ROLE OF THE INTERACTION OF REACTANTS WITH A PHONON FIELD IN ELECTRON-TRANSFER PROCESSES IN POLAR MEDIA

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The role of the interaction of electrons with optical phonons in the channel approach to the calculation of the probability of charge transfer in a polar medium has been considered. It has been shown that the part of the interaction of an electron with the polarization of the medium which creates a potential well for the electron near one of the ions, rather than the entire interaction, should be included in the determination of the reaction channel. At the same time, an additional term associated with the interaction with the polarization of the medium caused by a "foreign" ion appears in the interaction causing the reaction.

The interaction of electrons with polarization is known to play an important role in charge-transfer processes in polar media, such as electron transfer between impurities and F centers in polar crystals, polaron jumps in crystals, the reactions of solvated and trapped electrons in solid matrices and polar liquids, and electron-transfer reactions in solutions. If the overlap of the electronic wave functions between the first and second centers and the interaction between them are sufficiently small, the calculation of the mean probability of a transition per unit time W is usually carried out according to perturbation theory [1, 2]:

$$W=\frac{2\pi}{\hbar}\sum_{m,n}e^{(F_i-E_{im})\hbar/T}|\langle\varphi_f\chi_{fn}|\hat{V}_i|\varphi_i\chi_{im}\rangle|^2\delta(E_{im}-E_{fn}), \quad (1)$$

where φ_i, χ_{im}, and E_{im} are the electronic and phonon wave functions and the energies of the initial state in the first localization, center of the electron (A), φ_f, χ_{fn}, and E_{fn} are the corresponding quantities for the second center (b), F_i is the free energy of the initial state, and $\hat{V}_i$ is the interaction resulting in the electronic transition.

The electronic wave functions $\varphi_i(x; q)$ and $\varphi_f(x; q)$ used in the simplest variant of the theory are solutions of the equations

$$[T_e+V_{eA}+V_{ep}(q)]\varphi_i(x; q)=\varepsilon_i(q)\varphi_i(x; q), \quad (2)$$

$$[T_e+V_{eB}+V_{ep}(q)]\varphi_f(x; q)=\varepsilon_f(q)\varphi_f(x; q) \quad (3)$$

with fixed phonon coordinates q, where T_e is the kinetic energy of the electron, V_{eA} and V_{eB} are the interactions of the electron with centers A and B, and $V_{ep}(q)$ is the interaction of the electron with the phonons. The interactions V_{eB} and V_{eA} appear as the interactions $\hat{V}_i$ and $\hat{V}_f$ in (1), which result in the forward and reverse transitions, respectively.

A somewhat different definition of φ_i and φ_f was used in the work of Efrima and Bixon [3], where the equation defining these states were similar to (2) and (3) with the one difference that instead of $V_{ep}(q)$ they contain $V_{ep}(q_{oi})$, where q_{oi} are the equilibrium values of the phonon coordinates corresponding to the initial state. Accordingly, the interaction causing the transition contains the additional term $V_{ep}(q) - V_{ep}(q_{oi})$.

The distortion of the states φ_i (φ_f) by the interaction V_{eB} (V_{eA}), as well as the nonorthogonality of the wave functions φ_i and φ_f, have formally been taken into account in the calculation of the transition probability in a number of studies. The latter factor, in particular, results in renormalization of the interaction V_i and V_f as a consequence of the subtraction of matrix elements of the type $\langle\varphi_i|V_{eB}|\varphi_i\rangle$ and $\langle\varphi_f|V_{eA}|\varphi_f\rangle$ from them. In most studies

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on the theory of electron transfer, the dependence of the electronic wave functions φ_i and φ_f on the phonon coordinates is neglected in comparison to the dependence of the phonon wave functions on q, and the electronic matrix element $\langle\varphi_f|\hat{V}_i|\varphi_i\rangle$ is taken out of the integral sign with respect to q at the point q*, which corresponds to the maximum of the integrand (the Condon approximation).

In practical calculations in the framework of the Condon approximation the electronic matrix element is either not calculated or is evaluated with the use of the electronic wave functions of centers A and B without consideration of the interaction of the electrons with the phonon field. Such an approximation is apparently good for electron transfer between the deep states in A and B; however, it is inadequate for the transfer of weakly bound electrons (the transfer of trapped and solvated electrons and the transfer of electrons between F centers) owing to the strong dependence of the wave functions on the phonon coordinates. The purpose of the present work was to carry out a more detailed analysis of the role of the interaction of electrons with phonons (polarization) in electron-transfer processes.

First of all, let us consider the interaction of an electron with a phonon field in greater detail. The equilibrium distribution of the inertial polarization in a medium near centers A and B in the absence of an electron has the form

$$\mathbf{P}_0(\mathbf{r})=\frac{c}{4\pi}\mathbf{D}(\mathbf{r})=\frac{1}{4\pi}\left(\frac{1}{\varepsilon_0}-\frac{1}{\varepsilon_\infty}\right)[\mathbf{D}_A(\mathbf{r})+\mathbf{D}_B(\mathbf{r}-\mathbf{R})]\equiv\mathbf{P}_0^A(\mathbf{r})+\mathbf{P}_0^B(\mathbf{r}), \tag{4}$$

where D_A and D_B are the electrostatic inductances induced by the charges of centers A and B.

From (4) it is seen that in the definition of the initial and final electronic states φ_i and φ_f in Eqs. (2) and (3) it is unwise to include the entire interaction of the electron with the polarization $V_{ep}(x; q)$, which contains the interaction both with the polarization $P_0^A(r)$ near center A and with the polarization $P_0^B(r)$ near center B. This becomes most evident in cases in which centers A and B are negatively charged (z_A, $z_B < 0$). Then the potential energy V_{ep} for the distribution of the polarization described, for example, by Eq. (4) contains two potential wells $V_{ep} = V_{ep}^A + V_{ep}^B$, which are located near centers A and B. In this case, the solutions of Eqs. (2)-(3) generally do not describe states corresponding to the localization of an electron on the respective center.

As the basis wave functions $\varphi_{\gamma A}(x; q)$ and $\varphi_{\mu B}(x; q)$ for the initial and final states it is reasonable to choose solutions of the equations

$$[T_e+V_{eA}+V_{ep}^A(x; q)]\varphi_{\gamma A}(x; q)=\varepsilon_{\gamma A}(q)\varphi_{\gamma A}(x; q), \tag{5}$$

$$[T_e+V_{eB}+V_{ep}^B(x; q)]\varphi_{\mu B}(x; q)=\varepsilon_{\mu B}(q)\varphi_{\mu B}(x; q). \tag{6}$$

At arbitrary values of the phonon coordinates the potential energy V_{ep} may contain several potential wells. In V_{ep}^A and V_{ep}^B it is reasonable to include only the part of the potential energy which maintains the localization of an electron near the respective center. As will be seen from the following, the main role in the calculation of the transition probability is played by the oscillations of the polarization under which V_{ep}^A and V_{ep}^B maintain their form and vary only in intensity. Therefore a completely unequivocal division of V_{ep} into V_{ep}^A and V_{ep}^B can be made in a certain approximation.

Using the basis functions $\varphi_{\gamma A}(x; q)$ and $\varphi_{\mu B}(x; q)$, we can write the wave functions of the initial and final states in the form

$$\varphi_i(x; q)=\sum_\gamma C_{i\gamma}(q)\gamma_{\gamma A}(x; q), \tag{7}$$

$$\varphi_f(x; q)=\sum_\mu C_{f\mu}(q)\varphi_{\mu B}(x; q), \tag{8}$$

where the coefficients $C_{i\gamma}$ and $C_{f\mu}$ are determined from the equations

$$\langle\varphi_{\gamma' A}(x; q)|T_e+V_{eA}+V_{eB}+V_{ep}-\varepsilon_i(q)\left|\sum_\gamma C_{i\gamma}(q)\varphi_{\gamma A}(x; q)\right\rangle=0, \tag{9}$$

$$\langle\varphi_{\mu'B}(x;q)|T_e+V_{eA}+V_{eB}+V_{ep}-\varepsilon_f(q)\Big|\sum_{\mu}C_{f\mu}(q)\varphi_{\mu B}(x;q)\Big\rangle=0, \tag{10}$$

$$\langle\varphi_i|\varphi_i\rangle=1;\ \ \langle\varphi_f|\varphi_f\rangle=1. \tag{11}$$

If we neglect the terms on the order of $|S_{if}|^2=|\langle\varphi_i|\varphi_f\rangle|^2$, the electronic matrix elements V_i and V_f from the interaction operators $\hat{V}_i$ and $\hat{V}_f$, which cause the forward and reverse transitions, have the form

$$V_i=\langle\varphi_f|V_i|\varphi_i\rangle=\sum_{\mu,\gamma}C_{f\mu}^{*}C_{i\gamma}\langle\mu|\gamma\rangle[\varepsilon_{\gamma A}(q)-\sum_{\gamma'}\varepsilon_{\gamma' A}(q)|C_{i\gamma'}|^2]+$$

$$+\sum_{\mu,\gamma}C_{f\mu}^{*}C_{i\gamma}\langle\mu|(V_{eB}+V_{ep}^{B}-\sum_{\gamma',\gamma''}C_{i\gamma'}^{*}C_{i\gamma''}\langle\gamma'|V_{eB}+V_{ep}^{B}|\gamma''\rangle)|\gamma\rangle, \tag{12}$$

$$V_f=\langle\varphi_i|V_f|\varphi_f\rangle=\sum_{\gamma,\mu}C_{i\gamma}^{*}C_{f\mu}\langle\gamma|\mu\rangle[\varepsilon_{\mu B}(q)-\sum_{\mu'}\varepsilon_{\mu' B}(q)|C_{f\mu'}|^2]+$$

$$+\sum_{\gamma,\mu}C_{i\gamma}^{*}C_{f\mu}\langle\gamma|(V_{eA}+V_{ep}^{A}-\sum_{\mu',\mu''}C_{f\mu'}^{*}C_{f\mu''}\langle\mu'|V_{eA}+V_{ep}^{A}|\mu''\rangle)|\mu\rangle, \tag{13}$$

where $\langle\gamma|\mu\rangle=\langle\varphi_{\gamma A}|\varphi_{\mu B}\rangle$.

Thus, not only the interaction of the electron with center B(V_{eB}), but also the interaction of the electron with the inertial polarization near center B(V_{ep}^{B}) act as the perturbation causing electron transfer from center A to B. The latter interaction is especially significant for reactions involving solvated or trapped electrons. In particular, in the model of a polaron with a large radius, this interaction is the only interaction causing the formation of a solvated electron.

We shall calculate the transition probability in a very simple model, assuming that the adiabatic potentials in the initial and final states have the forms

$$U_i=\sum_{k}\frac{1}{2}\hbar\omega_k(q_k-q_{k0i})^2, \tag{14}$$

$$U_f=\sum_{k}\frac{1}{2}\hbar\omega_k(q_k-q_{k0f})^2+\Delta J, \tag{15}$$

where

$$q_{k0i}=-g_{ki}/\hbar\omega_k;\ \ q_{k0f}=-g_{kf}/\hbar\omega_k, \tag{16}$$

and g_{ki} and g_{kf} are the binding constants of the electron to the phonons in the initial and final states.

Such a form of writing the adiabatic potentials means that we postulate linear (with respect to the coordinates of the phonons) binding of the electrons to the phonon field and neglect the influence of the modulation of the electronic wave functions by the phonon field on the form of the adiabatic potentials. A treatment of this effect will be given in one of the subsequent communications.

Using a generating function, we can write the transition probability in the Condon approximation in the form

$$W=\int_{c-i\infty}^{c+i\infty}d\theta|V_i(q^{*}(\theta))|^2g(\theta)\int_{-\infty}^{\infty}\exp\left\{-\beta\theta\Delta J-\sum_{k}\left[(q_k-q_{k0i})^2\mathrm{th}\frac{\beta\hbar\omega_k(1-\theta)}{2}+(q_k-q_{k0f})^2\mathrm{th}\frac{\beta\hbar\omega_k\theta}{2}\right]\right\}\prod_{k}dq_k, \tag{17}$$

where $\beta = 1/kT$, $q^*(\theta)$ is the point of the maximum of the integrand in the integral with respect to q_k, i.e.,

$$q_k^*(\theta)=\left[q_{k0i}\,\mathrm{th}\frac{\beta\hbar\omega_k(1-\theta)}{2}+q_{k0f}\,\mathrm{th}\frac{\beta\hbar\omega_k\theta}{2}\right]\Big/\left[\mathrm{th}\frac{\beta\hbar\omega_k(1-\theta)}{2}+\mathrm{th}\frac{\beta\hbar\omega_k\theta}{2}\right], \tag{18}$$

and the expression for $g(\theta)$ is given in [2]. As will be seen from the following, expressions of type (18) make it possible to concretize the form of V_{ep}^{A} and V_{ep}^{B} in the evaluation of the influence of the modulation of the electronic wave functions on an electronic matrix element [4].

Integration over q_k yields

$$W=\int_{c-i\infty}^{c+i\infty} d\theta\,\tilde{g}(\theta)\,|V_i(q^*(\theta))|^2\exp[-\beta\theta\Delta J-\beta\mathcal{F}(\theta)], \tag{19}$$

where

$$\mathcal{F}(\theta)=\frac{1}{\beta}\sum_k (q_{k0i}-q_{k0f})^2\,\mathrm{sh}\frac{\beta\hbar\omega_k(1-\theta)}{2}\,\mathrm{sh}\frac{\beta\hbar\omega_k\theta}{2}\Big/\,\mathrm{sh}\frac{\beta\hbar\omega_k}{2}, \tag{20}$$

$$\tilde{g}(\theta)=g(\theta)\left\{\det\left\|\frac{1}{\pi}\delta_{\sigma\rho}\left(\mathrm{th}\frac{\beta\hbar\omega_\sigma(1-\theta)}{2}+\mathrm{th}\frac{\beta\hbar\omega_\sigma\theta}{2}\right)\right\|\right\}^{-1/2}. \tag{21}$$

The integral over θ is calculated by various methods, depending on the form of the phonon spectrum and the binding force of the electrons to the phonons. Below we shall restrict ourselves to the case of strong binding and a fairly broad phonon spectrum [1], in which the integral can be calculated by the saddle-point method. Then for W we have [1]

$$W\approx\tilde{g}(\theta^*)\Delta\,|V_i(q^*(\theta^*))|^2\exp\{-\beta\theta^*\Delta J-\beta\mathcal{F}(\theta^*)\}, \tag{22}$$

where Δ is the width of the saddle-point region and θ^* is determined by the equation

$$\Delta J+d\mathcal{F}/d\theta=\frac{1}{\beta}\frac{d}{d\theta}\ln|V_i(q^*(\theta))|. \tag{23}$$

We note that the dependence of V_i and θ is determined both by the modulation of the electronic wave functions by the phonon field and by the dependence on q^* (and consequently on θ) of the interaction of the electron with the phonons $V_{ep}^{B}(x;\,q)$, which appear in $\hat{V}_i$ [see (12) and (13)]. Equations (22) and (23) are the final general expressions for the transition probability in the approximation indicated. Their further concretization requires more detailed information on the properties of the system under consideration.

In conclusion, we note that the main result of the treatment carried out is the following. In the determination of reaction channels in the calculation of the probability of a nonadiabatic electronic transition between localized states in a polar medium it is wise to include only the part of the reaction of the electron with the inertial polarization of the medium (the phonon field) which provides for localization of the electron in the respective region in space, rather than the entire interaction. The interaction resulting in the transition, which has an additional term, viz., the off-diagonal part of the interaction with the inertial polarization of the medium having a "foreign" ion as its "localization" center, is appropriately renormalized. The basis wave functions of the electron needed for the calculation of the electronic resonance integral are determined by the solution of Eqs. (5) and (6), where $V_{ep}^{A}(x;\,q)$ and $V_{ep}^{B}(x;\,q)$ should be calculated at the point $q = q^*$.

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