Overpotential-induced lability of the electronic overlap factor in long-range electrochemical electron transfer: charge and distance dependence

Alexei A. Kornyshev,[ab] Alexander M. Kuznetsov,[b] Jens U. Nielsen[c] and J. Ulstrup[c]

[a] *Institut für Werkstoffe und Verfahren in der Energietechnik, Forschungszentrum Jülich, D-52425 Jülich, Germany*
[b] *The A.N. Frumkin Institute of Electrochemistry of the Russian Academy of Sciences, Leninskij prospect 31, Moscow 117071, Russia*
[c] *Department of Chemistry, Technical University of Denmark, DK-2800 Lyngby, Denmark*

Long-distance electrochemical electron transfer exhibits approximately exponential dependence on the electron transfer distance. On the basis of a jellium model of the metal surface we show that the slope of the logarithm of the current *vs.* the transfer distance also depends strongly on the electrode charge. The slope is smaller the more negative the charge density due to enhanced extension of the surface electronic density profile on the solution side, and thereby better electronic overlap with the reacting molecule. The effect is sensitive to the bulk electron density of the metal and the localization of the electronic state at the molecular reactant site. Effects similar to these have been observed experimentally and could be common for electronically light metals.

1. Introduction

The electronic tunnel factor in *homogeneous* long-range electron transfer (ET) processes has been in strong focus over the last decade.[1–7] Attention to the tunnel factor in *interfacial* electrochemical ET and *in situ* scanning tunnel microscopy (STM) has been less intense primarily due to the exclusive electronic and molecular structure of the electrode/electrolyte interface. Well characterized long-range electrochemical ET systems have, however, been reported recently. Systems based on self-assembled monolayers of functionalized aliphatic thiols[8–14] are central, where the length and chemical nature can be varied, to give currents spanning many orders of magnitude. This has also warranted new theoretical efforts in the area of long-range electrochemical ET.

Following an early suggestion[15] we have investigated the variation of the electrochemical tunnel factor at jellium-like metals with the excess electrode charge density.[16] The electronic jellium cloud at a given distance was found to follow the charge of the electrode, increasing on the solution side when charging is negative relative to the potential of zero charge (pzc), and contracting into the metal on positive charging. This lability is reflected in the electron exchange factor, facilitating tunnelling on the negative side of the pzc and impeding tunnelling on the positive side. The effects were found to be insignificant for contact ET distance but significant compared to the potential or charge dependence of the *nuclear* activation factor for longer-range ET and lower-electron density metals such as silver. The effect is small for electronically high-density metals such as gold and mercury.

The overpotential-induced electron tunnel lability effect has recently been addressed experimentally.[17,18] The electrochemical reduction of Zn^{2+} at In- and Tl-amalgam electrodes,[17] where the excess surface charge density can be controlled by the amalgam composition, is composed of two steps, *i.e.* Zn^{2+} is first reduced to Zn^+ on the solution side, followed by reductive amalgamation of Zn^+. The electro-chemical rate constant of the first step displays excess surface charge dependence following qualitatively the views in ref. 16. This system is not, however, a case for long-range ET and the observed effect is likely to have a different origin. The $[Cr(EDTA)]^- \rightarrow [Cr(EDTA)]^{2-}$ reduction at Hg-, Bi- and Cd-electrodes has also been reported to depend exponentially on the excess negative electrode surface charge, after correction for double layer effects.[18] This system is closer to the notion of long-range electrochemical ET as the metal centre is here spatially separated from the electrode by the voluminous ligand group.

In the light of such new perspectives for observation of quantum mechanical electrochemical charge lability, we provide some new theoretical results, addressing particularly the distance variation of the electrochemical current at jellium-like metals at different surface charge densities. We also rectify a few formal inconsistencies in the previous report.[16]

2. Jellium charge lability and electrochemical currents

The cathodic diabatic current density at the overvoltage η is[4–7,16,19,20]

$$j = eC\delta a \int \rho(\varepsilon) f(\varepsilon) W(\varepsilon; \eta) \, d\varepsilon \qquad (1)$$

where C is the concentration of the discharging (oxidized) molecule, e the electronic charge, δa a narrow distance range perpendicular to the surface, and $\rho(\varepsilon)$ the metallic electronic level density at the energy ε, $f(\varepsilon) = [1 + \exp(\varepsilon - \varepsilon_F)/k_B T]^{-1}$ is the Fermi function, ε_F the Fermi energy, k_B Boltzmann's constant and T the temperature. $W(\varepsilon; \eta)$ is the quantum mechanical transition probability per unit time for ET from a given level ε to the molecule. In terms of the widely used representation where nuclear reorganization involves displacement in a set of harmonic molecular and linear solvent modes $W(\varepsilon; \eta)$

takes the form[4−7,16,20]

$$W(\varepsilon; \eta) = [T_{\varepsilon A}]^2 \left(\frac{\pi}{E_r k_B T \hbar^2}\right)^{1/2} \exp\left(-\frac{G_c^{\neq}}{k_B T}\right)$$

$$G_c^{\neq} = \frac{[E_r + e\eta - (\varepsilon - \varepsilon_F)]^2}{4E_r} \qquad (2)$$

where E_r is the nuclear reorganization Gibbs free energy, $T_{\varepsilon A}(\varepsilon; \eta)$ the electron exchange factor coupling the level ε to the molecular acceptor level "A", and $2\pi\hbar$ Planck's constant.

$T_{\varepsilon A}(\varepsilon; \eta)$ incorporates the electronic wavefunctions of the metallic, $\psi_\varepsilon(x, R; \varepsilon; \eta)$, and molecular levels $\Psi_{mol}(x, R)$

$$T_{\varepsilon A} \approx V_{\varepsilon A} \int \psi_\varepsilon(x, R; \varepsilon; \eta)\Psi_{mol}(x, R) \, dx \, dR \qquad (3)$$

where x is the space coordinate perpendicular to the electrode and R the lateral coordinate, $V_{\varepsilon A}$ is the physical perturbation which induces the transition.

Following ref. 16 the overlap integral can be recast in terms of the electronic *densities*

$$M(\varepsilon; \eta) = \left| \int \psi_\varepsilon(x, R; \varepsilon; \eta)\Psi_{mol}(x, R) \, dx \, dR \right|^2$$

$$\approx (\Delta x)^2 \Delta R(\Delta R/\Delta \tilde{R})\Omega(x^*)\,|\,\psi_\varepsilon(x^*; \varepsilon; \eta)\,|^2 \qquad (4)$$

where $\Omega(x^*)$ is the density (length^{-1}) of the molecular electronic structure

$$\Omega(x^*) \approx |\,\Psi_{mol}(x, R^*)^2\,|\,\Delta\tilde{R} \qquad (5)$$

x^* in eqn. (4) is the value of x where the integrand is maximum and Δx (approximately coinciding with δa in eqn. (1)) the effective width of the x-integration. The definitions of R^* and ΔR are analogous regarding the lateral coordinate while $\Delta\tilde{R}$ is the extension of the molecular electronic distribution. Altogether the electronic factor $[T_{\varepsilon A}(\varepsilon; \eta)]^2$ is

$$[T_{\varepsilon A}(\varepsilon; \eta)]^2 \approx (V_{\varepsilon A})^2 M(\varepsilon; \eta) \approx (V_{\varepsilon A})^2(\Delta x)^2 \, \Delta R\Omega(x^*)$$

$$\times |\,\psi_\varepsilon(x^*; \varepsilon; \eta)\,|^2(\Delta R/\Delta\tilde{R}) \qquad (6)$$

A measure of the *metallic* electronic density at the energy ε (energy^{-1} length^{-3}) is

$$n(x; \varepsilon; \eta) = \rho(\varepsilon)f(\varepsilon)\,|\,\psi_\varepsilon(x, R^*; \varepsilon; \eta)\,|^2 \qquad (7)$$

The *total* density (length^{-3}), to be represented by a density functional such as jellium, is

$$n(x; \eta) = \int d\varepsilon n(x; \varepsilon; \eta) \approx \Delta\varepsilon n(x; \varepsilon^*(x); \eta) \qquad (8)$$

where ε^* is the maximum of $n(x; \varepsilon; \eta)$ and a principal ε^*-dependence on x is indicated. $\Delta\varepsilon$ is the width of $n(x; \varepsilon; \eta)$ around the maximum.

The current is then

$$j_c = eC\delta a \left(\frac{\pi}{E_r k_B T\hbar^2}\right)^{1/2} (\Delta x)^2 \Delta R(\Delta R/\Delta\tilde{R})\Omega(x^*)$$

$$\times \int d\varepsilon (V_{\varepsilon A})^2 n(x^*; \varepsilon^*; \eta)\exp\left[-\frac{G_c^{\neq}(\varepsilon; \eta)}{k_B T}\right]$$

$$\approx eC\delta a(V_{\varepsilon*A})^2 \left(\frac{\pi}{E_r k_B T\hbar^2}\right)^{1/2} (\Delta x)^2 \Delta R(\Delta R/\Delta\tilde{R})\Omega(x^*)$$

$$\times (\delta\varepsilon/\Delta\varepsilon)n(x^*; \varepsilon^*; \eta)\exp\left[-\frac{G_c^{\neq}(\varepsilon^*; \eta)}{k_B T}\right] \qquad (9)$$

where $\delta\varepsilon$ is the effective interval in the ε-integration. In general, $\varepsilon^* \neq \varepsilon_F$ and $\delta\varepsilon \neq \Delta\varepsilon$. Conversion back to integral form gives

$$j_c \approx eC\delta a(V_{\varepsilon*A})^2 \left(\frac{\pi}{E_r k_B T\hbar^2}\right)^{1/2} (\delta\varepsilon/\Delta\varepsilon)M(\eta)$$

$$\times \exp\left[-\frac{G_c^{\neq}(\varepsilon^*; \eta)}{k_B T}\right] \qquad (10)$$

The density overlap function $M(\eta)$ (dimensionless) now takes the form

$$M(\eta) \approx \Delta x\Delta R(\Delta R/\Delta\tilde{R})(\Delta x/\Delta\tilde{x}) \int dx\Omega(x)n(x; \eta) \qquad (11)$$

where $\Delta\tilde{x}$ is the effective extension of the x-integration in eqns. (10) and (11). In terms of the original electron exchange integral the current is

$$j_c \approx eC(\delta a)(\delta\varepsilon)\rho(\varepsilon_F)f(\varepsilon_F)\left(\frac{\pi}{E_r k_B T\hbar^2}\right)^{1/2} [T_{\varepsilon F A}]^2$$

$$\times \exp\left[-\frac{G_c^{\neq}(\varepsilon_F; \eta)}{k_B T}\right] \qquad (12)$$

Eqns. (9), (10) and (12) represent the general current–voltage form and eqn. (11) the electronic density overlap. These forms rectify eqns. (12)–(16) in ref. 16.

$M(\eta)$ can be given a simple form by using specific electronic density representations. The following exponential form is suitable for the *molecular* part

$$|\,\Psi_{mol}(x, R; a)\,|^2 = \frac{\gamma^3}{8\pi} \exp\{-\gamma[R^2 + (x - a)^2]\} \qquad (13)$$

corresponding to

$$\Omega(x; a) = \tfrac{1}{4}\gamma(1 + \gamma\,|\,x - a\,|)\exp(-\gamma\,|\,x - a\,|) \qquad (14)$$

where a is the centre of localization of the reacting molecule and γ the orbital decay factor. The *metallic* density is suitably
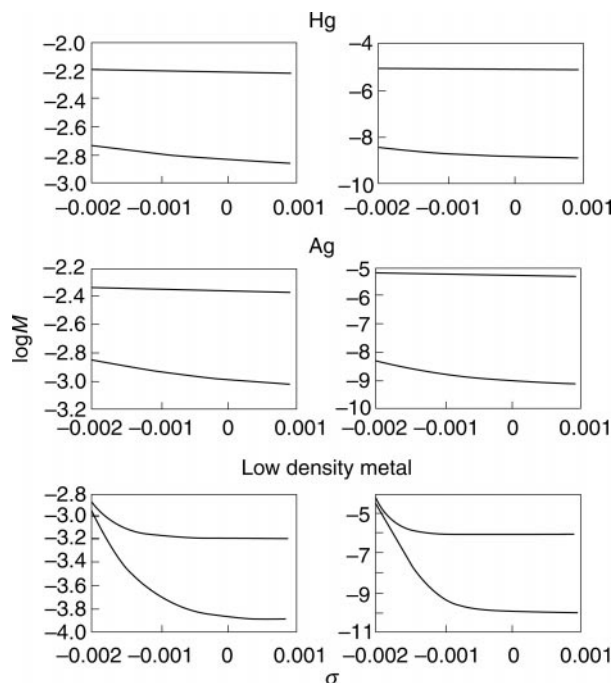

Fig. 1 Dependence of the electron density overlap $M(\eta)/\Delta x\Delta R$ ($\Delta R = \Delta\tilde{R}$ and $\Delta x = \Delta\tilde{x}$ in all the figures) on the electrode surface charge density σ (1 au $= 5.695 \times 10^3$ μC cm^{-2}), calculated from eqn. (17) for three metals (the low density corresponds to caesium). The lability coefficients are taken from ref. 22. Left column: "short-range": $a = 4.5$ a_0 (≈ 2.2 Å). Right column: "long-range: $a = 20$ a_0 (≈ 10 Å). Upper lines: electronic localization at the metal ($\gamma = 0.5$ au). Lower lines: electronic localization at the molecule ($\gamma = 1.0$ au).
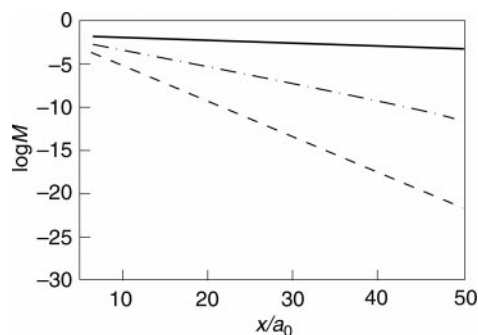
Fig. 2 The dependence of the electron density overlap $M(\eta)/\Delta x\Delta R$ (eqn. (17)) on the ET distance for uncharged silver for different degrees of localization of the wavefunction on the site of the discharging molecule. (———): $\gamma = 0.1$ au; (– · – · –): $\gamma = 0.5$ au (– – –): $\gamma = 1$ au.

represented by jellium density functionals of which the simplest is[16,21]

$$n(x; \eta) = n_+\{1 - \tfrac{1}{2}\exp[\beta(x - \bar{x})]\}\theta(\bar{x} - x) + \tfrac{1}{2}n_+$$

$$\times \exp[\beta(\bar{x} - x)]\theta(x - \bar{x}); \quad \bar{x} = -\frac{\sigma}{n_+} \quad (15)$$

where n_+ is the bulk density and σ the electrode charge density.† $\theta(x)$ is the step function, i.e. $\theta(x) = 1$ for $x > 1$ and 0 for $x < 1$. In the following we use atomic units ($e = m_e = \hbar = 1$, m_e being the electron mass). Both the jellium *front*, $\bar{x}$, and the *width* β^{-1} depend, moreover on the electrode charge or overpotential, by expansions such as[22]

$$\beta = \beta_0 + a\sigma + b\sigma^2 + d\sigma^3 \quad (16)$$

which give a much stronger jellium lability than the constant term β_0 alone. Analytical expressions for β_0 and the expansion coefficients a, b and d for metal/vacuum are available[22] but
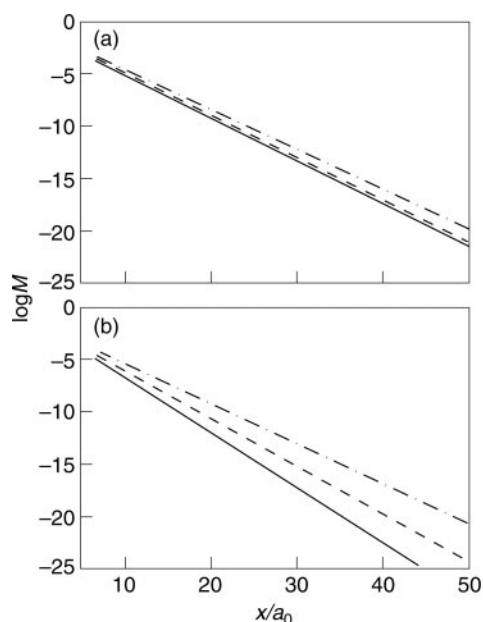

Fig. 3 The effect of excess electrode surface charge density on the distance relation for different localization degrees at the discharging molecule. The charge density corresponds to silver. (———): $\sigma = 0$. (– – –): $\sigma = -1 \times 10^{-3}$ au. (– · – · –): $\sigma = -2 \times 10^{-3}$ au. (a) $\gamma = 1$ au. (b) $\gamma = 2$ au.

† 1 au = 5.695×10^3 μC cm^{-2}.

the *procedure* can be brought to incorporate dielectric screening, pseudopotentials, etc.[23,24]

Eqns. (14) and (15) give, finally for $M(\eta)$

$$M(\eta) = \Delta x\Delta R(\Delta R/\Delta\tilde{R})(\Delta x/\Delta\tilde{x})\frac{n_+}{4(p^2 - 1)^2}$$

$$\times \{2\exp[-\beta(a - \bar{x})] + p^2\{(p^2 - 1)[\gamma(a - \bar{x}) + 2] - 2\}$$

$$\times \exp[-\gamma(a - \bar{x})]\}; \quad p = \beta/\gamma \quad (17)$$

This form replaces eqn. (20) in the previous report.[16]

3. Charge and distance dependence of the electrochemical electronic density overlap

Overvoltage variation affects the activation Gibbs free energy in eqns. (2), (9) and (12). The tunnel factor is *also* affected, *via* the jellium response to the surface charge density variation. The latter effect is summarized in Fig. 1. Ag and Hg are chosen as representatives of two common electrode materials of intermediate (8.73×10^{-3} au) and high (12.8×10^{-3} au) electron density, respectively, while the density corresponding to Cs (1.33×10^{-3} au) is the lowest jellium density available. Jellium lability is insignificant for Hg, i.e. less than an order of magnitude over 10 μC cm^{-2} variation of σ. The variation corresponds to ≈ 0.3 V for an inner layer capacitance of 30 μF cm^{-2}. The effect is significant for Ag even at the fairly small ET distance of 10 Å, increasing by up to two orders of magnitude over the same σ-range, and still more for the low-density metal. These effects approach the activation Gibbs free energy variation which would be three or four orders of magnitude over a 0.3 V overvoltage range.

The investigation of ref. 16 did not extend to charge lability effects on the distance variation of the density overlap. The distance dependence is approximately exponential but depends sensitively on the electrode charge or overvoltage. The distance dependence at different electrode charge densities is displayed in Figs. 2 and 3. Coulomb field and image charges[25–29] of the molecule surface interaction also depend
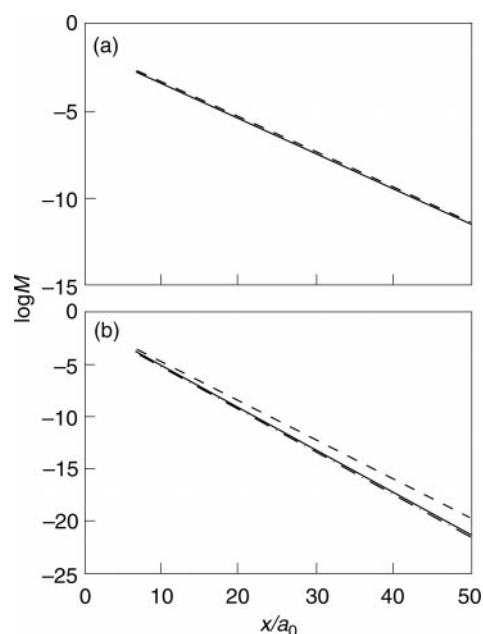

Fig. 4 The electron density overlap $M(\eta)/\Delta x\Delta R$ (eqn. (17)) as a function of the ET distance for different electrode charges. (– – –): $\sigma = -2 \times 10^{-3}$ au. (———): $\sigma = 0$. (– · – · –): $\sigma = 2 \times 10^{-3}$ au. The charge density corresponds to silver. The wavefunction localization on the reactant site: (a) $\gamma = 0.5$ au. (b) $\gamma = 1$ au.

on the distance but these effects are much smaller. The distance range 5–50 a_0 (2–20 Å) and a density corresponding to Ag are used, with different combinations of the decay factors β and γ. The lability coefficients are taken from ref. 22. Some observations follow from the figures.

(A) The distance relations are close to exponential, *cf.* eqn. (17).

(B) The decay factor, however, depends on *both* the molecular and jellium decay factors, where the smaller decay factor dominates. The smaller factor is mostly associated with the discharging molecule (Fig. 2). The effect of the metal is therefore most significant when negative electrode charging has brought the jellium decay length close to the molecular decay length.

(C) Following the observation in (B), the tunnel distance decay depends strongly on the electrode charge. This effect is larger, the more localized the charge distribution on the reactant (Fig. 3).

(D) The charge effect is notably nonlinear: charge variation from -0.001 to -0.002 au leads to a larger change of the slope of the log j_e *vs.* distance dependence than from 0 to -0.001 au. The effect is also notably asymmetric around zero electrode charge (Fig. 4). Negative electrode charging and spatial electron density expansion lower the decay factor significantly for (electronically) lighter metals but positive charging and electron density contraction give a weaker effect.

(E) The calculations in Figs. 1–4 rest on eqn. (17) and x-integration of the density overlap in eqn. (11) from $-\infty$ to $+\infty$. These limits overestimate the charge lability effects for weakly decaying molecular wavefunctions due to unphysical molecular wavefunction penetration into the metal.

4. Concluding remarks

The results above are of interest in the context of recent experimental data, particularly the strong (exponential) excess charge dependence of $[Cr(EDTA)]^-$ reduction at Cd, Bi, and Hg.[18] They hold, however, a broader perspective in the context of electron tunnelling across organized self-assembled films of alkane thiols and related compounds.[8–14] Electronic lability effects in these systems so far seem to be small. This could be associated with the high electron density of the gold substrates used, or the low capacitance of the films, leading to a need for large overvoltage ranges to induce sufficient excess surface charge variation. Lower-density metals such as silver, and distance variation at *different* charges or overpotentials might disclose these effects.

The results, however, need consolidation. The calculations so far rest on jellium at metal/vacuum interfaces. Inclusion of the solvent imposes both attractive and repulsive forces on the jellium density. The former are represented by solvent polarization or positively charged ions, the latter, for example, by pseudopotential forces or negatively charged ions. More composite jellium functionals including Friedel oscillations, dielectric screening, pseudopotential interactions, *etc.*, can, however, be treated by the same procedure.[24,29–31] Such calculations are voluminous but frame the different physical effects transparently. Electronic polarization, for example, enhances jellium expansion whereas retraction is induced by pseudopotential forces. The vacuum jellium representation is therefore a good starting point. Major steps forward should be associated with conversion of the density functionals to wavefunctions, either by Kohn–Sham schemes for jellium[32] or by full band structure calculations for low-density metals and semi-metals.

Acknowledgement

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