

Symmetry or asymmetry of k_{ET} and i_{STM} vs. potential curves

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The symmetry or asymmetry of STM current vs. bias potential and of electron transfer (ET) rate vs. overpotential curves is discussed for ET and for STM patterns across ordered monolayers. The superexchange expression for the electronic coupling matrix element, the Fermi–Dirac distribution and, for the ET reaction, the reorganization, are included. A mean potential approximation is assumed for the effect of bias or overpotential on the electronic orbitals or the ordered monolayer. Consequences for the symmetry vs. asymmetry of the $\ln(k_{\text{ET}})$ vs. overpotential and for the $\ln(i_{\text{STM}})$ and pattern vs. bias are described. Examples of some relevant experiments are considered.

1. Introduction

In some processes at electrodes the electron transfer proceeds across an ordered monolayer, adsorbed or chemically attached to the electrode. Such systems include electron transfer rates across an alkanethiol layer to a gold electrode.¹ They also include scanning tunnelling microscopy of organic monolayers, the electron transfer now being between a tip and the substrate electrode.^{2,3} In each case a superexchange mechanism utilizes the electronic orbital of the monolayer. One question which arises is how the potential drop between the two ‘reactants’ affects the behaviour. We explore this question and its implications for both sets of experiments, particularly with respect to symmetry toward the sign of the bias potential or overpotential.

The theoretical interpretation of the electron transfer (ET) rate vs. overpotential and the STM current vs. bias potential curves across monolayers has much in common. In ET reactions, energy conservation for the ET is assured, regardless of the intrinsic affinity of the electron or hole for each site, by fluctuations in the environment. These fluctuations lead to the exponential factors contained in eqn. (1), (8) and (10) below. As a result of this energy conservation condition, and of the restrictions imposed by the Fermi–Dirac factors in eqn. (8) and (10), most of the electron or hole transfer goes into or comes from an energy level in the electrode close to the Fermi level. Outside the ‘normal region’ ($|e\eta| > \lambda$ in those equations) the electron or hole goes into levels distant from the Fermi level, to avoid the ‘inverted effect.’ On the other hand, in STM, energy conservation at a substantial bias potential is assured by the electron or hole always going into the distant levels. Nevertheless, we shall see that in theoretical terms the two experiments are related. There will be some difference, it will be seen, in the behaviour of the superexchange electronic coupling elements, as a consequence of the difference in the energy-conservation mechanism described above.

In treating the intervening monolayer the analysis below includes a summation over all the filled and unfilled electronic orbitals of the monolayer. It includes, thereby, electron transfer *via* the unoccupied orbitals, hole transfer *via* the occupied ones, or both. We treat the electronic coupling occurring *via* a superexchange mechanism, as in eqn. (11) and (19) below.

2. Electron transfers at an electrode

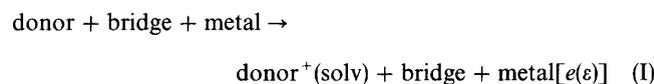
We first recall the intramolecular non-adiabatic expression for electron transfer between a donor, D, and an acceptor, A, each

at a fixed site in solution. The high-temperature limit is given by⁴

$$k_{\text{rate}} = \frac{2\pi}{\hbar} |H_{\text{DA}}|^2 \frac{1}{(4\pi\lambda k_{\text{B}} T)^{1/2}} \times \exp[-(\lambda + \Delta G^\circ)^2/4\lambda k_{\text{B}} T] \quad (1)$$

where the symbols have their customary significance. H_{DA} is the matrix element for transfer between a quantum electronic state of the donor, D, and a quantum electronic state of the acceptor, A, λ is the reorganization energy, and ΔG° is the standard Gibbs energy of reaction. Eqn. (1), and thereby eqn. (8) given later for electrode systems, make the approximation that there is no asymmetry in the reorganizational effects. We comment on this approximation in the Discussion section. It has no effect, we shall see, on the symmetry question at large overpotentials.

We consider the modification of eqn. (1) for an electron transfer reaction at an electrode. An expression for the non-adiabatic electron transfer rate constant can be obtained using arguments related to those used in ref. 5 to obtain an expression for the STM current (Please note some differences in notation, *e.g.*, in STM, $\eta = -v$ and $\bar{\mu} = \mu$ there.) We consider the reaction



where the energy, ε , is defined below. For simplicity of notation and presentation, we take D to be fixed to the solution side of the monolayer, and examine the energetics first. The results are readily extended to Ds that move in solution, just as eqn. (1) can be extended.

We consider the Gibbs energy change $\Delta G^\circ(\varepsilon, \eta)$ associated with reaction (I) for entering the metal (potential, ϕ_{m}) into an electronic orbital that has an energy ε with respect to the Fermi level $\bar{\mu}_{\text{m}}$. This $\Delta G^\circ(\varepsilon, \eta)$ is given by

$$\Delta G^\circ(\varepsilon, \eta) = \bar{\mu}_{\text{m}} + \varepsilon + \bar{\mu}_{\text{D}^+} - \bar{\mu}_{\text{D}} \quad (2)$$

where $\bar{\mu}_{\text{D}^+} - \bar{\mu}_{\text{D}}$ is the difference in electrochemical potential of D^+ and of D at the D site, for the prevailing electrolyte. We have

$$\begin{aligned} \bar{\mu}_{\text{m}} &= \mu_{\text{m}} - e\phi_{\text{m}} \equiv \bar{\mu}_{\text{m}}^\circ - e(\phi_{\text{m}} - \phi_{\text{m}}^\circ); \\ \bar{\mu}_{\text{D}^+} - \bar{\mu}_{\text{D}} &= \mu_{\text{D}^+} - \mu_{\text{D}} + e\phi_{\text{s}} \equiv \bar{\mu}_{\text{D}^+}^\circ - \bar{\mu}_{\text{D}}^\circ + e(\phi_{\text{s}} - \phi_{\text{s}}^\circ) \end{aligned} \quad (3)$$

where ϕ_s is the potential on the solution side at the D site and the $^\circ$ superscript on the $\bar{\mu}$ denotes a value for which the ϕ has been replaced by ϕ° .

We denote the overpotential by η , defined by

$$\eta = \phi_m - \phi_s - (\phi_m^\circ - \phi_s^\circ) \quad (4)$$

Here, $\phi_m^\circ - \phi_s^\circ$ is the potential difference which makes the $\Delta G^\circ(\varepsilon, \eta)$ in eqn. (2) vanish at $\varepsilon = 0$, and so

$$\bar{\mu}_m^\circ + \bar{\mu}_{D^+}^\circ = \bar{\mu}_D^\circ \quad (5)$$

The $\phi_m^\circ - \phi_s^\circ$ is the absolute 'standard' potential difference. From eqn. (2)–(5) we have

$$\Delta G^\circ(\varepsilon, \eta) = \varepsilon - e\eta \quad (6)$$

To obtain the electrochemical rate constant using eqn. (1) and (6) we use arguments similar to those given in ref. 5 for STM. The details are given elsewhere.⁶ Using eqn. (1) with eqn. (6), introducing the appropriate Fermi–Dirac weighting factor, and integrating over all states $|\mathbf{k}\rangle$, we have

$$k_{\text{rate}} = \frac{2\pi}{\hbar} \frac{1}{(4\pi\lambda k_B T)^{1/2}} \times \int |V(\varepsilon)|^2 \exp[-(\lambda - e\eta + \varepsilon)^2/4\lambda k_B T] \times \frac{\exp(\varepsilon/k_B T)}{1 + \exp(\varepsilon/k_B T)} d\varepsilon \quad (7)$$

where $|V(\varepsilon)|^2$ is an abbreviation for

$$|V(\varepsilon)|^2 = \int |\langle D | H | \mathbf{k} \rangle|^2 \delta(\varepsilon_k - \varepsilon) d\mathbf{k} \quad (8)$$

The last factor in eqn. (7) is the Fermi–Dirac distribution function for the probability that a state of energy ε is unoccupied. The wavefunctions $|\mathbf{k}\rangle$ in eqn. (8) are normalized to a Dirac delta function, $\langle \mathbf{k} | \mathbf{k}' \rangle = \delta(\mathbf{k} - \mathbf{k}')$.^{5,7} Eqn. (7) can also be derived using a formula⁸ for the crossing of a dense set of states by a single state. The details are given elsewhere.⁶

For the rate constant of the reverse reaction k_{rate}^r we have

$$k_{\text{rate}}^r = \frac{2\pi}{\hbar} \frac{1}{(4\pi\lambda k_B T)^{1/2}} \times \int |V(\varepsilon)|^2 \exp[-(\lambda + e\eta - \varepsilon)^2/4\lambda k_B T] \times \frac{1}{1 + \exp(\varepsilon/k_B T)} d\varepsilon \quad (9)$$

since the ΔG° for the step is $e\eta - \varepsilon$, i.e., is opposite in sign from before, and one uses the Fermi–Dirac factor for the probability distribution that a state of energy ε is occupied. The $|V(\varepsilon)|^2$ is again given by eqn. (8).

We consider next the superexchange expression for $H_{D\mathbf{k}}$ (i.e., for $\langle D | H | \mathbf{k} \rangle$). These matrix elements are

$$H_{D\mathbf{k}} = \sum_{\beta} H_{D\beta} H_{\beta\mathbf{k}} / \Delta E_{\beta} \quad (10)$$

where $H_{D\beta}$ is the matrix element coupling D to β , $H_{\beta\mathbf{k}}$ couples β to $|\mathbf{k}\rangle$, β is the β th orbital of the monolayer (the bridge), and ΔE_{β} is a vertical energy difference in the transition state. We discuss ΔE_{β} next.

To this end we consider the Gibbs energy vs. reaction coordinate q diagram in Fig. 1, which describes a reaction involving transfer of an electron from D to an electronic orbital of energy ε in the metal M, i.e., reaction (I). Curves I, II and III describe the left side of reaction (I), the right side of reaction (I), and the off-resonant (superexchange) system denoted by $D + B^-$ (unsolv) + M, respectively. The Gibbs energies $G(q)$

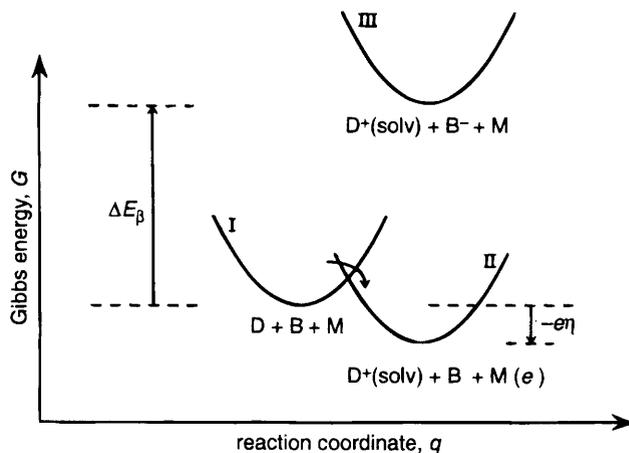


Fig. 1 Plot of Gibbs energy vs. reaction coordinate for the left-hand side of reaction (I) (curve I), the right-hand side (curve II) and the superexchange off-resonant state (curve III) where $B^-(\beta)$ indicates that the electron is in the orbital β of the bridge.

for I and II as a function of q can be written as

$$G_I(q) = G_D(q) + E_D \quad (11)$$

$$G_{II}(q, \varepsilon) = G_{D^+}(\text{solv}, q) + e\phi_s + \bar{\mu}_m + \varepsilon \quad (12)$$

In these equations, E_D is the energy of the electronic orbital of D with respect to vacuum (and so is negative); $G_D(q)$ is, apart from E_D , the Gibbs energy of D as a function of q ; $G_{D^+}(\text{solv}, q)$ is the solvation free energy of D^+ as a function of q , and the other symbols have been defined earlier. The sum $G_D(q) + E_D$, at the equilibrium value of q for the left side of reaction (I) is μ_D , while $G_{D^+}(\text{solv}, q)$ at the equilibrium value of q for the right side of reaction (I) is μ_{D^+} . A general definition of the reaction coordinate q for electron transfer processes is given in ref. 9. In eqn. (11), D is taken as uncharged. If, instead, it has a charge e' , a term $e'\phi_s$ is added to the right hand sides of eqn. (11) and (12) and to (13) below. It cancels in eqn. (14), given below, for ΔE_{β} .

The bridge B becomes a B^- in its supercharge state (or B^+ in the case of hole transfer) but because of the off-resonance this supertransient B^- is treated here as unsolvated, omitting at this time the question of an 'electronic solvation' of the electron in B^- by the remaining electrons in the system. In writing an expression for G_{III} , some estimate must be made of the effect of the electrostatic potential on the energy levels β of the monolayer B. If the potential change $\phi_m - \phi_s$ occurs almost entirely across B, rather than between B and the solution, then a first approximation would be to treat the electrons of B as being in a mean applied electrostatic potential $\frac{1}{2}(\phi_m + \phi_s)$. We comment in the Discussion section on the nature of this approximation and how it can be tested by a more detailed analysis of the effect of bias potential on the energies of the bridge orbitals.

We now have, from this last approximation,

$$G_{III}(q, \varepsilon, \beta) = G_{D^+}(\text{solv}, q) + e\phi_s + E_{\beta}^\circ - \frac{e}{2}(\phi_m + \phi_s) \quad (13)$$

where E_{β}° is the energy of the β orbital of B in the absence of the potentials.

The vertical difference between I and III, denoted by ΔE_{β} in Fig. 1, constitutes the denominator in the superexchange expression, eqn. (10). In the transition state $q = q^\ddagger$ it is seen from eqn. (3), (12) and (13) to be

$$\begin{aligned} \Delta E_{\beta}(q^\ddagger) &= G_I(q^\ddagger) - G_{III}(q^\ddagger) = G_{II}(q^\ddagger) - G_{III}(q^\ddagger) \\ &= \mu_m + \varepsilon - E_{\beta}^\circ - \frac{e}{2}(\phi_m^\circ - \phi_s^\circ) - \frac{1}{2}e\eta \end{aligned} \quad (14)$$

upon using the equality $G_i(q^\dagger) = G_{\text{II}}(q^\dagger)$. To obtain a useful expression for ΔE_β it was desirable to obtain a quantity, as in right side of eqn. (14), not explicitly dependent on q^\dagger , since q^\dagger is a function of η . It is seen that ΔE_β can be calculated from eqn. (14), using the energy of the LUMO of the bridge (one value of E_β°) relative to vacuum, the work function of the electrode ($-\mu_m$) relative to vacuum, the absolute standard metal-solution potential difference ($\phi_m^\circ - \phi_s^\circ$) of the electrode and the overpotential, η .

We consider next the question of symmetry or asymmetry of the rate expression in eqn. (7) and (9). Specifically, we compare the $\ln(k_{\text{rate}})$ vs. $e|\eta|$ and the $\ln(k_{\text{rate}}^r)$ vs. $-e|\eta|$ curves. It is seen from these equations that a change in the sign of η in eqn. (9) and a comparison of the result with eqn. (7) would yield

$$k_{\text{rate}}(\eta) \cong k_{\text{rate}}^r(-\eta) \quad (15)$$

if the effect of overpotential on H_{Dk} were neglected. However, we have already seen some effect of η on ΔE_β [eqn. (14)] and hence on H_{Dk} [eqn. (10)], and so there will be some deviation from the equality embodied in eqn. (15). We comment on this in the Discussion. There could also be some effect on $|H_{\beta k}|$ in eqn. (10). However, as we discuss in the next section, this latter dependence might be relatively small when one considers how the individual $|H_{\beta k}|$ values differ from each other. A detailed calculation of $|H_{\beta k}|$, coupled with the averaging appearing in eqn. (7) and (8), will permit this effect to be calculated.

3. STM expression

The net tip t to substrate electrode m current is given in ref. 5 as

$$i = \frac{2\pi e}{\hbar} \iint d\mathbf{k}_m d\mathbf{k}_t |H_{\text{mt}}(\mathbf{k}_m, \mathbf{k}_t)|^2 \times [f(\varepsilon_t) - f(\varepsilon_m)] \delta(\varepsilon_t - \varepsilon_m + e\eta) \quad (16)$$

where η is now the bias potential,

$$\eta = (\phi_m - \phi_t) - (\phi_m^e - \phi_t^e) \quad (17)$$

and the \mathbf{k} values refer to the respective electrodes. The superscript e in eqn. (17) indicates the ϕ value at zero bias potential. The $f(\varepsilon)$ is again the Fermi-Dirac distribution function (for t or m). The electronic coupling element, H_{int} , for a superexchange mechanism, is now given by

$$H_{\text{mt}}(\mathbf{k}_m, \mathbf{k}_t) = \sum_\beta H_{\text{m}\beta} H_{\beta t} / (E_t - E_\beta) \quad (18)$$

i.e., is given by the analogue of eqn. (10). $E_t = E_m$ in this denominator.

When the bias potential is changed, the value of $E_t - E_\beta$ is also changed. As a first approximation, we again assume that the monolayer is, on the average, at an electrostatic potential $\frac{1}{2}(\phi_m + \phi_t)$, *i.e.*, is the mean of the values at m and t. We again consider a superexchange mechanism for the transfer: $\text{TBM} \rightarrow (\text{T}^+\text{B}^-\text{M}) \rightarrow \text{T}^+\text{BM}^-$ where the electronic configuration in parentheses is off-resonance from the other two. We now have for the $E_t - E_\beta$ in eqn. (18),

$$E_t - E_\beta = [\mu_t - e\phi_t + \varepsilon_t] - [E_\beta^\circ - \frac{1}{2}e(\phi_t + \phi_m)] \\ = \mu_t - E_\beta^\circ + \varepsilon_t - \frac{e}{2}(\phi_t - \phi_m) \quad (19)$$

To see the effect of bias potential it is desirable to re-express eqn. (19) in a more symmetrical way. The ε_t and ε_m are related by

$$\bar{\mu}_t + \varepsilon_t = \bar{\mu}_m + \varepsilon_m \quad (20)$$

where the $\bar{\mu}$ values are again the electrochemical potentials, $\bar{\mu}_i = \mu_i - e\phi_i$ ($i = \text{t, m}$). In terms of the superscript e notation

in eqn. (17) we have $\bar{\mu}_m^e = \bar{\mu}_t^e$. From eqn. (19) and (20) we obtain the desired symmetric expression

$$E_t - E_\beta = \frac{1}{2}(\mu_t + \mu_m + \varepsilon_t + \varepsilon_m) - E_\beta^\circ \quad (21)$$

According to the delta function constraint in eqn. (16) a change in the sign of η is equivalent to interchanging the energies ε_t and ε_m and so to changing the sign of the term in square brackets in eqn. (16). Furthermore, it is seen from eqn. (21) that the denominator $E_t - E_\beta$ in eqn. (18) is unchanged in sign when ε_m and ε_t are interchanged. However, what is affected is the selection of ε_m and of ε_t values and thereby of \mathbf{k}_m and \mathbf{k}_t values. For the forward current (negative $e\eta$), the sampling is of \mathbf{k}_t with negative ε_t (occupied orbitals of the tip), while for the reverse bias the sampling is mainly, instead, of \mathbf{k}_t whose ε_t is positive (unoccupied orbitals of the tip). If we can neglect the dependence of the product $H_{\text{m}\beta} H_{\beta t}$ in eqn. (18) on this difference in sampling then it follows that

$$i(\eta) \cong i(-\eta) \quad (22)$$

As we discuss elsewhere,⁶ if the individual $H_{\beta t}$ matrix elements differ mainly in the phases associated with modulation factors such as $\exp(i\mathbf{k}_\parallel \cdot \mathbf{r}_i) \sin k_z z_i$ at each electrode site i in the state $|\mathbf{k}_t\rangle$, [$\mathbf{k}_t \equiv (k_\parallel, k_z)$], where k_\parallel and k_z are components of \mathbf{k}_t], then the $|H_{\beta t}|^2$ may be relatively insensitive to the difference in the ε_t samples at the two biases. A similar remark applies to the sampling of the $|\mathbf{k}_m\rangle$ values and hence to $|H_{\text{m}\beta}|^2$.

Discussion

In the above treatment only systems where there is no appreciable actual charge transfer between electrode and monolayer are considered. The approximation of a mean potential $\frac{1}{2}(\phi_m + \phi_s)$ acting on the monolayer orbitals, made in the calculation of ΔE_β , is examined next. The electric field due to the applied potential causes both a first-order and a second-order Stark effect on the energy levels of a molecule in the adsorbed monolayer. The first-order effect arises from the static charge distribution in the molecule interacting with the applied electrostatic potential function, and the second-order effect arises from the electronic polarization of the molecule by the field. When the extra electron in B is in the β th orbital, the second-order effect on ΔE_β arises from the polarizability of that orbital. We omit it, for the present, in comparison with the first-order effect. The first-order effect can be estimated by modifying, in an extended-Hückel calculation for example, the coulombic integral of each atom in the bridge molecule by an amount $-e\phi(\mathbf{r}_i)$ due to the applied potential $\phi(\mathbf{r}_i)$ at the site \mathbf{r}_i of that atom, and then calculating the new orbital energies of the molecule. As an initial approximation these $\phi(\mathbf{r}_i)$ values are replaced above by a mean value $\frac{1}{2}(\phi_m + \phi_s)$. This assumption, made in obtaining eqn. (10) in the present paper, can be tested by calculating the change in ΔE_β using the individual $\phi(\mathbf{r}_i)$ values to calculate the change in energy of each orbital β .

We have already mentioned that a possible asymmetry in the reorganization of the system, *e.g.*, due to a difference in vibrational force constants of corresponding vibrational modes of the oxidized and the reduced forms, was omitted in eqn. (1) and (7). (It is included for the force constants in ref. 13.) Any such effect would cause the electrochemical transfer coefficient at $\eta = 0$ to differ from the value of 0.5. At large values of η , both positive and negative, however, the effect of this asymmetry would disappear. The limiting rate constant does not involve any reorganization, and so in this region any difference in limiting rate constants at $+|\eta|$ and $-|\eta|$ would only reflect a dependence on the $|V(\varepsilon)|^2$ in eqn. (8)–(10) on the sign of η . Another potential source of asymmetry is the difference in the local electrostatic field around the site D due to the electrolyte, at $+|\eta|$ compared with $-|\eta|$. Any such effect

should again not affect the limiting k_{rate} values at large $|\eta|$. A comparison of experimental results for these two limiting k_{rate} values, namely at large $|\eta|$ and large $-|\eta|$, is therefore of special interest.

In summary, we have seen that in the ET rate *vs.* overpotential curve one expects a symmetry of k_{rate} values *vs.* $e|\eta|$, apart from any asymmetry caused by a dependence on the $|H_{\text{mt}}|$ values on η , *e.g.*, in the energy denominator in eqn. (14), and apart from other possible sources of asymmetry mentioned above. It should perhaps also be stressed that if the most important ΔE_{β} values are large, the effect of the $\frac{1}{2}e\eta$ term in eqn. (14) for ΔE_{β} would be relatively small.

In ref. 1(a)–(c) the $\ln(k_{\text{rate}})$ *vs.* $|\eta|$ [compared with $\ln(k_{\text{rate}}^r)$ *vs.* $-|\eta|$] showed an approximate symmetry, but there was some asymmetry. It will be interesting to see whether this behaviour is paralleled by that in other experimental systems and whether it is due to the small asymmetry represented by the η terms in eqn. (14). With the introduction of a detailed electronic coupling model¹⁰ for the monolayer, the donor and the electrode, the results in the present equations can be applied to the system in a quantitative way.

Turning next to STM, as the STM tip moves over the ordered monolayer, the H_{mt} will change, primarily because of a change in the value of the $H_{\beta\text{t}}$ in eqn. (16). Nevertheless, because of the symmetry in eqn. (22), there will correspondingly also be the same STM pattern, for a given $|\eta|$ regardless of the sign of η , according to the present results. This symmetry presumes an insensitivity of the $|H_{\text{m}\beta}|^2$ and $|H_{\beta\text{t}}|^2$ to the different sampling of $|k_{\text{m}}\rangle$ and of $|k_{\text{t}}\rangle$ at $+|\eta|$ and $-|\eta|$, as noted in the previous section.

In a recent study of STM pattern of monolayers of many organic molecules with various functional groups,³ this symmetry of STM pattern was observed for all cases but one. The STM current *vs.* overpotential curve also obeyed eqn. (22) approximately. The possible insensitivity of the squares of the matrix elements to η , discussed earlier, may be a key factor, as noted earlier, in the observed symmetry.

One further experimental result is that in ref. 3 the STM current is linear at low $|\eta|$ but for the system examined it showed a rapid increase at an η of about 0.5 eV. This behaviour may reflect either the onset of a decreased denominator in eqn. (18) or the contribution of another graphite band. Further experiments will help resolve this question.

It is a pleasure to dedicate this article to Roger Parsons, whose clear article¹¹ on electrified interfaces considerably facilitated my adapting to electrochemistry in 1957¹² some ideas that I had developed in the previous year for electron transfers in solution. I have acknowledged this special help in my Nobel address.¹⁴ It is a pleasure too, to acknowledge also

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