# INFLUENCE OF THE INTERACTION OF AN ELECTRON WITH A PHONON FIELD ON THE TRANSMISSION COEFFICIENT OF A NONADIABATIC TRANSITION IN THE CONDON APPROXIMATION

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The wave functions and electronic resonance integral in the transition configuration have been calculated for an outer-sphere electron-transfer reaction in the Condon approximation according to Pekar's model. It has been shown that upon transition of the system into the transition configuration the radius of localization of the electron on the donor increases, and the radius of localization of the electronic wave functions by a phonon field can strongly influence the value of the transmission coefficient. The effect increases with increasing electron-transfer distances.

In [1] there was a general discussion of the role of the dynamic interaction of electrons with phonon fields in the kinetics of electron transfer in polar media. In the present work we shall evaluate the change in the electronic resonance integral $V_i[q^*(\theta)]$, which, to a considerable extent, determines the value of the transmission coefficient of a nonadiabatic transition, due to the modulation of the electronic wave functions by a phonon field. The calculation will be carried out in the Condon approximation, in which the transition probability W is described by Eq. (19) from [1].

In order to evaluate the electronic resonance integral $V_i[q^*(\theta)]$ [Eq. (19) from [1]], we shall consider the transfer of a weakly bound electron in the Pekar model [2] and restrict ourselves to the two-level approximation with respect to the basis states $\varphi_{\gamma A}$ and $\varphi_{\mu B}$ ($C_{i\gamma} = \delta_{\gamma\gamma_0}$; $C_{f\mu} = \delta_{\mu\mu_0}$), i.e., we shall assume that $\varphi_i = \varphi_A$ and $\varphi_f = \varphi_B$ (the subscripts $\gamma_0$ and $\mu_0$ will be omitted) (for an explanation of the notation see [1]).

If the dielectric is described in terms of the specific inertial polarization of the medium $\mathbf{P}(\mathbf{r})$, to define the interactions of the electron with the phonon field which appear in the equations for $\varphi_A$ and $\varphi_B$ [Eqs. (5) and (6) in [1]], it is necessary to find the value of the polarization $\mathbf{P}^*(\mathbf{r})$ in the transition configuration $q^*$. Using Eq. (18) from [1] and the summation rule in [3], we can show that for spherical symmetric ions A and B

$$\mathbf{P}^*(\mathbf{r}) = R_i(\theta)\mathbf{P}_{0i}(\mathbf{r}) + R_f(\theta)\mathbf{P}_{0f}(\mathbf{r}), \tag{1}$$

where $\mathbf{P}_{0i}(\mathbf{r})$ and $\mathbf{P}_{0f}(\mathbf{r})$ are the equilibrium values of the polarization in the initial and final states.

The functions $R_i(\theta)$ and $R_f(\theta)$ are defined as

$$R_i(\theta) = \frac{4\pi}{c}\cdot\frac{2}{\pi}\int_0^{\omega_z} d\omega\,[\mathrm{Im}\,\varepsilon(\omega)/\omega|\varepsilon(\omega)|^2]\ \mathrm{th}\frac{\hbar\omega(1-\theta)}{2kT}\Big/\left[\mathrm{th}\frac{\hbar\omega(1-\theta)}{2kT}+\mathrm{th}\frac{\hbar\omega\theta}{2kT}\right], \tag{2}$$

$$R_f(\theta) = \frac{4\pi}{c}\cdot\frac{2}{\pi}\int_0^{\omega_z} d\omega\,[\mathrm{Im}\,\varepsilon(\omega)/\omega|\varepsilon(\omega)|^2]\mathrm{th}\frac{\hbar\omega\theta}{2kT}\Big/\left[\mathrm{th}\frac{\hbar\omega(1-\theta)}{2kT}+\mathrm{th}\frac{\hbar\omega\theta}{2kT}\right], \tag{3}$$

where $\varepsilon(\omega)$ is the complex dielectric constant of the medium, and $\omega_z$ is the characteristic frequency, which separates the inertial and inertialess polarization.

Everywhere below we shall restrict ourselves to the case in which the phonon spectrum is completely classical ($\hbar\omega_k \ll kT$). Then from (1) it follows that

$$\mathbf{P}^*(\mathbf{r}) = (1-\theta)\mathbf{P}_{0i}(\mathbf{r}) + \theta\mathbf{P}_{0f}(\mathbf{r}), \tag{4}$$

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and that $P_{0i}(\mathbf{r})$ and $P_{0f}(\mathbf{r})$ are related to the corresponding inductances $D_i$ and $D_f$ by the usual expressions [2]:

$$\mathbf{P}_{0i}(\mathbf{r})=\frac{c}{4\pi}\mathbf{D}_i(\mathbf{r}); \quad \mathbf{P}_{0f}(\mathbf{r})=\frac{c}{4\pi}\mathbf{D}_f(\mathbf{r}); \quad c=\frac{1}{\varepsilon_0}-\frac{1}{\varepsilon_\infty}. \tag{5}$$

It should be noted that Eqs. (1)-(5) comprise a very important result of the theory. They make it possible to express the potential energies of the interaction of an electron with a phonon field in terms of quantitites corresponding to the initial and final equilibrium states. This circumstance places the problem of calculating the electronic wave functions in the transition configuration on the same level with the simpler problems of calculating the electronic states of the reactants and products of a reaction in their equilibrium configurations.

The inductances $D_i(\mathbf{r})$ and $D_f(\mathbf{r})$ may be written in the form

$$\begin{aligned}\mathbf{D}_i(\mathbf{r})&=\mathbf{D}_A(\mathbf{r})+\mathbf{D}_{eA}(\mathbf{r})+\mathbf{D}_B(\mathbf{r}-\mathbf{R});\\ \mathbf{D}_f(\mathbf{r})&=\mathbf{D}_A(\mathbf{r})+\mathbf{D}_{eB}(\mathbf{r})+\mathbf{D}_B(\mathbf{r}-\mathbf{R}),\end{aligned} \tag{6}$$

where $D_A$ and $D_B$ are the inductances created by centers A and B, and $D_{eA}(\mathbf{r})$ and $D_{eB}(\mathbf{r}-\mathbf{R})$ are the inductances created by an electron localized near centers A and B.

Then for $P(\mathbf{r}, \theta)$ we have

$$\mathbf{P}(\mathbf{r},\theta)=\frac{c}{4\pi}[\mathbf{D}_A(\mathbf{r})+(1-\theta)\mathbf{D}_{eA}(\mathbf{r})+\mathbf{D}_B(\mathbf{r}-\mathbf{R})+\theta\mathbf{D}_{eB}(\mathbf{r}-\mathbf{R})]\equiv\mathbf{P}_A(\mathbf{r},\theta)+\mathbf{P}_B(\mathbf{r},\theta). \tag{7}$$

Accordingly, for the interactions of electrons with phonons $V_{ep}^{A}$ and $V_{ep}^{B}$ appearing in Eqs. (5) and (6) in [1], we obtain

$$V_{ep}^{A}(\mathbf{x};\theta)=-\int\mathbf{P}_A(\mathbf{r},\theta)\mathbf{D}_e(\mathbf{r},\mathbf{x})d^3r, \tag{8}$$

$$V_{ep}^{B}(\mathbf{x};\theta)=-\int\mathbf{P}_B(\mathbf{r},\theta)\mathbf{D}_e(\mathbf{r},\mathbf{x})d^3r. \tag{9}$$

In order to find the electronic wave functions, we shall use the direct variational method in [2]. For the initial state we start out from the functional

$$\begin{aligned}F_i[\varphi_i,P]=(\hbar^2/2m)\int d^3x|\nabla\varphi_i|^2-\int d^3r\,\mathbf{P}(\mathbf{r})\mathbf{D}_e^{(A)}(\mathbf{r})+(2\pi/c)\int d^3r[\mathbf{P}(\mathbf{r})]^2-\\ -(z_1e^2/\varepsilon_0)\int d^3r\,|\varphi_i|^2/r-\int d^3r\,\mathbf{P}(\mathbf{r})\mathbf{D}_A(\mathbf{r}),\end{aligned} \tag{10}$$

where $\varepsilon_0$ is the high-frequency limit of the dielectric constant of the medium, $ez_1$ is the charge of center A, and

$$\mathbf{D}_e^{(A)}(\mathbf{r})=-e\int d^3x\,|\varphi_i(\mathbf{x})|^2\frac{(\mathbf{r}-\mathbf{x})}{|\mathbf{r}-\mathbf{x}|^3}. \tag{11}$$

Since the inertialess polarization is adiabatically isolated from the motion of the electron being transferred, the interaction of the electron with center A in the case of a fixed value of the inertial polarization $P(\mathbf{r})$ is renormalized with consideration of the shielding of the field by the inertialess polarization.

Varying functional (11) with respect to $\mathbf{P}(\mathbf{r})$, we obtain the relationship between the initial equilibrium polarization $P_{0i}^{A}$ and the inductances

$$\mathbf{P}_{0i}^{A}(\mathbf{r})=(c/4\pi)\{\mathbf{D}_A(\mathbf{r})+\mathbf{D}_e^{(A)}[\varphi_i,\mathbf{r}]\}. \tag{12}$$

The wave function of the initial channel $\varphi_i(\mathbf{x};\mathbf{P}_{0i}^{A})$ in the initial equilibrium configuration $P_{0i}^{A}$ is found by minimizing the functional $F_i[\varphi_i, \mathbf{P}_{0i}^{A}]$, which is obtained after substituting (12) into (11):

$$\begin{aligned}F_i[\varphi_i,\mathbf{P}_{0i}^{A}]=(\hbar^2/2m)\int d^3x\,|\nabla\varphi_i|^2-(c/8\pi)\int d^3r[\mathbf{D}_e^{(A)}(\mathbf{r})]^2-\\ -(z_1e^2/\varepsilon_\infty)\int d^3r|\varphi_i|^2/r-(c/8\pi)\int d^3r[\mathbf{D}_A(\mathbf{r})]^2.\end{aligned} \tag{13}$$

If as the functions varied we choose, for example

$$\varphi_i(x;\ \mathbf{P}_{0i}^{A})=\varphi_A(x;\ \mathbf{P}_{0i}^{A})=A_i\exp(-\alpha_{0i}\cdot x), \tag{14}$$

then, according to [2], for $A_i$ and $\alpha_{0i}$ we have

$$\alpha_{0i}=(me^2/2\hbar^2)(2z_1/\varepsilon_s+5c/8);\quad A_i=(\alpha_{0i}^3/\pi)^{1/2}. \tag{15}$$

Similarly, for $\varphi_f(\mathbf{x};\ \mathbf{P}_{0f}^{B})$ we obtain

$$\varphi_f(\mathbf{x};\ \mathbf{P}_{0f}^{B})=\varphi_B(\mathbf{x};\ \mathbf{P}_{0f}^{B})=A_f\exp[-\alpha_{0f}|\mathbf{x}-\mathbf{R}|], \tag{16}$$

$$\alpha_{0f}=(me^2/2\hbar^2)(2z_2/\varepsilon_s+5c/8);\quad A_f=(\alpha_{0f}^3/\pi)^{1/2}. \tag{17}$$

To find the wave functions in the configuration corresponding to the polarization value $P(r,\theta)$ [see Eq. (4)], it is necessary to minimize the functionals $F_i[\varphi_i;\ \mathbf{P}_A(\mathbf{r},\theta)]$ and $F_f[\varphi_f;\ P_B(r,\theta)]$ at fixed $P_A(r,\theta)$ and $P_B(r,\theta)$ [see Eq. (7)]. For example, leaving only terms which are dependent on the electronic wave function $\varphi_i(x, P)$ in the functional of the initial channel $F_i[\varphi_i,\ P_A(r,\theta)]$, we obtain

$$F_i[\varphi_i;\mathbf{P}_A(\mathbf{r},\theta)]=(\hbar^2/2m)\int d^3x|\nabla\varphi_i|^2-\int d^3r\,\mathbf{P}_A(\mathbf{r},\theta)\mathbf{D}_e^{(A)}(\mathbf{r})-(z_1e^2/\varepsilon_0)\int d^3r\,|\varphi_i|^2/r=(\hbar^2/2m)\int d^3x\,|\nabla\varphi_i|^2$$
$$-(c/4\pi)R_i(\theta)\int d^3r\,\mathbf{D}_e^{(A)}(\mathbf{r};\mathbf{P}_{0i}^{A})\mathbf{D}_e^{(A)}(\mathbf{r})-(z_1e^2/\varepsilon_s)\int d^3r\,|\varphi_i|^2/r. \tag{18}$$

Similarly, for the final channel we have

$$F_f[\varphi_f,\mathbf{P}_B(\mathbf{r},\theta)]=(\hbar^2/2m)\int d^3x\,|\nabla\varphi_f|^2-(c/4\pi)R_f(\theta)\int d^3r\,\mathbf{D}_e^{(B)}(\mathbf{r}-\mathbf{R};\mathbf{P}_{0f}^{B})\mathbf{D}_e^{(B)}(\mathbf{r}-\mathbf{R})$$
$$-(z_2e^2/\varepsilon_s)\int d^3r\,|\varphi_f|^2/|\mathbf{r}-\mathbf{R}|. \tag{19}$$

For the case of a classical phonon spectrum considered here, we have

$$R_i(\theta)=1-\theta;\quad R_f(\theta)=\theta. \tag{20}$$

Using functions of type (14) and (16) as the functions varied, we find the dependence of $\alpha_i$ and $\alpha_f$ on $\theta^*$. At small values of $\theta^*$ we obtain

$$\alpha_i(\theta^*)\simeq\alpha_{0i}[{}^{11}/_5+16z_1/5c\varepsilon_s-\theta^*]/({}^{11}/_5+16z_1/5c\varepsilon_s). \tag{21}$$

Accordingly, when $\theta^*$ is close to unity ($|\eta|=|1-\theta^*|\ll 1$), we have

$$\alpha_f(\theta^*)\approx\alpha_{0f}[{}^{11}/_5+16z_2/5c\varepsilon_s-\eta^*]/({}^{11}/_5+16z_2/5c\varepsilon_s). \tag{22}$$

The dependence of $\alpha_i$ and $\alpha_f$ on $\theta$ at arbitrary real values of $\theta$ is shown in Fig. 1. As is seen from (21) and (22) and from Fig. 1, $\alpha_i$ decreases with increasing $\theta$, and $\alpha_f$ increases. The radius of localization of the electron in the initial and final states increases and decreases, respectively. For a rough estimate of the effect of the modulation of the electronic

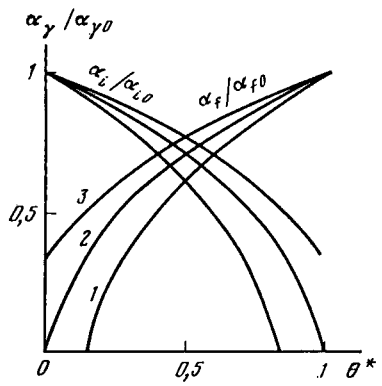


Fig. 1. Dependence of the reciprocal localization radii of an electron $\alpha_i$ and $\alpha_f$ on $\theta^*$ for various values of the parameter $P/S = 16z/5c\varepsilon_s$: 1) $P/S = -0.5$; 2) 0; 3) 0.5.

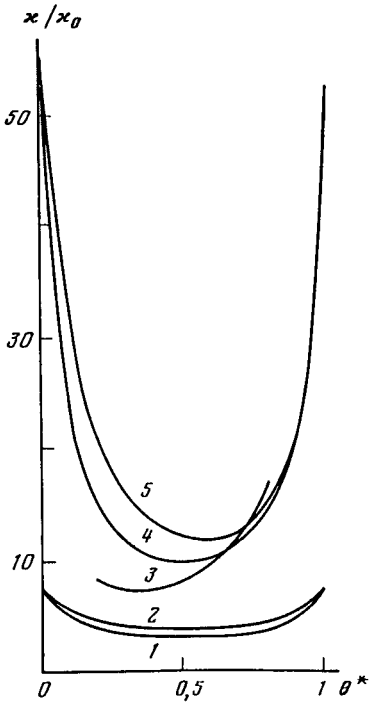


Fig. 2. Dependence of the transmission coefficient $\varkappa$ on $\theta^*$ for various values of the parameters P/S and $\alpha_0 x^* = 5mce^2x^*/16\hbar^2$: 1) $P_i/S = P_f/S = 0$; $\alpha_0 x^* = 1$; 2) $P_i/S = P_f/S = 0.5$, $\alpha_0 x^* = 1$; 3) $P_i/S = 0.5$, $P_f/S = -0.5$, $\alpha_0 x^* = 2$; 4) $P_i/S = P_f/S = 0$, $\alpha_0 x^* = 2$; 5) $P_i/S = 0$, $P_f/S = 0.5$, $\alpha_0 x^* = 2$.

wave functions by the phonon field in the transmission coefficient, we shall use the approximate expression for the electronic resonance integral

$$V_i \approx \Delta x V_i^0 \varphi_i(x^*, \mathbf{P}_A(\mathbf{r}, \theta^*))\varphi_f(x^*, \mathbf{P}_B(\mathbf{r}, \theta^*)),$$

$$V_i^0 = -e^2 z_2/\varepsilon_s |\mathbf{x}^* - \mathbf{R}| - \theta^* e^2 c/|\mathbf{x}^* - \mathbf{R}| - \tag{23}$$
$$-\langle\varphi_i|\left(-e^2 z_2/\varepsilon_s|\mathbf{x}-\mathbf{R}| - \theta^* e^2 c/|\mathbf{x}-\mathbf{R}|\right)|\varphi_i\rangle,$$

where $\theta^*$ is the Brønsted symmetry factor, R is the distance between centers A and B, $x^*$ is the point of the maximum of the integrand with respect to the coordinates of the electron, and $\Delta x$ is the width of the integration range which makes a significant contribution to the integral.

At the same time, for the sake of simplicity, we shall assume that $x^* \approx R/2$ and is constant. In such a case, Eq. (23) yields an underestimated value for the electronic matrix element. In the approximation indicated the expression for the transition probability may be written in the form

$$W \sim (S_{if}^0)^2 \exp\{-2[\alpha_i(\theta^*) - \alpha_{0i} + \tag{24}$$
$$+\alpha_f(\theta^*) - \alpha_{0f}]x^*\} \exp[-\beta(\theta^*)^2 E_r],$$

where $E_r$ is the energy of reorganization of the medium, and $S_{if}^0$ is the overlap integral calculated with the aid of the equilibrium electronic wave functions $\varphi_i(x; P_{0i}^A)$ and $\varphi_f(x; P_{0f}^B)$.

Figure 2 presents the dependence of $(S_{if}/S_{if}^0)^2$ on $\theta^*$. As is see from Fig. 2, the modulation of the electronic wave functions by the phonon field can have a very strong influence on the value of the transition probability, and this effect increases with increasing distance between centers A and B.

The symmetry factor $\theta^*$ is defined as the saddle point in the integral with respect to $\theta$ in Eq. (19) for the transition probability in [1]. As is seen from (21) and (22) and from Fig. 1, the dependence of $\alpha_i$ and $\alpha_f$ on $\theta$ is fairly weak, and when the conditions

$$[2x^*|d(\alpha_i+\alpha_f)/d\theta|]^2 \ll 4E_r/kT, \tag{25}$$
$$2x^*|d^2(\alpha_i+\alpha_f)/d\theta^2| \ll E_r/kT$$

are fulfilled it can be neglected in the determination of the saddle point $\theta^*$. If these conditions are not fulfilled, the dependence indicated should be taken into account. It is not

difficult to see [see (21) and (22)] that near $\theta^* = 0$ this results, in particular, in the displacement of $\theta^*$ by a value proportional to kT. In the case of light-induced electron-transfer processes, the latter, in particular, results in a temperature dependence of the absorption-band maximum.

In the present work the calculation was carried out in the framework of the Condon approximation. From the more general treatment in the next communication it will be seen that the applicability of the Condon approximation is determined by inequalities of type (25). In conclusion, we note that Eqs. (23) and (24) for the transition probability contain terms of the type $-\theta^* e^2 c/|x^* - R|$ besides the interaction with the "foreign" ion $-e^2 z_2/\varepsilon_s |x^* - R|$. When the difference between $\varepsilon_s$ and $\varepsilon_o$ is large and $\theta^* \sim 1/2$, the latter can significantly exceed the energy of the interaction with the ion in which the transition is completed.

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# ELECTROLYSIS OF WATER: REGIMES OF GAS EVOLUTION IN POROUS, HYDROPHILIC ELECTRODES


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The evolution with time of gas bubbles formed during the electrolysis of water at the front surface of a hydrophilic, porous electrode is studied. It is shown that two, qualitatively different regimes of gas evolution are possible: stepwise and pulsating.


In the electrolysis of water at a porous, hydrophilic electrode, the process of gas evolution begins with the formation of separate, microscopic gas bubbles. They form, primarily, on the front side of the electrode adjacent to the gas impermeable membrane separating the electrodes. This is because the ohmic loss of the electrode polarization $\eta$, is a maximum at the surface of the membrane/electrode separation. The number of gas bubbles increases stepwise, they agglomerate, and at some moment of time they coalesce into a single gas bubble (Fig. 1a). From this moment, earlier stages aside, we begin the analysis of gas

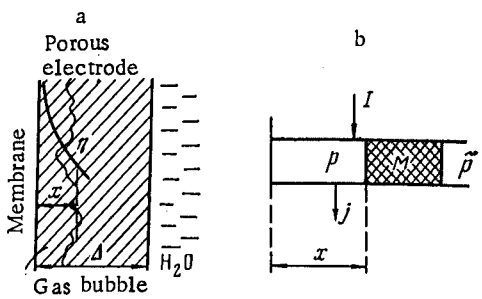


Fig. 1. Schematic representation of a porous electrode (a) and the model for calculating the regime of gas evolution (b). Explanation in text.


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