# QUASICLASSICAL CALCULATION OF THE PROBABILITY FOR ELECTRON TRANSFER VIA A VIRTUAL INTERMEDIATE STATE OF A BRIDGING GROUP

M. V. Vol'kenshtein,* R. R. Dogonadze, A. K. Madumarov, and Yu. I. Kharkats

UDC 539.194

The present paper represents the beginning of an investigation into the mechanism of fermentation processes based on the quantum-statistical theory of chemical reactions in condensed media [1]. As a first stage, it was found necessary to consider the transfer of an electron by a bridging mechanism. The system investigated consists of an electron donor A, an acceptor B, and a bridging ion C, located at fixed distances with respect to each other in a polar medium. It is assumed that, in addition to the direct transfer of an electron from A to B, an electron transfer from A to C and then subsequently to B is also possible and, moreover, that this latter process occurs in a single stage via a virtual intermediate state. Each charge state of the system possesses its own potential energy surface (electronic term) which describes the state of the polarization of the solvent. In the present paper these surfaces will be chosen so as to be linear and unidimensional for purposes of simplicity (see Fig. 1).

$$U_i = I_i - \varepsilon_i | q - q_i^0 |. \tag{1}$$

The quantities $q_i^0$ correspond to the equilibrium values of the dimensionless coordinates q, which describe the polarization of the solvent [2], for the initial (1), intermediate (2), and final (3) states of the system, $I_i$ are the values of the potential energy minima, and $\varepsilon_i$ are parameters characterizing the slopes of the terms. The electron-transfer process under investigation can be described within the framework of perturbation theory by a second order term, and one obtains the following expression for the transition probability per unit time:

$$W_{31} = \frac{2\pi}{\hbar} Av_1 \sum_3 \delta(E_3 - E_1) \left| \sum_2 \frac{\langle \Psi_3 | V_2 | \Psi_2 \rangle \langle \Psi_2 | V_1 | \Psi_1 \rangle}{E_1 - E_2 + i\eta} \right|^2. \tag{2}$$

Here $\Psi_i$ are the wavefunctions for the corresponding states of the system, $V_2$ and $V_1$ are the perturbations acting on the system in the intermediate and initial states, respectively, $AV_1$ denotes the Gibbs mean over the energies of the initial state, and $\eta \to +0$.

Since the energy spectra are assumed to be quasicontinuous, the summations can be replaced by integrations. Hence, after integration with respect to $E_3$, the transition probability per unit time can be written in the form:

$$W_{13} = \frac{2\pi}{\hbar} |V_2^{3,2} V_1^{2,1}|^2 \left[ \int_{I_1}^{\infty} \rho_1(E_1) e^{-\beta E_1} dE_1 \right]^{-1} \int_{\max\{I_1 I_3\}}^{\infty} \rho_1(E_1) \rho_3(E_1) \times e^{-\beta E_1} |M^{3,1}(E_1)|^2 dE_1, \tag{3}$$

where $p_i$ are the densities of energy levels of the corresponding states, $V_2^{3,2}$ and $V_1^{2,1}$ are the electronic exchange integrals from the perturbations, and $M^{3,1}(E_1)$ is given by the expression:

$$M^{3,1}(E_1) = \int_{I_2}^{\infty} \rho_2(E_2) \frac{\langle \Phi_3(E_1) | \Phi_2(E_2) \rangle \langle \Phi_2(E_2) | \Phi_1(E_1) \rangle}{E_1 - E_2 + i\eta}, \tag{4}$$

where $\Phi_i(E_i)$ are the wavefunctions of the solvent corresponding to the different electronic terms i.

* Corresponding Member, Academy of Sciences of the USSR.

Institute of Electrochemistry, Academy of Sciences of the USSR, Moscow. Translated from Doklady Akademii Nauk SSSR, Vol. 199, No. 1, pp. 124-127, July, 1971. Original article submitted January 29, 1971.

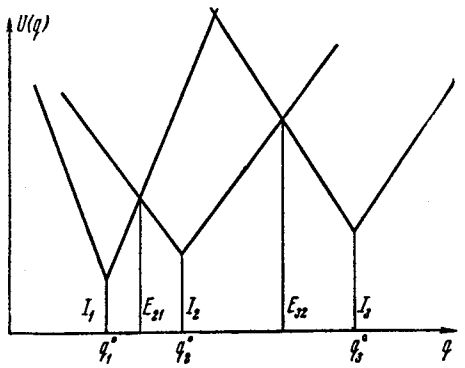


Fig. 1

Calculation of the Overlap Integrals $\langle\Phi_i|\Phi_j\rangle$. The quasiclassical wavefunctions for the linear terms in the classically accessible region can be represented in the form:

$$\Phi_i(E_i) = \frac{C_i(E_i)}{[(E_i - I_i)/\varepsilon_i - |q - q_i^0|]^{1/4}} \cos\left\{F_i[((E_i - I_i)/\varepsilon_i)^{3/2}(1 - \operatorname{sgn}(q - q_i^0)) - \operatorname{sgn}(q - q_i^0)((E_i - I_i)/\varepsilon_i - |q - q_i^0|)^{3/2} - \frac{\pi}{4}\right\}, \tag{5}$$

where

$$C_i(E_1) = 2^{-1/2}\varepsilon_i^{1/4}[E_i - I_i]^{-1/4}; \quad F_i = \pi/2\,(\varepsilon_i/\hbar\omega_i)^{3/2}, \quad \rho_i C_i^2 = {}^3/_4\,(\varepsilon_i/(\hbar\omega_i)^3)^{1/2},$$
$$E_i - I_i = \hbar\omega_i(n^{(i)} + {}^1/_2)^{2/3}\ (\hbar\omega_i \infty \varepsilon_i^{2/3}). \tag{6}$$

In the calculation of the overlap integrals, we shall neglect the exponentially small contribution from the classically inaccessible regions where the quasiclassical wavefunctions decay exponentially. The wavefunctions oscillate rapidly in the classically accessible regions and the neighborhoods of the stationary phase points [3] make the principal contribution to the overlap integral. Hence, for the overlap integral $\langle\Phi_i|\Phi_j\rangle$, we obtain the expression

$$\langle\Phi_i|\Phi_j\rangle = \frac{C_iC_j}{2}\sum_l \frac{\sqrt{8\pi F_j}\left[\frac{E_i - I_i}{\varepsilon_i} - |q_{ij}^l - q_i^0|\right]^{-1/4}\cos\Phi_{ij}^{(l)}}{[3|F_j^2\operatorname{sgn}(q_{ij}^l - q_j^0) - F_i^2\operatorname{sgn}(q_{ij}^l - q_i^0)|]^{1/2}}, \tag{7}$$

where the phase value at the stationary point $\Phi_{ij}^{(l)}$ is determined by

$$\Phi_{ij}^{(l)} = F_i\left[\frac{E_i - I_i}{\varepsilon_i} - |q - q_i^0|\right]^{3/2}\frac{F_j^2\operatorname{sgn}(q_{ij}^l - q_i^0) - F_i^2(q_{ij}^l - q_j^0)}{F_j^2} + F_i\left[\frac{E_i - I_i}{\varepsilon_i}\right]^{3/2}[1 + \operatorname{sgn}(q_{ij}^l + q_i^0)] + F_j\left[\frac{E_i - I_j}{\varepsilon_j}\right]^{3/2}[1 + \operatorname{sgn}(q_{ij}^l - q_j^0)]. \tag{8}$$

The stationary point $q_{ij}^{(l)}$ satisfies the condition that impulses in the i-th and j-th states should be equal, and is determined by the expression:

$$q_{ij}^l = \frac{(E_i - I_i) - (E_j - I_j) + \operatorname{sgn}(q_{ij}^l - q_i^0)F_i^2q_i^0 - \operatorname{sgn}(q_{ij}^l - q_j^l)F_j^2q_j^0}{\operatorname{sgn}(q_{ij}^l - q^0)F_i^2 - \operatorname{sgn}(q_{ij}^l - q_j^0)F_j^2}. \tag{9}$$

The various different possible arrangements of the points of the stationary phase with respect to the equilibrium coordinates $q_i^0$ and $q_j^0$ are denoted by the index $l$ in Eqs. (6)-(9).

$$q_{ij}^{\mathrm{I}} < q_i^0, \quad q_{ij}^{\mathrm{I}} < q_j^0; \quad q_{ij}^{\mathrm{III}} > q_i^0, \quad q_{ij}^{\mathrm{III}} > q_j^0; \quad \min(q_i^0, q_j^0) < q_{ij}^{\mathrm{II}} < \max(q_i^0, q_j^0); \tag{10}$$
$$(E_i - I_i)/\varepsilon_i - |q_{ij}^l - q_i^0| > 0; \quad (E_j - I_j)/\varepsilon_j - |q_{ij}^l - q_j^0| > 0.$$

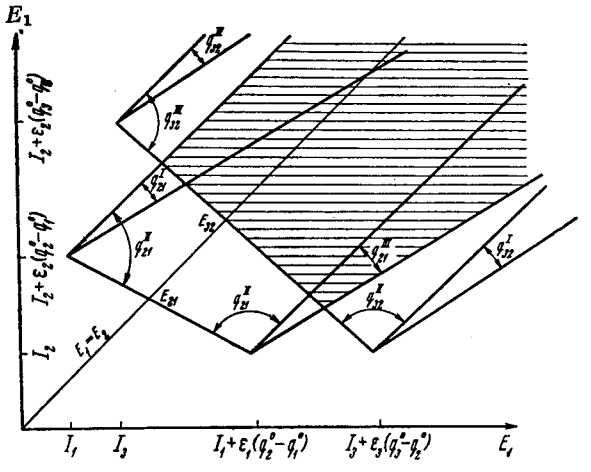

Fig. 2

The system of inequalities [Eq. (10)] can be represented as a system of inequalities bounding the region of integration with respect to the energies $E_1$ and $E_2$. The range of values of the energies $E_1$ and $E_2$ which satisfies such inequalities is shown in Fig. 2. The ranges of values of $E_1$ and $E_2$ which simultaneously satisfy the inequalities for the integrals $\langle\Phi_3|\Phi_2\rangle$ and $\langle\Phi_2|\Phi_1\rangle$ have been hatched in with lines in this figure.

Calculation of $M^{3,1}(E_1)$. Upon integration with respect to $E_2$, the integrand contains a slowly varying function $D^{l,k}$ in addition to an oscillating function of the energy $E_2$. The function $D^{l,k}$ is given by the expression:

$$D^{l,k} = {}^1/_3 C_1(E_1)\, C_3(E_1)\, C_2^2(E_2)\, \rho_2(E_2)\, 2\pi \sqrt{F_1 F_3} \left[\frac{E_2 - I_2}{\varepsilon_2} - |q_{21}^l - q_2^0|\right]^{-1/4}$$
$$\times \left[\frac{E_2 - I_2}{\varepsilon_2} - |q_{32}^k - q_2^0|\right]^{-1/4} [\,|F_1^2 \operatorname{sgn}(q_{1j}^l - q_1^0) - F_2^2 \operatorname{sgn}(q_{21}^l - q_2^0)| \tag{11}$$
$$\times |F_3^2 \operatorname{sgn}(q_{32}^k - q_3^0) - F_2^2 \operatorname{sgn}(q_{32}^k - q_2^0)|\,]^{-1/2}.$$

Using our present notation, $M^{3,1}(E_1)$ assumes the form

$$M^{3,1}(E_1) = \sum_{l,k} \int_{E_{2\min}^{l,k}}^{E_{2\max}^{l,k}} D^{l,k} \frac{\cos\Phi_{21}^{(l)} \cos\Phi_{32}^{(k)}}{E_1 - E_2 + i\eta} dE_2, \tag{12}$$

where $[E_{2\min}^{l,k}, E_{2\max}^{l,k}]$ is the interval of overlap of the accessible values of $E_2$ between the regions $l$ and k. It is apparent that regions which do not overlap for a given value of $E_1$ make no contribution to $M^{3,1}(E_1)$. Upon integration with respect to $E_2$, the point $E_1 = E_2$ can fall within the limits of integration, but cases are also possible when it lies outside the limits of integration.

In the former case the integral may be decomposed into real and imaginary parts.

$$\int_{E_{2\min}^{l,k}}^{E_{2\max}^{l,k}} D^{l,k} \frac{\cos\Phi_{21}^{(l)} \cos\Phi_{32}^{(k)}}{E_1 - E_2 + i\eta} dE_2 = -i\pi D^{l,k} \cos\Phi_{21}^{(l)} \cos\Phi_{32}^{(k)}\big|_{E_2 = E_1} + \int D^{l,k} \frac{\cos\Phi_{21}^{(l)} \cos\Phi_{32}^{(k)}}{E_1 - E_2} dE_2. \tag{13}$$

The integral, in the sense of its principal value, can be transformed to the form:

$$\frac{\mathrm{Im}}{2} \int D^{l,k} \frac{\exp\{i[\Phi_{21}^{(l)} + \Phi_{32}^{(k)} - \pi/2]\}}{E_1 - E_2} dE_2 + \frac{\mathrm{Re}}{2} \int D^{l,k} \frac{\exp\{i[\Phi_{21}^{(l)} - \Phi_{32}^{(k)}]\}}{E_1 - E_2} dE_2. \tag{13'}$$

It is easy to convince oneself that each of these integrals can be replaced by the limit of the sum of three integrals along the contours $C_\rho$, $C_1$, and $C_2$ as $\rho \to 0$ (see Fig. 3). The contribution from the integrals along $C_\rho$ is equal to

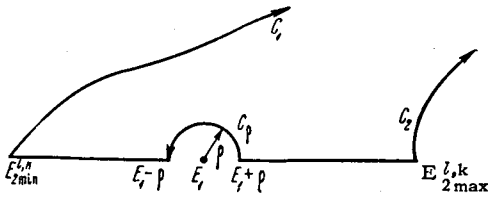


Fig. 3

$$\lim_{\rho\to 0}\frac{\mathrm{Re}}{2}\int\limits_{C_\rho} D^{l,k}\,\frac{\exp\{i\,[\Phi_{21}^{(l)}-\Phi_{32}^{(k)}]\}}{E_1-E_2}\,dE_2=\frac{\pi D^{l,k}}{2}\sin\,[\Phi_{21}^{(l)}-\Phi_{32}^{(k)}]_{E_2=E_1},$$
$$\lim_{\rho\to}\frac{\mathrm{Im}}{2}\int\limits_{C_\rho} D^{l,k}\frac{\exp\{i\,[\Phi_{21}+\Phi_{32}-\pi/2]\}}{E_1-E_2}\,dE_2=-\frac{\pi D^{l,k}}{2}\cos[\Phi_{21}^{(l)}+\Phi_{32}^{(k)}-\pi/4]_{E_2=E_1}. \qquad (14)$$

In order to calculate the integrals along the contours $C_1$ and $C_2$, it is necessary to investigate the behavior of the exponential function in the complex plane of $E_2$. The signs occurring before the i's in the exponents in Eq. (13') can always be chosen such that these exponents tend to zero as $E_2 \to \infty$ along the contours $C_1$ and $C_2$. The values of the integrals along the contours $C_1$ and $C_2$ are equal to the contributions from the end points of the contours and also, in those cases when the crossing points fall in the physically accessible region, to the contributions from these crossing points. These contributions from the terminal and crossing points are gathered together in very narrow regions of integration, since the integrands oscillate extremely rapidly due to the large parameter in the phase term. Hence, the above-mentioned contributions can be neglected in comparison with the integral along the contour $C_\rho$. For the same reason, the integrals with respect to $E_2$ from those regions in which $E_1$ does not fall within the limits of integration are small. Furthermore, investigations have shown that corresponding crossing points are found at the points of intersection of the terms 3 and 1, which correspond to large values of $E_1$, and the corresponding terms make a small contribution upon temperature averaging. Hence,

$$M^{3,1}(E_1)=\sum_{l,k} D^{l,k}\{-i\pi\cos\Phi_{(21)}^{l}\cos\Phi_{32}^{(k)}+\pi\sin\Phi_{21}^{(l)}\cos\Phi_{32}^{(k)}\}_{E_2=E_1}. \qquad (15)$$

Since $M^{3,1}(E_1)$ takes its value at $E_2 = E_1$, for practical purposes further integration with respect to $E_1$ is carried out along the line $E_1 = E_2$ in the $E_1$, $E_2$ plane starting from the value $E_1 = E_{23}$. The higher of the two values of the energies at the intersection of the 1,2 and 2,3 terms corresponds to this point (see Fig. 1). As can be seen from Fig. 2, at values of the energy $E_1$ close to the lower limit of integration $E_{23}$, which are also essential for the integral with respect to $E_1$, a term remains in the sums over $l$ and k which corresponds to $l$ = II and k = II. Allowing for this, we obtain

$$|M^{3,1}(E_1)|^2=\pi^2\,[D^{l,k}]^2\cos^2\Phi_{32}^{(\mathrm{II})}. \qquad (16)$$

By substituting (16) in (3), replacing $\cos^2\Phi$ by its mean value of $1/2$, and also taking into account Eq. (6) which relates the densities of states and the normalization coefficients, and using the result of the calculation of the statistical integral for the case $(E_{32}-E_{21})\ \beta \gg 1$, which is of interest to us, we finally obtain

$$W_{31}=\frac{3\pi^3}{4\hbar}|V_2^{3,2}V_1^{2,1}|^2\,\frac{(\hbar\omega_2)^3(\varepsilon_1\varepsilon_2\varepsilon_3)^2\,[(\hbar\omega_1)^3/(E_{32}-E_{21})]\,\beta\exp\{-\beta\,(E_{32}-I_1)\}}{[(\varepsilon_1\hbar\omega_2)^3+(\varepsilon_2\hbar\omega_1)^3]\,[(\varepsilon_3\hbar\omega_2)^3+(\varepsilon_2\hbar\omega_3)^3]}. \qquad (3')$$

The expression obtained shows that the transfer of an electron via a virtual state with the participation of bridging ions occurs with a lower activation energy than the direct transfer of an electron in that case when the minimum of the intermediate term is located lower than the point of intersection of the initial and final terms. This electron transfer mechanism can be put forward as one of the explanations for the increased rates of electron transfer observed when a bridging mechanism is operative.

## LITERATURE CITED

1. R. R. Dogonadze and A. M. Kuznetsov, Scientific Results, Electrochemistry [in Russian], Moscow (1969), p. 1961.
2. R. R. Dogonadze, Dokl. Akad. Nauk, 142, 1108 (1962).
3. L. D. Landau and E. M. Lifshits, Quantum Mechanics [in Russian], Moscow (1963).