Adiabatic polaron theory of electron hopping in crystals: A reaction-rate approach

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The paper presents an application of reaction-rate theory to nonradiative electron transitions in polar crystals based on a "two-site" model. For this purpose localized electronic states are described by using the adiabatic approximation. Both "large" polarons in ionic crystals and "small" polarons in molecular crystals are considered from a unified point of view. By assuming a single frequency of the lattice vibrations (Einstein model) one can calculate the transition probability for both the limits of adiabatic and nonadiabatic electron transfer as well as for the whole intermediate range. The relevant expressions, earlier derived in treating electron transfer in solution, are reviewed and discussed in order to give a justification of their application to polaron hopping in crystals. In a similar way, a review is made of the reaction-rate approach to electron transfer to obtain the appropriate rate equations for the low- and high-temperature limits and the intermediate temperature range as well. New expressions for the polaron-hopping rate are also derived. The conditions of its validity are discussed. This paper provides an essentially new approach to nonradiative electron transfer in polar crystals. It permits one to overcome the limitations of the usual methods, such as the multiphonon approach, entirely based on time-dependent perturbation theory and/or the Franck-Condon approximation which restrict their applicability only to nonadiabatic polaron hopping. The reaction-rate treatment exactly reproduces the results of the more rigorous multiphonon theory of nonadiabatic transitions. Moreover, it yields correct rate expressions for adiabatic transitions, in particular, in the high-temperature range, in which the classical occurrence-probability approach greatly overestimates the activation energy. Some problems concerning the Einstein one-frequency oscillator model assumed and the irreversibility of the electron transfer are discussed with some details from standpoint of both reaction-rate theory and multiphonon theory. The advantages of the reaction-rate approach are emphasized.

I. INTRODUCTION

The notion of polaron first introduced by Landau[1] is the basis of extensive theoretical studies on the interactions of an electron with the crystal lattice in both perfect and imperfect crystals. With the use of a continuum model for an ideal ionic crystal the polaron theory has been developed in different ways depending on the strength of the electron-lattice interaction.[2,3] A theory developed by Pekar[4] considers the case of strong interaction making use of the adiabatic approximation. Alternatively, Fröhlich[5] proposed a theory of slow electrons in polar crystals by assuming a weak electron-phonon interaction that allows application of perturbation theory. In a similar manner Lee et al.[6] treated the intermediate case of a moderate interaction of the electron with the crystal lattice. A generalization comprising weak, intermediate, and strong electron-lattice interactions is proposed by Feynman.[7] All these theories concern the "large" polarons in ionic crystals.

The continuum polarization model for "small" polarons was first considered by Tjablikov[8] and Yamashita and Kurosawa[9] making use of a perturbation approach. The same approach was then employed by Holstein[10] in treating small polarons in molecular crystals by using the adiabatic (tight-binding) approximation in a discrete (one-dimensional) model.

The polaron concept has been first applied to the theory of electron conduction in defect-free ionic and molecular crystals[4,10]; however, electron transitions via point defects have been also considered.[4] The adiabatic approach was used by Kubo and Toyozawa[11] to treat both radiative and nonradiative transitions of trapped electrons in insulating or semiconducting (ionic and covalent) crystals. Making use of Kubo density matrix formalism,[12] Lang and Firsov[13] further developed the small-polaron theory.

The polaron concept does not appear to give an

adequate description of electron motion in organic solids.[14] A variety of electron-transfer mechanisms have been proposed for an explanation of various phenomena in ordered and disordered molecular systems. A critical discussion of all these possibilities was recently made by Duke.[14]

The aim of the present paper is to consider a simple "two-site" polaron model of electron transfer in polar crystals based on the adiabatic approximation, which, however, is not restricted by the limitations of perturbation theory. It presents an extension of previous studies on similar problems in chemistry[15] and electrochemistry[16] in the framework of a general reaction-rate theory.[15,17] It is hoped that this extension may be useful in treating some important phenomena in solids such as the ionization of excited F centers in ionic crystals, the interimpurity electron transfer in covalent crystals, the electronic conductivity in molecular crystals, etc.

A comparison between the results of the reaction-rate approach and the usual multiphonon approach in studying large-polaron hopping in polar media was first made by Christov.[16] A similar comparison was recently done by Holstein[18] concerning the small-polaron hopping in molecular crystals. In this way some essential advantages of the reaction-rate approach are recognized. It will be, therefore, useful to give a critical discussion of the main results of reaction-rate theory[17] with regard to their applicability to the study of both large- and small-polaron hopping in crystals. This is the goal of the following considerations.

II. BASIC ASSUMPTIONS

We now consider a crystal as a system of oscillators (atoms, ions, or molecules) and an "extra" electron interacting with them. The crystal may have some point defects (such as ion vacancies) that can trap the electron, but a "self-trapping" is possible also in any lattice site of a defect-free crystal because of the lattice polarization due to the electron.

For ionic crystals one usually assumes that the electron motion is only coupled with the longitudinal-optical (LO) vibrations that consist of a relative displacement of the positive and negative ions in any elementary lattice cell (dielectric polarization). As is known, the frequency dispersion of these vibrations may be disregarded since the electron-phonon coupling is particularly strong for the vibrations for which the phonon wave number is

zero ($k_{\mathrm{ph}} = 0$). Therefore, at a later stage, we will consider only LO vibrations with a single frequency corresponding to the maximum of absorption of ionic crystals. The same one-frequency oscillator model (Einstein model) may be used when treating molecular crystals by assuming that the electron interacts most strongly with a particular vibration of the molecule at any site of the crystal lattice.

In ionic crystals the dielectric polarization is spread over a wide region around the instant electron position so that the linear dimensions of the polaron are large compared to the lattice constant. Therefore, the continuum model for the ionic crystal is justified for "large" polarons.[4] In molecular crystals, however, the polarization region (the polaron radius) is comparable with the spacing between the molecules; therefore, a molecular model for the "small" polaron must be used.[10] Our treatment will be based in both cases on models that consider the discrete structure of the crystal.

There are two approximations that are used, depending on whether the electron-phonon interaction is weak or strong. For ionic crystals, where the continuum theory of large polarons is applicable, one makes use of a criterion based on the value of the Fröhlich coupling constant

$$\alpha = \frac{e_0^2}{\bar{\epsilon}\hbar} \left[\frac{m^*}{2h\nu} \right]^{1/2} , \qquad (1)$$

where e_0 is the electron charge, m^* is the effective (conduction-band) mass of the electron, and $\bar{\epsilon}$ is an effective dielectric constant defined by

$$\frac{1}{\bar{\epsilon}} = \frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_0} , \qquad (2)$$

ϵ_0 and ϵ_∞ being the static and optic dielectric constant, respectively.

In the weak-coupling limit $\alpha \ll 1$ the electron is considered to move much slower than the lattice ions so that the dielectric polarization follows the electron motion immediately. In the strong-coupling limit $\alpha \gg 1$, in turn, the electron motion is much faster than the ion vibrations, which justifies the usual Born-Oppenheimer adiabatic separation of electron and ion motions. In practice, the adiabatic approximation seems to be good enough[3] if $\alpha > 4$, which is the case of alkali halides, for instance. We will, therefore, admit, that this condition is fulfilled when treating ionic crystals.

For molecular crystals the adiabatic approximation is justified as far as the overlap of the electronic wave functions of the neighbor molecules is small, which results in a relatively stable localiza-

tion of the electron in a molecule of the lattice. It is suitable in this case to consider the orientations and centers of gravity of molecules as being fixed,[10] since the localized electron is strongly coupled only with the intramolecular vibrations.

III. BASIC EQUATIONS FOR A LOCALIZED ELECTRONIC STATE

The time-independent Schrödinger equation of the crystal plus electron system

$$\hat{H}\psi = E\psi \tag{3}$$

involves the Hamiltonian operator

$$\hat{H} = \hat{H}_e + \hat{H}_v + \hat{H}_{ev} , \tag{4}$$

which is a sum of three terms corresponding to the electron motion, the lattice vibration motion, and their interaction, respectively.

The electron Hamiltonian

$$\hat{H}_e = -\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r}) \tag{5}$$

is a sum of the kinetic-energy operator that involves the free-electron mass m and the potential energy of the "static" interaction of the conduction electron with the crystal lattice as a function $V(\vec{r})$ of the electron position vector $\vec{r}$. In defect-free crystals $V(\vec{r})$ represents a periodic function if the lattice particles are fixed at their equilibrium positions but their electron clouds adiabatically follow the "slow" motion of the conduction electron. In the general case, however,

$$V(\vec{r}) = W(\vec{r}) + V^0(\vec{r}) , \tag{6}$$

where $W(\vec{r})$ denotes the periodic potential and $V^0(\vec{r})$ the electron potential energy of interaction with the distorted crystal lattice and some point defects (such as impurity atoms, ion vacancies, etc.), under the same adiabatic condition for the lattice electrons related to an "induced" polarization of the lattice.

If the conduction electron is *fixed* at some point of the crystal, then the lattice Hamiltonian can be written as

$$\hat{H}_v = \sum_i \frac{h\nu_i}{2}\left[\xi_i^2 - \frac{\partial^2}{\partial\xi_i^2}\right] + \sum_{i\neq k}\frac{h\nu_{ik}}{2}\xi_i\xi_k + \cdots \tag{7}$$

if we use the dimensionless coordinates

$$\xi_i = (2\pi\nu_i\mu_i/\hbar)^{1/2}x_i ,$$

where ν_i are the vibration frequencies, μ_i are the corresponding reduced masses, and x_i are the Cartesian normal coordinates of the harmonic oscillators relative to their equilibrium position $(x_i = 0)$, where account has been taken of the lattice distortion due to the presence of the electron and some lattice defect. The second term in (7) represents a weak coupling between the vibration coordinates that results from an expansion of the potential energy of the crystal about the configuration $\{\xi_i\}$ of its minimum value. This term is necessary to ensure the vibrational relaxation and the thermal equilibrium of the crystal; however, under certain conditions it may be neglected when considering the electron transfer from one to another localized state.

In band theory the lattice particles are fixed at their equilibrium positions $(\xi_i = 0)$ so that $\hat{H}_v = 0$ (and $\hat{H}_{ev} = 0$), and the electron-lattice interaction is described only by the periodic potential $W(\vec{r}) = W(\vec{r} + \vec{n})$, where $\vec{n}$ is the lattice vector. The solutions of (3) are Bloch functions

$$\psi_k(\vec{r}) = u_k(\vec{r})e^{i\vec{k}\cdot\vec{r}}, \quad u_k(\vec{r}) = u_k(\vec{r} + \vec{n}) \tag{8}$$

and the corresponding eigenvalues $E(\vec{k})$ are functions of the wave vector $\vec{k}$ whose components k_i $(i = 1,2,3)$ are usually restricted to vary between $-\pi/a$ and π/a (first Brillouin zone) when considering for simplicity a crystal of cubic symmetry with a lattice constant a. An energy band $E_\alpha(\vec{k})$ corresponds to a variation of $|k_i|$ from 0 to π/a. Near the minimum of $E_\alpha(\vec{k})$ (small $\vec{k}$ values) the parabolic approximation

$$E_\alpha(\vec{k}) = E_\alpha^0 + \frac{\hbar^2\vec{k}^2}{2m^*} \tag{9}$$

may be used, where $E_\alpha^0 = E_\alpha(0)$ and m^* is an effective electron mass. This is equivalent to replacing the periodic potential $W(\vec{r})$ by a constant potential and the Bloch functions (8) by plane waves [i.e., $u_k(\vec{r})$ by a constant mean value].

In the polaron theory one takes into account the dielectric polarization caused by the electron, which results in a shift of the equilibrium positions of the lattice particles in such a way that the electron is "self-trapped" at a given site of the crystal lattice. For a defect-free crystal this static interaction is represented by the second term $V^0(\vec{r})$ of the electron potential energy (6), which may include, however, also the interaction of the electron with a crystal imperfection.

The third term $\hat{H}_{ev}$ of the total Hamiltonian (4) describes the interaction between the electron motion and the lattice vibrations; hence it is essen-

tially a *dynamic* coupling term. If the lattice vibrations are restricted in the vicinity of the equilibrium configuration $\{\xi_i\}=0$ (harmonic approximation), then $\hat{H}_{ev}$ will be small compared to the static potential energy $V^0(\vec{r})$ and may be regarded as a small perturbation that depends linearly on the (small) lattice displacements ξ_i. Therefore, in such a case we may write

$$\hat{H}_{ev} \equiv V_\xi(\vec{r},\xi) = -\sum_i b_i(\vec{r})\xi_i \qquad (10)$$

where $b(\vec{r}) = -\partial V_\xi/\partial \xi_i$ is a force which tends to decrease the displacement ξ_i.

The adiabatic approximation consists of neglecting the kinetic energy operator of the lattice vibrations in (7), which means solving the wave equation (3) at fixed lattice coordinates $\{\xi_i\}$. With the use of (3)−(7) and (10) the adiabatic Hamiltonian of the system then becomes

$$\hat{H}_{ad} = -\frac{\hbar^2}{2m}\nabla^2 + W(\vec{r}) + V^0(\vec{r}) + \sum_i \frac{h\nu_i}{2}\xi_i^2$$

$$+ \sum_{i \neq k} \frac{h\nu_{ik}}{2}\xi_i\xi_k - \sum_i b_i(\vec{r})\xi_i \ . \qquad (11)$$

In the effective-mass approximation the free-electron mass m is replaced by m^* and the periodic potential $W(\vec{r})$ by a constant term that may be set equal to zero. The general solution of (3) is written as

$$\psi(\vec{r},\xi) = \sum_l \psi_l(\xi)\varphi_l(\vec{r},\xi) \ , \qquad (12)$$

which yields two separate equations for any bound electron state l:

$$\hat{H}_{ad}\varphi_l(\vec{r},\xi) = V_l(\xi)\varphi_l(\vec{r},\xi) \ , \qquad (13)$$

$$\left[-\sum_i \frac{h\nu_i}{2}\frac{\partial^2}{\partial \xi_i^2} + V_l(\xi) \right]\psi_l(\xi) = E_l\psi_l(\zeta) \ , \qquad (14)$$

where $\xi \equiv \{\xi_i\}$ denotes the set of coordinates ξ_i. These equations are obtained by a known standard procedure by neglecting the coupling terms between the electronic and lattice wave functions $\varphi_l(\vec{r},\xi)$ and $\psi_l(\xi)$, which is justified if $\varphi_l(\vec{r},\xi)$ is only weakly dependent on ξ, as is the case when the lattice particles make small (harmonic) vibrations.[17]

The electron energy $V_l(\xi)$ is given by the expression

$$V_l(\xi) = \int \bar{\varphi}_l(\vec{r},\xi)\hat{H}_{ad}\varphi_l(\vec{r},\xi)d^3r \ , \qquad (15)$$

which can be computed in continuum polaron theory by using the variational principle.[4] This approach is suitable only when treating "large" polarons in ionic crystals. A discrete-crystal model is necessary to describe "small" polarons in molecular crystals.[10] In both cases, use can be made of perturbation theory by considering the coupling terms $b_i(\vec{r})\xi_i$ in (10) as sufficiently small.

If we write the perturbed electronic wave function as

$$\varphi_l(\vec{r},\xi) = \varphi_l^0(\vec{r}) + \varphi_l'(\vec{r},\xi) \ , \qquad (16)$$

using the adiabatic Hamiltonian (11) with $m = m^*$ and $W(\vec{r}) = 0$, we obtain

$$V_l(\xi) = \sum_i \frac{h\nu_{il}}{2}(\xi_i - \xi_{il}^0)^2$$

$$+ \sum_{i \neq k} \frac{h\nu_{ikl}}{2}(\xi_i - \xi_{il}^0)(\xi_k - \xi_{kl}^0) + Q_l \ , \qquad (17)$$

where

$$\xi_{il}^0 = \bar{b}_{il}/h\nu_{il} \ , \quad \bar{b}_{il} = \int b_i(\vec{r}) |\varphi_l^0(\vec{r})|^2 d^3r \qquad (18)$$

and

$$Q_l = E_l^0 + \bar{V}_l^0 + E_{\xi^0 l}^0 \qquad (19)$$

with

$$E_l^0 = -\frac{\hbar^2}{2m^*}\int \bar{\varphi}_l^0(\vec{r})\nabla^2\varphi_l^0(\vec{r})d^3r \ ,$$

$$\bar{V}_l^0 = \int V^0(\vec{r}) |\varphi_l^0(\vec{r})|^2 d^3r \ , \qquad (20)$$

$$E_{\xi^0 l}^0 = -\sum_i \frac{h\nu_i}{2}\xi_{il}^{02} \ .$$

In (17) the small coupling terms,which may cause a change of the electronic state l (as well as of the vibration frequencies), are neglected.

Equation (18) gives the new equilibrium positions of the lattice particles that result from the dynamic interaction of the electron with the lattice vibrations. Equation (19) represents the "binding energy" Q_l of the electron as a sum of three terms corresponding to its mean kinetic energy E_l^0, its mean "static" potential energy $\bar{V}_l^0$ of interaction with the crystal lattice (including some imperfection), and the "dynamic" potential energy $E_{\xi^0 l}^0$ related to the displacement of the equilibrium lattice configuration. The energy is referred to the bottom of the conduction band $\alpha = \alpha_c$ by setting

$E_{\alpha_c}^0 = 0$ in (9) when the electron is at rest far from the imperfection. In defect-free crystals Q_l is simply the "polaron" binding energy in the adiabatic approximation.

The electron energy $V_l(\xi)$ defined by (17) plays the role of an adiabatic potential in the wave equation (14) of the lattice vibrations. The solution of this equation is simplified if the small second term in (17) is neglected ($v_{ikl} = 0$). This yields the known wave functions for a system of independent harmonic oscillators

$$\psi_n^l(\xi) = \prod_i (\sqrt{\pi} 2^{n_i} n_i!)^{-1/2} H_{n_i}^l(\xi_i - \xi_{il}^0)$$

$$\times e^{-(\xi_i - \xi_{il}^0)^2/2} \tag{21}$$

in terms of Hermitian polynomials of order n_i, and the corresponding eigenvalues are

$$E_n^l = \sum_i \frac{h \nu_{il}}{2}(n_i + \tfrac{1}{2}) , \tag{22}$$

where $n = \{n_i\}$ is a set of oscillator wave numbers.

The effective-mass approximation used to derive equations (11)–(20) is valid if the de Broglie wavelength $\lambda = h/m^* v$ ($v = \hbar |\vec{k}|$) exceeds the lattice constant a. In continuum polaron theory this corresponds to the condition

$$r_0 > a , \quad r_0 \simeq 2\hbar^2 \bar{\epsilon}/m^* e_0^2 \tag{23}$$

where r_0 is the polaron radius, $\bar{\epsilon}$ being the effective dielectric constant (2). On the other hand, according to (9) and (20) the effective-mass approximation is justified when the average kinetic energy E_l^0 of the trapped electron is considerably lower than the conduction-band width. Therefore, for ionic crystals for which $r_0 \gg a$ the concept of a "large" polaron is well applicable.

In a defect-free crystal the "large" polaron is allowed to move across the crystal. To take this translation motion into account the Hamiltonian should include the additional term

$$\hat{H}_p = -\frac{\hbar^2}{2M} \frac{\partial^2}{\partial \vec{R}^2} , \tag{24}$$

where $\vec{R}$ is the position vector of the polaron center and M is an effective polaron mass. In this situation the sums over the vibrational degrees of freedom in (7) must be reduced by three terms. The effective mass M has been estimated by Landau and Pekar[19] under the condition

$$v_p \ll 2\pi \nu r_0 , \tag{25}$$

which means that the polaron group velocity v_p is small, i.e, the translation motion of the polaron is slow compared to the ion vibrations. This condition is fulfilled when v_p is of the order of the thermal velocities ($M v_p^2/2 \sim kT$). Therefore, in such a case

$$\hat{H}_p \ll \hat{H}_v , \tag{26}$$

so that in some problems the adiabatic condition (25) allows us to disregard the translation motion of the polaron when using (15)–(20).

The effective-mass approximation is not justified for molecular crystals where the overlap of the electronic wave functions of neighbor molecules is small; therefore, the conduction electron can be easily localized at a lattice site in a deep potential well to form a "molecular ion." In this case the polaron radius is small ($r_0 \simeq a$) so that a tight-binding approximation seems to be very suitable.[10] With the use of this approach for fixed (equilibrium) positions of the lattice particles the band theory yields the well-known energy dispersion formula[3]

$$E_\alpha(\vec{k}) = E_\alpha^0 - z V_\alpha \cos(\vec{k} \cdot \alpha) , \tag{27}$$

where z is the coordination number and

$$V_\alpha = \int \bar{\varphi}_l(\vec{r} + \vec{a}) U(\vec{r}) \varphi_l(\vec{r}) d^3 r \tag{28}$$

is the mean value of the interaction potential $U(\vec{r}) = w(\vec{r}) - W(\vec{r})$ between two neighboring molecules, $w(\vec{r})$ being the unperturbed "molecular" interaction potential. One thus obtains narrow energy bands of width $2 z V_\alpha$ (corresponding to a variation of $|\vec{k}|$ between $-\pi/a$ and π/a). If $ka \ll 1$ from (27) the quadratic energy-momentum relation (9) follows, in which the effective mass is

$$m_\alpha^* = \hbar^2/z a^2 V_\alpha ,$$

but this approximation is not useful when treating "small" polarons in molecular crystals.

In the framework of the tight-binding approximation it is more reasonable to use the free-electron mass m but to disregard the periodic potential $W(r)$ in (6), as it represents a small perturbation of the electron energy due to the influence of the neighbor molecules.[10]

A full Hamiltonian of the form (11) with $W(\vec{r}) = 0$ may be used also for molecular crystals if the different terms are interpreted in a relevant manner. Thus $V^0(\vec{r})$ is to be considered a "static" potential energy of an "extra" electron in an isolated molecular ion, provided the nuclei are at rest at their (distorted) equilibrium positions $\xi_i = 0$ and the

other "fast" electrons are in a stationary quantum state that adiabatically follows the "slow" motion of the "extra" electron (induced polarization of the molecular ion). Then, the "lattice" Hamiltonian (7) will actually represent the intramolecular vibrations when the electron is fixed at the point $\vec{r}$. If both the "extra" electron and the nuclei are allowed to move, then, because of their "dynamic" interaction, an additional contribution $-b_i(\vec{r})\xi_i$ to the energy of any vibrational coordinate ξ_i arises.

Under these conditions the electronic energy $V_l(\xi)$ of the molecular ion can be evaluated by (15), making use of the above-mentioned perturbation approach, which implies that the "dynamic" coupling term $\sum b_i(\vec{r})\xi_i$ is small compared to the "static" potential energy of the electron $V^0(\vec{r})$. Then, using (16) one obtains again expression (17) for $V_l(\xi)$ in which ξ_{il}^0 and Q_l are defined by (18) and (20) in terms of the unperturbed electron wave functions $\varphi_l^0(\vec{r})$ of the molecular ion.

In this way we see that the "small" polaron in molecular crystals can be treated in a similar manner as the "large" polaron in ionic crystals when the conduction electron is localized at some point of the crystal (a molecule, or an ion, or a lattice defect). Under certain conditions this similarity provides a general basis for a treatment of the electron transfer from one to another lattice site.

IV. ELECTRON TRANSITIONS BETWEEN TWO LOCALIZED STATES

We have considered so far the electron localization at a given lattice site (point defect, ion, or molecule) on the basis of the adiabatic approximation. We will now investigate the radiationless electron transfer from one localized state to another in an ionic, atomic, or molecular crystal. The adiabatic energy of the crystal plus electron system for any of these two electronic state ($l=1$ and 2) is expressed by Eq. (17), which describes a many-dimensional paraboloid. The two corresponding paraboloids $V_1(\xi)$ and $V_2(\xi)$ intersect in a plane S along a line L, which represents a transition-state configuration of the crystal lattice. There is a minimum on this line that will be a saddle point between the two minima $V_1(\xi)=Q_1$ and $V_2(\xi)=Q_2$ of the two paraboloids if they are located sufficiently far from each other in the configuration space $\xi=\{\xi_i\}$.

In order to simplify the problem we will first neglect the small coupling terms in (17), i.e., we will set all $v_{ik}=0$ for both electronic states $l=1$

and 2. Furthermore, one can make use of two kinds of approximations.

The first approximation is to assume that all frequencies of lattice vibrations are equal ($v_i=v$) by neglecting the frequency dispersion, as is usual for the LO vibrations of ionic crystals. Then $V_1(\xi)$ and $V_2(\xi)$ will represent two similar rotational paraboloids and the saddle point will lie on a straight line ξ_r connecting the positions $\xi_1^0=\{\xi_{i1}^0\}$ and $\xi_2^0=\{\xi_{i2}^0\}$ of the minima of both paraboloids. We can conveniently change the origin of the coordinate system by setting $\xi_1^0=0$ and $\xi_2^0=\xi_0$.

The energy profiles along ξ_r are described by the equations

$$V_1(\xi)=\frac{hv}{2}\xi^2+Q_1 \, ,$$

$$V_2(\xi)=\frac{hv}{2}(\xi-\xi_0)^2+Q_2, \quad \xi_0=\left[\sum_i \xi_{i2}^{02}\right]^{1/2} , \tag{29}$$

by simply denoting ξ_r by ξ.

The second kind of approximation, which is suitable for molecular crystals, is to admit that the "dynamic" electron-lattice interaction is very weak for all vibrational modes except for a single mode. This means retaining only one term of the sum in the interaction Hamiltonian (10) that we denote by $b(\vec{r})\xi$ if ξ is simply the coordinate of the vibration concerned. Then, by rotation of the coordinate system we can make this coordinate coincide with the corresponding principal axis of the similar (ellipsoidal) paraboloids $V_1(\xi)$ and $V_2(\xi)$, where the set of coordinates $\xi=\{\xi_i\}$ is now replaced by a single coordinate ξ. In this way we come again to Eqs. (29), which represent the profiles of a cross cut of both paraboloids along the ξ axis. These profiles are two parabolic curves with a crossing point that corresponds to the saddle point of the two paraboloids. The height of this point is easily found to be

$$E_c'=\frac{(E_r+Q)^2}{4E_r} \, , \tag{30}$$

where $Q=Q_2-Q_1$ and

$$E_r=\frac{hv}{2}\xi_0^2 \, . \tag{31}$$

According to (30) it is convenient to measure the energy relative to the minimum (Q_1) of the electron energy $V_1(\xi)$ of the initial state by assuming $Q_2>Q_1=0$.

At the intersection line L of the paraboloids

$V_1(\xi)$ and $V_2(\xi)$ the system degenerates, since the electron energies of the initial and final states are equal. The degeneracy is removed by introducing the coupling between the two localized electronic states, which leads to a "resonance" splitting in the intersection region, i.e., to the formation of a lower and an upper adiabatic surface $V(\xi)$ and $V^1(\xi)$. Correspondingly, lower and upper adiabatic curves along the axes $\xi_r \equiv \xi$ arise.

The change of the lattice configuration can be described by the motion of a point from the initial state ($\xi=0$) to the final state ($\xi=\xi_0$) along ξ, which is the line of minimum energy, i.e., the most favorable path for a classical transition. It represents, however, a "reaction coordinate" that is dynamically separable from the other coordinates. Thus the many-dimensional "two-state" problem of calculating the quantum-mechanical transition probability can be reduced to a one-dimensional problem making use of the parabolic potential curves (29).

Using the linear combination (12) with $l=1,2$

$$\psi(\vec{r},\xi)=\psi_1(\xi)\varphi_1(\vec{r},\xi)+\psi_2(\xi)\varphi_2(\vec{r},\xi) , \qquad (32)$$

we can first solve the electron wave equation (13) at fixed ξ, which yields a system of two linear equations for the determination of ψ_1 and ψ_2. From the condition of resolubility of this system one obtains two eigenvalues $V(\xi)$ and $V^1(\xi)$, which represent two nonintersecting "adiabatic" potential surfaces: $V^1(\xi) > V(\xi)$. Their separation is given by the approximate expression[20]

$$\Delta V(\xi)=V^1(\xi)-V(\xi)$$
$$=\{[V_1(\xi)-V_2(\xi)]^2+4V_{12}^2(\xi)\}^{1/2} ,$$
$$\qquad (33)$$

where the nondiagonal matrix element

$$V_{12}(\xi)= \int \overline{\varphi}_1(\vec{r},\xi)\hat{H}_{ad}\varphi_2(\vec{r},\xi)d^3r \qquad (34)$$

(the electron "resonance" integral) is a measure of the interaction leading to the electron transfer from one localized state to another $(1\rightarrow 2)$ of the crystal lattice. The minimum value of $\Delta V(\xi)$ is at the crossing point ($\xi=\xi_c$) of the "diabatic" potential curves (29) (at which $V_1=V_2$), hence

$$\Delta V_{min}=2|V_{12}(\xi_c)| . \qquad (35)$$

Therefore, the maximum energy on the lower adiabatic surface is given by

$$E_c=E_c' - |V_{12}(\xi_c)| =\frac{(E_r+Q)^2}{4E_r} - |V_{12}(\xi_c)| ,$$
$$\qquad (36)$$

where E_c' is expressed by (30). This equation is a definition of the classical "activation energy" of the electron-transfer process considered.

A solution of the Schrödinger equation (3) by means of (32) yields two coupled differential equations for the lattice vibrations,

$$(E-\hat{H}_1)\psi_1(\xi)=V_{12}(\xi)\psi_2(\xi) ,$$

$$\hat{H}_1=-\frac{hv}{2}\frac{d^2}{d\xi^2}+V_1(\xi)$$

$$(E-H_2)\psi_2(\xi)=V_{12}(\xi)\psi_1(\xi) , \qquad (37)$$

$$\hat{H}_2=-\frac{hv}{2}\frac{d^2}{d\xi^2}+V_2(\xi)$$

where $V_1(\xi)$ and $V_2(\xi)$ are defined by (29) and $V_{12}(\xi)$ by (34).

We will now consider the conditions under which the probability of a radiationless electron transfer from state 1 to state 2 can be defined. Such a definition implies that there is no return from state 2 to state 1, at least within a time of the order of a period of vibration. This requires either a low transition probability or a fast relaxation of the vibrational state after the electron transfer. In the latter case one should take into account the small coupling terms in the lattice Hamiltonian (7) that lead to a frequency dispersion.[10] However, in order to simplify the calculations it is usual to neglect this frequency dispersion (Einstein model).

With the above-mentioned implications the transition probability can be defined in the familiar way[17] by considering a flux of system points moving along the reaction coordinate ξ from the initial state ($\xi=0$) towards to the transition state ($\xi=\xi_c$) of the lattice configuration. This flux is partially reflected back to the initial state ($\xi=0$) and partially transmitted to the final state ($\xi=\xi_0$). The transition probability is then given by the ratio

$$W =j_t/j_i ,$$
$$\qquad (38)$$
$$j_k=\frac{hv}{2i\hbar} \left[\overline{\psi}_k\frac{d\psi_k}{d\xi} -\psi_k\frac{d\overline{\psi}_k}{d\xi} \right]$$

of current densities j_t and j_i of the transmitted and the incident system points, the current density in the reverse direction in the final state being set equal to zero.

The transition probability W can be generally represented by the product

$$W =W_l W_e \qquad (39)$$

of two factors, where W_l is the probability for rearrangement of the lattice configuration and W_e that of the electron transfer when passing the transition lattice configuration ($\xi = \xi_c$), under the condition of energy conservation. If $W_e = 1$ the transition is called "adiabatic" and if $W_e \ll 1$ it is "nonadiabatic."

The possibility of an electron transfer leads to a perturbation of the initial state of the system (crystal plus electron), which will be small or large depending on whether the transition probability W is small or large. In an adiabatic transition ($W_e = 1$) W_l may be small for energies that lie considerably below the barrier peak ($E \ll E_c$), i.e., when a lattice rearrangement by quantum-mechanical "tunneling" is possible. In a proper one-dimensional treatment of the two-well problem the tunneling is related to a splitting of the vibrational levels in both wells, which is given in a quasiclassical approximation by the formula[21]

$$\Delta E_t = \frac{h\nu}{\pi} \exp\left[-\frac{2\pi i}{h} \int_{\xi_1}^{\xi_2} p_\xi \, d\xi \right] , \qquad (40)$$

$$p_\xi = \{2[E - V(\xi)]/h\nu\}^{1/2}$$

where ξ_1 and ξ_2 are the points of the potential barrier $V(\xi)$ between the initial and final configurations ($\xi = 0$ and $\xi = \xi_0$) at which the momentum p_ξ along ξ is zero, i.e., $E = V(\xi)$.

The tunneling probability can be calculated in the same approximation by (38) provided the other two classical turning points (ξ_1' and ξ_2') in the potential wells 1 and 2 are far away from ξ_1 and ξ_2, respectively.[17,22] In the low-energy range ($E \ll E_c$) one thus obtains the known WKB expression[21]

$$W_l = e^{-K(E)}, \quad K(E) = \frac{4\pi i}{h} \int_{\xi_1}^{\xi_2} p_\xi \, d\xi . \qquad (41)$$

Therefore, from (40) and (41)

$$\Delta E_t = \frac{h\nu}{\pi} W_l^{1/2} . \qquad (40')$$

Since $W_l \ll 1$, $\Delta E_t / h\nu \ll 1$, hence the tunneling splitting ΔE_t is small compared to the separation $\Delta E_n = h\nu$ between the unperturbed energy levels $E_n = (n + \frac{1}{2})h\nu$ of the lattice vibrations. If, however, the tunneling probability W_l is large, ΔE_t will be comparable with ΔE_n so that the discrete vibrational energy spectrum may be replaced by a continuous spectrum. This is, in particular, the case for energies which are somewhat below or higher than the barrier peak ($E \gtrsim E_c$); then, instead of (41), the more general quasiclassical formula[17,22]

$$W_l = (1 + e^{K(E)})^{-1} \qquad (42)$$

must be used, which involves (41) as a limiting case for $E \ll E_c$. It yields $W_l = 0.5$ for $E = E_c$ ($\xi_1 = \xi_2$) and $0.5 \le W_l \le 1$ for $E \ge E_c$ (ξ_1 and ξ_2 imaginary). The application of (42) to adiabatic transitions in the high-energy range $E \ge E_c$, in which W_l is large, implies a fast vibrational relaxation after the transition through energy exchange between the reaction coordinate and the nonreactive coordinates.

The phase integral in (40)–(42) can be easily calculated using the intersecting parabolic potentials (29) provided in (36) $|V_{12}| \ll E_c'$, i.e., $E_c \simeq E_c'$. The result is[16(a)]

$$K(E) = \frac{E_r}{h\nu} + \frac{Q^2}{E_r h\nu} - \frac{(E_r + Q)^2}{2E_r h\nu}[1 - \varphi(\alpha_1)]$$

$$- \frac{(E_r - Q)^2}{2E_r h\nu}[1 - \varphi(\alpha_2)] \qquad (42')$$

where

$$\varphi(\alpha) = \sqrt{\alpha} - (1 - \alpha)\ln\frac{\sqrt{1-\alpha}}{1-\sqrt{\alpha}} ,$$

$$\alpha_1 = 1 - (E/E_c) ,$$

$$\alpha_2 = 1 - [(E - Q)/(E_c - Q)] .$$

For a symmetric barrier ($Q = 0$) one has $E_r = 4E_c$ [see Eq. (36)] and $\alpha_1 = \alpha_2$; therefore

$$K(E) = \frac{4E_c}{h\nu}\left[\sqrt{1 - (E/E_c)} \right.$$

$$\left. - \frac{E}{E_c}\ln\frac{\sqrt{E/E_c}}{1 - \sqrt{1 - (E/E_c)}} \right] . \qquad (42'')$$

In the low-energy range the time-dependent perturbation theory may be used to calculate the tunneling probability $W_l \ll 1$ when assuming a quasicontinuous (weakly quantized) energy spectrum (for which $h\nu \ll E_c$) if in (36) $|V_{12}| \ll E_c'$. A modification of Bardeen's approach[23] then yields the expression[16,17]

$$W_l = \pi^2 \left[\psi_2 \frac{d\psi_1}{d\xi} - \psi_1 \frac{d\psi_2}{d\xi} \right]_{\xi = \xi_c} ,$$

$$\xi_c = \frac{\xi_0}{2} + \frac{n_1 - n_2}{\xi_0} ,$$

where ψ_1 and ψ_2 are the (real) oscillator wave functions of the initial and final states, respectively. This formula involves the current density in the

barrier region to be evaluated at the crossing point $\xi = \xi_c$ of the parabolic curves (29). This can be done accurately to give the formula[16(a)]

$$W_l \equiv W_{n_1 n_2} = \frac{\pi F_{n_1 n_2}^2 (\xi_0, \xi_c)}{2^{n_1 + n_2} n_1! n_2!}$$

$$\times e^{-(n_1 - n_2)^2 h v / E_r} e^{-E_r / h v}, \qquad (43)$$

$$E_r > Q = (n_1 - n_2) h v$$

where n_1 and n_2 are the vibrational quantum numbers of the initial and final states $(E_{n_1} = E_{n_2})$, E_r is the "reorganization energy" (31) and

$$F_{n_1 n_2}(\xi_0, \xi_c) = \xi_0 H_{n_1}(\xi_c) H_{n_2}(\xi_c - \xi_0)$$

$$- 2n_1 H_{n_1 - 1}(\xi_c) H_{n_2 - 1}(\xi_c - \xi_0)$$

$$+ 2n_2 H_{n_1}(\xi_c) H_{n_2 - 1}(\xi_c - \xi_0) ,$$

H_{n_i} being the Hermitian polynomials of order n_i.

Expression (43) agrees well with (41), with $K(E)$ given by (42'), in a range of variation of $E_r / h v$ between 10 and 100.[16(a)] This justifies its use even for a strongly quantized energy spectrum $(E_r / h v \sim 10)$ when there are a few energy levels below the barrier maximum $(E_n < E_c)$. In particular, it is to be preferred for the lowest vibration levels for which the WKB approximation (41) is inaccurate.

If the transition is nonadiabatic $(W_e \ll 1)$, the transition probability $W = W_l W_e$ may be small even when W_l is close to unity, i.e., when the lattice rearrangement occurs in a classical way (over barrier transition). Then, W_e can be calculated using Landau-Zener theory.[21]

In the general case of arbitrary value of W_l and W_e one must solve the system of coupled differential equations (37). This has been first done by Ovchinnikova[24] for the simplest case of two linear diabatic potentials that represent good approximations to the parabolic curves $V_1(\xi)$ and $V_2(\xi)$ only in the vicinity of their crossing point. It is assumed that $V_{12}(\xi)$ is a constant $V_{12}(\xi) = V_{12}(\xi_c)$. The formulas derived in this way are valid, however, for large absolute values of the energy variable $\epsilon = E - E_c$, i.e., for energy levels considerably above and below the crossing point $(\xi = \xi_c)$ where the linear approximations to $V_1(\xi)$ and $V_2(\xi)$ are not quite good $(E \gg E_c')$ or are completely inapplicable $(E \ll E_c')$. Nevertheless, it has been shown by Christov[16,17] that the expressions derived for linear adiabatic potentials are valid also for para-

bolic potentials, to a good approximation. This has been done by a comparison with the results of more accurate calculations for adiabatic and nonadiabatic transitions based on essentially different approaches.[16,25]

An important result of these investigations is that the transition probability can be well expressed by the product (39). For large positive values of $\epsilon(E \gg E_c')$, $W_l = 1$ and W_e is an oscillating function of $\epsilon = E - E_c^1$ which can be averaged over a small energy interval to obtain the expression[17,24]

$$W = \overline{W}_e = \frac{1 - e^{-2\pi\gamma}}{1 - \frac{1}{2} e^{-2\pi\gamma}}, \qquad (44)$$

where[16]

$$\gamma = |V_{12}|^2 / 2 h v (E_r | \epsilon |)^{1/2} \qquad (44')$$

and $\epsilon > 0$. This is a generalization of the semiclassical Landau-Zener formula[21]

$$W_e = 1 - e^{-2\pi\gamma} . \qquad (45)$$

Formula (45) gives the probability of a *one-way* transition (single passage of the crossing point of the diabatic curves) while (44) represents the probability of a *many-way* transition (multifold passage of the crossing point) as first shown by Holstein[10] in a direct intuitive way.

For large negative values of $\epsilon(E \ll E_c')$ one obtains for $W_l \ll 1$ the WKB expression (41) and for $W_e \leq 1$ the formula[16(b),24]

$$W_e = \frac{2\pi(2\gamma)^\gamma}{\gamma[\Gamma(\gamma)]^2} e^{-2\gamma} \qquad (46)$$

with γ defined by (44') and $\epsilon < 0$. For $\gamma > 1$ this formula yields $W_e \simeq 1$ (adiabatic transition) and for $\gamma \ll 1$, $W_e = 2\pi\gamma$ (nonadiabatic transition). Similar results for the case of linear diabatic curves are recently obtained by Holstein[18(a)] making use of an alternative approach.

Introducing (46) in (39) we may use the more accurate formula (43) for W_l for parabolic diabatic potentials instead of (41). As shown by Christov[16(b),17] the resulting expression for $W = W_l W_e$ agrees very well with earlier calculations[25] for nonadiabatic transitions $(\gamma \ll 1)$ for which (46) reduces to $W_e = 2\pi\gamma$. This justifies the use of (46) for any form of the diabatic curves and for arbitrary values of γ in the energy range $\epsilon \ll 0$ $(E \ll E_c^1)$ in which the lattice rearrangement is possible only by tunneling $(W_l \ll 1)$.

V. RATE EQUATIONS FOR POLARON HOPPING

According to the general formulation of reaction rate theory[15,17] the rate constant of any reaction can be conveniently written in the form

$$v = \kappa \frac{kT}{h} \frac{Z^*}{Z} e^{-E_c/kT} \qquad (47)$$

where E_c is the classical activation energy, Z is the full partition function, and Z^* is the partition function of the nonreactive modes (i.e., all motions normal to the reaction coordinate) of reactants, T is the absolute temperature, and k and h are Boltzmann and Planck constant, respectively. The factor κ considers the reaction dynamics through the statistical averages of the transition probabilities over the initial quantum states.

Equation (47) is based on the assumption that the reaction is irreversible, i.e., after the transition of the systems to the final state it is unlikely to return into the initial state. Expression (47) is closely related to the collision theory approach to gas-phase reactions but is essentially different from Eyring formulation of transition-state theory.[15,17] In particular, for unimolecular reactions from (47) one obtains[17,26]

$$v = 2\kappa \frac{kT}{h} \sinh \frac{h\nu_\xi}{2kT} \exp(-E_c/kT) , \qquad (48)$$

where ν_ξ is the frequency of a (harmonic) vibration of reactants along the reaction coordinate ξ and κ is defined by

$$\kappa = \sum_{n_\xi} \overline{W}(\epsilon_{n_\xi}) e^{-\epsilon_{n_\xi}/kT} \Delta\epsilon_{n_\xi}/kT , \qquad (49)$$

where n_ξ is the quantum number of the ξ vibration, and

$$\overline{W}(\epsilon_{n_\xi}) = \sum_n k_n(\epsilon_{n_\xi}) f(E_n, T) \qquad (49')$$

is the statistical mean value of the total transition probability

$$k_n = \sum_{n'} k_{nn'}$$

over the nonreactive quantum states n of reactants, $f(E_n, T)$ being the occupation probability of state n (with energy E_n) and n' denoting an energetically accessible nonreactive quantum state of products. The energy variable $\epsilon_{n_\xi} = E_{n_\xi} - E_c$ in (49) has discrete values in the low-energy range $(E < E_c)$, but the summation involves also the continuous part of the high-energy range $(E > E_c)$. If

$\Delta\epsilon_{n_\xi}/kT = h\nu_\xi/kT \ll 1$, the summation may be well replaced by integration in the whole energy range.

The rate equation (48) can be directly applied to the present two-site model for polaron hopping in crystals with the great simplification that the vibration frequency ν_ξ along the reaction coordinate ξ and the vibration frequencies of all nonreactive modes i are equal, i.e., $\nu_\xi = \nu_i = \nu$. The separability of the ξ vibration then leads to the result that the evaluation of the factor κ by (49) requires the solution of a one-dimensional dynamic problem, since the transition probabilities $k_n = \sum_{n'} k_{nn'}$ are independent of the initial and final states n and n' of the nonreactive modes. Therefore,

$$\overline{W} = \sum_n k_n(\epsilon_{n_\xi}) f(E_n, T) = k_n(\epsilon) \equiv W(\epsilon) \qquad (50)$$

so that $W(\epsilon)$ can be computed using the formulas of Sec. IV with $\epsilon_{n_\xi} \equiv \epsilon = E - E_c$ where E may have both discrete and continuous values.

We consider first adiabatic polaron hopping for which $\gamma/1$; hence, according to (45) and (46), $W_e = 1$. This will be, in particular, the case when the resonance energy V_{12} is sufficiently large. Then W_l can be computed by (42) in the whole energy range $(E \gtrless E_c)$. In this case κ represents the "tunneling factor" for lattice rearrangement.

At sufficiently high temperatures the tunneling transitions $(E < E_c)$ and the over-barrier transitions $(E > E_c)$ occur with a comparable probability $(W_e \sim 0.5 - 1)$ in an energy range[27]

$$\epsilon > -kT_k \text{ or } E > E_c - kT_k \qquad (51)$$

where T_k is a "characteristic temperature"[28-30]

$$T_k = h\nu^*/\pi k , \quad h\nu^* = (d^2V/d\xi^2)_{\xi=\xi_c} \qquad (52)$$

defined in terms of the barrier curvature at the maximum point $V(\xi_c) \equiv E_c$. A parabolic approximation

$$V(\xi) - E_c = -h\nu^* \xi^2/2 \qquad (53)$$

of the potential barrier in the energy range $\epsilon > -kT_k$ $(E > E_c - kT_k)$ allows an evaluation of the phase integral $K(E)$ in (42), which yields[17,31]

$$W_l = (1 + e^{-2\epsilon/kT_k})^{-1} . \qquad (54)$$

For $\epsilon > -kT_k$, $W_l > 0.12$, so that according to (40') $\Delta E_t/h\nu > 0.11$; hence a continuous energy spectrum can be used (see Sec. IV) to calculate κ by means of (49), (50), and (54) by replacing the n_ξ summation by an integration over $\epsilon = E - E_c$ (Δn_ξ

$= h\nu \rightarrow d\epsilon$) from $-\infty$ to ∞. We note first that the maximum of the integrand

$$W_l(\epsilon)e^{-\epsilon/kT} \qquad (55)$$

lies at the energy value

$$\epsilon_m = E_m - E_c = -\frac{kT_k}{2}\ln\frac{T_k \mid 2T}{1-(T_k \mid 2T)} , \qquad (56)$$

so that for $T = T_k$ we obtain $\epsilon_m = 0$ ($E_m = E_c$) and for $T = 0.567T_k$, $\epsilon_m = -kT_k$, which justifies the above approximations in the temperature range $T > T_k/2$. Thus, one obtains the simple expression[15-17]

$$\kappa = \frac{(\pi/2)(T_k/T)}{\sin[(\pi/2)(T_k/T)]} , \quad T > T_k/2 . \qquad (57)$$

This formula yields

$$\kappa \simeq 1 \text{ for } T > 2T_k ,$$

which defines the "classical temperature range" where the lattice reorganization occurs via over-barrier transitions. In this range from (48) the polaron hopping rate is found to be[16]

$$v = ve^{-E_c/kT} , \quad E_c = \frac{(E_r+Q)^2}{4E_r} - \mid V_{12} \mid \qquad (58)$$

under the conditions

$$T > 2T_k, \quad h\nu < kT/2, \quad (a^2/kT)^{1/3} > 1 \qquad (58')$$

where the adiabatic parameter a is defined below by (59'). Equation (58) represents the well-known Kramers formula.[32] The above derivation gives the *correct* activation energy E_c defined by (36) in contrast to the semiclassical approach,[2,10,33,35] which yields, instead, expression (58) with E_c replaced by E_c', i.e., it disregards the barrier lowering $\mid V_{12} \mid$, which may be considerable in adiabatic processes ($\mid V_{12} \mid \gg kT$).

We will now consider the classical temperature range ($T > 2T_k$) in the general case in which the polaron hopping is not adiabatic, hence $\gamma \lesssim 1$. Then, the semiclassical dynamic factor $\kappa = \chi \leq 1$ can be computed by (49) making use of the Landau-Zener formula (45) for $\overline{W} = W_e$ in order to evaluate the sum, by replacing it with an integral over ϵ from 0 to ∞ which can be calculated by the saddle-point method. Thus one obtains the expressions[16,17]

$$\chi = \frac{2}{\sqrt{\pi}}\left[\frac{a^2}{kT}\right]^{1/2} \ll 1 , \qquad (59a)$$

$$\chi = 1 - \frac{1}{2}\left[\frac{\pi}{3}\right]^{1/2}\left[\frac{a^2}{kT}\right]^{1/6}[1+\Phi(y)]$$

$$\times e^{-3(a^2/kT)^{1/3}} \leq 1 , \qquad (59b)$$

where[34]

$$a = \pi \mid V_{12} \mid^2 /2h\nu\sqrt{E_r} \qquad (59')$$

and the error integral

$$\Phi(y) = \frac{2}{\sqrt{2\pi}}\int_0^y e^{-t^2/2}dt, \quad y = \sqrt{3}\left[\frac{2a^2}{kT}\right]^{1/6} \qquad (59'')$$

is well tabulated. The formula (59a) is valid only for the nonadiabatic limit ($\chi \ll 1$), but (59b) applies to the remaining range of $\chi \leq 1$ including the adiabatic limit ($\chi = 1$) which is obtained for $(a^2/kT)^{1/3} > 1$.

From (48) and (59) we obtain in the high-temperature range the formula

$$v = \chi ve^{-E_c/kT} , \quad h\nu/kT < \frac{1}{2} . \qquad (60)$$

In particular, for nonadiabatic polaron hopping ($\chi \ll 1$) one has[16]

$$v = \frac{\mid V_{12} \mid^2}{\hbar}\left[\frac{\pi}{E_r kT}\right]^{1/2}e^{-(E_r+Q)^2/4E_r kT} ,$$

$$\qquad (61)$$

where $E_c \simeq E_c'$ is expressed by (30); this formula holds under the conditions

$$T > 2T_k, \quad h\nu < kT/2, \quad (a^2/kT)^{1/2} \ll 1 . \qquad (61')$$

For $Q = 0$ this formula coincides with the expression of Holstein[10] based on a semiclassical occurrence-probability approach (if we take into account that $E_r = 4E_c'$ when $Q = 0$). Similar expressions have been derived by using different other approaches.[2,25,35-37]

In the temperature range of moderate lattice tunneling

$$2T_k > T > T_k/2$$

a rough approximation for polaron hopping rate in the nonadiabatic limit ($\chi \ll 1$) and the intermediate range ($\chi < 1$) can be obtained by introducing in (60) an additional "tunneling" factor κ_t, i.e.,

$$v = \kappa_t \chi ve^{-E_c/kT} , \quad T > T_k/2 \qquad (62)$$

where κ_t is given by (57). This approximation is

justified as far as for $\kappa_t = 1$ or $X = 1$ it yields the correct results. In particular, in the adiabatic limit ($X = 1$) one obtains

$$v = \kappa_t v e^{-E_c/kT} , \qquad (62')$$

which is the Kramers equation (58) including the tunneling correction (57).

In the low-temperature range ($T < T_k/2$), according to (56) the maximum of the transfer probability (55) lies below the energy level $\epsilon_m = -kT_k$, hence the lattice rearrangement occurs almost entirely by tunneling. In this energy range, however, $W(\epsilon) \ll 1$ so that in the general case, as discussed in Sec. IV, a discrete energy variable

$$\epsilon_n = E_n - E_c = (n + \tfrac{1}{2})h v - E_c \qquad (63)$$

is to be used. Thus, from (48), (49), and (50) with (39) we obtain

$$v = v e^{hv/2kT} \sum_n W_l(E_{n_1}) W_e(E_{n_1}) e^{-E_{n_1}/kT} ,$$

$$E_{n_1} = E_{n_2} , \qquad (64)$$

under the conditions

$$T < T_k/2, \quad hv > 2kT . \qquad (64')$$

In (64) W_l can be computed by either (41) with (42') or (43) and W_e by (46).

At very low temperatures ($T \ll T_k/2$) only one term of the sum in (64) will contribute to the hopping rate. Then, a resonant transition ($E_{n_1} = E_{n_2}$) is possible only from a definite initial state n_1 to the ground final state $n_2 = 0$ so that

$$Q = (n_1 - n_2)h v = n_1 h v .$$

If $W_e(E_{n_1}) = 1$ (adiabatic transition) using (43) and (64) we obtain

$$v = \frac{\pi e^{-n_1 hv/kT}}{2^{n_1} n_1!} [\xi_0 H_{n_1}(\xi_c) - 2n_1 H_{n_1 - 1}(\xi_c)]^2$$

$$\times e^{-n_1 hv/E_r} e^{-E_r/hv} . \qquad (65a)$$

In particular, for a symmetric barrier for which $n_1 = 0$ ($Q = 0$)

$$v = \frac{2\pi E_r}{h} e^{-E_r/hv} . \qquad (65a')$$

If $W_e(E_{n_1}) \ll 1$ (nonadiabatic transition), using (43) and (46) with (44') for $\gamma \ll 1$ (when $W_e = 2\pi\gamma$) from (64) one finds

$$v = \frac{2\pi^2 |V_{12}|^2 e^{-n_1 hv/kT}}{h v E_r 2^{n_1} n_1!}$$

$$\times [\xi_0 H_{n_1}(\xi_c) - 2n_1 H_{n_1 - 1}(\xi_c)]^2$$

$$\times e^{-n_1 hv/E_r} e^{-E_r/hv} , \qquad (65b)$$

which yields for $n_1 = 0$ ($Q = 0$)

$$v = \frac{1}{v} \left[\frac{2\pi |V_{12}|}{h} \right]^2 e^{-E_r/hv} . \qquad (65b')$$

Equation (65) can be compared with the result of a perturbation treatment of Levich and Dogonadze[25] that was also derived more recently by Mott et al.[25] and Robertson and Friedman[37] using other approaches. See, for instance, Eq. (1) in Ref. 37(b) by noting that the reverse transition rate is

$$v_{0n_1} = v_{n_1 0} \exp(+n_1 h v/kT) .$$

Despite the different mathematical form for $n_1 \neq 0$, this equation gives for $n_1 = 0$ the same expression as (65b), namely (65b'). For $n_1 \neq 0$ a very good numerical agreement between both expressions is found.[17]

Our approach yields somewhat more complicated expressions for nonadiabatic transitions at low temperatures ($T < T_k/2$); however, it is applicable also to adiabatic transitions and the whole intermediate range between them, which cannot be treated by the methods used by other authors[25,37] based entirely on time-dependent perturbation theory and/or the Condon approximation. Indeed, the general rate expression (64) is not limited to nonadiabatic transitions, since $W_e(E_n)$ as given by (46) ranges between 0 and 1 ($0 \leq \gamma \leq \infty$) [although $W_l(E_n) \ll 1$].

If the number of energy levels below the barrier peak is relatively large so that $hv \ll E_c$ and $hv \ll E_c - Q$, then the sum in (64) may be well replaced by an integral over E even when $hv > kT$. In this case it is more convenient to use (41) with (42') to calculate W_l. Thus from (48) one obtains in the adiabatic limit ($W_e = 1$)

$$v = \frac{2kT}{h} \sinh \frac{hv}{2kT} \int_0^\infty e^{-K(E)} e^{-E/kT} dE / kT . \qquad (66)$$

The integral has been evaluated[16(a)] by the saddle-point method, which yields the expression

$$v = \sinh \frac{h\nu}{2kT} \left[\frac{2\pi}{h^2 K''(E_m)} \right]^{1/2} [1 + \Phi(y_m)]$$

$$\times e^{-F(E_m)}, \tag{67}$$

where E_m is the energy value at which the function

$$F(E) = K(E) + (E/kT) \tag{68}$$

has a minimum; hence $F'(E) = dF/dE = 0$, or

$$K'(E_m)kT = -1, \tag{69}$$

and $K''(E_m) = (d^2 K/dE^2)_{E_m}$. The Gaussian error integral

$$\Phi(y_m) = \frac{2}{\sqrt{2\pi}} \int_0^{y_m} e^{-t^2/2} dt, \quad y_m = E_m \sqrt{K''(E_m)} \tag{70}$$

is a function of E_m through y_m; it can be easily computed from tabulated data.

Expressions for all parameters in (67) can be derived.[16(a)] In particular, for $Q = 0$ using (42'') from the condition (69) we obtain

$$\frac{(E_m/E_c)^{1/2}}{1 - [1 - (E_m/E_c)]^{1/2}} = \exp(h\nu/4kT). \tag{71}$$

A solution of this equation is

$$E_m/E_c = \operatorname{sech}^2(h\nu/4kT). \tag{72}$$

From (42''), (68), and (71) one has

$$F(E_m) = \frac{4E_c}{h\nu} \left[1 - \frac{E_m}{E_c} \right]^{1/2} \tag{73}$$

so that using (72) we find

$$F(E_m) = \frac{4E_c}{h\nu} \tanh \frac{h\nu}{4kT}. \tag{74}$$

From (42'') and (72) one further obtains

$$K''(E_m) = \frac{2}{h\nu E_c} [\operatorname{sech}(h\nu/4kT)$$

$$\times \tanh(h\nu/4kT)]^{-1}. \tag{75}$$

Introducing (74) and (75) in (67) yields the rate equation

$$v = \frac{2[1 + \Phi(y_m)]}{h} \left[\pi h\nu E_c \sinh^3 \frac{h\nu}{4kT} \right]^{1/2}$$

$$\times \exp \left[-\frac{4E_c}{h\nu} \tanh \frac{h\nu}{4kT} \right]. \tag{76}$$

Expressions (67) and (76) are applicable as approximations under the conditions

$$0 \leq E_m < E_c - kT_k$$

or from (70) and (56)

$$E_m \sqrt{K''(E_m)} \geq 0, \quad T < T_k/2 \tag{77}$$

where E_m and $K''(E_m)$ are given by (72) and (75), while T_k is defined by (52). It should be noted, however, that the first condition (77) is not very stringent, i.e., (67) and (76) are still valid also for small negative values of E_m ($E_m \lesssim 0$), for which $\Phi(y_m)$ becomes negative.[27] This is due to the fact that the error function (70) arises in (67) because the integral in (66) comprises only positive E values.

The limitations of the second condition (77) can be avoided if we use in the energy range $E > E_c - kT_k$ the more general formula (42) for W_l by replacing (66) by the expression[27]

$$v = \frac{2kT}{h} \sinh \frac{h\nu}{2kT} \left[\int_0^{E_c - kT_k} e^{-F(E)} \frac{dE}{kT} \right.$$

$$\left. + \int_{E_c - kT_k}^{\infty} \frac{e^{-E/kT}}{1 + e^{K(E)}} \frac{dE}{kT} \right], \tag{78}$$

where $F(E)$ is given by (68). The first integral can be evaluated again by the saddle-point method and the second by means of expression (54) in which $K(E) = -2\epsilon/kT_k = 2(E_c - E)kT_k$. We thus obtain

$$v = \frac{2kT}{h} \sinh \frac{h\nu}{2kT} \left[\left[\frac{2\pi}{K''(E_m)} \right]^{1/2} \frac{\Phi(y_m) + \Phi(y_m')}{2kT} \right.$$

$$\left. \times e^{-F(E_m)} + \kappa_t' e^{-E_c/kT} \right], \tag{79}$$

where

$$y_m' = (E_c - kT_k) - E_m \gtrless 0 \tag{80}$$

and

$$\kappa_t' = \frac{(\pi/2)(T_k/T)}{\sin[(\pi/2)(T_k/T)]}$$

$$- \frac{\frac{1}{2}(T_k/T)}{1 - \frac{1}{2}(T_k/T)} e^{(T_k/T)-2}, \quad T > T_k/2 \tag{81a}$$

$$\kappa_t' = T_k/T, \quad T \simeq T_k/2 . \tag{81b}$$

If $T > \frac{2}{3}T_k$ the first term in (79) and the second term in (81a) can be neglected so that we obtain expression (62') with κ given by (57). For $T < T_k/2$ the second term in (79) becomes small and in the first term y_m' is so large that $\Phi(y_m') \simeq 1$; hence (79) turns into (67).

Recently, using a similar reaction-rate approach, Holstein[18(a)] has derived by the saddle-point method an equation for the hopping rate of small polarons in the nonadiabatic limit ($W_e \ll 1$). In our notations it is written as

$$v = \frac{|V_{12}|^2}{2\hbar} \left[\frac{2\pi}{E_c hv \operatorname{csch}(hv/2kT)} \right]^{1/2}$$
$$\times \exp\left[-\frac{4E_c}{hv} \tanh\frac{hv}{4kT} \right] . \tag{82}$$

This equation is based on the parabolic potentials (29) for the special case $Q = Q_2 - Q_1 = 0$ for which according to (36) $E_r = 4E_c(|V_{12}| \ll E_c)$; therefore, it corresponds to Eq. (76), which is valid for $Q = 0$ in the adiabatic limit ($W_e = 1$). For $hv/kT \ll 1$, Eq. (82) turns into Eq. (61) (with $E_r = 4E_c$, $Q = 0$); however, the actual high-temperature limit of validity of Eq. (82) is $E_m < E_c - kT_k$ or according to Eq. (77) $T < T_k/2$. The low-temperature limit, however, is not well defined.[38] When E_m is near to zero Eq. (82) comprises a considerable range of integration over negative E values; therefore it implies a sufficiently large positive E_m value. We may, however, modify Eq. (82) in order to extend its validity to lower temperatures at which $E_m \sim 0$ by using the same improvement of the saddle-point method,[27] which yields the corresponding adiabatic equation (76). Thus, instead of Eq. (82), we obtain

$$v = \frac{[1 + \Phi(y_m)]|V_{12}|^2}{4\hbar}$$
$$\times \left[\frac{2\pi}{E_c hv \operatorname{csch}(hv/2kT)} \right]^{1/2}$$
$$\times \exp\left[-\frac{4E_c}{hv} \tanh\frac{hv}{4kT} \right] . \tag{83}$$

It should be emphasized that at very low temperatures ($T \to 0$) the correct expressions for the hopping rate in the adiabatic and nonadiabatic limit for $Q = 0$ are given by Eqs. (65a') and (65b'), respectively. This implies, of course, that the electron transport via polaron band states is disregarded, although it actually is the prevailing conduction mechanism in molecular crystals at $T \to 0$.[10]

VI. DISCUSSION

The present treatment of polaron hopping in crystals is based on a reaction-rate approach[15,17] which has been previously applied to chemical reactions in both gas and dense phases[16,26] and, in particular, to electron transfer processes in solution.[16] In the latter case a two-site model, including a donor and acceptor center, is used under the assumption that the medium represents a system of harmonic oscillators. It has been noted,[16(b)] however, that such a description is much more suitable for electron transfer in polar crystals than in liquids where not only vibrations but also relative translations and rotations of molecules must be included in the reaction dynamics.[16,17] This is the actual motivation of the present work, which presents a consideration of the applicability of the reaction-rate approach to polaron hopping in crystals where the vibrations of atoms (ions and molecules) are the only modes which are coupled to the electron transitions.

The current theories of electron transfer in polar media are usually based on a perturbation treatment,[2,8-10,25,35-37] which restricts their applicability to nonadiabatic transitions. It has been shown,[16-17] however, that the reaction-rate approach is equally well applicable to both the nonadiabatic and adiabatic limits as well as to the whole intermediate range between them. It reproduces exactly the results of the multiphonon approach for the nonadiabatic hopping rate[10,25,35-37] and yields correct results for the adiabatic hopping, in particular, for the high-temperature activation energy which is overestimated by the classical occurrence-probability approach to the vibrational motion.[10,33,35]

The advantages of the reaction-rate treatment of small-polaron hopping in molecular crystals have been recently recognized by Holstein,[18] who derived in this way the rate equation (82) that refers to the limiting case of nonadiabatic transitions. The latter equation agrees completely with the result of the more rigorous multiphonon theory.[10] This agreement can be considered as an indirect justification of the reaction-rate approach also for the case of adiabatic hopping for which the multiphonon method is very difficult to apply. It should be also emphasized that, in principle, the reaction-rate theory[17] is not restricted by the assumptions of harmonic lattice vibrations and linear electron-lattice interaction as is usually the case of multiphonon theory.[10,35-37]

An inherent shortcoming of the Einstein one-

frequency model of the lattice vibrations is the neglect of their coupling, which is a necessary condition for the thermal equilibrium of the crystal. The influence of the frequency dispersion, resulting from the vibrational coupling, on the electron-transfer probability has been studied by Holstein,[10] Soules and Duke,[35] and Robertson and Friedman[37(b)] in the framework of multiphonon theory. Recently, Holstein[18] investigated the role of the vibrational relaxation after the electron transfer in order to give a justification of the simplest version of the reaction-rate approach in which the vibrational coupling is not explicitly included in the transition probability.[39] In this way Holstein[18] has shown that Eq. (82) for the nonadiabatic hopping rate follows from an expression of the type (64), by replacing the summation by integration over energy, when the effective "transition-time" τ_t is much shorter than the period $\tau_v = 1/\nu$ of the lattice vibrations $(\tau_t \ll \tau_v)$. The same conclusions are certainly valid for Eq. (76) for the adiabatic hopping rate that results from (66). The physical reason is that if the lattice tunneling is presumed to be a relatively fast process, it will lead to a broadening of the discrete vibration energy spectrum into a continuum, as discussed in Sec. IV. At this situation the validity of rate equations of the type (66) or (78) implies a fast vibrational relaxation.[18]

If, however, the tunneling probability is so low that the "transition time" is much greater than the vibration period $(\tau_t \gg \tau_v)$, then a definition of the transition probability by Eq. (38) is possible without the implication of a fast vibrational relaxation. This is so because before the transition the system has enough time to reach a stationary quantum state (within an equilibrium energy distribution), and after the transition there is also enough time for a relaxation (after many vibrations). Therefore, the vibrational coupling must be taken into account before and after the hopping event, but may be disregarded when calculating the probability of a "slow" tunneling transition along the reaction coordinate ξ, which can be separated by imposing suitable boundary conditions.[17,35] In this case, in principle, a discrete vibrational spectrum should be used. However, in practical calculations one is allowed to replace (64) by an integral expression like (66) if the number of energy levels in the energy range $0 < E_n < E_c - kT_k$ is sufficiently large so that $h\nu \ll E_c$. In this situation one is allowed also to use time-dependent perturbation theory[16,17] to derive expression (43) for the probability of lattice rearrangement. It is important to stress again that this expression yields numerical results in good agreement with those obtained from formula (41), based on the time-independent definition (38), even when applied to a properly discrete (strongly quantized) one-frequency oscillator model.[16(a)]

It should be recalled that the present reaction-rate treatment of polaron hopping is based on the adiabatic approximation, i.e., the motion of the trapped electron is assumed to be much faster than the lattice vibrations. Therefore, the electron potential energy $V(\vec{r},\xi)$ changes slowly with time[40] so that the electron remains in the same quasistationary quantum state α corresponding to a *discrete* energy value $V_\alpha(\xi) = E_\alpha(t)$. If the frequency dispersion of the lattice vibrations is neglected, then a change of the electron energy E_α at a given lattice site by absorption or emission of phonons $h\nu$ is excluded, since the adiabatic condition means that $h\nu \ll \Delta V_\alpha$, where $\Delta V_\alpha = \Delta E_\alpha = E_\alpha - E_{\alpha-1}$ is the energy difference between any two nearest electron energy levels. At this situation the electron transfer by tunneling from one site to another of the crystal lattice is possible only in the transition region of the lattice configuration space $\xi = \{\xi_i\}$, i.e, near the intersection line of the potential-energy surfaces $V_1(\xi)$ and $V_2(\xi)$ where the electron energies of the initial and final states are either equal $(V_1 = V_2)$ or differ by $h\nu(|V_2 - V_1| = h\nu)$. Therefore, one distinguishes between *elastic* (or "resonant") electron tunneling and *inelastic* (or "phonon-assisted") tunneling. In the case of a discrete vibration-energy spectrum the probability of inelastic electron tunneling is actually very small; however, it increases greatly when considering the frequency dispersion that facilitates the absorption and emission of many phonons by the electron before and after the tunneling process. This *dynamic* electron-transfer mechanism is an essential feature of the adiabatic multiphonon theory of (nonadiabatic) polaron hopping.[10,18,35−37] In the semiclassical Landau-Zener theory,[21] instead, one introduces a *static* perturbation, resulting in an avoided crossing of the diabatic potential curves $V_1(\xi)$ and $V_2(\xi)$, which produces an elastic (resonant) electron transfer. Nevertheless, in the framework of reaction-rate approach this theory as well as its quantal generalization[16,17,24] yields the same equations for the nonadiabatic polaron hopping rate as the multiphonon theory.[10,18,35−37]

In the general formulation of reaction-rate theory,[17] based on the adiabatic approximation, the detailed mechanism of electronic rearrangement is not specified so that it comprises many kinds of

adiabatic and nonadiabatic reactions. In particular, when applied to electron-transfer processes in solids both elastic and inelastic electron tunneling can be incorporated into the rate equation (48) through the transition probabilities $k_n(\xi)$ by using corresponding models for the transfer mechanism.

An essentially different approach to polaron hopping implies that the motion of the trapped electron is much slower than the lattice vibrations, which results in a very fast fluctuation of the electron potential energy $V(\vec{r},\xi)$ and thereby in a broadening of the discrete electron-energy value into a continuous spectrum.[40] The dispersion of the lattice vibrations plays an important role in these electron density-of-states effects. Soules and Duke[35] showed that these effects are responsible for the elastic electron tunneling provided the electron is coupled at the two lattice sites to different lattice vibrations. In contrast to this, inelastic electron tunneling occurs by emission or absorption of many phonons when the electron at both sites is coupled to the same lattice vibrations.[35] In the case of a strong electron-vibration interaction, the elastic and inelastic electron tunneling are connected with two essentially different mechanisms of activation of the electron transfer. Nevertheless, they lead in the high-temperature limit ($h\nu \ll kT$) to similar equations for the nonadiabatic transition rate[35] that have the same form as Eq. (61). Therefore, the experimental verification of a rate expression of this form is not a sufficient criterion for the actual mechanism of the hopping process. The unambiguous determination of this mechanism appears to be a very difficult problem[14]; however, for the purposes of rate calculations it is evidently of secondary importance. In this respect the reaction-rate approach, when applied to simple models for the hopping event, may be very useful.

An inherent assumption of reaction-rate theory is that Eq. (47) describes an irreversible process.

In the present case of electron transfer in solids this assumption requires a justification as discussed, in particular, by Duke[14,35] and Holstein[18] from the standpoint of multiphonon theory, which is based on a perturbation treatment. They showed that the coupling of the electron to a quasicontinuous energy spectrum of lattice vibrations plays an essential role for the irreversibility of the electron transfer. Beyond the perturbation approach a simple way of introducing irreversibility is the imposition of appropriate boundary conditions[17,33,35] when calculating the transition probability.

It should be noted that the general reaction-rate theory, used here in treating polaron hopping, is essentially different from Eyring "activated complex theory" in two points: (1) It is based on a quantum-mechanical description of the vibrations. (2) A thermal equilibrium is postulated only for the initial and not for the transition state of the system. The first assumption can be introduced in a formal generalization of Eyring theory,[15(b),17] while the second one is usual in the collision theory of chemical reactions.[17] Both theories become identical only in the particular case of a dynamically separable reaction coordinate, in which the Eyring concept of the "activated complex" loses its usefulness. This is just the situation in a theory of polaron hopping in which the coupling between the lattice vibrations is ignored. This situation is sometimes misunderstood.[18]

The reaction-rate theory is certainly applicable to small-polaron hopping in molecular crystals; however, it may be used also in some cases of electron transitions in ionic crystals in which the concept of large polaron is adequate. Such is, for instance, the electron hopping from a F center to an ion vacancy or a localized polaron state outside the F center. This may be, in particular, the mechanism of ionization of excited F centers which will be considered elsewhere.[41]

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[39]In a discrete (strongly quantized) one-frequency model for the lattice vibrations, specific problems arise in the application of time-dependent perturbation theory, since it yields, at condition of energy conservation, a transition probability proportional to t^2, i.e., a hopping rate proportional to time t. As first shown by Holstein (Ref. 10) introducing a small frequency dispersion leads to the correct expression of a time-independent rate. The same result is obtained more recently by Robertson and Friedman (Ref. 37) for a more general molecular crystal model ($Q\neq0$). It is shown that the neglect of the frequency dispersion yields infinite transition rates in the resonant case (equal vibration energies in the initial and final states) in which $Q=ph\nu$ ($p=n_1-n_2$ is an integer number). This may be considered as a fundamental weakness of the model [Ref. 37(b)]. Such "pathological" results (Ref. 18) do *not* appear in the time-independent treatment based on the definition (38) of the transition probability, which yields constant transition rates for a discrete one-frequency oscillator model. The agreement between the results of both approaches means that the frequency dispersion is *implicitly* included in the time-independent approach [Ref. 37(b)]. This conclusion seems to be the outcome of the apparent controversy considered.

[40]In the Hamiltonian (11) the full electron potential energy is $V(\vec{r},\xi)=W(\vec{r})+V^0(\vec{r})+V_\xi(\vec{r},\xi)$, where V_ξ is defined by (10). The adiabatic condition is that the dynamic coupling term V_ξ varies slowly with the lat-

tice coordinates $\xi=\xi(t)$ compared to its dependence on the electron coordinate $\vec{r}=\vec{r}(t)$. Consequently, the "adiabatic" electron energy $V_\alpha(\xi)$ has a discrete value at any lattice configuration $\xi=\xi(t)$. If, in turn, V_ξ varies slowly with $\vec{r}=\vec{r}(t)$ relative to its variation with $\xi=\xi(t)$, then the discrete V_α values are broadened out into continua.

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