In analyzing experiments, this effect might be misinterpreted as being due to the absence of a potential jump in the Helmholtz layer, especially when semiconductor/electrolyte boundaries are being studied. Another important conclusion is that, as follows from the substitution of concrete parameters, the shift is always less than φ_0. Thus, when $E_{2n+1} \approx 1$ eV, $E_{2n} \approx -5$ eV, $E_p \approx -2$ eV (the surface level is in the center of the band) and $x_1 \approx 1$ A, then $\Delta E_p \approx -\varphi_0/5$.

In conclusion, we should point out that the whole of the above treatment was one-dimensinal. However, the basic results also hold in the three-dimensional case, where the surface states may be extended into surface bands. We will return to the complex question of the effect of nonuniformity in our next work.

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SEMICLASSICAL THEORY OF ADIABATIC AND NONADIABATIC ELECTRON-TRANSFER BRIDGING REACTIONS

A. M. Kuznetsov and Yu. I. Kharkats

UDC 541.138

A semiclassical description of slow subsystems (solvents) has been used to calculate the probability of electron transfer in systems with three intersecting energy levels. Expressions are obtained for the activation energies and preexponential factors at high and low values of the Landau—Zener parameters, corresponding to adiabatic and nonadiabatic electron transfer.

In theoretical studies of nonadiabatic electron-transfer processes taking place by a bridging mechanism, the quantum-mechanical calculation of the transfer probability is generally performed using perturbation-theory formulas of second order with respect to the interactions between the reactants and the bridging species. Calculations of this type have been performed for a one-dimensional model in [1-3], in which quasiclassical wave functions were used to describe the state of the slow subsystem. It was also assumed that relaxation of the slow subsystem does not take place in the intermediate state in the course of a quantum-mechanical transition. The result obtained in this way describes the probability W_{if} of a nonadiabatic transition with allowance for virtual transitions into all possible vibrational

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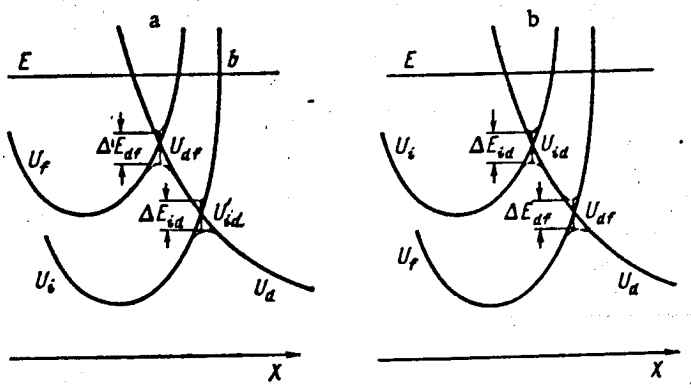

Fig. 1

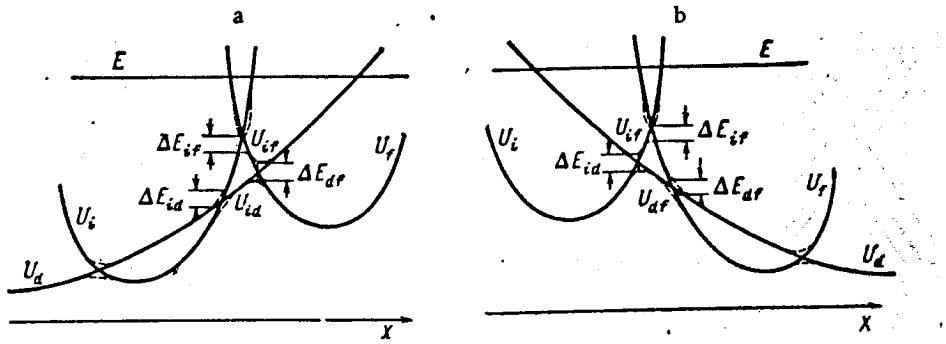

Fig. 2

levels of the intermediate electronic energy level U_d (corresponding to localization of the electron on the bridging species); for levels of fairly arbitrary form, this probability can be written as

$$W_{if} = \frac{2\pi^{1/2}(\Delta E_{id}/2)^2(\Delta E_{df}/2)^2 m \exp(-\beta E_a)}{Z(\beta)\hbar^3 \left(\frac{dU_i}{dx} - \frac{dU_d}{dx}\right)^* \left(\frac{dU_d}{dx} - \frac{dU_f}{dx}\right)^* \sqrt{\beta |U_{fd} - D_{di}|}}, \quad (1)$$

where $Z(\beta)$ is the statistical sum of the initial state; E_{id} and E_{df} are resonance splittings of the electronic energy levels† at the points of intersection of the levels in the zero approximation of the initial U_i and intermediate U_d states and the intermediate U_d and final U_f states; m is the effective mass corresponding to motion along the reaction coordinate; $\beta = 1/kT$; $E_a = \max(U_{fd}, U_{di})$ is the activation energy; U_{fd} and U_{di} are the energies at the points of intersection of the U_f and U_d levels and the U_d and U_i levels; and the superscript asterisks indicate that the values of the derivatives are taken at the points of intersection of the corresponding levels (see Figs. 1 and 2).

In the particular cases of linear and parabolic energy levels, Eq. (1) transforms into the expressions obtained in [1, 2] within the limits of the symbols used. In deriving Eq. (1) it was essentially assumed that the slow subsystem is classical [4] and that $|U_{fd} - U_{di}| \gg kT$.

As will be evident from what follows, Eq. (1) corresponds to the arrangement of energy levels shown in Figs. 1 and 2. A calculation on the basis of a harmonic approximation using the density-matrix method leads to a transition probability which is twice as high as that obtained from (1) [5]. As will be seen from what follows, this result corresponds to the arrangement of energy levels shown in Fig. 3.

Calculations performed in [1-3, 5] show that the activation energy of electronic transitions corresponding to the arrangement of levels shown in Figs. 1-3 is determined by the higher of the points of intersection of the intermediate level with the initial and final levels (points U_{fd} in Figs. 1a and 2a, and points U_{di} in Figs. 1b and 2b), and is considerably lower than the activation energy for direct electron transfer between the reactants (U_{if}).

†More strictly, ΔE is the minimum distance between the adiabatic levels.

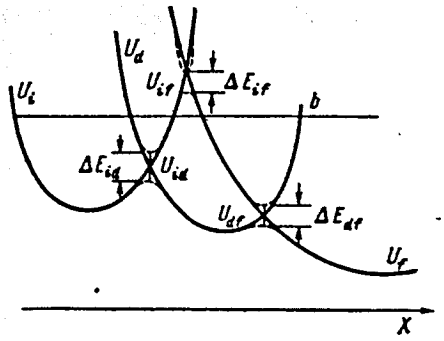

Fig. 3

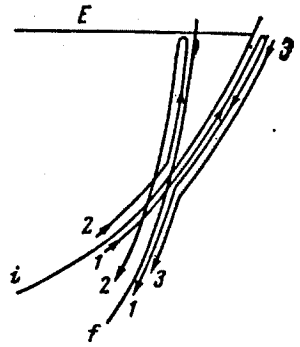

Fig. 4

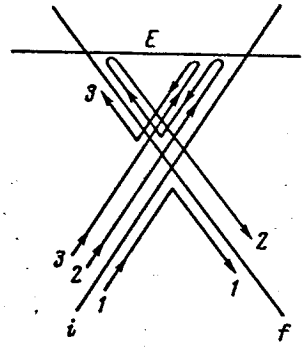

Fig. 5

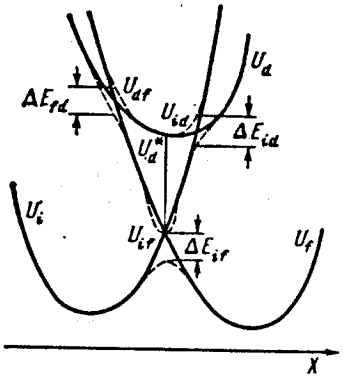

Fig. 6

One important result emerging from the calculations in [1-3, 5] is that although the formal expression for the transition probability contains a summation over all intermediate energy levels, including those not satisfying the law of conservation of energy, the main contribution to the transition probability is made by intermediate states whose energies are equal to the energies of the corresponding initial and final states. Since the slow subsystem is semiclassical, this result means that the transition of the system from the initial into the final state can be regarded as classical motion through a set of levels with constant energy with allowance for the probability of reorganization of the electronic state in the vicinity of the intersections of the zero-approximation levels [6]. The latter means that expressions can be obtained for the transition probability both in the case of nonadiabatic and in the case of adiabatic reactions.

As shown in [6], transitions between different levels in a multilevel system can be regarded as being independent provided that certain conditions with respect to the slope of the levels and their relative positions are met (one of these conditions is that the points of intersection of the levels should be far enough away from one another). In the following, we will assume that these conditions are met.

We will first consider the case where the levels are arranged as shown in Fig. 1a. In the initial state, the system is at level U_i. As the system moves in the positive direction along the x axis, it reaches an intersection region where transitions between the levels become possible. Transition into the final state is possible only if the systems remains on the initial level as it passes the point of intersection of the U_i and U_d levels in the positive direction along the x axis. It then reaches the turning point b and changes direction. As it moves backwards, the system can transfer to the U_d level and then, by moving along this level, it can complete its transition to the level of the final state U_f at the point U_{fd}.

The probability of a transition between two levels in a single pass through their point of intersection is defined by the Landau–Zener formula [7]: $[1 - \exp(-2\pi\gamma)]$, where $\gamma=(\Delta E/2)^2/\hbar v|U_i'-U_f'|$. If the levels have slopes with the same sign at the point of intersection and the direction of motion changes during the transition, a transition between the levels can only take place by two trajectories (1 and 2 in Fig. 4), and the probability of this transition is defined by the expression $2\exp(-2\pi\gamma)[1 - \exp(-2\pi\gamma)]$. In the case of motion without a change of direction (right to left in Fig. 4), the transition i → f is possible only by one

trajectory (3) and its probability is equal to $[1 - \exp(-2\pi\gamma)]$. If, however, the slopes of the levels have different signs at their point of intersection (Fig. 5), there are an infinite number of possible trajectories, including multiple reflections, for transfer without a change of direction (two such trajectories are shown in Fig. 5). In this case, the probability of a transition without a change of direction [8] is $f(\gamma) = (1-e^{-2\pi\gamma}) \Big/ \left(1 - \frac{1}{2} e^{-2\pi\gamma}\right)$, while transfer with a change of direction is possible only by one trajectory (3) with a probability $\exp(-2\pi\gamma) \cdot [1 - \exp(-2\pi\gamma)]$. In the more complicated case where the system has three levels (i, d, and f), the probability of an i → f transition is defined by more complicated expressions. For the arrangement of levels shown in Fig. 1a,

$$W_{1a} = \frac{e^{-2\pi\gamma_{id}}(1-e^{-2\pi\gamma_{id}}) f(\gamma_{df})}{1-(1-e^{-2\pi\gamma_{id}})^2 [1-f(\gamma_{df})]}, \tag{2}$$

$$\gamma_{id} = \frac{(\Delta E_{id}/2)^2}{\hbar v_{id} \left| \frac{dU_i}{dx} - \frac{dU_d}{dx} \right|_{\cdot}}; \quad \gamma_{df} = \frac{(\Delta E_{df}/2)^2}{\hbar v_{df} \left| \frac{dU_d}{dx} - \frac{dU_f}{dx} \right|_{\cdot\cdot}}. \tag{3}$$

In the case of 1b, γ_{id} and γ_{df} must be interchanged in (2). For the arrangement of levels shown in Fig. 2a and b,

$$W_{2a} = f(\gamma_{id})[1-\exp(-2\pi\gamma_{fd})]; \; W_{2b} = f(\gamma_{df})[1-\exp(-2\pi\gamma_{id})]. \tag{4}$$

The average probability of a transition in unit time is defined by the expression

$$\overline{W}_{if} = A v_i \left[\frac{1}{T_i(E)} W_{if}(E) \right], \tag{5}$$

where T_i is the period of the vibrations in the initial state and averaging with respect to the energy E is carried out with the aid of a Gibbs distribution.

Various limiting cases are possible depending on the splitting of the levels.

1) With small splittings:

$$2\pi\gamma_{id} \ll 1, \; 2\pi\gamma_{df} \ll 1 \tag{6}$$

Eq. (2) takes the form

$$W_{1a} = 4\pi\gamma_{df} \cdot 2\pi\gamma_{id}, \tag{7}$$

and averaging of probability (7) leads to an expression exactly the same as (1).

2) Let us consider the case where the parameter corresponding to the higher of the intersection points of the levels has a high value ($\gamma_{df} \gg 1$ for Figs. 1a and 2a; $\gamma_{id} \gg 1$ for Figs. 1b and 2b). Then,

$$W_{1a} = e^{-2\pi\gamma_{id}}(1-e^{-2\pi\gamma_{id}}); \; W_{1b} = e^{-2\pi\gamma_{df}}(1-e^{-2\pi\gamma_{df}}); \tag{8}$$

$$W_{2a} = (1-e^{-2\pi\gamma_{id}}); \; W_{2b} = (1-e^{-2\pi\gamma_{df}}). \tag{8'}$$

In these cases, the transition from the intermediate to the final level ($\gamma_{df} \gg 1$) or from the initial to the intermediate level ($\gamma_{id} \gg 1$) takes place adiabatically. The transition probabilities defined by Eqs. (8) are low at both low and high values of the parameters γ_{id} and γ_{df}, while the transition probabilities defined by Eqs. (8') are low only at low γ_{id} and γ_{df}. Averaging probabilities (8) and (8') gives

$$W_{1a} = \frac{k\tau \exp[-(U_{df} - \Delta E_{df}/2)/kT]}{Z(kT) 2\pi\hbar} e^{-2\pi\gamma_{id}^{\circ}}(1-e^{-2\pi\gamma_{id}^{\circ}}), \tag{9}$$

$$W_{2a} = \frac{kT \exp[-(U_{df} - \Delta E_{df}/2) kT]}{Z(kT) 2\pi\hbar} (1-e^{-2\pi\gamma_{id}^{\circ}}), \tag{9'}$$

where

$$\gamma_{id}^{\bullet}=\frac{(\Delta E_{id}/2)^2}{\hbar\sqrt{2|U_{id}-U_{df}|/m}\left|\frac{dU_i}{dx}-\frac{dU_d}{dx}\right|^{\bullet}}.$$

$$\Delta E_{df}=2V_{df}\sqrt{FF'}/(F+F');\quad F=\left|\frac{dU_d}{dx}\right|^{\bullet},\quad F'=\left|\frac{dU_f}{dx}\right|^{\bullet}.$$

Analogous expressions are obtained for $\bar{W}_{1b}$ and $\bar{W}_{2b}$.

As follows from expressions (9) and (9'), the activation energy of the process decreases during the adiabatic transition, while the preexponential factor is determined by the parameters δ_{id}^{*} characterizing the degree of nonadiabaticity of the passage of the system through the region in the vicinity of the lower point of intersection of the levels.

Let us now consider the case where the levels are arranged as shown in Fig. 3. In this case, the expression for $W_{if}(E)$ is of the form†

$$W_{if}(E)=f(\gamma_{id})\cdot f(\gamma_{df}). \tag{10}$$

1) At low γ_{id} and γ_{df} values, when conditions (6) are met, Eq. (10) takes the form

$$W_{if}(E)=4\pi\gamma_{id}\cdot 4\pi\gamma_{df}. \tag{11}$$

This expression differs from (7) by a factor of 2. Accordingly, the expression $\bar{W}_{if}$ for the average transition probability in unit time differs from (1) only by this factor.

2) When one of the γ parameters is small (for example γ_{id}) and the other is large ($\gamma_{df} \gg 1$), we obtain‡

$$W=\frac{(2m)^{1/2}kT(\Delta E_{id}/2)^2\exp(-E_a/kT)}{Z(kT)\hbar^2\left|\frac{dU_i}{dx}-\frac{dU_d}{dx}\right|^{\bullet}\sqrt{|U_{fd}-U_{df}|}}, \tag{12}$$

$$E_a=\max\ (U_{di}-\Delta E_{id}/2,\ U_{df}-\Delta E_{df}/2).$$

In this case, transfer from the U_i level to the U_d level takes place nonadiabatically, whereas the transition between the U_d and U_f levels is adiabatic.

3) Finally, when $\gamma_{id} \gg 1$ and $\gamma_{fd} \gg 1$, we have

$$W=\frac{kT\exp(-E_a/kT)}{Z(kT)2\pi\hbar}$$

$$E_a=\max\ (U_{di}-\Delta E_{id}/2,\ U_{df}-\Delta E_{df}/2). \tag{13}$$

Here, the transitions at each point of intersection of the U_{id} and U_{df} levels take place adiabatically.

It should be noted that in the mixed case described by formula (12), we can expect that, other conditions being equal, an adiabatic transition will be observed in the vicinity of the higher point of intersection, since the effective velocity at this point, which is equal to the thermal velocity, is considerably lower than the effective velocity at the lower point of intersection, which is determined by the difference in the energies of these two intersects.

†In deriving Eq. (10), account was taken of the fact that real systems involve multidimensional levels, so there is no need to allow for the contribution from trajectories (Fig. 3) in which the system is first reflected from the turning point b on level U_d and then passes twice through the minimum in this level and finally returns to the point of intersection U_{df} of the U_d and U_f levels.

‡When Gibbs averaging is employed, the parameter γ generally changes since the rate v entering into it is a function of the energy. In the inequalities $\gamma \gg 1$ and $\gamma \gg 1$, therefore, the term v implies the thermal velocity. In averaging the expression for the probability of a nonadiabatic transition with respect to energy, it is assumed that the range of low, superthreshold energy values in which the nonadiabatic expression is not applicable is very narrow ($\ll kT$) and does not make a significant contribution to the averaged probability.

Finally, let us consider the situation represented in Fig. 6. In this case, we will assume that the electronic matrix element of the interaction energy between the reactants V_{if} is negligible, so that resonance splitting of the U_i and U_f levels can be disregarded in the absence of a bridging species. According to a quantum-mechanical calculation of the transition probability by second-order perturbation theory, the presence of a bridging species will result in the activation energy of the process being determined by the point of intersection of the U_i and U_f levels.

The method set forth in the present article allows us to obtain both the above result and the probability of an adiabatic transition, and also the corresponding criteria. In fact, the transition probability $W_{if}(E)$ at the energies below the point of intersection of the U_i and U_f levels is exponentially small. At energies within the $U_{if} < E < \min(U_{id}, U_{df})$ range (see Fig. 6), the probability $W_{if}(E)$ is mainly determined by the Landau–Zener formula:

$$W_{if}(E)=f(\gamma_{if}), \tag{14}$$

where

$$\gamma_{if}=(\Delta E_{if}/2)^2/\hbar v\left(\frac{dU_i}{dx}-\frac{dU_f}{dx}\right). \tag{15}$$

At energies higher than $\tilde{E}_a = \min(U_{id}, U_{df})$, transfer into the final state by movement along the intermediate level becomes possible. The probability of such a transition when the splitting of the levels is small is determined by the formula

$$W_{if}'=4\pi\gamma_{id}\cdot 4\pi\gamma_{df}, \tag{16}$$

and is exponentially small with respect to the parameters $2\pi\gamma_{if}$, $2\pi\gamma_{id}$, and $2\pi\gamma_{df}$ when the splitting of the levels is large.

On the basis of the above hypotheses, the splitting ΔE_{if} of the zero-approximation levels U_i and U_f (and consequently γ_{if}) is equal to zero according to first-order perturbation theory. When we allow for the interaction with the bridging species, however, ΔE_{if} proves to be nonzero, the minimum distance between the adiabatic levels being

$$\Delta E_{if}=2\frac{V_{id}V_{df}}{U_d^*-U_{if}}. \tag{17}$$

Averaging expression (14) with respect to energy leads to the normal expression for the transition probability in unit time between two levels [4] (the only difference being that ΔE_{if} is defined by Eq. (17)]. At the limit of low γ_{if} values (nonadiabatic transition), it is of the form

$$W_{if}=\frac{(\pi mkT)^{1/2}(\Delta E_{if}/2)^2}{Z(kT)\left(\frac{dU_i}{dx}-\frac{dU_f}{dx}\right)^*\hbar^2 2^{1/2}}e^{-U_{if}/kT}. \tag{18}$$

When $\gamma_{if} \gg 1$ (adiabatic transition), the transition probability can be written as

$$W_{if}=\frac{kT\exp[-(U_{if}-\varepsilon)/kT]}{Z(kT)2\pi\hbar},$$

$$\varepsilon=\frac{(|V_{id}|\sqrt{F'}+|V_{df}|\sqrt{F})^2}{(U_d^*-U_{if})(F-F')},\quad F=\left|\frac{dU_i}{dx}\right|^*,\quad F'=\left|\frac{dU_f}{dx}\right|^*. \tag{19}$$

It is easy to ascertain that transfer into the final state by movement along the intermediate level U_d does not make a significant contribution to the averaged transition probability, since it is exponentially small compared with the probability defined by Eqs. (18) and (19). Thus, in the case of a nonadiabatic reaction the transition probability is defined by Eq. (18), which is the same as the corresponding formula obtained by Madumarov, while in the case of an adiabatic reaction W_{if} is defined by Eq. (19).

It follows from the treatment in the present article that the semiclassical method of calculation is suitable for finding the probabilities of electron-transfer processes taking place by a bridging mechanism. In the case of nonadiabatic reactions, it gives the same

results as quantum-mechanical calculations on the basis of perturbation theory. In addition, it allows expressions to be obtained for the transition probability in adiabatic reactions.

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KINETICS OF ELECTRON TRANSFER REACTIONS BETWEEN MOLECULES OF POLYCYCLIC AROMATIC HYDROCARBONS AND THEIR RADICAL ANIONS

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A comparison is made of the experimental data for electron transfer between molecules of polycyclic aromatic hydrocarbons and their radical anions [1] with the quantum theory of charge transfer in a polar medium. An expression is derived for solvent reorganization energy when electron transfer occurs between nonspherical reactants, which is described by a model based on triaxial ellipsoids.

In a recent study [1] an attempt was made to compare the experimental data for the kinetics of electron transfer between molecules of polycyclic aromatic hydrocarbons and their radical anions $R_1^- + R_2 = R_1 + R_2^-$ with the Marcus theory of electron transfer [2]. In agreement with the Marcus theory it was reckoned that in the absence of Coulombic interaction between the reactants, the rate constant for the electron transfer could be represented as

$$k = A \exp(-\Delta G^*/RT), \quad (1)$$

$$\Delta G^* = E_r/4 + \Delta G^0/2 + (\Delta G^0)^2/4E_r, \quad (2)$$

$$E_r = E_s + E_i, \quad (3)$$

$$E_s = e^2(1/\varepsilon_{op} - 1/\varepsilon_{st})\,(1/2a_1 + 1/2a_2 - 1/r). \quad (4)$$

In expressions (1)-(4) the value of the preexponential coefficient A is identified with Z, the number of collisions of the reactants in unit time, ΔG^* and ΔG^0 are the free energy of activation and the free energy of reaction, E_r is the total energy of reorganization of the system, consisting of the solvent reorganization energy E_s and the reorganization energy of the chemical bonds of the reactants E_i, a_1 and a_2 are the radii of the reactants, r is the distance between the reactant centers, ε_{op} and ε_{st} are the optical and static dielectric constants of the solvent. The further development of the quantum theory of electron transfer reactions in

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