

**PCCP****Q-model of electrode reactions: Altering force constants of intramolecular vibrations**

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Q-model of electrode reactions: Altering force constants of intramolecular vibrations

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A theory of redox reactions involving electron transfer between a metal electrode and a molecule in solution is formulated in terms of two types of nuclear coordinates of the thermal bath: electrostatic polarization of the medium and local low-frequency vibrations. The polarization fluctuations follow Gaussian statistics. In contrast, the vibrational coordinate is allowed to change its force constant between two oxidation states of the reactant, which is projected onto non-Gaussian fluctuations of the reactant's electronic states. A closed-form analytical theory for the electrode redox reactions is formulated in terms of three reorganization energies: the reorganization energy for the electrostatic polarization of the medium and two internal (vibrational) reorganization energies for the reduced and oxidized states of the reactant. The theory predicts asymmetry between the cathodic and anodic branches of the electrode current driven by the corresponding difference in the vibrational force constants.

1 Introduction

Reactions between the metal electrode and a redox active molecule in solutions belong to a broad class of problems where the interaction between the reacting molecule and the surrounding medium changes because of a chemical transformation (a change of the oxidation state for electrochemistry^[1]). For many such problems, the interaction between the reactant and the medium is of primary importance, while the structure and dynamics of the surrounding medium is not affected by the reaction. The medium in this scenario plays a somewhat passive role of a source of thermal noise allowing the barrier passage. Since fluctuations of such media typically involve many molecules or molecular groups, the central limit theorem applies and the thermal noise follows the statistical rules of the Gaussian distribution.

This physics is the focal point of the Marcus theory of electron transfer.^[2] It considers the coupling of the electric field of the transferring electron to a polarizable medium characterized by the polarization density \mathbf{P} .^[3] The medium is allowed to fluctuate, and each fluctuation carries a free energy penalty quadratic in the polarization field \mathbf{P} . Since the structure of the medium is not affected by the reaction (linear response approximation^[4]), the only effect of the reaction on the system's energy is in shifting the equilibrium medium polarization, which minimizes the quadratic functional describing deviations from equilibrium.^[3,5] The re-

sult of this perspective is the picture of shifted equal-curvature parabolas with the crossing point specifying the activation barrier of the reaction.

The Gaussian character of the fluctuations describing many degrees of freedom of the medium does not have to extend to local properties describing the electronic state and nuclear structure of the reactant. A number of nonlinearities potentially generalizing the problem from the standard picture of equal-curvature parabolas can be identified here. The proposal that local vibrational frequencies of the molecules participating in the reaction can be altered by changing electronic state was put forward already at the very early stages of the progress in the field^[6] (e.g., Duschinsky rotations of normal modes^[7]), when the problem of radiationless transitions in molecules was originally advanced.^[8] Another possibility of distinct non-linearities comes from linear and higher-order polarizabilities of the reactants, which allow terms in the system Hamiltonian of nonlinear orders in the electric field produced by the medium, as is well recognized in applications related to non-linear spectroscopies.^[9] Some early suggestions of non-linearities arising from solvation have not received support by computations, which showed that Gaussian statistics and linear solvation are very robust for reactions in condensed media.^[10,11]

Despite the general recognition that force constants of intramolecular vibrations depend on the oxidation state,^[12–15] no closed-form solution including such effects and broadly applicable to the analysis of reaction rates has been achieved.^[16] A difficulty in this development is the need for such solutions to satisfy a number of exact constraints discussed below, which signifi-

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cantly limit the space for analytical approximations and functionalities. We start our discussion below with these general results, followed by a more specific theory development focused on combining medium polarization with localized intramolecular vibrations whose vibrational force constants (frequencies) are altered in the course of an electrode reaction.

Electrode reactions have an important advantage for testing fundamental theoretical concepts compared to redox reactions in solution due to the fact that the free energy of the reaction (the negative of the driving force^[17]) can be continuously changed by altering the electrode potential. In this regard, a fundamental result of standard theories of electrochemistry is the equality between the activation barrier for the cathodic reaction at the overpotential η and the activation barrier for the anodic reaction at the overpotential $-\eta$.^[18,19] In other words, one expects equal currents when changing the electrode overpotential in either positive or negative direction.^[1] Nevertheless, a number of recent observations^[20–24] and theoretical developments^[25,26] have pointed to a possibility that this prediction might be violated. Specifically, Compton and co-workers,^[23] inspired by an earlier model of Marcus,^[27] have assigned the violation of the symmetry between the anodic and cathodic branches to oxidation-state dependence of force constants of intramolecular vibrations of the reactants. Here, we address this problem by providing a closed-form analytical solution for electrode reactions in polar media involving reactants changing their vibrational force constants.

The theory developed here combines the standard Gaussian picture of the Marcus theory for electron transfer in polar media^[3] with a non-Gaussian picture developed within the Q-model for electronic transitions in molecules^[28] and more recently extended to electrode reactions involving polarizable reactants.^[25,26] The previous formulations of the model focused on the effect of the solute polarizability on the energetics of electron-transfer reaction and the corresponding alteration of the “force constant” (susceptibility) of the collective solvent coordinate between two electron-transfer states. In contrast, we address here changes of force constants of internal molecular vibrations caused by electronic transitions. We show that the general mathematical framework of the Q-model can be mapped on this specific problem of electron-transfer reactions involving changes of force constants of discrete intramolecular vibrations. The asymmetry between the cathodic and anodic electrode currents then follows from the asymmetry of vibrations in two oxidation states and the non-Gaussian statistics of the corresponding contribution to the activated transitions leading to the electrode current.

2 Conceptual framework

We start with reviewing the general theoretical framework for electronic transitions in molecules and exact relations which a successful theory has to satisfy. These constraints strongly limit the mathematical solutions applicable to the problem. In fact, the Marcus model of crossing parabolas^[2] and the Q-model of non-parabolic free energy surfaces^[28] are nearly the only exactly solvable mathematical models established in the field that satisfy all known constraints.

The modern theory of radiationless transitions in molecules,

and of electron-transfer reactions as a specific application, considers the vertical energy gap, i.e., the difference of energies at a fixed set of nuclear coordinates, as the best-defined one-dimensional collective coordinate describing the progress of the reaction.^[8,29,30] It is given by the difference of Hamiltonians (energies) of the system after ($H_2(\mathbf{q})$) and before ($H_1(\mathbf{q})$) the electronic transition

$$X = \Delta H(\mathbf{q}) = H_2(\mathbf{q}) - H_1(\mathbf{q}). \quad (1)$$

Here, \mathbf{q} denotes the entire manifold of nuclear coordinates of the medium and of the reactant itself affecting its electronic energy levels. The theory then proceeds to find the free energy required to establish a specific value X . This is accomplished by identifying the free energy surface for electron transfer $F_a(X)$, where $a = 1 = \text{Ox}$ corresponds to the oxidized form (Ox) and $a = 2 = \text{Red}$ refers to the reduced form (Red) when applications to electrode reactions are concerned. Below we will mostly use $a = 1, 2$ to simplify notations, but will specifically emphasize which oxidation states (Ox or Red) is considered to avoid potential confusion. In some equations for the activation barriers derived below \pm or \mp signs appear. We always follow the convention that the upper sign refers to the reduction reaction and the lower sign refers to the oxidation reaction.

The deviation of the partial free energy $F_a(X)$ (at a given X , similarly to the Landau functional for phase transitions^[31]) from the thermodynamic free energy F_{0a} can be mathematically expressed as taking a constrained statistical average

$$e^{-\beta F_a(X) + \beta F_{0a}} = A \langle \delta(X - \Delta H(\mathbf{q})) \rangle_a, \quad (2)$$

where A is some constant with the unit of energy and

$$\langle \dots \rangle_a = Q_a^{-1} \int \dots e^{-\beta H_a(\mathbf{q})} d\mathbf{q}. \quad (3)$$

Further, Q_a is the corresponding partition function and the standard free energy in each oxidation state is $F_{0a} = -\beta^{-1} \ln[Q_a]$; $\beta = (k_B T)^{-1}$ is the inverse temperature.

The statistical average in Eq. (2) satisfies the following identity

$$\langle \delta(X - \Delta H(\mathbf{q})) \rangle_2 = e^{\beta(\Delta F_0 - X)} \langle \delta(X - \Delta H(\mathbf{q})) \rangle_1 \quad (4)$$

where $\Delta F_0 = F_{02} - F_{01}$ is the reaction free energy. Expressed in terms of the free energies $F_a(X)$ this result transforms to the linear relationship between the free energy surfaces^[32]

$$F_2(X) = F_1(X) + X. \quad (5)$$

This relation, when strictly enforced, severely limits potential functionalities that can describe free energy surfaces for electron transfer. The Marcus parabolas

$$F_a(X) - F_{0a} = \frac{(X - X_a)^2}{4\lambda} \quad (6)$$

satisfy the linear relation provided that the distance between the minima of the parabolas X_a is equal to twice the reorganization energy, $|X_1 - X_2| = 2\lambda$. The free energy surfaces produced by the Q-model discussed below also satisfy the linear relation. An

equally accurate formulation is attainable for the binding model of electron transfer considering local binding/unbinding events (telegraphic noise^[33]) as a part of the fluctuation spectrum of the medium.^[34]

The physical meaning of the linear relation between $F_a(X)$ [Eq. (5)] is the law of conservation of energy. Since electronic transitions are instantaneous on the nuclear time-scale (Frank-Condon principle), the configuration and the entropy of the system do not change in the transition. The difference of free energies at any given X is, therefore, the energy supplied to allow the transition between the states (e.g., the energy of a photon), which is the energy X . When $X = 0$, the transition is radiationless, and this is the transition state for the electron-transfer reaction. The rates of reactions from right to left and from left to right through $X = 0$ should satisfy the detailed balance, which imposes another exact constraint between the activation barriers ΔF_a^\ddagger for the forward and backward reactions

$$\Delta F_1^\ddagger - \Delta F_2^\ddagger = \Delta F_0. \quad (7)$$

Since for electron transfer the activation barrier is given by the vertical separation of the activated state and the minimum of the free energy surface, $\Delta F_a^\ddagger = F_a(0) - F_{\min,a}$ and $F_1(0) = F_2(0)$, this relation also implies

$$\Delta F_{\min} = \Delta F_0. \quad (8)$$

This equation implies that the shift^[35] between $F_{\min,a}$ and F_{0a} should cancel in the difference.

The reaction free energy is also related to the electrode overpotential η

$$\Delta F_0 = e\eta. \quad (9)$$

Equation (9) is the Nernst equation^[1] connecting ΔF_0 to the electrode overpotential and, through detailed balance in Eq. (7), to the reaction barriers for cathodic and anodic processes. Negative overpotential $\eta < 0$ favors the cathodic (reduction) process, while the anodic (oxidation) reaction dominates at $\eta > 0$. We now turn to a specific model for electrode reactions in which the manifold of the nuclear degrees of freedom \mathbf{q} is replaced with two nuclear modes, the vector field of the medium nuclear polarization density \mathbf{P} and a scalar coordinate q representing a low-frequency intramolecular vibrational mode.

3 Theory

We consider a reactant placed into a polarizable medium which develops the polarization density field $\mathbf{P}(\mathbf{r})$ in response to the electric field of the solute $\mathbf{E}_a(\mathbf{r})$. The linear response is given by the local susceptibility χ , which neglects the non-local microscopic correlations in the liquid.^[36] This form is adopted here for simplicity and can always be lifted to extend the model to more realistic calculations based on structural properties of polar liquids.^[37] In this simplified formulation, the Hamiltonian of the polarizable medium containing the solute is given by the following equation

$$H_P^{(a)}[\mathbf{P}] = I_a - \mathbf{E}_a * \mathbf{P} + \frac{1}{2\chi} \mathbf{P} * \mathbf{P}, \quad (10)$$

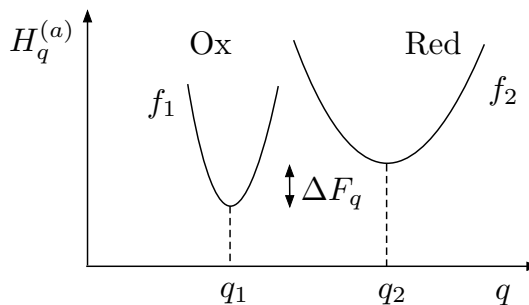


Fig. 1 Schematic representation of the potential energy surfaces [Eq. (11)] along the vibrational coordinate q ($1 \equiv \text{Ox}$ and $2 \equiv \text{Red}$). Indicated in the plot are the different force constants of vibrations f_a , the position of parabolae minima $q_a = C_a/f_a$ (Eq. (11)) and the free energy gap ΔF_q (Eqs. (12) and (13)) vertically separating the minima.

where the asterisk is used to denote both the tensor contraction and integration of the corresponding fields over the volume occupied by the polar medium. Further, I_a denotes the gas-phase energy of the reactant and all solvation free energies due to electronic polarizability of the solvent. Because of this separation, the term $-\mathbf{E}_a * \mathbf{P}$ describes the interaction of the reactant with the nuclear polarization of the medium.^[5]

As explained above, we assume that the structure of the medium is not affected by the electric field of the reactant and the susceptibility χ does not depend on the reactant's oxidation state. On the contrary, the force constant f_a of the local low-frequency (classical) vibration is altered by changing the oxidation state and thus carries the subscript a in the quadratic term of the vibrational Hamiltonian

$$H_q^{(a)}(q) = -C_a q + \frac{1}{2} f_a q^2. \quad (11)$$

The linear and quadratic terms here can be associated with the corresponding expansion terms of the potential energy $U(q)$ of the local vibrational coordinate q : $U(q) = U(0) + (\partial U/\partial q)q + \dots$

The schematic representation of our model of localized intramolecular vibrations is shown in Fig. 1. We thus consider two parabolic potential energy surfaces $H_q^{(a)}(q)$ with unequal curvatures and with minima at $q_a = C_a/f_a$. The minima are vertically displaced by the difference of free energies corresponding to the vibrational coordinate

$$\Delta F_q = F_{q2} - F_{q1}. \quad (12)$$

Here, we have included the common vibrational entropy term in the free energy of the vibrational coordinate

$$F_{qa} = -C_a^2/(2f_a) + k_B T \ln[\omega_a], \quad (13)$$

where $\omega_a^2 \propto f_a$ is the square of the vibrational frequency. The entropic term of course does not appear in the Hamiltonian function and instead comes from the statistical average over the coordinate q discussed below. It is incorporated directly in the vertical shift of the potential energies for convenience. The corresponding entropic contributions are therefore omitted when performing the statistical average over the intramolecular vibrations.

Combining the medium polarization and the intramolecular vi-

brational mode, the total system Hamiltonian in our model is

$$H_a[\mathbf{P}, q] = H_P^{(a)}[\mathbf{P}] + H_q^{(a)}(q). \quad (14)$$

Correspondingly, the energy gap between the reduced ($a = 2$) and oxidized ($a = 1$) states is a function of two nuclear coordinates which are constrained to satisfy Eq. (1). One gets

$$\Delta H[\mathbf{P}, q] = \Delta H[\mathbf{P}] + \Delta H(q), \quad (15)$$

where

$$\Delta H[\mathbf{P}] = \Delta I - \Delta \mathbf{E} * \mathbf{P}, \quad (16)$$

$$\Delta H(q) = -\Delta Cq + \frac{1}{2}\Delta f q^2,$$

$$\Delta C = C_2 - C_1, \Delta f = f_2 - f_1, \text{ and } \Delta \mathbf{E} = \mathbf{E}_2 - \mathbf{E}_1.$$

The major distinction of Eqs. (15) and (16) from the standard Marcus model of internal reorganization^[27] appears in Eq. (16) in the form of the linear-quadratic dependence of $\Delta H(q)$ on the vibrational coordinate q (in contrast to a linear dependence in the Marcus theory). In the case of multiple normal modes of vibrations, this functionality is isomorphic to Duschinsky effect^[7,38] in which the normal modes of two electronic states of a molecule are related by a linear shift-rotation transformation.

For reductive electrode reactions $\text{Ox} + e \rightarrow \text{Red}$, the final reduced state corresponds to the electron localized on the reactant with the gas-phase energy $I_2 = I_{\text{Red}}$ and the initial state corresponds to the reactant with the gas-phase energy $I_1 = I_{\text{Ox}}$ and the electron in the conduction state of the metal with the energy $\varepsilon_k = \bar{\mu}_m + \varepsilon$, where $\bar{\mu}_m$ is the electrochemical potential of the metal electrons. We therefore have for ΔI in Eq. (16)

$$\Delta I = I_2 - I_1 - \bar{\mu}_m - \varepsilon. \quad (17)$$

The offset ε is used below in the calculation of the electrode reaction rate, where integration over the conduction states of the metal populated according to the Fermi-Dirac distribution is performed.

We further assume that the fluctuations of the medium polarization are statistically independent from fluctuations of the nuclear coordinate q , which essentially implies that $\Delta \mathbf{E}$ is independent of q .^[28] The additivity of the Hamiltonian implies that the Boltzmann factor $e^{-\beta F_a(X)}$ can be cast as the convolution of probabilities along coordinates \mathbf{P} and q . Specifically, one writes

$$\langle \delta(X - \Delta H[\mathbf{P}, q]) \rangle_{\mathbf{P}, q, a} = \int_{-\infty}^{\infty} dy \langle \delta(X - y - \Delta H[\mathbf{P}]) \rangle_{\mathbf{P}, a} \langle \delta(y - \Delta H(q)) \rangle_{q, a}. \quad (18)$$

The first angular bracket represents the standard Marcus model [Eq. (6)] and is given by the Gaussian distribution

$$G_P^{(a)}(X - y) = \langle \delta(X - y - \Delta H[\mathbf{P}]) \rangle_{\mathbf{P}, a} \propto \exp \left[-\frac{\beta(X - y - \langle X \rangle_a)^2}{4\lambda_M} \right], \quad (19)$$

where

$$\lambda_M = (\chi/2)\Delta \mathbf{E} * \Delta \mathbf{E} \quad (20)$$

is the standard Marcus reorganization energy of a polar medium,^[3] the minima are equal to the averages $X_a = \langle X \rangle_a$ (cf. to Eq. (6)), and

$$\langle X \rangle_a = \Delta I + \Delta F_P \pm \lambda_M. \quad (21)$$

Here, the upper sign (+) and the lower sign (−) refer, respectively, to reduction/oxidation and $\Delta F_P = F_{P, \text{Red}} - F_{P, \text{Ox}}$ is the difference of solvation free energies due to the nuclear polarization of the medium in the reduced and oxidized states of the reactant.

The second bracket in Eq. (18) represents the novel component of the present theory, applying the framework of the Q-model to the energy gap which is linear-quadratic in the nuclear coordinate q . The statistical average over the nuclear coordinate q depends on the oxidation state, as reflected by the subscript a . We now turn our attention to the calculation of this function.

3.1 Intramolecular vibrational mode

Here we address the calculation of the distribution of the component of the reaction coordinate relevant to the classical, low-frequency vibrations of the reactant. The distribution of the vibrational component of the energy gap convoluting with the corresponding distribution due to the medium polarization in Eq. (18) is given by the following equation

$$G_q^{(a)}(y) = \langle \delta(y - \Delta H(q)) \rangle_{q, a}. \quad (22)$$

This function is conveniently written as the Fourier integral involving the cumulant-generating function $A_a(\xi)$

$$G_q^{(a)}(y) = \beta \int_{-\infty}^{\infty} \frac{d\xi}{2\pi} \exp[i\xi\beta y + A_a(\xi)], \quad (23)$$

where

$$e^{A_a(\xi)} = \left\langle e^{-i\xi\beta\Delta H(q)} \right\rangle_{q, a}. \quad (24)$$

The cumulant generating function $A_a(\xi)$ determines the statistics of the stochastic variable y . This implies that successive cumulants of y are given as the derivatives of $A_a(\xi)$

$$\langle (\delta y)^n \rangle_a = \left(\frac{i}{\beta} \right)^n \frac{\partial^n A_a(\xi)}{\partial \xi^n} \Big|_{\xi=0}, \quad (25)$$

where $\delta y = y - \langle y \rangle_a$. Only two cumulants, the first, $\langle y \rangle_a$, and the second, $\langle \delta y^2 \rangle_a$, are non-zero for the Gaussian statistics of y . This latter case corresponds to the Marcus treatment of internal reorganization, when intramolecular vibrations provide an additional source of Gaussian fluctuations of the energy gap and the outer and inner reorganization energies simply add up.^[27] In the present model of intramolecular vibrations allowing a change of the vibrational force constant (frequency), the statistics of y is non-Gaussian. This is seen directly from performing the statistical average over the variable q in Eq. (24), which leads to the following cumulant generating function^[26]

$$A_a(\xi) = -i\xi\beta Y_0 - \frac{\beta\xi k_a^2}{\xi - i\kappa_a} \lambda_{qa}, \quad (26)$$

with parameters defined below.

It is easy to see that an infinite series of derivatives in Eq. (25) can be produced from Eq. (26), implying an infinite series of cumulants contributing to $A_a(\xi)$. One therefore expects a non-Gaussian form for the function $G_a(y)$, which can indeed be obtained in the closed form^[26,28]

$$G_q^{(a)}(y) = \frac{\beta e^{-\beta \kappa_a^2 \lambda_{qa}/2}}{2 \sinh(\beta \kappa_a^2 \lambda_{qa}/2)} \sqrt{\frac{|\kappa_a|^3 \lambda_{qa}}{|y - Y_0|}} \times e^{-\beta |\kappa_a| |y - Y_0|} I_1 \left(2\beta \sqrt{|\kappa_a|^3 \lambda_{qa} |y - Y_0|} \right). \quad (27)$$

Here, $I_1(x)$ is the modified Bessel function of the first order.^[39] Before turning to a general theory combining both polarization and vibrational coordinates into one formalism, we first discuss the parameters entering Eqs. (26) and (27) and some physical consequences of altering the force constant of intramolecular vibrations.

The most important parameter in the theories of activated electron-transfer reactions is the reorganization energy. The Q-model predicts a major change from the Marcus model in this regard since, instead of a single reorganization energy characterizing both oxidation states, two intramolecular (vibrational) reorganization energies $\lambda_a = \beta \langle \delta y^2 \rangle_a / 2$ appear in Eq. (26)

$$\lambda_{q1} = \frac{1}{2} (f_2^2 / f_1) \Delta q^2, \quad \lambda_{q2} = \frac{1}{2} (f_1^2 / f_2) \Delta q^2, \quad (28)$$

where $\Delta q = q_2 - q_1$ is the separation between the parabolas' minima along the q -coordinate (Fig. 1). Further, in Eq. (27), the parameters

$$\kappa_a = f_a / \Delta f \quad (29)$$

quantify the relative change in the vibrational force constants; $\kappa_a \rightarrow \infty$ corresponds to $\Delta f = 0$ and the return to the Gaussian statistics of the variable y .

Figure 2 illustrates the results of the model. It shows the free energy surfaces $g_a(y) = -\beta^{-1} \ln[G_a(y)]$ along the vibrational component of the energy gap y . They obtained by an asymptotic expansion of $G_a(y)$ in Eq. (27) at values of y sufficiently far from Y_0 and given by the relation

$$g_a(y) - F_{qa} = \left(\sqrt{|\kappa_a| |y - Y_0|} - \sqrt{\kappa_a^2 \lambda_{qa}} \right)^2, \quad (30)$$

where F_{qa} is given by Eq. (13).

The free energy surfaces are obviously non-parabolic, with a linear tail at one side of the minimum y_a and a limiting value Y_0 (fluctuation boundary) on the other side of the minimum. The latter is given by the expression

$$Y_0 = \Delta F_q - \frac{f_1 f_2}{2 \Delta f} \Delta q^2. \quad (31)$$

The appearance of this parameter in the theory is related to the linear-quadratic dependence of y on the vibrational coordinate q : $y = -\Delta C q + (1/2) \Delta f q^2$. Because of the parabolic form of this function, possible values of y are restricted from above by parabola's maximum at $\Delta f < 0$ and from below by parabola's minimum at

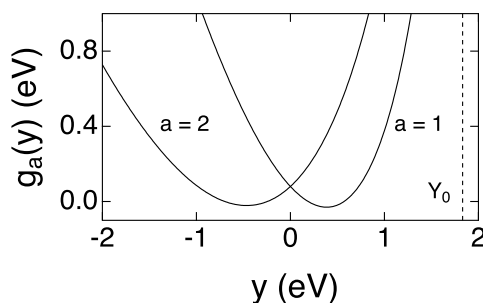


Fig. 2 $g_a(y) = -\beta^{-1} \ln[G_q^{(a)}(y)]$ calculated from Eq. (27) at $\lambda_{q1} = 0.3$ eV, $\lambda_{q2} = 0.6$ eV, and $\Delta F_q = 0$. The vertical dashed line marks the position of the fluctuation boundary Y_0 in Eq. (31). The probability of reaching $y > Y_0$ is identically zero in the Q-model.

$\Delta f > 0$. Based on this constraint, we have

$$\begin{aligned} y < Y_0 & \text{ at } \Delta f < 0, \\ y > Y_0 & \text{ at } \Delta f > 0. \end{aligned} \quad (32)$$

Since the regions of y outside these intervals cannot be reached, one gets an infinite value of the free energy at Y_0 and zero probability $G_q^{(a)}(y) = 0$ for reaching the forbidden regions

$$g_a(Y_0) = \infty. \quad (33)$$

Despite a number of parameters used for algebraic convenience in Eqs. (27), (30), and (31), the free energy surfaces $g_a(y)$, and all corresponding observables, depend on three parameters only: two reorganization energies λ_{qa} and the free energy difference ΔF_q (Fig. 1). This needs to be contrasted with the standard Marcus formulation, such as in Eq. (6), which depends on two parameters: the free energy difference and a single reorganization energy. The complication of altering vibrational force constant thus adds one additional theory parameter, the second reorganization energy. In turn, the reorganization energies are expressed in terms of the vibrational force constants by Eq. (28). Further, the parameters κ_a , given in terms of the force constants by (29), can be also fully specified in terms of λ_{qa} by the following equation

$$\kappa_1^{-1} = (\lambda_{q1} / \lambda_{q2})^{1/3} - 1, \quad \kappa_2 = \kappa_1 + 1. \quad (34)$$

In the numerical examples and figures below we, therefore, distinguish vibrations in different oxidation states by specifying the corresponding reorganization energies instead of force constants. Along the same lines, the parameter Y_0 in Eq. (31) can be rewritten as

$$Y_0 = \Delta F_q - \text{sign}(\Delta f) [\lambda_{q1} \lambda_{q2} \kappa_1 \kappa_2]^{1/2}. \quad (35)$$

When $\kappa_a \rightarrow \infty$, the fluctuation boundary shifts to infinity, $|Y_0| \rightarrow \infty$, and becomes irrelevant.

The free energy surfaces $g_a(y)$ are plotted in Fig. 2 at $\lambda_{q1} \neq \lambda_{q2}$ and $\Delta F_q = 0$. We use a hypothetical example of $\lambda_{q1} = 0.3$ eV and $\lambda_{q2} = 0.6$ eV, which corresponds to $\Delta f < 0$ and $Y_0 = 1.8$ eV. The functions $g_a(y)$ are clearly non-parabolic, while satisfying the fundamental constraints given by Eqs. (5) and (7). The average

values $\langle y \rangle_a$ satisfy the relation

$$\langle y \rangle_a = \Delta F_q \pm \lambda_{qa} \kappa_a / (\kappa_a \pm 1), \quad (36)$$

where κ_a are given through Eq. (34) or, alternatively, in terms of the vibrational force constants in Eq. (29). Further, similarly to Eq. (21), +/− refer, respectively, to reduction/oxidation. Because the free energy surfaces are asymmetric in respect to mirror reflections about their minima, the minima y_a are distinct from the averages $\langle y \rangle_a$.

The difference of the average values $\langle y \rangle_a$, an analog of the Stokes shift in spectroscopy, carries a clear physical meaning of the internal reorganization energy characterized by the mean vibrational force constant

$$\bar{\lambda}_q = \frac{1}{2} |\langle y \rangle_1 - \langle y \rangle_2| = \frac{1}{2} \bar{f} \Delta q^2 \quad (37)$$

where $\bar{f} = (f_1 + f_2)/2$. Alternatively to this definition, an effective “symmetric” internal reorganization energy

$$\lambda_i = [(f_1 f_2) / (f_1 + f_2)] \Delta q^2 \quad (38)$$

was suggested by Marcus^[27] and Kuznetsov^[40] to incorporate the alteration of the vibrational frequencies. This form of the internal reorganization energy, which is distinct from the standard Marcus reorganization energy of the polarizable medium λ_M [Eq. (20)], does not appear in the exact solution presented here. Instead, $\bar{\lambda}_q$ plays the role of an effective vibrational (internal) reorganization energy in our formulation.

3.2 Free energy surfaces

The convolution of the probability densities $G_{P,q}^{(a)}$ along the coordinate y in Eq. (18) can be calculated numerically or, alternatively, approximated analytically by assuming a Gaussian shape for the function $G_q^{(a)}$. In the latter case, the convolution of two Gaussian functions is given by a Gaussian function. The resulting free energy surfaces do not exactly satisfy the linear relation in Eq. (5), but nevertheless provide a reasonable numerical solution of the problem with two classical nuclear modes activating electron transfer. They are given by the relation similar to Eq. (6), where the curvature of the free energy surface gains a dependence on the oxidation state through the corresponding dependence of the vibrational reorganization energies in Eq. (28)

$$F_a(X) - F_{0a} = \frac{(X - X_a)^2}{4\lambda_a}. \quad (39)$$

In this equation,

$$\lambda_a = \lambda_M + \lambda_{qa} \quad (40)$$

and

$$X_a = \langle X \rangle_a + \langle y \rangle_a. \quad (41)$$

Here, $\langle X \rangle_a$ and $\langle y \rangle_a$ are given by Eqs. (21) and (36), respectively. Combining these equations, we obtain

$$X_a(\eta) = e\eta \pm \lambda_M \pm \lambda_{qa} \kappa_a / (\kappa_a \pm 1), \quad (42)$$

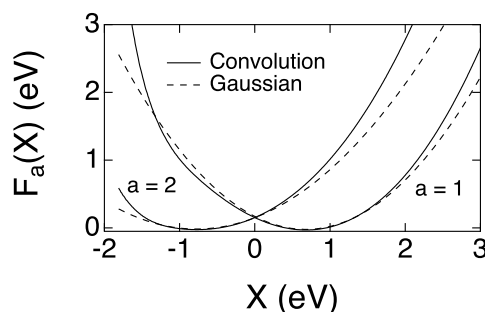


Fig. 3 Free energy surfaces for electron transfer calculated from the direct numerical convolution in Eq. (18) (solid lines) and from the effective Gaussian approximation leading to Eq. (39) (dashed lines). The reorganization energies adopted in the calculations are: $\lambda_M = 0.3$ eV, $\lambda_{q1} = 0.3$ eV, and $\lambda_{q2} = 0.6$ eV; $\Delta F_0 = 0$.

where $e\eta = \Delta F_0 = \Delta I + \Delta F_P + \Delta F_q$ is the total reaction free energy [Eq. (9)] including the free energy due to internal vibrations and the free energy of solvation by both electronic and nuclear polarization of the medium.

Combining Eqs. (21) and (37), we conclude that half of the separation between the minima of the free energy surfaces is the sum of the Marcus reorganization energy for the medium polarization and the reorganization energy $\bar{\lambda}_q$ given in terms of the mean vibrational force constant [Eq. (37)]

$$\frac{1}{2} |X_1 - X_2| = \lambda_M + \bar{\lambda}_q. \quad (43)$$

On the contrary, the curvatures of the effective parabolas are given by λ_a specified by Eqs. (40) and (28).

One expects that inaccuracies introduced by replacing the exact $G_q^{(a)}(y)$ with its Gaussian approximation in the convolution integral are insignificant when reorganization due to solvent polarization dominates. On the other hand, when $\lambda_M \approx \lambda_{qa}$ non-quadratic shape of the free energy surfaces $g_a(y)$ can affect $F_a(X)$. This less favorable for our approximation case is shown in Fig. 3 where we use $\lambda_M = \lambda_{q1} = 0.3$ eV and $\lambda_{q2} = 0.6$ eV, as adopted in Fig. 2. This extent of deviation between the internal reorganization energies in different oxidation states was reported for the $\text{Cr}(\text{edta})^{-2-}$ redox pair.^[12] Even in this case of relatively low λ_M , the effective Gaussian approximation used in deriving Eq. (39) is still quite accurate, in particular in the region between the minima X_a ,^[41] which is of primary significance for determining the activation barrier.

3.3 Electrode currents

A significant advantage of the effective Gaussian solution in Eq. (39) is that it allows one to use the standard set of tools developed over the years to calculate the electrode currents from the picture of crossing parabolas.^[2,18,42] In the limit of weak electronic coupling between the reactant and the conduction electronic states of the metal, the rate constant is found by integrating the golden-rule transition rates to individual conduction states with the Fermi-Dirac distribution of the conduction elec-

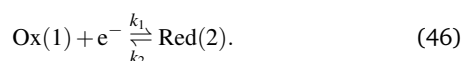
trons^[18,42–46]

$$k_a(\eta) = \frac{\Delta}{\hbar} \left(\frac{\beta}{\pi\lambda_a} \right)^{1/2} \int_{-\infty}^{\infty} e^{-\beta\Delta F_a^\ddagger(\eta-\varepsilon/e)} f_F(\pm\varepsilon) d\varepsilon. \quad (44)$$

Here, $f_F(\varepsilon) = [\exp(\beta\varepsilon) + 1]^{-1}$ is the Fermi-Dirac population function and $\Delta = \pi V^2 \rho_F$;^[25,47,48] V is the electron-transfer matrix element between the electronic state on the reactant and a single electronic state in the metal and ρ_F is the density of states at the metal's Fermi level. Further, $\Delta F_a^\ddagger = F_a(0) - F_{0a}$ in Eq. (44) is the activation barrier

$$\Delta F_a^\ddagger(\eta) = [X_a(\eta)]^2 / (4\lambda_a), \quad (45)$$

where $X_a(\eta)$ is from Eq. (42) and λ_a is from Eq. (40). Finally, similarly to Eqs. (21) and (36), $a = 1, +$ and $a = 2, -$ refer, respectively, to reduction and oxidation. The rate constants in Eq. (44) are therefore assigned to the following half reaction



The linear shift in the function $X_a(\eta - \varepsilon/e)$ with the offset energy ε in Eq. (44) originates from the corresponding shift of the energy of the conduction electron from the electrochemical potential of the metal in Eq. (17). When $\Delta f \rightarrow 0$, $\kappa_a \rightarrow \infty$ [Eq. (29)], one arrives at the standard Marcus solution

$$\Delta F_{M,a}^\ddagger(\eta) = (e\eta \pm \lambda)^2 / (4\lambda), \quad (47)$$

where

$$\lambda = \lambda_M + \bar{\lambda}_q \quad (48)$$

is the total reorganization energy due to classical nuclear modes including the medium polarization (λ_M) and intramolecular vibrations ($\bar{\lambda}_q$). The latter is equivalent to λ_i in Eq. (38) in this limit.

Integration over the conduction electrons can be performed numerically in Eq. (44) or through a number of analytical approximations.^[44,48] When $\beta\lambda_a \gg 1$, the Fermi-Dirac population $f_F(\varepsilon)$ can be taken at zero temperature,^[47,49] yielding the rate in terms of the complementary error function^[39]

$$k_a(\eta) = \frac{\Delta}{\hbar} \operatorname{erfc} \left([\beta\Delta F_a^\ddagger(\eta)]^{1/2} \right). \quad (49)$$

As is shown by the blue lines in Fig. 4, this approximation is very reasonable for typical parameters encountered in electrochemistry (exact integration in Eq. (44) is shown by the black lines).

Figure 4 shows the cathodic and anodic currents calculated from Eq. (44) for the reorganization parameters used in Fig. 3 (solid lines). It is clear that the model leads to asymmetry between the cathodic and anodic branches with respect to the sign change $\eta \rightarrow -\eta$. Formal Tafel slopes are calculated as the derivatives of ΔF_a^\ddagger with respect to $\pm e\eta$ (equivalent to Eqs. (9.4) and (9.5) in Ref. 47). The transfer coefficient at $\eta = 0$ can be alternatively calculated as the first-order coefficient in the series expansion of $\Delta F^\ddagger(\eta)$ in Eq. (45) in the powers of η . The result is given

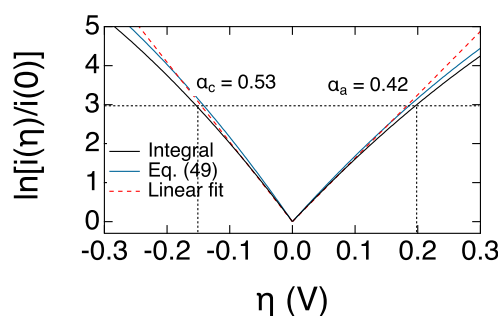


Fig. 4 Cathodic (left) and anodic (right) currents vs the electrode overpotential η calculated from Eq. (44) (black lines) and from Eq. (49) (blue lines). The red dashed straight lines are extensions of the linear curves found at small $|\eta|$, corresponding to the transfer coefficients $\alpha_c = \alpha_1 = 0.53$ and $\alpha_a = \alpha_2 = 0.42$ for the cathodic and anodic currents, respectively [Eq. (50)]. The reorganization parameters are the same as in Fig. 3. The vertical and horizontal dotted lines are drawn to visualize the asymmetry of cathodic anodic current branches.

by the following equation

$$\alpha_a(\eta = 0) = \frac{1}{2} \mp \frac{\lambda_{qa}}{2\lambda_a} \frac{1}{\kappa_a \pm 1}, \quad (50)$$

where, for guidance, upper and lower signs are combined with $a = \text{Ox}$ and $a = \text{Red}$, respectively. The values obtained, which are distinct for reduction and oxidation, define the slopes for small deviations from $\eta = 0$, as indicated in Fig. 4. A higher reorganization energy in the reduced state ($\lambda_{q2} = 0.6$ eV) compared to the oxidized state ($\lambda_{q1} = 0.3$ eV) leads to an effectively lower transfer coefficient for the anodic current. We note that the condition $\alpha_{\text{Ox}}(0) + \alpha_{\text{Red}}(0) = 1$ is not exactly satisfied in Eq. (50) because of the approximation used in solving the convolution over the coordinate y in Eq. (18). Direct integration in Eq. (18) leads to fully consistent results since both the Gaussian solution for the polarization coordinate \mathbf{P} and the Q-model for the coordinate q are exact.

Compton and co-workers,^[23] motivated by earlier work of Marcus,^[27] have proposed a correction to the activation barrier caused by changes in intramolecular vibrational force constants. Their definition of the intramolecular reorganization energy is based on the Marcus expression in Eq. (38), while only the mean $\bar{\lambda}_q$ given by Eq. (37) appears in our theory. Following previous work,^[23,27] we define the asymmetry parameter $\gamma = (\bar{\lambda}_q/\lambda)\Delta f/(2\bar{f})$, in which λ is given by Eq. (48). Note that our γ is the negative of the parameter used in Ref. 23 since the convention $\Delta f = f_2 - f_1 = f_{\text{Red}} - f_{\text{Ox}}$ is adopted here. The parameter in Ref. 23 also does not involve the sign alteration in the Marcus parameter^[27] $l_s = (f_r - f_p)/(2\bar{f})$ (“r” and “p” are for the reactant and products, respectively), which changes sign depending on whether reduction or oxidation reaction is considered. Independently of the definition, the first-order expansion of the activation free energy is linear in $\Delta f \propto \gamma \propto l_s$. In order to calculate this linear term, we expand our solution for the activation barrier in Eq. (45) in series of powers of κ_a^{-1} assuming that the relative change of the vibrational force constant is small, $\Delta f \ll f_a$. When

the expansion is truncated after the first order in γ , we obtain

$$\Delta F_a^\ddagger(\eta) = \Delta F_{M,a}^\ddagger(\eta) \mp \gamma \frac{(e\eta \pm \lambda)(3e\eta \pm \lambda)}{4\lambda}, \quad (51)$$

where $\Delta F_{M,a}^\ddagger(\eta)$ is the Marcus solution given by Eq. (47).

The first-order expansion term is different from the Compton *et al* result,^[23] which should read in our notation $-\gamma(e\eta/4)[1 - (e\eta/\lambda)^2]$. Our expansion in Eq. (51) shares, however, a problem present in their solution: the activation barrier becomes negative in some limits (e.g., when “-” at $\eta \rightarrow \infty$ is taken in Eq. (51)), as identified by Bazant and co-workers.^[16] This difficulty does not appear in our solution given by Eqs. (44) and (45). The integral over the energies of the conduction electrons of the metal in Eq. (44) is well-defined. It is also important to note that the term of the first-order in γ disappears from the formula by Compton *et al*,^[23] at $\eta = 0$ (similarly through first order in γ to Eq. (A13) in Ref. 27). This disappearance of the first-order in $\gamma \propto \Delta f$ correction implies no skewness (asymmetry in respect to reflection about the minimum) of the free energy surfaces at $\eta = 0$. This outcome is not shared by the present exact solution since skewness is present in the Q-model (Fig. 2). The first-order correction to the Marcus result is non-vanishing and is equal to $\mp(\gamma/4)\lambda$ at $\eta = 0$ [Eq. (51)].

4 Discussion

Activation of chemical reactions occurs by rare events of barrier crossing promoted by fluctuations of the thermal bath. The rare character of such fluctuations implies that many particles should be involved in the delivery of the thermal energy and one might anticipate that central-limit theorem should apply. The result is the dominance of Gaussian statistics describing activated events. This indeed turns out to be the case for electron-transfer reactions driven by fluctuations of the medium polarization. The statistics of these collective fluctuations is well described by the Gaussian distribution, as successfully captured by the Marcus theory. The probability of reaching the activation barrier much higher than $k_B T$ is governed by the fast decaying Gaussian tail. This picture, while quite reasonable from the basic principles, could be detrimental for the design of artificial and natural systems transporting electrons through molecular arrays: the activation barrier grows too fast with the driving force when moving away from the top activationless rate. One therefore wonders if there are potential mechanisms to counter the design deficiencies associated with the Gaussian statistics and to produce “fat tails” deviating from the fast probability decay of the Gaussian distribution.

A potential recipe applicable to the transfer of electron in molecular systems is to replace the noise produced by a collective Gaussian bath with a set of local variables, which do not have to follow the central-limit theorem. The standard formulation of the theory convolutes the collective medium polarization with the long-ranged electrostatic field of the solute. Even though one might think of such variables as local, the long range character of both the electric field and the medium polarization combine into Gaussian fluctuations of the electron-transfer vertical energy gap viewed as the reaction coordinate. An alternative approach is to “localize” the response even stronger by adding the polariz-

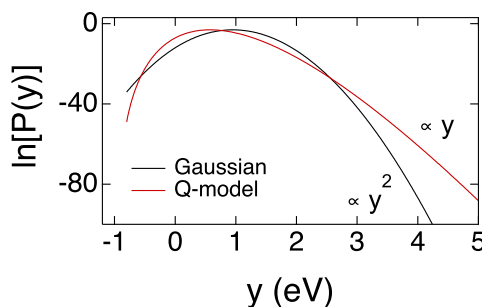


Fig. 5 Gaussian (black) and Q-model (red) distributions $P(y)$ along the reaction coordinate y . $\ln[P(y)]$ has a harmonic $\propto y^2$ (Gaussian) asymptote at $y \gg 1$, while the Q-model has a linear asymptote $\propto y$. The calculations for the Q-model are done at $\kappa = 1.5$; $\kappa \rightarrow \infty$ corresponds to the Gaussian distribution.

ability of the solute, as was recognized in the construction of the Q-model. This alteration of the physical model makes the vertical energy gap a non-Gaussian variable with a physically distinct statistics of fluctuations: the probability of reaching a large value of the energy gap decays exponentially with the driving force, instead of the quadratic exponential decay of the Gaussian distribution (Fig. 5). This advantage applies mostly to the inverted region of electron transfer, but it also changes the energetics of the model, requiring now two reorganization energies instead of one in the standard models. However, the main fundamental accomplishment of the new perspective is in changing the statistics of the energy gap fluctuations and producing much higher probabilities of rare events (linear decay in place of the Gaussian quadratic decay).

The strategy of introducing local nuclear modes and electronic energies nonlinear in bath coordinates to defeat the central limit theorem must be a general principle. Obviously, local low-frequency vibrations are a good candidate in this general design scheme. This possibility is explored here, where we have analyzed a fairly old suggestion that a change in the frequencies of localized vibrations can occur upon electron transfer. The vertical energy gap between the reactant electronic states then becomes a linear-quadratic function of the vibrational coordinate described by the Q-model.

As we have mentioned in the text above, deviations from the standard Gaussian picture of crossing parabolas have appeared in the literature.^[20–24] Among possible candidates for the theory application is oxygen reduction, currently actively studied,^[50] particularly in application to Li-air batteries.^[51] Electrochemical reduction of oxygen in ionic liquids shows high asymmetry between the cathodic and anodic branches.^[52] In addition, anomalously low transfer coefficients were reported for oxygen reduction.^[52,53] The electrode reduction occurs to a chemisorbed oxygen molecule with altered bond distance and potential change of the force constant depending on the oxidation state.^[54] The quantum character of oxygen vibration precludes, however, a direct application of the present theory, which is limited to the classical domain of frequencies.

The theory proposed here employs a convolution of the Gaus-

sian statistics of the standard models with the non-Gaussian statistics linked to localized vibrations. The result is an analytical model predicting the activation barrier of electrode reactions based on three reorganization energies: the reorganization energy of the Gaussian bath (medium polarization here) and two reorganization energies describing the non-Gaussian statistics of the Q-model type (local vibrations here). It is obvious that the physical meaning of these two types of nuclear modes does not constrain the formalism and the model can be extended to any problem where a combination of a Gaussian and non-Gaussian components of the thermal bath affecting electronic transitions need to be involved.

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