Effects of Configurational Fluctuation on Electronic Coupling for Charge Transfer Dynamics*

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Abstract—We advance a theory for the effects of bridge configurational fluctuations on the electronic coupling for electron transfer reactions in donor-bridge-acceptor systems. The theory of radiationless transitions was applied for activationless electron transfer, where the nuclear Franck–Condon constraints are minimized, with the initial vibronic state interacting directly with the final vibronic manifold, without the need for thermal activation. Invoking the assumption of energy-independent coupling, the time-dependent initial state population probability was analyzed in terms of a cumulant expansion. Two limiting situations were distinguished, i.e. the fast configurational fluctuation limit, where the electron transfer rate is given in terms of the configurational average of me squared electronic coupling, and the slow configurational fluctuation limit, where the dynamics is determined by a configurational averaging over a static distribution of electron transfer probability densities. The correlation times for configurational fluctuations of the electronic coupling will be obtained from the analysis of molecular dynamics, in conjunction with quantum mechanical calculations of the electronic coupling, to establish the appropriate limit for electron transfer dynamics.

INTRODUCTION

Levich and Dogonadze [1, 2] and Dogonadze [3, 4] advanced the quantum mechanical theory of chemical electron transfer (ET) in solution. Their work provided the first description of ET as a quantum transition between two electronic Born–Oppenheimer potential surfaces, which is induced perturbatively by electronic coupling. This pioneering work constituted a cornerstone for the theoretical studies of ET in physical chemistry and electrochemistry. ET between localized, widely spaced, donor and acceptor sites is ubiquitous and central in chemistry, physics and biology [5, 6]. The ET process can be considered as a nonradiative transition between vibronic levels corresponding to two electronic states, which are determined by both the coupling between electronic states and the nuclear Franck–Condon factors. The conceptual framework for ET dynamics encompasses the nonadiabatic microscopic rates, k_i, from a vibronic state ($|I\rangle$) (with energy E_i), to the initial vibronic manifold [6, 7]

$$k_i = (2\pi/\hbar)|V|^2 F_i, \qquad (1)$$

where V is the electronic coupling, which can involve either direct donor–acceptor exchange or bridge-mediated superexchange, and F_i is the nuclear Franck–Condon weighted density of states between $|I\rangle$ and the final manifold. The separation between the electronic and nuclear contributions to k_i, Eq. (1), rests on the Condon approximation [7, 8]. Under the common circumstances of the applicability of the separation of the time scales between fast medium-induced fluctuations of the

energetics, i.e. excitation and relaxation (time scale τ_m), and slow microscopic electronic-nuclear ET, i.e. $k_i \ll \tau_m^{-1}$, the thermally averaged ET rate is

$$k_{ET} = (2\pi/\hbar)|V|^2 F, \qquad (2)$$

with the thermally averaged nuclear Franck–Condon factor being

$$F = (1/Z)\sum_i \exp(-E_i/k_B T)F_i, \qquad (3)$$

where Z is the partition function in the initial manifold. For activated ET, F is maximized at the crossing of the nuclear potential surfaces of the initial and final electronic states. F manifests the celebrated Marcus parabolic activation energy [5], i.e. $F \propto \exp(-E_A/k_B T)$, $E_A = (\Delta G + \lambda)^2/4\lambda k_B T$ in the "normal" region, where nuclear quantum effects are small. For activationless ET, F_i exhibits a weak dependence on E_i and k_{ET} manifests a very weak (inverted) dependence on the temperature [5, 6], i.e. $k_B \propto T^{-1/2}$. In the "inverted" region nuclear quantum effects are often important and k_{ET} exhibits a weak T dependence [6].

Long-range ET (over a distance of a few to tens of angstroms) plays a pivotal role in large-scale chemical systems and biological systems [6, 9–17]. The role of the bridge electronic structure in a donor–bridge–acceptor system can be inferred from the unistep superexchange rate, Eqs. (1) and (2), where V is the off-resonance electronic coupling, which is often expressed in terms of a perturbation expression with the parameters $v/\Delta E$, where v are the nearest-neighbor matrix elements and $\Delta E > 0$ are the energy gaps [6]. The superex-

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change mechanism was widely applied for ET in chemical systems, consisting of rigid or nonrigid covalently bridged donor–acceptor supramolecules [9–13, 18], for ET in globular proteins [19, 20], for some aspects of ET in the photosynthetic reaction centers, e.g. quinone reduction [15], for primary ET in chemically engineered reaction centers [6–14], as well as for hole transfer in DNA [17, 21–29], where unistep hole hopping between adjacent guanine (G) nucleobases is induced by superexchange mediation via short adenine–thymine $(T–A)_n$ $(n \leq 3)$ bridges.

The first approach to the structure-dynamics-function analysis of ET mediated by nonrigid bridges, such as floppy long chemical bridges [10, 18], by the polypeptide backbone in proteins [30] and by the $(T–A)_n$ bridges in DNA [31–35] was based on "frozen" ideal X-ray crystallographic structures (or energy minimized structures). However, it is well recognized that the positions of bridge molecular components, e.g. the intervening protein bridge or fee base pairs in DNA, undergo significant internal motions, which will grossly modify the electronic coupling. Theoretical model calculations of fluctuating bridge effects on ET were advanced by several groups [36–43]. Ulstrup and his colleagues [36, 37] considered free energy functionals for nonequilibrium inertial polarization. Configurational static averaging was considered by Onuchic et al. [38, 39] who treated configurational thermal averaging of the electronic coupling, and by Medvedev and Stuchebrukhov [42] who treated an inhomogeneous distribution of inelastic tunneling processes. Attempts to treat time-dependent autocorrelation functions were reported by Tang [40] and by Goychuk et al. [41] who considered an exponential time correlation function for the electronic coupling in a two-state model within the framework of the spin-boson model. Finally, Xie et al. [43] developed a two-state approximation for the electronic coupling. Several recent simulations, based on molecular dynamics, in conjunction with quantum-mechanical calculations of the sensitivity of the electronic couplings to conformational changes for ET in donor–acceptor bound polyproline [30], for other polypeptides, e.g. in azurine [43] and for hole transfer in DNA [32, 34], reveal large (one to two orders of magnitude) variations of the electronic couplings. These large effects of fluctuating bridges on the electronic coupling raise the distinct possibility that charge transfer may occur from specific accessible (nonequilibrium) conformations of the system.

In this paper we apply the theory of radiationless transitions [6] for the development of a model system for the effects of configurational fluctuations on ET dynamics. Two major issues will be addressed in the context of the effects of configurational fluctuations on superexchange mediated charge transfer via floppy bridges. First, when are the configurationally-averaged electronic couplings applicable? Second, what is the interrelationship between the time scales for the effect of configurational fluctuations on V for the medium induced relaxation/excitation and the microscopic ET lifetimes?

A MODEL FOR ELECTRONIC COUPLING FLUCTUATION EFFECTS ON ET DYNAMICS

In the application of the theory of radiationless transitions [6] for the effects of (bridge) configurational fluctuations on electron transfer dynamics, the microscopic ET rate, Eq. (1), will be extended to incorporate the effects of such fluctuations. We consider an (initial) electronic-vibrational doorway state $|I\rangle$ coupled to a (final) vibronic quasi-continuum $\{|F\rangle\}$. Casting the dynamics of the model system within the framework of the Born–Oppenheimer approximation for the diabatic-electronic vibrational state, we invoke time-dependent coupling to mimic the effects of the configurational fluctuations in direct exchange (i.e. for nearest neighbor D and A) or in superexchange (for DBA).

We shall consider ET dynamics from a single initial state, implying that the microscopic ET rates depend weakly on the nature of the initial vibronic state. This physical situation prevails for activationless ET [6]. In this case the initial state $|I\rangle$ interacts directly with the manifold of final states, without the need for thermal activation. Accordingly, the microscopic ET rate (i.e. from the zero-point vibrational level of the initial manifold) provides a good approximation for the activationless ET rate constant. Activationless ET processes optimize the constraints imposed by the nuclear Franck–Condon factor, with the corresponding rate constant being ultrafast, falling in the temporal range of hundreds of femtoseconds to picoseconds [6]. Such activationless processes are common in biophysics for the primary charge separation in photosynthesis [6, 44, 45]. In the treatment of the effects of configurational and medium fluctuations on the activationless ET rate, the energy gap fluctuations exert only a minor effect on the overall process, and the only relevant effects of fluctuations involve the imposed time-dependent electronic coupling.

The total Hamiltonian is

$$H = H_0(r, Q) + V(r, Q), \qquad (4)$$

where r and Q are the electronic and nuclear coordinates, respectively, H_0 is the Hamiltonian for the diabatic states, while V is the electronic coupling.

The zero-order states $|I\rangle$ and $\{|F\rangle\}$ correspond to vibronic levels (with energies E_I and (E_F)) of two diabatic electronic states, corresponding to me eigenstates of the Hamiltonian H_0, i.e.

$$\begin{aligned} H_0|I\rangle &= E_I|I\rangle \\ H_0|F\rangle &= E_F|F\rangle. \end{aligned} \qquad (5)$$

Within the framework of the Born–Oppenheimer approximation we set the diabatic wavefunction as products of electronic wavefunctions $\varphi(r, Q)$, and the nuclear wavefunction $\chi(Q)$, in the form

$$|I\rangle = \varphi_i(r, Q)\chi_i(Q),$$
$$|F\rangle = \varphi_f(r, Q)\chi_f(Q). \tag{6}$$

The dynamics of the system is specified in terms of the time-dependent Schroedinger equation $ih\dot{\Psi}(t) = \hat{H}\Psi(t)$ with the initial condition $\psi(t=0) = |I\rangle$, i.e. $|I\rangle$, constituting the doorway state. In the interaction representation

$$\Psi(t) = \alpha(t)\exp(-iE_I t/\hbar)|I\rangle$$
$$+ \sum_F \gamma_F(t)\exp(-iE_F t/\hbar)|F\rangle \tag{7}$$

the time evolution is determined by the non-Markovian equation

$$\dot{\alpha}(t) = \int_0^t dt' K_{II}(t-t')\alpha(t') \tag{8}$$

with the memory kernel being given by

$$K_{II}(\tau) = \left(\frac{1}{\hbar^2}\right)\sum_F V_{IF}\exp[i(E_I - E_F)\tau/\hbar]V_{FI}, \tag{9}$$

where $V_{IF} = \langle I|V|F\rangle$, being explicitly expressed with the help of Eq. (9), in the form

$$V_{IF} = \int dQ\chi_i(Q)\chi_f(Q)\int dr\varphi_i(r, Q)V\varphi_f(r, Q), \tag{10}$$

$$V_{IF} = \int dQ\chi_i(Q)V_{if}(Q)\chi_f(Q), \tag{10a}$$

where $V_{if}(Q) = \int dr\varphi_i(r, Q)V\varphi_f(r, Q)$ and the Condon approximation need not be introduced at this stage.

We now invoke the assumption of energy-independent coupling, which means that on the average the coupling is independent on the final state in the relevant range. To be more precise, the condition can apply if the coupling is small enough such that the line width $2\pi V^2\rho$ (where ρ is the density of finial states) is small compared to the Franck–Condon width. Under this assumption, a summation over the final states in Eq. (9) results in the following expression

$$K_{II}(t-t') \longrightarrow (2\pi/\hbar)V_{IF}V_{FI}\rho\delta(t-t'), \tag{11}$$

where ρ is the density of final states. At this stage we move to a semiclassic description, with $Q(t)$ being time dependent nuclear coordinates due to configurational fluctuations. We replace V_{IF} in Eq. (11) by a time-dependent effective coupling, setting $V_{IF} \longrightarrow v(t)$. So we finally approximate

$$K_{II}(t-t') = (2\pi/\hbar)v(t)v(t')\rho\delta(t-t'). \tag{12}$$

The dynamics of the system is given by

$$\dot{\alpha}(t) = -(\pi/\hbar)\rho v(t)v(t)\alpha(t). \tag{13}$$

The time-dependent initial state probability is

$$P(t) = \langle|\alpha(t)|^2\rangle, \tag{14}$$

where $\langle\ \rangle$ denotes averaging over the system's trajectories and $P(t)$ is given from Eq. (13), by

$$P(t) = P(0) = \left\langle \exp\left[-\int_0^t (2\pi\rho/\hbar)v^2(\tau)d\tau\right]\right\rangle. \tag{15}$$

The effective time-dependent rate

$$k(t) = -\dot{P}(t)/P(t) \tag{16}$$

is given from Eq. (16) in the form

$$k(t) = \frac{\left\langle (2\pi\rho/\hbar)v^2(t)\exp\left[-\int_0^t (2\pi\rho/\hbar)v^2(\tau)d\tau\right]\right\rangle}{\left\langle \exp\left[-\int_0^t (2\pi\rho/\hbar)v^2(\tau)d\tau\right]\right\rangle}. \tag{17}$$

CUMULANT EXPANSION AND CORRELATION TIMES

We apply standard techniques of statistical mechanics to express the time-dependent probability density, Eq. (15), in terms of a cumulant expansion [46]. The cumulant expansion is useful if it is possible to truncate the expansion after the second order term. This is permissible when the fluctuation's correlation time is short on the time scale of the charge transfer process. Keeping the expansion up to the second order results in the following expression for the time-dependent probability

$$P(t)/P(0) = \left\langle \exp\left[-\int_0^t (2\pi\rho/\hbar)v^2(\tau)d\tau\right]\right\rangle$$

$$= \exp\left[-(2\pi\rho/\hbar)\int_0^t \langle v^2(\tau)\rangle d\tau \right. \tag{18}$$

$$\left. + (2\pi\rho/\hbar)^2\int_0^t d\tau\int_0^t d\tau_1\langle v^2(\tau)v^2(\tau_1)\rangle_c\right],$$

where

$$\langle v^2(\tau)v^2(\tau_1)\rangle_c = \langle(v^2(\tau) - \langle v^2\rangle)(v^2(\tau_1) - \langle v^2\rangle)\rangle. \tag{19}$$

As the simplest approximation we take a time-dependent coupling in the form

$$v(t) = v_0 + f(t) \tag{20}$$

with the finite time-averaged value

$$\langle v(t)\rangle = v_0, \tag{21}$$

where $f(t)$ is a stationary stochastic process with a vanishing average, i.e.

$$\langle f(t) \rangle = 0 \tag{21a}$$

and an exponentially decaying autocorrelation function

$$\langle f(\tau)f(\tau_1) \rangle = \sigma^2 \exp[-(\tau - \tau_1)/\tau_c], \tag{22}$$

where τ_c is the characteristic decay time of the autocorrelation function for the coupling. Thus the effects of medium fluctuation dynamics are subsummed in the autocorrelation time. A Gaussian joint probability distribution for the process $\Phi(f(0); f(t))$ has taken in the form

$$\Phi(f(0); f(t))$$

$$= \frac{1}{\sqrt{2\pi\sigma^2}} \exp\left\{-\frac{f^2}{2\sigma^2}\right\} \frac{1}{\sqrt{2\pi(1 - \exp(-t/\tau_c))\sigma}} \tag{23}$$

$$\times \exp\left\{-\frac{(f(t) - f\exp\{-t/\tau_c\})^2}{2\sigma^2(1 - \exp(-t/\tau_c))}\right\}.$$

Making use of Eqs. (18)–(23) we obtain for the time-dependent probability

$$P(t)/P(0) = \exp\{-[(2\pi\rho/\hbar)(v_0^2$$

$$+ \langle\sigma^2\rangle\{1 - (8\pi\rho/\hbar)v_0^2\tau_c\})]t\} \tag{24}$$

$$\times \exp\{-(4\pi\rho/\hbar)^2 v_0^2\sigma^2\tau_c^2[1 - \exp(-t/\tau_c)]\}$$

and the effective rate, Eq. (17), takes on the form

$$k(t) = (2\pi\rho/\hbar)[v_0^2 + \sigma^2\{1 - (8\pi\rho/\hbar)v_0^2\tau_c\}]$$

$$+ (4\pi\rho/\hbar^2)v_0^2\sigma^2\tau_c\exp(-t/\tau_c). \tag{25}$$

The final, rather cumbersome, results, Eqs. (24) and (25), determine the dynamics of the model system subjected to configurational fluctuations, which are characterized by the parameters τ_c and $\langle f^2 \rangle = \sigma^2$.

THE LIMITING CASES OF FAST AND SLOW FLUCTUATIONS

We shall consider two limiting cases for the dynamics of ET via a configurationally-fluctuating bridge, which are determined by the relative time scales for the nonradiative process and the correlation time τ_c.

(1) Fast configurational fluctuations. The time scale for the nonradiative process, $\tau_{NR} \sim k^{-1}$ corresponds to $\tau_c \ll \tau_{NR}$. Accordingly, the relevant time scale is $t \gg \tau_c$. Under these circumstances, $k(t)$ is time independent and Eq. (25) reduces to the following expression for the rate

$$k = (2\pi\rho/\hbar)(v_0^2 + \langle f^2 \rangle). \tag{26}$$

The rate is now determined by the configurational average of the electronic coupling $\langle v^2(t) \rangle$. In the fast configurational fluctuations limit the effective rate, Eqs. (17)

arid (25), is time independent, with the population probability $P(t)$, Eqs. (15) and (18), being expressed in terms of a single exponential decay.

For fast configurational fluctuations of the electronic coupling $V_{if}(Q)$, with the Franck–Condon factor being weakly time dependent, we use Eq. (10a) and invoke the Condon approximation, setting

$$\langle v^2(t) \rangle \simeq \langle V_{if}^2(Q) \rangle F_i. \tag{27}$$

The microscopic ET rate from a single doorway state is given by

$$k_i \simeq (2\pi/\hbar)\langle V_{if}^2(Q) \rangle F_i, \tag{28}$$

where the FC factor is

$$F_i = \left| \int \chi_i(Q)\chi_f(Q)dQ \right|^2. \tag{29}$$

The replacement of the absolute square of the electronic coupling in Eq. (4) by its configurational average in Eq. (28) was previously considered by Newton and his colleagues [30] for protein ET. It is imperative to bear in mind that this physical situation corresponds to the fast fluctuations limit.

(2) Slow configurational fluctuations. Slow fluctuations are characterized by the condition $\tau_c k > 1$. This physical situation implies a quasi-statical distribution of the couplings, resulting in inhomogeneous broadening of the individual population probabilities. Making use of Eq. (15) the configurational averaging is taken over a static distribution $F_{static}(f)$, in the form

$$P(t)/P(0) = \int df F_{static}(f)$$

$$\times \exp\{-(2\pi\rho/\hbar)[v_0^2 + 2v_0 f + f^2]t\}. \tag{30}$$

Taking a Gaussian static distribution

$$F_{static}(f) = (2\pi\sigma^2)^{-1} \exp(-f^2/2\sigma^2) \tag{31}$$

results in

$$P(t)/P(0) = [1 + (4\pi\rho\sigma^2/\hbar)t]^{-1/2}$$

$$\times \exp\left\{-\frac{(2\pi\rho V_0^2/\hbar)t}{1 + (4\pi\rho\sigma^2 t/\hbar)t}\right\}. \tag{32}$$

Replacing ρ by the Franck–Condon density $\rho \longrightarrow F_i$ the final result for the static distribution is obtained. The time-resolved decay, Eq. (32), is determined by the rate $k_{ET} \simeq (2\pi\rho V_0^2/h)$ with the (time-dependent) correction terms being of the order $(4\pi V_0\sigma\rho/\hbar)/k_{ET} \simeq 2\sigma/V_0$ and $(4\pi\sigma\rho^2/\hbar)/k_{ET} \simeq (\sigma/V_0)^2$. In the slow configurational fluctuations limit the inhomogeneous broadening effects result in the deviation of the population probability $P(t)$, Eq. (18), from a simple exponential decay, with the effective rate constant, Eqs. (17) and (25), being time dependent.

CONCLUDING REMARKS

From the foregoing analysis of the effects of bridge configurational fluctuations on the dynamics of activationless ET, two limiting situations were distinguished. In the fast fluctuations limit the microscopic ET rate is considerably slower than the correlation time τ_c for the fluctuations in the coupling, Eq. (22), and the activationless ET rate is determined by the configurational average of the squared electronic coupling, Eq. (28). In the slow fluctuations limit, when the activationless ET rate is comparable to, or faster than τ_c the dynamics of the system is determined by configurational averaging over a static distribution of the ET probability density, Eqs. (30) and (32), manifesting the effects of inhomogeneous broadening. To determine the appropriate limit for ET dynamics, the analysis of molecular dynamics results for the electronic coupling in realistic chemical or biophysical systems are called for. Molecular dynamics simulations, in conjunction with quantum mechanical calculations of the electronic coupling, will determine the characteristic decay time τ_c of the auto-correlation function for the electronic coupling. This will be of considerable interest, as these will establish the appropriate limit for the ET dynamics.

Our treatment of activationless ET dynamics was restricted to the simplest model of direct time-dependent coupling between the initial and final manifolds, without the need of activation (triggered by medium-induced energy gap fluctuations) in the initial manifold. When activation in the initial manifold is important one also has to consider the time scale τ_m for energy gap fluctuations, in addition to the time scales for microscopic ET and for the fluctuations of the electronic coupling. An important related issue in this context is the correlation between fluctuations in the electronic coupling and fluctuations in the energy gap. The absence of coupling between these two types of fluctuations may permit us, in the case of solvent dependent ET dynamics together with fast fluctuating coupling, to use the results obtained for energy gap fluctuations [6] with the averaged squared coupling. When all the fluctuations are fast on the time scale of the charge transfer process, one can use the standard nonadiabatic ET rate [5, 6] with the averaged square coupling.

EPILOGUE

This paper is devoted to the memory of R.R. Dogonadze, whose scientific work shaped our perception of electron transfer in physical chemistry and electrochemistry.

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