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Outer-sphere electron transfer in polar solvents: Quantum scaling of strongly interacting systems

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The spin–boson Hamiltonian model is used to study electron transfer (ET) reactions of strongly interacting systems in polar solvents in the limit of fast dielectric relaxation of the solvent. The spectrum of polarization modes consists of low frequency modes which are treated classically, and high frequency modes which are treated quantum mechanically. A general explicit formula for the rate valid in all orders of perturbation theory in electronic coupling is derived. The rate formula is applicable in a wide range of parameters, including the inverted region of the reaction where the quantum tunneling corrections give the main contribution to the rate. It is found that the quantum degrees of freedom can be effectively eliminated from the model by renormalizing the electronic coupling matrix element. This renormalization results in the following scaling property of the electron transfer systems: a system containing both classical and quantum degrees of freedom is equivalent to a system of lower dimensionality, containing only classical degrees of freedom, with renormalized electronic coupling matrix element. An explicit formula for the renormalization is obtained.

I. INTRODUCTION

In the present paper outer-sphere electron transfer (ET) reactions in polar media in the limit of fast dielectric relaxation are discussed. In this limit the reaction rate is independent of the relaxation properties of the solvent and can be studied within the traditional statistical equilibrium formulation of the problem. 1,2 In recent years the opposite case of reactions controlled by the solvent dynamics has attracted the most attention. 3,4 In particular, a clear understanding of all possible limiting cases has been achieved. 5–7

The case of fast dielectric relaxation is commonly believed to be well understood 5,6—for weakly interacting systems a well developed nonadiabatic theory is applicable, and for strongly interacting systems a reaction taking place on an adiabatic potential surface is described by transition state theory. 1,2 The latter case, however, is much less studied than the former one. Moreover, neither the rate expression has actually been rigorously derived from the electron transfer Hamiltonian of a strongly interacting system, nor has a general rigorous theory unifying two extreme cases been ever formulated, although numerous attempts to do so have been undertaken from the early stages of the development of the electron transfer theory. 1,8 The unsatisfactory situation with the strongly interacting systems has renewed interest in such systems 9–12 recently. In particular, the role of the fast electronic component of the solvent polarization in the reaction rate has been extensively discussed although the picture is far from clear.

The spin–boson Hamiltonian model of ET provides an excellent tool for studying the strong coupling limit and discussing a unified approach to adiabatic and nonadiabatic regimes. 7,10,12,13 In particular, the free energy of strongly interacting electron transfer systems has been calculated 10,12 and the role of the electronic polarization has been studied within this model. In Refs. 10 and 12 an exponential part of the rate for symmetric ET systems is obtained and it is shown that the activation energy depends on the electronic coupling matrix element. This result has never been rigorously derived before, although it has been commonly accepted. As far as the electronic polarization is concerned the authors reached a conclusion that it does not affect the free energy of ET reaction.

In this paper we continue development of the spin–boson Hamiltonian model of ET. In comparison with Refs. 10 and 12 we discuss not only the exponential factor of the rate, the free energy, but also a pre-exponential factor. The spectrum of the system is assumed to contain low (classical) as well as high (quantum) frequencies, the latter ones describe the high frequency part of the solvent polarization, including the electronic part. We derive an explicit expression for the rate, Eq. (4.13), which is a sum of all perturbation orders in electronic coupling, and show how the general formula reduces to a traditional golden rule formula and to the transition state theory for electron transfer in two extremes of a small and a strong coupling. The general formula is applicable in a wide range of parameters, including the inverted region of the reaction, 1 where the quantum tunneling corrections give the main contribution to the rate.

To study the quantum corrections we develop a quantum-classical approximation for the correlation function of the solvent. Our quantum correlation function is exponential, and is essentially the next order approximation to the δ-function approximation proposed in Ref. 10. The latter approximation formally corresponds to infinitely large (∞) quantum frequencies of the solvent polarization. For this reason the δ-function approximation does not describe the quantum effects in the system. In a recent paper Gehlen and Chandler 12 have developed an approximate

a) Contribution No. 8799.
method to account for the effect of high (but finite) frequency polarization modes in the free energy of the reaction. According to their approximation the quantum corrections can be described as an additional quantum part of the activation energy of the reaction, which vanishes as frequency of the polarization becomes infinitely high. In the present paper we have developed a different approximation and found that the quantum modes modify the classical ET system in a different way. It turns out that all quantum tunneling effects can be incorporated into a renormalized (reduced) electronic coupling matrix element of the system, Eq. (4.10). This result reveals an interesting scaling property of the ET systems. We find that a system with both classical and quantum degrees of freedom is equivalent to a system of lower dimensionality, containing only classical degrees of freedom, with a renormalized electronic coupling matrix element.

The method of our calculation is based on a correlation function expression for the rate constant,\textsuperscript{14-17}

\[ k(r) = \frac{Z_R^k}{Z_R} = \text{Im} \langle \tilde{\mathcal{N}}(\tau) \tilde{\mathcal{N}}(0) \rangle, \] \tag{1.1a} \]

\[ k = \lim_{\tau \to r} k(\tau + it), \] \tag{1.1b} \]

where \( \tilde{\mathcal{N}}(\tau) \) is the occupation operator of the reactant state in Matsubara representation. The dot above \( \tilde{\mathcal{N}}(\tau) \) is a derivative with respect to \( \tau \), \( \tau_p \) is the plateau time, \( Z^0 \) is the partition function of the whole system (reactants plus products), and \( Z_R^k \) is the partition function of the reactants. Using the path integral representation of the correlation function and introducing a quantum centroid reaction coordinate of the system,\textsuperscript{18-20} the rate can be expressed as (\( k_B = 1 \))\textsuperscript{20}

\[ k = A \frac{2 \text{Im} \int Z(R) dR}{Z_R^1} = A \frac{2 \text{Im} Z}{Z_R^1}, \] \tag{1.2} \]

where

\[ A = \begin{cases} T_r, & \text{if } T < T_c = \omega_b/2\pi \\ T_c, & \text{if } T > T_c \end{cases} \] \tag{1.3} \]

and \( Z(R) \) is the partition function of the system with a fixed centroid \( R \). In Ref. 20 a simplified \textit{ad hoc} derivation of Eq. (1.2) is discussed. In the temperature dependence of the prefactor \( A \) there is a crossover between two different regimes\textsuperscript{7,18,20,21} at \( T_c = \omega_b/2\pi \), where \( \omega_b \) is the activation barrier frequency. Below \( T_c \) the reaction takes place primarily from the metastable quantum states lying below the activation barrier, i.e., due to tunneling, while for temperatures above \( T_c \) the states lying above the activation barrier mainly contribute to the reaction, which is a classical activation process.

An imaginary part of the partition function of the reaction appears in an analytical continuation of the partition function into a complex plane \( R \). The final formula for the rate constant has the form\textsuperscript{20}

\[ k = A \frac{\text{Re} \int \frac{Z(iR)dR}{Z_R^1}}{Z_R^1}, \] \tag{1.4} \]

The structure of the paper is as follows. In Sec. II a general expression for the partition function \( Z(R) \) of the spin–boson Hamiltonian is derived. In Sec. III it is shown how the method of the present paper exactly reproduces the conventional nonadiabatic quantum rate expression in the lowest perturbation order. In Sec. IV results of the previous section are generalized to strongly interacting systems which require summation of all perturbative terms. A general formula for the rate constant is obtained. The quantum renormalization of the electronic coupling constant and scaling in the ET reactions are discussed. In Sec. V nonadiabatic and adiabatic asymptotics are discussed along with a saddle point approximations of the general formula for the rate constant. Section VI concludes this paper with some remarks on the limitations of the method and discussion of an experiment to check the scaling prediction of the present paper.

II. PARTITION FUNCTION OF THE SPIN–BOSON HAMILTONIAN

The Hamiltonian of ET system is written in a conventional form,\textsuperscript{1,2,13}

\[ H = \frac{\Delta}{2} \sigma_x + \frac{\epsilon}{2} \sigma_z + \frac{\sigma_z^2}{2} \sum_{i=1}^N 2c_y p_i + \sum_{i=1}^N \left( \frac{p_i^2}{2m_i} + \frac{m_i \omega_i^2 y_i^2}{2} \right), \] \tag{2.1} \]

where \( \Delta/2 \) is the electronic matrix element coupling the reactant state, \( - \), and the product state, \( + \), \( y_i \) and \( p_i \) are the nuclear motion coordinates and conjugated momenta, respectively, \( \epsilon \) is the exothermicity of the reaction, \( \sigma_z \) and \( \sigma_x \) are the Pauli matrices in a two-state \(( |+\rangle \) and \((-\rangle \) representation. The Hamiltonian is written as a two-state system coupled linearly to a harmonic bath which describes the nuclear motion of the environment (e.g., polarization of the solvent) as well as the nuclear motion of the reactant and product molecules. The harmonic bath for the reactant and product states is assumed to have the same frequencies. This assumption is a good approximation for most of the electron transfer systems.\textsuperscript{1,2}

The key role in the present theory is played by the partition function of the whole system, which is written as

\[ Z = \langle + | \text{Tr} e^{-\beta H'} | + \rangle + \langle - | \text{Tr} e^{-\beta H'} | - \rangle = Z_+ + Z_-, \] \tag{2.2} \]

where the trace is taken over all of the bath coordinates. Following the standard procedure of calculations\textsuperscript{22-25} the harmonic nuclear coordinates can be integrated out and the trace over the spin coordinate can be conveniently written as a path integral. The result of such calculation is given by Eq. (2.10). For the convenience of those who are not familiar with this technique, and in order to introduce some useful notations, the sketch of the derivation is shown below.

The electronic coupling in Eq. (2.1) is treated as a perturbation and the Hamiltonian is written as \( H = H_0 + H' \), where \( H' = (\Delta/2) \sigma_z \) and \( H_0 \) is the rest of the Hamiltonian. The density operator can be written as (hereafter \( \tilde{\mathcal{N}} = 1 \))

\[
e^{-\beta H} = e^{-\beta H_0} \times \sum_{n=0}^{\infty} (-1)^n \int_0^\beta d\tau_1 \cdots \int_0^\beta d\tau_1^n H'(\tau_2) \cdots H'(\tau_1),
\]
(2.3)

where \( H'(\tau) = e^{\tau H_0} H e^{-\tau H_0} \). After that, the partition function of the \(|+\rangle\) state reads

\[
Z_+ = \langle + | \text{Tr} e^{-\beta H} | + \rangle
= \text{Tr} \sum_{n=0}^{\infty} \left( \frac{\Delta}{2} \right)^n \int_0^\beta d\tau_1 \cdots \int_0^\beta d\tau_n e^{-\beta(\tau_n - \tau_0 - 1)} H_{0+},
\]
\[
\times e^{-\beta(\tau_n - \tau_{n-1} - 1)} H_{0-} \cdots e^{-\beta(\tau_2 - \tau_1)} H_{0-} e^{-\beta \tau_1},
\]
(2.4)

where

\[
H_{0\pm, n} = H_b \pm \frac{1}{2} \left( \sum_{i=1}^{n} \frac{2c_p y_i + \epsilon}{l} \right),
\]
(2.5)

\[
H_b = \sum_{i=1}^{n} \left( \frac{p_i^2}{2m_i} + \frac{m \omega_i^2 y_i^2}{2} \right).
\]
(2.6)

\( H_b \) in Eqs. (2.5) and (2.6) is the harmonic bath Hamiltonian.

Now a \( \tau \)-dependent Hamiltonian, \( H_{0n}(\tau) \), is defined by

\[
H_{0n}(\tau) = H_b + \frac{\sigma_n(\tau)}{2} \left( \sum_{i=1}^{n} 2c_p y_i + \epsilon \right),
\]
(2.7)

\[
\sigma_n(\tau) = \begin{cases} 1 & \text{if } \tau \in [\tau_{2i-1}, \tau_{2i-2}), 1 \leq i \leq n+1; \\ -1 & \text{if } \tau \in [\tau_{2i-1}, \tau_{2i}), 1 \leq i \leq n; \end{cases}
\]
(2.8)

where \( 0 < \tau < \beta \), \( \tau_0 = 0 \), and \( \tau_{2n+1} = \beta \). Thus \( \sigma_n(\tau) \) takes values \( \pm 1 \) in the interval \( 0 < \tau < \beta \) and changes sign sequentially \( n \) times at the points \( \tau_1, \tau_2, \ldots, \tau_{2n} \). This variable explicitly describes the quantum paths of the two-state electronic coordinate.

In terms of the \( \tau \)-dependent Hamiltonian, \( H_{0n}(\tau) \), the partition function of the \(|+\rangle\) state, Eq. (2.4), can be written in a compact form\textsuperscript{23}

\[
Z_+ = \sum_{n=0}^{\infty} \left( \frac{\Delta}{2} \right)^n \int_0^\beta d\tau_1 \cdots \int_0^\beta d\tau_1 \text{Tr} \left[ \hat{T} e^{-\beta H_{0n}(\tau) d\tau} \right],
\]
(2.9)

where \( \hat{T} \) is the \( \tau \)-ordering operator. A similar procedure can be done for the \(|-\rangle\) state and, finally, making use the cumulant expansion for the harmonic variables \( \{y_i^s\} \), \( Z_{\pm} \) takes the form:

\[
Z(R) = Z_+(R) + Z_-(R),
\]

\[
Z_{\pm} = Z_b \sum_{n=1}^{\infty} \left( \frac{\Delta}{2} \right)^n \int_0^\beta dx_{2n} \cdots \int_0^\beta dx_1 \exp \left[ -\beta \epsilon + \frac{1}{4} \int_0^\beta d\omega J(\omega) \right] \int_0^\beta d\tau^* \int_0^\beta d\tau^* \cdot \sigma_n(\tau) \sigma_n(\tau^*) \cdot \frac{\cosh \left( \frac{\beta(\omega/2) - \omega}{\sinh(\beta(\omega/2))} \right)}{\sinh(\beta(\omega/2))} \cdot \left[ \theta(\beta - (x_1 + x_2 + \cdots + x_{2n})) \right] \left[ \frac{1}{\beta^2} x_1 + x_2 + \cdots + x_{2n} \right],
\]
(2.16)

The sum over all nuclear coordinates in Eq. (2.10) is conventionally written with a spectral density, \( J(\omega) \), defined by the following equation:

\[
J(\omega) = \sum_{i=1}^{N} \pi \delta(\omega - \omega_i) \frac{c_i^2}{m_i \omega_i}.
\]
(2.12)

Up to this point the transformations of the initial Hamiltonian have been known for a very long time. Recently Chandler and co-workers\textsuperscript{13,19} suggested a new idea to use the centroid \( R \) of the spin coordinate \( u(\tau) \) as a reaction coordinate of the electron transfer. In a different situation the centroid approach has been discussed before in Refs. 18–20. In our notation the centroid reaction coordinate, \( R \), is written as

\[
R = \frac{1}{\beta} \int_0^\beta \sigma_n(\tau) \frac{1}{2} d\tau = \frac{1}{2} \frac{x_2 + x_4 + \cdots + x_{2n}}{\beta},
\]
(2.13)

where \( x_n = \tau_n - \tau_{n-1} \).

In order to calculate the imaginary part of the partition function we first calculate it as a function of the real parameter \( R \) and then analytically continue it into complex plane of \( R \), as required by Eq. (1.4).

With the introduced notations and with the definition of the reaction coordinate (2.13), the partition function at a fixed real \( R \) can be written as

\[
Z(R) = Z_+(R) + Z_-(R),
\]

\[
Z_{\pm} = Z_b \sum_{n=1}^{\infty} \left( \frac{\Delta}{2} \right)^n \int_0^\beta dx_{2n} \cdots \int_0^\beta dx_1 \exp \left[ \frac{1}{\beta} \int_0^\beta d\omega J(\omega) \right] \int_0^\beta d\tau^* \int_0^\beta d\tau^* \sigma_n(\tau) \sigma_n(\tau^*) \cdot \frac{\cosh \left( \frac{\beta(\omega/2) - \omega}{\sinh(\beta(\omega/2))} \right)}{\sinh(\beta(\omega/2))} \cdot \left[ \theta(\beta - (x_1 + x_2 + \cdots + x_{2n})) \right] \left[ \frac{1}{\beta^2} x_1 + x_2 + \cdots + x_{2n} \right].
\]
In the above formula the $\theta$ function is introduced in order to change variables from $\tau_a$ to $x_a$ and the $\delta$ function fixes the centroid at $R$. Notice that summation in the above formula begins with $n=1$. The zero-order term was omitted since it only gives the partition function of the unperturbed system ($\Delta=0$) and does not contribute to the rate.

The above formula is the central point of our calculation of rate constant of electron transfer. The sum over $n$ represents summation of all orders of perturbation theory. One needs first to evaluate Eqs. (2.15) and (2.16) for a real reaction coordinate $R$, then make an analytical continuation into the complex plane of $R$, and use Eqs. (1.4) and (1.3) to find the rate constant.

A critical step for further transformation of Eq. (2.16) is to analytically evaluate the double integral in the exponent involving spin variable,

$$I_n = \frac{1}{\pi} \int_0^\infty d\omega J(\omega) \int_0^\beta d\tau d\tau' \frac{\sigma_a(\tau)\sigma_a(\tau') \cosh[(\beta\omega/2) + \tau - \tau']}{4 \sinh(\beta\omega/2)} \tag{2.17}$$

for an arbitrary value of $n$. We recall that, according to Eq. (2.8), $\sigma_a(\tau)$ is a function which takes values of $\pm 1$ in the interval $0<\tau<\beta$ and changes sign $n$ times. It turns out that this integral can be taken exactly only in $n=1$ case. This is the lowest order of perturbational theory which corresponds to a nonadiabatic case. This case is considered in the next section. For a general case of arbitrary matrix element $A$, Eq. (2.17) can be evaluated approximately for most realistic systems. This approximation will be developed in Sec. IV.

III. NONADIABATIC CASE

In order to show how the method of the present paper works, in this section the golden rule formula for a nonadiabatic electron transfer rate is reproduced. This case will also help to clarify some subtle points of the analytical continuation required for the rate calculations.

The nonadiabatic case corresponds to a small $\Delta$, hence, only the first term, $n=1$, of the perturbation expansion in Eq. (2.15) can be taken into account. This term is proportional to $\Delta^2$ and obviously corresponds to the golden rule. For $n=1$ the double integral involving the spin variable, Eq. (2.17), can be taken exactly,

$$I_1 = E\beta \int_0^\infty d\omega \frac{J(\omega) \cosh(\beta\omega/2) - \cosh(\beta R\omega)}{\sinh(\beta\omega/2)} \tag{3.1}$$

where

$$E_a = \sum_{i=1}^N \frac{c_i^2}{2m_i\omega_i^2} = \frac{1}{2\pi} \int_0^\infty d\omega \frac{J(\omega)}{\omega} \tag{3.2}$$

The remaining two integrals in Eq. (2.16) over $x_1$, $x_2$ are easy to take directly returning to $\tau_1$, $\tau_2$ variables. The result is

$$Z^{(1)}(R) = Z_b \left( \frac{\Delta R}{2} \right)^2 \frac{1}{2 \pm R} \exp \left[ -\beta Re + E\beta \right]$$

$$- \frac{2}{\pi} \int_0^\infty d\omega \frac{J(\omega) \cosh(\beta\omega/2) - \cosh(\beta R\omega)}{\sinh(\beta\omega/2)} \tag{3.3}$$

Now it is recalled that the reactant partition function, $Z^0_R$, is the partition function of the unperturbed $\pm$ state and, according to (2.5) can be conveniently expressed as

$$Z^0_R = \text{Tr} e^{-\beta H_R} = e^{\beta(\langle 0 | + E\beta Z_b)} \tag{3.4}$$

Thus

$$Z^{(1)}(R) = Z^0_R \left( \frac{\Delta R}{2} \right)^2 \exp \left[ -\left( \frac{\beta}{2} + R\beta \right) \right]$$

$$- \frac{2}{\pi} \int_0^\infty d\omega \frac{J(\omega) \cosh(\beta\omega/2) - \cosh(\beta R\omega)}{\sinh(\beta\omega/2)} \tag{3.5}$$

Finally, using Eq. (1.4) with a prefactor $A=1/\beta$, the nonadiabatic rate can be written as

$$k = \beta \left( \frac{\Delta}{2} \right)^2 \text{Re} \int_{-\infty}^{+\infty} dR \exp \left[ -\left( \frac{\beta}{2} + i\beta R \right) \right]$$

$$- \frac{2}{\pi} \int_0^\infty d\omega \frac{J(\omega) \cosh(\beta\omega/2) - \cosh(\beta R\omega)}{\sinh(\beta\omega/2)} \tag{3.6}$$

This is a well-known quantum rate expression of the electron transfer in nonadiabatic case. In the classical approximation, $\beta\omega \ll 1$, Eq. (3.6) reduces to Marcus' nonadiabatic rate expression.\(^{1,2}\) Eq. (3.6) was first derived from the golden rule by the Soviet researchers\(^ {26,27}\) and after that was rederived by many authors, e.g., Refs. 2 and 28.

In the original derivation a variable corresponding to our $R$ (in Refs. 2 and 26 it is $\alpha = -\frac{1}{2}$) was introduced as a formal integration parameter to represent a $\delta$ function from the golden rule. As it is seen from the above derivation, $R$ is a centroid of the electron coordinate. It has a clear physical meaning of the reaction coordinate of the system.

Notice that for the nonadiabatic case the prefactor $A$ is always $1/\beta$. As it was discussed in Sec. I, in the normal region there are two regimes, quantum and classical, with a crossover temperature $T_c$. However, in a nonadiabatic case, $\Delta \to 0$, the crossover temperature, $T_c = \omega_b/2\pi$, is indefinitely high and for this reason any finite temperature of the system is always below $T_c$, i.e., in the quantum regime where prefactor $A=1/\beta$. As it is shown in Appendix B, the barrier frequency $\omega_b$, given by Eq. (B14), becomes indefinitely large when $\Delta \to 0$, so $T_c \to \infty$. In the inverted region, on the other hand, there is no classical barrier crossing at all, and the electron transfer always takes place from the quantum metastable states. In this case the prefactor is again $1/\beta$. 

In many practical cases Eq. (3.6) can be further simplified by making use of the fact that the low and high frequency modes in the system are well separated. The low frequency modes can be treated classically, and the high frequency modes, quantum mechanically. To make use of this approximation two cutoff frequencies, classical, $\omega_{cl}$, and quantum, $\omega_q$, are introduced. In the integral expression of the exponent of Eq. (3.6), for all $\omega < \omega_{cl}$ the classical limit ($\beta \omega < 1$) is used and for $\omega > \omega_q$ the quantum limit ($\beta \omega > 1$) is used. In a general case only one separation frequency is usually employed, $\omega = \omega_{cl} = \omega_q - T$. Two corresponding asymptotics of the hyperbolic functions give

$$k = \beta \left( \frac{\Delta}{2} \right)^2 \text{Re} \int_0^\infty dR \exp \left[ -\left( \frac{\beta}{2} + iR \right) \frac{2\beta}{\pi} \right]$$

$$\times \int_0^\infty d\omega \frac{J(\omega)}{\omega} \left[ \frac{1}{4} + R^2 \right] \frac{2}{\pi} \int_0^\infty d\omega \frac{J(\omega)}{\omega^2}. \quad (3.7)$$

In this approximation the integral over $R$ can be taken exactly. It should be recalled at this point that $R$ in Eqs. (3.6) and (3.7) is in fact a pure imaginary reaction coordinate which becomes complex in the transformation $R \rightarrow iR$ in Eq. (3.6), according to the prescription of Eq. (1.4). The integrand is exponentially decaying for large $R$ in the complex plane, and for this reason the integral converges. This became possible only after the analytical continuation of the partition function, $Z(R)$, into the complex plane was done.

Integration in Eq. (3.7) gives

$$k = \left( \frac{\Delta}{2} \right)^2 \left[ \frac{\beta \pi}{\beta_{\text{rec}}} \exp \left[ -\frac{\beta \omega_{\text{rec}}}{4} \left( 1 + \frac{\varepsilon}{\omega_{\text{rec}}} \right) \right] \right]$$

$$\times \left[ \frac{2}{\pi} \int_0^\infty d\omega \frac{J(\omega)}{\omega^2} \right]. \quad (3.8)$$

where $\beta_{\text{rec}} = 4\beta_{\text{ac}}$ is the classical reorganization energy. The classical activation energy is

$$\beta_{\text{ac}} = \frac{1}{2\pi} \int_0^{\omega_{\text{cl}}} d\omega \frac{J(\omega)}{\omega}. \quad (3.9)$$

As it is seen from Eq. (3.8), the classical modes contribute to the activation energy of the reaction and quantum modes give a temperature independent tunneling factor.\textsuperscript{1,2}

Thus for $n=1$, our approach reproduces exactly all known results for the nonadiabatic case of the electron transfer theory. In the next section generalization of the theory to the case of arbitrary $n$, which corresponds to a strongly interacting system, is developed.

**IV. ELECTRON TRANSFER RATE FOR STRONGLY INTERACTING SYSTEMS**

In the case of strongly interacting systems, large $\Delta$, all perturbation orders of the expansion in Eq. (2.16) must be taken into account. First, the integral involving spin variable, $I_n$, of Eq. (2.17), has to be evaluated for an arbitrary value of $n$. This can be done as follows.

We notice that the integral is a sum of contributions of all frequencies in the system. The spectrum of the system is assumed to be divided into a low frequency region, $\omega \leq \omega_{cl}$, and a high frequency region, $\omega > \omega_q$. In the approximation of this section the low frequency modes are treated classically, $\beta \omega q < 1$, and the high frequency modes are treated quantum mechanically, $\beta \omega q > 1$. In many realistic systems the low and high frequencies are indeed well separated. For a system where this is not the case the separation can be made by a single frequency $\omega_q = T$. Such an approximation has been previously discussed in the literature.\textsuperscript{2}

The correlation function of the classical modes is constant,

$$\langle \tilde{T} y_\tau \tilde{T} y_\tau' \rangle_b = \frac{1}{2m \omega q} e^{-\omega q |\tau - \tau'|}. \quad (4.1)$$

and their contribution is easy to evaluate. For an arbitrary $n$, the classical contribution to $I_n$ is

$$I_{ncl} = \beta \omega_{ac} \frac{2\beta}{\pi} \int_0^{\omega_{cl}} d\omega \frac{J(\omega)}{\omega} \left( \frac{1}{4} - R^2 \right). \quad (4.2)$$

The quantum contribution is more difficult to evaluate. To understand the general case of arbitrary $n$, it is convenient to start from the analysis of the case $n=1$, which can be treated exactly and, hence, our approximation can be verified. When $n=1$, the integration area in the $\tau, \tau'$ plane is divided into nine regions, as shown in Fig. 1(a). In each of the nine regions the product of two spin variables is $\pm 1$. The quantum correlation function has a sharp maximum along the diagonal of the square integration area and exponentially decays in the regions away from the diagonal. The quantum approximation for the correlation function (2.11) is

$$\langle \tilde{T} y_\tau \tilde{T} y_\tau' \rangle_b = \frac{1}{2m \omega q} e^{-\omega q |\tau - \tau'|}. \quad (4.3)$$

The integral is calculated in the following way. First it is assumed that the product of the spin variables is $\pm 1$ everywhere and the integral is taken with the exact correlation function (2.11). The result of the integration is $E_{\omega q} \beta$, where

$$E_{\omega q} = \sum_{i=1}^{N_q} \frac{e_i^2}{2m \omega q^2} \frac{1}{2\pi} \int_0^\infty \frac{J(\omega)}{\omega} d\omega. \quad (4.4)$$

Then, a double contribution of the negative regions of the spin variables (those regions are shaded in Fig. 1) is subtracted from $E_{\omega q} \beta$. An additional factor of two comes from the fact that one should first compensate a positive contribution which was overcounted in $E_{\omega q} \beta$, and then add a negative contribution, as is required by Eq. (2.17). There are four such equal contributions for $n=1$ case. Because of the sharp exponential decay of the correlation function, each of the negative contributions can be calculated independently of the others. This can be done for most of the points $\tau_1, \tau_2$ inside of the interval $(0,\beta)$ which are separated from each other farther than $1/\omega q$. The negative contribution is calculated with the quantum approximation (4.2). Each of the four shaded regions in Fig. 1(a) gives a negative contribution.
FIG. 1. The integration area for $I_n$, Eq. (2.17), in the $n=1$(a) and $n=2$(b) cases. The integration function is exponentially decaying in the regions away from the diagonal. In shaded regions the integration function is negative. Contribution of such negative regions is proportional to $n$ for $\beta > 1/\omega_q$, Eq. (4.5).

$$ \frac{1}{4\pi} \int_{\omega_q}^{\infty} \frac{J(\omega)}{\omega^2} d\omega. \quad (4.5) $$

The final result of such calculations is $E_{0\beta} \beta$ minus the eight contributions of Eq. (4.5). It can be verified that the same result is obtained in the quantum limit of the exact formula, Eq. (3.1).

In a general case of arbitrary $n$, as it clearly follows from Fig. 1(a) and Fig. 1(b), instead of eight contributions (4.5), there will be eight times $n$ such negative contributions. So, the quantum contribution into Eq. (2.17) is

$$ I_{nq} = E_{0\beta} \beta - \frac{2\pi}{4\pi} \int_{\omega_q}^{\infty} \frac{J(\omega)}{\omega^2} d\omega. \quad (4.6) $$

The first temperature dependent term, $E_{0\beta} \beta$, can be also obtained from the $\delta$-function approximation of the correlation function. Indeed, the correlation function is very sharp and one would think that it is possible to approximate it by a $\delta$ function. Such an approximation was used by Gehlen et al.\textsuperscript{10} It turns out, however, as shown below, that this temperature dependent term does not correspond to any physical effects. The same term is present in the denominator of the rate expression, and two terms cancel each other. The true quantum effects are incorporated in the second temperature independent term which can not be reproduced with the $\delta$-function approximation. The way in which the integral in the general $n$ case has been taken is essentially equivalent to a so-called independent blip approximation of Garg, Onuchic, and Ambegaokar,\textsuperscript{29} see also Ref. 25. This approximation is correct for all $n < n_q = \omega_q \beta > 1$.

Thus the contribution of classical and quantum modes to the integral $I_n$, Eq. (2.17), for an arbitrary $n$ is

$$ I_n = \beta E_{0\beta} - \frac{2\beta}{\pi} \int_{0}^{\omega_q} d\omega \frac{J(\omega)}{\omega} \left( \frac{1}{4} - R^2 \right) + E_{0\beta} \beta $$

$$ - \frac{2\pi}{\pi} \int_{\omega_q}^{\infty} \frac{J(\omega)}{\omega^2} d\omega. \quad (4.7) $$

From the above expression it is seen that the exponential factor in the partition function (2.16) depends only on $R$ and can be taken out of the integral. The remaining multidimensional integral of $\theta$ and $\delta$ functions represents a purely geometrical factor. It is easy to recognize in it a cross section area of the $\eta$-dimensional cube. The calculation is rather straightforward although a bit tedious. Details for the purpose of references are given in Appendix A. The result of the calculation is

$$ Z_{\pm 1}(R) = Z_0 \sum_{n=1}^{\infty} \left( \frac{\beta \Delta}{2} \right)^{2n} \frac{1}{n!} \frac{1}{n!(n-1)!} \left( \frac{1}{2} \right)^{n-1} \left( R^2 - \frac{1}{2} \right)^{n-1} $$

$$ \times \left( \frac{1}{\sqrt{2}} R \right)^{2n} \exp \left[ 4\beta E_{0\beta} R^2 - \beta R \epsilon + \beta E_{0\beta} \right]. \quad (4.8) $$

In the sum of the above expression the Bessel function can be recognized. Thus

$$ Z(R) = Z_+(R) + Z_-(R) $$

$$ = Z_0 I_1 \left( \frac{\beta \Delta}{\sqrt{2}} R \right) \left( \frac{1}{\sqrt{2}} R \right) \left( \frac{1}{\sqrt{2}} R \right)^{-1} $$

$$ \times \exp \left[ 4\beta E_{0\beta} R^2 - \beta R \epsilon + \beta E_{0\beta} \right], \quad (4.9) $$

where $I_1(x)$ is the modified Bessel function.\textsuperscript{30}

$\Delta'$ in the partition function of the system (4.9) is an effective matrix element modified by quantum modes in the system,

$$ \Delta' = \Delta \exp \left( -\frac{1}{\pi} \int_{\omega_q}^{\omega_q} d\omega \frac{J(\omega)}{\omega^2} \right). \quad (4.10) $$

This modification (renormalization) of the electronic coupling matrix element is one of the central results of the present paper. The expression for the partition function, Eq. (4.9), shows that there are no other effects due to the
quantum degrees of freedom except for the renormalization of the electronic coupling. This fact results in a very interesting scaling property of the electron transfer systems. Namely, a system with classical and “frozen” quantum degrees of freedom is equivalent to a system of lower dimensionality, containing only classical degrees of freedom, with renormalized electronic coupling (4.10).

As it will be made clear below, the decrease of the matrix element due to renormalization by quantum modes results in an increase of the reaction rate compared with the case when all modes, including quantum ones, are treated classically.

Gehlen et al.10 calculated the partition function of the spin–boson Hamiltonian and they also obtained the modified Bessel function. Their result, however, contains an unchanged electronic matrix element, because a δ-function approximation for the correlation function of nuclear coordinates was used in the calculations. In a later publication Gehlen and Chandler12 developed an approximation which extends their previous result with an additional quantum exponential factor. In our case the quantum corrections, as it is seen from Eq. (4.9), are incorporated into argument of the Bessel function.

In Eq. (4.9), \( Z_b \) should be substituted in the form [cf. Eq. (3.5)]

\[
Z_b = e^{-\beta\pi/2 - E_{ac} - E_{eq}^b Z_R^0}.
\]

(4.11)

It is seen that the quantum part of the activation energy, \( E_{eq} \), cancels out of the final expression of the partition function and, hence, from the corresponding rate expression, see Eq. (4.13) below.

A general expression for the rate constant is written as

\[
k=A \text{Im} \int I_{1} \left( \beta \Delta' \sqrt{1-R^2} \right) \left( \frac{\beta \Delta'}{2} \right)^{-1} \exp \left\{ 4\beta E_{ac} R^2 - \beta E_{ac} - \frac{\beta}{2} \right\} dR.
\]

(4.12)

After transformation of the integration contour into the complex plane according to Eq. (1.4) it takes the final form

\[
k=A \int_{-\infty}^{+\infty} I_{1} \left( \beta \Delta' \sqrt{1+R^2} \right) \left( \frac{\beta \Delta'}{2} \right)^{-1} \exp \left\{ -4\beta E_{ac} R^2 - \beta E_{ac} - \frac{\beta}{2} \right\} \cos(\beta R)e \; dR.
\]

(4.13)

This is the main result of the present paper. The electron transfer rate constant is given for an arbitrary electronic matrix element where both quantum and classical modes are taken into account. All known results for the electron transfer theory can be reproduced as different asymptotics of this formula. In addition, it predicts several new results for strongly interacting electron transfer systems.

V. NONADIABATIC AND ADIABATIC ASYMPTOTICS OF THE GENERAL FORMULA (4.13)

As Gehlen et al.10 pointed out, the nonadiabatic and adiabatic limits can be obtained from two asymptotics of the Bessel function10

\[
I_1(x) \sim \begin{cases} 
\frac{x^2}{2}, & \text{if } x \to 0; \\
\exp \left( \frac{1}{2} \sqrt{\frac{2}{\pi x}} \right), & \text{if } x \to \infty; 
\end{cases}
\]

(5.1)

For the nonadiabatic rate [small \( x \) in Eq. (5.1)], as discussed in the previous section, \( A=1/\beta \). In a saddle point approximation Eq. (4.13) reduces to

\[
k=\left( \frac{\Delta'}{2} \right)^2 \frac{\beta}{E_{ac}} \exp \left( \frac{1}{4} \frac{E_{ac}}{E_{ac}} \right) \left( 1 + \frac{1}{E_{ac}} \right)^2 \]

(5.2)

which is the Marcus nonadiabatic electron transfer formula with quantum corrections.1,2 In the above expression \( E_{ac}=4E_{ac} \) is the classical part of the reorganization energy. This result also coincides with Eq. (3.8) which was derived in a different way as an approximation for the exact result (3.7). The nonadiabatic quantum correction in Eq. (3.8) has been known for a long time, although it was not recognized that this correction, in fact, is connected with modification of the electronic matrix element, as seen from Eqs. (5.2) and (4.10).

The exact condition for the nonadiabatic asymptotics \( (x\ll 1) \) is written as

\[
\frac{\beta \Delta'}{2} \left( 1 + \frac{1}{\beta E_{ac}} \right) \ll 1.
\]

(5.3)

Usually \( \beta E_{ac} \gg 1 \) and, thus condition (5.3) is defined solely by the coupling matrix element and temperature. It should be noticed it is the modified electronic matrix element, \( \Delta' \), and not the initial one, that enters the nonadiabatic condition (5.3). An important consequence is that the applicability of the classical formula, Eqs. (3.8) and (5.2), can be extended to some cases of the conventional strong coupling,3 \( \Delta \beta \gg 1 \). In this situation, due to the quantum modes in the system, the effective interaction can still be small, \( \Delta \beta = 1 \), and the nonadiabatic asymptotics, Eqs. (3.8) and (5.3), valid. In this case, the nonadiabaticity of the reaction is induced by the quantum modes in the system.

The adiabatic asymptotics, large arguments of the Bessel function, is more difficult to study. There are two cases of large and small \( |R| \) contributing to the integral (4.13) which are important in dealing with square roots in expression (4.13). In both cases the saddle point approximation is used in the evaluation of the integral in Eq. (4.13).

A large value of \( \epsilon \) corresponds to the inverted region12 of the reaction. In this case the prefactor \( A=1/\beta \), as was explained in the previous section. If

\[
\epsilon \gg 8E_{ac} \gg \Delta'
\]

and

\[
\Delta' \beta \gg 1
\]

(5.4)

(5.5)
then the adiabatic asymptotics of the Bessel function [second line in Eq. (5.1)] can be used, and at the same time the saddle point $|R^*|=\varepsilon/8E_{ac}\gg 1$. The rate of reaction (4.13) in this approximation is

$$k=\frac{E_{sc}}{\varepsilon^2} \frac{8\Delta'}{\varepsilon} e^{-\beta\varepsilon/16E_{ac}}. \quad (5.6)$$

Unfortunately, the saddle point approximation (and this estimate) in this case is very inaccurate because of the presence of the branch cuts on the complex plane of the integrand in Eq. (4.13).

In case of small $\varepsilon$,

$$\frac{\varepsilon}{4E_{ac}-\Delta'}<1 \quad (5.7)$$

and large $\Delta'$, Eq. (5.5), the saddle point $|R^*|=\varepsilon/2(4E_{ac}-\Delta')<1$. In this case the square roots in the integral of Eq. (4.13) can be expanded in small $R$, and the saddle point approximation can be simply obtained. This case corresponds to a normal region, where there is an activation barrier for the reaction. Let the frequency of the barrier be $\omega_b$ (this frequency will be found below). There are two regimes in the temperature dependence of the prefactor $A$ with the crossover temperature $T_c=\omega_b/2\pi$.

For the low temperature regime, $T<T_c$, the prefactor $A=1/\beta$ and the adiabatic rate is

$$k=\frac{1}{\beta} \left[ \frac{\Delta'}{4E_{ac}-\Delta'} \exp \left( -\frac{4E_{ac}-\Delta'}{4} \beta \right) \right]^{1/2} \left( 1+\frac{\varepsilon}{4E_{ac}-\Delta'} \right)^2 \left( \frac{\beta\Delta'}{4} \right). \quad (5.8)$$

Because of condition (5.7) the rate is essentially proportional to

$$k \sim e^{-\beta(E_{ac}-\Delta'/2)}. \quad (5.9)$$

Modification of the activation energy of the reaction in a classical system by the electronic interaction (due to splitting of two potential surfaces by $\pm \Delta/2$ at the intersection points) is a well known result.\(^\ast\)\(^\ast\)\(^\ast\) However, the exponential factor obtained in Eq. (5.9) is not at all trivial. First, because $E_{ac}$ is not a total activation energy but only the classical part of it, second, and more surprisingly, because $\Delta'$ above is not the original matrix element of the Hamiltonian (2.1) but is the one renormalized by quantum modes in the system. This result is a direct consequence of the scaling nature of the quantum interactions.

In the regime corresponding to Eq. (5.8), many vibrational states of the classical modes are thermally excited, $\omega_b/T<1$, however, because of the condition $T<T_c$, the reaction mainly takes place from the metastable quantum states below the barrier top, i.e., due to tunneling. Thermal excitation of those states is described by the Arrhenius factor in Eq. (5.8). The high frequency quantum modes are not excited and the reaction takes place from the ground state of those modes. The contribution of the quantum modes to the reaction rate is described by the modification of the electronic matrix element, Eq. (4.9). Thus, in this regime the reaction takes place due to tunneling of both low and high frequency modes. The difference between them is that in the former case the tunneling takes place from the ground state, and in the latter case from the highly excited states, just under the classical barrier top.

In the high temperature regime, $T>T_c$, the prefactor $A$ is $\omega_b/2\pi$. The frequency of the classical barrier found in Appendix B is

$$\omega_b=\sqrt{\frac{4E_{ac}}{\Delta'}-1} \prod_{i=1}^{N_c} \omega_i \prod_{i=2}^{N_c} \omega_i', \quad (5.10)$$

where $\omega_i$ and $\omega_i'$ are the classical frequencies of the reactant well and of the transition state respectively.

Thus, for the same condition as above, but for $T>T_c$, the reaction rate takes the following form

$$k=\frac{1}{2\pi} \prod_{i=1}^{N_c} \omega_i \prod_{i=2}^{N_c} \omega_i' \exp \left[ -\frac{4E_{ac}-\Delta'}{4} \beta \left( 1+\frac{\varepsilon}{4E_{ac}-\Delta'} \right)^2 \right] \left( \frac{\beta\Delta'}{4} \right). \quad (5.11)$$

Again, due to condition (5.7) the exponential factor in the above expression is in fact simplified to Eq. (5.9). This formula exactly reproduces the well known result of the multidimensional transition state theory for the electron transfer when all modes in the system are classical,\(^\ast\)\(^\ast\)\(^\ast\)\(^\ast\) in which case $\Delta'=\Delta$ and $E_{ac}=E_c$. Eq. (5.11) shows how the strong electronic interaction and the quantum modes modify the classical transition state theory expression. Surprisingly, all changes are incorporated in the modified electronic matrix element $\Delta'$.

VI. CONCLUSION

In this paper a theory for strongly interacting electron transfer systems is proposed. The theory is based on the spin–boson Hamiltonian model of the electron transfer. A general formula for the rate is derived such that all of the electron transfer rate cases (weakly and strongly interacting systems, nonadiabatic and adiabatic cases) can be derived as different asymptotics of the general formula. There are several limitations for this treatment. First of all, in the strong coupling case the electronic coupling matrix element should be still small enough so that the coupling would not affect the reactant and the product wells dramatically. Second, our treatment is not applicable to infinitely low temperature. Even for the low temperature regime, $T<T_c$, the temperature must be higher than the typical classical bath frequency. Otherwise the bath will be frozen in the ground state and the dynamics of the system will consist of coherent oscillations between reactants and products instead of exponential decay.\(^\ast\)\(^\ast\)\(^\ast\)

It is shown that the quantum degrees of freedom can be effectively eliminated from the model by renormalizing the electronic coupling matrix element according to Eq. (4.10). This renormalization results in the following scaling property of the electron transfer systems: a system containing both classical and quantum degrees of freedom is equivalent (the same reaction rate) to a system of lower
dimensionality containing only classical degrees of freedom, with renormalized electronic coupling matrix element. It would be interesting to check this theoretical prediction experimentally.

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APPENDIX A: EVALUATION OF THE GEOMETRICAL FACTOR IN EQ. (2.16)

In Sec. IV the calculation of the partition function (2.16) is reduced to evaluation of the following geometrical factor (for \( Z^+ \)):

\[
G = \sum_{n=1}^{\infty} \left( \frac{\Delta}{2} \right)^{2n+1} \int_0^\beta dx_{2n} \cdots \int_0^\beta dx_1 \times \theta[\beta - (x_1 + x_2 + \cdots + x_{2n})] \times \delta\left( R - \frac{1}{2} + \frac{x_2 + x_4 + \cdots + x_{2n}}{\beta} \right).
\]

(A1)

Using the integral representations of \( \delta \) and \( \theta \) functions,

\[
\delta(x) = \int_{-\infty}^{+\infty} \frac{dk}{2\pi} e^{ikx}, \quad \theta(x) = \int_{-\infty}^{+\infty} \frac{dk}{2\pi i} \frac{e^{ikx}}{k}\]

and defining dimensionless variables \( z_i = x_i/\beta \), \( G \) is written in the following form:

\[
G = \sum_{n=1}^{\infty} \left( \frac{\beta\Delta}{2} \right)^{2n} \int_0^{+\infty} \frac{dk}{2\pi i} \int_{-\infty}^{+\infty} dt \int_{-\infty}^{+\infty} \frac{dt}{2\pi} \exp[iR - ik z_1 + \cdots + ik z_{2n}]
\]

(A2)

Integration over \( \{x_1, x_2, \cdots, x_{2n}\} \) gives

\[
G = \sum_{n=1}^{\infty} \left( \frac{\beta\Delta}{2} \right)^{2n} \int_{-\infty}^{+\infty} \frac{dk}{2\pi i} \int_{-\infty}^{+\infty} dt \int_{-\infty}^{+\infty} \frac{dt}{2\pi} \exp[\frac{-ik z_1}{R} + \cdots + \frac{-ik z_{2n}}{R}] \times \frac{1}{\{n-1\}} C_n^m (-1)^{m+n}(R+m-1/2)^{n-1} e^{ik(R-1/2)}. \]

(A3)

Expanding Eq. (A4) in \( t \) and then integrating over \( t \) in the complex plane results in

\[
G = \sum_{n=1}^{\infty} \left( \frac{\beta\Delta}{2} \right)^{2n} \int_{-\infty}^{+\infty} \frac{dk}{2\pi i} \int_{-\infty}^{+\infty} \frac{dt}{2\pi} \int_{-\infty}^{+\infty} \frac{dt}{2\pi} \exp[\frac{-ik z_1}{R} + \cdots + \frac{-ik z_{2n}}{R}] \times \frac{1}{\{n-1\}} C_n^m (-1)^{m+n}(R+m-1/2)^{n-1} e^{ik(R-1/2)}. \]

(A4)

Applying the summation formula:

\[
\sum_{m=1}^{\infty} \left( \frac{-1}{n} \right)^n (R+m-1/2)^{n-1} = \frac{\pi}{2},
\]

\[
\int_0^{+\infty} \frac{dx}{\pi x} e^{-x} = \frac{\pi}{2},
\]

we obtain

\[
G = \sum_{n=1}^{\infty} \left( \frac{\beta\Delta}{2} \right)^{2n} \frac{1}{n!} (R+1/2)^n \times \sum_{m=1}^{\infty} C_n^m (-1)^m(R+m-1/2)^{n-1}.
\]

(A5)

APPENDIX B: EVALUATION OF THE BARRIER FREQUENCY

The barrier frequency is evaluated for only classical degrees of freedom and for the renormalized coupling matrix element \( \Delta' \). Here we follow the method of Dakhnovskii and Ovchinnikov.\(^{31,32}\)

The uncoupled reactant and product harmonic potentials in the mass-weighted coordinates are written as

\[
U_i = \sum_{i=1}^{N_c} \left( \frac{\omega_i^2 y_i^2}{2} + c y_i \right), \quad i = +, - \]

(B1a, B1b)

Electronic coupling with matrix element \( \Delta'/2 \) results in two adiabatic surfaces, the lower one is

\[
U_i = \frac{U_+ + U_-}{2} - \sqrt{\left( \frac{U_+ - U_-}{2} \right)^2 + \frac{(\Delta')^2}{2}} = \sum_{i=1}^{N_c} \frac{\omega_i^2 y_i^2}{2} + \frac{(\Delta')^2}{2}
\]

(B2)

In order to find a saddle point we set

\[
\frac{\partial U_i}{\partial y_i} = 0.
\]

(B3)

Thus we find

\[
y_i^+ = \frac{2B e_i}{\omega_i^2}, \quad (B4)
\]

where \( y_i^+ \) is the saddle point coordinate, and \( B \) satisfies the following equation

\[
B = \frac{e + BEr}{2} + \sqrt{\left( \frac{e + 2BEr}{2} \right)^2 + \left( \frac{\Delta'}{2} \right)^2}.
\]

(B5)
If $\Delta'/E_r \ll 1$ one can solve the equation for $B$ approximately. We find $B = \epsilon / 2E_r$, which gives the saddle point coordinates by Eq. (B4).

To calculate the frequencies of the barrier one needs to calculate the second derivative of $U$,

$$\frac{\partial^2 U}{\partial y_1 \partial y_j} = \omega_1^2 \delta_{ij} - c_j C,$$

(B6)

where

$$C = \left( \frac{\Delta'}{2} \right)^2 \left[ \left( \frac{\epsilon + 2BE_r}{2} \right)^2 + \left( \frac{\Delta'}{2} \right)^2 \right]^{3/2}. \quad \text{(B7)}$$

The eigenvalue equation for frequencies can be written as follows:

$$\sum_{i=1}^{N_x} (\omega_1^2 \delta_{ij} - c_j C \psi_i) = \lambda \psi_j,$$

(B8)

where $\psi_j$ is an eigenvector corresponding to $\lambda$. Thus

$$\psi_j = \frac{C_j \sum_{i=1}^{N_x} c_i \psi_i}{\omega_j^2 - \lambda}.$$

(B9)

Summation over $j$ on both sides of this equation results in

$$\sum_{j=1}^{N_x} c_j \psi_j = \sum_{j=1}^{N_x} \frac{C_j \sum_{i=1}^{N_x} c_i \psi_i}{\omega_j^2 - \lambda}.$$

(B10)

Thus

$$1 = \sum_{j=1}^{N_x} \frac{C_j^2}{\omega_j^2 - \lambda}.$$

(B11)

The product of the roots of this equation equals to the constant term (the Vieta's theorem), hence

$$\prod_{j} \frac{\lambda_j}{\omega_j^2} = 1 - \frac{E_r C}{2},$$

(B12)

when $\Delta'/2E_r \ll 1$ and $\epsilon \ll \Delta'/2$ we have

$$\prod_{j} \frac{\lambda_j}{\omega_j^2} \approx 1 - \frac{E_r}{\Delta'}.$$

(B13)

Defining the barrier frequency by $\lambda_1 = -\omega_2^2$ and the stable frequencies of the transition state by $\lambda_j = \omega_j^2$ we finally obtain the equation for the barrier frequency

$$\omega_b = \prod_{j=2}^{N_x} \omega_j / \prod_{j=1}^{N_x} \omega_j = \sqrt{\frac{E_r}{\Delta'}} - 1.$$

(B14)