phys.* B **15** 405–21