A Nonlinear Dynamical Model for Ultrafast Catalytic Transfer of Electrons at Zero Temperature

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The complex amplitudes of the electronic wavefunctions on different sites are used as Kramers variables for describing Electron Transfer. The strong coupling of the electronic charge to the many nuclei, ions, dipoles, etc, of the environment, is modeled as a thermal bath better considered classically. After elimination of the bath variables, the electron dynamics is described by a discrete nonlinear Schrödinger equation with norm preserving dissipative terms and Langevin random noises (at finite temperature).

The standard Marcus results are recovered far from the inversion point, where atomic thermal fluctuations adiabatically induce the electron transfer. Close to the inversion point, in the non-adiabatic regime, electron transfer may become ultrafast (and selective) at low temperature essentially because of the nonlineairities, when these are appropriately tuned. We demonstrate and illustrate numerically that a weak coupling of the donor site with an extra appropriately tuned (catalytic) site, can trigger an ultrafast electron transfer to the acceptor site at zero degree Kelvin, while in the absence of this catalytic site no transfer would occur at all (the new concept of Targeted Transfer initially developed for discrete breathers is applied to polarons in our theory).

Among other applications, this theory should be relevant for describing the ultrafast electron transfer observed in the photosynthetic reaction centers of living cells.

1. Introduction

According to transition state theory, chemical reactions decompose into elementary reactions among which electron transfer is ubiquitous. The time required for an electron transfer (ET) between different molecules is expected to be minimum at the so-called Marcus inversion point in the space of parameters. However, it is precisely in the vicinity of this inversion point that the standard adiabatic (Born-Oppenheimer) approximation used in Marcus theory, breaks down. We propose a non adiabatic dimer model which should improve the Marcus theory in this regime.

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We also show that our approach extended to trimer models predicts the possibility of catalytic ultrafast electron transfer when appropriate conditions are fulfilled.

The Marcus theory well describes in many cases the features observed for ET between two molecules. It is essentially an adiabatic theory where the atomic fluctuations are supposed to be slow at the scale of the characteristic time of the electron dynamics so that the wavefunction of the electron may remain practically an eigenstate of the time dependent potential created by the atoms. This adiabatic assumption is valid when the largest phonon energy $\hbar \omega_{ph}$ remains much smaller than the smallest excitation energy of the electron. In a two level system, this energy is essentially the distance $\hbar \omega_{el}$ between the two levels. This condition is very often fulfilled in real systems because electronic energies are generally much larger than phonon energies.

![Diagram](image.jpg)

**Fig. 1.** Free energy versus Reaction Coordinates of the system Donor-Acceptor when the electron is on the Donor (top left curve $D$) or on the Acceptor for several redox potentials in the normal regime (top right curve), at the inversion point (middle right curve) and in the inverted regime (bottom right curve). The chemical reaction energy is the distance between the energy minima $\Delta G^0$. The energy barrier is $\Delta G^*$. The electronic excitation energy on the Donor at fixed Reaction Coordinates is $\Delta_{el}$.

Since in the adiabatic case the electron dynamics is essentially driven by the dynamics of the atoms, ET is essentially induced by their fluctuations. The free energy of the system as a function of the reaction coordinates (describing the global atomic configuration), depends on the electronic state which could be either on the Donor molecule or the Acceptor molecule. The well-known Marcus scheme is represented in fig.1 (see ref.2 for details). In the normal regime, the ET from the
Donor to the Acceptor at fixed Reaction Coordinates requires a positive energy \( \hbar \omega_{el} = -\Delta_{el} \). ET is a thermally activated process since thermal fluctuations of the lattice are necessary to overcome the energy barrier \( \Delta G^\star \). In the inverted regime, this energy \( -\Delta_{el} \) is negative. Although ET could be achieved at low temperature by a photon emission at frequency (energy) \( \hbar \omega_{el} = \Delta_{el} \) (photoluminescent chemical reaction \(^2\)), activation processes above the energy barrier \( \Delta G^\star \) become by far more efficient and prevalent at higher temperature.

\( \Delta G^\star \) turns out to be just zero at the inversion point when \( \Delta_{el} = 0 \) (see fig.1). This is the regime where ET is expected to be at maximum speed and still effective at low temperature because of the absence of energy barrier. However, in the vicinity of this inversion point the validity of the adiabatic hypothesis necessarily breaks down, since the characteristic energy \( -\Delta_{el} \) of the electronic excitation becomes small. Our approach improves the theory for ET to be valid in this non-adiabatic regime as well.

2. A Non-adiabatic Model for ET

We consider a single electron tunneling between Donor (D) and Acceptor (A) systems representing large molecules with many vibrational degrees of freedom (see fig.3). Each of these molecules \( \alpha \) (\( \alpha = D \) or \( A \) but more molecules may be involved) is supposed to involve for simplicity a single electronic state with a wavefunction \( |\Psi_\alpha > = \Psi_\alpha (r; \{u^\alpha_i\}) \), where \( r \) is the space coordinate, \( u^\alpha_i \) the phonon coordinates, and we assume that the Born-Oppenheimer (adiabatic) approximation. This approximation is valid when the other electronic states on this molecule are far apart in energy from the considered state \( |\Psi_\alpha > \) at the scale of the maximum phonon energy. Then this electronic wavefunction can be considered as a function of the molecule phonon coordinates \( \{u^\alpha_i\} \), including possibly those of the environment and in particular, the solvent.

Within a standard tight-binding representation, the state of the electron in the whole system, has the form \( \sum_\alpha \psi_\alpha |\Psi_\alpha > \). We use as Kramers reaction coordinates \( \psi_\alpha \) the complex amplitudes of the electronic wavefunction. We have the normalization condition \( \sum_\alpha |\psi_\alpha|^2 = 1 \).

It is convenient to define first the minimum energy of the system of the two coupled electronic states \( H_T(\{\psi_\alpha\}) \) at fixed collective variables \( \{\psi_\alpha\} \). Then, the Hamiltonian of the interacting electron-phonon system can be written as

\[
H = H_T(\{\psi_\alpha\}) + \sum_\alpha H^{ph}_\alpha (|\psi_\alpha|^2, u^\alpha_i, p^\alpha_i)
\]

The electronic density \( |\psi_\alpha|^2 \) on each molecule \( \alpha \) couples to the coordinates of the same molecule assumed to be harmonic and thus consisting of a collection of independent harmonic oscillators \( i \) with position-momentum coordinates \( u_{\alpha,i}, p_{\alpha,i} \), mass \( m_{\alpha,i} \), and frequencies \( \omega_{\alpha,i} \).

\[
H^{ph}_\alpha (|\psi_\alpha|^2, u_{\alpha,i}, p_{\alpha,i}) = \sum_i \frac{1}{2} m_{\alpha,i} \omega_{\alpha,i}^2 (u_{\alpha,i} - k_{\alpha,i} |\psi_\alpha|^2)^2 + \frac{1}{2} m_{\alpha,i} p_{\alpha,i}^2
\]
In principle this coupling energy involves all possible interactions with the atomic coordinates and in particular, the chemical energies and the electrostatic energies. The latter ones could be especially important in biomolecules which are polyelectrolytes surrounded by ions and highly polarizable water.

In general $H_T(\{\psi_\alpha\})$ has not the Hermitian form $<\{\psi_\alpha\}|H_T|\{\psi_\alpha\}>$ where $H_T$ is a linear operator but is highly non-linear as a consequence of the electric field and the molecule reorganization generated by the density variations of $\psi_\alpha$. It is convenient to split this Hamiltonian in several parts

$$H_T(\{\psi_\alpha\}) = \sum_\alpha H_\alpha(|\psi_\alpha|^2) + H_f(\{|\psi_\alpha|^2\}) + H_t(\{\psi_\alpha\})$$

(3)

where $H_\alpha(|\psi_\alpha|^2)$ is the energy of the isolated molecule $\alpha$ which depends only on its electron density $I_\alpha = |\psi_\alpha|^2$. It is sufficient to expand this energy at second order in electronic density for obtaining the main physical features

$$H_\alpha(|\psi_\alpha|^2) = \mu_\alpha |\psi_\alpha|^2 + \frac{1}{2} \chi_\alpha |\psi_\alpha|^4$$

(4)

$\mu_\alpha$ is the linear electronic level at zero occupation. $\chi_\alpha = \chi^C_\alpha + \chi^R_\alpha$ is the sum of two contributions. $\chi^C_\alpha$ is the positive coefficient for the energy of the electric field generated by the charge $I_\alpha$ without lattice reorganization (capacitive energy). This coefficient takes into account the electronic dielectric constant $\epsilon_\infty$.

$\chi^R_\alpha$ is the negative coefficient of the energy gain from the local reorganization due to the presence of the electron. This energy involves for a part chemical bond energies which could be broken or created and electrostatic terms involved in the static dielectric constant. Actually, in our model (3) the reorganization energy can be explicitly calculated and we get $\chi^R_\alpha = -\sum_i m_{a,i} \omega_{a,i}^2 k_{a,i}^2$. 

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**Fig. 2.** Schematic representation of a Donor-Acceptor pair with electronic levels interacting with phonon baths in the normal Marcus regime.
It is essential to remark that the sum of the two contributions \( \chi_\alpha \) might be positive or negative depending whether it is the electrostatic energies or the chemical energies which are prevalent. We expect for example that when the electronic state \( \alpha \) belong to the inner shell of a transition metal ion (which could be embedded in a large biomolecule), the electrostatic energy is prevalent so that \( \chi_\alpha \) is positive. When it belongs to a chemical bond (or a ring of bonds), it is more likely negative. Actually, only \textit{ab initio} calculations could estimate the real values of these coefficients. The essential physical consequence of the nonlinearity is that the electronic level on molecule \( \alpha \)

\[
E_\alpha = \frac{\partial H_\alpha}{\partial I_\alpha} = \mu_\alpha + \chi_\alpha |\psi_\alpha|^2
\]  

(5)

depends on its electronic occupation density.

\( H_f(|\psi_\alpha|^2) \) in (3) is a small extra term due to molecule interactions which could be for example the Coulomb interaction energy

\[
H_f(|\psi_\alpha|^2) = \sum_{\alpha,\beta} C_{\alpha,\beta} |\psi_\alpha|^2 |\psi_\beta|^2
\]  

where \( C_{\alpha,\beta} \) are mutual capacitance coefficients.

\( H_t(|\psi_\alpha|) \) in (3) is also a small extra energy term due to orbital overlaps but it is essential because it allows ET. We may choose for simplicity the form

\[
H_t(|\psi_\alpha|) = \lambda_{\alpha,\beta} \psi^*_\alpha \psi_\beta + c.c.
\] 

The transfer integrals \( \lambda_{\alpha,\beta} \) are assumed to be small (compared to differences of electronic energy levels) and may be of the order of phonon energies.

In an ideal anti-adiabatic regime (but non-realistic) where the transfer integrals \( \lambda_{\alpha,\beta} \) between different molecules would be much smaller than all phonon energies \( \hbar \omega_{\alpha,i} \), ET would be much slower than the phonon dynamics. Then, the phonons could be eliminated as fast variables following adiabatically the slow electron variables and \( H_T(|\psi_\alpha|) \) would be the exact Hamiltonian describing the electron dynamics through the set of nonlinear Hamilton equations

\[
\dot{\psi}_\alpha = \frac{\partial H_T}{\partial \psi^*_\alpha}.
\]

Actually, nonlinearities may generate energy barriers and even in the absence of energy barriers, the absence of energy dissipation does not allow ET to a lower energy level. Ultrafast ET requires an efficient energy dissipation which can be obtained only by interaction of the electron with a phonon bath in the regime intermediate between adiabatic and anti-adiabatic

Usually, the lattice reorganization due to the presence of an electron on a molecule is large and involves the coherent creation of many phonons. It is thus legitimate to treat this phonon bath classical while the electron dynamics remains quantum. The dynamical equations of the coupled system (12) are

\[
\dot{\psi}_\alpha = \frac{\partial H_T}{\partial \psi^*_\alpha} - \sum_i m_{\alpha,i} k_{\alpha,i} \omega^2_{\alpha,i} (u_{\alpha,i} - k_{\alpha,i} |\psi_\alpha|^2) \psi_\alpha
\]  

(6)

\[
\ddot{u}_{\alpha,i} + \omega^2_{\alpha,i} (u_{\alpha,i} - k_{\alpha,i} |\psi_\alpha|^2) = 0
\]  

(7)

*The dynamical coupling of the electron with the electromagnetic field also generates energy dissipation. However, this coupling which is weak has to be treated quantum using Fermi golden rule which yields relatively long life time to quantum excitations. We neglect here this energy dissipation since we are interested in ultrafast ET.*
The harmonic motions $u_{\alpha,i}(t)$ can be explicitly obtained from the linear equations as the sum of functions of the time dependent driving force $|\psi_{\alpha}(t)|^2$ and a solution of the equation without driving force. Actually, this term physically corresponds to thermal fluctuations of $u_{\alpha,i}$ and thus is random. Then, substituting $u_{\alpha,i}(t)$ in eq.\ref{eq5} yields the fundamental equation for non-adiabatic electron dynamics (which preserves the norm $\sum_\alpha |\psi_{\alpha}|^2$)

$$i\hbar \dot{\psi}_\alpha = \frac{\partial H_T}{\partial \psi^*_\alpha} + \left( \int_{-\infty}^{t} \Gamma_\alpha(t-\tau) \frac{d|\psi_\alpha|^2}{d\tau} d\tau + \zeta_\alpha(t) \right) \psi_\alpha$$\hspace{1cm} (8)

where $\Gamma_\alpha(t) = \sum_i m_{\alpha,i}\omega_{\alpha,i}^2 k^2 \cos(\omega_{\alpha,i} t)$. If there are many phonon modes with a rather uniform distribution, $\Gamma_\alpha(t)$ can be assumed to be a smooth decaying function of time. It generates energy dissipation as a kernel in eq.\ref{eq8} (the absorption rate in energy of a charge fluctuation at site $\alpha$ at frequency $\omega$ is nothing but the product of the square of its amplitude with the Fourier transform of $\Gamma_\alpha(t)$). We also have $\Gamma_\alpha(0) = -\chi_\alpha^R$. The time dependent potential $\zeta_\alpha(t)$ is produced by the thermal fluctuations of the lattice. It is a colored random Langevin force with correlation function which fulfills $<\zeta_\alpha(t+\tau)\zeta_\alpha(\tau)> = \Gamma_\alpha(t) k_B T$ at temperature $T$.

Thus, the effect of non-adiabaticity is to transform the standard linear Schrödinger equation describing the dynamics of the electron into a nonlinear Schrödinger equation \ref{eq8} with norm preserving energy dissipation terms and with random colored time dependent potentials generated by atomic thermal fluctuations.

### 3. ET in the Dimer Model

We first show that far from the Marcus inversion point we essentially recover the basic result of the standard theory. The initial Hamiltonian \ref{eq12} restricted to a dimer model ($\alpha = D$ or $A$) readily yields the energy surfaces schematically shown in fig.\ref{fig1}. Neglecting the small interaction energy terms between the molecules we obtain the essential parameters of this theory which are $\Delta G^0 = \mu_D + \frac{1}{2}\chi_D - \mu_A - \frac{1}{2}\chi_A$, $\Delta_{el} = \Delta G^0 + \frac{1}{2}(\chi_D^R + \chi_A^R) = \mu_D' + \chi_D^R - \mu_A'$ and $\Delta G^* = -\Delta_{el}^2/(2(\chi_D^R + \chi_A^R))$ where $\mu_A' = \mu_A + \chi_A^R/2$.

The energy variation $E_T(I_A) = H_D(1-I_A) + H_A(I_A) - H_D(1)$ of our dimer as a function of the electron density $I_A = |\psi_A|^2$ on the acceptor is

$$E_T(I_A) = (\mu_A - \mu_D - \chi_D)I_A + \frac{1}{2}(\chi_D + \chi_A)I_A^2$$\hspace{1cm} (9)

and $-E_T(1) = \Delta G^0$ is the chemical reaction energy. There is always an energy barrier between Donor and Acceptor when $\frac{dE_T}{dI_A}(0) > 0$ or equivalently $\mu_A < \mu_D + \chi_D$. Otherwise, the minimum of energy is not necessarily obtained for a total transfer at the Acceptor when $\chi_D + \chi_A > 0$. The derivative $dE_T/dI_A = E_A - E_D$ (see eq.\ref{eq9}) is the difference of the electronic levels on the Acceptor and the Donor at the transfer $I_A$. Thus, resonance between Donor and Acceptor implies a zero derivative.

For recovering the same results as the Marcus theory from our equation, it is essential to note that the phonon spectrum has a cut-off at relatively small frequen-
Beyond this frequency, the Fourier spectrum of $\Gamma(t)$ is zero. Thus, when the characteristic energy of the electron dynamics, which is the energy difference $E_D - E_A$ between the electronic levels, eq.(5), is larger than the phonon energy $\hbar \omega_c$, there is no more energy dissipation. Then ET cannot be achieved at zero degree K but requires thermal fluctuations. Actually, this is the regime of validity of the adiabatic approximation.

The electron density which is initially on the Donor $|\psi_D|^2 = 1$ and $|\psi_A|^2 = 0$ remains practically constant. Eq.(6) gives in this case the random potential as due to phonon variables, $\zeta(t) = - \sum m_{\alpha,i} k_{\alpha,i} \omega_{\alpha,i}^2 (u_{\alpha,i} - k_{\alpha,i} |\psi_\alpha|^2)$. The slowly varying potential $\zeta_D(t)$ makes the energy level of the electron $E_D(t) = \mu_D + \chi_D + \zeta_D(t)$ on the Donor time dependent. The unoccupied energy level on the acceptor $E_A(t) = \mu_A + \zeta_A(t)$ fluctuates similarly. It occurs statistically that $E_D(t) \approx E_A(t)$ or

$$\mu_D + \chi_D - \mu_A + \zeta_D(t) - \zeta_A(t) \approx 0 \quad (10)$$

induces an almost resonance between Donor and Acceptor so that the electron could tunnel (see fig.4). If we discard the details concerning the probability of this tunneling process and neglect its intrinsic time which is generally short compared to the characteristic time for reaching the resonance, the characteristic time for ET is mostly related to the time required to reach the resonance.

Condition (10) may be compared with the condition for the intersection of the two free energy surfaces shown in fig.2, which can be written as

$$\mu_D^R + \chi_D^R - \mu_A^R + \zeta_D(t) - \zeta_A(t) = \Delta = \zeta_D(t) - \zeta_A(t) = 0 \quad (11)$$

This condition is similar but different from our resonance condition (10). The reason is that the energy level variations due to the Coulomb energies are not taken into account.

\footnote{The electron tunneling problem has been considered differently in the literature which distinguishes between adiabatic processes (strong reactants) and diabatic processes (weak reactants). Our non-adiabatic theory (potentially) describes both cases as well as the intermediate cases.}
account in the Marcus theory unlike the reorganization energy (if $\chi^C_\alpha = 0$ conditions (10) and (11) become identical). Nevertheless, we can also interpret the probability of reaching the resonance as shown in Fig. 4 in terms of an activation process with an activation energy $\Delta'G^* = -\Delta'_d/(2(\chi^R_D + \chi^R_A)) \neq \Delta G^*$ where $\Delta'_d = \Delta_{el} + (\chi^C_D + \chi^C_A)/2 = \mu_D + \chi_D - \mu_A$ is different from $\Delta_d$ because of the Coulomb terms.

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"The only case implicitly considered in the Marcus theory is for negative $\chi_\alpha = \chi^R_\alpha < 0$."

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Fig. 4. Sketch of the electronic level fluctuations in the normal regime (left) and in the Marcus inverted regime (right).

Fig. 5. Electron density on the Donor and the Acceptor versus time for the dimer model at the inversion point and zero degree $K$ where $\mu_D = 2, \chi_D = -1$, $\mu_A = 1, \chi_A = -0.75$, $\lambda_{AD} = 10^{-2}$, $\gamma_D = \gamma_A = 1$. (left) or 20. (right) (the time unit is 1 ps=$10^{-12}$ s for energy in units of eV)

Nevertheless, our approach confirms the existence of an inversion point when resonance is obtained at zero degree $K$ for $\zeta_D = \zeta_A = 0$. Then, (10) yields $\Delta'_d = 0$ or $\mu_D + \chi_D = \mu_A$ which again is different from the condition $\Delta_d = 0$ in the original Marcus theory.

At our inversion point, the energy profile $E_T(I_A)$ has a zero derivative at the origin $I_A = 0$. Fig. 3 shows that there is no energy barrier only when $\chi_D + \chi_A \leq 0$ We check that the initial resonance $E_D = E_A$ triggers ET. If the derivative
$dE_T/dI_A$ remains smaller than $\hbar \omega_c$ which is equivalent to a small reaction energy $\Delta G^0 < \hbar \omega_c/2$, ET can be achieved at zero degree K without thermal fluctuations. Fig.5 shows two examples. The speed of ET strongly depends on the damping which is related to the coupling to the phonon bath. In these examples and in the following we chose for simplicity $H_f(|\psi_\alpha|^2) = 0$ in (3). If the phonon frequency cutoff $\omega_c$ is large compared to the characteristic electronic frequencies, a reasonable approximation is to assume that $\Gamma(t) = 2\gamma_\alpha \delta(t)$ is a Dirac function. Then, 

$$\int_{t-\infty}^t \Gamma(t-\tau) \frac{d|\psi_\alpha|^2}{d\tau} d\tau \approx \gamma_\alpha \frac{d|\psi_\alpha|^2}{dt}(t)$$

in eq.(8). There is an optimal damping constant ($\gamma_\alpha \approx 40$) where the characteristic time required for ET is minimum.

ET is triggered at zero degree (but slows down) when escaping only on one side of the inversion point when $\mu_A < \mu_D + \chi_D$. On the other side, it is blocked at zero degree K because of the appearance of an energy barrier. However it is complete only when $dE_T/dI_A$ remains always negative with a modulus which never exceeds the phonon cutoff energy $\hbar \omega_c$ (for having efficient energy dissipation). In summary, our approach yields results which are qualitatively similar to those of the Marcus theory far from the inversion point but with a redefinition of characteristic parameters. It yields more detailed features not predicted by the original Marcus theory, close to the inversion point.

4. Principle of Catalytic ET in a trimer model

ET could be fast for a Donor-Acceptor system only in special conditions close to the Marcus inversion point and when the chemical reaction energy is small compared to the phonon energy cutoff.

We now show that we can take advantage of a third catalytic site weakly coupled to the Donor for triggering at zero temperature an ultrafast ET from the Donor to the Acceptor while in the absence of catalyst, a large energy barrier would prevent any transfer at zero degrees.

It is clear that ET could become fast only in case of resonance or almost resonance within the phonon energy range. Otherwise, the electronic level $E_\alpha$ on a molecule depends on its occupation density $E_\alpha = \partial H_\alpha(I_\alpha)/\partial I_\alpha = \mu_\alpha + \chi_\alpha I_\alpha$

How to get complete ultrafast ET between Donor and Acceptor at zero degree K not at the Marcus inversion point? We suggest to take advantage of the nonlinearities for inducing relatively slow oscillations of the electronic level on the Donor (or on the acceptor) which could produce a resonance between Donor and Acceptor.

The simplest way is to obtain these energy oscillations by thermal fluctuations as shown fig.4. This is the standard situation described above where Marcus theory is recovered.

Another way is to induce artificially these electronic level oscillations by exciting a specific phonon well coupled to the electronic level. Note that this is what happens systematically when creating an exciton by the absorption of a photon before the Franck-Condon relaxation. This situation very likely occurs in some real systems but we shall not discuss it here.
For inducing these level oscillations, we propose to use a third site, a “Catalyst”, which is appropriately tuned on the Donor. For that purpose, we use the phenomenon of Targeted Energy Transfer (or Targeted ET in this case) for a Donor and an Acceptor at the inversion point are in resonance but in general they do not remain in resonance during the transfer. However, there is a specially interesting case, when $\chi_D + \chi_A = 0$ (which is exactly solvable) for which the resonance persists all along the transfer. Since $dE_T(I_A)/dI_A \equiv 0$, $E_T(I_A) \equiv 0$, the reaction energy is zero. As shown in the absence of damping, the electron slowly oscillates between the Donor and the Acceptor, which is now the Catalyst ($C$), with a frequency corresponding to the transfer integral $\lambda_{CD}$. The electronic level oscillates with the half period. This situation requires to associate a soft electronic level with an appropriate and well defined hard electronic level (which could involve a metallic ion as suggested above) ($\mu_C = \mu_D + \chi_D$ and $\chi_C = -\chi_D$). When there is energy dissipation, this oscillation is damped and converges to the covalent state with equal density on Donor and Catalyst (see fig.6). Indeed, the small transfer integral raises the degeneracy at zero coupling. The range of variation of the energy level, which is the interval $[\mu_D + \chi_D, \mu_D]$ in the undamped case, is reduced to the interval $[\mu_D + \chi_D/2, \mu_D]$ in the overdamped case. However, this binding energy is very weak and negligible since $\lambda_{CD}$ is small. Then, small thermal fluctuations become sufficient to generate giant charge fluctuations. In practice, Donor and Catalyst do not bind chemically but they could trigger ultrafast ET to another molecule.

We now test the principle of catalysis suggested by fig.6. We consider a trimer model with Hamiltonian

$$H_{tr} = \mu_D|\psi_D|^2 + \frac{1}{2}\chi_D|\psi_D|^4 + \mu_C|\psi_C|^2 + \frac{1}{2}\chi_C|\psi_C|^4 + \mu_A|\psi_A|^2 + \frac{1}{2}\chi_A|\psi_A|^4 + \lambda_{CD}(\psi_D^*\psi_C + cc) + \lambda_{CA}(\psi_A^*\psi_C + cc) + \lambda_{AD}(\psi_D^*\psi_A + cc)$$

We assume that Donor and Acceptor are both soft ($\chi_D < 0, \chi_A < 0$). The transfer energy is positive which means $\mu_A + \chi_A/2 < \mu_D + \chi_D/2$. 

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Fig. 6. Sketch of electronic level oscillations on the donor system inducing resonance with the acceptor level.
Fig. 7. Electron density oscillations on the Donor and its Catalyst at zero degree K, without damping $\gamma_D = \gamma_C = 0$ (left) and with damping $\gamma_D = \gamma_C = 1$ (right). $\mu_D = 2$, $\chi_D = -1$, $\mu_C = 1$, $\chi_C = -1$, $\lambda_{CD} = 10^{-2}$.

In the absence of Catalyst ($\lambda_{CD} = \lambda_{CA} = 0$) there is a large Kramers energy barrier between Donor and Acceptor, which implies $\mu_D + \chi_D < \mu_A$. Thus, we are in the normal Marcus regime. ET is impossible at zero degree K and remains slow up to relatively high temperature.

We now introduce the Catalyst. Donor and Catalyst are tuned for Targeted Electron Transfer which requires $\chi_C = -\chi_D$ and $\mu_C = \mu_D + \chi_D$. The initial electronic level $\mu_A$ of the acceptor should belong to the variation interval of the electronic level of the Donor-Catalyst system which yields $\mu_D + \chi_D < \mu_A < \mu_D$ at weak damping or $\mu_D + \chi_D/2 < \mu_A < \mu_D$ at strong damping. Fig. 8 sketches $H_D(I_D)$, $H_C(I_C)$ and $H_A(I_A)$ when all these conditions are fulfilled.

Fig. 8 shows that under these conditions, huge charge fluctuations suddenly appear between between weakly coupled Donor Acceptor and Catalyst, while the Donor-Acceptor system alone does not exhibit any fluctuations. However, the absence of energy dissipation prevents the electron from falling on its ground-state, which is on the acceptor. The same model with damping shows that the electron finally falls on the acceptor while the catalyst has only taken transitively a fraction of the electronic charge (see Fig. 9).

This ET is highly sensitive to small perturbations of the Donor-catalyst system which easily breaks the Targeted Transfer. We have shown for example that relatively small electric fields are sufficient for blocking ET at zero degree K. These principles may be extended to many-site networks of electronic levels where the electron can choose a specific path very selectively. This path can be blocked and switched under small perturbations. Logical functions with one or few electrons could be built at the molecular level suggesting potential nanodevice applications and complex biological functions to be studied in living cells. These studies are left for further developments.
Fig. 8. Energies $H_D(I)$, $H_C(I)$ and $H_A(I)$ versus electron density $I$ for the Donor, Catalyst and Acceptor in the situation of Ultrafast ET. The energy barrier between Donor and Acceptor without Catalyst is plotted in gray.

Fig. 9. Electron density on Donor Acceptor and Catalyst versus time in the trimer in the absence of damping $\gamma_D = \gamma_C = \gamma_A = 0$ at two different time scales $\mu_D = 2$, $\chi_D = -1$, $\mu_C = 1$, $\chi_C = 1$, $\mu_A = 1.5$, $\chi_A = -0.75$, $\lambda_{AD} = \lambda_{AC} = \lambda_{CD} = 10^{-2}$. The electron is initially on the Donor.

5. Concluding Remarks

We presented in this short paper basic principles for a non-adiabatic theory of ET. We briefly sketched new perspectives for understanding ultrafast ET and catalysis. A more complete description of this work with mathematical details, developments and applications shall be published elsewhere.

A precise example of application of our trimer model to real and well studied experimental problems concerns the photochemical reaction in the reaction cen-
Fig. 10. Same as fig. 9 but with damping $\gamma_D = \gamma_C = \gamma_A = 2$ (left) or 10 (right)

ter, where the electronic sites involved have been well identified. In this system
the photons collected in an antenna of pigment molecules funnel to a specific site
of the reaction center. Then, an electron is ejected and transferred within few ps
over relatively long distances of about one nm (e.g. see ref. for a review). Further
subsequent ETs follow in the biomachinery. Besides theoretical studies and numerical
investigations of the molecules involved confirming the high efficiency of this
molecular system, the Marcus theory is not sufficient for a global understanding
of all experimental features. We shall propose that, out of the apparent system
complexity, our simple basic principles could help understand ultrafast ET as well
as the puzzling features associated with it.

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