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Theory of the transition from sequential to concerted electrochemical proton-electron transfer

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Abstract

A theory for the calculation of potential energy surfaces of electrochemical proton-coupled electron transfer is considered and parameterized on the basis of thermodynamic relations. The paper discusses the qualitatively different potential energy surfaces predicted by the theory, and their relation to the existence of sequential and concerted proton-electron transfer pathways. The concomitant activation energies for sequential and concerted PET are calculated. The applied overpotential may change the qualitative shape of the PES and therefore the mechanism of the proton-coupled electron transfer reaction.

1. Introduction

Proton-coupled electron transfer (PCET) reactions are central to many processes in chemistry, including organic chemistry, biochemistry and electrochemistry.^{1,2,3,4,5,6} One of the key mechanistic issues in the understanding of PCET reactions is whether the proton and the electron are transferred sequentially, for which proton transfer (PT) either precedes or follows electron transfer (ET), or whether their transfer takes place in a concerted manner. The latter pathway is often referred to as concerted proton-electron transfer (CPET). The former case will be referred to as sequential proton-electron transfer (SPET). The relation between the different pathways is commonly illustrated in a so-called square scheme for a single proton-electron transfer reaction as shown in Figure 1.

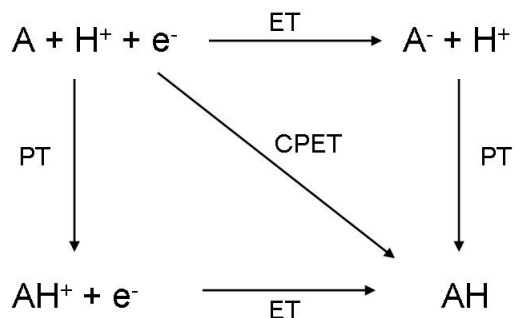
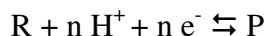


Figure 1. Square scheme for proton-coupled electron transfer.

PCET reactions are ubiquitous in redox electrochemistry and electrocatalysis. Many redox reactions that are currently under detailed scrutiny because of their importance to fuel cells and (electrochemical) solar fuel production, are of the following type:



Although it is well accepted and well known in the molecular electrochemistry literature that such reactions may follow SPET pathways,^{3,5} in the surface electrochemistry literature, one practically always assumes CPET pathways. The concerted character of PCET reactions is implicit in many recent theoretical treatments of reactions such as the oxygen reduction reaction, the oxygen evolution reaction, the hydrogen evolution and oxidation reactions, and carbon dioxide reduction. It is in fact the basis of the applicability of the computational hydrogen electrode (CHE) introduced by Nørskov et al.^{7,8} for the simulation of electrode reactions using first-principles density functional theory calculations. In such calculations, the pH does not play an active role, as it always scales with the electrochemical potential of the electrons. However, there are now ample experimental examples of electrocatalytic reactions on metal surfaces in which the decoupling of proton and electron transfer is deemed important, including the oxidation

of alcohols and formic acid on gold and platinum electrodes,^{9,10,11,12} and the reduction of carbon monoxide on copper electrodes.^{13,14}

The theory of PCET reactions is well developed^{15,16,17,18,19,20,21,22,23,24,25,26,27,28,29,30,31} and recent treatments and reviews are available.^{32,33} There are various thoughts about the determining factors that make a PCET reaction choose a SPET or CPET pathway. The most prevalent though often implicit idea in many theoretical studies of PCET is that the CPET happens because the thermochemistry of the SPET pathways is unfavorable,^{22,32,34,35} i.e. the energies of the “off-diagonal” states in Figure 1 are too high with respect to the “diagonal states”, thereby making the CPET pathway the only feasible route. A second school of thought is that there is cross coupling between the reaction coordinates for proton and electron transfer that favors concerted transfer over sequential transfer.^{22,32,25,26}

The aim of this paper is to merge the first two approaches into a single quantitative theory, allowing the prediction of SPET vs CPET pathways on the basis of measurable or computable physico-chemical quantities. The paper will specifically deal with redox reactions of the type illustrated in Figure 1, studied in a half cell under electrochemical conditions, where the proton and the electron are at different locations in the reactant state. Hence, the theory is not applicable to the related class of hydrogen atom transfer (HAT) reactions.

2. The model

2.1 Model equations

We model a simple one-proton one-electron transfer reaction:



We will assume an electrochemical PCET redox reaction, as mentioned in the Introduction. The model is based on the idea that the activation energy for both electron and proton transfer depend on the reorganization of the surrounding solvent, or more

generally on the molecular reorganization of the nearby environment. This reorganization will be modeled using two separate reaction coordinates: one solvent coordinate accommodating electron transfer, and one solvent coordinate accommodating proton transfer. The transition state follows from the Franck-Condon principle applied to both electron and proton transfer. In essence, this is a straightforward extension of the Marcus electron transfer theory. The potential free energy surface for this reaction will be calculated from a Hamiltonian suggested by Schmickler et al.²⁶ This Hamiltonian is based on the well-known Anderson-Newns^{36,37} Hamiltonian from surface physics, and has been used extensively in the modeling of various aspects of electrochemical reactions.^{38,39,40,41,42,43} The model is very similar to the formalism introduced by Soudackov and Hammes-Schiffer for homogeneous multiple charge transfer reactions in solution,²¹ later extended to electrochemical PCET by the same group.^{30,31} The Hamiltonian for PCET reactions describes the electron transfer between an isolated energy level and a multitude of energy levels modeling the solid (metal) surface, augmented by a term modeling the coupling between the solvent and the isolated energy level (the redox level of species A), and a term describing the interaction between the proton and the solvent and the proton and the species A. The Hamiltonian consists of five terms:

$$H = H_{et} + H_{e,solv} + H_{pt} + H_{p,solv} + H_{ep} \quad (2)$$

The first term H_{et} describes the electronic part of the interaction between the redox level and the metal electrons, in second-quantized form:

$$H_{et} = \varepsilon_A n_A + \sum_k \varepsilon_k n_k + \sum_k (V_k c_k^\dagger c_A + V_k^* c_A^\dagger c_k) \quad (3)$$

where n denotes a number operator, ε an energy, $c^\dagger$ and c creation and annihilation operators, and k is an index running over the electronic energy levels of the metal. The last two terms describe the exchange between the redox level and the metal levels, with

V_k the corresponding matrix elements. We are considering only a single electron, so the model does not account explicitly for spin.

The solvent and the other modes coupled to the electron transfer are presented by a set of harmonic oscillators, with a linear coupling to the transferring electron, in agreement with the Marcus theory of electron transfer:⁴⁴

$$H_{e,solv} = \frac{1}{2} \sum_v \hbar \omega_v (p_v^2 + q_v^2 - 2n_A g_v q_v) \quad (4)$$

where q_v and p_v are the dimensionless coordinates and momenta of the solvent oscillators with frequency ω_v ; the last term in Eq.4 accounts for the interaction of the oscillator bath with the transferring electron as characterized by the coupling constants g_v .

The proton transfer term H_{pt} is also modeled using a number operator formalism, as suggested by Schmickler.²⁶ There are two states for the proton and two corresponding number operators, n_1 and n_2 , where “1” denotes the state where the proton is in solution and “2” denotes the state when it is on A. Since we consider the transfer of a single proton, $\langle n_1 \rangle = 1 - \langle n_2 \rangle$. This formalism does not consider the wavefunctions of the proton explicitly, and since to a first approximation we are only interested in the potential energy surface, we will omit the kinetic energy of the proton. Therefore we neglect nuclear tunneling, although approximate effects of nuclear tunneling may be estimated after having established expressions for the activation free energy, as discussed by Marcus.²⁸ Thus, H_{pt} reads as:

$$H_{pt} = \epsilon_{p,1} n_1 + \epsilon_{p,2} n_2 + V_{pt} c_1^+ c_2 + V_{pt}^* c_2^+ c_1 \quad (5)$$

and the interaction of the proton with the solvent is again treated within the linear response model:

$$H_{p,solv} = -n_2 \sum_v \hbar \omega_v f_v q_v \quad (6)$$

where f_v are the coupling constants. Finally, we need to account for the interaction between the proton and the electron on the A species:

$$H_{ep} = \beta n_A n_2 \quad (7)$$

where β has been called the Coulomb attraction by Schmickler et al.²⁶, and is expected to be negative.

At this point, it is useful to introduce two separate solvent coordinates, one coupling to the electron, and one to the proton, q_e and q_p , resp.²¹ The introduction of these two reaction coordinates also introduces a cross term into the Hamiltonian. It is convenient to define the two coordinates in the following way:

$$q_v = g_{v_e} q_e + f_{v_p} q_p \quad (8)$$

where v_e is an index for the solvent modes that couple to electron transfer, and v_p is an index for the solvent modes that couple to proton transfer. In the absence of cross coupling, v_e and v_p belong to different sets that do not overlap; in the case of cross coupling, v_e and v_p will index over two sets of modes that have non-zero overlap. This yields the following expression for the Hamiltonian:

$$\begin{aligned} H(q_e, q_p) = & \varepsilon_A n_A + \sum_k \varepsilon_k n_k + \sum_k (V_k c_k^+ c_A + V_k^* c_A^+ c_k) + \varepsilon_{p,1} n_1 + \varepsilon_{p,2} n_2 + V_{pt} c_1^+ c_2 + V_{pt}^* c_2^+ c_1 \\ & + \lambda_e q_e^2 + \lambda_p q_p^2 - 2\bar{\lambda} q_e q_p - 2\lambda_e q_e - 2\lambda_p q_p + \beta n_A n_2 \end{aligned} \quad (9)$$

in which

$$\lambda_e = \frac{1}{2} \sum_v \hbar \omega_v g_{v_e}^2 \quad (10)$$

$$\lambda_p = \frac{1}{2} \sum_v \hbar \omega_v f_{v_p}^2 \quad (11)$$

and in which $\bar{\lambda}$ has been called the solvent overlap by Schmickler et al.²⁶, and the cross-reorganization energy by Kuznetsov and Ulstrup,²⁵ and is given by the following equation

$$\bar{\lambda} = \frac{1}{2} \sum_v \hbar \omega_v f_{v_e} g_{v_p} \quad (12)$$

where the summation is only over those modes that couple to both proton and electron. Note that this quantity may be negative, 0, or positive. When the modes do not overlap, $\bar{\lambda} = 0$. If $\bar{\lambda} < 0$, the cross term facilitates CPET. If $\bar{\lambda} > 0$, the cross term opposes CPET. We note that this cross coupling term was already considered by Dogonadze et al.¹⁵ in 1968, but was put equal to zero in their paper. This “cross reorganization energy” plays an important role in the more recent theories of Soudackov and Hammer-Schiffer,^{21,45,46,47} and influences the shape of the PES significantly⁴⁶ (see also section 3.2 below). The introduction of the cross coupling term is a straightforward consequence of the linear response model. The real coupling of the solvent to the proton and electron transfer is likely to be more complex and non-linear. Insight into such effects requires detailed molecular simulations.⁴⁸

2.2 Solution and parameterization of the potential energy surface

We will solve for the ground state potential energy surface (PES) of the ANS Hamiltonian in the weak adiabatic limit, where the electronic coupling elements are sufficiently strong to assure adiabaticity but not strong enough to significantly affect the energies, especially those near the saddle points of the energy surface. In parameterizing the various energies in the model, it helps to make use of the fact that the model predicts four minima in the energy landscape, corresponding to $\{A + H^+ + e^-\} = (q_e=0, q_p=0)$, $\{AH^+ + e^-\} = (q_e=0, q_p=1)$, $\{A^- + H^+\} = (q_e=1, q_p=0)$, and $\{AH\} = (q_e=1, q_p=1)$. These four states are illustrated in the square scheme in Figure 1.

Let us first consider the transition from A to A⁻; this is a classical ET reaction. The Hamiltonian simplifies to $H_{et} + H_{e,solv}$, which is the ET model first suggested by Schmickler in 1986.⁴⁹ It has a well-known solution for the adiabatic ground state PES:

$$E(q_e) = \tilde{\varepsilon}_A(q_e)n(q_e) + \frac{\Delta}{2\pi} \ln[\tilde{\varepsilon}_A^2(q_e) + \Delta^2] + \lambda_e q_e^2 + 2z\lambda_e q_e \quad (13)$$

In this equation, z is the charge of the reactant core (in our this case, $z = 0$),

$$\Delta = 2\pi \sum_v |V_k|^2 \delta(\varepsilon - \varepsilon_k) \quad (14)$$

is the orbital broadening introduced by the interaction with the metal levels, and

$$n_A(q_e) = \frac{1}{\pi} \operatorname{arccot}\left(\frac{\tilde{\varepsilon}_A(q_e)}{\Delta}\right) \quad (15)$$

is the expectation value of the orbital occupation of the reactant. Finally,

$$\tilde{\varepsilon}_A(q_e) = \varepsilon_A - 2\lambda_e q_e \quad (16)$$

is the renormalized energy level of the reactant. In order to obtain the correct value for the equilibrium potential of the ET reaction, the reactant energy level must be equal to

$$\varepsilon_A = -EA(A) + \Delta G_{solv}(A^-) + \lambda_e + e_0\phi \quad (17)$$

where $EA(A)$ is the electron affinity of A, $\Delta G_{solv}(A^-)$ is the solvation energy of A⁻, e_0 is unit of charge (defined as positive), and ϕ is the electrostatic potential at the location of A/A⁻ compared to that in the metal. Requiring the energies of the reduced ($n_e=q_e=1$) and oxidized state ($n_e=q_e=0$) to be equal at equilibrium, we obtain the desired Born-Haber expression for the equilibrium potential of the ET reaction:

$$\phi_{A,A^-}^{eq} = \frac{1}{e_0} (EA - \Delta G_{solv}(A^-)) \quad (18)$$

All the above expressions neglect the effect of work terms,^{28,44} for simplicity.

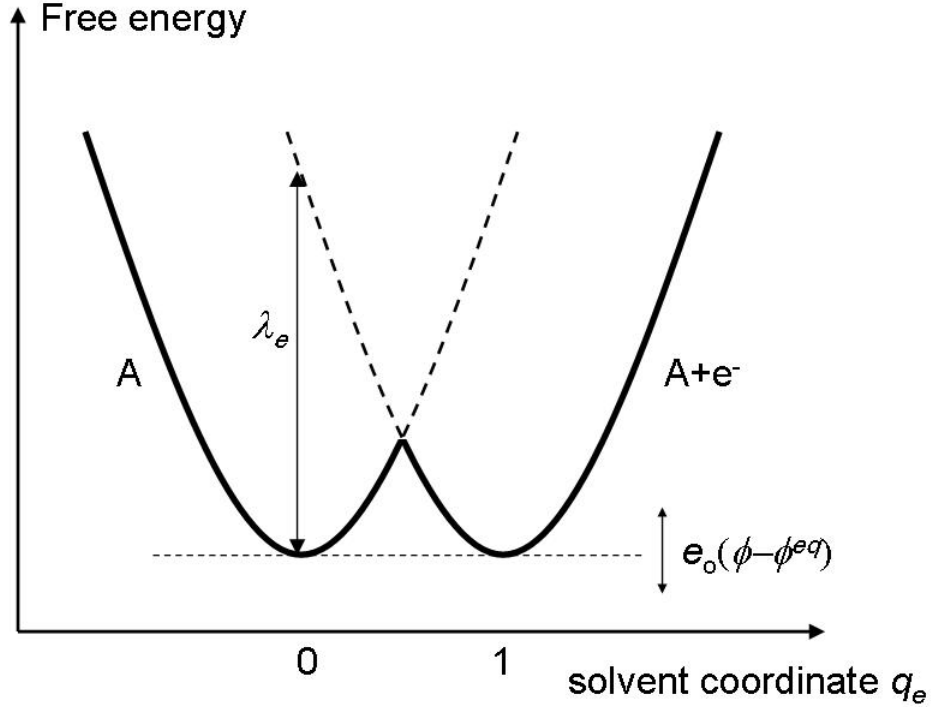


Figure 2. Potential free energy surface for an electron transfer (ET) reaction.

Next, let us consider the transition from $A + H^+$ to AH^+ ; this is a classical proton transfer reaction, or acid-base equilibrium. The corresponding Hamiltonian simplifies to $H_{pt} + H_{p,solv}$. This is a two-level problem with two diabatic energy curves $E_{p,1}(q_p)$ and $E_{p,2}(q_p)$, coupled by the coupling matrix element $|V_{pt}|^2$. The expressions for the diabatic energy curves are:

$$E_{p,1}(q_p) = \varepsilon_{p,1} + \lambda_p q_p^2 \quad (19)$$

$$E_{p,2}(q_p) = \varepsilon_{p,2} + \lambda_p (q_p - 1)^2 \quad (20)$$

The adiabatic potential energy curve is given by the well-known expression:

$$E_p(q_p) = \frac{1}{2} \left(E_{p,1}(q_p) + E_{p,2}(q_p) - \left[(E_{p,1}(q_p) - E_{p,2}(q_p))^2 - 4|V_{pt}|^2 \right]^{1/2} \right) \quad (21)$$

This is essentially our version of Schmickler's double-well potential for the proton transfer,²⁶ which in the limit of small coupling simplifies to taking the lowest value of the two energy surfaces. Again, we parameterize the Hamiltonian by requiring that we obtain the correct equilibrium expressions. State “1” has the proton in solution, and we follow the usual definition that $G^0(\text{H}^+) = 0$. We will set the value of $G(\text{A})$ to zero so that

$$\varepsilon_{p,1} = 0; \quad \varepsilon_{p,2} = G(\text{HA}^+) - G(\text{A}) - \lambda_p = \Delta G_{\text{prot}}(\text{A}) - \lambda_p = 2.303\text{RT}pK_a(\text{HA}^+) - \lambda_p \quad (22)$$

The energy level of state “2” therefore depends on the free energy of protonation of A in solution, $\Delta G_{\text{prot}}(\text{A})$, or, equivalently, the acidity constant $pK_a(\text{HA}^+)$.

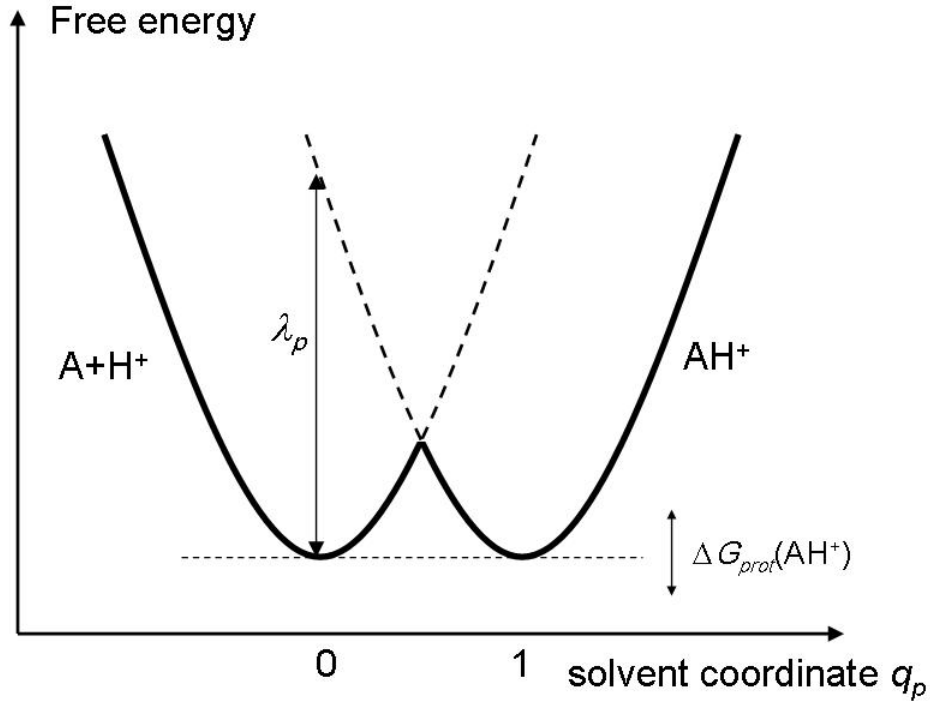


Figure 3. Potential free energy surface for a proton transfer (PT) reaction.

We can perform the same analysis for the $\text{HA}^+ + \text{e}^- \rightleftharpoons \text{HA}$ electron transfer reaction and the $\text{A}^- + \text{H}^+ \rightleftharpoons \text{HA}$ proton transfer reaction. This defines the value of the Coulomb attraction β as:

$$\beta = \Delta G_{\text{prot}}(\text{A}^-) - \Delta G_{\text{prot}}(\text{A}) + 2\bar{\lambda} \quad (23)$$

showing that this parameter is related to the acidity constants of HA^+ and HA and the solvent overlap. If A^- has a higher proton affinity than A , this term will normally indeed be negative.

What we have done in the above is not much more than parameterize the ANS Hamiltonian using thermodynamic cycles. In the next section, we will discuss the resulting PES, the concomitant activation energies for sequential and concerted PET,

illustrate the different classes of PES predicted by the model, and show how the applied overpotential can change the qualitative shape of the PES.

3. Analysis and discussion of the model

Our main aim is to analyze the PES and different reaction paths and their corresponding activation energies at the overall equilibrium potential of reaction 1, which is given by:

$$\phi = \phi_{A, H^+/HA}^{eq} = \frac{1}{e_0} (EA(A) - \Delta G_{solv}(A^-) - \Delta G_{prot}(A^-)) \quad (24)$$

and (small) deviations from this equilibrium potential given by the overpotential η . We will consider the limit of no solvent overlap, $\bar{\lambda} = 0$ (Section 3.1), as well as finite solvent overlap, both negative and positive (Section 3.2), in the weakly adiabatic limit.

3.1 No solvent overlap $\bar{\lambda} = 0$

In this case, the PES of the ANS Hamiltonian in the weakly adiabatic simplifies to the interaction of four two-dimensional parabola. The analysis is very straightforward and insightful in this limit. We label the states $\{A + H^+ + e^-\}$, $\{AH^+ + e^-\}$, $\{A^- + H^+\}$, and $\{AH\}$ by “1”, “2”, “3” and “4”, respectively. Their energies are given by:

$$\begin{aligned} E_1(q_e, q_p) &= \lambda_e q_e^2 + \lambda_p q_p^2 \\ E_2(q_e, q_p) &= \lambda_e q_e^2 + \lambda_p (q_p - 1)^2 + E_2^0 \\ E_3(q_e, q_p) &= \lambda_e (q_e - 1)^2 + \lambda_p q_p^2 + E_3^0 + \eta \\ E_4(q_e, q_p) &= \lambda_e (q_e - 1)^2 + \lambda_p (q_p - 1)^2 + \eta \end{aligned} \quad (25)$$

where the values for the various offset parameters follow from the previous section:

$$\begin{aligned}
E_2^0 &= \Delta G_{prot}(A) \\
E_3^0 &= -EA(A) + \Delta G_{solv}(A^-) \\
\eta &= e_0(\phi - \phi_{A,H^+/HA}^{eq})
\end{aligned} \tag{26}$$

The overall PES E_{PET} is now:

$$E_{PET}(q_e, q_p) = \min[E_1(q_e, q_p), E_2(q_e, q_p), E_3(q_e, q_p), E_4(q_e, q_p)] \tag{27}$$

Transition states are located at the minima of the intersections of the two E_i surfaces. In the q_e, q_p plane, these intersections are lines, and the minima are points on those lines. Since we consider the reaction from state “1” to state “4”, we will consider all intersections apart from the intersection between E_2 and E_3 . This intersection only plays a role if both state “2” and state “3” are more stable than state “1” and “4”, in which case the reaction considered would be thermodynamically unfavorable. Therefore, we have the following five lines in the q_e, q_p plane:

$$E_1 \cap E_2 : q_p = \frac{1}{2} + \frac{E_2^0}{2\lambda_p} \tag{28}$$

$$E_1 \cap E_3 : q_e = \frac{1}{2} + \frac{E_3^0 + \eta}{2\lambda_e} \tag{29}$$

$$E_2 \cap E_4 : q_e = \frac{1}{2} + \frac{\eta - E_2^0}{2\lambda_e} \tag{30}$$

$$E_3 \cap E_4 : q_p = \frac{1}{2} - \frac{E_3^0}{2\lambda_p} \tag{31}$$

$$E_1 \cap E_4 : q_p = -\frac{\lambda_e}{\lambda_p} q_e + \frac{\lambda_e + \lambda_p + \eta}{2\lambda_p} \tag{32}$$

The lines have the following minima (which are saddle points or “transition states”) with corresponding energies:

$$\text{TS } 1 \rightarrow 2: \left(q_e = 0, q_p = \frac{1}{2} + \frac{E_2^0}{2\lambda_p} \right), E_{12}^{ST} = \frac{(\lambda_p + E_2^0)^2}{4\lambda_p} \quad (33)$$

$$\text{TS } 1 \rightarrow 3: \left(q_e = q_e = \frac{1}{2} + \frac{E_3^0 + \eta}{2\lambda_e}, q_p = 0 \right), E_{13}^{ST} = \frac{(\lambda_e + E_3^0 + \eta)^2}{4\lambda_e} \quad (34)$$

$$\text{TS } 2 \rightarrow 4: \left(q_e = \frac{1}{2} + \frac{\eta - E_2^0}{2\lambda_e}, q_p = 1 \right), E_{24}^{ST} = \frac{(\lambda_e + \eta - E_2^0)^2}{4\lambda_e} \quad (35)$$

$$\text{TS } 3 \rightarrow 4: \left(q_e = 1, q_p = \frac{1}{2} - \frac{E_3^0}{2\lambda_p} \right), E_{12}^{ST} = \frac{(\lambda_p - E_3^0)^2}{4\lambda_p} \quad (36)$$

$$\text{TS } 1 \rightarrow 4: \left(q_e = q_p = \frac{1}{2} + \frac{\eta}{2(\lambda_p + \lambda_e)} \right), E_{12}^{ST} = \frac{(\lambda_p + \lambda_e + \eta)^2}{4(\lambda_p + \lambda_e)} \quad (37)$$

Note that these energies are the energies with respect to zero, not with respect to corresponding reactant states. Also note that if all steps are thermodynamically neutral, the corresponding activation energies would be $\lambda_p/4$, $\lambda_e/4$, $\lambda_e/4$, $\lambda_p/4$ and $(\lambda_e + \lambda_p)/4$, respectively. Further analysis shows that there are five qualitatively different E_{PET} with corresponding transitions between them. We will discuss them below.

1. PES with 4 TS

This type of PES happens if $E_2^0 = -E_3^0$, i.e. if $\Delta G_{prot}(A) = -EA(A) + \Delta G_{solv}(A^-)$. The resulting PES for $\eta=0$ and the location of the intersection lines between states “1”, “2”, “3” and “4” are shown in Figure 4. This is the only kind of PES where the transition state corresponding to the transition from “1” to “4”, i.e. the concerted proton-electron transfer (CPET), is a local maximum. This situation does not change if an overpotential is applied. Since it is physically impossible that the above equality is satisfied exactly, this kind of PES is in fact unphysical. Still, it is interesting to note that in and close to this situation, i.e. $E_2^0 = \Delta G_{prot}(A) \approx 0$ and $E_3^0 = -EA(A) + \Delta G_{solv}(A^-) \approx 0$, sequential PET (SPET) is always preferred over CPET, because the activation energies for the separate ET and PT steps are $\lambda_e/4$ and $\lambda_p/4$, which is always lower than that of the CPET step, $(\lambda_e + \lambda_p)/4$.

An illustration of the physically more realistic situation corresponding to $E_2^0 \approx 0$ and $E_3^0 \approx 0$ is shown in Figure 5. This situation is observed if either E_2^0 or E_3^0 is negative, such that the line corresponding to the intersection of “1” and “4” does not include the saddle point, and the other state satisfies $E_2^0 < \lambda_p$ or $E_3^0 + \eta < \lambda_e$. In this case, the system will choose the pathway with the negative E_2^0 or $E_3^0 + \eta$. If both E_2^0 and E_3^0 are negative, there is no intersection between “1” and “4” for the PES defined by Eq.27, and we will not consider this situation, although the general conclusion regarding the pathway chosen is not significantly different from the one just stated.

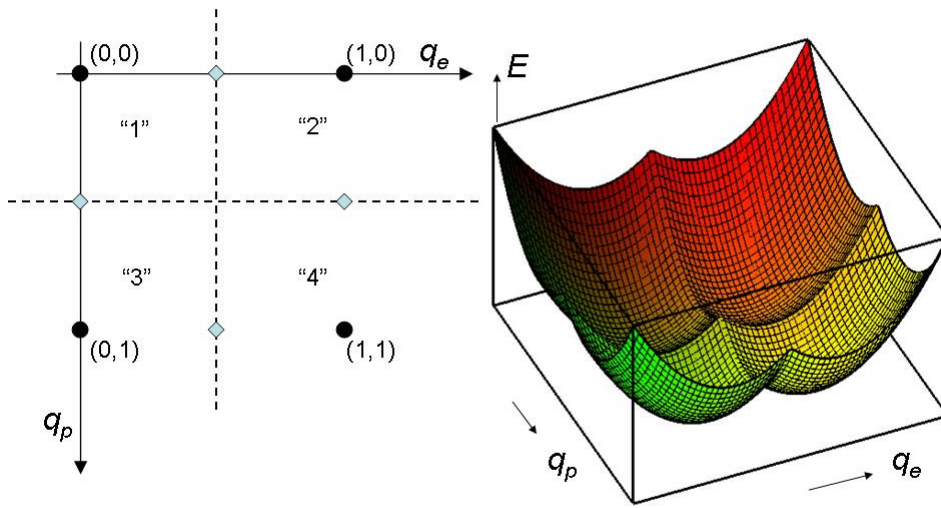


Figure 4. Predicted potential energy surface Eq.27 for $E_2^0 = E_3^0 = \eta = 0$, for $\lambda_e = \lambda_p = 1$ (arbitrary units).

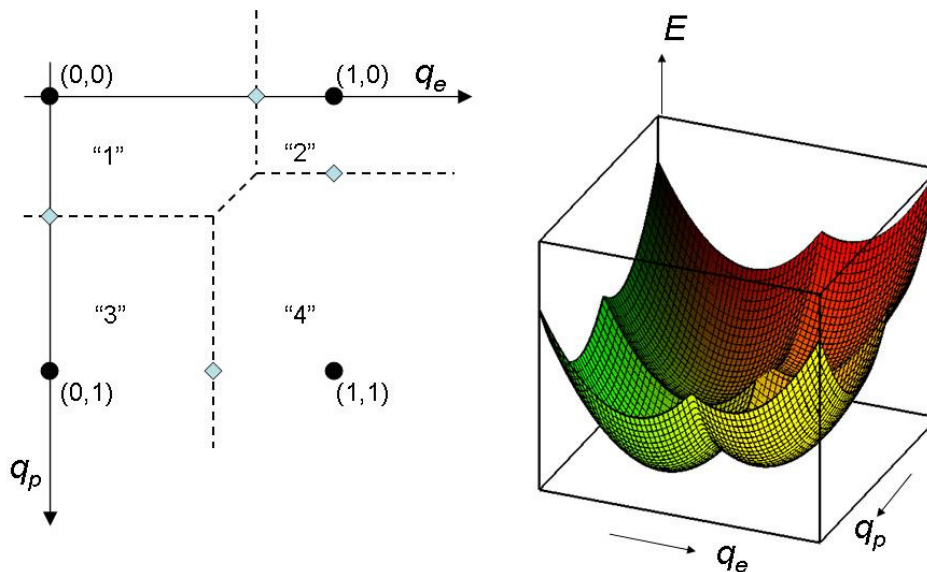


Figure 5. Predicted potential energy surface Eq.27 for $E_2^0 > 0$, $E_3^0 < 0$, $\eta = 0$, for $\lambda_e = \lambda_p = 1$ (arbitrary units).

2. PES with 5 TS

A special version of the PES shown in Figure 5 is the one for which the line corresponding to the intersection of “1” and “4” includes the TS. This happens when both $E_2^0 = \Delta G_{prot}(A)$ and $E_3^0 = -EA(A) + \Delta G_{solv}(A^-)$ are positive, and $E_2^0 = \Delta G_{prot}(A) < \lambda_p$ and $E_3^0 + \eta = -EA(A) + \Delta G_{solv}(A^-) + \eta < \lambda_e$. In this case, a PES develops with 5 TS, as illustrated for $\eta=0$ with the location of the intersection lines between states “1”, “2”, “3” and “4” as shown in Figure 6. In this case, the system has the choice between three pathways. The CPET pathway will have the lowest overall barrier if $(\lambda_p + \lambda_e)/4$ is smaller than the highest barrier in the SPET pathway, as given by Eqs.33-36. Typically, if the proton affinity and the electron affinity of A (including the resulting gain in solvation energy) are significantly larger than the smallest of the reorganization energies, the CPET pathway will be favored.

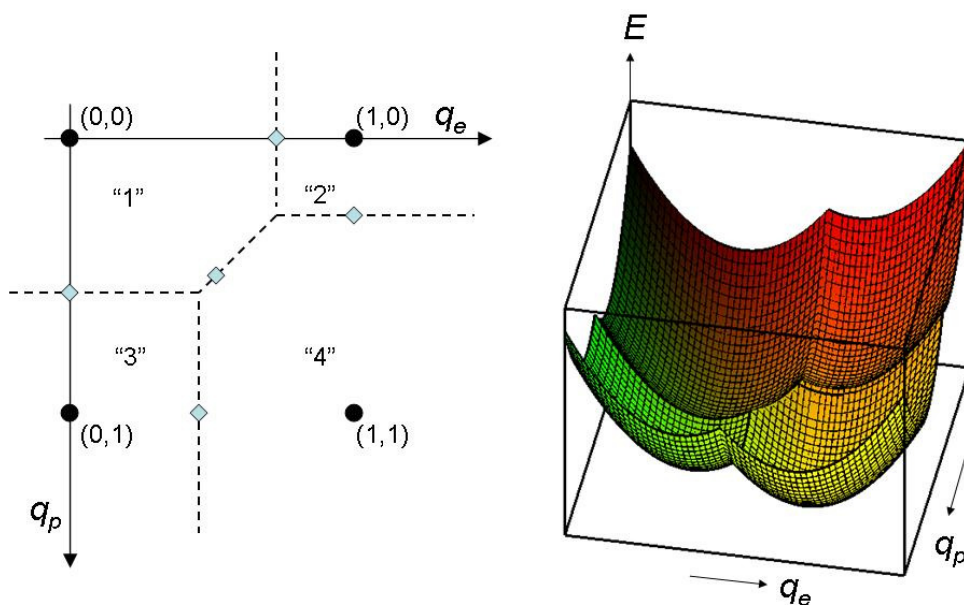


Figure 6. Predicted potential energy surface Eq.27 for $0 < E_2^0 < \lambda_p$, $0 < E_3^0 < \lambda_e$, $\eta = 0$, for $\lambda_e = \lambda_p = 1$ (arbitrary units).

3. PES with 1 TS

This type of surface is observed when the minima in region “2” and “3” are no longer (local) minima of the overall PES. This happens if both the proton affinity and the electron affinity of the reactant are very energetically unfavorable, i.e. and $E_2^0 = \Delta G_{prot}(A) > \lambda_p$ and $E_3^0 + \eta = -EA(A) + \Delta G_{solv}(A^-) + \eta > \lambda_e$. In this case, there are only a single TS and a single pathway. This corresponds to a true CPET reaction, as other pathways are not available.

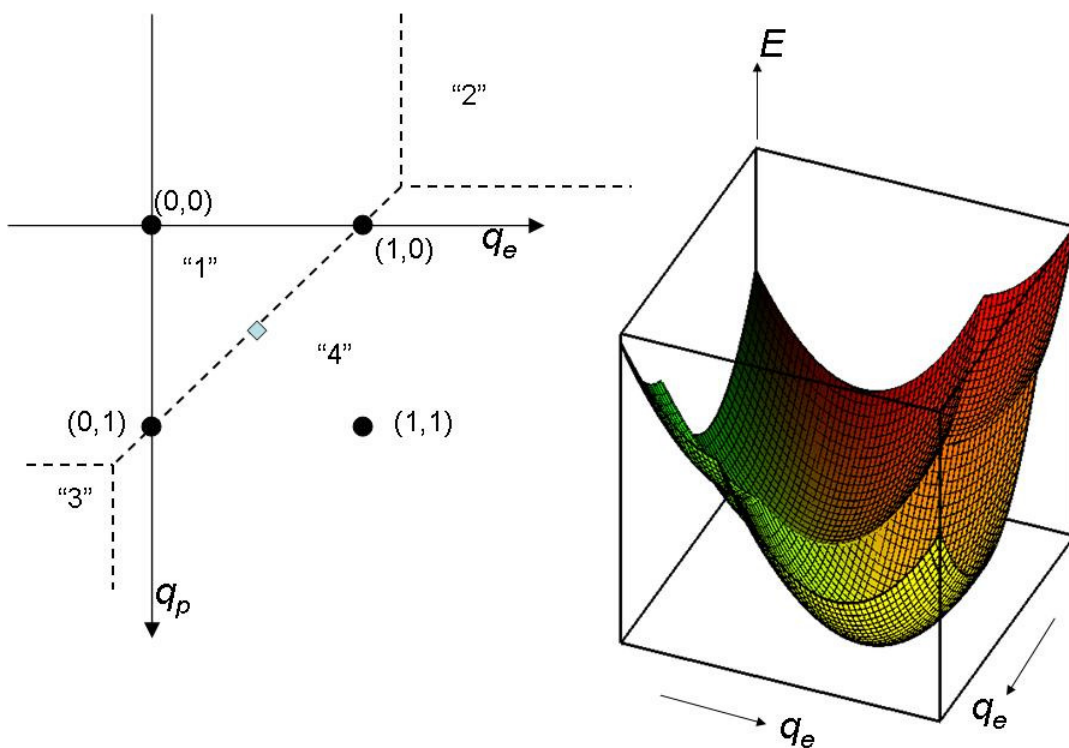


Figure 7. Predicted potential energy surface Eq.27 for $E_2^0 > \lambda_p$, $E_3^0 > \lambda_e$, $\eta = 0$, for $\lambda_e = \lambda_p = 1$ (arbitrary units).

4. PES with 3 TS

This type of surface is observed when one of the minima in region “2” and “3” is no longer a (local) minimum of the overall PES, either because $E_2^0 = \Delta G_{prot}(A) > \lambda_p$ or $E_3^0 + \eta = -EA(A) + \Delta G_{solv}(A^-) + \eta > \lambda_e$. In such a case there is the simultaneous possibility of SPET and CPET, as there are two pathways on the PES. This is presumably a rather typical case, in which the CPET pathway competes with a SPET pathway, the latter rendered possible by either a high proton affinity or a high electron affinity.

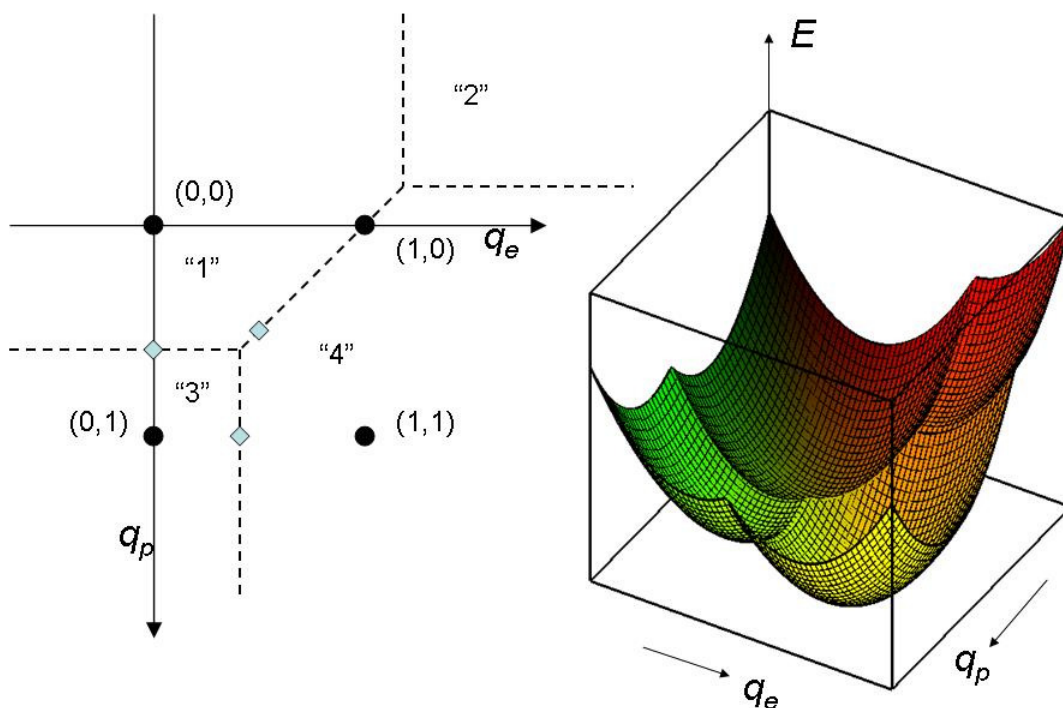


Figure 8. Predicted potential energy surface Eq.27 for $E_2^0 > \lambda_p$, $0 < E_3^0 < \lambda_e$, $\eta = 0$, for $\lambda_e = \lambda_p = 1$ (arbitrary units).

5. PES with 2 TS

This type of surface is observed when one of the minima in region “2” and “3” is no longer a local minimum of the overall PES, and also the TS corresponding to the transition from region “1” to “4” is no longer a saddle point of the overall PES. This situation is observed if one of the off-diagonal states has high energy, and the other one satisfies either $E_2^0 = \Delta G_{prot}(A) < 0$ or $E_3^0 + \eta = -EA(A) + \Delta G_{solv}(A^-) + \eta < 0$. In such a case there are two TS corresponding to the two steps of the SPET pathway.

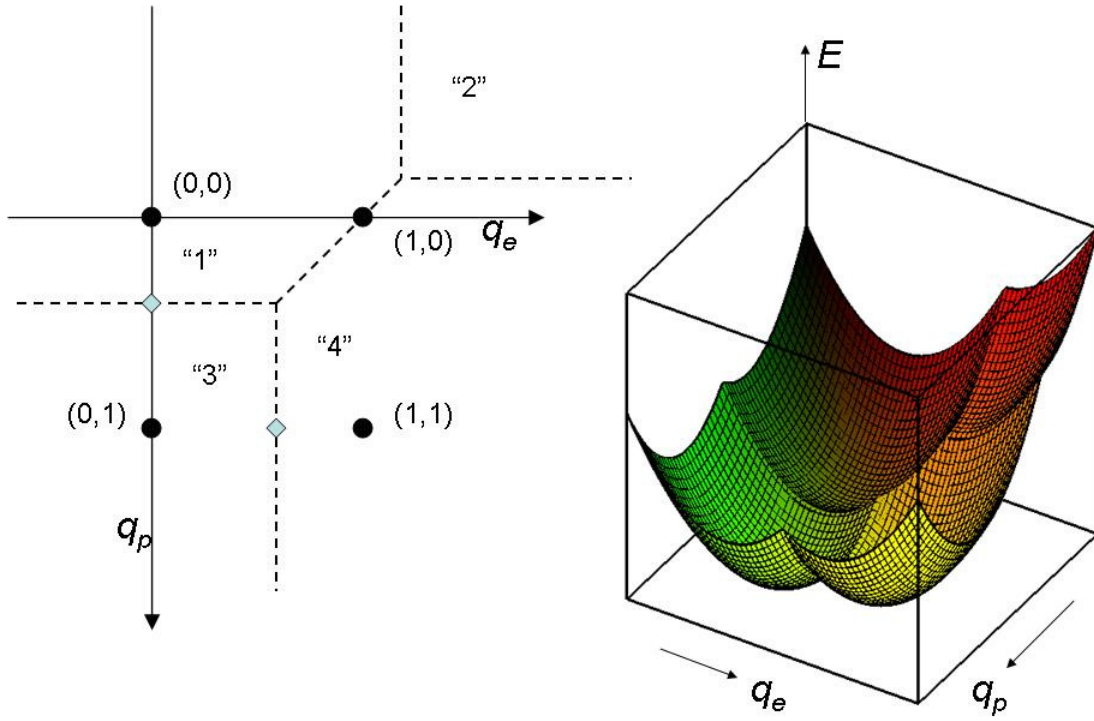


Figure 9. Predicted potential energy surface Eq.27 for $E_2^0 > \lambda_p$, $E_3^0 < 0$, $\eta = 0$, for $\lambda_e = \lambda_p = 1$ (arbitrary units).

3.2 Solvent overlap $\bar{\lambda} \neq 0$

In the case of non-zero solvent overlap, the four states are given by:

$$\begin{aligned}
 E_1(q_e, q_p) &= \lambda_e q_e^2 + \lambda_p q_p^2 + 2\bar{\lambda} q_e q_p \\
 E_2(q_e, q_p) &= \lambda_e q_e^2 + \lambda_p (q_p - 1)^2 + 2\bar{\lambda} q_e (q_p - 1) + E_2^0 \\
 E_3(q_e, q_p) &= \lambda_e (q_e - 1)^2 + \lambda_p q_p^2 + 2\bar{\lambda} (q_e - 1) q_p + E_3^0 + \eta \\
 E_4(q_e, q_p) &= \lambda_e (q_e - 1)^2 + \lambda_p (q_p - 1)^2 + 2\bar{\lambda} (q_e - 1)(q_p - 1) + \eta
 \end{aligned} \tag{38}$$

The parameters E_2^0, E_3^0 and η have the same meaning as in the previous section. The intersections between two paraboloids are now given by:

$$E_1 \cap E_2 : q_p = \frac{1}{2} + \frac{E_2^0 - 2\bar{\lambda}q_e}{2\lambda_p} \quad (39)$$

$$E_1 \cap E_3 : q_e = \frac{1}{2} + \frac{E_3^0 + \eta - 2\bar{\lambda}q_p}{2\lambda_e} \quad (40)$$

$$E_2 \cap E_4 : q_e = \frac{1}{2} + \frac{\eta - E_2^0 - 2\bar{\lambda}(q_p - 1)}{2\lambda_e} \quad (41)$$

$$E_3 \cap E_4 : q_p = \frac{1}{2} - \frac{E_3^0 + 2\bar{\lambda}(q_e - 1)}{2\lambda_p} \quad (42)$$

$$E_1 \cap E_4 : q_p = -\frac{\lambda_e + \bar{\lambda}}{\lambda_p + \bar{\lambda}}q_e + \frac{\lambda_e + \lambda_p + 2\bar{\lambda} + \eta}{2\lambda_p + 2\bar{\lambda}} \quad (43)$$

and the corresponding minima on these intersections, i.e. the saddle points of the PES, and their energies are given by the same expressions as in the previous section, except for the saddle point corresponding to the concerted transfer:

$$\text{TS } 1 \rightarrow 4: \left(q_e = q_p = \frac{1}{2} + \frac{\eta}{2(\lambda_p + \lambda_e + 2\bar{\lambda})} \right), E_{12}^{ST} = \frac{(\lambda_p + \lambda_e + 2\bar{\lambda} + \eta)^2}{4(\lambda_p + \lambda_e + 2\bar{\lambda})} \quad (44)$$

At equilibrium, the activation energy for CPET is $(\lambda_e + \lambda_p + 2\bar{\lambda})/4$. This expression shows that if $\bar{\lambda} < 0$, the activation energy for CPET decreases with respect to the activation energies for SPET. The cross reorganization energy also significantly changes the shape of the PES. Again, there are essentially four qualitatively different PES, with 1, 2, 3, or 5 TS. The PES with 4 TS is atypical and occurs only for a very specific set of parameters.

Figure 10 shows an example for $\bar{\lambda} < 0$ (in fact $\bar{\lambda} = -\lambda_e/2 = -\lambda_p/2$) in which now the concerted pathway is favored over the sequential pathway (which had lowest activation

energy for $\bar{\lambda}=0$). Note that the entire potential energy surface has been deformed to favor the concerted proton-electron transfer. The PES with 3 and 2 TS are straightforward deformations of this PES obtained by disfavoring one of the off-diagonal states and favoring the other off-diagonal state.

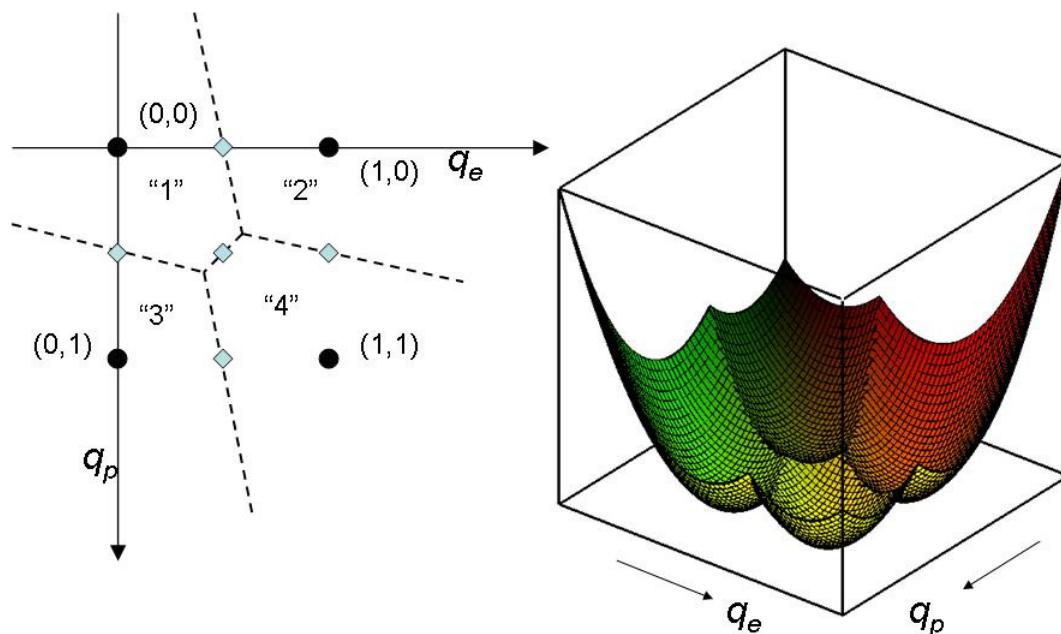


Figure 10. Predicted potential energy surface Eq.27 for $E_2^0 = E_3^0 = \eta = 0$, for $\lambda_e = \lambda_p = 1$, $\bar{\lambda} = -1/2$ (arbitrary units).

For completeness' sake, we also illustrate two cases where $\bar{\lambda} > 0$. In fact, some interesting behavior is observed. Figure 11 shows a situation where the off-diagonal states are endothermic, but the positive value of $\bar{\lambda}$ still removes the possibility of a CPET pathway. With increasing endothermicity of the off-diagonal states, the CPET pathway reappears, as shown in Figure 12, however with a higher activation energy than in the case of $\bar{\lambda} = 0$. These examples show that not only the thermochemistry of the off-diagonal states matters in determining the preferred PCET pathway, but also the extent of cross-coupling between the solvent modes for electron and proton transfer. In the case of

unfavorable cross coupling, the reaction will favor SPET even if this pathway involves a (mildly) thermodynamically unfavorable intermediate.

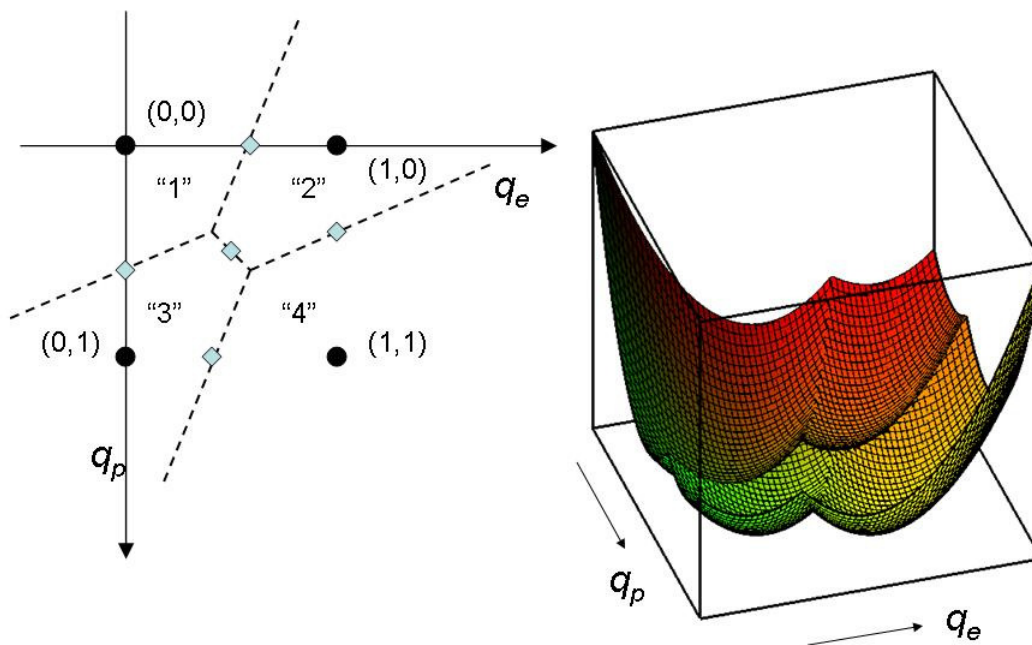


Figure 11. Predicted potential energy surface Eq.27 for $0 < E_2^0 < \lambda_p$, $0 < E_3^0 < \lambda_e$, $\eta = 0$, for $\lambda_e = \lambda_p = 1$, $\bar{\lambda} = 1/2$ (arbitrary units).

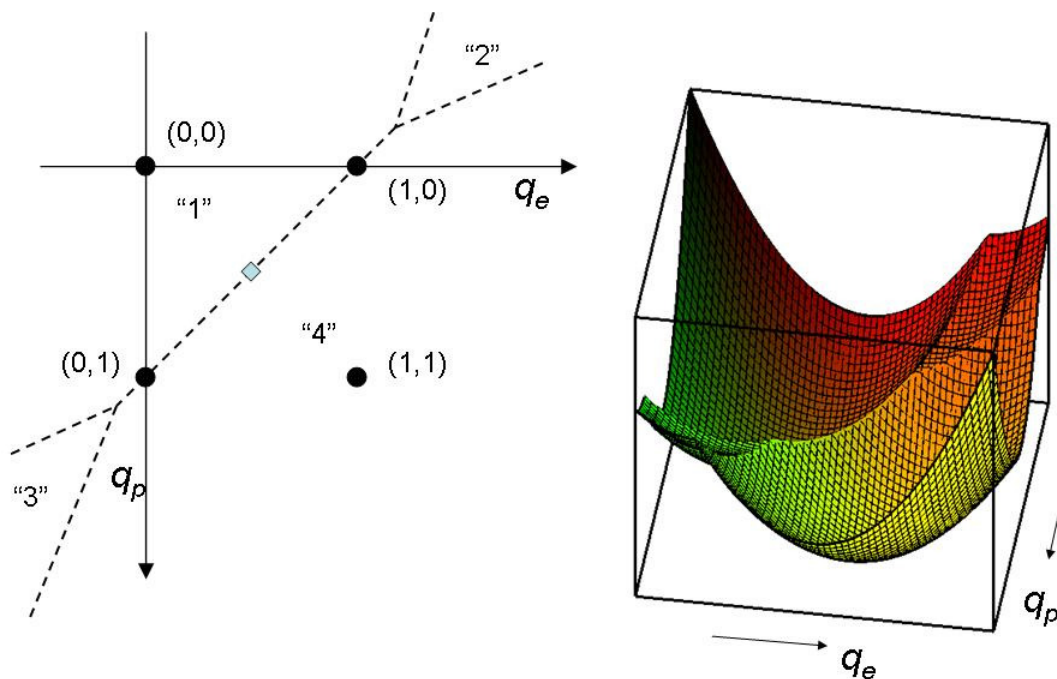


Figure 12. Predicted potential energy surface Eq.27 for $E_2^0 > \lambda_p$, $E_3^0 > \lambda_e$, $\eta = 0$, for $\lambda_e = \lambda_p = 1$, $\bar{\lambda} = 1/2$ (arbitrary units).

3.3 Changes in the PES by application of an overpotential

The qualitative shape of the PES may change as one varies the overpotential, leading to a change in reaction mechanism.^{26,50} Figure 13 shows a typical example. The PES on the left is similar to that in Fig.9, with two transition states, giving rise to a SPET pathway. As an overpotential η is applied, the energy of states 2 and 4 is lowered compared to the energy of states 1 and 3. This leads to the favoring of new pathways, as the transition states corresponding to the transition from 1→4, 1→2, and 2→4 become saddle points on the overall PES. For intermediate η (the middle PES in Fig.13), the CPET pathway will compete with the 1→3→4 SPET, whilst at high η (PES on the right in Fig.13), the 1→2→4 SPET pathway appears as the most favorable pathway. The

competition between stepwise/sequential and concerted pathways in PCET reactions has also been discussed in some detail by Costentin et al.⁵¹.

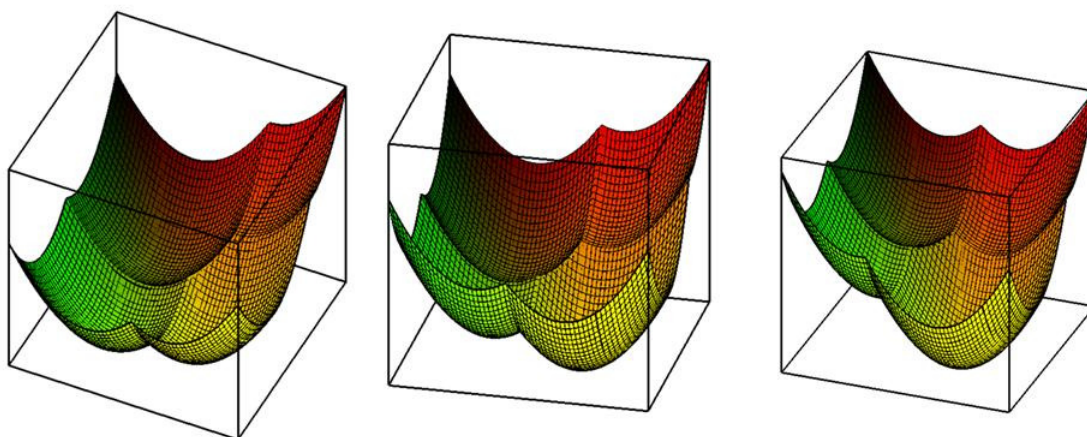


Figure 13. Predicted potential energy surfaces for varying overpotential illustrating how the qualitative shape of the PES may change with η .

4. General discussion and conclusion

The analysis presented above demonstrated that the pathway followed by a general PCET reaction primarily depends on the energy of the off-diagonal states and the cross-coupling between the solvent coordinates related to proton and electron transfer, as has been pointed out in the literature.^{2,24,25,26,27,32} The treatment given here has focused entirely on the shape of the PES and the corresponding energies of the saddle points and intermediate states as they follow from a thermodynamic analysis of the energies of the various (meta)stable states. The derivation or calculation of actual rate constants requires treatment of the solvent dynamics and proton tunneling.

For a reduction reaction, the reactant A will prefer to protonate first if it has a high proton affinity or low pK_a ; for an oxidation reaction, the reactant AH will deprotonate first if it has a low proton affinity, or high pK_a . The latter case seems more typical from the experimental point of view; examples would include the oxidation of alcohols or formic acid on gold and platinum electrodes.^{10,11,12} The oxidation of alcohols prefers a high pH because the deprotonation of the alcoholic proton is key to a high reactivity.¹⁰ Formic acid oxidation is also enhanced by the deprotonation into formate, which is complete at $pH > 4$.¹² An example of the former case would include the reduction of nitrate and nitrate on platinum electrodes, although other side reactions are known to play a role in these processes as well.^{52,53,54} The protonated form of nitrite, nitrous acid, is known to be the more reactive species of the two. Nitrate reduction is also significantly faster in acidic media,⁵² and the availability of protons should be considered as one of the determining factors for nitrate activation. A possible example of an electrocatalytic reaction in which an electron is transferred first before proton transfer takes place, is the reduction of carbon monoxide to ethylene on copper electrodes. Hori et al.¹³ have shown that the rate of this reaction depends on potential but not pH. The decoupling of proton-electron transfer in this reaction has been ascribed to the formation of CO dimer on the copper surface.^{14,55} The CO dimer is known to have a high electron affinity (eventually leading to acetelynediolate, in the absence of water), and we have suggested that this effectively decouples the electron from the proton transfer in the rate determining step of the overall mechanism.⁵⁵

The approach suggested in this paper, which essentially follows earlier works of Soudackov and Hammer-Schiffer,^{21,32} Kuznetsov et al.²⁵ and Schmickler et al.^{26,29}, ascribes the mechanism of the overall reaction in terms of a SPET vs a CPET pathway to the qualitative shape of the PES. This shape is determined by the energy of the off-diagonal states and the cross reorganization energy. At present, there seems to be limited experimental or computational evidence for the importance for the cross-coupling effect. Molecular dynamics simulations mapping the system's free energy onto a two-dimensional PES (as has been done for electrochemical bond breaking and ion transfer reactions^{56,57,58}) will shed light on the issue of solvent cross coupling in PCET reactions,

essentially following the original approach of Kobrak and Hammes-Schiffer⁵⁹ who combined a multi-state valence bond model with an explicit treatment of the solvent.

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