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PAPER

# A general theoretical model for electron transfer reactions in complex systems

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In this paper we present a general theoretical–computational model for treating electron transfer reactions in complex atomic–molecular systems. The underlying idea of the approach, based on unbiased first-principles calculations at the atomistic level, utilizes the definition and the construction of the Diabatic Perturbed states of the involved reactive partners (*i.e.* the quantum centres in our perturbation approach) as provided by the interaction with their environment, including their mutual interaction. In this way we reconstruct the true Adiabatic states of the reactive partners characterizing the electron transfer process as the fluctuation of the electronic density due to the fluctuating perturbation. Results obtained by using a combination of Molecular Dynamics simulation and the Perturbed Matrix Method on a prototypical intramolecular electron transfer (from 2-(9,9'-dimethyl)fluorene to the 2-naphthalene group separated by a steroidal 5- $\alpha$ -androstane skeleton) well illustrate the accuracy of the method in reproducing both the thermodynamics and the kinetics of the process.

## 1 Introduction

In the second part of the last century the theory and modelling of electron transfer (ET) reactions have intensively occupied the interests of a large number of scientists as witnessed by the huge amount of fundamental and applied research papers produced in this field covering different areas of biological, chemical and physical science.<sup>1–4</sup> The common features of many of these theoretical–computational advances are based on the seminal work of Rudolph Marcus<sup>5–7</sup> who first provided the conceptual basis for understanding this peculiar class of reactions. The work of Marcus proposed a non-Adiabatic representation of the ET phenomenon by including energy terms acting as a coupling between the involved Diabatic states. The important work of Warshel<sup>8</sup> has been extending and further developing ET modelling by introducing the microscopic treatment of the fluctuating environment and the use of computational strategies such as the Empirical Valence Bond (EVB), the Frozen Density Functional Theory (FDFT) and the Full Density Functional Theory (DFT) allowing us to model adiabatic reactions. As a consequence, owing to the huge increase recently undergone by the computational resources allowing studies of large molecular systems at increasing accuracy, the popularity of the Marcus model is even increased in the last decades<sup>9–14</sup> also inspiring possible alternative viewpoints.<sup>15,16</sup>

The theoretical characterization of the kinetics and thermodynamics of ET processes must address two main points:

- the role of the environment perturbation and semi-classical internal motions in the ET reaction for a given covalent structure of the reaction centre, *i.e.* the reaction due to the fluctuating perturbation and structure occurring independently of covalent rearrangements;
- the effects of the covalent rearrangements in the occurrence of the ET process, *i.e.* the role of the nuclei reaction coordinates variation.

The theoretical modelling of ET reactions present in the literature typically makes use of the following approximations: (i) the reaction is described *via* the explicit use of a reaction coordinate, often given by the transition energy (*i.e.* the whole system energy change associated with the electron transition), defining two crossing Diabatic (free) energy surfaces approximated by two simple quadratic functions differing only for the minima positions (note that the environment perturbation affecting the Diabatic surfaces, if included, is usually treated with simplified approaches); (ii) the ET is assumed to occur only within a specific and very limited range of the reaction coordinates, *i.e.* the crossing of the Diabatic (free) energy surfaces or transition state, assuming a pre-equilibrium condition for the reactants to transition state interconversion. Such an approach, although provided a large body of valuable information on many different ET reactions, due to the above approximations may be inaccurate especially when we deal with processes not involving relevant covalent rearrangements as in many biochemical redox reactions.

In the last few years we have been developing an increasing interest in the modelling of chemical reactions in complex

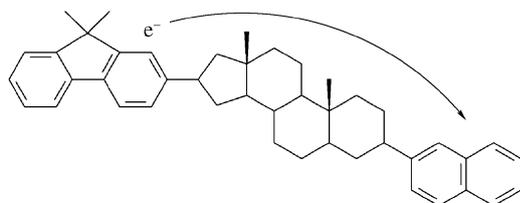
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molecular systems.<sup>17,18</sup> Our first aim is to provide a physically coherent theoretical–computational approach specifically devoted to preserve both the configurational complexity of the overall atomic–molecular system and the quantum-chemical description of the chemical event. Our methodology, based on a joint application of Molecular Dynamics (MD) simulations and Quantum-chemical (QM) calculations, *i.e.* the Perturbed Matrix Method (PMM),<sup>19–21</sup> constructed within a basic statistical–mechanical formulation, repeatedly showed to be able to provide a valid complementary viewpoint to the more popular Quantum Mechanics/Molecular Mechanics (QM/MM)<sup>22,23</sup> approaches, for modelling several chemical processes both in dilute solution<sup>24,25</sup> and in protein.<sup>26–29</sup> As a natural consequence of our efforts in this direction ET reactions represent a crucial step and, although in some of our previous studies examples of charge-transfer processes have been encountered and investigated,<sup>26,30,31</sup> a systematic and general PMM-based approach is still missing.

In this paper we specifically address the problem of modelling the effects on ET processes of the fluctuating environment perturbation and reaction centre internal configuration, occurring within a given covalent structure, *i.e.* processes not involving covalent reorganization and hence not modelled *via* the use of explicit nuclei reaction coordinates. By the use of fluctuating reactants and products perturbed Diabatic energies, provided by explicitly treating the perturbation effects at the atomistic level, we may reconstruct the Adiabatic process in principle reproducing the experimentally observed transitions given by the fluctuations of the perturbed quantum states.

In the first part of the manuscript the proposed theoretical framework of this study will be outlined in detail, then the kinetic model will be presented and, finally, a simple application to a model reaction in solution will be presented. The process under consideration is the intramolecular electron transfer reaction occurring in the species shown in Fig. 1 concisely named as 2FSN which contains a 2-(9,9'-dimethyl)fluorene, which in the anionic form acts as the electron donor, and the 2-naphthalene group acts as the electron acceptor both separated by the steroidal 5- $\alpha$ -androstane skeleton. This reaction, belonging to a widely investigated class of processes in the middle eighties as examples of intramolecular long-distance electron transfer in solution,<sup>32</sup> has been rather well characterized both by a thermodynamic and kinetic point of view<sup>33</sup> and, because of its well assessed and well accepted experimental data, has provided<sup>34</sup> and still provides a rather good test for the theoretical modelling of electron transfer reactions.



**Fig. 1** Chemical structure of the molecular system used to study the intramolecular ET reaction in the present paper. The molecule contains a 2-(9,9'-dimethyl)fluorene that in the anionic form acts as the electron donor, and the 2-naphthalene group acting as the electron acceptor both separated by the steroidal 5- $\alpha$ -androstane skeleton.

## 2 Theory

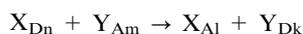
### 2.1 General considerations

In this paper we present a general theoretical model to treat ET reactions as occurring without involving any covalent reorganization hence corresponding either to reactions which take place in a truly covalently stable system (as in many ET reactions in solution or within a protein matrix) or, for reactions associated with covalent rearrangements, to the reactive process occurring at a fixed nuclei reaction coordinates position. Note that a productive ET reaction should occur only when no concomitant spin-state transition is present (see the Appendix). The inclusion of covalent reorganization in the present theoretical approach, *i.e.* modelling the reaction process beyond the usual approximation of assuming the reaction kinetics as provided only by the diffusion along the reaction (free) energy surface, will be specifically addressed in forthcoming papers. In the ET reactions we consider here (*i.e.* with no covalent reorganization), the fluctuations of the perturbing electric potential and field exerted by the atomic–molecular environment and the semiclassical internal motions of the reactive center, the Quantum Centre (QC) in our calculations, provide the ultimate causes of the reaction determining the changes of the QC quantum state properties to the ET process. Note that we always consider instantaneous relaxation of the Hamiltonian eigenstate, *i.e.* Adiabatic approximation, see the Appendix, and hence within such an approximation no transmission coefficient, *e.g.* as in the Landau–Zener model, is involved in the ET rate constant. However, in future works we will specifically address the actual accuracy of the Adiabatic approximation utilized in this paper, explicitly modelling the wavefunction time evolution without assuming instantaneous relaxation.

### 2.2 The diabatic perturbed energy surfaces

When the charge donor (D) and acceptor (A) can be well included in a single QC, PMM calculations may provide a direct evaluation of the actual QC perturbed quantum states and hence, for ET reactions which can be well modelled as a diffusive process over the proper reaction (free) energy surface, the reaction kinetics can be obtained by a relatively simple procedure based on using MD simulations in the reactants ensemble to reconstruct the reaction (free) energy surface to be used in the diffusion equations.<sup>17,26,30,35</sup> However, many ET reactions, *i.e.* those processes where no generalized coordinate can be identified such that all the other relevant orthogonal coordinates relax instantaneously, cannot be properly described by such a diffusion model, then requiring the use of complex, often unaffordable, MD simulations attempting to describe the D and A charge exchange. Moreover, in many ET reactions not involving covalent reorganization A and D cannot be properly considered as parts of a single QC, either because of their relative motions or, when A and D are parts of a rigid or semirigid molecule, due to their distance. Such conditions make it very difficult and inefficient to treat the ET process within the usual framework and hence a different PMM approach is needed based on considering the quantum states obtained by fixing the exchanging charge alternatively on one

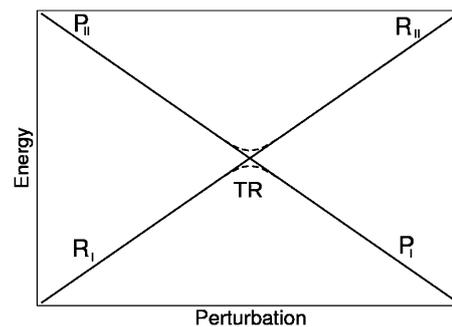
of the chemical species involved in the ET reaction. Warshel introduced the concept of Diabatic Perturbed energy surface as obtained by atomistic simulations,<sup>8</sup> showing that it is possible to reconstruct the reactive adiabatic process through the evaluation of such perturbed diabatic states.<sup>36–39</sup> Here, focussing on ET reactions not involving covalent reorganization, A and D are considered as different QC's interacting with each other as well as with their environment, thus allowing a relatively straightforward calculation of the effects of A and D relative semiclassical motions, typically computationally expensive when considering A and D within a single QC. The basic approximation to be used in this approach is that at virtually every D–A and environment configuration, except for a very limited number of specific configurations corresponding to the charge transition (the transition region, *vide infra*), the true vibronic eigenstate of the whole system (adiabatic state) be well approximated by a combination of D and A perturbed vibronic eigenstates with the environment in its electronic ground state, *i.e.* the product of the corresponding eigenfunctions,<sup>21</sup> with the exchanging charge fully located in one of the chemical species involved in the reaction (diabatic state). Let us consider the ET process involving the chemical species X and Y



where the subscripts A and D stand for the acceptor and donor, respectively, and the subscripts n, l, m and k indicate the corresponding X and Y perturbed vibronic quantum states. We define the transition energy as the whole system energy change ( $\Delta\mathcal{H}$ ) due to the whole system Diabatic state transition associated to the reactants (R) to products (P) transition. Therefore, the ET reaction occurs each time the transition energy changes its sign hence corresponding to a crossing of the Diabatic energy surfaces (the semiclassical kinetic energy is always considered independent of quantum transitions and thus it is constant in the ET reaction), indicating that the Adiabatic state has changed its electron distribution for the X and Y species. Introducing the Diabatic Perturbed vibronic energy surface (*i.e.* the Diabatic Perturbed vibronic energy of the QC's involved in the ET, including their mutual interaction and the environment perturbation) for the R ( $\mathcal{U}_{vb,R}$ ) and P ( $\mathcal{U}_{vb,P}$ ) QC's chemical state, we can write the transition energy for each D–A and environment configuration, with the environment in its  $j$ th vibrational state, as  $\Delta\mathcal{H} = \mathcal{U}_{vb,P,j}^e - \mathcal{U}_{vb,R,j}^e + \mathcal{U}_{vb,P} - \mathcal{U}_{vb,R} \cong \mathcal{U}_{vb,P} - \mathcal{U}_{vb,R}$ , where  $\mathcal{U}_{vb,P,j}^e$  and  $\mathcal{U}_{vb,R,j}^e$  are the environment vibronic internal energies when the X and Y species are in their R or P vibronic states and we used  $\mathcal{U}_{vb,P,j}^e \cong \mathcal{U}_{vb,R,j}^e \cong \mathcal{U}_{vb,j}^e$  (*i.e.* we disregard the environment vibronic internal energy change associated to the QC's state transition which is typically negligible<sup>21</sup>). From the last equation we then obtain that we can express the transition energy using only the QC's perturbed energy

$$\begin{aligned} \Delta\mathcal{H} &\cong \mathcal{U}_{vb,P} - \mathcal{U}_{vb,R} = \Delta\mathcal{U} \\ &= \Delta\mathcal{U}_{X_{Dn},Y_{Am} \rightarrow X_{Al},Y_{Am}} + \Delta\mathcal{U}_{X_{Al},Y_{Am} \rightarrow X_{Al},Y_{Dk}} \\ &= \Delta\mathcal{U}_{X_{Dn},Y_{Am} \rightarrow X_{Dn},Y_{Dk}} + \Delta\mathcal{U}_{X_{Dn},Y_{Dk} \rightarrow X_{Al},Y_{Dk}} \end{aligned} \quad (1)$$

hence implying that the ET reaction actually corresponds to the crossings of the reactants and products Diabatic Perturbed



**Fig. 2** Schematic view of the reactants and products Diabatic Perturbed energy surfaces (solid lines) and their relation with the QC's Adiabatic energy surfaces (dashed lines). In the figure the chemical states relevant to the ET reaction have been evidenced (see the text).

energy surfaces, approximating the QC's Adiabatic energy surfaces (*i.e.* the energy of the true perturbed vibronic eigenstates of the QC's involved in the ET reaction, see Fig. 2). It is worthy of note that the use of approximating the transition energy *via* the QC's Diabatic Perturbed energy variation, provided by atomistic simulations, has been introduced by Warshel.<sup>8</sup> The direct evaluation of the Diabatic Perturbed energies has been typically carried out by using empirical or semiempirical approaches or, more recently, by FDFT or DFT methods.<sup>38</sup> In our approach the QC's perturbed energy variations due to each chemical species transition (see eqn (1)) are obtained by PMM calculations for the corresponding QC within the perturbing field of its environment including the perturbation due to the other QC (for each QC we again disregard the environment vibronic internal energy change associated with the QC state transition). In the present study we address ET processes where, typically, the Diabatic Perturbed energy variation accompanying the vibronic transitions relevant for the reaction can be well approximated by using only the QC's electronic perturbed energies, *i.e.* the vibrational energy difference is neglected and D–A excitonic coupling is disregarded (note that although such simplifications are not necessary to use the present approach, for the sake of simplicity and given their usual accuracy for chemical reactions they are adopted in this paper).

Within such approximation<sup>19,21</sup> we can express at each MD frame the perturbed energy variation due to a chemical species transition *via* the perturbed electronic Hamiltonian matrix eigenvalues ( $\varepsilon$ ) corresponding to the electronic states which best approximate the vibronic states involved in the reaction

$$\Delta\mathcal{U}_{X_{Dn},Y_{Am} \rightarrow X_{Al},Y_{Am}} \cong \varepsilon_{X_{Al}'}^{Y_{Am}'} - \varepsilon_{X_{Dn}'}^{Y_{Am}'} \quad (2)$$

$$\Delta\mathcal{U}_{X_{Dn},Y_{Am} \rightarrow X_{Dn},Y_{Dk}} \cong \varepsilon_{Y_{Dk}'}^{X_{Dn}'} - \varepsilon_{Y_{Am}'}^{X_{Dn}'} \quad (3)$$

$$\Delta\mathcal{U}_{X_{Al},Y_{Am} \rightarrow X_{Al},Y_{Dk}} \cong \varepsilon_{Y_{Dk}'}^{X_{Al}'} - \varepsilon_{Y_{Am}'}^{X_{Al}'} \quad (4)$$

$$\Delta\mathcal{U}_{X_{Dn},Y_{Dk} \rightarrow X_{Al},Y_{Dk}} \cong \varepsilon_{X_{Al}'}^{Y_{Dk}'} - \varepsilon_{X_{Dn}'}^{Y_{Dk}'} \quad (5)$$

where, for example,  $\varepsilon_{X_{Al}'}^{Y_{Am}'}$  is the  $l'$  eigenvalue of the  $X_A$  perturbed electronic Hamiltonian matrix in the presence of the  $Y_A$  species in its  $m'$  state, with the latter providing a

perturbation term in the overall perturbing field (note that using different QC internal configurations to evaluate the electronic states, we may approximate any vibronic state involving either the ground or an excited vibrational state).

Following the usual PMM approach, the perturbed electronic Hamiltonian operator in the matrix form for each QC is expressed *via*<sup>19,21</sup>

$$\tilde{H} = \tilde{H}^0 + q_T \mathcal{V} \tilde{I} + \tilde{Z} + \Delta V \tilde{I}$$

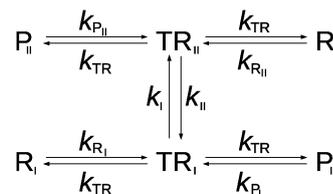
$$[\tilde{Z}]_{l,l'} = -\mathbf{E} \langle \Phi_l^0 | \hat{\mu} | \Phi_{l'}^0 \rangle$$

with  $\tilde{H}^0$  being the unperturbed electronic Hamiltonian matrix,  $\tilde{I}$  the identity matrix,  $q_T$  the QC total charge,  $\mathcal{V}$  and  $\mathbf{E}$  the perturbing electric potential and field as evaluated at the QC reference position (typically the QC centre of mass),  $\langle \Phi_l^0 | \hat{\mu} | \Phi_{l'}^0 \rangle$  the  $l, l'$  electronic transition dipole in the unperturbed QC electronic state basis set ( $\Phi^0$ ) and  $\Delta V$  a short range potential energy term approximating the higher order terms (note that  $\Delta V$  can be usually neglected in the calculation of the perturbed energy variation as this is typically independent of such a term). Eqn (2)–(5) may then be used to readily obtain the Diabatic Perturbed energy variation (eqn (1)) at each MD configuration, provided diagonalization of the perturbed electronic Hamiltonian matrices at each MD frame corresponding to the X and Y chemical species both under the acceptor and donor conditions. Note that the matrix  $\tilde{Z}$  implies that the QC's perturbed electronic eigenstates are in general linear combinations of the unperturbed basis set states and, hence, the perturbation results in mixing the unperturbed electronic eigenstates.

### 2.3 Modelling the electron transfer reaction kinetics

In Fig. 2 we show a schematic picture illustrating the reactants and products Diabatic Perturbed energy surfaces and their relation with the QC's Adiabatic energy surfaces involved in the reaction (*i.e.* the energy surfaces of the QC's Hamiltonian eigenstates defined as surfaces I and II). It must be remarked that the energy surfaces we consider provide the energy of the corresponding quantum state as a function of the perturbation and thus they should not be confused with the free energy surfaces often used in Marcus theory. In the figure it is evidenced that the R and P Diabatic Perturbed states coincide with the Adiabatic states except within a tiny perturbation interval centered at the R and P surface crossing, the transition region (TR), where the Adiabatic states are quasi-degenerate being defined by a mixture of the R and P Diabatic Perturbed states (note that within the TR even a slight coupling provides a relevant mixing as the R and P Diabatic Perturbed states are degenerate or nearly degenerate). Therefore, according to Fig. 2 six chemical states relevant for the ET reaction can be identified:

- The  $R_I$  and  $P_I$  chemical states corresponding, respectively, to the branches of the reactants and products Diabatic Perturbed energy surfaces coinciding with the Adiabatic energy surface I. Such chemical states define the reactants and products for the ET reaction occurring within the Adiabatic surface I (*i.e.* the reaction given by the charge distribution changes of the corresponding Adiabatic state).



**Fig. 3** Reaction scheme for the ET process occurring over the Adiabatic energy surfaces.

- The  $R_{II}$  and  $P_{II}$  chemical states corresponding, respectively, to the branches of the reactants and products Diabatic Perturbed energy surfaces coinciding with the Adiabatic energy surface II. Such chemical states define the reactants and products for the ET reaction occurring within the Adiabatic surface II (*i.e.* the reaction given by the charge distribution changes of the corresponding Adiabatic state).

- The  $TR_I$  and  $TR_{II}$  chemical states corresponding, respectively, to the Adiabatic energy surfaces I and II tiny subparts within the TR. Such chemical states define the transition states for the ET reaction occurring within the corresponding Adiabatic surface.

Given the above definitions, we may construct a general reaction scheme (Fig. 3) describing the ET process occurring over the two Adiabatic energy surfaces. In such a reaction scheme we have considered that the only possible transitions between the Adiabatic states may occur within the TR (we of course do not consider transitions due to photon absorption–emission) and that, given its extremely limited size, the TR exit rate constants be all the same. The basic meaning of this approximation is that, given a reference perturbation value, the local small fluctuations of the perturbation may be safely assumed to be symmetrical and hence for the tiny TR perturbation range the mean crossing times corresponding to both its exit rates can be considered as virtually identical. According to the reaction scheme and considering the Adiabatic state transitions too slow to be relevant for the reaction kinetics (*i.e.*  $k_I \cong k_{II} \cong 0$  corresponding to the Adiabatic approximation), we obtain the following rate equations for the ET process occurring over the two Adiabatic energy surfaces

$$\dot{P}_{R_I} = -k_{R_I} P_{R_I} + k_{TR} P_{TR_I} \quad (6)$$

$$\dot{P}_{P_I} = -k_{P_I} P_{P_I} + k_{TR} P_{TR_I} \quad (7)$$

$$\dot{P}_{TR_I} = k_{R_I} P_{R_I} + k_{P_I} P_{P_I} - 2k_{TR} P_{TR_I} \quad (8)$$

$$\dot{P}_{R_{II}} = -k_{R_{II}} P_{R_{II}} + k_{TR} P_{TR_{II}} \quad (9)$$

$$\dot{P}_{P_{II}} = -k_{P_{II}} P_{P_{II}} + k_{TR} P_{TR_{II}} \quad (10)$$

$$\dot{P}_{TR_{II}} = k_{R_{II}} P_{R_{II}} + k_{P_{II}} P_{P_{II}} - 2k_{TR} P_{TR_{II}} \quad (11)$$

where we used for each chemical state the corresponding probability instead of the molecular density. By using the stationary condition for  $TR_I$  and  $TR_{II}$  (*i.e.*  $\dot{P}_{TR_I} \cong \dot{P}_{TR_{II}} \cong 0$ ), we can simplify the rate equations

$$\dot{P}_{R_I} \cong -\frac{k_{R_I}}{2} P_{R_I} + \frac{k_{P_I}}{2} P_{P_I} \quad (12)$$

$$\dot{P}_{P_I} \cong \frac{k_{R_I}}{2} P_{R_I} - \frac{k_{P_I}}{2} P_{P_I} \quad (13)$$

$$\dot{P}_{R_{II}} \cong -\frac{k_{R_{II}}}{2} P_{R_{II}} + \frac{k_{P_{II}}}{2} P_{P_{II}} \quad (14)$$

$$\dot{P}_{P_{II}} \cong \frac{k_{R_{II}}}{2} P_{R_{II}} - \frac{k_{P_{II}}}{2} P_{P_{II}} \quad (15)$$

readily providing the reaction kinetics for the Adiabatic energy surfaces I and II (we assume that at the beginning of the reaction only the reactant states are present and due to the TR negligible size  $P_{TR_I} \cong P_{TR_{II}} \cong 0$ )

$$P_{R_I}(t) \cong P_{R_I}(0) [\chi_{P_I} e^{-(k_{R_I} + k_{P_I})t/2} + \chi_{R_I}] \quad (16)$$

$$P_{P_I}(t) \cong -\chi_{P_I} e^{-(k_{R_I} + k_{P_I})t/2} + \chi_{P_I} \quad (17)$$

$$P_{R_{II}}(t) \cong P_{R_{II}}(0) [\chi_{P_{II}} e^{-(k_{R_{II}} + k_{P_{II}})t/2} + \chi_{R_{II}}] \quad (18)$$

$$P_{P_{II}}(t) \cong -\chi_{P_{II}} e^{-(k_{R_{II}} + k_{P_{II}})t/2} + \chi_{P_{II}} \quad (19)$$

with  $P_{R_I}(0) + P_{R_{II}}(0) = 1$  and

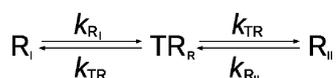
$$\chi_{R_I} = \frac{k_{P_I}}{k_{R_I} + k_{P_I}} \quad (20)$$

$$\chi_{P_I} = \frac{k_{R_I}}{k_{R_I} + k_{P_I}} \quad (21)$$

$$\chi_{R_{II}} = \frac{k_{P_{II}}}{k_{R_{II}} + k_{P_{II}}} \quad (22)$$

$$\chi_{P_{II}} = \frac{k_{R_{II}}}{k_{R_{II}} + k_{P_{II}}} \quad (23)$$

From the last eqn (16)–(23) it is evident that we only need to evaluate  $k_{R_I}, k_{P_I}, k_{R_{II}}, k_{P_{II}}$  to reconstruct the complete ET kinetics. Unfortunately, as briefly mentioned in the previous subsection, any direct evaluation of the reaction kinetics would require the use of simulations in the Adiabatic states ensembles resulting in many theoretical–computational problems to be addressed. On the other hand the use of the Diabatic Perturbed energy surfaces, described in the previous subsection, provides a simple and very efficient approach, *via* the Diabatic Perturbed energy variation, to obtain the  $R_I \rightarrow R_{II}$  and  $R_{II} \rightarrow R_I$  transitions as provided by MD simulations in the reactants ensemble (*i.e.* MD simulations where no charge exchange occurs and then based on the usual atomistic force fields). Note that the Diabatic Perturbed energy variation which is the natural observable to track the  $R_I, R_{II}$  interconversion over the R Diabatic Perturbed energy surface, providing a direct measure of the ET events in the Adiabatic ensemble (see the previous subsection) may furnish the proper means to reconstruct the reaction process of the Adiabatic surfaces *via* simulations in the reactants ensemble.



**Fig. 4** Reaction scheme for the transitions occurring over the reactants Diabatic Perturbed energy surface.

The reaction scheme for the reactants ensemble is shown in Fig. 4 where  $TR_R$  is the reactants Diabatic Perturbed energy surface transition region and, of course, the rate constants for the  $R_I, TR_R$  and  $R_{II}, TR_R$  interconversions are by definition identical to the ones for the  $R_I, TR_I$  and  $R_{II}, TR_{II}$  interconversions in the Adiabatic surfaces I and II, respectively. Therefore, the rate equations in the reactants ensemble are (using derivations similar to the ones employed for the Adiabatic surfaces I and II)

$$\dot{P}_{R_I} \cong -\frac{k_{R_I}}{2} P_{R_I} + \frac{k_{R_{II}}}{2} P_{R_{II}} \quad (24)$$

$$\dot{P}_{R_{II}} \cong \frac{k_{R_I}}{2} P_{R_I} - \frac{k_{R_{II}}}{2} P_{R_{II}} \quad (25)$$

readily providing (considering, for instance,  $P_{R_{II}}(0) = 0$ )

$$P_{R_I}(t) \cong \chi_{R_{II}}^R e^{-(k_{R_I} + k_{R_{II}})t/2} + \chi_{R_I}^R \quad (26)$$

$$P_{R_{II}}(t) \cong -\chi_{R_{II}}^R e^{-(k_{R_I} + k_{R_{II}})t/2} + \chi_{R_{II}}^R \quad (27)$$

$$\chi_{R_I}^R = \frac{k_{R_{II}}}{k_{R_I} + k_{R_{II}}} \quad (28)$$

$$\chi_{R_{II}}^R = \frac{k_{R_I}}{k_{R_I} + k_{R_{II}}} \quad (29)$$

Eqn (24)–(29) show that full information on the  $R_I \rightarrow P_I$  or  $R_{II} \rightarrow P_{II}$  transitions occurring over the Adiabatic surfaces can be obtained by MD simulations in the reactants ensemble (*i.e. via* the  $R_I \rightarrow R_{II}$  and  $R_{II} \rightarrow R_I$  transitions occurring over the R Diabatic Perturbed energy surface). In practice, given the negligible TR size, we may obtain the rate constants simply by monitoring the time length distributions for the first *abscissa* crossing as obtained by a set of independent MD simulations in the reactants ensemble, starting either with positive or negative Diabatic Perturbed energy variation (the former corresponds to the kinetic trace for the  $R_I \rightarrow R_{II}$  transition providing  $k_{R_I}/2$  and the latter corresponds to the  $R_{II} \rightarrow R_I$  transition providing  $k_{R_{II}}/2$ ). Once  $k_{R_I}, k_{R_{II}}$  are obtained we may easily evaluate the other two missing rate constants of the reaction (*i.e.*  $k_{P_I}, k_{P_{II}}$ ) *via* the following relations for the rate constants and chemical states free energy changes

$$k_{P_I} = k_{R_I} e^{\beta(A_{P_I} - A_{R_I})} \quad (30)$$

$$k_{P_{II}} = k_{R_{II}} e^{\beta(A_{P_{II}} - A_{R_{II}})} \quad (31)$$

$$\begin{aligned} A_{P_I} - A_{R_I} &= A_{P_I} - A_{R_{II}} + A_{R_{II}} - A_{R_I} \\ &= -kT \ln \langle e^{-\beta(\mathcal{U}_{vb,P} - \mathcal{U}_{vb,R})} \rangle_{R_{II}} - kT \ln \frac{P_{R_{II}}^{\text{eq}}}{P_{R_I}^{\text{eq}}} \\ &= kT \ln \langle e^{\beta(\mathcal{U}_{vb,P} - \mathcal{U}_{vb,R})} \rangle_{P_I} - kT \ln \frac{P_{R_{II}}^{\text{eq}}}{P_{R_I}^{\text{eq}}} \end{aligned} \quad (32)$$

$$\begin{aligned}
 A_{P_{II}} - A_{R_{II}} &= A_{P_{II}} - A_{R_I} + A_{R_I} - A_{R_{II}} \\
 &= -kT \ln \langle e^{-\beta(\mathcal{U}_{vb,P} - \mathcal{U}_{vb,R})} \rangle_{R_I} + kT \ln \frac{P_{R_{II}}^{eq}}{P_{R_I}^{eq}} \\
 &= kT \ln \langle e^{\beta(\mathcal{U}_{vb,P} - \mathcal{U}_{vb,R})} \rangle_{P_{II}} + kT \ln \frac{P_{R_{II}}^{eq}}{P_{R_I}^{eq}}
 \end{aligned} \quad (33)$$

where  $1/\beta = kT$ , the angular brackets subscripts indicate that averaging is performed in the  $R_I$  or  $R_{II}(P_I, P_{II})$  ensemble,  $P_{R_I}^{eq}$ ,  $P_{R_{II}}^{eq}$  are the equilibrium probabilities for the  $R_I$  and  $R_{II}$  chemical states as provided by the MD simulations in the reactants ensemble and clearly

$$A_{R_{II}} - A_{R_I} = -kT \ln \frac{P_{R_{II}}^{eq}}{P_{R_I}^{eq}} \quad (34)$$

The reaction free energy can be also easily obtained by MD simulations performed over the R Diabatic Perturbed energy surface *via*

$$\begin{aligned}
 \Delta A_{\text{reac}} &= A_{X_{A_I, Y_{Dk}}} - A_{X_{Dn, Y_{Am}}} = A_P - A_R \\
 &= -kT \ln \frac{e^{-\beta A_{P_I}} + e^{-\beta A_{P_{II}}}}{e^{-\beta A_{R_I}} + e^{-\beta A_{R_{II}}}} \cong -kT \ln \langle e^{-\beta(\mathcal{U}_{vb,P} - \mathcal{U}_{vb,R})} \rangle_R \\
 &= kT \ln \langle e^{\beta(\mathcal{U}_{vb,P} - \mathcal{U}_{vb,R})} \rangle_P
 \end{aligned} \quad (35)$$

with the angular brackets subscript  $R(P)$  indicating that averaging is obtained in the ensemble provided by the whole  $R(P)$  Diabatic Perturbed energy surface including the TR perturbation range.

It must be remarked that within our approach neither we assume Gaussian fluctuations for the transition energy nor pre-equilibrium between reactants and TR states. As a consequence the activation free energy for the ET reaction, which without assuming the Gaussian approximation cannot be expressed *via* the reaction free energy and reorganization energy, is not needed within our theoretical model which in principle may treat both pre-equilibrium and not-pre-equilibrium reaction conditions.

### 3 Computational methods

In order to apply the PMM/MD procedure it is first necessary to preselect the QCs, *i.e.* the subportions of the simulated system to be treated explicitly at the electronic level providing the acceptor and donor within the ET process. In the present case the naphthalene and fluorene moieties of 2FSN were obviously selected as QCs. In order to properly treat the effect of the alkyl spacer on the unperturbed electronic properties of the two QCs we considered also methyl groups as substituents in the gas-phase calculations. Consequently four sets of unperturbed calculations were carried out on 2-methylnaphthalene and 2-methyl(9,9'-dimethyl)fluorene in their neutral and radical anionic state. Note that for the radical species the most stable magnetic state (the doublet state) was utilized. Each calculation consisted in a full-geometry relaxation using Density Functional Theory with the hybrid Becke3LYP

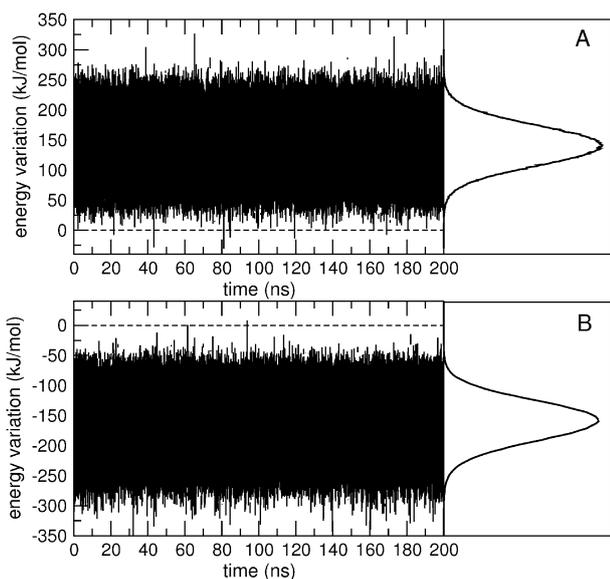
functional<sup>40,41</sup> in conjunction with the Dunning's correlation-consistent triple zeta (cc-PVTZ) basis set.<sup>42</sup> On each of the optimized geometries eight unperturbed electronic states (*i.e.* the ground and seven excited states) were evaluated using Time Dependent Density Functional Theory with the same functional and basis set.<sup>43</sup> It must be noted that TD-DFT is not used for directly evaluating the charge transfer process (many doubt the capability of a DFT to treat ET) but rather to provide a reliable unperturbed basis set for both the donor and acceptor QCs, hence not involving any charge exchange.

MD simulations of 2FSN were performed in tetrahydrofuran, THF (two 200 ns-long trajectories), and in  $\text{CCl}_4$  (one 50 ns-long trajectory) at 296 K in the NVT ensemble using the Gromacs software package;<sup>44</sup> the temperature was kept constant using the isokinetic temperature coupling,<sup>45,46</sup> bond length vibrational motions were removed by applying the LINCS algorithm and a time step of 2 fs was used for the numerical integration. Long-range electrostatics was calculated *via* the Particle Mesh Ewald (PME) procedure.<sup>47</sup> Atomic point charges for the solute were evaluated by means of the ESP procedure<sup>48</sup> from the quantum mechanical calculations described above. The rest of the parameters for the solute, including the Lennard-Jones terms, were adapted from the Gromos96 (ffG43a1) force field.<sup>49</sup> The parameters for  $\text{CCl}_4$  were adapted from the opls-AA force field.<sup>50</sup> The parameters for THF were taken from Briggs *et al.*<sup>51</sup>

At each MD frame we obtained, by means of PMM, the terms required for the evaluation of the Diabatic Perturbed energy variation, *i.e.* eqn (2)–(5), using the following scheme: the electronic states of the X chemical species, either under the donor or acceptor conditions, were obtained considering the corresponding QC as perturbed by the electric field provided by the Y chemical species as well as the rest of the atomic-molecular system, both treated within the semiclassical approximation; the same procedure was performed for the Y chemical species (in this case obviously the QC corresponds to the Y chemical species and the X chemical species and the rest of the atomic-molecular system were treated within the semiclassical approximation) hence providing all the energy changes necessary to evaluate the Diabatic Perturbed energy variation in time.

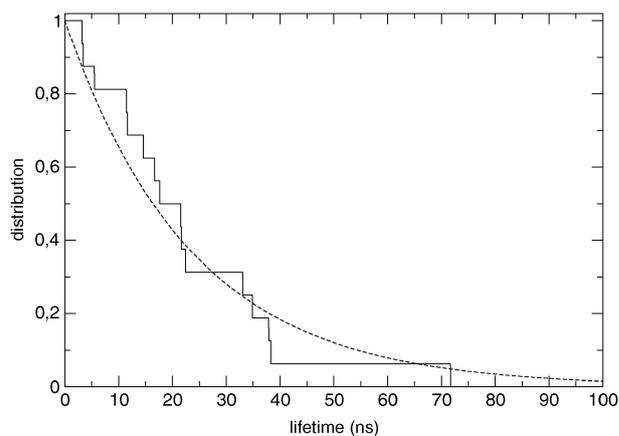
### 4 Results and discussion

As already reported in the Introduction, we test the validity of the general theoretical methodology described in the Theory section, by modelling the intramolecular electron transfer reaction rate of 2FSN in THF at 296 K in order to provide a direct comparison with experimental data obtained approximately under the same conditions of our simulations.<sup>33</sup> Within our theoretical framework the investigated electron transfer reaction can be characterized by the time course of the Diabatic Perturbed energy variation (for transition energy, see the Theory section) as obtained by the MD simulations in the reactants ensemble. Each electron transfer event is indicated by the *abscissa* crossing of this observable corresponding to the crossing of the Diabatic Perturbed energies of the donor and acceptor (see Fig. 2), *i.e.* the  $R_I \rightarrow R_{II}$  or  $R_{II} \rightarrow R_I$  transitions. This is illustrated in Fig. 5 where we show the time



**Fig. 5** Diabatic Perturbed energy variation, see eqn (1), time-course and corresponding distribution of 2FSN in THF at 296 K, as obtained by the MD simulations in the reactants ensemble (panel A) and products ensemble (panel B).

course of the Diabatic Perturbed energy variation ( $\Delta\mathcal{U} = \mathcal{U}_{vb,P} - \mathcal{U}_{vb,R}$ ) for the electron transfer from the fluorene (Fl) anion to naphthalene (Nf) of 2FSN in THF as obtained by 200 ns MD simulations and PMM calculations in either the R (panel A) and P (panel B) ensembles (note that in this ET reaction only the electronic ground states are involved). From the figure it is evident that only a limited number of surface crossings, *i.e.* *abscissa* crossings, are present with a unimodal distribution of the Diabatic Perturbed energy variation peaked at about 140 and  $-160 \text{ kJ mol}^{-1}$  for the R and P ensemble, respectively. The latter result clearly implies that in the present electron transfer reaction the  $R_{II}$  branch of the reactants Diabatic Perturbed energy surface is thermodynamically unstable (from our calculations  $A_{R_{II}} - A_{R_I} \cong 29.6 \text{ kJ mol}^{-1}$ ). It is worthy of note that although the distributions of the Diabatic Perturbed energy variation are rather close to a Gaussian distribution, their low and high energy tails, essential for determining the reaction free energy, deviate significantly from the Gaussian behaviour, as also reported in the literature for other reactions.<sup>52</sup> The reaction rate for the electron transfer occurring over the Adiabatic surface I, *i.e.* the  $R_I \rightarrow P_I$  transition rate, can be obtained by the distribution of the time lengths needed to reach the first crossing of the Diabatic Perturbed energy surfaces as provided by a set of independent reactants ensemble MD trajectories starting in the  $R_I$  state. Such a time length distribution of the positive Diabatic Perturbed energy variation, corresponding to the  $R_I \rightarrow R_{II}$  transitions in the MD reactants ensemble (see the Theory section), can be also estimated by using the (uncorrelated) subtrajectories of the positive Diabatic Perturbed energy variation provided by one or a few extended MD simulations, as done in this paper. In Fig. 6 we report such  $R_I \rightarrow P_I$  transition time distribution, providing the kinetic profile of this reaction. In the figure we show both the actual profile as



**Fig. 6** Kinetic trace, *i.e.* time length distribution, for the  $R_I \rightarrow P_I$  reaction of 2FSN in THF as provided by the 200 ns-long MD trajectories at 296 K (solid line) and the corresponding exponential fitting curve (dashed line).

obtained by analyzing the Diabatic Perturbed energy variation time course and its exponential fitting characterized by a mean lifetime ( $2/k_{R_I}$ ) of  $27 \pm 4 \text{ ns}$ , reproducing reasonably well the corresponding experimental value of about 80 ns.<sup>33</sup> Interestingly, a similar evaluation for the Adiabatic surface II, providing the  $R_{II} \rightarrow P_{II}$  rate constant, results in a mean lifetime of 100–200 fs clearly indicating that the electron transfer kinetics monitored in the experiments is the one occurring over the Adiabatic surface I. By using the Diabatic Perturbed energy variation fluctuations as obtained by the MD simulations in the reactants ensemble, we may also calculate the reaction free energy according to eqn (35), *via*

$$\Delta A_{\text{reac}} = A_{\text{Fl,Nf}^-} - A_{\text{Fl}^-, \text{Nf}} \cong -kT \ln \langle e^{-\beta \Delta\mathcal{U}} \rangle_{\text{Fl}^-, \text{Nf}} \quad (36)$$

where the angular brackets subscript indicates that the average is obtained in the  $\text{Fl}^-$ , Nf ensemble. Such a calculation provides a reaction free energy reasonably close, within the noise, to the free energy estimate obtained, again *via* eqn (35), by the products ensemble, hence indicating a good level of convergence in each of the ensembles used. By averaging the reactants and products ensembles theoretical-computational values, we then obtain our best estimate of the reaction free energy well matching the experimental value<sup>33</sup> (see Table 1), thus confirming the high quality of the model employed. Interestingly, when using the linear response approximation<sup>53,54</sup> to evaluate the reorganization energy of the reaction, *i.e.*  $\lambda = (\langle \Delta\mathcal{U} \rangle_R + \langle \Delta\mathcal{U} \rangle_P)/2$ , we obtain a rather high value

**Table 1** Comparison of the estimated reaction free energies (in  $\text{kJ mol}^{-1}$ ) for the  $\text{Fl}^-, \text{Nf} \rightarrow \text{Fl, Nf}^-$  transition in THF, as obtained by PMM/MD calculations using both the R and P ensembles. In the table we also show our best estimate of the reaction free energy as obtained by averaging the R and P ensemble values and the corresponding experimental value. The standard errors are given within parentheses and the unperturbed energy variation of the reaction, as obtained by *in vacuo* calculations on the isolated donor and isolated acceptor, is also reported

	R ensemble	P ensemble	Average	Experimental
THF	4.1 (9.0)	-26.2 (13.0)	-11.0 (7.9)	-5.7 (1.0)
Unperturbed	-1.3	-1.3	-1.3	

( $\sim 151 \text{ kJ mol}^{-1}$ ) suggesting a large solute–solvent reorganization upon the ET process. However, it must be remarked that such a reorganization energy estimate, differently from the reaction free energy we in principle obtained by means of an exact expression, is based on an approximated relation with hence a possible significant systematic error.

It is worth noting that within the usual Marcus approach to treat ET reactions, the assumed exact Gaussian behaviour of the transition energy distribution (*i.e.* the Diabatic Perturbed energy variation distribution) provides for the present reaction a wrong estimate of  $\Delta A_{\text{reac}}$  in THF as a consequence of the non-Gaussian low energy tail of the MD sampled distribution. In fact, by using the mean ( $\langle \Delta \mathcal{U} \rangle_{\text{R}}$ ) and variance ( $\sigma^2$ ) of the Diabatic Perturbed energy variation in the R ensemble to reconstruct the assumed Gaussian distribution we obtain<sup>55</sup>  $\Delta A_{\text{reac}} = \langle \Delta \mathcal{U} \rangle_{\text{R}} - \sigma^2/2 = -81.3 \pm 0.4 \text{ kJ mol}^{-1}$ . Such a result when compared with the corresponding experimental value ( $-5.7 \pm 1.0 \text{ kJ mol}^{-1}$ ) clearly indicates the inadequacy of the Gaussian approximation. This is further shown by the calculation of the same reaction free energy within the Gaussian approximation utilizing the P ensemble, which provides  $\Delta A_{\text{reac}} = 70.9 \pm 0.4 \text{ kJ mol}^{-1}$ . Comparison of these latter results with our calculations based on the general, in principle exact, expression for the free energy change, indicates that when dealing with ET reactions occurring in a polar environment with hence relevant low and high energy tails in the transition energy distribution, the Gaussian approximation may be inaccurate if not misleading. In  $\text{CCl}_4$  where no strong solute–solvent interactions are present, and hence the transition energy distribution is highly peaked around its mode, the ET reaction free energy we obtain ( $-3.7 \pm 0.1 \text{ kJ mol}^{-1}$ ), rather close to the unperturbed value (see Table 1), is almost exactly reproduced by the value obtained by assuming a Gaussian behaviour.

## 5 Conclusions

In this paper we describe a general theoretical–computational model to treat electron transfer reactions in complex atomic–molecular systems as obtained by explicitly modelling the quantum-mechanical events and their coupling with the atomic–molecular motions, avoiding the use of the typical approximations adopted in the framework of Marcus theory. In fact, differently from the Marcus theory where the electron transfer is essentially modelled as the hopping between two coupled Diabatic surfaces occurring at their crossing, in the present model, based on the Adiabatic approximation, the electron transfer is described in terms of the time variation of the relevant Adiabatic state properties. In line with the method introduced by Warshel,<sup>8</sup> this is accomplished by approximating the Adiabatic energy surface relevant for the ET process *via* the Diabatic Perturbed energy surfaces (as obtained in our model by the PMM/MD approach described in this paper) and hence reconstructing the electron transfer kinetics and thermodynamics. Results obtained for intramolecular electron transfer of solvated 2FSN show that such a method can quantitatively reproduce the main features of the process as experimentally observed. This approach, specifically designed for efficiently modelling electron transfer processes in complex

environments, may be applied to model also other quantum-mechanical tunnelling processes such as proton transfer or vibrational energy redistribution. At the same time the basic features of the method make it possible, at least in principle, to address the quantum energy transfers taking place in very complex atomic–molecular environments, allowing the modelling of the kinetics and thermodynamics of processes of biophysical–biochemical interest.

## Appendix

We consider that the time evolution of a quantum centre embedded in a semi-classical atomic–molecular environment be physically equivalent to the time evolution of a quantum system interacting with an external time dependent field. Within such an approximation, except for a possible phase factor irrelevant for the quantum state physical properties, we can obtain the quantum centre time dependent wave function by solving the time dependent Schrödinger equation for the quantum system interacting with an external field reproducing the perturbing field of the atomic–molecular environment. The implications and limitations of such approximation, although very interesting, are beyond the scope of the present paper and therefore they will not be addressed here.

Let us assume that the quantum system interacting with its atomic–molecular environment at a given time, say  $t_0$ , be in one of the perturbed Hamiltonian eigenstates, *e.g.* the quantum state defined by the  $j$ th eigenvector of the perturbed Hamiltonian matrix at  $t_0$ ,  $\tilde{H}(t_0) = \tilde{H}_{t_0}$ . Note that here  $\tilde{H}$  indicates the system Hamiltonian operator for the complete set of quantum degrees of freedom, hence corresponding to either the electronic, the vibronic or even the whole energy Hamiltonian matrix. We can therefore express the perturbed Hamiltonian matrix at any time as

$$\tilde{H}(t) = \tilde{H}_{t_0} + \Delta\tilde{H}(t) \quad (37)$$

$$\Delta\tilde{H}(t_0) = \tilde{0} \quad (38)$$

where  $\Delta\tilde{H}$  is the change of the Hamiltonian operator as a function of time, providing the perturbation acting on the initial quantum state and given by the change of the perturbation operator (see the Theory section). We may obtain the quantum state time evolution *via* the time dependent Schrödinger equation (in a matrix form) expressed in the basis set of the Hamiltonian eigenstates at  $t = t_0$

$$i\hbar\dot{c} = [\tilde{H}_{t_0} + \Delta\tilde{H}]c \quad (39)$$

$$c(t) = e^{-i\mathcal{U}(t_0)(t-t_0)/\hbar} w(t) \quad (40)$$

$$[\tilde{H}_{t_0}]_{l,l'} = \mathcal{U}(t_0)\delta_{l,l'} \quad (41)$$

with  $\mathcal{U}(t_0)$  being the  $l$ th Hamiltonian eigenvalue at  $t_0$  and  $\delta_{l,l'}$  the Kroenecker's delta. From the last equations we then obtain

$$i\hbar\dot{w} = \Delta\tilde{H}^{\#}w \quad (42)$$

$$[\Delta\tilde{H}^{\#}]_{l,l'} = [\Delta\tilde{H}]_{l,l'} e^{i[\mathcal{U}(t_0) - \mathcal{U}'(t_0)](t-t_0)/\hbar} \quad (43)$$

Eqn (42) can be used to obtain general approximated solutions of the Schrödinger equation according to two basic conditions: the  $j$ th eigenstate is not degenerate or quasi-degenerate

(i.e. solution outside the transition region); the  $j$ th eigenstate is degenerate or quasi-degenerate (i.e. solution within the transition region).

### Solution outside the transition region

If we consider a finite time interval small enough that within the whole interval the perturbation given by  $\Delta\tilde{H}$  is small, say a first order perturbation compared to  $\tilde{H}_{t_0}$ , then the corresponding solution of eqn (42) should be very close to the solution we would obtain in case  $\Delta\tilde{H}^{\#}$  were made of null elements except for its  $j,j$  diagonal element (corresponding to the initial state). We can define such a solution and the corresponding perturbation as the reference solution  $\mathbf{w}^{\text{ref}}$  and reference perturbation  $\Delta\tilde{H}_{\text{ref}}^{\#}$  with clearly  $w_l^{\text{ref}}(t) = 0$ ,  $l \neq j$  and

$$w_j^{\text{ref}}(t) = e^{-i \int_{t_0}^t [\Delta\tilde{H}_{j,j}^{\#} dt'] / \hbar} \quad (44)$$

Expressing  $\mathbf{w}$  via the reference solution and correction terms of increasing order (i.e.  $\mathbf{w} = \mathbf{w}^{\text{ref}} + \mathbf{w}^{(1)} + \mathbf{w}^{(2)} + \dots$ ) and the first order perturbation  $\Delta\tilde{H}^{\#}$  via  $\Delta\tilde{H}^{\#} = \Delta\tilde{H}_{\text{ref}}^{\#} + \Delta\tilde{H}^{\#} - \Delta\tilde{H}_{\text{ref}}^{\#}$ , we can rewrite eqn (42) as

$$i\hbar\dot{\mathbf{w}} = \Delta\tilde{H}_{\text{ref}}^{\#}\mathbf{w} + (\Delta\tilde{H}^{\#} - \Delta\tilde{H}_{\text{ref}}^{\#})\mathbf{w} \quad (45)$$

which, keeping only up to the first order terms, reduces to

$$i\hbar\dot{\mathbf{w}}^{(1)} = (\Delta\tilde{H}^{\#} - \Delta\tilde{H}_{\text{ref}}^{\#})\mathbf{w}^{\text{ref}} \quad (46)$$

Expanding the Hamiltonian operator change to the first order, i.e.  $\Delta\tilde{H} \cong \tilde{\Gamma}(t - t_0)$ , with  $\tilde{\Gamma}$  the time independent matrix of the first order time derivatives of the  $\Delta\tilde{H}$  elements evaluated at  $t_0$ , we obtain for each  $l$ th component (with  $l \neq j$ ) of the first order correction of the quantum state

$$\begin{aligned} i\hbar\dot{w}_l^{(1)} &\cong e^{i[\mathcal{U}_l(t_0) - \mathcal{U}_l(t_0)](t-t_0)/\hbar} \Gamma_{l,j}(t - t_0) w_{\text{ref},j} \\ &\cong e^{i[\mathcal{U}_l(t_0) - \mathcal{U}_l(t_0)](t-t_0)/\hbar} \Gamma_{l,j}(t - t_0) \end{aligned} \quad (47)$$

where  $\Gamma_{l,j} = [\Delta\tilde{\Gamma}]_{l,j}$  and in eqn (47) we made use of the approximation  $w_j^{\text{ref}} \cong 1$  due to the fact we are considering a small time interval allowing the Hamiltonian operator change to correspond only to a first order perturbation (from eqn (46) we also have  $w_j^{(1)} = 0$ ). From eqn (47), using only up to the first order correction to express the quantum state (i.e.  $\mathbf{w} \cong \mathbf{w}^{\text{ref}} + \mathbf{w}^{(1)}$ ), and integrating by parts we readily obtain  $w_l(t) \cong w_j^{\text{ref}} \cong 1$  and for each  $l$ th component with  $l \neq j$

$$\begin{aligned} w_l(t) &\cong -\frac{i}{\hbar} \int_{t_0}^t e^{i[\mathcal{U}_l(t_0) - \mathcal{U}_j(t_0)](t-t_0)/\hbar} \Gamma_{l,j}(t' - t_0) dt' \\ &= -\frac{e^{i[\mathcal{U}_l(t_0) - \mathcal{U}_j(t_0)](t-t_0)/\hbar} \Gamma_{l,j}(t - t_0)}{\mathcal{U}_l(t_0) - \mathcal{U}_j(t_0)} \\ &\quad + \frac{i}{\hbar} \int_{t_0}^t \frac{e^{i[\mathcal{U}_l(t_0) - \mathcal{U}_j(t_0)](t-t_0)/\hbar} \Gamma_{l,j} dt'}{i[\mathcal{U}_l(t_0) - \mathcal{U}_j(t_0)]/\hbar} \quad (48) \\ &= \frac{e^{i[\mathcal{U}_l(t_0) - \mathcal{U}_j(t_0)](t-t_0)/\hbar} [\Delta\tilde{H}]_{l,j}}{\mathcal{U}_j(t_0) - \mathcal{U}_l(t_0)} \\ &\quad \times \left[ 1 + i \frac{1 - e^{-i[\mathcal{U}_l(t_0) - \mathcal{U}_j(t_0)](t-t_0)/\hbar}}{[\mathcal{U}_l(t_0) - \mathcal{U}_j(t_0)](t-t_0)/\hbar} \right] \end{aligned}$$

For solutions outside the transition region we can in general assume that  $|\mathcal{U}_l(t_0) - \mathcal{U}_j(t_0)|/\hbar \gg |\Gamma_{l,j}[\mathcal{U}_l(t_0) - \mathcal{U}_j(t_0)]|$

(Adiabatic approximation) hence implying that, except for a tiny initial time window, within the considered time interval we have

$$w_l(t) \cong \frac{e^{i[\mathcal{U}_l(t_0) - \mathcal{U}_j(t_0)](t-t_0)/\hbar} [\Delta\tilde{H}]_{l,j}}{\mathcal{U}_j(t_0) - \mathcal{U}_l(t_0)} \quad (49)$$

providing

$$c_l(t) \cong \frac{e^{-i\mathcal{U}_j(t_0)(t-t_0)/\hbar} [\Delta\tilde{H}]_{l,j}}{\mathcal{U}_j(t_0) - \mathcal{U}_l(t_0)} \quad (50)$$

$$c_j(t) \cong e^{-i\mathcal{U}_j(t_0)(t-t_0)/\hbar} \quad (51)$$

which exactly corresponds to the  $j$ th perturbed Hamiltonian eigenstate according to first order time independent perturbation theory.<sup>56,57</sup> Therefore we may safely conclude that within the considered condition, provided that at  $t_0$  the quantum centre is in a given Hamiltonian eigenstate, the quantum state virtually instantaneously relaxes into the corresponding perturbed Hamiltonian eigenstate determined by the  $\Delta\tilde{H}$  perturbation.

### Solution inside the transition region

When dealing with the time evolution of a quantum state within the transition region (TR) two main differences with respect to the previous case must be considered: (i) in the subspace involved in the ET process, the Hamiltonian eigenstates (the QC's Adiabatic states) no longer coincide with the Diabatic Perturbed states and (ii) the eigenstates are quasi-degenerate with time, say  $t_d$ , corresponding to the crossing of the Diabatic Perturbed energy surfaces (see Fig. 2) where the Adiabatic states can be considered as virtually degenerate. We may therefore expand the Hamiltonian matrix around  $t_d$  within the approximation that in the tiny TR time range the two quasi-degenerate Hamiltonian eigenstates involved in the ET belong almost exactly to the 2-dimensional subspace defined by the degenerate Hamiltonian eigenstates at  $t_d$  (i.e. only such degenerate eigenstates may be significantly affected by the tiny  $\Delta\tilde{H}$  perturbation), thus reducing the calculations to the 2-dimensional subspace  $\Sigma$  defined by these eigenstates

$$\begin{aligned} \tilde{H}_{\Sigma}(t) &= \tilde{H}_{\Sigma,t_d} + \Delta\tilde{H}_{\Sigma}(t) = \mathcal{U}_d \tilde{I}_{\Sigma} + \tilde{\Gamma}_{\Sigma}(t - t_d) \\ &\quad + \tilde{\Theta}_{\Sigma} \frac{(t - t_d)^2}{2} + \dots \end{aligned} \quad (52)$$

In the previous equation the subscript  $\Sigma$  indicates that we are considering the  $2 \times 2$  matrices of the  $\Sigma$  subspace,  $\tilde{H}_{\Sigma,t_d} = \tilde{H}_{\Sigma}(t_d)$ ,  $\mathcal{U}_d$  is the degenerate energy at  $t_d$ ,  $\tilde{I}$  is the identity matrix and  $\tilde{\Gamma}$  and  $\tilde{\Theta}$  are the Hermitian matrices of the first and second order time derivatives, respectively, of  $\Delta\tilde{H}$  as evaluated at  $t_d$ . From eqn (52) it is evident that when the time interval considered is small enough that only the terms up to first order time derivatives must be retained, the  $\tilde{\Gamma}_{\Sigma}$  eigenvectors (the  $\Sigma_I$  and  $\Sigma_{II}$  quantum states) provide the Hamiltonian eigenstates of the subspace, thus implying that the corresponding eigenvalues ( $\mathcal{U}_{\Sigma_I}, \mathcal{U}_{\Sigma_{II}}$ ), the first order approximation of the Hamiltonian eigenvalues  $\mathcal{U}_I, \mathcal{U}_{II}$ , with  $\mathcal{U}_{II} \geq \mathcal{U}_I$ , of the

corresponding full space perturbed eigenstates (the QC's Adiabatic states I and II), be defined by

$$\mathcal{U}_I(t) \cong \mathcal{U}_{\Sigma_I}(t) = \mathcal{U}_d + \Gamma_{\Sigma_I}(t - t_d) \quad (53)$$

$$\mathcal{U}_{II}(t) \cong \mathcal{U}_{\Sigma_{II}}(t) = \mathcal{U}_d + \Gamma_{\Sigma_{II}}(t - t_d) \quad (54)$$

with  $\Gamma_{\Sigma_I}$  and  $\Gamma_{\Sigma_{II}}$  being the eigenvalues of the  $\tilde{T}_{\Sigma}$  matrix. From eqn (53) and (54) we then obtain  $\mathcal{U}_{II} - \mathcal{U}_I(t) \cong (\Gamma_{\Sigma_{II}} - \Gamma_{\Sigma_I})(t - t_d)$  clearly showing that in order to have continuous eigenstate energies and derivatives, as it is assumed in productive ET reactions, we must necessarily have  $\Gamma_{\Sigma_I} = \Gamma_{\Sigma_{II}} = \Gamma_{\Sigma}$ . It is worth noting that when the Diabatic Perturbed energy surfaces possibly involved in the ET reaction correspond to different spin-states, then the QC's Adiabatic states always coincide with the Diabatic Perturbed ones and hence no TR is present anymore. In such a condition where a singular point is present at  $t_d$ , i.e.  $\Gamma_{\Sigma_I} \neq \Gamma_{\Sigma_{II}}$ , the time evolution of the QC's starting at  $t_d$  in one of their eigenstates (now identical to the Diabatic Perturbed states) will keep them as before in the same quantum state (the same Diabatic Perturbed state) therefore avoiding the ET process to occur.

For productive ET reactions we consider that a second order expansion is accurate in the whole TR time range, and so we can rewrite eqn (52) as

$$\begin{aligned} \tilde{H}_{\Sigma}(t) &= \tilde{H}_{\Sigma,t_d} + \Delta\tilde{H}_{\Sigma}(t) \cong \mathcal{U}_d\tilde{I}_{\Sigma} + \Gamma_{\Sigma}\tilde{I}_{\Sigma}(t - t_d) \\ &+ \tilde{\Theta}_{\Sigma} \frac{(t - t_d)^2}{2} \end{aligned} \quad (55)$$

providing as Hamiltonian eigenstates of the  $\Sigma$  subspace the (time independent) eigenvectors of the  $\tilde{\Theta}_{\Sigma}$  matrix (the best approximation within  $\Sigma$  of the Adiabatic states I and II, now defining the  $\Sigma_I$  and  $\Sigma_{II}$  quantum states) with Hamiltonian eigenvalues (the first order approximation of the Adiabatic state energies) expressed *via* the corresponding eigenvalues  $\Theta_{\Sigma_I}$  and  $\Theta_{\Sigma_{II}}$  (note that we assume  $\Theta_{\Sigma_{II}} > \Theta_{\Sigma_I}$ )

$$\mathcal{U}_I(t) \cong \mathcal{U}_{\Sigma_I}(t) = \mathcal{U}_d + \Gamma_{\Sigma}(t - t_d) + \Theta_{\Sigma_I} \frac{(t - t_d)^2}{2} \quad (56)$$

$$\mathcal{U}_{II}(t) \cong \mathcal{U}_{\Sigma_{II}}(t) = \mathcal{U}_d + \Gamma_{\Sigma}(t - t_d) + \Theta_{\Sigma_{II}} \frac{(t - t_d)^2}{2} \quad (57)$$

$$\mathcal{U}_{II}(t) - \mathcal{U}_I(t) \cong (\Theta_{\Sigma_{II}} - \Theta_{\Sigma_I}) \frac{(t - t_d)^2}{2} \quad (58)$$

We can therefore construct the reference perturbation  $\Delta\tilde{H}_{\Sigma}^{\#}$  by using  $\Delta\tilde{H}_{\Sigma}$  to define its non-zero elements, thus providing from eqn (42) expressed utilizing the  $\tilde{\Theta}_{\Sigma}$  eigenvectors (i.e. the  $\Delta\tilde{H}_{\Sigma}$  eigenvectors) as a basis set of the  $\Sigma$  subspace, the equations for the relevant (i.e. non-zero) components of  $w^{\text{ref}}$

$$i\hbar w_{\Sigma_I}^{\text{ref}} \cong \Gamma_{\Sigma}(t - t_d) + \Theta_{\Sigma_I} \frac{(t - t_d)^2}{2} \quad (59)$$

$$i\hbar w_{\Sigma_{II}}^{\text{ref}} \cong \Gamma_{\Sigma}(t - t_d) + \Theta_{\Sigma_{II}} \frac{(t - t_d)^2}{2} \quad (60)$$

with solution

$$\begin{aligned} w_{\Sigma_I}^{\text{ref}}(t) &\cong w_{\Sigma_I}^{\text{ref}}(t_d) e^{-\frac{i}{\hbar} \int_{t_d}^t [\mathcal{U}_{\Sigma_I}(t') - \mathcal{U}_d] dt'} \\ &= w_{\Sigma_I}^{\text{ref}}(t_d) e^{-\frac{i}{\hbar} \left[ \frac{\Gamma_{\Sigma}(t-t_d)^2}{2} + \frac{\Theta_{\Sigma_I}(t-t_d)^3}{6} \right]} \end{aligned} \quad (61)$$

$$\begin{aligned} w_{\Sigma_{II}}^{\text{ref}}(t) &\cong w_{\Sigma_{II}}^{\text{ref}}(t_d) e^{-\frac{i}{\hbar} \int_{t_d}^t [\mathcal{U}_{\Sigma_{II}}(t') - \mathcal{U}_d] dt'} \\ &= w_{\Sigma_{II}}^{\text{ref}}(t_d) e^{-\frac{i}{\hbar} \left[ \frac{\Gamma_{\Sigma}(t-t_d)^2}{2} + \frac{\Theta_{\Sigma_{II}}(t-t_d)^3}{6} \right]} \end{aligned} \quad (62)$$

Eqn (61) and (62) clearly show that if we assume that at the initial time  $t_d$  the quantum centre be either in the  $\Sigma_I$  or  $\Sigma_{II}$  state (at  $t = t_d$  full space Hamiltonian eigenstates) then at any time within the TR time interval the reference solution QC state will coincide with such a quantum state, except for a phase factor. Finally, using the expressions derived for the previous case (see eqn (45)–(51)), we can obtain the first order corrections by assuming  $w_{\Sigma_I}(t_d) = 1$ ,  $w_{\Sigma_{II}}(t_d) = 0$ , readily providing

$$c_I(t) \cong \frac{e^{-i\mathcal{U}_d(t-t_d)/\hbar} [\Delta\tilde{H}]_{I,\Sigma_I}}{\mathcal{U}_d - \mathcal{U}_I(t_d)} \quad (63)$$

$$c_{\Sigma_I}(t) \cong e^{-i\mathcal{U}_d(t-t_d)/\hbar} \quad (64)$$

$$c_{\Sigma_{II}}(t) \cong 0 \quad (65)$$

with  $l \neq \Sigma_I, \Sigma_{II}$ . Eqn (63)–(65) provide expressions for the perturbed quantum state exactly reproducing the  $\Sigma_I$  perturbed Hamiltonian eigenstate as obtained in the case of degenerate unperturbed eigenstates, according to first order time independent perturbation theory.<sup>56,57</sup>

We may hence conclude, merging this result valid inside the TR with the result obtained for the solution outside the TR, that once at an arbitrary initial time the QC state coincides with one of the Hamiltonian eigenstates then, within an excellent approximation, at any other time the QC state will be indistinguishable from the corresponding perturbed Hamiltonian eigenstate determined by the perturbation matrix  $\Delta\tilde{H}$ .

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