CALCULATION OF THE ACTIVATION PROBABILITY FOR A JUMP OF A SMALL-RADIUS POLARON

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We analyze a formula for the high-temperature jump probability of a small-radius polaron onto neighboring lattice points of the lattice, which is suitable for larger values of the resonance integral J than was the case in earlier obtained results. The magnitude of J determines the width of the initial band (ignoring the strong electron-phonon interaction) and occurs in the determination of one of the basic parameters of the theory η_2 ($\eta_2 \sim J^2$). We show that the problem of constructing a theory for any η_2 reduces to solving a set of two first-order equations which describe the motion of an "effective" particle along two intersecting terms. We solve the equations using methods which are employed in the theory of non-adiabatic transitions.

YAMASHITA and Kurosawa [1] and Holstein [2] suggested a theory of the mobility of small-radius polarons to elucidate the activation-like temperature dependence of the mobility of charge carriers which was experimentally observed in a number of semiconducting compounds. In [1,2] the possibility that the mobility might depend on the temperature as $u \sim \exp(-E_a/kT)$ (E_a—activation energy) at high temperatures[1] $kT > \hbar\omega_0/2$ (ω_0: limiting frequency of an optical phonon) was predicted. This result was founded in [3] by using a density matrix method. The contribution to the mobility which depends in an activation way on the temperature was called the Holstein contribution and denoted by u_H. The quantity u_H was written as a series in powers of the parameters:

$$\eta_1 \approx \frac{J}{E_a},\quad \eta_2 \approx \frac{J^2}{(E_a kT)^{1/2}\hbar\omega_0},\quad \eta_3 \approx \frac{J^2}{E_a kT},\qquad \eta_1^2 < \eta_3 < \eta_2, \tag{1}$$

where J is the "resonance" integral which determines the width ΔE of the "initial" band (apart from a renormalization taking the strong electron-phonon interaction into account).[2] Data on the magnitude of ΔE can be derived from numerical calculations or from optical experiments.[4] For a whole number of substances for which the electron-phonon coupling constant is large ($E_a \gg \hbar\omega_0$) the values of J are such that the parameters η_2 and η_3 are not small (see, for instance,[4,5]). This makes comparison of theory with experiment difficult, since all formulae for transport coefficients obtained earlier in the theory of small-radius polarons are only valid under the conditions: $\eta_1 \ll 1$, $\eta_2 \ll 1$, $\eta_3 \ll 1$.

The first step in widening the limits of applicability of the theory must consist in getting away from the condition $\eta_2 \ll 1$ while retaining the conditions $\eta_1 \ll 1$, $\eta_3 \ll 1$. The condition $\eta_1 \ll 1$ guarantees that the polaron radius is small.[2] When $\eta_3 > 1$ the problem involves in an essential way more than two sites [3,6-8] and the mathematical methods used below to solve it are insufficient. If $\eta_3 \ll 1$ effectively two sites take part in the transition process [8] and the parameter η_2 may have any value. The physical reason for the occurrence of the parameter η_2 is the following one (see also [2,6]). The jump of a polaron occurs only when another polarization well is formed through fluctuations on a neighboring site. It is unstable if there is no electron on this site, i.e., when the formation of such a well is energetically disadvantageous, and the probability of the occurrence of such a fluctuation is proportional to $\exp(-E_a/kT) \ll 1$. The electron tunnels from one well into another in a time $t_1 \approx \hbar/J$, if the transition takes place under conditions of symmetric resonance, i.e., when the electron energy levels are the same in both wells. The time during which the conditions favorable for symmetric resonance are conserved (see below) is

$$\bar{t} \approx \hbar(4E_a kT)^{-1/4}(\hbar\omega_0)^{-1/2}.$$

The parameter η_2 is the square of the ratio of these two characteristic times $\eta_2 \approx 2(\bar{t}/t_1)^2$. Because of mathematical difficulties it was not possible to generalize the theory to the case of arbitrary η_2 before now, but the way to solving this problem was shown in [7], where a closed expression was obtained for u_H in the form

$$u_H = \frac{e}{2kT}\sum_G W(G)\,G_x^2. \tag{2}$$

Here G is a lattice vector connecting any two sites of the same kind (the smallest value of G is g, $|g| = a$), W(G) the probability for an activation jump of a polaron between them.

1. It was shown earlier [8] that in zeroth approximation in η_1 and η_3 but for arbitrary values of η_2 we can restrict ourselves to the "two-site" approximation to evaluate (2). In the two-site approximation we take in (2) only jumps between nearest neighbors (G = g) into account, dropping contributions to W(G) from such processes where the transition of an electron from site 0 to site g (on which fluctuations have created a potential well) takes place with the participation of an intermediate state of the electron on a third site g′ which is adjacent to the sites 0 and g, and so on.

[1] More precisely, $kT > \hbar\omega_0[2\ln(2E_a/\hbar\omega_0)]^{-1}$.

[2] For instance, for a simple cubic lattice $\Delta E = 12J$ and the "bare" effective mass $m^* = \hbar^2/2Ja^2$, where a is the lattice constant.

In the two-site approximation W(g) has the form [8]

$$W(g)=\frac{\bar{\omega}}{2\pi}\exp\left[-\frac{E_a(g)}{kT}\right]F(\eta_2(g),t_0(g)), \tag{3}$$

where

$$t_0^4(g)=\left\langle\frac{E_a(\mathbf{q},g)}{kT}\left(\frac{\hbar\omega_\mathbf{q}}{2kT}\right)^2\right\rangle=\frac{1}{N}\sum_\mathbf{q}|\gamma_\mathbf{q}|^2\frac{\hbar\omega_\mathbf{q}}{4kT}(1-\cos\mathbf{qg})\left(\frac{\hbar\omega_\mathbf{q}}{2kT}\right)^2 \tag{3a}$$

$$E_a(g)=\langle E_a(\mathbf{q},g)\rangle=\frac{1}{N}\sum_\mathbf{q}|\gamma_\mathbf{q}|^2\frac{\hbar\omega_\mathbf{q}}{4}(1-\cos\mathbf{qg}), \tag{3b}$$

$$\bar{\omega}=\frac{\langle E_a(\mathbf{q},g)\omega_\mathbf{q}^2\rangle^{1/2}}{E_a^{1/2}(g)},\qquad \eta_2(g)=\frac{J^2(g)}{\hbar\langle E_a(\mathbf{q},g)\omega_\mathbf{q}^2\rangle^{1/2}(kT)^{1/2}}. \tag{3c}$$

Here $\mathbf{q}$ is a phonon wave vector; $|\gamma_\mathbf{q}|^2$ is a dimensionless function of $\mathbf{q}$ introduced in [3] which characterizes the coupling of the electrons with the phonons; $F(\eta_2, t_0)$ is a dimensionless function of η_2 and t_0.

It was also shown in [8] that when $kT > \hbar\omega_0/2$ the quantity $F(\eta_2(g), t_0(g))$ in (3) can be determined using the solution of an auxiliary problem (a model two-site problem with one vibrational degree of freedom) through the following rigorous mathematical method. In the expression for the probability

$$W=\frac{\omega_0}{2\pi}\exp\left(-\frac{E_a}{kT}\right)F(\eta_2,t_0), \tag{4}$$

obtained by solving this model problem we must make the substitution

$$\omega_0\to\bar{\omega},\quad t_0=\left(\frac{\hbar\omega_0}{2kT}\right)^{1/2}\left(\frac{E_a}{kT}\right)^{1/4}\to t_0(g),\quad E_a\to E_a(g),$$
$$\eta_2=\frac{J^2}{(E_akT)^{1/2}\hbar\omega_0}\to\eta_2(g), \tag{5}$$

where $t_0(g)$, $E_a(g)$, $\bar{\omega}$, and $\eta_2(g)$ are defined in (3a) (3b) and (3c).

Moreover, it follows from [8] that we can in the model problem with the exact quantum-mechanical averaging over the phonon equilibrium distribution associate the averaging over E and φ (energy and phase of the "effective particle"). We show in Appendix 2 that as the result of the approximate averaging over the phase φ we get for $F(\eta_2, t_0)$ in (4) the following expression:

$$F(\eta_2,t_0)=\int_{-x_0}^{\infty}e^{-x}F(\eta_2,t_0,x)\,dx, \tag{6}$$

where $x = (E - E_0)/kT$, $x_0 = E_a/kT$, i.e., the integral over x corresponds to an averaging over the energy E of the "effective particle" and the function $F(\eta_2, t_0, x)$ is

$$F(\eta_2,t_0,x)=|Z(\infty)|^2, \tag{7}$$

where $Z(\tau)$ is determined from the set of equations

$$idZ/d\tau=\alpha R_0^*(\tau)\Phi(\tau),\qquad id\Phi/d\tau=-\alpha R_0(\tau)Z(\tau) \tag{8}$$

with boundary conditions

$$\Phi(\infty)=1,\qquad Z(-\infty)=0. \tag{9}$$

We have introduced here the following notation

$$\tau=\frac{(4E_akT)^{1/4}}{(\hbar\omega_0)^{1/2}}\omega_0t=\frac{t}{\bar{t}},\qquad \alpha=\frac{J}{(E_akT)^{1/4}(2\hbar\omega_0)^{1/2}}=\left(\frac{\eta_2}{2}\right)^{1/2},$$
$$R_0=\exp\left[i\left(\frac{x\tau}{t_0}-\frac{\tau^3}{3}t_0\right)\right]. \tag{10}$$

We shall show in the following that Eqs. (8) describe the motion of some particle with intersecting terms and that one can solve them using well-known methods which are used in problems about non-adiabatic transitions [9-17] (for instance, for slow collisions of atoms and molecules).

We express (7) in terms of the solution of the system of Eqs. (8) satisfying the boundary conditions

$$Z'(-\infty)=1,\qquad \Phi'(-\infty)=0. \tag{11}$$

We note beforehand that all solutions of the set (8) satisfy the relation (conservation law for currents)

$$|Z(\tau)|^2-|\Phi(\tau)|^2=\text{const}, \tag{12}$$

which can easily be proved by taking the derivative of the left-hand side of (12) and using (8) to show that it vanishes.

The solutions Z′ and Φ′ of the set (8) satisfying the boundary conditions (11) are connected with the solutions Z and Φ satisfying the boundary conditions (9) by the relations

$$Z=\xi Z'+\zeta\Phi'^*,\qquad \Phi=\xi\Phi'+\zeta Z'^*, \tag{13}$$

where ξ and ζ are complex coefficients. From the first of Eqs. (13) we get $\xi = 0$ as $\tau = -\infty$, and from the second one we find $\zeta = 1/(Z'(\infty))^*$ as $\tau = \infty$. Using these values for ξ and ζ we get from the first of Eqs. (13) as $\tau = +\infty$

$$Z(\infty)=\left(\frac{\Phi'(\infty)}{Z'(\infty)}\right)^*. \tag{14}$$

We find then from Eq. (7), using (11) and (12) for $F(\eta_2, t_0, x)$,

$$F(\eta_2,t_0,x)=\left|\frac{\Phi'(\infty)}{Z'(\infty)}\right|^2=\frac{|Z'(\infty)|^2-1}{|Z'(\infty)|^2}=\frac{|\Phi'(\infty)|^2}{1+|\Phi'(\infty)|^2}. \tag{15}$$

It is interesting to note that Eqs. (8) are the same as those which are obtained for the wavefunctions of the relative nuclear motion in the problem of non-adiabatic transitions between two linear terms when atoms and molecules collide. [12-14] Indeed, introducing instead of τ the variable $\tau' = \tau/2d = 2Jt/\hbar$, the parameters

$$\varepsilon=(E-E_a)/J,\qquad b=2J^{3/2}/E_a^{1/2}\hbar\omega_0$$

and writing $Z = A_1$, $\Phi = A_2$, we can write the set (8) in the form

$$idA_1/d\tau'=\tfrac{1}{2}R_0^*A_2,\qquad idA_2/d\tau'=-\tfrac{1}{2}R_0A_1, \tag{16}$$

where

$$R_0=\exp[i\varepsilon\tau'-(\tau')^3/3b^2]. \tag{17}$$

This is the form in which the set of equations (which is not Hermitean) was written in [13]. The minus sign in the second Eq. (16) correspond to the difference in sign of the slopes of the intersecting linear terms [14] and the quantity J can be compared with the constant interaction matrix element. The boundary conditions (11) for Z′ and Φ′ were chosen such that they are the same as the boundary conditions for A_1 and A_2 in [14].

The above-mentioned correspondence is obvious if we remember that the solution of the model problem can be reduced to the solution of the following set of quantummechanical equations (compare Eq. (21) in [8]):

$$i\hbar\frac{\partial\Psi_1}{\partial t}=\hbar\omega_0\left[-\frac{\partial^2}{\partial Q^2}+Q^2-2Q\bar{Q}\right]\Psi_1+J\Psi_2,$$

$$i\hbar\frac{\partial\Psi_2}{\partial t}=\hbar\omega_0\left[-\frac{\partial^2}{\partial Q^2}+Q^2+2Q\bar{Q}\right]\Psi_2+J\Psi_1, \quad (18)$$

in which the dimensionless coordinate Q describes the relative displacement of the nuclei at the first and second sites (cf.[6]), $\bar{Q}=(E_a/\hbar\omega)^{1/2}$ is a constant displacement caused by the polaron effect. On the other side, the set of Eqs. (16) was in[13,14] introduced in the approximation of linear terms from a set of time-independent wavefunctions ψ_1 and ψ_2. This set can be obtained from (18) by substituting $\psi_{1,2}(t)=\psi_{1,2}e^{-iEt/\hbar}$ and dropping on the right-hand sides of (18) the quadratic terms $\hbar\omega_0 Q^2$. Eqs. (8) thus reflect all peculiarities of the quantummechanical problem without any additional assumptions bar the approximation of the linearity of the terms.

In the figure we have drawn two electronic-vibrational terms corresponding to the set of Eqs. (8) (cf.[6], and also[2]). By the dashed line we have shown the behavior of the terms (two displaced parabolae) when the splitting is not taken into account. Along the vertical axis we have put the energy of the "effective particle" $E=E_a+kTx$. The point of intersection of the terms corresponds on the energy scale to $E_a=\hbar\omega_0\bar{Q}^2$. The magnitude of the term splitting is 2J. It is clear that when averaging over E (or x) the energies $E\approx E_a+kT$, i.e., $x\approx 1$ are important. If $kT\ll E_a$ this will be just the region close to the intersection of the original terms where the terms may be assumed to be linear. When determining the main contribution to $F(\eta_2, t_0, x)$ only the region of small values of $\omega_0 t$ and φ is important (see Appendix 1). We show that the expansion of $\sin\omega_0 t$ and $\sin\varphi$ in power series for small $\omega_0 t$ and φ corresponds to the linear term approximation. Since the phase φ and energy E are connected with the initial values of the coordinate (q_0) and momentum (p_0) of the classical oscillator describing the motion of the "effective particle" in the right-hand parabola in the figure by the relations

$$\varphi=\arccos\frac{\bar{q}-q_0}{[(q_0-\bar{q}_0)^2+(p_0/M'\omega_0)^2]^{1/2}},\quad E=\frac{p^2}{2M'}+\frac{M'\omega_0^2}{2}(q-\bar{q})^2, \quad (19)$$

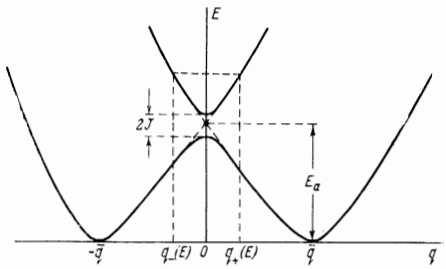
while the running values of the coordinate $q(t)=(2\hbar/M'\omega_0)^{1/2}Q(t)$ and momentum $p(t)$ are equal to

$$q(t)-\bar{q}=(q_0-\bar{q})\cos\omega_0 t+\frac{p_0}{M'\omega_0}\sin\omega_0 t=-\bar{q}\left(\frac{E}{E_a}\right)^{1/2}\cos(\omega_0 t+\varphi),$$

$$p(t)=\left(\frac{E}{E_a}\right)^{1/2}M'\omega_0\bar{q}\sin(\omega_0 t+\varphi) \quad (20)$$

($M'=M/2$ is the mass of the "effective particle"[6]) small values of $\omega_0 t$ and φ for E close to E_a correspond to small values of q_0, $q(t)$ and p_0, $p(t)$ which corresponds to a small region near the point of intersection of the terms where these are linear.

The transition of the "particle" with energy $E\approx E_a+kTx$ in the region above the barrier $x\gg J/kT$ from one term to the other is contained near the point $q(t)=0$ (the "transition time" is of order $\bar{t}\,x^{-1/4}$). Moving, for instance, from the right to the left the particle can at once go over to the second term when passing the point $q=0$; if, however, it remains on the first term then after reflection at the point



Electronic-vibrational terms in the two-site model.

$q_-=-\bar{q}kTx/E_a$ it can go to and fro many times between the two turning points $q_-=-\bar{q}kTx/E_a$ and $q_+=\bar{q}kTx/E_a$ changing over near $q=0$ from one term to the other (see[2]). The terms may be assumed to be linear only when in the points $q_\pm$ the energy $M'\omega_0^2 q^2/2$ is negligibly small compared with $M'\omega_0^2\bar{q}q$ (see (19)) which is satisfied provided $xkT/E_a\ll 1$.

We note also that the time to move between the points q_+ and q_- or between two consecutive passages of the point $q=0$ is equal to

$$\omega_0(t_1-t_2)=2(kTx/E_a)^{1/2}. \quad (21)$$

The condition necessary for the applicability of the approximation of linear terms is thus the same as the condition $\omega_0(t_1-t_2)\ll 1$ which allows us to expand the index in (A2.3) (see Appendix 2) in a series in $\omega_0 t+\varphi$ and φ.

We must thus solve the problem of a multiple passage of the non-adiabatic region when the two turning points may be close to the point of intersection of the two terms.

2. We proceed now to solve Eqs. (8) which describe the process of the motion of an "effective particle" near the intersection of terms. The shortest method is the following. We express (15) by means of the solutions $\bar{Z}$ and Φ of a system differing from (8) by replacing the minus sign by a plus sign in the right-hand side of the second equation which would correspond to the case of linearly intersecting terms with slopes of the same sign. We choose the boundary conditions for $\bar{Z}$ and Φ in the form $\bar{Z}(-\infty)=0$, $\Phi(-\infty)=1$. The solutions, for instance for Φ' and $\bar{Z}$ can be written in the form

$$\Phi'(\tau)=\sum_{n=0}^{\infty}\Phi'_{2n+1}(\tau),\quad \bar{Z}(\tau)=\sum_{n=0}^{\infty}\bar{Z}_{2n+1}(\tau), \quad (22)$$

where

$$\Phi'_{2n+1}(\tau)=(-i\alpha)^{2n+1}(-1)^{n+1}I^*_{2n+1}(\tau),\quad \bar{Z}_{2n+1}(\tau)=(-i\alpha)^{2n+1}I_{2n+1}(\tau), \quad (23)$$

$$I_{2n+1}(\tau)=\int_{-\infty}^{\tau}d\tau_{2n+1}\int_{-\infty}^{\tau_{2n+1}}d\tau_{2n}\ldots\int_{-\infty}^{\tau_2}d\tau_1 R_0^*(\tau_{2n+1})R_0(\tau_{2n})\ldots R_0^*(\tau_1). \quad (24)$$

The absolute squares of $\Phi'(\tau)$ and $\bar{Z}(\tau)$ are, according to (23) equal to

$$|\Phi'(\tau)|^2=\sum_{n=0}^{\infty}\sum_{m=0}^{\infty}(\alpha^2)^{n+m+1}I_{2n+1}(\tau)I^*_{2m+1}(\tau), \quad (25)$$

$$|\bar{Z}(\tau)|^2=-\sum_{n=0}^{\infty}\sum_{m=0}^{\infty}(-\alpha^2)^{n+m+1}I_{2n+1}(\tau)I^*_{2m+1}(\tau). \quad (25a)$$

Comparing (25) and (25a) we find that $|\Phi'(\tau)|^2$ differs

from $|\bar{Z}(\tau)|^2$ by the total sign and by the replacement of α^2 by $-\alpha^2$ (i.e., J^2 by $-J^2$) in the final solution. The approximate solution for $|\bar{Z}(\infty)|^2$ in the region above the barrier when

$$x \gg x_1 \approx J/kT, \quad x \gg x_2 \approx t_0^{4/3} \tag{26}$$

is given by the well-known Landau-Zener formula formula[9,12,13] [3)]

$$|\bar{Z}(\infty)|^2 = 2e^{-2\pi\delta}(1 - e^{-2\pi\delta}) 2\sin^2(\rho + \pi/4), \tag{27}$$

where $\delta = \eta_2/4\sqrt{x}$, ρ the phase determined in[12] and equal to the dimensionless (in units of $\hbar$) action between the point of quasi-intersection of the terms and the turning point. The phase ρ depends on J^2 and in our notation has the form

$$\rho = \frac{x^{3/2}}{2t_0^2} \int_{-1}^{\infty} \left[(1-u^2)^2 + \left(\frac{J}{kTx}\right)^2 \right]^{1/2} du, \tag{28}$$

where we have introduced the variable $u = \omega_0 t (E_a/kTx)^{1/2}$.

Bearing in mind the above-mentioned connection between $|\Phi'(\tau)|^2$ and $|\bar{Z}(\tau)|^2$ we find that in the above-barrier region I ($x > x_1$, $x > x_2$)

$$|\Phi'(\infty)|_I^2 \approx -2e^{2\pi\delta}(1 - e^{2\pi\delta}) 2\sin^2(\bar{\rho} + \pi/4). \tag{29}$$

We note that it is impossible to obtain the value of the phase $\bar{\rho}$ in (29) taking the dependence on J^2 into account directly by the substitution of $-J^2$ for J^2 in the approximate expression (28) since as the result of this substitution we obtain a complex expression for the phase. To find the correction in J^2 in the phase of the solution (29) we must solve the set of Eqs. (8) by the WKB method with the boundary conditions (11) which is equivalent to the analytical continuation of the asymptotic expansions for Φ' and Z' through the two pairs of "turning points" (τ_1, τ_2) and (τ_3, τ_4) (where $\tau_2 - \tau_1 = \tau_4 - \tau_3$, $\tau_4 - \tau_1 \gg \tau_2 - \tau_1$, $\tau_3 - \tau_2 \gg \tau_2 - \tau_1$) lying on the real axis. Near each pair of points (τ_1, τ_2) or (τ_3, τ_4) Eqs. (8) can be simplified and their exact solutions are two linearly independent parabolic cylinder functions. Moving along the real axis (just along it the WKB solutions are of the same order) and joining the approximate WKB solutions[11] with the exact ones in the regions (τ_1, τ_2) and (τ_3, τ_4) allows us to show that the solution for $|\Phi'(\infty)|_I^2$ has, indeed, the form (29) and to find the expression $\bar{\rho}$ for the phase depending on J^2. However, it turns out that in the region I under the conditions (26) $\rho \approx \rho_0 = \frac{2}{3}x^{3/2}/t_0^2$ and the corrections to ρ_0 are small. We drop therefore the calculations by the WKB method described here and put in (29) $\bar{\rho} \approx \rho_0$. We then get according to (15)

$$F_I(\eta_2, t_0, x) \approx \frac{2e^{2\pi\delta}(e^{2\pi\delta} - 1)(1 + \sin 2\rho_0)}{2e^{2\pi\delta}(e^{2\pi\delta} - 1)(1 + \sin 2\rho_0) + 1}. \tag{30}$$

Since under the conditions (26) the phase $\rho_0 \gg 1$ we can average (30) over a small interval $\Delta x \ll 1$ of values of x along which $\sin 2\rho_0$ goes through many oscillations. We then neglect small corrections connected with the inteference of the amplitudes when the transition region is passed through (this is, apparently, equivalent to the procedure of summing the series in front of (III.6) in[2]). As the result of the averaging which reduces to integrating (30) over ρ_0 between 0 and 2π and dividing by 2π we have[4)]

$$F_I(\eta_2, t_0, x) \approx 2\frac{1 - e^{-2\pi\delta}}{2 - e^{-2\pi\delta}}. \tag{31}$$

Equations (30) and (31) were checked by us by evaluating $F_I(\eta_2, t_0, x)$ using (7)—(9) in the form of a series in $2\pi\delta = \frac{1}{2}\pi\eta_2 x^{-1/2}$ up to δ^3 (just in that order is there a difference between the Landau-Zener formula and (31)). Integration over all variables is performed by the saddle-point method (see footnote[3)]). The set of all terms which do not contain $\sin 2m\rho_0$ or $\cos 2n\rho_0$ (where n and m are integers) corresponds to the expansion (31).

Holstein[2] was the first to obtain Eq. (31) from qualitative considerations.[5)]

Elucidating the problem of the correspondence between quantal and classical equations for a system of linear terms (applying this to the problem of slow collisions between atoms and molecules), Ovchinnikova[14] obtained also (31) by a somewhat different method.[6)]

[3)] One can check that Eq. (25a) for the quantity $|Z(\tau)|^2$ as a power series in α^2 corresponds to the expansion of (27) in a series in J. To do this we evaluate the multiple integrals in (24) by the saddle-point method assuming (for $x > 0$) the existence of two saddle-points $\tau_{1,2} = \pm\sqrt{x}/t_0$ (as follows from the definition of R_0 in (10)). Splitting off in the separate terms a series of diverging contributions corresponding to expanding the phase ρ of (28) in a series in J we find that the series (25a) is the same as the series obtained by means of a direct expansion of (27) which is the confirmation of the validity of the solution (27).

[4)] The small contribution to the integral contribution to $F(\eta_2, t_0)$ from region I which is connected with the finite value of the phase ρ_0 and which comes from the first term ($\sim \delta$) in the expansion of (30) turns out to be of order $\eta_2 t_0^{2/3}$. However, the problem of corrections requires a more careful consideration. Indeed, we show in Appendix 1 that the correction $\eta_2 t_0^{2/3}$ from region I is cancelled by a small contribution from regions II and III and the true magnitude of the correction is of order $\eta_2 t_0^4 \ll \eta_2 t_0^{2/3}$.

[5)] We note that the set (II.1) in Appendix II of [2] does not, strictly speaking, follow from the initial quantum-mechanical problem which differs from (8) by the change in sign in the second equation which corresponds to the case of identical signs for the slopes of the terms and not to the case depicted in the figure.

For large times of the order of (21) the solution of these equations would lead to the Landau-Zener formula and not to (30). In fact, Holstein assumed that for small times $t \sim \bar{t}/x^{1/4}$ when the effective particle is near $q = 0$ and far from the turning points q_+ and q_- the expression for the transition probability from one term to the other term, $P_{12} = 1 - e^{-2\pi\delta}$, has the same form for both signs of the slope of the terms. Using this expression for P_{12} and assuming in his physical considerations that the terms all have slopes of a different sign, Holstein arrives at the result (31).

[6)] Dubrovskiĭ [18] considered the process of the decay of diatomic molecules (for the case when the angles of inclination of the terms have different signs near the intersection of the terms) and obtained for the lifetime in the above-barrier region a result which differs from ours (the latter can conditionally be written in the form $(\bar{\omega}F_I/2\pi)^{-1}$) in that in the expression for F_I there is missing as compared to (31) the denominator which, as is clear from the calculations (see (15)) is caused by the precise statement of the problem solved here. We note that the use of Eqs.(8) with the boundary conditions (11) and Eq.(15), the necessity of which follows from the original expression for W(g), is equivalent to stating the problem in terms of incident and transmitted currents (see [14]).

The main point of the problem solved by Dubrovskiĭ lies in finding non-stationary levels in a potential well (mathematically the problem reduces to finding the resonance scattering phase). It is possible that the cause of the difference between the results for the above-barrier region lies in a different statement of the problem.

The authors are grateful to G. V. Dubrovskiĭ for the opportunity to get acquainted with his work prior to publication.

In the deep sub-barrier region III ($x < 0$, $|x| \gg x_1$, $|x| \gg x_2$), where a non-adiabatic tunnelling transition takes place, we use the result of [13] for $|\bar{Z}(\infty)|^2$ which has the form

$$|\bar{Z}(\infty)|^2_{III} = B(\delta)e^{-2|\rho_0|}, \quad B(\delta) = \begin{cases} 2\pi\delta, & \delta \ll 1, \\ 2\pi\delta(\Gamma(1-\delta))^{-2}\delta^{-2\delta}e^{2\delta}, & \delta \gg 1, \end{cases} \tag{32}$$

where

$$|\rho_0| = {}^2/_3|x|^{3/2}/t_0^2 \gg 1,$$

and $\Gamma(x)$ is the gamma-function.
In accordance with (15), (25), (25a) we get

$$F_{III}(\eta_2, t_0, x) = \frac{\bar{B}(\delta)e^{-2|\rho_0|}}{\bar{B}(\delta)e^{-2|\rho_0|}+1} \approx \bar{B}(\delta)e^{-2|\rho_0|}. \tag{33}$$

Since $\delta^{-2\delta}$ occurs in $B(\delta)$ in the transition to $\bar{B}(\delta)$ we must specify the way to make the change $\delta \to -\delta$ in (32):

$$\delta^{-2\delta} = \left(\frac{1}{\delta^2}\right)^{\delta} \to \left(\frac{1}{\delta^2}\right)^{-\delta} = \delta^{2\delta}.$$

Only when such a transition is made do we not obtain a superfluous factor $(-1)^{2\delta}$ in the limit $\delta \ll 1$, i.e., the prescription is in accordance with the requirement that $|\Phi'(\infty)|^2$ be real. We thus obtain

$$\bar{B}(\delta) = \begin{cases} 2\pi\delta & \delta < 1, \\ 2\pi\delta(\Gamma(1+\delta))^{-2}\delta^{2\delta}e^{-2\delta} & \delta \gg 1, \end{cases} \tag{33a}$$

which is the same as the expression for $\bar{B}(\delta)$ found in [14,15].

If $x_1 > x_2$ then even at the upper limit of the region III ($x \approx J/kT$) F_{III} will be small as $\exp(-{}^2/_3 b)$, i.e., the region III makes an exponentially small contribution to $F(\eta_2, t_0)$, and we shall in the following not take it into account. The contribution to $F(\eta_2, t_0)$ from the intermediate region II in which $-x_{max} < x < x_{max}$ (where x_{max} is the largest of the quantities (26)),

$$F_{II}(\eta_2, t_0) = \int_{-x_{max}}^{x_{max}} e^{-x}F_{II}(\eta_2, t_0, x)\,dx \tag{34}$$

could have been obtained by a numerical integration of the set (8) with the boundary conditions (9) or by means of Eq. (15) and integrating Eqs. (8) with the boundary conditions (11). But this could hardly be done if $x_1 \approx J/kT \ll 1$ since the integral over x the function $F(\eta_2, t_0, x)$ by its definition (see (15)) is less than unity and the region of integration in (34) is small compared to unity.

Thus, when

$$J/kT \ll 1 \tag{35}$$

the above-barrier region I is the important one. Using the prescription for changing from the model problem to the exact one (see (5)) we finally get

$$W(g) = \frac{\bar{\omega}}{2\pi}\exp\left\{-\frac{E_a(g)}{kT}\right\}\int_{x_{max}}^{\infty} e^{-x}\frac{2[1-e^{-2\pi\delta(x)}]}{2-e^{-2\pi\delta(x)}}\,dx, \tag{36}$$

where $2\pi\delta(x) = \pi\eta_2(g)/2\sqrt{x}$ (apart from small corrections the limit x_{max} in (36) can be replaced by 0). In the limit $\eta_2 \ll 1$ Eq. (36) changes to

$$W(g) \approx \bar{\omega}\frac{\pi^{1/2}}{2}\eta_2(g)\exp\left[-\frac{E_a(g)}{kT}\right], \tag{36a}$$

which is the same as an expression obtained earlier.[2,3,7] However, when $\eta_2 \gtrsim 1$ the expression for $W(g)$ (and thus also for the mobility (2)) has a different form:[7)]

$$W(g) \approx \frac{\bar{\omega}}{2\pi}\exp\left[-\frac{E_a(g)}{kT}\right]. \tag{36b}$$

3. When

$$J/kT \gg 1 \tag{37}$$

region II gives the main contribution to W. In that case the actual values of the energy E lie in the interval between the split upper and lower adiabatic terms (see the figure and also [6]). It is clear that in that case Eq. (36) is inapplicable since, assuming $J/kT \ll 1$, we neglect the splitting of the terms. However, Eqs. (8) take into account the possibility of a splitting of the terms. This is confirmed in particular by the fact that in [8] we were able by means of (A2.1) to (A2.3) (see Appendix 2) to get agreement with the results of the quantummechanical averaging of each term in the "series in J" amongst which we also found agreement for the contributions proportional to $(\eta_2 t_0^2)^n \approx (J/2kT)^{2n}$, which just describe the splitting of the terms. However, when $\eta_2 \gg 1$, $b \approx 2\eta_2(kT/J)^{1/2} \gg 1$ the result for the case (37) is rather obvious:[8)] we neglect transitions from the lower to the upper term and we change to Kramers' problem [20] of the passage above a barrier the height of which is equal to $E_a - J$. As a result we have

$$W(g) = \frac{\bar{\omega}}{2\pi}\exp\left[-\frac{E_a(g)-J}{kT}\right]. \tag{38}$$

The mathematical case with spaced terms was analyzed in some detail by Dykhne and Chaplik [15,16] (see also Sec. 53 in Landau and Lifshitz's book [9]). The methods developed there can be used to base (38) on. Equation (38) changes to (36b) when $J/kT \ll 1$ as should be expected.[9)]

In conclusion the authors thank G. F. Drukarev, G. V. Dubrovskiĭ, and E. K. Kudinov for interesting discussions.

APPENDIX 1

We shall illustrate some properties of the functions $F(\eta_2, t_0, x)$ and $F(\eta_2, t_0)$ by the example of the contribution to the jump probability which is lowest in J.

7) This last fact emphasizes the importance of the problem of the true small parameters in the theory. Denying the existence of the independent parameter η_2, Klinger (see the discussion in [6,19]) assumes that Eq.(36a) is always valid provided only that $\eta_2 \ll 1$ and $\eta_3 \ll 1$. From the result given in the foregoing it follows that the problem of dimensionless parameters in the theory of small-radius polarons is not exhausted by the problem of the true smallness of the neglected corrections and that an error in the determination of the complete set of parameters can lead to errors in the evaluation of quantities which can be compared with experiment.

8) The combination of the inequalities $\eta_2 \lesssim 1$ and $J/kT \gg 1$ clearly corresponds to the case $t_0 \gg 1$ which was not considered.

9) We note that the qualitative consideration of Holstein's (see [2], summation of the series in front of (III.6)) also leads to the conclusion that when $2\pi\delta(x) \gg 1$ the motion takes place only along the lower adiabatic term: "the effective particle" moving, for instance, along the right-hand terms from the right to the left has a probability 1 to change in the point $q = 0$ to the left-hand term (since $P_{12} = 1 - e^{-2\pi\delta(x)} \approx 1$), i.e., it continues to move along the lower adiabatic term starting to the left. For W(g) Eq.(36b) is then valid.

Starting from the Eqs. (A2.1) to (A2.4) given below we get

$$F_1(\eta_2, t_0, x) = \left(\frac{J}{\hbar\omega_0}\right)^2 \int_{-\pi}^{\pi} d\varphi \int_{-\omega_0 T}^{\omega_0 T} \exp\left\{ ia\left[\left(1+\frac{xkT}{E_a}\right)^{1/2} \times (\sin(v+\varphi) - \sin\varphi) - v\right]\right\} dv. \quad (A1.1)$$

Here $a = 4E_a/\hbar\omega_0 \gg 1$, $v = \omega_0 t$, $x = (E - E_a)/kT$. We assume that $\hbar\omega_0/kT \ll 1$ (high temperature).

A. Exact integration over φ and over v. We write the difference of the sines in the index in the form $2\cos(v/2 + \varphi)\sin(v/2)$, displace φ by v/2 without changing the limits of φ (periodicity condition), and integrate over φ:

$$F_1(\eta_2, t_0, x) = \left(\frac{J}{\hbar\omega_0}\right)^2 2\pi \int_{-\omega_0 T}^{\omega_0 T} e^{-iav} J_0\left[2a\left(1+\frac{xkT}{E_a}\right)^{1/2} \sin\frac{v}{2}\right] dv. \quad (A1.2)$$

Substituting (A1.2) into (6) we get after integrating over x

$$F_1(\eta_2, t_0) = \left(\frac{J}{\hbar\omega_0}\right)^2 \pi \int_{-\omega_0 T}^{\omega_0 T} e^{-iav} \exp\left[-16\frac{E_a kT}{(\hbar\omega_0)^2}\sin^2\frac{v}{2} + \frac{E_a}{kT}\right] dv. \quad (A1.3)$$

When there is no dispersion the integrand in (A1.3) oscillates and does not decrease. However, taking dispersion into account leads to a decrease of the exponent as $t \to \infty$ (see [2,3,8]). Integrating in (A1.3) over v from $-\pi$ to π (i.e., over a complete period of oscillation in the well) we get

$$F_1(\eta_2, t_0) \approx (2\pi)^2 \left(\frac{J}{\hbar\omega_0}\right)^2 \exp\left[\frac{E_a}{kT} - 8\frac{E_a kT}{(\hbar\omega_0)^2}\right]\left\{ I_a\left(a\frac{2kT}{\hbar\omega_0}\right) + \ldots\right\}. \quad (A1.4)$$

The dropped terms are small at least as $\exp[-8E_a kT/(\hbar\omega_0)^2] \ll 1$.

Using a formula of the kind [21]

$$I_p(z) = \left(\frac{1}{2\pi}\right)^{1/2} (p^2+z^2)^{-1/4} \exp\left[\sqrt{p^2+z^2} - p\,\mathrm{Arsh}\frac{p}{z}\right], \quad (A1.5)$$

putting $p = a = 4E_a/\hbar\omega_0$, $z = 8E_a kT/(\hbar\omega_0)^2 = 2akT/(\hbar\omega_0) > a$ and expanding in $(\hbar\omega_0/2kT)^2$ we get

$$F_1(\eta_2, t_0) = \pi^{3/2}\eta_2 \exp(t_0^4/12). \quad (A1.6)$$

We recall that the factor $\exp(t_0^4/12)$ occurs in the exact Eq. (3) in [8].

Integrating (A1.2) over v from $-\pi$ to π (over a complete cycle) without expanding $\sin(v/2)$ we get

$$F_1(\eta_2, t_0, x) \approx \left(2\pi\frac{J}{\hbar\omega_0}\right)^2 J_a^2\left[a\left(1+x\frac{kT}{E_a}\right)^{1/2}\right]. \quad (A1.7)$$

Using the asymptotic expressions for the Bessel functions (approximation by tangents [22]) we find the following values:

$$\pi\eta_2 x^{-1/2}\left[1+\sin\left(\frac{4}{3}\frac{x^{3/2}}{t_0^2}\right)\right] \text{ for } x > t_0^{4/3}, \text{ region I,}$$

$$b^{4/3} = \frac{\eta_2}{t^{2/3}} \text{ for } -t_0^{4/3} < x < t_0^{4/3}, \text{ region II,}$$

$$\frac{\pi}{2}\eta_2 x^{-1/2}\exp\left(-\frac{4}{3}\frac{|x|^{3/2}}{t_0^2}\right) \text{ for } x < 0,\ |x| > t_0^{4/3}, \text{ region III.} \quad (A1.8)$$

The exact integration over v gives a small contribution to $F_1(t_0, \eta_2)$ from the sub-barrier region III while in the above-barrier region I there is an oscillating term. The integral contribution to $F_1(\eta_2, t_0)$ from the region II is small as $t_0^{2/3}\eta_2$. Corrections of the same kind to the main term $\pi^{3/2}\eta_2$ from $F_1(\eta_2, t_0)$ are obtained from the integration over the regions I and III (cf. (5) in [8]). However, all these corrections are cancelling one another as is clear from substituting (A1.7) into (6) and integrating over x using the equations

$$\int_0^{\infty} e^{-vy} J_a^2(ay^{1/2})\,dy = e^{-a^2/2} I_a\left(\frac{a^2}{2}\right) \quad (A1.9)$$

and (A1.5). We are then led to (A1.6), i.e., we obtain a correction $\sim t_0^4/12$, and not $\sim t_0^{2/3}$.

B. Exact integration over φ and over v after expanding sin v up to v^3. Using the approximate Eq. (7) we get (cf. [7])

$$F_1(\eta_2, t_0, x) = \left(\frac{J}{\hbar\omega_0}\right)^2 \left| \int_{-\infty}^{\infty} dv \exp\left\{ ia\left[\frac{1}{2}\frac{xkT}{E_a}v + \frac{v^3}{3!}\right]\right\}\right|^2 = \eta_2 \frac{2\pi}{t_0^{4/3}} \Phi^2\left(-\frac{x}{t_0^{4/3}}\right), \quad (A1.10)$$

where

$$\Phi(\alpha) = \frac{1}{\sqrt{\pi}} \int_0^{\infty} du \cos\left(u\alpha + \frac{u^3}{3}\right)$$

is the Airy function. Using the asymptotics for the Airy function we are led to (A1.8), i.e., the integration over the complete period of v and integration using (7) to (9) leads to the same results in the regions I and III. Indeed, one can show somewhat more, viz., that (A1.10) is the same as (A1.7). We show this for the above-barrier region. Using the connection between $\Phi(\alpha)$ and $K_{1/3}(\frac{2}{3}\alpha^{3/2})$ and Watson's formula (see [21])

$$K_{1/3}\left(\frac{pw^3}{3}\right) = \frac{\sqrt{3}\pi}{w} J_p(z) \quad (A1.11)$$

(where $z = p(1-w^2)^{1/2}$), putting $p = 4E_a/\hbar\omega_0$, $w = ((E_a - E)/E_a)^{1/2}$ we obtain for $x < 0$

$$\Phi\left(-\frac{x}{t_0^{4/3}}\right) = \pi^{1/2}\left(\frac{2E_a}{\hbar\omega_0}\right)^{1/3} J_a\left[a\left(\frac{E}{E_a}\right)^{1/2}\right]. \quad (A1.12)$$

Thus a comparison of the results of the exact integration (A) over φ and v and of the approximate integration (B) shows that the main contribution to $F_1(\eta_2, t_0, x)$ is given by the regions $v \ll 1$ and $\varphi \ll 1$, which corresponds to the regions near the intersection of the terms.

C. Integration over φ and v of the approximate Eq. (A1.10) by the saddle-point method. When $x > 0$ the index $f(v)$ of the integrand in (A1.10) has two saddle points $v_{1,2} = \pm(kTx/E_a)^{1/2}$ where $f'(v_{1,2}) = 0$. The difference $f(v_1) - f(v_2) = \frac{2}{3}x^{3/2}/t_0^2$ is the phase ρ_0.

Integration by the saddle-point method near the two saddle-points is allowed only when $\frac{2}{3}x^{3/2}/t_0^2 \gg 1$, that is, when the points are sufficiently far apart, leads also to the result (A1.8) for the region I.

APPENDIX 2

In [8] we obtained for W the result in the form of an average over E and φ:

$$W = \mathrm{Re}\left\{\left(-\frac{iJ}{\hbar}\right)^2 \int_0^{\infty} \frac{dE}{kT} e^{-E/kT} \frac{1}{2\pi} \int_{-\pi}^{\pi} d\varphi \Phi(0, E, \varphi) Z^*(T, E, \varphi)\right\}. \quad (A2.1)$$

The functions $\Phi(t, E, \varphi)$ and $Z(t, E, \varphi)$ are determined from the set of equations

$$i\hbar\, dZ/dt = JR^*\Phi, \qquad i\hbar\, d\Phi/dt = -JRZ, \quad (A2.2)$$

in which the quantity R is, according to [8], equal to

$$R(t,E,\varphi)=\exp\left\{i\frac{4E_a}{\hbar\omega_0}\left[\left(\frac{E}{E_a}\right)^{1/2}(\sin(\omega_0 t+\varphi)-\sin\varphi)-\omega_0 t\right]\right\}. \quad (A2.3)$$

The boundary conditions have the form

$$\Phi(T)=1, \quad Z(-T)=0. \quad (A2.4)$$

Iterating Eqs. (A2.2) in powers of J, substituting the result in (A2.1) and averaging over E and over φ we get W as a power series in J while the term in the series proportional to J^{2n} contains an integral over the variables $t_1,\ldots,t_{2n-1}$ of multiplicity 2n-1. As was shown in [8] for small values of the integration variables $\omega_0 t \ll 1$ the integrands in all terms of the series obtained by the method described above are the same as the integrands in the corresponding terms of the series obtained as the result of the exact quantum-mechanical averaging in each order in J. However, just the regions of small times $\omega_0 t \ll 1$ are important in the multiple integrals over t when evaluating the main contribution to W. The index in (A2.3) can thus be expanded in a series in $\omega_0 t$ up to $(\omega_0 t)^3$ inclusively and we let the quantity T in (A2.1) and (A2.4) tend to infinity since the quantity W(T) in (A2.1) reaches its asymptotic value and ceases to depend on T when $\omega_0 T < 1$.

We shall consider the variable φ from (A2.3) on a par with the other integration variables bearing in mind that the main contribution to (A2.1) is given by values of $\varphi \ll 1$. This was shown in Appendix 1 by the example of calculating W_2. Using (A2.2) and (A2.4) we get for Z(t) and $\Phi(t)$ power series in J

$$Z(t)=\sum_{n=0}^{\infty}Z_{2n+1}(t), \quad \Phi(t)=\sum_{n=0}^{\infty}\Phi_{2n}(t), \quad (A2.5)$$

$$Z_{2n+1}(t)=\left(-\frac{iJ}{\hbar}\right)^{2n+1}\int_{-T}^{t}dt_{2n+1}\int_{t_{2n+1}}^{T}dt_{2n}\ldots\int_{t_3}^{T}dt_2\int_{-T}^{t_2}dt_1 R^*(t_{2n+1})R(t_{2n})\ldots R(t_2)R^*(t_1), \quad (A2.6)$$

$$\Phi_{2n}(t)=\left(-\frac{iJ}{\hbar}\right)^{2n}\int_{t}^{T}dt_{2n}\int_{-T}^{t_{2n}}dt_{2n-1}\ldots\int_{t_3}^{T}dt_2\int_{-T}^{t_2}dt_1 R(t_{2n})R^*(t_{2n-1})\ldots R(t_2)R^*(t_1). \quad (A2.7)$$

In all terms of the series (A2.6) and (A2.7) for the quantities $\Phi(0)$ and Z(T) occurring in (A2.1) we perform a change of variables according to the rule $t_i' = t_i + \varphi/\omega_0$. As a result we obtain

$$W=\mathrm{Re}\left\{-\frac{iJ}{\hbar}\left\langle R_0^*\left(\frac{\varphi}{\omega_0}\right)\Phi_0\left(\frac{\varphi}{\omega_0}\right)Z_0^*(T)\right\rangle_{E,\varphi}\right\}, \quad (A2.8)$$

where

$$R_0(t)=\exp\left\{i\frac{4E_a}{\hbar\omega_0}\left[\left(\frac{E}{E_a}\right)^{1/2}\sin\omega_0 t-\omega_0 t\right]\right\}. \quad (A2.9)$$

$\Phi_0(t)$ and $Z_0(t)$ are determined by means of (A2.6) and (A2.7) with the change $R \to R_0$. In (A2.8) we neglected the difference of the limits $T+\varphi/\omega_0$ and $-T+\varphi/\omega_0$ from T and -T since in (A2.1) values of $\varphi \ll 1$ are important and the value of T is chosen such that it exceeds by far the values of the variables which are important for the integration.

Noting that

$$\frac{1}{2\pi}\left(-\frac{iJ}{\hbar}\right)\int_{-\pi}^{\pi}R_0^*\left(\frac{\varphi}{\omega_0}\right)\Phi_0\left(\frac{\varphi}{\omega_0}\right)d\varphi = \frac{\omega_0}{2\pi}\left[Z_0\left(\frac{\pi}{\omega_0}\right)-Z_0\left(-\frac{\pi}{\omega_0}\right)\right]\approx\frac{\omega_0}{2\pi}Z_0(T), \quad (A2.10)$$

we have finally

$$W=\frac{\omega_0}{2\pi}\lim_{T\to\infty}\left\{\int_0^{\infty}\frac{dE}{kT}e^{-E/kT}|Z_0(T,E)|^2\right\}, \quad (A2.11)$$

whence we get (7) using (3) and (6) (in the text we dropped the index zero of Z_0). Expanding the index of the exponent of $R_0(t)$ in a series in $\omega_0 t$ and $xkT/E_a = (E-E_a)/E_a \ll 1$ and changing to the dimensionless variable $\tau = t/\bar{t}$ we get the equation for R_0 from (10).

We note that in principle Eq. (A2.1) is more exact than (A2.11). In (A2.1) the integration over φ is between the limits $-\pi$ and π, i.e., we take into account the initial parts of the trajectories far from q = 0 where the terms are essentially non-linear. We obtained Eq. (A2.11) from (A2.1) as a result of an approximate integration over φ over the region $\varphi \ll 1$ (near q = 0) where the terms are linear. However, as we have already noted earlier, the main contribution in the result averaged over E and φ is given by small times $\omega_0 t \ll 1$. Therefore the physical reason for the small difference between (A2.1) and (A2.11) is clear: when $\varphi \sim \pi$ the particle is so far from the point q = 0 near which the transition from term to term takes place that over a time $\omega_0 t \ll 1$ it does not succeed in approaching that point, i.e., such initial values of φ do not give an appreciable contribution to the transition probability. These conclusions are confirmed by the example analyzed in Appendix 1.

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