Elementary electron transfer reactions: from basic concepts to recent computational advances

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11 May 2024

UNIVERSITÀ DEGLI STUDI DI TORINO

Elementary Electron Transfer reactions: from basic concepts to recent computational advances

Raffaele Borrelli[a] and Andrea Peluso[b]

[a] Dipartimento di Scienze Agrarie, Forestali e Alimentari, Università di Torino,
I-10095 Grugliasco (TO), Italy

[b] Dipartimento di Chimica e Biologia, Università di Salerno,
I-84084 Fisciano, Salerno, Italy,

E-mail apeluso@unisa.it.

March 5, 2013

Abstract

The basic chemico-physical concepts and the most recent developments in the dynamics of the elementary electron transfer reactions are reviewed, posing particular attention to discrete state approaches, which combine use of a few experimental data with reliable *ab initio* calculations of the equilibrium nuclear configurations and normal coordinates of vibration of the redox partners.

Introduction

Elementary electron transfer (ET) reactions play a prominent role in chemistry and biochemistry. Many fundamental processes in biosystems as the respiration, the process by which living organisms obtain energy from food and oxygen, and the photosynthesis, the process by which plants transform the solar energy in the food and the oxygen we consume, mainly rely on electron transfer reactions between cofactors in proteins.

Here we will mainly focus on the computational aspects of ET processes. Indeed, the last two decades have witnessed the great impact of reliable *ab initio* computations and molecular dynamics simulations on the understanding of molecular properties and chemical processes both in the gas phase and in condensed phase.

Before considering modern computational approaches to ET in biosystems and in condensed phase, with the intent of providing as much as possible a thorough picture of theoretical aspects of ET processes to non-expert readers, we start from the basic chemico-physical concepts contained in the seminal papers of Lax and Kubo on radiationless transitions in condensed phase,[1, 2, 3, 4] and of Marcus on ET processes in solution,[5, 6] which provided the cornerstones of our actual understanding of ET processes in condensed phases. Excellent reviews are already available in the literature on those topics.[7, 8, 9, 10]

The other important breakthrough in the field of ET processes was provided by realizing how realistic simulations of ET processes can be carried out on complex systems; the surface hopping and the dispersed polaron models were the first computational approaches by which complex biochemical systems could be realistically handled.[11, 12, 13, 14] We will shortly discuss the basic ideas which those methods rely on, for an excellent review see ref. [15]. Later on, fully quantum dynamics simulations of ET rates employing the results of highly reliable ab-initio computations on single molecules have appeared.[16, 17, 18, 19, 20, 21, 22, 23] Combining the results of highly reliable computations with quantum dynamics simulations of ET rates is still a challenging task, but efforts along this line should hopefully provide a significant contribution towards the achievement of a deeper knowledge

of the structure-function relationships in complex systems, where single molecule properties and the supramolecular structure of the systems concur to determine the behavior of molecular machines.

Basic concepts of ET theory

Classical and semiclassical approaches

It is difficult to overemphasize the impact that Marcus' ET theory had and still has in Chemistry and Biochemistry.[5, 6, 7] Indeed, although its limitations inherent to its classical nature, the theory provides all the basic physical concepts for understanding ET processes in condensed media. Marcus was among the first to realize that ET rates are regulated by the nuclear motions both of the two molecules which exchange an electron and of the surrounding environment. Within the framework of the absolute reaction rate theory, he thus wrote the rate expression of an elementary ET process as:

$$k_{\mathrm{ET}} = \alpha f e^{-\frac{\Delta G^{\#}}{k_B T}}, \qquad (1)$$

where α is a parameter related to the probability of ET and f is the collision frequency in the liquid phase, ca. 10^{11} M^{-1} s^{-1} or a suitable vibrational frequency, ca. 10^{13} s^{-1} for intramolecular ET.

The great merit of Marcus' theory is in its ability of relating the ET activation free energy to physically well sound quantities, i.e. the free energy change of the ET reaction ΔG^0, and the reorganization energy, λ, which is the energy to bring ET reactants in the nuclear configuration of the products without changing electronic state:

$$\Delta G^{\#} = \frac{\lambda + \Delta G^0}{4\lambda}. \qquad (2)$$

The geometrical derivation of Eq. 2 is reported in the caption of Fig. 1 for the simplest case of a system characterized by a single vibrational degree of freedom, exhibiting the same vibrational frequency in both electronic states, a model which does not account for entropic changes upon ET, but Marcus derived it for a multi-

dimensional system, characterized by different frequencies, applying a full statistical mechanics treatment.[5, 24, 25, 26, 27, 28, 29] An additional "work" term can be added in order to account for other energy requirements, such as for the formation of a binary complex leading to ET or for a conformational change.

The reorganization energy λ has been further separated into the sum of two contributions, one coming from the nuclear degrees of freedom of the two molecules which exchange an electron, the internal reorganization energy, the other from the changes in the environment, the solvent reorganization energy. The former is immediately seen to be:

$$\lambda_{int} = \frac{1}{2} \sum_j \omega_j^2 \Delta_j \tag{3}$$

where ω_j and Δ_j are the vibrational frequency and the displacement upon ET of the equilibrium position of the j-th vibrational mode of the whole system, acceptor plus donor, the latter can be related to solvent polarizability by the expression: [5, 25]

$$\lambda_{solv} = \frac{e^2}{4\pi\epsilon_0} \left(\frac{1}{2r_1} + \frac{1}{2r_2} - \frac{1}{r_1 + r_2} \right) \left(\frac{1}{D_{op}} + \frac{1}{D_s} \right), \tag{4}$$

where e is the electron charge, r_1 and r_2 are the molecular radii of the acceptor and donor molecule, D_{op} is the square of the refractive index of the medium, D_s its static dielectric constant, and ϵ_0 the vacuum permittivity.

Marcus equation is classical and its use is therefore limited to temperature high enough that all vibrations are fully excited. Notwithstanding, it has been the headlight for a huge number of experimental works. Marcus' theory predicts a quadratic dependence of $\Delta G^{\#}$ on ΔG^0, so that maximum ET rates occur when $\Delta G^0 = -\lambda$, a case for which no thermal activation is necessary, and the rate is predicted to decrease for more negative values of ΔG^0. The free energy region where $\Delta G^0 << -\lambda$ has been called the Marcus inverted region; several experimental efforts were devoted to search for the existence of the inverted region, which would have provided a stringent proof of the theory, but all experiments carried out on a series of reactions exhibiting more and more negative ΔG^0 revealed only an increase of the reaction rate up to the diffusion limit. It was only after about 30 years that studies of intramolecular electron transfer in systems where donor and acceptor groups

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are separated by a stiff spacer have undoubtedly substantiated the existence of the inverted region.[30]

The classical Marcus' equation can also been obtained in a very different way,[31, 8] by considering ET as a radiationless transition between two electronic states $|A\rangle$ and $|B\rangle$ and resorting to the Landau-Zener expression for evaluating the transition probability P_{AB} per passage of the system through the intersection region:[32, 33]

$$P_{AB} = \frac{2\pi}{\hbar} \frac{|H_{BA}|^2}{v\Delta F}, \qquad (5)$$

where $|H_{BA}|^2$ is the coupling between the initial and final ET states, v is the velocity with which the system passes through $X^{\#}$, see fig. 1, and ΔF is the difference in the slopes of the potential energy surfaces of the initial and final states at the crossing point. For a classical harmonic oscillator with mass M and frequency ω, $v = \omega\sqrt{X_{max}(E)^2 - X^{\#2}}$ and $\Delta F = \omega\sqrt{2\lambda M}$, where $X_{max}(E)$ is the maximum amplitude of oscillation at a given energy E, $X_{max}(E) = \sqrt{2E/M\omega^2}$. Considering that the system passes through $X^{\#}$ twice per vibration cycle, the rate at a given energy E can be defined as $k_{B\leftarrow A}(E) = \omega P_{AB}/\pi$ and the mean ET rate k_{ET} is obtained by averaging over a Boltzmann distribution, integrating over $E \geq E^{\#}$, since lower energies are ineffective:

$$k_{ET} = \frac{\int_{E^{\#}}^{\infty} k_{B\leftarrow A}(E)e^{-\beta E}dE}{\int_0^{\infty} e^{-\beta E}dE} = \frac{|H_{BA}|^2}{\hbar} \sqrt{\frac{\pi}{\lambda k_b T}} \exp\left(-E^{\#}/k_B T\right), \qquad (6)$$

where $E^{\#} = (\lambda + \Delta E)/4\lambda$. The semi-classical rate expression is equivalent to the classical one, upon assuming that ET does not involve entropy changes and volume work.

An analogous rate expression was later obtained by Hopfield, using a completely different approach.[34] Following a previous treatment of the energy transfer between two chromophores in a matrix,[35, 36] Hopfield wrote the ET probability per unit time as:

$$k_{ET} = \frac{2\pi}{\hbar} |H_{BA}|^2 \int_{-\infty}^{\infty} D_a(E)D_b(E)dE \qquad (7)$$

where H_{BA} is the coupling term between the two electronic states involved in ET, $D_a(E)$ represents the probability of removing an electron from the molecule A at a given energy E, and $D_b(E)$ the analogous for adding an electron to the molecule B.

The Franck-Condon principle states that ET occurs at fixed nuclei, therefore $D_a(E)$ is given by the probability that molecule A is in the nuclear configuration at which the process occurs at a given energy E. Since the equilibrium positions of A and A^+ are different, the maximum probability of ET will not occur at E_a, the electronic energy difference between neutral and ionized states, but at a certain $E_a + \lambda_a$, see figure 2, where λ_a depends on the displacement of the equilibrium positions upon removing an electron from A. Similar considerations also hold for adding an electron to B. Hopfield considered a one-dimensional harmonic system, with force constants K_a and K_b. The classical probability distribution of A being at the coordinate x is:

$$P_a(x) = \left(\frac{K_a}{2\pi k_B T} \right)^{1/2} \exp \left(-\frac{K_a (x - x_a)^2}{2 k_B T} \right). \tag{8}$$

with x_a denoting the equilibrium position. Then by considering that in harmonic approximation, with equal force constants for both A and A^+, and with equilibrium positions 0 and x_a, respectively, the energy required for ET to occurr at x is:

$$E = E_a + 1/2 K_a (x - x_a)^2 - 1/2 K_a x^2, \tag{9}$$

Hopfield obtained:

$$D_a(x) = \left(\frac{1}{2\pi k_B T K_a x_a^2} \right)^{1/2} \exp \left(\frac{-(E - E_a + 1/2 K_a x_a^2)^2}{2\pi k_B T K_a x_a^2} \right). \tag{10}$$

A similar equation holds for an electron injection at B. By susbstituting $D_a(E)$ and $D_b(E)$ in eq. 7, the ET rate expression (probability per unit time) is easily obtained:

$$k_{ET} = \left(\frac{1}{2\pi \hbar^2 \sigma^2} \right)^{-1/2} |H_{BA}|^2 \exp \left(\frac{-(E_a - E_b - \Delta)^2}{2\sigma^2} \right), \tag{11}$$

with:

$$\sigma^2 = \sigma_a^2 + \sigma_b^2, \qquad \Delta = 1/2 K_a x_a^2 + 1/2 K_b x_b^2, \tag{12}$$

and

$$\sigma_i^2 = k_B T K_i x_i^2 \qquad \text{or} \qquad \sigma_i^2 = \hbar \omega_i (K_i x_i^2 / 2) \coth \frac{\hbar \omega_i}{2 k_B T}, \qquad i = a, b \tag{13}$$

according to whether the classical or the quantum mechanical distribution is used for $P(x)$.

Equation 11 is completely equivalent to the semiclassical Marcus equation, of course upon assumption that $K_a = K_b$ and $\omega_a = \omega_b$.

Noteworthy, Marcus' rate expression can also be obtained by the surface-hopping approach,[11] see below; for the derivation the interested reader can consult ref.s [12, 37, 15]

The quantum mechanical approach

Most of the quantum mechanical treatments of ET reactions are strictly based on the standard theory of non-radiative processes, developed by Lax and Kubo in the fifties, often denoted as the generating function (GF) approach.[2, 3, 4]

Let $|A\rangle$ and $|B\rangle$ be the initial and final ET electronic states, each of them with a manifold of vibrational states, denoted by $|Am\rangle$ (shortly $|m\rangle$) and $|Bn\rangle$ ($|n\rangle$). According to first order time dependent perturbation theory, the transition probability $B \leftarrow A$ is given by the sum over all vibrational states of $|Bn\rangle$, thermally averaged over the vibrational states of the initial state:

$$k_{B \leftarrow A} = \text{Av}_m \frac{2\pi}{\hbar} \sum_n \langle m| H_{BA}^\dagger |n\rangle \langle n| H_{BA} |m\rangle \delta(E_n - E_m - \Delta E), \qquad (14)$$

where Av_m stands for the Boltzmann average over the initial vibrational states, and $\Delta E = E_A - E_B$. Introducing the integral representation of the delta function:

$$\delta(E_n - E_m - \Delta E) = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\tau \exp\left[i\left(E_n - E_m - \Delta E\right)\tau\right], \qquad (15)$$

and by assuming that the electronic coupling term H_{BA} is independent of nuclear coordinates, Eq. 14 can be rewritten:

$$k_{B \leftarrow A} = \frac{2\pi}{\hbar} |H_{BA}|^2 \text{Av}_m \int_{-\infty}^{\infty} d\tau \, \langle m| e^{i\mathcal{H}_A \tau} e^{-i\mathcal{H}_B \tau/\hbar} |m\rangle \, e^{-i\Delta E \tau}, \qquad (16)$$

where E_n and E_m have been replaced by the corresponding Hamiltonian operators, $\mathcal{H}_A$ and $\mathcal{H}_B$, in order to permit the closure sum over n. By performing the Boltzmann average in the standard way, the transition probability per unit time can finally be written as:

$$k_{B\leftarrow A} = \frac{|H_{BA}|^2}{\hbar} \int_{-\infty}^{+\infty} e^{-i\Delta E\tau} f(\tau) d\tau, \tag{17}$$

with

$$f(\tau) = \text{Tr}\{e^{i\mathcal{H}_A\tau} e^{-(\beta+i\tau)\mathcal{H}_B\tau}\}/\text{Tr}\{e^{-\beta\mathcal{H}_A}\}, \tag{18}$$

where $\beta = 1/K_B T$ with K_B the Boltzmann constant.

The transition probability is thus recast in terms of the Fourier transform of a correlation function f in the dummy variable τ. As we will see later that is very convenient for numerical approaches.

In order to highlight the physical meaning of Eq.s 17 and 18, let us first consider the simplest case consisting of a single harmonic oscillator with unit mass, whose equilibrium position is displaced upon ET by an amount Δ, without frequency change, namely the same model used before for discussing Marcus' classical treatment. In order to obtain an expression of ET rate as a function of the equilibrium position displacement Δ along the coordinate q, we have to evaluate the matrix elements of the density operator:

$$\rho_W(\xi) = \exp\left(-\xi\mathcal{H}_W\right) = \sum_n \exp\left(-\xi E_{Wn}\right) |n\rangle \langle n|, \tag{19}$$

in the coordinate representation. By using the Mehler formula for Hermite polynomials:

$$\sum_{n=0}^{\infty} \frac{(Z/2)^n}{n!} H_n(x) H_n(y) = \left(1 - Z^2\right)^{-1/2} \exp\left\{\frac{Z\left(2xy - Zx^2 - Zy^2\right)}{2\left(1 - Z^2\right)}\right\}, \tag{20}$$

the matrix elements of ρ are:

$$\langle q| \rho(\xi) |q'\rangle = \{2\pi\hbar \sinh(\xi\hbar\omega)/\omega\}^{-1/2}$$

$$\times \exp\left[-(\omega/4\hbar)\tanh(\xi\hbar\omega/2)(q + q')^2 - (\omega/4\hbar)\coth(\xi\hbar\omega/2)(q - q')^2\right] \tag{21}$$

By substituting Eq. 21 in Eq. 18, with the appropriate ξ, using $\bar{q}$ and $\bar{q}'$ ($\bar{q} = q - \Delta$), for the density matrix elements involving $\mathcal{H}_B$, and performing the trace operation, corresponding to the integration over q, q', $\bar{q}$, and $\bar{q}'$, one obtains:

$$f(\tau) = \exp\left\{-\frac{\Delta^2\omega}{2\hbar} \frac{1 - e^{-(\beta\hbar+i\tau)\omega} - e^{-i\omega\tau} + e^{-\beta\omega\tau}}{1 - e^{-\beta\hbar\omega}}\right\}. \tag{22}$$

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Noting that $\Delta^2 \omega/(2\hbar) = \lambda/\hbar\omega = S$, where λ is the Marcus internal reorganization energy, Eq. 3, and that the average quantum number, $\bar{n}$, in an ensemble of identical oscillator at thermal equilibrium is $(e^{\beta\hbar\omega} - 1)^{-1}$, $f(\tau)$ becomes:

$$f(\tau) = \exp\{-S\left[2\bar{n} + 1 - (\bar{n} + 1)e^{i\omega\tau} - \bar{n}e^{-i\omega\tau}\right]\}$$
$$= \exp\left[-S(2\bar{n} + 1)\right] \exp\left[\frac{x}{2}\left(y + \frac{1}{y}\right)\right], \tag{23}$$

with $x = 2S\sqrt{\bar{n}(\bar{n} + 1)}$ and $y = \sqrt{\frac{\bar{n}+1}{\bar{n}}}e^{i\omega\tau}$.

After expressing the τ dependent exponential factor in terms of the modified Bessel functions $I_p(Z)$ defined as:

$$I_p(Z) = \sum_{k=0}^{\infty} \frac{(Z/2)^{p+2k}}{k!(p+k)!},$$

for which the following identity holds:

$$e^{(x/2)(t+1/t)} = \sum_{n=-\infty}^{\infty} I_n(x)t^n,$$

integration over τ finally yields:

$$k_{B\leftarrow A} = \frac{|H_{BA}|^2}{\hbar} \left(\frac{\bar{n} + 1}{\bar{n}}\right)^{\frac{1}{2}p} e^{-S(2\bar{n}+1)} I_p\left(2S\sqrt{\bar{n}(\bar{n} + 1)}\right), \tag{24}$$

with p taken as the integer closest to $\Delta E/\hbar\omega$.

At very low temperature $\bar{n} \rightarrow 0$ and Eq. 24 becomes:

$$k_{B\leftarrow A} \approx \frac{|H_{BA}|^2}{\hbar} e^{-S} \frac{1}{p!}. \tag{25}$$

At high temperature $\bar{n}$ becomes large and the Bessel function can be approximated by the asymptotic expression:[38]

$$I_p(Z) \approx (2\pi Z)^{-1/2} \exp(Z - p^2/2Z),$$

which leads to:

$$k_{B\leftarrow A} \approx \frac{2\pi}{\hbar} \frac{|H_{BA}|^2}{(4\pi\lambda k_B T)^{-1/2}} \exp\left\{-\frac{(\Delta E - \lambda)^2}{4\lambda k_b T}\right\}. \tag{26}$$

Thus in the limit of very high temperature the quantum mechanical approach reproduces the classical behaviour, exhibiting an exponential dependence on an activation energy, even though no potential energy barrier has been considered.

In the case of a multi-dimensional system with frequencies and normal mode directions identical in the initial and final states, $f(\tau)$ is obtained by simply taking the product of the density matrix elements for all normal modes $q_i - q_i^0$. Written in a compact form $f(\tau)$ takes the form:[39, 40, 9]

$$f(\tau) = \exp(-G)e^{-i\Delta E\tau}\exp\{G_+(t) + G_-(t)\} \tag{27}$$

with:

$$G_+(t) = \sum_k S_k(\bar{n}_k + 1)\exp(i\omega_k t),$$
$$G_-(t) = \sum_k S_k\bar{n}_k\exp(-i\omega_k t),$$
$$G = G_+(0) + G_-(0),$$

where the summations run over all normal modes of the system. This formula has been the starting point of several works on ET.[31, 8, 40, 41, 42, 43, 44, 10, 45]

The role of solvent

A major contribution toward the development of the quantum mechanical theory of ET processes in solution was initially provided by Levich[31] and his school,[43, 46] and subsequently extended by Jortner and others.[40, 42, 41, 44] All those approaches start from Eq.s 17 and 27: the ET rate is expressed in terms of thermally averaged transition probabilities from the vibronic states of the reactants to those of the products. In the work of Levich the reactants with their first coordination layers are regarded as rigid metallic spheres, neglecting changes in their nuclear configurations. The solvent bulk, which in Levich's scheme provide the whole contribution to reactions rates, is considered as a continuous dielectric, and its polar normal modes are treated in harmonic approximation, usually by approximating the frequencies of the medium polar modes by a single frequency.[31, 8]

Levich's treatment was mainly intended for ET between metal ions in solution; in the case ET involves two polyatomic molecules in solution it is no longer possible

to neglect configurational changes of the two molecules and of their first solvation shell. Kestner, Logan, and Jortner have extended Levich's theory along that direction.[40, 42, 41] They considered a model in which the two ions strongly interact with their first solvation shell and exert long-range electrostatic interactions on the bulk of solvent. The first coordination layers of the two ions are treated as a sort of supermolecules, each of them represented in their simplified model by only a totally symmetric mode, q_A and q_B, whose vibrational frequencies are not allowed to change upon ET, whereas the polar modes of the medium, q_s, are considered by polaron theory, as in Levich's work. The equilibrium positions of q_A, q_B, and q_S's are all displaced upon ET by an amount Δ_A, Δ_B, and Δ_k^s, respectively. The vibrational wavefunctions are then written as the direct product of harmonic wavefunctions of the two symmetric modes of the first coordination layer and of the polar solvent coordinates. It is straightforward to verify that with the above separation of intramolecular and solvent modes the correlation function $f(\tau)$ of Eq. 23 comes out to be the product of two correlation functions, one for the coordination layer, the other for the solvent bulk. Then the transition rate can be recast in terms of a convolution of two line shape functions, F_s and F_c:

$$k_{B \leftarrow A} = 2\pi \frac{|H_{BA}|^2}{\hbar} \int d\epsilon F_s(\Delta E - \epsilon) F_c(\epsilon), \tag{28}$$

which represent generalized transition probabilities at a given energy ϵ, obtained by applying Eq. 17 to the modes of the solvent bulk and of the first coordination layer. Since the former ones are characterized by low frequencies, the high temperature limit can be used leading to:

$$F_s(\Delta E - \epsilon) \approx \frac{2\pi}{\hbar} \frac{|H_{BA}|^2}{(4\pi\lambda_s k_B T)^{-1/2}} \exp\left\{ -\frac{(\Delta E - \lambda_s - \epsilon)^2}{4\lambda_s k_b T} \right\}. \tag{29}$$

For the coordination layer, assuming the same frequency for both oscillators in both electronic states:

$$F_c(\epsilon) = \exp[(-\Delta_c^2/2)(2\bar{n}_c + 1) \times$$
$$\int d\tau \exp(i\epsilon\tau) \exp\left[\frac{\Delta_c^2}{2}(\bar{n}_c + 1)\exp(i\hbar\omega_c\tau) + \frac{\Delta_c^2}{2}\bar{n}_c \exp(-i\hbar\omega_c\tau) \right], \tag{30}$$

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with:

$$\Delta_c^2 = \Delta_A^2 + \Delta_B^2.$$

Eq. 28, together with Eq.s 29 and 30, provides a manageable quantum mechanical expression for the transition probability per unit time, in which Δ_c and ω_c can be obtained from experimental results, whereas λ_s can be evaluated from polaron theory.

Jortner applied his approach to rationalize the non-Arrhenius behavior of ET from bacteriopheophytin anion (BPh) to primary quinone (Q_A) in bacterial photosynthetic reaction centers. That ET step is characterized by a temperature independent rate up to T=130 K and a rough $T^{-\frac{1}{2}}$ dependence at higher temperatures.[47] Jortner's quantum theory predicts a $T^{-\frac{1}{2}}$ dependence for an activationless ET, a process for which the nuclear potential energy surfaces of the initial and final electronic states cross at the minimum energy configuration of the initial state. Bixon and Jortner obtained a reasonable fit of the experimental data by using the single mode approximation of the multiphonon ET theory and by setting the average wavenumber of the displaced modes at $100\ cm^{-1}$.[48] From that low value a dominant contribution of the vibrational modes of the protein medium was argued. Although the theoretical curve is in reasonable agreement with the experimental results, the theoretical ET rates are temperature independent up to T=50 K, rather than 130 K as observed. Inclusion of a few higher energy quantum modes did not improve the situation, whereas a very satisfying fit of ET rates was obtained by using a slightly modified version of Jortner's quantum theory, including quadratic coupling terms originated by the vibrational frequency changes.[44] Recently, a very satisfying simulation of the temperature dependence of ET from BPh to Q_A has been obtained by applying a generalized Kubo formalism, which allows for using in computations the whole set equilibrium position displacements and of normal modes of the two isolated partners, calculated by reliable DFT computations, see infra.[23]

The importance of quadratic coupling terms in ET processes is now well recognized.[49, 50, 51, 52, 53] Those terms arise both from normal mode mixing and frequency changes. Frequency changes have an important physical meaning, inasmuch they

lead to different densities of vibrational states for the initial and final electronic states, allowing for entropy changes, which make ΔG to be a function of temperature. In order to include those effects in the computation of ET transition probabilities numerical approaches are needed.

Numerical approaches

Numerical approaches based on the generating function method

The evaluation of the time correlation function of Eq. 18 is not an easy task, and can be carried out analytically only for a few selected model Hamiltonians. However, within the limits of applicability of the Fermi golden rule, Kubo's GF method is an extremely powerful and convenient method for numerical approaches. In the case of weak coupling between the electron donor and acceptor redox pair, the most frequent situation in biosystems, the electronic coupling term between the initial and final states can be considered independent of nuclear coordinates, so that the expression for ET rate can be written:

$$k_{B \leftarrow A} = \frac{2\pi}{\hbar} |H_{BA}|^2 F(\Delta E, T), \tag{31}$$

where $F(\Delta E, T)$ is the Franck-Condon weighted density of states (FCWDS), given by:

$$F(\Delta E; T) = \frac{1}{Z} \sum_{m,n} e^{-\beta E_m} |\langle m|n \rangle|^2 \delta(E_n - E_m - \Delta E) \tag{32}$$

where $\langle m|n \rangle$ is the Franck-Condon integral, Z is the vibrational partition function of the initial electronic state $|A\rangle$, and the sum runs over all vibrational states $|m\rangle$ and $|n\rangle$ of $|A\rangle$ and $|B\rangle$.

The evaluation of $F(\Delta E, T)$ for large ET cofactors is not an easy task, even in the harmonic approximation. The calculation of FC integrals by use of multi-index recurrence relations,[54, 55, 56, 57, 58, 59, 60] poses problems for the extremely large amount of data which has to be stored. Data storage problems can be somewhat limited by using algorithms based on an judicious way of choosing normal mode ex-

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citations, and completely overcome by using a perturbative treatment of the normal mode mixing effect.[61]

From a computational point of view, the most efficient method for evaluating $F(\Delta E, T)$ is just the generating function discussed in the previous section, consisting in writing $F(\Delta E, T)$ as the inverse Fourier transform of a correlation function

$$F(\Delta E, T) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} e^{i\Delta E\tau} f(\tau) d\tau, \tag{33}$$

where

$$f(\tau) = \mathrm{Tr}\{e^{-i\tau\mathcal{H}_B} e^{-(\beta - i\tau)\mathcal{H}_A}\}/\mathrm{Tr}\{e^{-\beta\mathcal{H}_A}\}. \tag{34}$$

Harmonic approximation can be used for modeling $\mathcal{H}_A$ and $\mathcal{H}_B$, assuming that the normal modes of vibration ($\mathbf{Q}_A$ and $\mathbf{Q}_B$) differ both for equilibrium positions, frequencies, and directions.

The equilibrium position displacements and the elements of the rotation matrix, which describe normal mode mixing upon ET, can be determined by Duschinsky's normal mode transformation, a fundamental tool for understanding mechanistic details of both radiative and radiationless photochemical processes in polyatomic molecules.[62] Let $\mathbf{Q}_A$ and $\mathbf{Q}_B$ be the normal mode vectors of a molecule in the electronic states $|A\rangle$ and $|B\rangle$, respectively. According to Duschinsky, the two sets of normal coordinates are related by the expression:

$$\mathbf{Q}_A = \mathbf{J}\mathbf{Q}_B + \mathbf{K}, \tag{35}$$

where $\mathbf{J}$ is a rotation matrix and $\mathbf{K}$ a displacement vector, the former accounts for mixing of normal modes upon electronic transition, the latter for changes in the nuclear equilibrium configurations.[62, 55, 63, 54, 58, 60]

If $\mathbf{Q}_A$ and $\mathbf{Q}_B$ are expressed in terms of Cartesian displacement coordinates $\xi_i = q_i - q_i^0$, which is the most convenient representation for small equilibrium displacements,

$$\mathbf{Q}_\alpha = \mathbf{T}_\alpha^+ \mathbf{m}^{1/2}(\boldsymbol{\xi} - \boldsymbol{\xi}_\alpha^0) \qquad \alpha = A, B \tag{36}$$

then:

$$\mathbf{J} = \mathbf{T}_A^+ \mathbf{m}^{-1} \mathbf{T}_B, \qquad \mathbf{K}^{(x)} = \mathbf{T}_A^+ \mathbf{m}^{-1/2}(\boldsymbol{\xi}_B^0 - \boldsymbol{\xi}_A^0), \tag{37}$$

where $\mathbf{m}$ is the diagonal matrix of the atomic masses, and $\mathbf{T}_\alpha$ and $\boldsymbol{\xi}_\alpha^\circ$ are the normal mode matrix and the equilibrium position vector of the electronic state $|\alpha\rangle$.

In the case the two electronic states exhibit large equilibrium geometry differences, the normal mode transformation in the rectilinear Cartesian coordinates can pose problems in harmonic approximation, which can be partially solved by using the internal coordinate representation.[64, 65, 66, 67]

Performing the Gaussian integration over normal modes in Eq. 34, which corresponds to the trace operation, and taking into account Eq. 35, $f(\tau)$ takes the form:[23]

$$f(\tau) = [\det \boldsymbol{\Phi}]^{-1/2} \exp\left(-\tilde{\mathbf{K}} \mathbf{J} \mathbf{T}_g (\mathbf{T}_g + \mathbf{T}_e)^{-1} \mathbf{T}_e \tilde{\mathbf{J}} \mathbf{K}\right), \qquad (38)$$

where

$$\mathbf{T}_g = \boldsymbol{\omega}_g \tanh[(\beta - i\tau)\boldsymbol{\omega}_g/2]; \qquad \mathbf{T}_e = \tilde{\mathbf{J}} \boldsymbol{\omega}_e \tanh(i\tau\boldsymbol{\omega}_e/2) \mathbf{J} \qquad (39)$$

$$\mathbf{C}_g = \boldsymbol{\omega}_g / \tanh[(\beta - i\tau)\boldsymbol{\omega}_g/2]; \qquad \mathbf{C}_e = \tilde{\mathbf{J}} \boldsymbol{\omega}_e / \tanh(i\tau\boldsymbol{\omega}_e/2) \mathbf{J} \qquad (40)$$

$$\boldsymbol{\Phi} = [2\sinh(\beta\boldsymbol{\omega}_g/2)]^{-2} \boldsymbol{\omega}_g^{-1} \sinh[(\beta - i\tau)\boldsymbol{\omega}_g](\mathbf{T}_g + \mathbf{T}_e)(\mathbf{C}_g + \mathbf{C}_e)\boldsymbol{\omega}_e^{-1} \sinh(i\tau\boldsymbol{\omega}_e), \qquad (41)$$

$\boldsymbol{\omega}_g, \boldsymbol{\omega}_e$ being the diagonal matrices of the vibrational frequencies of the initial and final states.

The above formulation is very efficient for numerical treatments because the calculation of $F(\Delta E, T)$ can be recast into a discrete Fourier transform problem

$$F(\Delta E, T) = \frac{1}{N} \sum_{k=1}^{N} w(\tau_k) f(\tau_k) e^{i\Delta E \tau_k} \qquad (42)$$

where $w(\tau)$ is a proper window function, necessary to avoid boundary and spectral leakage problems.[68]

The appealing feature of the GF approach is in the fact that its computational cost is independent on the value of the temperature used in calculation, making thus it possible the analysis of the temperature dependence of ET rates between large redox cofactors.

Thermally averaged FCWDS's computed with the above approach for ET from BPh anion to Q$_A$ at different temperatures, ranging between 5 and 300 K, are shown

in Fig 3 as a function of the electronic energy difference between the initial and the final state ΔE. Equilibrium positions and vibrational frequencies and normal modes of the pairs BPh^-/BPh and Q_A/Q_A^- were computed by reliable DFT/B3LYP calculations of the isolated molecules in the gas phase.

At very low temperature and for lower values of ΔE, the FCWDS's show peaks characteristic of a system consisting of a discrete set of quantum states superimposed to a continuum. As ΔE increases, the FCWDS's become a smooth function of the vibrational energy of the final state for all T, exhibiting a broad maximum, which shifts at longer wavenumbers as the temperature increases.

The computed temperature dependence of ET rates, obtained from the Fermi Golden rule expression 31 using FCWDS's of Fig. 3, are shown in Fig. 4, together with the experimental results. The temperature dependence of the ET rates is well reproduced by computations. At lower temperatures there is a close agreement between theoretical and experimental data, the computed rates being within the range of the experimental error reported by Kirmaier et al. At higher temperatures, above 250 K, the computed rates are slightly underestimated, suggesting that the role of the surrounding medium in promoting ET dynamics, not explicitly considered in the present treatment, but for the adopted values of ΔE and H_{BA}, becomes more important.

The dispersed polaron model

A different approach to the calculation of ET rates has been developed by Warshel and collaborators who have pioneered the use of molecular dynamics in the computation of electron transfer rates in complex biochemical systems, using fully microscopic models including both reactants and their environment (solvent or protein matrix).[12, 13, 15, 37, 69, 70] The approach is based on the semi-classical surface hopping method,[11] according to which the rate of hopping from one electronic state to another can be obtained by running classical molecular mechanics trajectories on the potential energy surface of the reactants, and considering that each time the energy gap between the two potential energy surfaces vanishes a transition (ET)

occur with a certain probability factor.

The surface hopping is a semi-classical approach inasmuch the probability of reaching a crossing point is evaluated classically, whereas ET transition probabilities at the crossing point are evaluated at quantum mechanical level. In principle, a rigorous treatment would require an energy average over a large number of trajectories and the consideration of quantum interference effects arising because of trajectory branching in the phase space. In practice, the approach works quite well in complex biochemical systems, where the high dimensionality of the system provides for a fast energy redistribution and makes quantum interference effects negligibly small, because of the low probability that two trajectories originated at a crossing point come back in a same point of the phase space. Thus the only significant drawback is in the neglect of nuclear tunneling, which makes the method not suitable at low temperatures.

As discussed before, inclusion of tunneling effects requires the knowledge of the vibrational frequencies and equilibrium nuclear configurations of both reactants and products. Warshel realized that those pieces of information can be obtained from the Fourier transform of the time dependence of the energy difference between reactant and product states computed from classical trajectory simulations. This was the basic idea behind the dispersed polaron model; the Fourier transform of the reactant (R) autocorrelation function $A_R(t)$,

$$A_R(t) = <u(\tau+t)u(\tau)>_R, \qquad u(t) = \Delta E_{RP}(t) - <\Delta E_{RP}>_R, \qquad (43)$$

yields the spectral density function $J(\omega)$,

$$J(\omega) = \int_{-\infty}^{\infty} dt A_R(t) e^{i\omega t}, \qquad (44)$$

which picks out the ET active vibrational normal modes, namely those modes which exhibit significant displacements (Δ) of their equilibrium positions upon ET, with an amplitude $J(\omega_i)$ proportional to $\omega_i \Delta_i^2$. Thus, by properly scaling the spectral density function to yield the overall reorganization energies, Eq. 3, the key parameters (ω_i and Δ_i) for evaluating tunneling effects can be obtained. Many interesting applications of the dispersed polaron model were concerned with the early electron transfer steps in photosynthetic reaction centers.[13, 14, 15]

17

The Spin-Boson Hamiltonian

The general model provided by Kubo and Toyozawa can be simplyfied in a variety of ways. A common approximation is to assume that frequencies and directions of the normal modes of vibration do not change upon ET. The resulting so called spin-boson (SB) model is representative of a wide class of problems in physics and chemistry, and describes two (or more generally a few) discrete states of a subsystem linearly coupled to one or many harmonic oscillators (the boson field). Using the standard formalism in the literature the SB Hamiltonian can be written as:

$$H = -\frac{H_{AB}}{2}\sigma_x - \frac{\Delta E}{2}\sigma_z + \frac{1}{2}\sigma_z \sum_k \omega_k \Delta_k q_k + \frac{1}{2}\sum_k \omega_k(p_k^2 + q_k^2) \qquad (45)$$

where $\sigma_x = |A\rangle\langle B| + |B\rangle\langle A|$ and $\sigma_z = |A\rangle\langle A| - |B\rangle\langle B|$, are the standard Pauli operators, H_{AB} is the "bare" coupling between the two electronic states (the tunneling matrix element), and the parameters Δ_k describe the interaction between the discrete (electronic) states and the bath of oscillators.

The seminal work of Leggett[71, 72] and co-workers has provided an in depth and systematic analysis of the rich dynamical features of the SB Hamiltonian. The rate constant for a SB Hamiltonian has already been given in Eq.s 17 and 27 and can be written in the form

$$k_{B \leftarrow A} = \frac{H_{BA}^2}{\hbar} \int_{-\infty}^{+\infty} \exp[-i\tau\Delta E + G(\tau) - G(0)]d\tau \qquad (46)$$

with:

$$G(\tau) = \sum_k S_k(\bar{n}_k + 1)\exp(i\omega_k\tau) + \sum_k S_k\bar{n}_k\exp(-i\omega_k\tau).$$

Within this model the sign of the system-bath coupling parameters Δ_k is irrelevant in the computation of the decay rate, however this does not hold for more sophisticated models including, for example, Duschinsky effects. The effect of the system-bath interaction on the rate constant can be condensed in the spectral density function defined as

$$J(\omega) = \sum_k \Delta_k^2\delta(\omega - \omega_k). \qquad (47)$$

Using the above definition of spectral density it is possible to rewrite the function $G(\tau)$ as[72, 37, 73, 74]

$$G(\tau) = \int_0^\infty d\omega \{(1 + \bar{n}(\omega))J(\omega)e^{-i\omega\tau} + \bar{n}(\omega)J(\omega)e^{i\omega\tau}\} \quad (48)$$

$n(\omega)$ being the mean number of vibrational quanta for an oscillator of frequency ω at thermal equilibrium.

The calculation of the rate constant has been thus traced back to the calculation of a suitable spectral density, describing the process under investigation. In solid state processes usually a power law $J(\omega) \propto \omega^s$ with a cutoff frequency is employed. The so-called Ohmic, sub-ohmic and super-ohmic spectral-densities, as well as the Debye one have been widely investigated and much is known about their physics,[72, 75] but what is the correct spectral density for a given molecular redox pair process remains an open question. Indeed, in most cases a discrete subset of the molecular vibrations of the redox couple is strongly coupled to the ET process, giving rise to a highly structured and non-uniform spectral density (see infra).[76, 77, 20] Bath spectral densities having distinct resonances have been recently discussed, mainly in relation with the field of quantum computation.[78]

Since the microscopic parameters Δ_k can be related to the change of the equilibrium positions of the atoms of the reacting systems upon ET, it is possible to directly determine the bath spectral density, from first principles calculations, using the tools of modern quantum chemistry. This approach, pursued by the authors for ET in biochemical systems, requires the calculations of the normal vibrations of the entire reacting system, being therefore effective only for medium sized redox pairs when the driving force of the reaction is associated mainly to intramolecular motion of the two redox partners. Extension of this approach to ET between a redox pair embedded in a protein matrix has been discussed by Basu et al.[79].

When the role of the environment can not be neglected, *ab initio* calculations can be quite troublesome and different techniques have been developed to indirectly obtain an "effective" spectral density. In particular molecular dynamics calculations have been used to numerically estimate $J(\omega)$ for ET processes in solution;[80, 81] in that case the spin-boson and the dispersed polaron are clearly identical models.[73]

A similar approach has been used by Zheng *et al.*[82], Marchi *et al.*[83], and Xu and Schulten[84] who have computed numerical spectral densities for the primary ET in bacterial photosynthetic reaction centers. The spectral density can then be plugged into the rate expression of the SB model.

Quantum dynamics

Another approach pursued by several authors consists in the numerical resolution of the time dependent Schrödinger equations, using special algorithms for handling the diagonalization of very large matrices.[85, 86, 87, 60, 88, 89, 90] In short, the approach consists in expressing the time dependent wavefunction of the whole system in terms of a time independent manifold of vibronic states, one set of which, denoted by $\overline{|A\rangle}$, corresponds to ET reactants, the other, $\overline{|B\rangle}$, to ET products, with time dependent expansion coefficients:

$$|\Psi(t)\rangle = \overline{|A\rangle}\mathbf{C}_A(t) + \overline{|B\rangle}\mathbf{C}_B(t), \tag{49}$$

In the Born-Oppenheimer approximation the elements of the $\overline{|B\rangle}$ and $\overline{|A\rangle}$ are given by the direct product of the electronic and vibrational wavefunctions:

$$|A, \bar{v}\rangle = |\psi_A\rangle \otimes |\bar{v}_A\rangle, \qquad |B, \bar{w}\rangle = |\psi_B\rangle \otimes |\bar{w}_B\rangle, \tag{50}$$

where $\bar{v}$ and $\bar{w}$ denote the set of the vibrational quantum numbers associated to each normal mode of vibration. Therefore $\mathbf{C}_A$ and $\mathbf{C}_B$ of Eq. 49 are column vectors, whose sizes are given by the dimensions of the vibrational subspaces of $\overline{|A\rangle}$ and $\overline{|B\rangle}$ considered relevant to the problem under consideration. The time dependence of the expansion coefficients $\mathbf{C}(t)$ of eq. 49 determines the time evolution of $|\Psi(t)\rangle$ and therefore the dynamics of ET. $\mathbf{C}_A(t)$ and $\mathbf{C}_B(t)$ are obtained by solving the time dependent Schrödinger equation:

$$-i\hbar \begin{pmatrix} \dot{\mathbf{C}}_A(t) \\ \dot{\mathbf{C}}_B(t) \end{pmatrix} = \begin{pmatrix} \mathbf{H}_{AA} & \mathbf{H}_{AB} \\ \mathbf{H}_{AB}^{\dagger} & \mathbf{H}_{BB} \end{pmatrix} \begin{pmatrix} \mathbf{C}_A \\ \mathbf{C}_B \end{pmatrix}, \tag{51}$$

with initial conditions specifying the initial state of the system, where each $\mathbf{H}_{XY}$ in equation 51 is a matrix, with dimensions corresponding to those of $\mathbf{C}_A$ and $\mathbf{C}_B$.

The matrix elements of the diagonal and extradiagonal blocks of H are:

$$H_{A\bar{w}A\bar{v}} = \langle A\bar{v}| \mathcal{H}^{el} + \mathcal{T}_N |A\bar{w}\rangle = \langle \bar{v}_A| \mathcal{E}_A(R) + \mathcal{T}_N |\bar{w}_A\rangle = E_{A\bar{v}}^{tot}\delta_{\bar{w},\bar{v}} \qquad (52)$$

$$H_{A\bar{w}B\bar{v}} = \langle A\bar{v}| \mathcal{H}^{el} + \mathcal{T}_N |B\bar{w}\rangle = \langle \bar{v}_A| \lambda(R) + \langle A| \mathcal{T}_N |B\rangle |\bar{w}_B\rangle , \qquad (53)$$

where $\mathcal{T}_N$ is the nuclear kinetic energy operator, $\mathcal{E}_A(r)$ is the potential energy operator of $\overline{|A\rangle}$ and:

$$\lambda(R) = \langle A| \mathcal{H}^{el} |B\rangle . \qquad (54)$$

The extradiagonal terms can be further simplified by making the reasonable assumption that:

$$\lambda(R) >> \langle A| \mathcal{T}_N |B\rangle . \qquad (55)$$

Furthermore, since ET takes place in a small region of nuclear coordinates, see *infra*, the dependence of the electronic coupling term $\lambda(R)$ on the nuclear coordinates can be usually neglected, although it seems to play a role in some biosystems,[91] leading to the well known result that the off-diagonal terms of the Hamiltonian matrix are proportional to the overlap of the vibrational states of $|A\rangle$ and $|B\rangle$, the so called Franck-Condon (FC) integrals:

$$H_{A\bar{w}B\bar{v}} = \lambda\langle \bar{v}_A|\bar{w}_B\rangle. \qquad (56)$$

In a discrete state approach to ET dynamics, such as that outlined before, the selection of the vibronic states to be used in the time evolution is probably the most important problem to deal with. In fact, as shown in figure 5, the density of the vibrational states increases very rapidly as the internal energy increases, see fig. 5 Thus a selection of the most important state for ET dynamics becomes mandatory.

The assumptions that the nuclear dependence of the electronic coupling term can be neglected allows to easily identify the active modes for ET, namely those modes whose quantum number can change during the electronic transition. Since the coupling term is proportional to the Franck-Condon integral, eq. 56, and since FC integrals between vibronic states with different quantum numbers are vanishingly

small whenever changes in quantum numbers are associated to normal coordinates whose equilibrium positions or directions are the same in the two electronic states, only displaced or rotated normal modes can change their quantum numbers for degeneracy condition needed for ET is met; all other modes will act as spectators in dynamics, inasmuch their quantum numbers are frozen to the initial values. The displaced and mixed modes can be determined by Duschinsky's normal mode transformation previously discussed, Eq. 35.

With the modern technologies for electronic computations, reliable estimates of the equilibrium positions and normal modes of vibration of ET reactants and products can be obtained, even for large size molecules. That has opened the way to several works in which ET dynamics have been computed completely from first principles, using parameters obtained by highly reliable *ab initio* computations, and choosing the ET active modes by employing Duschinsky's transformation. That kind of calculations was pionereed by Warshel at empirical level of computation,[92] and subsequently reconsidered at ab-initio level.[88, 87, 16, 76, 21] The main problem to be faced with in the discrete state approach is the huge number of vibronic states which should be considered. The situation for the case of the redox pair bacteriochlorophyll (BChl) anion/pheophytin (BPh), two cofactors involved in the early ET steps occurring in bacterial reaction centers, is illustrated in Fig. 6, where the displacements of the modes of the two pairs $BChl^-/BChl$ and BPh/BPh^- have been reported as a function of the vibrational wavenumber. There are tens of displaced modes in the region 0-1700 cm^{-1}, many of them falling at wavenumbers less than 100 cm^{-1},[93] in substantial good agreement with dispersed polaron results.[13, 15] A such large number of displaced modes can not be taken into account in quantum dynamics, so that a judicious choose of the active modes is necessary. By taking only ten displaced modes for the $BChl^-$ molecule and six for the BPh partner, and limiting the maximum excitation numbers to 2 and 1 for the low and high frequency modes, respectively, dynamics showing essentially an irreversible decay toward the products have been obtained.[93]. That is a very important point, showing that the use of the whole set of the normal coordinates of the redox molecular pair into

Duschinsky's transformation and the use of simple algorithms, based on the energy difference between initial and final state and on the strength of the coupling factors, i.e. Eq. 56, allows to partially include in dynamics the faster dephasing effects, inasmuch there would be several final states, with different vibrational frequencies, which are populated in the electronic transition, a situation which makes the recurrence times much longer than the transition time.[16, 93]

BChl and BPh are two large size cofactors of bacterial reaction centers leading to fast ET; for such a system it is largely expected that models including only intramolecular vibrational modes are sufficient to account for ET transition times. The situation is somewhat different for ET from BPh to the primary quinone Q_A, an ET step which takes a significantly longer time. Although Q_A is much smaller than BChl, the density of vibrational states of the ET products which are quasi-degenerate with the ground vibronic state of the reactants is as large as 10^{13}, see Fig. 5. In Fig 7 the absolute values of the FC integrals between the vibronic ground state of the reactants with a selected manifold of states of products, falling at about the same total energy of the initial state (ΔE for ET between BPh and Q_A is in the range 4500–5000 cm^{-1}[94, 95]), are reported.

Fig. 7 shows the existence of a quasi-continuum of states which are weakly coupled with the initial ground state. However, quantum dynamics simulations computed by using the coupling terms of Fig. 7 are characterized by recurrence times of the same order of magnitude of the transition time,[16] showing that only a few states are effectively coupled with the initial ground state.[16, 87] That undesired behaviour, no oscillations are experimentally observed, is mainly due both to the paucity of vibrational states considered in dynamics and to the fact that the results of dynamical simulations have not been temperature averaged.

With the development of the multi-configuration time dependent Hartree (MCTDH) methodology [96] and of its multi-layer extension [97, 98, 99] for the solution of the time-dependent Schrödinger equation, it has been possible to provide exact numerical simulations for such large size systems, thus opening new perspectives for the study of ET processes in large chemical systems.

The MCTDH algorithm was introduced in 1990 by Meyer, Manthe and Cederbaum[96], and its theoretical aspects can be found in several papers[100, 101]. In its standard formulation the method is based on the expansion of the nuclear wavepacket in terms of a time-dependent basis set

$$|\Psi(t)\rangle = \sum_{j_1} \sum_{j_2} \cdots \sum_{j_p} A_{j_1 j_2 \dots j_p}(t) \prod_{\kappa=1}^{p} |\varphi_{j_\kappa}^{(\kappa)}(Q_\kappa, t)\rangle = \sum_{J} A_J(t)|\Phi_J(t)\rangle \qquad (57)$$

where the $\varphi^{(\kappa)}$ are known as single particle functions (SPF). The coordinate for each set of n_κ functions is a composite coordinate of one or more system coordinates, $i.e.$ $Q_\kappa = (q_a, q_b, ...)$, thus the SPFs basis functions are d-dimensional where d is the number of degrees of freedom that have been grouped into a single coordinate.

The above equation is very similar to the standard wavepacket expansion with the exception that the Φ_J, $i.e.$ the direct product of the SPFs, form a time-dependent basis set $i.e.$

$$|\varphi_{j_\kappa}^{(\kappa)}(t)\rangle = \sum_{i_1} \sum_{i_2} \cdots \sum_{i_{N_\kappa}} B_{i_1 i_2 \dots i_{N_\kappa}}^{\kappa, j_\kappa}(t) \prod_{q=1}^{N_\kappa} |v_{i_q}^{(\kappa,q)}\rangle \qquad (58)$$

Where the coefficients $B(t)$ of the expansion are time-dependent, and the $|v_{i_q}^{(\kappa,q)}\rangle$ functions are time-independent primitive functions. N_κ is the number of degrees of freedom which have been grouped into the j_κ SPFs. With the above ansatz one obtains a set of non-linear coupled differential equations for the time-dependent coefficients, A_J, and for the SPFs, $i.e.$ for the $B(t)$ coefficients. From this point of view the MCTDH method can be considered as a time-dependent contraction of the basis set: the number of physically significant SPFs is usually much smaller than the number of time-independent primitive functions. Furthermore, a key advantage of the MCTDH formulation is in its flexibility to combine more degrees of freedom and represent them through a single particle time-dependent wavefunction. Usually tens degrees of freedom are combined to give a much lower number of SPFs. This techniques allows to strongly reduce the computational effort of the time-dependent calculation by drastically reducing the size of the basis set.

The multi-layer formulation of MCTDH[97, 98, 102] has extended the basic MCTDH approach by introducing other layers of time-dependent contractions. The

wave function is represented by a recursive, layered expansion of time dependent SPFs, the final layer is expanded, as for the standard MCTDH, in terms of a time-independent basis set. The inclusion of several dynamically optimized layers in the ML-MCTDH method provides more flexibility in the variational functional, which significantly advances the capabilities of performing wavepacket propagations in complex systems.

The possibility to numerically solve the TDSE for systems with a large number of degrees of freedom has also opened the way to a significant number of applications to homogeneous as well as heterogeneous ET processes. Model systems with different spectral densities and coupling parameters were solved numerically, [97, 103, 104]; quantum dynamics of heterogeneous ET between organic dyes (alizarin and coumarin derivatives) and semiconductors (TiO_2) were studied by using electronic structure calculations to obtain a microscopic Hamiltonian[105, 17, 18, 19, 22]; full quantum dynamics of ET in model biochemical systems comprised of a porphyrin-quinone redox pair has also been recently studied including more than 130 vibrational degrees of freedom, with a full *ab initio* microscopic Hamiltonian.[106, 107]

The ML-MCTDH techniques is a quite impressive methodology for studying exact quantum dynamical problems, but it requires a careful attention in choosing how nuclear degrees of freedom are grouped to form a single particle and in testing the convergence of the SPFs basis for each layer.

Future perspectives

The comprehension of ET processes in complex systems at atomistic level has largely grown in the last years. The development of the modern computational techniques for the electronic properties of large size molecules have allowed the implementation of several computational approaches to ET, in which the evaluation of rate constants or of the time evolution of the reactants configuration is carried out from first principles, starting from realistic microscopic models of the two redox partners, and employing a few selected experimental data, which often serve to account for the role of the environment. Further progresses are expected in short time, which

should hopefully open the way toward a detailed microscopic understanding of the mechanisms regulating molecular machines.
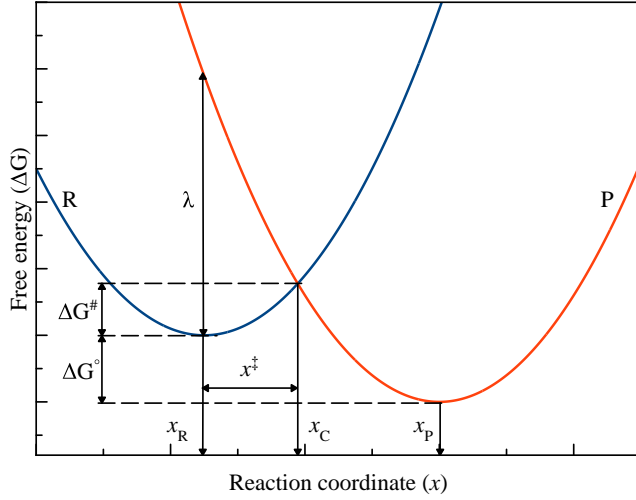
Acknowledgments

FIG. 1: The role of nuclear motion in electron transfer. Curve R and P represent schematic profiles of the change of Gibbs free energy with the nuclear coordinate for ET reactants and products. In the classical Marcus theory the passage from R to P can occur at x_C where R and P cross each other. λ is the reorganization energy, i.e. the energy the system has to spend to reach the equilibrium position of one state, but staying in the other state. ΔG^0 and $\Delta G^\#$ indicates the ET free energy change and the free energy activation energy. In a one dimensional system with equal curvatures for the curves R and P, the free energy activation energy can be easily related to λ and ΔG^0 by noting that, since $G_R = Kx^2/2 + \Delta G^0$ and $G_P = K(x - x_P)^2/2$, $x_C = x_P/2 - \Delta G^0/Kx_P$, so that $G_R(x_C) - \Delta G^0 = \Delta G^\# = \lambda/4 + (\Delta G^0)^2/4\lambda - \Delta G^0/2 = (\lambda - \Delta G^0)^2/4\lambda$.
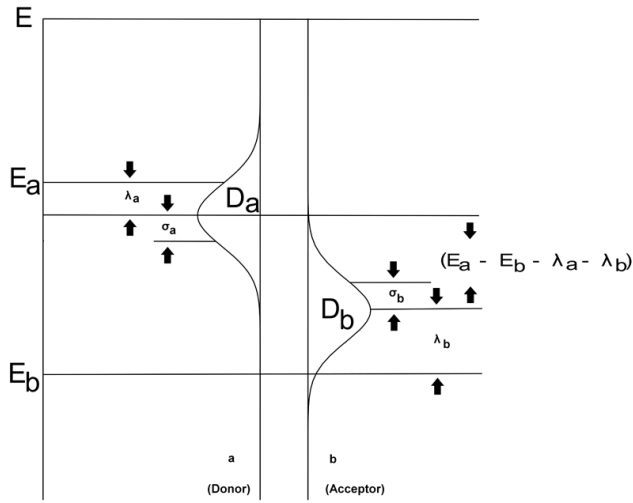
FIG. 2: Probability energy distributions for removing an electron from the donor and for releasing an electron to the acceptor, in the framework of the Franck-Condon principle. E_A is the energy required to adiabatically extract an electron from donor, and E_B that gained for the injection of an electron to the acceptor. Because the potential energy profiles corresponding to the neutral and charged (initial and final) states are displaced each other, the maximum probability for removing an electron occurs at $E_A + \lambda_A$, and that for releasing an electron to the acceptor at $E_B - \lambda_B$
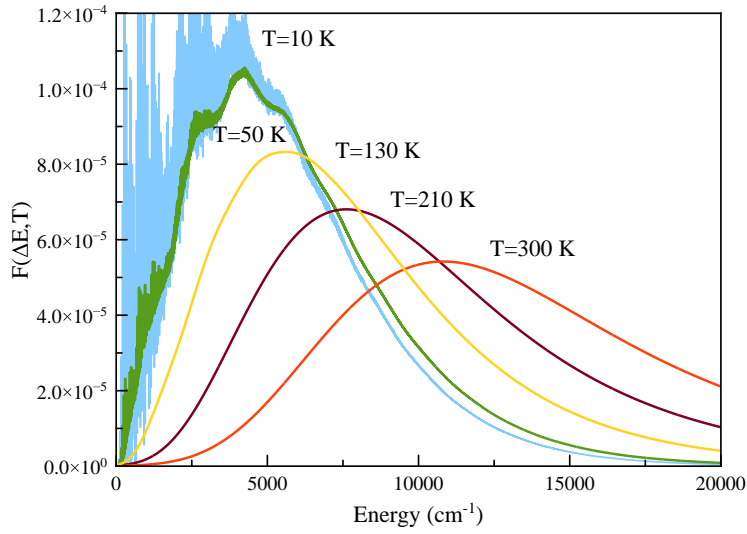
FIG. 3: Thermally averaged FranckCondon weighted density of states for ET from B^- to Q_A as a function of the electronic energy difference between initial and final states. The FC weighted density of states has been computed by the generating function method, including the whole sets of normal coordinates of the two redox pairs, without posing any limit to normal modes excitation numbers.
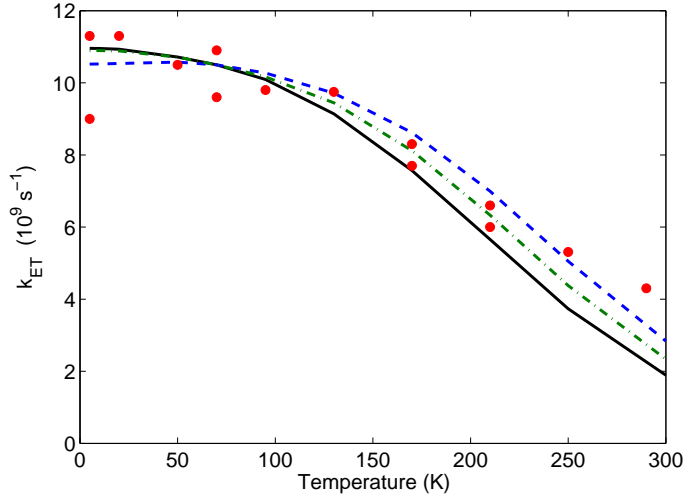
FIG. 4: Computed (lines) and observed (squares and circles) temperature dependence of ET rates for the redox pair BPh/Q_A of bacterial photosynthetic reaction centers. Circles and squares refer to measurements at 545 nm and 665 nm, respectively. Computed curves: DE = 5400 cm^{-1}(dashed line), DE = 6200 cm^{-1}(dotted line), DE = 5830 cm^{-1}(full line). Experimental values are taken from ref. 58. Theoretical rates have been obtained by evaluating the two parameters ΔE and $|H_{BA}|^2$ by a least squares fit of the experimental data, which yielded 5830 and 10.0 cm^{-1}, respectively. The other two curves have been obtained by setting ΔE to 5400 and 6200 cm^{-1}, and evaluating the electronic coupling term by least squares, which yielded $|H_{BA}|^2$ = 9.9 and 10.1 cm^{-1}, respectively. Reprinted with permission from ref. [23]
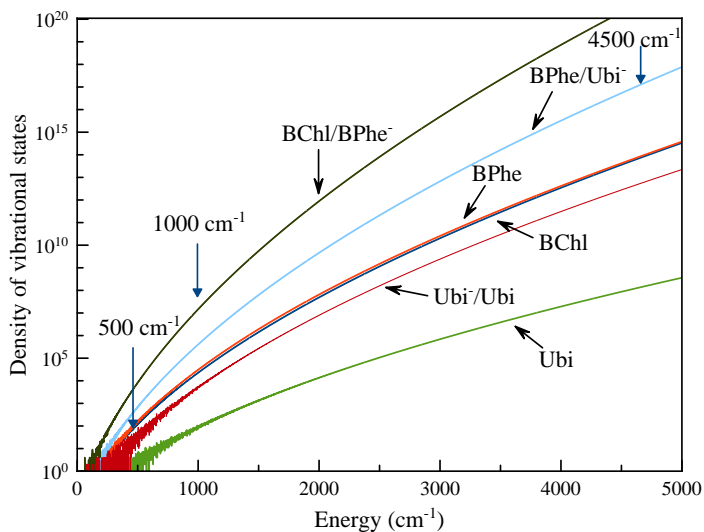
FIG. 5: Total density of states versus energy for some of the redox pairs present in bacterial photosynthetic reaction centers: bacteriochlorophyll/pheophytin, pheophytin/ubiquinone, and ubiquinone/ubiquinone. The curves have been calculated by using the vibrational frequencies obtained at DFT/B3LYP level for the isolated molecules in the gas phase and the Beyer-Swinehart algorithm. The curves indicate how the density of the manifold of vibrational states of the ET products change as the exothermicity of the ET reactions increases. The experimental ΔE of the three processes are also reported.[108, 109] The case of the pair ubiquinone/ubiquinone anion is intriguing for the huge the difference with respect to the other two long range ET processes, which would suggest that different mechanisms must probably be invoked.[110, 111, 112, 113, 114, 115, 116, 117, 118]
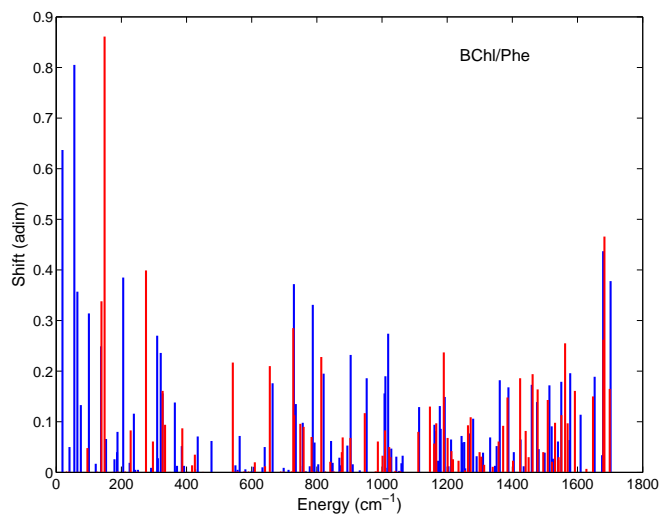
FIG. 6: Displaced modes of bacteriochlorophyll anion (blue) and bacteriopheophytin (red) upon relieving and accepting an electron. Displacements are in dimensionless units.
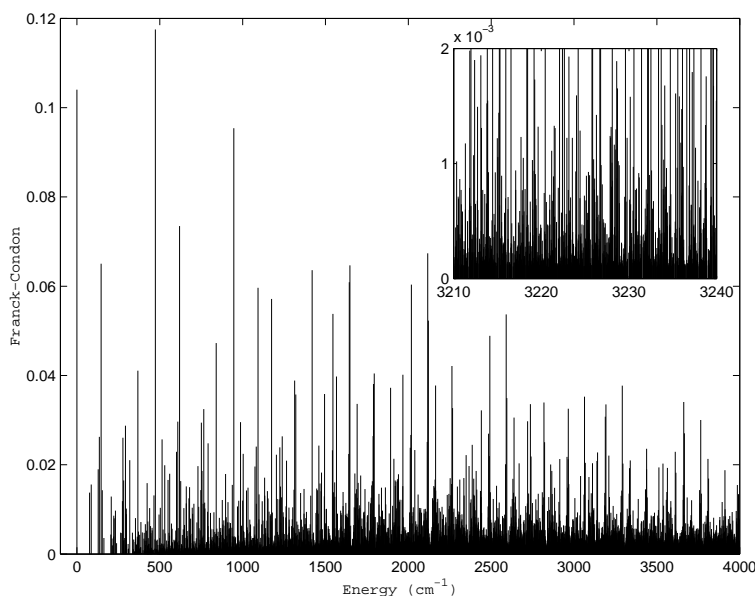
FIG. 7: Franck-Condon integrals (absolute values) for ET from bacteriopheophytin (BPh) to ubiquinone (Q_A) as a function of the energy difference between the ground vibronic state of BPh$^-$-Q_A and the final state of BPh-Q_A^-. Twenty vibrational states were allowed to change quantum number, with a maximum change of three quanta.

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