The Relationship between Electron Transfer Rate and Molecular Conduction. 2. The Sequential Hopping Case

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Abstract. This note discusses the relationship between a given bridge-assisted electron transfer rate and the corresponding zero-bias molecular conduction of the same molecular species, in the limit where both processes occur by sequential hopping. It follows a previous publication (A. Nitzan, *J. Phys. Chem. A* **2001**, *105*, 2677–2679) in which the same issue was discussed for coherent tunneling transfer.

1. INTRODUCTION

Molecular electron transfer, one of the most basic chemical processes, has been an active field of research for over half a century.[1–6] Investigations of this reaction on the fundamental level focus on the rate of the transfer process between donor and acceptor species that exist in solution either as free solutes or as separate sites of a bigger molecule. Theoretical studies of such reactions aim to understand the effect of molecular and solvent properties on observed rates and yields of electron transfer reactions, mostly following the Marcus theory.[7,8] Another manifestation of molecular electron transfer that is gaining increasing attention in recent years is the conduction of a molecule (or a molecular layer) connecting two metal leads (see, e.g., refs 9–12). Clearly, the conduction property of a given molecular system and the electron transfer properties of the same system should be closely related. One should keep in mind that because of either tunneling or thermal activation, there is always an ohmic regime near zero bias. Obviously, this conduction may be extremely low, implying in practice an insulating behavior.[13] Of particular interest is estimating the electron transfer rate in a given donor–bridge–acceptor (DBA) system that will translate into a measurable zero-bias conduction of the same system when used as a molecular conductor between two metal leads.

In an earlier paper,[14] I analyzed the relationship between molecular electron transfer rates and molecular zero-bias conduction for cases where the electron trans-mission is dominated by coherent tunneling. Denoting the molecule by M = D–B–A, in which the segment B = 1–2–...–N may be viewed as a bridge connecting the donor (D) and acceptor (A) segments, the Marcus theory for the electron transfer rate yields (for weak coupling between the bridge and the donor/acceptor species, and in the non-adiabatic electron transfer limit relevant for this case)

$$k_{D \to A} = \frac{2\pi}{\hbar} |V_{DA}|^2 \, \mathcal{F}(E_{AD})$$

$$= \frac{2\pi}{\hbar} \left|V_{D1}V_{NA}\right|^2 \left|G_{1N}^{(B)}(E_D)\right|^2 \mathcal{F}(E_{AD}) \quad (1)$$

where $\mathcal{F}$ is the Franck–Condon weighted density of states

$$\mathcal{F}(E) = \frac{e^{-(\lambda+E)^2/4\lambda k_B T}}{\sqrt{4\pi\lambda k_B T}} \quad (2)$$

in which k_B is the Boltzmann constant, T is the temperature, λ is the reorganization energy, and $G_{1N}^{(B)}(E) = \langle 1|(E - H_B)^{-1}|N \rangle$ (H_B is the bridge Hamiltonian) is a matrix element of the bridge Green's function. The second part of eq 1 is written for a model in which the coupling between the donor and acceptor species is mediated by the coupling of D and A to the first (1) and last (N) bridge levels, respectively. Note that the explicit form (eq 2) of the Marcus factor $\mathcal{F}$ is a classical, high T

limit, and that more rigorous expressions for this factor can be used.

The corresponding conduction problem is usually described using variants of the Landauer formula.[15–17] In a simple model in which the molecule–metal leads interactions are localized at the D and A segments, this approach leads to

$$g(E) = \frac{e^2}{\pi\hbar} |G_{DA}^{(M)}(E)|^2 \, \Gamma_D^{(L)}(E)\Gamma_A^{(R)}(E) \qquad (3)$$

where e is the electron charge, $\Gamma_D^{(L)}$ and $\Gamma_A^{(R)}$ are widths (imaginary parts of the corresponding self energies $\Sigma_D^{(L)}$ and $\Sigma_A^{(R)}$) of the D and A levels due to their couplings to the left and right metal leads, respectively, and $G_{DA}^{(M)}$ is the D–A matrix element of the Green's function $(E-H)^{-1}$ projected on the molecular (DBA) subspace. In the model that yields the result (eq 1), $G_{DA}^{(M)}(E)$ of eq 3 is related to the bridge Green's function by

$$G_{DA}^{(M)}(E) =$$

$$\frac{\bar{V}_{D1}\bar{V}_{NA}}{\left(E - E_D - \Sigma_D^{(L)}(E)\right)\left(E - E_A - \Sigma_A^{(R)}(E)\right)}\bar{G}_{1N}^{(B)}(E) \qquad (4)$$

where bars above $\bar{G}_{1N}^{(B)}$ and the coupling elements represent the fact that their values for the chemisorbed molecule may be different from the corresponding values in the free DBA complex. Equations 1, 3, and 4 lead to[14]

$$\frac{g}{k_{D\to A}} = \frac{e^2}{2\pi^2}\frac{X}{\mathcal{F}} \qquad (5)$$

where

$$X = \frac{|\bar{V}_{D1}\bar{V}_{NA}|^2}{|V_{D1}V_{NA}|^2}\frac{|\bar{G}_{1N}(E_F)|^2}{|G_{1N}(E_D)|^2} \times$$

$$\frac{\Gamma_D^{(L)}\Gamma_A^{(R)}}{\left[\left(E_F - \tilde{E}_D\right)^2 + \left(\Gamma_D^{(L)}/2\right)^2\right]\left[\left(E_F - \tilde{E}_A\right)^2 + \left(\Gamma_A^{(R)}/2\right)^2\right]} \qquad (6)$$

where $\tilde{E}_D$ and $\tilde{E}_A$ are the donor and acceptor energies shifted by the real parts of the self energies Σ, respectively, and where all width parameters Γ are computed at E_F. A rough approximation to (eq 5) is obtained by assuming that energy shifts occur uniformly in the DBA complex, without distorting its internal electronic structure, and that shifted energies $\tilde{E}_D$ and $\tilde{E}_A$ lie within distances of order Γ from the Fermi energy. This leads to[14]

$$g \approx \frac{8e^2}{\pi^2\Gamma_D^{(L)}\Gamma_A^{(R)}\mathcal{F}}k_{D\to A} \qquad (7)$$

An order of magnitude estimate was obtained[14] by using, e.g., $\lambda = 0.5eV$ in $\mathcal{F} \approx (\sqrt{4\pi\lambda k_B T})^{-1}\exp(-\lambda/4k_B T)$ and taking $\Gamma_D^{(L)} = \Gamma_A^{(R)} \sim 0.5eV$, to give for the coherent transfer case $g \sim (e^2/\pi\hbar)\,(10^{-13}\,k_{D\to A}\,(s^{-1})) \cong [10^{-17}\,k_{D\to A}\,(s^{-1})]\Omega^{-1}$.

In the present paper I discuss a similar issue, the relation between electron transfer rate and molecular conduction, for the case where both processes proceed via incoherent sequential hopping between nearest-neighbor bridge sites. The next section presents the technical analysis and the following one discusses the implication of the resulting relationship.

2. CONDUCTION AND TRANSFER RATE IN THE SEQUENTIAL HOPPING CASE

Consider first the electron transfer rate problem. In what follows, we will use alternately the notations $k_{i,j}$ and $k_{i\to j}$ for the rate of transition from state j to state i. It is convenient to denote the donor and acceptor states by the labels 0 and $N+1$, respectively. The sequential transition from donor to acceptor starting through the N-state bridge may be described by a master equation for the time evolution of the occupations P_k of the different $N+2$ states.

$$\dot{P}_0 = -k_{1,0}P_0 + k_{0,1}P_1 \qquad (8a)$$

$$\dot{P}_1 = -(k_{0,1} + k_{2,1})P_1 + k_{1,0}P_0 + k_{1,2}P_2 \qquad (8b)$$

$$\vdots$$

$$\dot{P}_N = -(k_{N-1,N} + k_{N+1,N})P_N + k_{N,N-1}P_{N-1}$$
$$+ k_{N,N+1}P_{N+1} \qquad (8c)$$

$$\dot{P}_{N+1} = -k_{N,N+1}P_{N+1} + k_{N+1,N}P_N \qquad (8d)$$

with $P_0(t=0) = 1$. We are interested in the situation where beyond a short transient time, the $0 \to N+1$ transition can be described by a simple exponential decay of the donor population, implying a single and well-defined electron transfer rate. When this holds, the corresponding rate may be obtained using the steady-state flux method. In this approach, we consider the steady-state obtained after a long time under the restriction that state 0 is a constant source (P_0 = constant) while state $N+1$ is a drain (P_{N+1} = 0). The corresponding steady-state equations are

$$0 = -(k_{0,1} + k_{2,1})P_1 + k_{1,0}P_0 + k_{1,2}P_2 \qquad (9a)$$

$$0 = -(k_{1,2} + k_{3,2})P_2 + k_{2,1}P_1 + k_{2,3}P_3 \qquad (9b)$$

$$\vdots$$

$$0 = -(k_{N-2,N-1} + k_{N,N-1})P_{N-1} + k_{N-1,N-2}P_{N-2}$$
$$+ k_{N-1,N}P_N \tag{9c}$$

$$0 = -(k_{N-1,N} + k_{N+1,N})P_N + k_{N,N-1}P_{N-1} \tag{9d}$$

This set of N equations yields a simple solution[18] in the case where all rates that do not involve the donor and acceptor states are the same, i.e., when $k_{j,j\pm1} = k$ for j, $j \pm 1$ different from 0 and/or $N + 1$. The steady-state population of state N is obtained in the form

$$P_N = \frac{(k/k_{N+1,N})(k_{1,0}/k_{0,1})P_0}{(k/k_{N+1,N}) + (k/k_{0,1}) + N - 1} \tag{10}$$

This implies that the steady-state flux is $k_{N+1,N}P_N$, yielding the electron transfer rate

$$k_{N+1,0} = \frac{k_{N+1,N}P_N}{P_0}$$
$$= \frac{(k_{1,0}/k_{0,1})k}{(k/k_{N+1,N}) + (k/k_{0,1}) + N - 1} \tag{11}$$

Using detailed balance and resorting to the usual notation for the donor and acceptor species, we finally get

$$k_{D\to A} \equiv k_{A,D} = \frac{ke^{-(E_B/k_BT)}}{\dfrac{k}{k_{N\to A}} + \dfrac{k}{k_{1\to D}} + N - 1} \tag{12}$$

where E_B is the energy gap between the bridge and the donor state. It is important to note that in these expressions, the rates $k_{j,j+l}$ are "regular" Marcus-type electron transfer rates between the corresponding species. This holds because the assumption that fast nuclear relaxation relative to the electron hopping timescale is inherent in the incoherent hopping model.

Next consider the conduction problem. The molecular chain now connects two metal leads, and I assume the binding involved is chemically strong. An important aspect of the new physics is expressed by the assumption, similar to that I made in ref 14, that the electron does not stay localized on the donor and acceptor species, and escapes into the corresponding metals on a fast timescale relative to nuclear relaxation on these species. The donor and acceptor species effectively become parts of the left and right electrodes, respectively. If we represent the donor/left electrode species by a single state L and similarly the acceptor/right electrode species by a single state R, eq 12 would still be valid:

$$k_{L\to R} = \frac{ke^{-(\bar{E}_B/k_BT)}}{\dfrac{k}{k_{R,N}} + \dfrac{k}{k_{L,1}} + N - 1} \tag{13}$$

The bar on $\bar{E}_B$ reflects the fact that the bridge height above the relevant electrode levels may be different than in the free molecule. The rates $k_{L,1}$ and $k_{R,N}$ are essentially electron transfer rates from the leftmost and rightmost bridge states into their corresponding electrodes. These can again be calculated using Marcus-type theory for electron transfer from a molecular state into a metal surface,[19-21] except that the coupling involved is mediated by the corresponding donor or acceptor states: If l denotes a state in the continuous manifold of free electron states in the left metal, we will have

$$V_{1,l} = \frac{V_{1,D}V_{D,l}}{E_1 - E_D - (i/2)\Gamma_D} \tag{14}$$

where Γ_D is the width acquired by the donor state because of its interaction with the metal. Note that the rates $k_{L,1}$ and $k_{R,N}$ depend on nuclear reorganization in the corresponding bridge states 1 or N, but not on the nuclear reorganization at the donor and acceptor species.

In zero-biased junctions the relevant energy is that of the leads' Fermi energy, and $\bar{E}_B$ denotes the energy spacing between this energy and the bridge levels. The net current resulting from an infinitesimal potential bias $\delta\Phi$ between the two electrodes is

$$I = -e(k_{L\to R} - k_{R\to L})$$
$$= -e \times \frac{ke^{-(\bar{E}_B/k_BT)} - e^{-((\bar{E}_B - e\delta\Phi)/k_BT)}}{\dfrac{k}{k_{R,N}} + \dfrac{k}{k_{L,1}} + N - 1} \tag{15}$$

implying the following expression for the conduction:

$$g = \frac{e^2}{k_BT} \frac{ke^{-(\bar{E}_B/k_BT)}}{\dfrac{k}{k_{R,N}} + \dfrac{k}{k_{L,1}} + N - 1} \tag{16}$$

Equations 12 and 16 lead to the following approximate relationship between the conduction and the electron transfer rate

$$g \approx \frac{e^2}{k_BT} e^{-\Delta E/k_BT} \times$$
$$\frac{k\left((k_{D,1})^{-1} + (k_{A,N})^{-1}\right) + N - 1}{k\left((k_{L,1})^{-1} + (k_{R,N})^{-1}\right) + N - 1} k_{D\to A} \tag{17}$$

where $\Delta E = \bar{E}_B - E_B$.

3. DISCUSSION

The result (eq 17) reflects the fact that the bridge dynamics is the same in both experimental situations: donor-to-acceptor electron transfer in a D–B–A complex on one hand, and conduction through the same D–B–A species used as a molecular wire connecting two metal leads. However, the rates to populate and depopulate the bridge are different for these two cases in two ways. First, the activations energies involved may be different (ΔE is their difference). Secondly, the Marcus-type rates $k_{D,1}$ and $k_{A,N}$ from the bridge states 1 and N into their neighboring donor and acceptor states are different from the corresponding rates into the left and right electrodes. The relationships between these rates may in principle be estimated from eq 14 if the corresponding coupling terms are known. Perhaps more significant is the fact that for large N, eq 17 yields the remarkably simple result

$$g \approx \frac{e^2}{k_B T} e^{-\Delta E / k_B T} k_{D \to A} \qquad (18)$$

or $g(\Omega^{-1}) \approx \left(5 \cdot 10^{-18}\right) e^{-\Delta E / k_B T} k_{D \to A}(s^{-1})$ at $T = 300$ K. Note that for $\Delta E \leq k_B T$, this numerical estimate is remarkably close to that obtained using eq 7 for the coherent case.

The relationships (eqs 5–7) and (eqs 17–18) make it possible to set criteria for observing ohmic behavior for small voltage biases in molecular junctions. For example, eqs 7 or 18 imply that with a current detector sensitive to pico-amperes, $k_{D \to A}$ has to exceed ~$10^6 s^{-1}$ before measurable current can be observed at 0.1 V voltage across such a junction. These results provide practical expressions for making such estimates, but their use should be exercised with attention paid to the principal assumption under which they were derived, that the electronic structure of the molecular bridge, when connecting the metal leads, is not considerably different from the electronic structure of the corresponding species in solution. In the more general case, eqs 5–6 and eq 17 should be used, implying the need to have information about the way binding to the electrodes affects the molecular electronic structure. Another point to emphasize is that these results correspond only to conduction at zero bias. An important attribute of experimental setups involving molecular conductors is the possibility to employ their finite bias conduction, which is not directly related to the corresponding electron transfer property.[22] Keeping these limitations in mind, eqs 5–7 and eqs 17–18 provide, in the coherent and incoherent transport regimes, respectively, useful approximate relationships between two extremely important molecular transport observables.

REFERENCES AND NOTES

(1) *Advances in Chemical Physics: Electron Transfer–from Isolated Molecules to Biomolecules*; Bixon, M.; Jortner, J., Eds. Wiley: New York, 1999; Vol. 106.

(2) Kuznetsov, A.M. *Charge Transfer in Physics, Chemistry and Biology*; Gordon & Breach: New York, 1995.

(3) Kuznetsov, A.M.; Ulstrup, J.; Kuzne, A.M.; Sov, T. *Electron Transfer in Chemistry and Biology*: *an Introduction to the Theory*; Wiley: New York, 1998.

(4) Lamb, D.R. *Electrical Conduction Mechanisms in Thin Insulating Films*; Methuen: London, 1967.

(5) Miller, R.J.; McLendon, G.; Nozik, A.; Schmickler, W.; Willig, F. *Surface Electron Transfer Processes*; VCH Publishers: New York, 1995.

(6) Schmickler, W. *Interfacial Electrochemistry*; Oxford University Press: Oxford, 1996.

(7) Marcus, R.A. *J. Chem. Phys.* **1956**, *24*, 966.

(8) Marcus, R.A. *J. Chem. Phys.* **1956**, *24*, 979.

(9) Reed, M.A.; Zhou, C.; Muller, C.J.; Burgin, T.P.; Tour, J.M. *Science* **1997**, *278*, 252–254.

(10) Tian, W.D.; Datta, S.; Hong, S.H.; Reifenberger, R.; Henderson, J.I.; Kubiak, C.P. *J. Chem. Phys.* **1998**, *109*, 2874–2882.

(11) Porath, D.; Bezryadin, A.; De Vries, S.; Dekker, C.; *Nature* **2000**, *403*, 635–8.

(12) Weber, H.B.; Reichert, J.; Weigend, F.; Ochs, R.; Beckmann, D.; Mayor, M.; Ahlrichs, R.; Lohneysen, H.V. *Chem. Phys.* **2002**, *281*, 113–125.

(13) Magoga, M.; Joachim, C. *Phys. Rev. B* **1997**, *56*, 4722–4729.

(14) Nitzan, A. *J. Phys. Chem. A* **2001**, *105*, 2677–2679.

(15) Landauer, R. *IBM J. Res. Dev.* **1957**, *1*, 223.

(16) Landauer, R. *Philos. Mag.* **1970**, *21*, 863–867.

(17) Imry, Y. *Introduction to Mesoscopic Physics*; Oxford University Press: Oxford, 1997.

(18) Kehr, K.W.; Mussawisade, K.; Wichmann, T.; Dieterich, W. *Phys. Rev. E* **1997**, *56*, R2351–R2354.

(19) Marcus, R.A. *J. Chem. Phys.* **1965**, *43*, 679.

(20) Gosavi, S.; Marcus, R.A. *J. Phys. Chem.* **2000**, *104*, 2067–2072.

(21) Nitzan, A. *Annu. Rev. Phys. Chem.* **2001**, *52*, 681–750.

(22) In a conduction process, a potential bias may be partly distributed along the molecular wire, implying a position change in the wire energy levels. This is different from changing the relative energies of the donor and acceptor case in the electron transfer problem.