Lecture 13. Thermal Activated Conduction in Molecular Wires

For a one step coherent tunneling, the conductance a molecular junction (consisting of a molecule connected to two electrodes) at low bias voltage is given by (Lecture 12)

\[ G(E_F) = G_c e^{-\beta(E_F)L} . \]  \hspace{1cm} (1)

At high temperature, however, the transport process may proceed by thermally populating the bridge states followed by hopping diffusion along the molecular wire. Theoretical description of the transition from the coherent tunneling to the bridge-hopping transfer modes was provided by Ref.1. The work allows one 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.

We note that for the coherent tunneling processes, the Landauer formula has been applied to understand electrical conduction in mesoscopic and molecular systems. This formulation connects the conduction of a given molecular junction to its transmission properties either obtained from the quantum scattering theory in the case of coherent tunneling or from stochastic transport theory when dephasing is dominant. These formulations have so far excluded the possibility of activated transport, i.e., the enhancement of conduction by thermal activation. The possible role of thermally activated transport in molecular wires is the subject of this lecture.

Thermal Landauer Formula

For simplicity we consider a molecular junction with only a single conduction channel. The conductance, \( G \), of the molecular junction is given by the Landauer formula,

\[ G = \frac{2e^2}{h} T(E_F) , \]  \hspace{1cm} (2)
where $T$ is the transmission probability. In this simple formulism thermal relaxation processes are not included. An equivalent form is obtained by invoking the formal relationship between $T$ and the *steady state* transition rate $k_{ss}$, $k_{ss}(E) = L^{-1}(2q_i(E)/m)T(E)$, where $q_i$ is the incident momentum and $L$ is the normalization length (so that $L^{-1}$ is the single electron density), and $m$ is the effective electron mass. For a one-dimensional system, the density of states is $\rho = Lm(2\pi^2q_i)^{-1}$, which allows us to express $G$ in terms of $k_{ss}$ and given by

$$G = e^2k_{ss}(E_F)\rho(E_F).$$  \hfill (3)

When the electron transport involves thermal activation in the molecular wire, the energy of the transmitted electron can be different from that which enters the junction. It has been recently shown (Ref. 3) that $k_{ss}$ can be approximated a sum of coherent tunneling and sequential hopping contributions

$$k_{ss} = k_{ss}^{tun} + k_{ss}^{hop},$$  \hfill (4)

where $k_{ss}^{tun}$ depends exponentially on the molecular length, $N$. The dependence of $k_{ss}^{tun}$ on $N$ is discussed below. Assume now that $k_{ss}$ 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 $V_{bias}$ across the junction is
\[ I^{\text{tun}} = e \int_0^\infty dE \rho_i(E) k^{\text{tun}}_{ss}(E) \left[ f(E + eV_{\text{bias}})(1 - f(E)) - f(E)(1 - f(E + eV_{\text{bias}})) \right] \]
\[ \approx e^2 V_{\text{bias}} \rho_i(E_F) k^{\text{tun}}_{ss}(E_F) \]  

(5)

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

\[ G^{\text{tun}} = \frac{I^{\text{tun}}}{V_{\text{bias}}} = e^2 k_{ss} (E_F) \rho_i(E_F) . \]  

(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 molecular wire with energy \( E_F + \Delta E \). The net inelastic current is

\[ I^{\text{hop}} = e \int_0^\infty dE \rho_i(E) k^{\text{hop}}_{ss}(E) \left[ f(E + eV_{\text{bias}})(1 - f(E_F + \Delta E_F)) - f(E)(1 - f(E + \Delta E_F + eV_{\text{bias}})) \right] \]

(7)

For small \( V_{\text{bias}} \) and \( k_B T < \Delta E \) we may take \( f(E + e\Phi)[1 - f(E_F + \Delta E)] \approx f(E + e\Phi) \) and \( f(E)[1 - f(E_F + \Delta E + e\Phi)] \approx f(E) \), which leads to

\[ G^{\text{hop}} = \frac{I^{\text{hop}}}{V_{\text{bias}}} = e^2 k_{ss}^{\text{hop}}(E_F) \rho_i(E_F) \]  

(8)

\( k_{ss}^{\text{hop}} \) depends on \( \Delta E \) like \( \exp(-\Delta E/k_B T) \), and the first correction to (8) is of order \( \exp(-2\Delta E/k_B T) \). 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 $k_{ss}$ in Eq. 3 is the electron rate from one metal electrode through the molecular bridge to another metal electrode. It is related to the electron transfer rate, $k_{ET}$, which describes electron transfer between a donor and an acceptor separated with the same molecular bridge. Of course, 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

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

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

$$G = \frac{2e^2}{\hbar} T_{\text{eff}} \quad , \quad (10)$$

with an effective transmission probability

$$T_{\text{eff}} = l_M k_{ET} \sqrt{\frac{\hbar}{2E_F}} \quad (11)$$

Notice that, as is physically required, the final result is independent of the normalization length $L$. 
Using typical numbers we find $G(\mathcal{O}^{-1}) \sim 10^{20} k_{\text{ET}} \text{ (s}^{-1})$. 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 $10^8 \text{ s}^{-1}$.

**Dependence on the length of the molecular wires**

The Hamiltonian for a molecular wire connected between a donor and an acceptor is $H_M = H_0 + V$, where $H_0$ corresponds to the states of the wire 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. By solving the steady state Liouville equation, Segal et al (Ref. 1) calculated the steady state rate as a function of the bridge length $N$ at different temperatures (Fig. 1). 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., $k_{\text{ET}} \sim N^{-1}$. Further analysis of the numerical results yields the following functional form

$$k_{\text{ET}} = \frac{1}{\alpha_1 + \alpha_2 N} e^{-\Delta E / k_B T}, \quad (12)$$

This $N$ dependence is clearly seen in Figure 2 that depicts both $k_{\text{ss}}$ and $k_{\text{ss}}^{-1}$ as functions of $N$. Only when $N$ is large enough we obtain the Ohmic, $N^{-1}$, behavior.

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

$$a_i^{-1} \approx \frac{V^2}{\Delta E^2 \kappa}, \quad (13)$$
and $\alpha_2$ is the characteristic hopping time that may be approximated by

$$\alpha_2^{-1} \approx \frac{4V^2}{\kappa} \quad (14)$$

where $\kappa$ determines the relaxation and dephasing rates. This leads, for the choice of parameters, to $\alpha_1 \approx 5.5 \times 10^{-13}$ s and $\alpha_2 \approx 1.2 \times 10^{-14}$ s, in reasonable agreement with the numerical findings ($\alpha_1 \approx 8.2 \times 10^{-13}$ s and $\alpha_2 \approx 1.4 \times 10^{-14}$ s). The apparent independence on the molecular 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 $N$.

Fig. 1 Finite temperature conduction of a simple tight-binding model of a molecular junction as a function of bridge length $N$. (See text for details.)
Figure 2 $k_{ET}$ (full line, left axis), and $k_{ET}^{-1}$ (dotted line, right axis), plotted against $N$. Parameters are the same as in Figure 1. $T = 300$ K.

References


HOMEWORK:

13-1 (a) Show $k_{ss}(E) = L^{-1}(\hbar q_i(E)/m)T(E)$, 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). Hint: Galperin, M.; Segal, D.; Nitzan, A. *J. Chem. Phys.* **1999**, *111*, 1569-1579.

(b) Using the above result and $\varrho_i = \frac{Lm}{n\hbar^2 q_i}^{-1}$, where $m$ is the effective electron mass in the metal, for the density of initial electron states (including spin degeneracy), show Equation 3.