Activated Conduction in Microscopic Molecular Junctions

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We analyze the connection between the electron transfer (ET) rate through a given molecular bridge, and the conduction of a junction based on the same bridge between two metals. The Landauer relation between the conduction of a junction and its transmission properties is generalized to yield a relation between conduction and ET rate, including transfer processes dominated by thermal activation. The relation between the orders of magnitude of these observables involves an additional length parameter, of the order of the range of the donor wave function. We find that the functional dependence of these observables on the bridge length (N) and on the temperature (T) changes from the exponential and temperature independent, $\exp(-\beta N)$ for small N, to algebraic and thermally activated form, $(\alpha_1 + \alpha_2 N)^{-1} \exp(-\Delta E/k_B T)$, as N increases. An intermediate range of apparent independence on N exists if $\alpha_1 \gg \alpha_2$. This behavior is the analogue to the quantum Kramers (barrier crossing) problem, analyzed with respect to the barrier length.

1. Introduction

The Landauer formula[1] for the conduction of a small one-dimensional junction between two macroscopic metals, and its generalizations to multichannel situations and to the presence of dephasing phenomena,[2] have been central to the development and understanding of electrical conduction in mesoscopic systems. These formulations connect the conduction of a given junction to its transmission properties as obtained from quantum scattering theory in the coherent transmission case, and from stochastic transport theory when dephasing becomes dominant. These formulations have so far excluded the possibility of activated transport, i.e., the enhancement of conduction by thermal activation onto and within the junction barrier. The possible role of thermally activated transport has been recently considered in attempts to understand long-range bridge-mediated electron transfer in molecular systems.[3] The analysis of such processes usually focuses on the *rate* of electron transfer (ET) between donor (D) and acceptor (A) molecules connected by a molecular bridge (B) (Figure 1). Standard theory of such DBA-ET ("superexchange") processes follows the original formulation of McConnell,[4] and predicts an exponential dependence of the rate on the bridge length:

$$k_{ET} = A e^{-\beta R_{DA}} \tag{1}$$

where R_{DA} is the donor−acceptor distance and β is a constant characterizing the DBA system. (We ignore here the possible dependence on R_{DA} of reorganization energies associated with the charge migration, though these are certainly important in some cases.[5]) This is clearly a coherent tunneling process, whereupon β increases with the energy gap ΔE (see Figure 1). Weak dependence on R_{DA} is predicted for small ΔE. Alternatively, at high temperature T the transmission may proceed by thermally populating the bridge states followed by hopping diffusion on the bridge. Theoretical description of the transition from the coherent tunneling to the bridge-hopping transfer modes usually invoke the reduced Liouville equation for the system's density matrix.[3,6] This makes it possible to consider on equal footing the molecular coupling responsible for the transfer process, as well as the system−solvent interactions that cause dephasing and thermal relaxation.

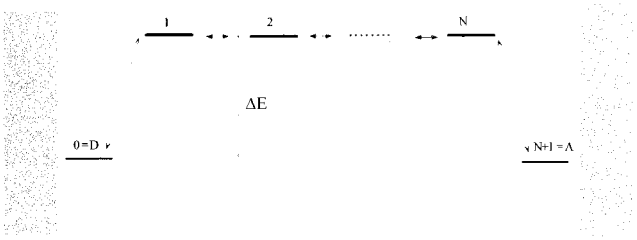

Figure 1. A schematic representation of DBA system discussed in the text. Levels 1, ..., N represent the molecular bridge. For the molecular ET problem D and A represent donor and acceptor levels (also marked 0 and $N + 1$), and the continuous manifolds correspond to molecular or solvent vibronic states. In a metal−molecular layer−metal junction these continua are quasi-free electron states in the metal. In this case D and A may denote the positions of the corresponding Fermi energies. In simplified models the effect of the acceptor continuum is sometimes replaced by assigning a damping rate Γ_A to the acceptor level.

This Letter considers the relationship between the steady state ET rate that is the central observable in ET measurements, and the conduction of a junction based on the same molecular bridge. We first show that the Landauer formula can be generalized to situations involving thermal activation and relaxation in the bridge and thus can account for the overall current, including the elastic/quasi-elastic and the inelastic (energy relaxed) fluxes. Second, we consider the relationship between the ET rate and

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the conduction properties associated with the same molecular bridge and show that while both describe essentially the same phenomenon, their exact relationship involves a nontrivial length parameter, of the order of the size of the donor-localized electronic wave function. Finally, we consider the bridge length (N) dependence of the ET rate and the associated conduction and show that beyond the coherent tunneling regime they behave like $(\alpha_1 + \alpha_2 N)^{-1}$, where α_1 and α_2 depend on molecular properties and on the strength of coupling to the thermal environment. In many situations $\alpha_1 \gg \alpha_2$, implying a range of bridge length where the transmission appears almost N independent.

2. Thermal Landauer Formula

For simplicity we focus on the single channel Landauer formula

$$g = \frac{e^2}{\pi\hbar} T(E_F) \tag{2}$$

which constitutes a relation between the (linear) conductance g and the transmission probability T in a system without thermal relaxation *in the junction*. An equivalent form is obtained by invoking the formal relationship[7] between T and the *steady state* transition rate k_{ss}, $k_{ss}(E) = L^{-1}(\hbar q_i(E)/m)T(E)$, where $\hbar q_i$ is the incident momentum and L is the normalization length in the metal (so that L^{-1} is the single electron density). Using also $\rho_i = Lm(\pi\hbar^2 q_i)^{-1}$, where m is the effective electron mass in the metal, for the density of initial electron states (including spin degeneracy) we get

$$g = e^2 k_{ss}(E_F)\rho_i(E_F) \tag{3}$$

When the transfer involves thermal activation onto the bridge, the energy of the transmitted electron can be different from that which enters the junction. We have recently shown[3b,8] that k_{ss} can be approximated in this case as a sum of coherent tunneling and sequential hopping contributions

$$k_{ss} = k_{ss}^{tun} + k_{ss}^{hop} \tag{4}$$

k_{ss}^{tun} depends exponentially on the bridge length N. The dependence of k_{ss}^{hop} on N is discussed below. Assume now that k_{ss}^{tun} corresponds to an elastic or quasi-elastic process so that the energy of the transmitted electron is essentially the same as the incident one. Taking into account the Fermi occupations $f(E)$ on the two sides, the net quasi-elastic tunneling current for a given voltage drop ϕ across the junction is

$$J^{tun} = e\int dE\, \rho_i(E)k_{ss}^{tun}(E)(f(E+e\phi)(1-f(E)) - f(E)(1-f(E+e\phi))$$
$$\approx e^2\phi\rho_i(E_F)k_{ss}^{tun}(E_F) \tag{5}$$

This leads to the familiar expression (3) for the elastic tunneling part of the conductance

$$g^{tun} = \frac{J^{tun}}{\phi} = e^2 k_{ss}^{tun}(E_F)\rho_i(E_F) \tag{6}$$

Consider now the hopping contribution. This part of the transmitted flux results from electrons that physically occupy the bridge, and we may assume that they emerge from the bridge with energy $E_F + \Delta E$. The net inelastic current is

$$J^{hop} = e\int dE\, \rho_i(E)k_{ss}^{hop}(E)[f(E+e\phi)(1-f(E_F+\Delta E)) - f(E)(1-f(E_F+\Delta E+e\phi))] \tag{7}$$

For small ϕ and $k_BT < \Delta E$ we may take $f(E+e\phi)[1-f(E_F+\Delta E)] \cong f(E+e\phi)$ and $f(E)[1-f(E_F+\Delta E+e\phi)] \cong f(E)$, which leads to

$$g^{hop} = \frac{J^{hop}}{\phi} \cong e^2 k_{ss}^{hop}(E_F)\rho(E_F) \tag{8}$$

k_{ss}^{hop} depends on ΔE like $\exp(-\Delta E/k_BT)$, and the first correction to (8) is of order $\exp(-2\Delta E/k_BT)$. It follows that in the lowest order in this thermal activation parameter, the form (3) of the Landauer formula is satisfied also in the presence of inelastic processes that result in occupying the bridge, where k_{ss} is the rate associated with the total: elastic, quasi-elastic, and inelastic flux.

The rate k_{ss} that appears in eq 3 depends, in addition to the molecular bridge, also on the electronic structure of the donor and acceptor molecules and on the interaction between them and the bridge.[9] When the "bulk metal donor" is replaced by a molecular donor, the bridge electronic structure and charging state may change in a way which is specific to the particular system considered. Here we focus on generic aspects and disregard this possible change of electronic structure. The other main effect enters in the relationship between the matrix elements, V_{BD} between the bridge and the donor molecule and V_{BM} between the bridge and the metal, connecting the corresponding initial states to the neighboring bridge state. The ratio between these elements should scale like $(l_M/L)^{1/2}$, where L is the normalization length introduced above and l_M is the characteristic size of the donor state, typically the size of a molecular site. Consequently[10]

$$\frac{k_{ss}}{k_{ET}} = \left|\frac{V_{BM}}{V_{BD}}\right|^2 = \frac{l_M}{L} \tag{9}$$

Using also $\rho_i(E_F) = (L/2\pi\hbar)\sqrt{(2m/E_F)}$ leads to

$$g = \frac{e^2}{\pi\hbar} T_{eff} \tag{10}$$

with an effective transmission probability

$$T_{eff} = l_M k_{ET}\sqrt{\frac{m}{2E_F}} \tag{11}$$

Notice that, as is physically required, the final result is independent of the normalization length L. Using typical numbers we find $g(\Omega^{-1}) \sim 10^{-20}k_{ET}$ (s^{-1}). This implies that a measurable current in, e.g., an STM junction can be observed only if the electron-transfer rate through the same electronic structure exceeds 10^8 s^{-1}.

3. Bridge Length Dependence

The Hamiltonian for the system depicted in Figure 1 is $H_M = H_0 + V$, where H_0 corresponds to the states shown and V is the coupling between them. The Hamiltonian for the overall system is $H = H_M + H_B + F$, where H_B is the Hamiltonian of the free thermal environment ("bath") and F is the molecule−bath coupling. The steady state Liouville equation for the reduced system density matrix σ in the local representation

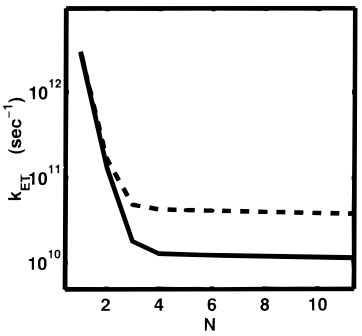

Figure 2. k_{ET} plotted against the bridge length N, for the model of Figure 1, using parameters given in the text. The steady state electron transfer rate is obtained by holding the population of level 0 fixed, and assigning a damping rate, Γ_A, to level $N + 1$. Full line, $T = 250$ K; dashed line, $T = 350$ K.

(eigenstates of H_0) is of the form[3,8]

$$-i\omega_{nn'}\sigma_{nn'} - i[V,\sigma]_{nn'} + \sum_l\sum_{l'} R_{nn'll'}\sigma_{ll'} = J_{nn'} \qquad (12)$$

where $J_{nn'}$ represent the boundary conditions, and where the dephasing and relaxation terms R are obtained as Fourier transforms of time correlation functions involving system matrix elements of the operator F. For the present application the relevant boundary conditions are

$$J_{DD} = -J$$

$$J_{AA} = \Gamma_A\sigma_{AA}$$

$$J_{An} = {}^1/_2\Gamma_A\sigma_{An}; \quad J_{nA} = {}^1/_2\Gamma_A\sigma_{nA}$$

$$J_{nn'} = 0 \qquad \text{for } n,n' \neq A \qquad (13)$$

where J is the total current through the system and Γ_A represents the decay of the acceptor state $|A\rangle \equiv |N + 1\rangle$. We note that the derivation of eqs 12 should be done with care because the Redfield approximation[6] is valid only in the molecular representation (eigenstates of H_M) so that repeated transformations between the molecular and the local representations are needed.[8] Solving (12) yields the steady state elements of σ and in particular σ_{DD} and σ_{AA}, the populations in the donor and acceptor states. The steady state electron transfer rate is obtained from

$$k_{ET} = J/\sigma_{DD} = \Gamma_A\sigma_{AA}/\sigma_{DD} \qquad (14)$$

Figure 2 shows some model results based on this procedure. In this calculation we took the donor and acceptor energies equal, $E_D^{(0)} = E_A^{(0)} \equiv 0$, and all bridge levels placed 0.1 eV above them. A tight-binding model was taken for the molecular coupling, $V_{nn'} = V\delta_{n,n'\pm1}$ with $V = 0.02$ eV. The molecule−bath coupling was taken to be diagonal in the local representation (i.e., $F = \sum_n F_{nn}|n\rangle\langle n|$, with $|n>$ eigenvectors of H_0) and correlations between thermal operators on different sites were assumed to vanish, i.e., $\langle F_{nn}(t)F_{jj}(0)\rangle = 0$ if $j \neq n$. This implies the existence of correlations in the molecular states representation. Temperature and thermal relaxation enter through the detailed balance property of such correlation functions. In the Markovian limit this is taken to be of the form

$$\int_{-\infty}^{\infty} dt\, e^{i\omega t}\langle F(0)\, F(t)\rangle = \kappa;\ \omega \geq 0$$

$$= \kappa \exp(-|\omega|/k_BT); \quad \omega < 0 \qquad (15)$$

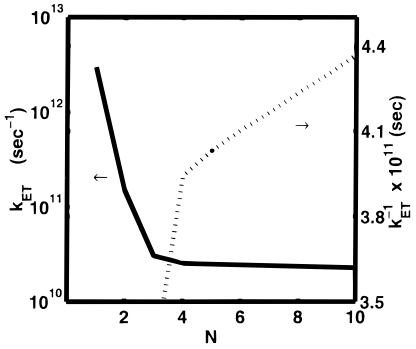

Figure 3. k_{ET} (full line, left axis), and k_{ET}^{-1}(dotted line, right axis), plotted against N. Parameters are the same as in Figure 2. $T = 300$ K.

The parameter κ determines the relaxation and dephasing rates in the model. In the following calculations we take it to be 0.03 eV. A similar value is assigned to the parameter Γ_A in eq 13. Assuming the process to be Markovian overestimates the relaxation and dephasing rates, but it does not change the qualitative effects of relaxation and is relatively simple to analyze. (See ref 8 for a discussion of the non-Markovian case.)

Figure 2 shows the resulting steady state rate displayed as a function of the bridge length N for temperatures 250 and 350 K. For $N < 3$ the superexchange transfer mode prevails, and the dependence on N is exponential. Beyond the crossover region, the rate depends on temperature and the dependence on N is very weak. This weak dependence on the bridge length may seem odd, since in the hopping transport regime one may expect an Ohmic behavior, i.e., $k_{ET} \sim N^{-1}$. Further analysis of the numerical results yields the following functional form

$$k_{ET} = (\alpha_1 + \alpha_2 N)^{-1} e^{-\Delta E/k_BT} \qquad (16)$$

This N dependence is clearly seen in Figure 3 that depicts both k_{ss} and k_{ss}^{-1} as functions of N. Only when N is large enough we obtain the Ohmic, N^{-1}, behavior. α_2 is the characteristic hopping time that may be approximated by[11]

$$\alpha_2^{-1} \sim \frac{4V^2}{\kappa} \qquad (17)$$

and α_1 may be identified as the inverse rate associated with the transition between the donor the bridge levels, given approximately by

$$\alpha_1^{-1} \sim \frac{V^2}{\Delta E^2}\kappa \qquad (18)$$

This leads, for our choice of parameters, to $\alpha_1 \cong 5.5 \times 10^{-13}$ s and $\alpha_2 \cong 1.2 \times 10^{-14}$ s, in reasonable agreement with the numerical findings ($\alpha_1 \cong 8.2 \times 10^{-13}$ s and $\alpha_2 \cong 1.4 \times 10^{-14}$ s). The apparent nondependence on the bridge length N in the intermediate N regime results from $\alpha_1 \gg \alpha_2$ and reflects the existence of a range of N for which the electron transfer is dominated by the rate to thermally occupy the bridge. This rate is obviously independent of N. This behavior is reminiscent of the underdamped limit of the Kramers' barrier crossing problem. In fact, the model considered here is a discrete level analogue of the quantum Kramers problem, except that the *barrier length* is here a controlled variable. In this respect the present discussion provides the first analysis of the transition from the

tunneling to the thermally activated regime in a variant of the quantum Kramers problem *as a function of the barrier length*.

4. Conclusions

We have analyzed the connection between the *electron transfer rate* through a given molecular bridge and the *conduction* of a junction based on the same bridge. Three new results were obtained: First, we have generalized the Landauer relation between a junction conduction and its transmission properties, to yield a connection between conduction and ET rate, *including transfer processes dominated by thermal activation in the bridge*. Second, we found that in orders of magnitude these variables can be associated with each other by adding a length parameter of the order of the range of the donor wave function. Quantitative comparison requires of course knowledge of the coupling between the donor/acceptor (molecule or metal) and the bridge. Finally, we have shown that the bridge length dependence of the ET rate and of the conduction, which reflects a transition from tunneling to thermally activated diffusion through the bridge, is analogous to the quantum Kramers problem, now analyzed as a function of barrier *length*. The possible existence of a regime where electron transport depends weakly on the bridge length was demonstrated and was argued to be the analogue of the underdamped−activated regime of the quantum Kramers problem.

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