


THEORY OF BRIDGE-ASSISTED ELECTRON TRANSFER IN SYSTEMS WITH AN INTERMEDIATE LINK AT HIGH TEMPERATURES

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From solution of the time-dependent wave equation by specifying the Ψ(t) function in the form of a linear combination \( a_1(t)\Psi_1 + a_2(t)\Psi_2 + a_3(t)\Psi_3 \) (\( \Psi_1, \Psi_2, \Psi_3 \) are the wave functions corresponding to localization of the electron on the donor, the intermediate link, and the acceptor), we obtain an expression for the electron transfer probability in a system consisting of six components: one direct transfer and five interference components. We have studied the effect of electronic structure and vibrational motion of the components of the system on the probability components. This has allowed us to find the dependence of the electron transfer probability on the ionization potential or the electron affinity of the intermediate link, playing the role of a catalyst or inhibitor of the process.

A bridge (indirect) mechanism for electron transfer has been considered within second-order perturbation theory, with and without taking into account the dynamic role of the condensed medium in [1, 2] and [3] respectively. This report is a continuation of [4], in which we obtained a formula for the electron transfer probability in systems with an intermediate link (ion, molecule, protein, a solid and its surface for reactions within the volume and on the surface respectively, the solvated or free state of the electron in a medium). In the proposed theory, in the electron transfer probability components, distinguished from the components of first and second order perturbation theory, explicit allowance is made for the potential surfaces of the components of the system (the donor, the intermediate link, the acceptor, the medium) in the initial, the intermediate, and the final states. This makes it possible to establish the dependence of the electron transfer probability on the experimentally measured ionization potentials and electron affinities of the components of the system and thus to explain and predict the changes in the reaction rate constants, analogous to the case of direct electron transfer [5-7]. Of special interest is the selection rule for indirect electron transfer.
transfer with respect to spin, orbital symmetry, and number of electrons to be transferred, which can be obtained by the method developed for the direct reaction mechanism in [8-10].

The electron transfer probability \( W \) in systems with an intermediate link is expressed by the formula

\[
W = \frac{2\pi}{\hbar} \left| H_{ii} - H_{id}H_{df}\Delta E_{df} \right|^2 \delta(\Delta E_{ii}) + 
\]

\[
+ \frac{2\pi}{\hbar} \sum_{\xi, \xi'} H_{id}H_{df}H_{\xi\xi'}H_{df}\{[(\Delta E_{if}\Delta E_{if}^{-1})^{-1}\delta(\Delta E_{if}) + 
\]

\[
+ (\Delta E_{if}\Delta E_{if}^{-1})^{-1}\delta(\Delta E_{if}) + (\Delta E_{if}\Delta E_{if}^{-1})^{-1}\delta(\Delta E_{if})\}. \tag{1}
\]

The expressions for the difference in vibronic energies (\( \Delta E \)) and the matrix elements (\( H \)) of the Hamiltonian \( \hat{H} \) of the system in the initial state (\( i \)), the intermediate state (\( d \)) (the \( d' \) state has the same electronic component as \( d \), but a different vibrational component), and the final state (\( f \)), and also the physical meaning of the probability terms are given in [4, ii].

We can persuade ourselves that we need to take into account the off-diagonal \( d \) and \( d' \) terms from calculation of the probability

\[
W = \lim_{t \to +\infty} \frac{\partial}{\partial t} \sum_{d} a_{f}(i, d)|^2/\partial t,
\]

if we use the explicit form \( a_{f}(t, d) \) and the calculation method in [4], and also the similar identity \( x^a\delta(x) = 0 \).

Let us compare formula (1) with the corresponding formula in perturbation theory, and let us study the effect of the electronic structure and vibrational motion of the components of the system on the components of the electron transfer rates, expressed by the last term in (1). According to the perturbation theory in [12], in the case of a single intermediate electronic state the transition probability

\[
W = 2\pi^{-1} |H_{ii} - H_{id}H_{df}\Delta E_{df} |^2 \delta(\Delta E_{ii})
\]

is obtained by neglecting the last term in the amplitude:

\[
a_{f} = \Delta E_{if}^{-1}(H_{ii} - H_{id}H_{df}\Delta E_{df}) \exp(i\hbar^{-1}\Delta E_{if}) - 1 + 
\]

\[
+ H_{id}H_{df}(\Delta E_{if}\Delta E_{if}^{-1})^{-1} \exp(i\hbar^{-1}\Delta E_{if}) - 1
\]

This is possible when the condition \( |\Delta E_{if}| \ll |\Delta E_{df}| \) is satisfied, i.e., when the intermediate level is located far from the levels \( E_i \) and \( E_f \). Consequently, for the intermediate levels \( E_d \) located close to the \( E_i \) and \( E_f \) levels, the indicated condition is not satisfied. If in the amplitude \( a_{f} \) we do not neglect the last term and use the real wave functions, the transition to which is accomplished using a linear transformation (see, for example, [13]), then by calculating \( \lim_{t \to +\infty} \frac{\partial}{\partial t} |\sum_{d} a_{f}(i, d)|^2/\partial t \) we obtain the probability \( W \) coinciding with the correct formula (1).

Substituting the wave functions, the energy differences (expressions (20)-(23) from [1]), the integral representations for \( \delta(\Delta_{mn}) \) and the denominators \( (\Delta_{nm} + i\gamma_{nm})^{-1} (\gamma_{nm} + 0) \) [ii] in (1), after summing over the final vibrational states and averaging over the initial vibrational states for the last three terms in the Franck-Condon approximation, we obtain (\( s = 4, 5, 6 \))

\[
W_s = \frac{2\pi}{\hbar} \left| H_{id}H_{df} \right|^2 \sum_{n_1} \sum_{n_2} \exp\left[ iF_{id}\omega_{ip_1}(n_{1p_1} - n_{1p_2}) + iF_{id}\omega_{ip_2}(n_{1p_1} - n_{1p_2}) + 
\]

\[
+ iF_{id}\omega_{ip_1}(n_{1p_1} - n_{1p_2})M_{n_1p_1n_{1p_1}}M_{n_1p_2n_{1p_2}}M_{n_1p_2n_{1p_1}}M_{n_1p_1n_{1p_2}}\right]
\]

where

\[
\Delta_{s_1}, \Delta_{s_2}, \Delta_{s_3}, \gamma_{1s}, \gamma_{2s}, F_{s}, F_{s'}, F'_{s},
\]

\[
\Delta_{s_1}, \Delta_{s_2}, \Delta_{s_3}, \Delta_{s_4}, \gamma_{1s}, \gamma_{2s}, t_1, t_2;
\]

\[
(\Delta_{s_1}, \Delta_{s_2}, \Delta_{s_3}, \gamma_{1s}, t_1, t_2, t_3, t_4) \tag{3}
\]