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Citation: The Journal of Chemical Physics 113, 10438 (2000); doi: 10.1063/1.1323723
View online: http://dx.doi.org/10.1063/1.1323723
View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/113/23?ver=pdfcov
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(Received 18 July 2000; accepted 19 September 2000)

A concerted electron–proton transfer reaction is discussed, in which proton tunneling occurs simultaneously with electronic transition. It is assumed that the potential in which the proton moves is formed by two electronic states, which in the absence of their interaction would cross in the region between the two minima of the proton adiabatic potential. The proton tunneling between the two wells is, therefore, coupled to a switch between the two electronic states. The later occurs only when the proton is in the tunneling region under the barrier. A simple analytical expression for the tunneling matrix element \( T_{DA} \) is derived, which is uniformly correct for small and large values of the electronic coupling. For small electronic coupling our expression coincides with that obtained in the nonadiabatic theory of proton-coupled electron transfer reactions. For large electronic coupling the expression is reduced to that obtained in the Born–Oppenheimer approximation. The transition from nonadiabatic to adiabatic tunneling is governed by the magnitude of the Landau–Zener parameter defined for the tunneling process. The obtained result is discussed in the context of the proton tunneling time.

I. INTRODUCTION

In biological redox reactions and in other reactions that occur in aqueous solutions, electron transfer is often coupled to proton transfer. There is a growing interest in understanding the mechanistic details of this type of redox processes. It has been recognized that such reactions can occur either in a concerted or in a sequential fashion. In sequential process, the electron and proton transfers can be described independently and the overall reaction rate is determined by the slowest step. Theories of both electron and proton transfer reactions have been considered in great detail in the past. At the same time, concerted reactions, in which electron and proton transfers occur as a single quantum-mechanical event, received much less attention, and only recently have become the focus of detailed theoretical investigation.

In this paper a concerted electron–proton transfer reaction is discussed in which both an electron and a proton change their quantum states simultaneously. We consider the case when the proton transfer can be described as a quantum tunneling between two wells formed by two interacting electronic states. The proton potentials in both electronic states are schematically shown in Fig. 1. The transfer of the proton from one well to the other is associated with a change of an electronic state of the system, i.e., in our case with an electron transfer. This situation is interesting, because the switch between the electronic states can only occur when the proton tunnels through the barrier. Naturally, the relation between the time scale of the proton tunneling and that of the electronic transition plays a central role in the problem. As can be seen from Fig. 1, without the switch of the electronic states, the proton would not be able to tunnel from one well to the other. The question then is what is the probability of such an event, in which, while the proton tunnels through the barrier from the donor well, the switch of the electronic states will occur and the proton will exit on the other side of the barrier, into the acceptor well?

In one form or another the above question arises in the context of quantum transition state theory and the theory of nonadiabatic reactions and reactive scattering that involves tunneling, see, e.g., Refs. 7–19. Yet another area in which this question has been discussed extensively is radiationless processes.

Kinetically, the situation is characterized by the tunneling matrix element \( T_{DA} \) between the initial and final vibrational states of the proton. If the tunneling matrix element is known for a pair of the donor and acceptor states then its contribution to the reaction rate can be easily evaluated. The transition state of the reaction corresponds to the resonance between the initial and final vibrational states of the proton, which is brought about by a thermal fluctuation of other, slower modes considered as an environment. Every time the two levels cross in the course of a thermal fluctuation of the medium, there is a nonzero probability that the concerted electron–proton transfer will occur. The probability of the transfer \( P_{DA} \) can be evaluated by the well-known Landau–Zener (LZ) formula

\[
P_{DA} = 1 - \exp(-2\pi p_{LZ}),
\]

where the adiabaticity parameter \( p_{LZ} \) with respect to motion of the medium is determined by the tunneling matrix element \( T_{DA} \), and the velocity of level crossing, \( \dot{\epsilon}, \epsilon = E_A - E_D \), as

\[
p_{LZ} = \frac{T_{DA}^2}{\hbar |\dot{\epsilon}|}.
\]
The velocity of level crossing $|\epsilon|$ is determined by the motion of the medium.

The overall rate of the reaction then is the frequency of occurrence of the transition state times the probability of the transfer. In the simplest case, when only one initial and one final vibrational state are involved in the reaction for sufficiently small $T_{DA}$, the rate of the proton transfer $k_{pt}$ can be written in a form similar to that given by the nonadiabatic electron transfer theory:\textsuperscript{2,3,24}

$$k_{pt} = \frac{\tau_{DA}^2}{\hbar} \sqrt{\frac{\pi}{\lambda k_B T}} e^{-\Delta G^\dagger/k_B T}, \quad (1.3)$$

where $\lambda$ is the energy of reorganization of the environment in response to the proton transfer, $\Delta G^\dagger$ is the activation (free) energy necessary to bring the two quantum states of the proton into the resonance, $k_B$ is the Boltzmann constant, and $T$ is the temperature.\textsuperscript{25}

If the tunneling matrix element is large, the contribution to the reaction rate will be determined by the corresponding adiabatic formulas of the rate theory\textsuperscript{2,14,26–28} and will be essentially independent of the tunneling matrix element.\textsuperscript{29}

Thus, the key parameter which determines the dynamics of the system is the tunneling matrix element $T_{DA}$. This parameter is the focus of discussion of the present paper.

One of the crucial characteristics of the system is the coupling of the two electronic states, $V_{12}$. In two limiting cases of small and large electronic couplings, the expression for $T_{DA}$ can be written out in a straightforward way. If $V_{12}$ is small, the expression for the tunneling matrix element can be obtained using first order perturbation theory in the electronic coupling

$$T_{DA}^{(1)} = V_{12}(\chi_D^{(1)} | \chi_A^{(2)}), \quad (1.4)$$

where $\chi_D^{(1)}$ and $\chi_A^{(2)}$ are the initial and final vibrational states of the proton in the initial (first) and final (second) electronic states, correspondingly, and $\langle \chi_D^{(1)} | \chi_A^{(2)} \rangle$ is their Franck–Condon overlap.

The above expression naturally appears in the theory which treats the proton motion as an additional quantum mode in the otherwise standard electron transfer system.\textsuperscript{30–32}

The nonadiabatic theory of electron transfer gives, in this limit, expressions similar to those obtained by nonadiabatic proton-coupled electron transfer theory (PCET), developed recently by Cukier\textsuperscript{33,34} and Hammes–Schiffer and co-workers.\textsuperscript{35,36}

On the other hand, when electronic coupling $V_{12}$ is sufficiently large one expects that the proton dynamics, as well as the dynamics of other nuclei in the system, can be adequately described as occurring on the adiabatic potential surface. The reaction, then, is usual tunneling of the proton through the barrier from one well to the other. In this limit too, the tunneling matrix element can be readily evaluated using standard methods.\textsuperscript{37,38} For example, for two ground states of the proton in both wells the following expression can be obtained using quasiclassical approximation (see below):

$$T_{DA}^{(ad)} = 0.17 \hbar \sqrt{\omega_D \omega_A} e^{\int_{x_p}^{x_A} \sqrt{2m[V(x) - E]} dx}, \quad (1.5)$$

where $\omega_D$ and $\omega_A$ are the vibration frequencies in the donor (left) and the acceptor (right) wells, $x_p$ and $x_A$ are the left and right turning points of the classical trajectories of energy $E$ on both sides of the barrier, $m$ is the proton mass, and $\hbar$ is the Planck constant. The potential energy $V(x)$ of the proton should be calculated in the Born–Oppenheimer approximation as an eigenvalue of the electronic part of the Hamiltonian (the kinetic energy of the nuclei being excluded) in which the proton coordinate is equal to $x$, and the coordinates of the heavy nuclei playing the role of the medium are such that there is a resonance between vibrational states in both wells.

In this paper an expression for $T_{DA}$ is derived which is uniformly correct in the whole range of variation of the electronic coupling $V_{12}$. The expression has the following form:

$$T_{DA} = \kappa T_{DA}^{(ad)}, \quad (1.6)$$

where $T_{DA}^{(ad)}$ is the tunneling matrix element calculated for the adiabatic potential barrier, e.g., as in Eq. (1.5), and the factor $\kappa$ is

$$\kappa = \sqrt{2 \pi p} \frac{e^{\rho \ln p - p}}{\Gamma(p + 1)}. \quad (1.7)$$

Here, $\Gamma(x)$ is the gamma-function and $p$ is the proton adiabaticity parameter. The parameter $p$ has a form similar to that of the parameter of the Landau–Zener theory, but which is defined for a tunneling process

$$p = \frac{|V_{12}|^2}{\hbar |\Delta E| v_i}, \quad (1.8)$$

where $|\Delta E|$ is the difference of the slopes of the potential energy curves, and $v_i$ is the “tunneling velocity” of the proton at the point where the potential energy curves cross

$$v_i = \sqrt{2(V_i - E)/m}. \quad (1.9)$$
Here, $V_c$ is the energy at which the potential energy curves cross, $E$ is the tunneling energy, and $m$ is the mass of the proton.

In the weak electronic coupling limit, our expression for the tunneling matrix element, Eq. (1.6), is reduced to the nonadiabatic expression, Eq. (1.4). In the strong electronic coupling limit, the factor $\kappa = 1$ and the expression for $T_{DA}$ is reduced to the adiabatic one, $T_{DA}^{(ad)}$.

The rest of the paper describes the derivation of Eq. (1.6), which is followed by an additional discussion of the main result.

II. THE MODEL AND THE METHOD OF CALCULATION OF $T_{DA}$

The model consists of a classical medium and a quantum subsystem which includes a proton and all electrons. In what follows the electron–proton subsystem will be referred to as the “system.” The medium represents all the heavy nuclei and is assumed to move slowly compared with the proton and electrons. At a fixed configuration of the medium we consider the coupled dynamics of the proton and electrons. We assume that there are only two electronic states $|\phi_1\rangle$ and $|\phi_2\rangle$ which are relatively weakly coupled and which come into resonance in the process of the proton tunneling from the left well to the right well. All other electronic states are separated from these two states by few eV and, therefore, satisfy the Born–Oppenheimer approximation, and can be excluded from the consideration. The Hamiltonian of the system has the form

$$\hat{H} = |\phi_1\rangle\langle\phi_1|\hat{h}_1(x) + |\phi_2\rangle\langle\phi_2|\hat{h}_2(x) + V_{12}(|\phi_1\rangle\langle\phi_2| + |\phi_2\rangle\langle\phi_1|),$$

where $V_{12}(x)$ is the coupling matrix element between the electronic states. The coordinates of the medium are implicitly present in the above Hamiltonian via dependence of the proton potentials on the configuration of the medium. For a specific configuration of the medium, the potentials are schematically shown in Fig. 1. We assume that the electronic coupling $V_{12}$ is constant and does not depend on either the coordinate $x$ of the proton, or that of the medium.

The wave function which describes the quantum state of the system can be written as

$$|\psi\rangle = \chi^{(1)}(x)|\phi_1\rangle + \chi^{(2)}(x)|\phi_2\rangle,$$

where $\chi^{(1)}(x)$ and $\chi^{(2)}(x)$ are the amplitudes for finding the proton at the position $x$ and the electronic subsystem in the states $|\phi_1\rangle$ and $|\phi_2\rangle$, correspondingly. Thus, we can say that the quantum state of the system is described by the two-component wave function $\chi(x)$

$$\chi = \begin{pmatrix} \chi^{(1)} \\ \chi^{(2)} \end{pmatrix}.$$

The eigenstates of our system (for a fixed configuration of the medium) are found from the Schrödinger equation

$$\hat{H}|\psi\rangle = E|\psi\rangle,$$

or, equivalently, from the following system of coupled equations for $\chi^{(1,2)}(x)$:

$$\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \chi^{(1)}(x) + V_1(x)\chi^{(1)}(x) + V_{12}\chi^{(2)}(x) = E\chi^{(1)}(x),$$

$$\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \chi^{(2)}(x) + V_2(x)\chi^{(2)}(x) + V_{12}\chi^{(1)}(x) = E\chi^{(2)}(x).$$

For most configurations of the medium, the eigenstates of the system are such that the proton is almost entirely localized either in the left, or in the right wells. We focus on a pair of such states, $|\psi_+\rangle$ and $|\psi_-\rangle$. Suppose the configuration of the medium is close to the transition state, which corresponds to resonance between the $|\psi_+\rangle$ and $|\psi_-\rangle$ states. As the coordinates of the medium are adiabatically changed and cross the transition state configuration, the energies of the two states will experience the avoided crossing. The minimum splitting of two eigenstates is twice the value of the tunneling matrix element, $|\Delta E_\pm| = 2|T_{DA}|$. At the transition state configuration, when the energy difference between the two states is minimum, the proton is delocalized between the left and the right wells.

In the vicinity of the transition state the eigenstates $|\psi_\pm\rangle$ can be described in terms of two localized diabatic states, $|\psi_D\rangle$ and $|\psi_A\rangle$, which are coupled with a constant matrix element $T_{DA}$. The diabatic states $|\psi_D\rangle$ and $|\psi_A\rangle$ can be defined as linear combinations of the two exact eigenstates of the system which are localized in either well. In contrast to the adiabatic states, $|\psi_+\rangle$ and $|\psi_-\rangle$, the diabatic states $|\psi_D\rangle$ and $|\psi_A\rangle$ are not very sensitive to the medium configuration. The diabatic states satisfy the Schrödinger equation, Eq. (2.6), in the region of their localization and under the barrier. Since the diabatic states are not eigenstates of the system, they are not well defined in the area where another diabatic state is localized. The energies of the diabatic states, $E_D$ and $E_A$, depend on the medium configuration. At the transition state configuration of the medium the diabatic states come into resonance and have equal energies.

If the system, initially in one of the localized states, $|\psi_D\rangle$, passes the transition state due to the thermal fluctuation of the medium, the probability $P_{DA}$ of transition from $|\psi_D\rangle$ to $|\psi_A\rangle$, upon the level crossing, is given by the Landau–Zener formula,22,23 Eq. (1.1), in which the tunneling matrix $T_{DA}$ element is a key parameter. To calculate the tunneling matrix element $T_{DA}$, one can use the method of the tunneling current, which was developed originally to describe the electron tunneling in proteins.39 In Appendix A it is shown using similar arguments as in Ref. 39 that the tunneling matrix element $T_{DA}$ is related to the tunneling current $J_{DA}$ as follows:

$$T_{DA} = \hbar J_{DA}(x_0),$$

where the tunneling current $J_{DA}(x_0)$ at the point $x_0$ is given by
\[ J_{DA}(x_0) = -i(\psi_d)[\hat{J}(x_0)]\psi_A, \]  
(2.8)  
where \( \hat{J}(x_0) \) is the proton flux operator  
\[ \hat{J}(x_0) = \frac{1}{2m}[\delta(x-x_0)\hat{P} + \hat{P} \delta(x-x_0)], \quad \hat{P} = -i\hbar \frac{d}{dx}, \]  
(2.9)  
where \( \delta(x-x_0) \) is the Dirac delta-function. The tunneling current \( J_{DA}(x_0) \) should not depend on the position of \( x_0 \) when \( x_0 \) lies in the barrier region between the donor and acceptor wells. The advantage of calculating of the matrix element using the method of tunneling current is that the region of coordinates where the diabatic states are ill-defined (the other well) does not enter into calculation. To calculate the tunneling current one only needs to evaluate the "tails" of the two diabatic states in a common area under the barrier, where they are both well defined.

In terms of the two-component wave function, Eq. (2.4), the diabatic wave function \( \chi^D(x) \) which is localized in the left well consists mostly of the first component \( \chi_1^D(x) \) while \( \chi_2^D(x) \approx 0 \). This wave function corresponds to the initial state of the system in which the proton is localized in the left well and the electronic subsystem is approximately in the first state. Similarly, \( \chi_A(x) \) describes the proton in the right well and the electronic subsystem in the second state.

### III. FINDING DIABATIC STATES \( |\psi^D_d\rangle \) AND \( |\psi^D_A\rangle \) AND TUNNELING CURRENT CALCULATION

To calculate the tunneling current the diabatic wave functions \( \chi^D(x) \) and \( \chi_A(x) \) must be calculated under the resonance condition in some common area deeply under the barrier. The two-component functions \( \chi^D(x) \) and \( \chi_A(x) \) satisfy the same system of equations, Eq. (2.6), with the same energy \( E \), however, in different but overlapping regions of the coordinate \( x \) (see above the discussion about the diabatic states). The boundary conditions for \( \chi^D(x) \) and \( \chi_A(x) \) are different. The function \( \chi^D(x) \) decays as \( x \) increases, while \( \chi_A(x) \) decays as \( x \) decreases. To find the diabatic wave functions \( \chi^D(x) \) and \( \chi_A(x) \) the whole range of variation of \( x \) in which Eq. (2.6) should be solved will be separated into several regions and approximate solutions will be found in these regions. After that, the derived solutions will be combined in the areas where their regions of applicability overlap. We will focus on the solution of Eq. (2.6) for the donor wave function \( \chi^D(x) \). The solution of Eq. (2.6) for the acceptor wave function \( \chi_A(x) \) can be found in a similar way.

Four such regions can be identified, cf. Fig. 1. The region \( DW \) (donor well) corresponds to the donor well. In this region, one can use the Born–Oppenheimer approximation and also approximate the adiabatic potential in which the proton moves as a harmonic one. The corresponding solution is given in Appendix B. The region DB (donor barrier) corresponds to the classically forbidden region under the barrier to the left of the crossing point \( x_c \) at which \( V_1(x_c) = V_2(x_c) \). In this region the Born–Oppenheimer approximation and the quasiclassical approximation to describe the proton motion are applicable. The region AB (acceptor barrier) corresponds to the classically forbidden region under the barrier on the acceptor side. It is similar to the DB region.

Finally, the region AW (acceptor well) corresponds to the acceptor well and should be considered only for the calculation of the acceptor wave function \( \chi_A(x) \). We will also define a small transition region \( C \) near the crossing point region. In this transition region Eq. (2.6) should be solved explicitly (see below).

In the DB and AB regions, the Born–Oppenheimer approximation is applicable, which means that the dynamics of the proton can be described as occurring on the lowest adiabatic energy surface, \( V_-(x) \)

\[ V_-(x) = \frac{1}{2}[V_1(x) + V_2(x) - \Delta V(x)], \]  
(3.1)  
\[ \Delta V(x) = \sqrt{[V_1(x) - V_2(x)]^2 + 4V_{12}^2}. \]  
(3.2)

The quantum state of the system (electrons plus the proton) can then be written as  
\[ |\psi\rangle = |\phi_-(x)\rangle \chi^{(0)}_{ad}(x), \]  
(3.3)  
where \( \chi^{(0)}_{ad}(x) \) is a one-component proton wave function which satisfies the Schrödinger equation for the proton in the adiabatic potential \( V_-(x) \)

\[ -\frac{\hbar^2}{2m} \frac{d^2 \chi^{(0)}_{ad}(x)}{dx^2} + V_-(x) \chi^{(0)}_{ad}(x) = E \chi^{(0)}_{ad}(x), \]  
(3.4)  
and \( |\phi_-(x)\rangle \) is the lowest adiabatic electronic wave function formed from \( |\phi_1\rangle \) and \( |\phi_2\rangle \) at a fixed position of the proton \( x \)

\[ |\phi_-(x)\rangle = |\phi_1^{(1)}\rangle |\phi_1\rangle + |\phi_2^{(2)}\rangle |\phi_2\rangle. \]  
(3.5)

In the \( |\phi_{1,2}\rangle \) basis, the two-component wave function \( \phi_-(x) \) can be written as

\[ \phi_-(x) = \begin{pmatrix} \phi^{(1)}_1 \\ \phi^{(2)}_2 \end{pmatrix} = \frac{1}{\sqrt{2\Delta V(x)}} \begin{pmatrix} -\sqrt{\Delta V(x) - V_1(x) + V_2(x)} \\ \sqrt{\Delta V(x) + V_1(x) - V_2(x)} \end{pmatrix}. \]  
(3.6)

To the left of the crossing point \( x_c \) \( \phi_-(x) = (-1,0) \), i.e., the system is in the first electronic state. To the right of the crossing point \( \phi_-(x) = (0,1) \), i.e., the system is in the second electronic state.

To calculate \( \chi^{(0)}_{ad}(x) \), the quasiclassical approximation can be used. For the donor state it will give

\[ \chi^{(0)}_{ad}(x) \approx \frac{1}{\sqrt{k_-}(x)} \exp\left[ -\int_{x}^{x_\infty} k_-(x') dx' \right]. \]  
(3.7)  
where \( k_-(x) \) is the wave vector in the low adiabatic state

\[ k_-(x) = \sqrt{2m(V_-(x) - E)/\hbar}. \]  
(3.8)

For the acceptor state, the sign of the power of the exponent in Eq. (3.7) is different.

Thus, in the DB and AB tunneling regions, the two-component wave functions \( \chi^D(x) \) and \( \chi_A(x) \) can be written as...
To find the proportionality coefficient for the donor wave function \( \chi_D(x) \) in Eq. (3.9) in the DB region this solution should be correlated with the corresponding solution in DW region. Similarly, the solution for the acceptor wave function \( \chi_A(x) \) in the AB region, Eq. (3.10), should be correlated with the appropriate solution in the AW region. In Appendix B it is shown that

\[
\chi_D(x) = C_{n_D} \phi_-(x) \frac{\sqrt{m \omega_D / \hbar}}{\sqrt{k_-(x)}} \exp \left[ - \int_{x_D}^{x} k_-(x') dx' \right],
\]

(3.9)

\[
\chi_A(x) = C_{n_A} \phi_-(x) \frac{\sqrt{m \omega_A / \hbar}}{\sqrt{k_-(x)}} \exp \left[ - \int_{x}^{x_A} k_-(x') dx' \right],
\]

(3.10)

where \( x_D \) and \( x_A \) are the left and right turning points of the tunneling trajectory (cf. Fig. 1). \( \omega_D \) and \( \omega_A \) are the vibration frequencies in the left (donor) and right (acceptor) wells, and \( C_{n_D} \) and \( C_{n_A} \) are numerical coefficients corresponding to the \( n_D \)th and \( n_A \)th excited states of the proton in the donor and acceptor wells, respectively. These coefficients are given in Appendix B by Eq. (B.10). For the ground-state \( C_0 = 0.41 \) and for the first excited-state \( C_1 \approx 0.40 \). Equations (3.11) and (3.12) are not applicable very close to the turning and crossing points. The intervals corresponding to the appropriate transition regions are shown in the applicability conditions of Eqs. (3.11) and (3.12) as \( \delta_D \), \( \delta_A \), and \( \delta_c \). The transition regions around the turning points are well known from standard quantum mechanics. The size of the transition region \( C \), \( \delta_c \), is given by Eq. (C.22) (see also below).

To obtain the wave functions \( \chi_D(x) \) and \( \chi_A(x) \) in the whole region under the barrier, one must correlate the solutions to the left and to the right of the crossing point by solving Eq. (2.6) in the crossing point region \( C \). In this region, the Born–Oppenheimer approximation is not valid and Eq. (2.6) must be solved explicitly. To this end, Eq. (2.6) can be rewritten as

\[
\frac{d^2 \chi^{(1)}}{dx^2} = k_1^2(x) \chi^{(1)}(x) + 2 \frac{m V_{12}}{\hbar^2} \chi^{(2)}(x),
\]

(3.13)

\[
\frac{d^2 \chi^{(2)}}{dx^2} = k_2^2(x) \chi^{(2)}(x) + 2 \frac{m V_{12}}{\hbar^2} \chi^{(1)}(x),
\]

where the wave vectors \( k_1(x) \) and \( k_2(x) \) are defined as

\[
k_1(x) = \sqrt{2 m [V_1(x) - E]} / \hbar,
\]

(3.14)

\[
k_2(x) = \sqrt{2 m [V_2(x) - E]} / \hbar.
\]

(3.15)

The potentials \( V_1(x) \) and \( V_2(x) \) can be expanded near the crossing point \( x_c \) up to the linear terms

\[
k_1^2(x) = k_2^2 + 2k_c q_1(x-x_c),
\]

\[
k_2^2(x) = k_2^2 + 2k_c q_2(x-x_c),
\]

(3.16)

where \( k_c \) is the wave vector at the crossing point

\[
k_c = k_1(x_c) = k_2(x_c),
\]

(3.17)

and the parameters \( q_1 \) and \( q_2 \) are

\[
q_1 = \frac{dk_1}{dx} \bigg|_{x=x_c} = \frac{m}{\hbar^2 k_c} \frac{dV_1}{dx} \bigg|_{x=x_c},
\]

(3.18)

\[
q_2 = \frac{dk_2}{dx} \bigg|_{x=x_c} = \frac{m}{\hbar^2 k_c} \frac{dV_2}{dx} \bigg|_{x=x_c},
\]

(3.19)

\[
q = q_1 - q_2.
\]

(3.20)

We look for \( \chi_D(x) \) and \( \chi_A(x) \) in the form

\[
\chi_D(x) = \tilde{\chi}_D(x) e^{-k_c x},
\]

(3.21)

\[
\chi_A(x) = \tilde{\chi}_A(x) e^{k_c x},
\]

(3.22)

where \( \tilde{\chi}_D(x) \) and \( \tilde{\chi}_A(x) \) are slowly changing two-component functions of \( x \). We will consider the donor wave function \( \chi_D(x) \) and the acceptor wave function \( \chi_A(x) \) separately. As \( \chi_D(x) \) is a slowly changing function of \( x \), one can neglect the second derivative of \( \tilde{\chi}_D(x) \) over \( x \) after the substitution of Eq. (3.21) into Eq. (3.13). As a result, the following system of equations for \( \chi_D(x) \) is obtained:

\[
- \frac{d \chi^{(1)}}{dx} = q_1(x-x_c) \tilde{\chi}^{(1)}(x) + \gamma \tilde{\chi}^{(2)}(x),
\]

(3.23)

\[
- \frac{d \chi^{(2)}}{dx} = q_2(x-x_c) \tilde{\chi}^{(2)}(x) + \gamma \tilde{\chi}^{(1)}(x),
\]

where the coupling parameter \( \gamma \) is

\[
\gamma = \frac{m V_{12}}{\hbar^2 k_c}.
\]

(3.24)

Similarly, for \( \chi_A(x) \) one obtains

\[
\frac{d \chi^{(1)}}{dx} = q_1(x-x_c) \tilde{\chi}^{(1)}(x) + \gamma \tilde{\chi}^{(2)}(x),
\]

(3.25)

\[
\frac{d \chi^{(2)}}{dx} = q_2(x-x_c) \tilde{\chi}^{(2)}(x) + \gamma \tilde{\chi}^{(1)}(x).
\]

The solution of Eq. (3.23) is given in Appendix C [the solution of Eq. (3.25) is similar]. It is also shown there that the adiabatic factor \( \kappa \), which reflects the deviation of the wave function \( \chi_D(x) \) from its adiabatic approximation, is given by

\[
\kappa = \sqrt{2 \pi p} e^{p \ln p - p} \frac{1}{\Gamma(p+1)},
\]

(3.26)

where \( \Gamma(x) \) is the gamma-function. The adiabatic parameter \( p \) is given by
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\[ p = \frac{\gamma^2}{q} = \frac{m V_{12}^2}{\hbar^2 k_c} \left[ d(V_1 - V_2) \right]_{x=x_c}^{-1}. \]  

(3.27)

The wave functions \( \chi_D(x) \) and \( \chi_A(x) \) in the AB and DB regions, correspondingly, are given by [cf. Eqs. (3.11) and (3.12)]

\[ \chi_D(x) = \kappa C_{n_D} \phi_{-}(x) \frac{\sqrt{m \omega_D / \hbar}}{\sqrt{k_{-}(x)}} \exp \left[ - \int_{x_D}^{x} k_{-}(x') dx' \right], \]

(3.28)

\[ x_c + \delta_c < x < x_A - \delta_A, \]

\[ \chi_A(x) = \kappa C_{n_A} \phi_{-}(x) \frac{\sqrt{m \omega_A / \hbar}}{\sqrt{k_{-}(x)}} \exp \left[ - \int_{x}^{x_A} k_{-}(x') dx' \right], \]

(3.29)

\[ x_D + \delta_D < x < x_c - \delta_c. \]

To calculate the tunneling current, Eq. (2.8) can be used at some point in the AB region. Equations (3.28) and (3.12) should then be used for the donor and acceptor diabatic wave functions \( \chi_D(x) \) and \( \chi_A(x) \), respectively. Using Eq. (2.7) the following expression for the tunneling matrix element \( T_{DA} \) is readily obtained:

\[ T_{DA} = \hbar \kappa C_{n_D} C_{n_A} \sqrt{\omega_D \omega_A} \exp \left[ - \int_{x_D}^{x_A} k_{-}(x') dx' \right], \]

(3.30)

where the adiabatic factor \( \kappa \) is given by Eq. (3.26) and the numerical coefficients \( C_{n_D} \) and \( C_{n_A} \), which depend on the excitation levels \( n_D \) and \( n_A \) of the proton in the donor and acceptor states, are given by Eq. (B10).

We finally notice that if \( \kappa = 1 \) the above formula coincides with the quasiclassical expression for tunneling matrix element \( T_{DA}^{(ad)} \) in an adiabatic potential. Therefore, Eq. (3.30) can be rewritten as

\[ T_{DA} = \kappa T_{DA}^{(ad)}. \]

(3.31)

Equation (3.30) is the main result of this paper. It gives the expression for the tunneling matrix element \( T_{DA} \) in the whole range of variation of the electronic coupling \( V_{12} \). To calculate the rate of the coupled electron–proton transfer reaction, one should calculate \( T_{DA} \) for each possible pair of the initial and final vibrational states of the proton, \( n_D \) and \( n_A \), substitute it into Eq. (1.3), and thermally average the obtained partial rates over the initial \( n_D \) and sum up over the final states \( n_A \) of the proton. In the next section, we will discuss different asymptotic regimes of the proton tunneling, which correspond to the small and large electron coupling.

**IV. DISCUSSION**

**A. Limiting cases**

First of all, we would like to show that in both adiabatic and nonadiabatic limits Eq. (3.30) is reduced to the known expressions for the adiabatic and nonadiabatic tunneling, respectively. At large values of the electronic coupling \( V_{12} \) the adiabatic parameter \( p \) is large, \( p \gg 1 \). The adiabatic factor \( \kappa \), which comes into Eq. (3.30) is given by Eq. (3.26). In Fig. 2, \( \kappa \) is shown as a function of the adiabatic parameter \( p \), Eq. (3.27). The asymptotic behavior of the adiabatic factor \( \kappa \) is as follows:

\[ \kappa = \begin{cases} 1, & p \gg 1 \\ \sqrt{2 \pi p}, & p \ll 1 \end{cases} \]

(4.1)

and so Eq. (3.31) is reduced to the adiabatic expression for \( T_{DA} \) in the strong electronic coupling limit. Thus, as it is expected, at strong electronic coupling, the proton tunneling occurs adiabatically and the Born–Oppenheimer approximation is recovered in the whole range of variation of \( x \).

Next, we will show that in the case of the weak electron coupling, \( p \ll 1 \), Eq. (3.30) is reduced to Eq. (1.4). To this end one can rewrite Eq. (1.4) as

\[ T_{DA}^{(na)} = V_{12} \int dx \chi_D^{(1)}(x) \chi_A^{(2)}(x), \]

(4.2)
where $\chi^{(1)}_D(x)$ and $\chi^{(2)}_A(x)$ refer to the case of zero electronic coupling, $V_{12}=0$. Under the barrier, they are given by [cf. Eqs. (3.11) and (3.12)]

$$
\chi^{(1)}_D(x) = C_D \sqrt{\frac{m \omega_{D}}{\hbar}} \frac{1}{\sqrt{k_1(x)}} \exp \left[ -\int_{x_p}^{x} k_1(x') dx' \right],
$$

$$
\chi^{(2)}_A(x) = C_A \sqrt{\frac{m \omega_{A}}{\hbar}} \frac{1}{\sqrt{k_2(x)}} \exp \left[ -\int_{x_c}^{x} k_2(x') dx' \right].
$$

One notes that the main contribution to the integral in Eq. (4.2) comes from the vicinity of the crossing point $x_c$. One can use the saddle point method to estimate this integral thereby obtaining

$$
T_D^{(na)} \approx C_D C_A \sqrt{\frac{m V_{12}}{\hbar k_c}} \frac{\sqrt{2 \pi / q}}{\sqrt{2 \pi / q}} \exp \left[ -\int_{x_c}^{x} k_1(x) dx - \int_{x_c}^{x} k_2(x) dx \right],
$$

where $k_c$ and $q$ are given by Eqs. (3.17) and (3.20), respectively.

On the other hand, one can utilize the asymptotic behavior of the adiabatic factor $\kappa$ at small values of $p \ll 1$, and the definition of the adiabatic parameter $p$, Eq. (3.27) to obtain

$$
\kappa = \frac{m V_{12}}{\hbar^2 k_c} \sqrt{2 \pi / q}, \quad p \ll 1.
$$

Substituting Eq. (4.6) into Eq. (3.30) and comparing the result with Eq. (4.5) one can see that they coincide if one also takes into account the fact that in the weak electronic coupling limit, $V_{12} \rightarrow 0$,

$$
k_-(x) = \begin{cases} 
  k_1(x), & x < x_c \\
  k_2(x), & x > x_c 
\end{cases}.
$$

Thus, the tunneling matrix element $T_{DA}$ is recovered.

The solution of Eq. (3.23) in the crossing region given in Appendix C shows that even in the weak electronic coupling case, when one can talk about “nonadiabatic” proton tunneling, the right asymptotic behavior of the wave function sufficiently far from the crossing point is described by an adiabatic approximation, and not by a nonadiabatic one. For example, the correct asymptotic behavior of $\chi(x)$ for large negative $x$ is given by Eq. (C18), while the nonadiabatic approximation would simply give a constant, $\chi(x) = (1.0)$. Therefore, even in a relatively weak coupling regime one may have to use the adiabatic $k$-vector $k_-(x)$ instead of the nonadiabatic $k_1(x)$ and $k_2(x)$ to calculate the tunneling matrix element $T_{DA}$ [cf. Eq. (4.5)].

In Fig. 2 numerical values of the adiabatic factor $\kappa$ are shown. It is seen that the crossover between two adiabatic and nonadiabatic regimes occurs in a relatively narrow region of the parameter $p$. For values $p$ roughly less than $\frac{1}{2} \pi$ the factor $\kappa$ is equal to its nonadiabatic limit $\sqrt{2 \pi p}$, while for $p > 1$ it is very accurately approximated by unity, and for values of $p$ in between $\frac{1}{2} \pi$ and 1, the factor $\kappa$ is different from unity by less than 50%.

### B. Analogy with the Landau–Zener problem

The problem of the proton tunneling which is complicated by a simultaneous electronic transition is somewhat analogous to the Landau–Zener problem of a nonadiabatic transition between two electronic surfaces. There is, however, a considerable difference: Equations (3.23) and (3.25), which describe the nonadiabatic coupling between two electronic states in the process of the proton tunneling, while formally analogous to the corresponding equations in the Landau–Zener problem [cf. Eqs. (2) and (3) in Ref. 23], do not contain the imaginary unity. One can loosely say that the nonadiabatic transition occurs in “imaginary time.” Mathematically, this fact implies that the imaginary phase of a quantum state in the Landau–Zener problem, which does not change the transition probability and can, therefore, be disregarded, becomes real in our case and modifies the final result for the “transition amplitude,” Eq. (3.26). One must also keep in mind that while in the case of the real nonadiabatic transition both states do exist after passing the level crossing point, in the case of the proton tunneling only the exponent with the largest power is defined as there is no way to extract an exponentially small term on the background of an exponentially large one.

It is worth noting that these subtle mathematical differences between the usual Landau–Zener transition occurring above the barrier and that for the tunneling process, result in qualitatively similar, and yet different, expressions for the probability of transition between two electronic states. Our factor $\kappa$ is to be compared with the amplitude (instead of probability) of the usual Landau–Zener transition

$$
\kappa_{LZ} = \sqrt{1 - \exp(-2 \pi p_{LZ})}.
$$

In both cases for the nonadiabatic regime the amplitude is $\sqrt{2 \pi p}$ and for large $p$ the amplitude is unity. However, for the tunneling system, the approach to the adiabatic regime is much slower. It occurs as $1/p$ with increasing $p$ instead of an exponential law in the usual Landau–Zener transition.

The expression for the adiabatic parameter, Eq. (3.27), can be rewritten in such a way so the similarity to the Landau–Zener theory becomes obvious

$$
p = \frac{V_{12}}{h \Delta F V_1}.
$$

where $\Delta F = dV_1/dx - dV_2/dx$ is the difference of the forces acting on the proton in the two electronic states at the crossing point, and $v_t$ is the “tunneling velocity” of the proton moving in the inverted potential, either $-V_1(x)$ or $-V_2(x)$, at the crossing point with the “energy” $-E$

$$
v_t = h k_c / m = \sqrt{(2V_c - E) / m}, \quad V_c = V_1(x_c) = V_2(x_c).
$$

Equation (4.9) allows one to estimate the adiabaticity parameter $p$ in a realistic situation (see below).
C. Physical meaning of the adiabaticity parameter

As in the standard real-time avoided crossing situation, the adiabaticity parameter \( p \) given by Eq. (4.9) is determined by how quickly the proton moves through the region where electronic states are sufficiently close to each other and where the electronic transition can occur. The width of such a region is

\[
\delta x \sim \frac{V_{12}}{\Delta F}. \tag{4.11}
\]

Hence, the "tunneling time" through this region is

\[
\tau_{\text{tun}} \sim \frac{V_{12}}{\Delta F |v_t|}. \tag{4.12}
\]

On the other hand, the time required to change the electronic state is

\[
\tau_{\text{el}} \sim \frac{\hbar}{V_{12}}. \tag{4.13}
\]

Now, the ratio of the electron transition time and the time of tunneling through the region of level crossing is just our adiabaticity parameter

\[
p = \frac{\tau_{\text{tun}}}{\tau_{\text{el}}}. \tag{4.14}
\]

Thus, one can say that the small values of \( p \) correspond to a small fraction of time spent by the tunneling proton in the region of level crossing. Indeed, in this case perturbation theory should be applicable and the nonadiabatic result Eq. (1.4) makes complete sense. On the other hand, if \( p \) is large, the electronic subsystem has enough time to completely mix two states and to form an adiabatic surface on which the proton moves. This picture is a direct analogy with the usual Landau–Zener transition, when level crossing occurs at energies above the barrier, except that now the motion of the heavy particle, the proton, is quantum tunneling.

In the past, there has been an extensive discussion of the nature of tunneling, the tunneling time, and the tunneling velocity of the tunneling particle. In the present problem, the concepts of the tunneling velocity and tunneling time appear naturally, as a means to describe the relative importance of the processes occurring in the barrier region during the tunneling event. Our results support the proposal of Landauer and Buttiker according to which the tunneling time is defined in a usual way by the tunneling velocity, which is given by Eq. (4.10). This latter expression also appears naturally in Bohm’s interpretation of quantum mechanics. It is also worth mentioning that the description of long distance electron tunneling in proteins with tunneling currents, the stream lines of which represent the manifold of all possible Bohmian trajectories, is based on a similar view of the tunneling process as that of Bohm, Landauer, and Buttiker.

D. Some estimates and applicability condition

To estimate the parameters which come into Eq. (4.9) in a realistic situation one notes that the total potential, either \( V_1(x) \) or \( V_2(x) \), in which the proton moves consists of two parts. The main contribution to the potential comes from the local electrons which participate in the formation of the valence and/or hydrogen bonds of the proton with the heavy atoms involved in the proton exchange. This part of the potential denoted as \( V_b(x) \) does not depend on the electron transfer state and so does not contribute to the difference of \( V_2(x) \) and \( V_1(x) \). The potential \( V_b(x) \) is responsible for the vibrational frequencies \( \omega_p \) and \( \omega_a \) in the donor and acceptor wells and for the tunneling velocity \( v_t \), Eq. (4.10). The electronic redistribution which is associated with making the second part of the proton potential, which is somewhat smaller than the first part and depends on the electron transfer state, is due to the electrostatic interaction with the tunneling electron. Typically the tunneling distance for the electron (~10 Å) is by order of value larger than the one for the proton (~1 Å) and the proton tunneling occurs in a spatial region separated from the regions of localization of the electron both in the initial and final electronic states. As a result, in a good approximation the electric field created by the electron, either in the initial or in final states, is a constant in the whole range of variation of the proton coordinate. The difference of the forces \( \Delta F \) can then be estimated as

\[
\Delta F = e(\mathcal{E}_1 - \mathcal{E}_2), \tag{4.15}
\]

where \( e \) is the (positive) elementary charge and \( \mathcal{E}_1 \) and \( \mathcal{E}_2 \) are the electric fields created by the tunneling electron in the proton tunneling region in the initial and final electronic states, respectively.

Using the cosine potential as a model potential for the proton bonding

\[
V_b(x) = \frac{m \omega_0^2 J_p^2}{4 \pi^2} \cos(2\pi x / l_p), \tag{4.16}
\]

where \( \omega_0 \) is the vibrational frequency of the proton in the donor and acceptor wells and \( l_p \) is the distance of the proton tunneling, the following estimate for the tunneling velocity is easily obtained:

\[
v_t \sim \pi^{-1} \omega_0 l_p. \tag{4.17}
\]

Assuming that the electron transfer occurs along the same line as the proton transfer and that the regions of localization of the electron in the initial and final electronic states are equidistant from the proton transfer region, \( \Delta F \) can be approximated as

\[
\Delta F = \frac{1}{2 \epsilon_{el} l_p^2}, \tag{4.18}
\]

where \( \epsilon_{el} \) is the electronic dielectric constant of the medium and \( l_p \) is the electron transfer distance. Substituting Eqs. (4.17) and (4.18) into Eq. (4.9), the following estimate for the adiabaticity parameter \( p \) is readily obtained:

\[
p \sim 2 \pi \epsilon_{el} \frac{V_{12}^2 l_p^2}{\hbar e^2 l_p \omega_0}, \tag{4.19}
\]

or in the atomic units

\[
p \sim 2 \pi \epsilon_{el} \frac{V_{12}^2 l_p^2}{l_p \omega_0}. \tag{4.20}
\]
The transition region $C$ in which the electronic transition actually occurs in the process of proton tunneling should be small in comparison to the whole transition region. This restriction constitutes the main applicability condition of Eq. (3.30). The size of the transition region is given by Eq. (C22). The expression for the parameter $q$, Eq. (3.20), which comes into Eq. (C22), can be rewritten in terms of the tunneling velocity $v_t$ and $\Delta F$ as

$$q = \frac{\Delta F}{h v_t}.$$  \hfill (4.21)

Using the estimates for the tunneling velocity, Eq. (4.17), and for $\Delta F$, Eq. (4.18), the applicability condition of Eq. (3.30) can be written as

$$\frac{e^2 p}{\hbar \omega_0 l_c^2} > 1,$$  \hfill (4.22)

or in the atomic units

$$\frac{l_p}{\omega_0 l_c^2} > 1,$$  \hfill (4.23)

where the factor $\pi/(2 \epsilon_d)$ has been disregarded.

The applicability condition of the quasiclassical approximation can be written as

$$\int_{x_D}^{x_A} k(x) dx \gg 1, \quad k(x) = \sqrt{2m[V(x) - E]/\hbar}.$$  \hfill (4.24)

Using the potential given by Eq. (4.16), Eq. (4.24) can be rewritten as

$$\frac{2}{\pi^2} \frac{m \omega_0 l_c^2}{\hbar} \gg 1.$$  \hfill (4.25)

Taking $\omega_0 \sim 10^{-2}$ a.u. as a typical value for the proton frequency and $l_p \sim 2$ a.u., one can estimate the left hand side of Eq. (4.25) as 15 and see that Eq. (4.25) is indeed satisfied.

E. Multidimensional generalization

The expression for the adiabaticity parameter given by Eq. (4.9), allows for an obvious generalization on the multidimensional case when several quantum nuclear modes are involved and the tunneling trajectory is multidimensional. In this situation both the potential gradients $\nabla V(x)$ and the tunneling velocity $v_t$ in Eq. (4.9) must be considered as vectors of an appropriate dimensionality. The tunneling velocity $v_t$ should be calculated along the tunneling trajectory at the crossing point as well as $\nabla V(x)$. One can expect that the tunneling matrix element $T_{DA}$ in the multidimensional case will be related to the one calculated in an adiabatic approximation $T_{DA}^{ad}$ by Eq. (3.31), as in the one-dimensional case.

ACKNOWLEDGMENTS

We would like to acknowledge stimulating discussions with Sharon Hammes-Schiffer, and Bob Cukier during their visits to UC Davis. We also thank Professor Bill Miller for helpful comments and for pointing out several important references. This work was supported by the National Institutes of Health (GM54052-02), and by the Sloan and Beckman Foundations.

APPENDIX A: THE EXPRESSION OF $T_{DA}$ IN TERMS OF THE TUNNELING CURRENT

In this appendix Eqs. (2.7) and (2.8) which express the tunneling matrix element $T_{DA}$ in terms of the tunneling current (2.7) $J_{DA}$ between the donor $|\psi_D\rangle$ and acceptor $|\psi_A\rangle$ states is derived. To this end the quantum dynamics of the effective two-level system consisting of the two states $|\psi_D\rangle$ and $|\psi_A\rangle$, which are assumed to be in resonance, is considered. This type of dynamics is described by the nonstationary Schrödinger equation with the Hamiltonian given by Eq. (2.6).

The system which is initially prepared in the donor state $|\psi_D\rangle$ will oscillate with the frequency $T_{DA}/\hbar$ between the donor $|\psi_D\rangle$ and acceptor $|\psi_A\rangle$ states. Using our two-component notation for the wave function it can be written as

$$\chi(x,t) = \cos \theta \chi_D(x) - i \sin \theta \chi_A(x), \quad \theta = T_{DA}/\hbar.$$  \hfill (A1)

One notes that the equation of continuity holds for our system

$$\frac{\partial \rho(x,t)}{\partial t} + \frac{\partial J(x,t)}{\partial x} = 0,$$  \hfill (A2)

which can be confirmed by the direct calculation. The probability density $\rho(x,t)$ is given by

$$\rho(x,t) = \langle \psi(t) | \hat{\rho}(x) | \psi(t) \rangle = |\chi^{(1)}(x,t)|^2 + |\chi^{(2)}(x,t)|^2,$$  \hfill (A3)

and the probability current density $J(x,t)$ is the average of the probability flux operator given by Eq. (2.9)

$$J(x,t) = \langle \psi(t) | \hat{J}(x) | \psi(t) \rangle.$$  \hfill (A4)

Substituting Eq. (A1) into Eq. (A3) one will find

$$\rho(x,t) = \rho_D(x) \cos^2 \theta + \rho_A(x) \sin^2 \theta,$$  \hfill (A5)

$$\rho_D(x) = \langle \psi_D | \hat{\rho}(x) | \psi_D \rangle,$$  \hfill (A6)

$$\rho_A(x) = \langle \psi_A | \hat{\rho}(x) | \psi_A \rangle.$$  \hfill (A7)

Similarly, substituting Eq. (A1) into Eq. (A4) one will find

$$J(x,t) = -J_{DA}(x) \sin 2 \theta,$$  \hfill (A8)

where $J_{DA}(x)$ is given by Eq. (2.8). Substituting Eqs. (A5) and (A8) into Eq. (A2) one arrives at the following equation which couples the tunneling current with the probability distributions in the donor and acceptor states:

$$\frac{T_{DA}}{\hbar} \left[ \rho_A(x) - \rho_D(x) \right] = \frac{dJ_{DA}}{dx}.$$  \hfill (A9)

Integrating this equation from $-\infty$ to some point between the donor and acceptor wells and taking into account the fact that the donor and acceptor wave functions, $\chi_D(x)$ and $\chi_A(x)$, are localized near the donor and acceptor wells, respectively, one obtains Eq. (2.7).
APPENDIX B: ASYMPTOTE OF THE PROTON WAVE FUNCTION UNDER THE BARRIER

In this appendix the asymptote of the wave function of the proton in the \( n \)th excited state will be found under the barrier and before the crossing point. As the proton coordinate is far from the crossing point \( x_c \) one can use the Born–Oppenheimer approximation and consider the proton wave function to be one-component. The potential \( V(x) \) in which the proton moves is schematically shown in Fig. 3. The well minimum is assumed to be at \( x=0 \).

At small \( x \) one can approximate the potential as a harmonic one:

\[
V(x) = \frac{m\omega_0^2}{2} x^2. \tag{B1}
\]

In the \( n \)th excitation state the wave function in this region is given by

\[
\chi_n(x) = \pi^{-1/4} a^{-1/2} \frac{1}{\sqrt{2^n n!}} e^{-x^2/2a^2} H_n(x/a), \tag{B2}
\]

where \( H_n(\xi) \) is the Hermite polynomial, and the parameter \( a \) is given by

\[
a^2 = \frac{\hbar}{m \omega_0}. \tag{B3}
\]

The position \( x=a \) is a turning point in the ground state, \( V(a) = \hbar \omega_0 a/2 \).

At sufficiently large values of \( x \) the quasiclassical approximation is applicable and the wave function \( \chi_n(x) \) can be written as

\[
\chi_n(x) = \frac{C_n}{\sqrt{k(x)}} \exp \left[ -\int_{x_n}^{x} k(x') dx' \right], \tag{B4}
\]

\[
k(x) = \sqrt{2m[ V(x) - E_n]} / \hbar, \tag{B5}
\]

where \( E_n = (n+1/2) \hbar \omega_0 \) is the energy of the proton in the \( n \)th excited state and \( x_n = \sqrt{2n+1}a \) is a turning point. In the region where both Eqs. (B1) and (B4) are valid, \( k(x) \) can be written as

\[
k(x) = \sqrt{x^2-(2n+1)a^2}/a^2. \tag{B6}
\]

It is easy to show that in this region

\[
\int_{x_n}^{x} k(x') dx' = (2n+1) \int_{1}^{x/\sqrt{2n+1}a} \sqrt{y^2-1} dy
\]

\[
\approx \frac{x^2}{2a^2} - \frac{2n+1}{2} \ln \frac{x}{a} + \frac{2n+1}{4}
\]

\[
\times [\ln(2n+1) - 2 \ln 2 - 1], \tag{B7}
\]

where the following identity has been used:

\[
\int_{1}^{y} \sqrt{y^2-1} dy = \frac{1}{4}[y \sqrt{y^2-1} - \ln(y + \sqrt{y^2-1})] \bigg|_{1}^{y}
\]

\[
= \frac{1}{4}(y^2 - \ln y) - \frac{1}{4}(2 \ln 2 + 1), \quad y \gg 1. \tag{B8}
\]

Only the terms which are not small in comparison with unity have been retained in Eq. (B7) while the terms which are small in comparison with unity have been neglected. Substituting Eq. (B7) into Eq. (B4) and approximating \( k(x) \approx x/a^2 \) one obtains for this region

\[
\chi_n(x) = C_n a^{-1/2} (x/a)^n e^{-x^2/2a^2} e^{-(2n+1)/4[\ln(2n+1) - 2 \ln 2 - 1]}, \tag{B9}
\]

Comparing Eqs. (B2) and (B9) and taking into account that at large \( \xi \), \( H_n(\xi) \approx 2^n \xi^n \), one finds that the coefficient \( C_n \) is equal to

\[
C_n = \pi^{-1/4} \sqrt{\frac{2^n n!}{\Gamma(2n+1)}} e^{(2n+1)/4[\ln(2n+1) - 2 \ln 2 - 1]}. \tag{B10}
\]

APPENDIX C: SOLUTION OF EQ. (3.23) IN THE CROSSING POINT REGION

In this section the solution of Eq. (3.23) will be found in the vicinity of the crossing point \( x = x_c \) which describes the donor state localized in the left well. For simplicity of notation we will assume that \( x_c = 0 \). It will be shown that for large values of \( x \), both negative and positive, the solution is asymptotically equal to an adiabatic one and the adiabatic factor, \( \kappa \), will be found which couples the adiabatic asymptote of \( \chi_D(x) \) on the left of the crossing point to the one on the right.

Using the standard substitution

\[
\tilde{\chi}^{(1)}_D(x) = e^{-q x^2/2} \chi^{(1)}_D(x),
\]

\[
\tilde{\chi}^{(2)}_D(x) = e^{-q x^2/2} \chi^{(2)}_D(x), \tag{C1}
\]

Eq. (3.23) is reduced to the following form:

\[
-\frac{d}{dx} \chi^{(1)}(x) = \gamma \chi^{(2)}(x), \tag{C2}
\]

where \( \gamma = \kappa \).
Substituting Eq. (C2) into Eq. (C3) one comes to the following second-order differential equation in $\chi^{(1)}(x)$:
\[
\frac{d^2}{dx^2} \chi^{(1)}(x) - q x \frac{d}{dx} \chi^{(1)}(x) - \gamma^2 \chi^{(1)}(x) = 0.
\] (C4)

To solve Eq. (C4), the Laplace transform method can be used. The solution of Eq. (C4) is sought in the form:
\[
\chi^{(1)}(x) = A_0 \int_C e^{-ax} v(u) du.
\] (C5)

where the constant $A_0$ will be defined later [see below Eq. (C15)]. The contour of integration $C$ in the imaginary plane of $u$ will be chosen in such a way, so that the function $e^{-u} v(u)$ and its derivatives disappear at its boundaries at all values of $x$ (see also below). Substituting Eq. (C5) into Eq. (C4) and allowing it to be satisfied at any value of $x$, the following equation for $v(u)$ is obtained
\[
u u \frac{dv}{du} + (u^2 - \gamma^2 + q)v(u) = 0.
\] (C6)

The solution of this equation is
\[
v(u) = \exp[-u^2/2q + (p+1)\ln u],
\] (C7)

where $p$ is given by Eq. (3.27). Thus, the solution of Eq. (C4) can be written as
\[
\chi^{(1)}(x) = A_0 \int_C e^{\Phi(u)} du,
\] (C8)

\[
\Phi(u) = -u^2/2q + (p-1)\ln u - u x.
\] (C9)

To choose the contour of integration one notes that at asymptotically large values of $x$, both negative and positive, the largest contribution to the integral in Eq. (C8) occurs in the vicinities of the points which are defined by $d\Phi/du=0$. There are two saddle points for $\Phi(u)$, which can be approximated at large values of $x$ as
\[
u 1 \approx \frac{p-1}{x},
\] (C10)

\[
u 2 \approx -q x + \frac{p-1}{x}.
\] (C11)

The first saddle point $u_1$ corresponds to the solution which describes the proton tunneling along the first electronic energy surface $V_1(x)$ and the second saddle point $u_2$ corresponds to the solution which describes the proton tunneling along the second electronic energy surface $V_2(x)$. At large negative $x$ the proton should be in the first electronic state. Therefore, the contour of integration should be chosen in such a way that the contribution from the second saddle point $u_2$ disappears at large negative values of $x$. Such a contour is schematically shown in Fig. 4.

Next, we focus on the asymptotic behavior of $\chi(x)$ which satisfies Eqs. (C2) and (C3). First the $x \to -\infty$ limit will be considered. As stated earlier, in this limit the main contribution to the integral in Eq. (C8) comes from the vicinity of the first saddle point $u_1$, Eq. (C10). In this region, one can neglect the term $-u^2/2q$ in the power of exponent, Eq. (C9). As a result, the following expression for $\chi^{(1)}(x)$ is obtained:
\[
\chi^{(1)}(x) = A_0 \int_C u^{p-1} e^{-ax} du,
\] (C12)

which is reduced to the following expression by the substitution $y = ux$:
\[
\chi^{(1)}(x) = -|x|^{-p} A_0 \int_{C_1} (-y)^{p-1} e^{-y} dy,
\] (C13)

where the contour of integration $C_1$ is shown on Fig. 5. Representing $-1$ as either $e^{-i\pi}$ or $e^{i\pi}$, depending on the way the branching point $u=0$ is circumvented, one finds that,
\[
\chi^{(1)}(x) = A_0 2i \sin(\pi p) \Gamma(p)|x|^{-p} = -|xy|^{-p} e^{p \ln p - p/2},
\] (C14)

were the constant $A_0$
\[
A_0 = \frac{i}{2 \sin(\pi p) \Gamma(p)} y^{-p} e^{p \ln p - p/2},
\] (C15)

has been defined in such a way so that the asymptote given by Eq. (C14) will coincide with the adiabatic approximation, Eq. (C34) below.

FIG. 4. The integration contour $C$ in the imaginary plane of $u$. The stationary points $u_1$ and $u_2$ for large positive $x$ are shown as small crosses.

FIG. 5. The integration contour in the imaginary plane of $y$. 
To obtain the asymptote for $\chi^{(2)}(x)$ one can use Eq. (C2), which can be rewritten as

$$\chi^{(2)}(x) = -\gamma^{-1} \frac{d}{dx} \chi^{(1)}(x).$$  \hspace{1cm} (C16)

Substituting Eq. (C14) into Eq. (C16) one finds that

$$\chi^{(2)}(x) \approx \frac{\gamma}{q^2} \chi^{(1)}(x).$$  \hspace{1cm} (C17)

Equations (C14) and (C17) can be rewritten in a matrix form:

$$\chi(x) \approx e^{p \ln p - p^2 (1/2)} \chi^{(1)}(x)$$

for large negative $x$ the electronic state of the system is close to $(1,0)$ as it should be in the low adiabatic state [cf. Eq. (3.6) and the discussion thereafter].

Next the $x \to +\infty$ limit is considered. In this limit the main contribution to the integral in Eq. (C8) comes from the second saddle point, C11. There are actually two contributions to the integral from this point, which come from the integration over the low and upper branches of the contour C. Using the saddle point method of integration for each contribution the following result is obtained:

$$\chi^{(1)}(x) \approx A_0 2i \sin \left( \pi p \right) \sqrt{2 \pi q} \exp \left[ \frac{q x^2}{2} + (p - 1) \ln(xq) \right]$$

$$a_1 \gamma \chi^{(1)}(x).$$ \hspace{1cm} (C20)

Equations (C19) and (C20) can be rewritten in a matrix form

$$\chi(x) \approx \frac{\sqrt{2 \pi \gamma}}{\sqrt{\pi \Gamma(p)}} e^{-p^2 / 2} (\gamma x)^p e^{q x^2 / 2}. \hspace{1cm} (C19)$$

Substituting Eq. (C19) into Eq. (C16) and retaining the largest term, which comes from the differentiation of the $-q x^2 / 2$ term in the power of the exponent, the following asymptote for $\chi^{(2)}(x)$ is obtained:

$$\chi^{(2)}(x) \approx -\frac{q x}{\gamma} \chi^{(1)}(x).$$ \hspace{1cm} (C20)

At large positive $x$ the electronic wave function is approximately equal to $(0, 1)$, as it should be for the low adiabatic state to the right from the crossing point [cf. Eq. (3.6) and the discussion thereafter].

The distance at which the asymptotic solution given by Eq. (C19) is formed provides the width $\delta_x$ of the transition region C. Using the applicability condition of the saddle point method for the integral given by Eq. (C8) one can readily show that $\delta_x$ is given by

$$\delta_x \approx q^{-1/2}. \hspace{1cm} (C22)$$

Equations (C18) and (C21) provide the asymptotic behavior of the donor wave function $\chi(x)$ to the left and to the right of the crossing point. These asymptotes should be compared with the adiabatic approximation. To this end, it is convenient to rewrite Eqs. (C2) and (C3) in the matrix form

$$-\frac{d}{dx} \chi^{(2)}(x) = \begin{pmatrix} 0 & \gamma \\ \gamma & -q x \end{pmatrix} \chi^{(1)}(x).$$ \hspace{1cm} (C23)

The adiabatic approximation for Eq. (C23) can be written as [cf. Eq. (3.9)]

$$\chi_{ad}(x) = \phi_{\gamma}(x) e^{-\int_0^x k_{\gamma}(x') dx'},$$ \hspace{1cm} (C24)

where $k_{\gamma}(x)$ and $\phi_{\gamma}(x)$ are the lowest eigenvalue and the corresponding eigenvector of the matrix in the right-hand side of Eq. (C23)

$$\begin{pmatrix} 0 & \gamma \\ \gamma & -q x \end{pmatrix} \phi_{\gamma}(x) = \begin{pmatrix} \phi_{\gamma}^{(1)}(x) \\ \phi_{\gamma}^{(2)}(x) \end{pmatrix}.$$ \hspace{1cm} (C25)

They are equal to [cf. Eqs. (3.8) and (3.6)]

$$k_{\gamma}(x) = -\frac{1}{2}(q x + \sqrt{q^2 x^2 + 4 \gamma^2})$$ \hspace{1cm} (C26)

and

$$\phi_{\gamma}(x) = 2^{-1/2} \left[ \frac{q x + \sqrt{q^2 x^2 + 4 \gamma^2}}{2} \right]^{-1/4} \left( \frac{\sqrt{q^2 x^2 + 4 \gamma^2} - q x}{\sqrt{q^2 x^2 + 4 \gamma^2} + q x} \right).$$ \hspace{1cm} (C27)

At large $x$, $\phi_{\gamma}(x)$ can be approximated as

$$\phi_{\gamma}(x) \approx \begin{pmatrix} -1 \\ \gamma \\ \gamma \ln(xq) \end{pmatrix}, \hspace{1cm} (C28)$$

$$\phi_{\gamma}(x) \approx \begin{pmatrix} -\gamma \\ q x \\ 1 \end{pmatrix}, \hspace{1cm} x \gg \gamma / q. \hspace{1cm} (C29)$$

The power of the exponent in Eq. (C24)

$$-\int_0^x k_{\gamma}(x') dx' = q x^2 / 4 + \frac{1}{2} \int_0^x \sqrt{q^2 x^2 + 4 \gamma^2} \, dx'$$

$$= q x^2 / 4 + 2p \int_0^{x/2} \sqrt{y^2 + 1} \, dy, \hspace{1cm} (C30)$$

can be approximated at large $x$ as

$$-\int_0^x k_{\gamma}(x') dx' \approx -p \ln|\gamma x| + p \ln|p - p / 2|, \hspace{1cm} (C31)$$

$$-\int_0^x k_{\gamma}(x') dx' \approx q x^2 / 4 + p \ln|\gamma x| - p \ln|p + p / 2|,$$ \hspace{1cm} (C32)

where the following identity has been used:
\[
\int_0^y \sqrt{y'^2 + 1} \, dy' = \frac{1}{2} \left[ \sqrt{y'^2 + 1} + \ln(y' + \sqrt{y'^2 + 1}) \right]_0^y \\
\approx \frac{1}{2} (y^2 + \ln y) + \frac{1}{2} (2 \ln 2 + 1), \quad y \gg 1.
\]

(C33)

Using Eqs. (C28), (C29), (C31), and (C32), Eq. (C24) can be written for large \( x \) as

\[
\chi_{ad}(x) \approx e^{-p \ln p - p^2/2} \left| \frac{1}{y^2} \right|^{p/2} \left( \frac{-1}{q^2 x^2} \right), \quad x \to -\infty, \quad (C34)
\]

\[
\chi_{ad}(x) \approx e^{-p \ln p + p^2/2} \left( \frac{y}{x} \right)^p e^{q^2 x^2/2} \left( \frac{-1}{q^2 x^2} \right), \quad x \to +\infty.
\]

(C35)

One can see that the adiabatic approximation, Eq. (C34), coincides with the asymptote of the wave function, Eq. (C18), to the left of the crossing point. Comparing the adiabatic approximation, Eq. (C35), with the asymptote of the wave function given by Eq. (C21) to the right of the crossing point one finds that they differ by the factor \( \kappa \) which is given by Eq. (3.26).

4. A. M. Kuznetsov, Charge Transfer in Physics, Chemistry and Biology (Gordon and Breach, Amsterdam, 1995).
25. If several vibrational states are participating in the reaction, the corresponding averaging over the initial and final states is necessary and the resulting equation for the rate is slightly more complicated than Eq. (1.3), see, e.g., Refs. 32,33,35.
29. It is worth noticing that although in both adiabatic and nonadiabatic regimes the reaction is due to quantum mechanical tunneling of the proton, it is only in the latter case a significant isotope effect should be expected.