

## Modulating electron dynamics: Modified spin-boson approach

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Vibrationally modulated electron transfer in polar media is considered in the framework of a modified spin-boson approach when modulation and solvation degrees of freedom are independent of each other. The transition probability is presented in terms of the infinite series of multidimensional integrals. The solution is rigorously derived in the noninteracting blip approximation for symmetric electron transfer. It is proved that in this approximation the procedure of the direct averaging of the rate constant over modulation bath appears to be correct. Possible applications in molecular electronics, vibrational coherence, long range electron transfer, and solar cells are discussed.

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### I. INTRODUCTION

In the last two decades there has been a growing interest in proton transfer modulated by nuclear vibrations<sup>1–6</sup> as well as electron transfer through a bridge.<sup>7–16</sup> However, with increasing complexity of the systems under investigation in chemistry<sup>7,8,17–21</sup> and biology,<sup>22–32</sup> the evidence of vibrational modulation has become more convincing and many new results justify the increasing interest in this field.

In many systems a bridge undergoes conformational changes and alters the charge transfer dynamics, i.e., controls the electron motion by modulating a transition matrix element.<sup>1–6,11–16</sup> Sometimes this effect is called conformational gating in the rate constant.<sup>11,33</sup> In the fast reactions of electron transfer in photosynthetic bacteria,<sup>22–32</sup> the conformational gating manifests itself in strong oscillations of the transition probability.

A non-Condon effect is important in the context of electron transfer in biological membranes discussed by Medvedev and Stuchebrukhov<sup>12,13</sup> and Daizadeh *et al.*<sup>34</sup> and in molecular electronics discussed by Ranter.<sup>35,36</sup> In this context, Nitzan showed that there is an intrinsic connection between the electron transfer rate and electrical current in molecular wires.<sup>37,38</sup> Thus, the study of modulation in an electron transfer reaction becomes an important problem in molecular electronics as well.

There is another fundamental issue that should be addressed to this problem, i.e., how to average over modulation degrees of freedom. Indeed, in quantum mechanics a time-dependent absolute value of the square of the electron wave function,  $\langle \psi_1^*(t) \psi_1(t) \rangle_T$  (rather than the reaction rate) thermodynamically averaged over both modulation and solvation nuclear degrees of freedom, represents the true transition probability for the electron to be in the initial electronic state.<sup>39,40</sup> There is a group of the authors who directly average the rate constant.<sup>1–6,13</sup> This issue should be resolved by direct solution of the whole time-dependent quantum mechanical problem. In the context of the modulated electron transfer, the former approach was employed by several groups<sup>14–16</sup> where Creechley and Dahnovsky<sup>14</sup> found the exact solution for the transition probability for an electron shuttling between the levels. As shown by them, in the absence

of solvation degrees of freedom, the electron evolution reveals strong oscillations with (or without) decay depending on temperature, the frequencies, and the vibronic coupling constants of the modulation oscillators. Such a behavior was also found in numerical solutions by Coalson and Evans.<sup>15</sup> Kilin and coworkers<sup>16</sup> discussed a different model where the same nuclear oscillator participates in both modulation and solvation interactions with the electron. In all of this research, a spin-boson model was employed. In this model a Hamiltonian describing both types of nuclear vibrations for the symmetric electron transfer ( $\epsilon=0$ ), can be written as follows:

$$H = -\frac{1}{2} \left( \hbar \Delta_0 + \sum_i C_i q_i \right) \sigma_x + \frac{1}{2} \sum_i \left( \frac{p_i^2}{M_i} + M_i \Omega_i^2 q_i^2 \right) - \frac{1}{2} \sigma_z \sum_k g_k x_k + \frac{1}{2} \sum_i \left( \frac{p_i^2}{m_i} + m_i \omega_i^2 x_i^2 \right), \quad (1)$$

where  $p_i$ ,  $q_i$  (or  $p_k$ ,  $x_k$ ) are the momentum and coordinate of a mediated  $i$ th oscillator (or a solvation  $k$ th oscillator) with the frequency  $\Omega_i$  (or  $\omega_k$ ), the mass  $M_i$  (or  $m_k$ ), and the coupling constant  $C_i$  (or  $g_k$ ). In the absence of modulation ( $C_i=0$ ), the electron dynamics obey the exponential evolution described by the golden rule expression for the rate constant with the transition matrix element  $\Delta_0$ . The main assumptions made in Eq. (1) is the independence of the mediation and solvation degrees of freedom. No oscillators from the modulation oscillator group participate in the solvation process and vice versa. Usually it is a good approximation for a polar environment where the main contribution to the rate constant is owing to a continuous polar environment.

This work differs from the previous research of Creechley and Dahnovsky<sup>14</sup> where only a modulation bath  $\{q_i\}$  was included. It was found that the transition probability never exhibits exponential evolution described by the rate constant. Moreover, strong oscillations in the time-dependent transition probability were found. In the most studied case of electron-solvation bath interaction, the transition probability evolution is exponential in the noninteracting blip approximation.<sup>39</sup> It becomes unclear how strong coherence

oscillations and slow nonexponential decay due to a modulation bath will change the transition probability of a system that includes interaction with a solvation bath as well. It is unclear either whether a frequently employed procedure of the averaging of the electron transfer constant with respect to modulation vibrations is correct since according to statistical mechanics one should average an observable operator—a transition probability—in a manner, for example, presented by Leggett and coworkers.<sup>39</sup> Thus, it is methodologically important to find the limits where a thermodynamic averaging of the rate constant is true procedure.

To study a time-dependent behavior of a transferring electron, we employ the Hamiltonian (1) that is capable of describing non-Condon effects in fast electron transfer (vibrational coherence), long-range electron transfer in proteins, and electrical current in molecular electronics, and find the exact expression for the time-dependent transition probability for the electron transfer in Sec. II by making use of a path-integral technique (the same approach was used by Leggett *et al.* in Ref. 39). For the Hamiltonian (1), derivation becomes more complicated and technical details are moved to the Appendix. In Sec. III, a solution is rigorously found in the noninteracting-blip approximation (NIBA) (such an approximation results in the golden rule expression for the rate constant<sup>39,40</sup> [see Eq. (1)] using the method of *asymptotic symmetrization*. The obtained results are discussed in Sec. IV. Possible applications to molecular electronics, long-range electron transfer, and solar cells are also discussed.

## II. TIME-DEPENDENT TRANSITION PROBABILITY

### A. General expression

The probability to find an electron in the initial state  $|\uparrow\rangle$  is determined from the thermodynamic averaging of the  $|\psi_{\uparrow}(t)\rangle^2$ . The electron wave function depends on two types of variables  $\{q_i\}$  and  $\{x_k\}$ . Thus, the thermodynamic averaging should be performed with respect to both sets of the coordinates. Such an average can be presented in terms of a path integral over the electron and oscillator trajectories. This method works well for oscillator environments. According to Feynman and Vernon,<sup>41</sup> the oscillator paths can be integrated out simplifying the expression for the transition probability with

$$W_{\uparrow}(t) = \int \int Dx(t)Dy(t)A[\sigma_x(t)]A^*[\tilde{\sigma}_x(t)] \times F_M[\sigma_x(t), \tilde{\sigma}_x(t)]F_S[\sigma_z(t), \tilde{\sigma}_z(t)], \quad (2)$$

where the amplitudes of electron motion in the absence of an environment are defined as follows:<sup>39</sup>

$$A[\sigma_x(t)] = \exp\left[-i\frac{\Delta_0}{2}\int_0^t \sigma_x d\tau\right],$$

$$A^*[\tilde{\sigma}_x(t)] = \exp\left[+i\frac{\Delta_0}{2}\int_0^t \tilde{\sigma}_x d\tau\right]. \quad (3)$$

The double path  $[x(\tau), y(\tau)]$ , defined in the same way as in Ref. 39, corresponds to  $[+, +]$ ,  $[+, -]$ ,  $[-, +]$ , and  $[-, -]$

where the initial and final states are the same

$$x(\tau) = y(\tau) = +q_0$$

for  $\tau \leq 0$ , and

$$x(t) = y(t) = +q_0$$

for  $\tau = t$ . In Eq. (2)  $F_M[\sigma_x(t), \tilde{\sigma}_x(t)]$  is a modulation influence functional

$$F_M[\sigma_x(t)(t), \tilde{\sigma}_x(t)] = \exp\left\{-\frac{1}{\pi\hbar}\int_0^t d\tau \int_0^\tau ds[-iM_1(\tau-s)[\sigma_x(\tau) - \tilde{\sigma}_x(\tau)] \times [\sigma_x(s) + \tilde{\sigma}_x(s)] + M_2(\tau-s)[\sigma_x(\tau) - \tilde{\sigma}_x(\tau)] \times [\sigma_x(s) - \tilde{\sigma}_x(s)]\right\}, \quad (4)$$

where the functions  $M_1$  and  $M_2$  are defined as

$$M_1(\tau-s) \equiv \int_0^\infty d\omega J_M(\omega)\sin[\omega(\tau-s)],$$

$$M_2(\tau-s) \equiv \int_0^\infty d\omega J_M(\omega)\cos[\omega(\tau-s)]\coth\left(\frac{\beta\omega}{2}\right). \quad (5)$$

The effect of the interaction with the modulation medium is determined by the spectral density  $J_M(\omega)$ <sup>39</sup>

$$J_M(\omega) \equiv \frac{\pi}{2}\sum_i \frac{C_i^2}{M_i\Omega_i}\delta(\omega - \Omega_i). \quad (6)$$

The solvation influence functional  $F_S[\sigma_z(t)(t), \tilde{\sigma}_z(t)]$  is defined in an usual manner<sup>39,40</sup>

$$F_S[\sigma_z(t)(t), \tilde{\sigma}_z(t)] = \exp\left\{-\frac{1}{\pi\hbar}\int_0^t d\tau \int_0^\tau ds[-iL_1(\tau-s)[\sigma_z(\tau) - \tilde{\sigma}_z(\tau)] \times [\sigma_z(s) + \tilde{\sigma}_z(s)] + L_2(\tau-s)[\sigma_z(\tau) - \tilde{\sigma}_z(\tau)] \times [\sigma_z(s) - \tilde{\sigma}_z(s)]\right\}, \quad (7)$$

where the functions  $L_1$  and  $L_2$  are given by the following equations:

$$L_1(\tau-s) \equiv \int_0^\infty d\omega J_S(\omega)\sin[\omega(\tau-s)],$$

$$L_2(\tau-s) \equiv \int_0^\infty d\omega J_S(\omega)\cos[\omega(\tau-s)]\coth\left(\frac{\beta\omega}{2}\right). \quad (8)$$

As in Eq. (6), the interaction with the solvation medium is determined by the spectral density,  $J_S(\omega)$ <sup>39,40</sup>

$$J_S(\omega) \equiv \frac{\pi}{2} \sum_i \frac{g_i^2}{m_i \omega_i} \delta(\omega - \omega_i). \quad (9)$$

The term  $F_S[\sigma_z(t)(t), \tilde{\sigma}_z(t)]$ , is a familiar influence functional that causes the solvation and reorganization in the electron transfer while the less known modulation influence functional,  $F_M[\sigma_x(t)(t), \tilde{\sigma}_x(t)]$ , corresponds to the double electron flips at different moments.<sup>14</sup> The flips can be due to the amplitudes (3) as well. Thus, the two transitions at the times  $t_i$  and  $t_j$  are due to the following terms:

$$\left(\pm i \frac{\Delta_0}{2}\right) \left(\pm i \frac{\Delta_0}{2}\right) dt_i dt_j, \quad \pm \frac{i}{\hbar \pi} M_1 dt_i dt_j,$$

and

$$\pm \frac{1}{\hbar \pi} M_2 dt_i dt_j. \quad (10)$$

The signs “+” or “-” in the pairs of the flips are determined by the signs of  $\sigma$  and  $\tilde{\sigma}_x$  in the influence functional (4). All of the flips due to the terms (10) should be presented in the expression (2) for the transition probability. As shown in Ref. 14, the contribution from the  $M_1$  flips vanishes for symmetry reasons (see the proof in the Appendix). However, the  $M_2$  flips do not cancel despite having both signs, “+” or “-.” Such a choice stems from the fact that the number of  $\sigma$  as well as  $\tilde{\sigma}_x$  should be even since the electron starts from the state (++) and ends up in the same state, (++) . The complete discussion of this property is given in the Appendix .

Just as in Ref. 14, the transition probability difference  $P(t) = [1 + W_1(t)]/2$  yields

$$P(t) = \sum_{n=0}^{\infty} \sum_{p_1=0}^n (-\Delta_0^2)^{p_1} \int_0^t dt_{2n} \cdots \int_0^{t_2} dt_1 S_{p_2}(t_1, \dots, t_{2n}) \times F_n(t_1, \dots, t_{2n}). \quad (11)$$

Here

$$p_1 + p_2 = n.$$

The function,  $S_{p_2}(t_1, \dots, t_{2n})$ , is symmetric with respect to the times  $t_1, \dots, t_{2n}$  and the index  $p_2$  determines the number of the terms in the product

$$S_{p_2}(t_1, \dots, t_{2n}) \equiv \sum_{\{t\text{-perm}\}} \left( -\frac{1}{\pi \hbar} M_2(t_{i_1} - t_{j_1}) \right) \cdots \left( -\frac{1}{\pi \hbar} M_2(t_{i_{p_2}} - t_{j_{p_2}}) \right). \quad (12)$$

The term  $F_n(t_1, \dots, t_{2n})$  is defined in the way presented by Leggett *et al.*<sup>39</sup>

$$F = \frac{1}{2^n} \exp\left(-\frac{1}{\pi \hbar} \sum_{j=1}^n S_j\right) \sum_{\zeta_j=\pm 1} \left[ \exp\left(-\frac{1}{\pi} \cdot \sum_{j>k=1}^n \Lambda_{jk} \zeta_j \zeta_k\right) \times \prod_{k=0}^{n-1} \cos\left(\frac{1}{\pi} \zeta_j X_{jk}\right) \cos\left(\frac{1}{\pi \hbar} \sum_{j=1}^n \zeta_j X_{j0}\right) \right]. \quad (13)$$

The functions  $S_j$ ,  $\Lambda_{jk}$ , and  $X_{jk}$  are given by

$$S_j \equiv Q_2(t_{2j} - t_{2j-1}),$$

$$\Lambda_{jk} \equiv Q_2(t_{2k} - t_{2j-1}) + Q_2(t_{2k-1} - t_{2j}) - Q_2(t_{2k} - t_{2j}) - Q_2(t_{2k-1} - t_{2j-1}),$$

$$X_{jk} \equiv Q_1(t_{2j} - t_{2k+1}) + Q_1(t_{2j-1} - t_{2k}) - Q_1(t_{2j} - t_{2k}) - Q_1(t_{2j-1} - t_{2k-1}), \quad (14)$$

where the functions  $Q_1$  and  $Q_2$  stand for<sup>39,40</sup>

$$Q_1(t) \equiv \int_0^\infty \frac{d\omega}{\omega^2} J_S(\omega) \sin(\omega t),$$

$$Q_2(t) \equiv \int_0^\infty \frac{d\omega}{\omega^2} J_S(\omega) [1 - \cos(\omega t)] \coth\left(\frac{\beta\omega}{2}\right). \quad (15)$$

Equations (11)–(15) describe the complete dynamics of the transfer an electron interacting with the modulation and solvation oscillator baths.

## B. Exact solution

In this section we prove that the solution given by Eqs. (11)–(15) reproduces the well-known exact result<sup>14,42,43</sup> that describes vibrational coherence in the framework of a model which only includes the modulation of the transition matrix element by vibrational modes. This model does not consider the effect of dissipation due to a solvation or polaron mechanism, i.e.,

$$g_i = 0 \quad (16)$$

for all  $i$ . In this section we follow the description given by the authors in Ref. 14.

The number of  $M_2$  terms is  $p_2$  with the relation  $n = p_1 + p_2$ . The  $M_2$  terms are distributed in all time positions in the integrand. The sum over these terms makes the integrand a symmetric function with respect to all time permutations. Hence, the upper limits of the multiple integral (11) can be taken as  $t$  for all integrals with the respective combinatorial denominator  $(2n)!$ . Finally, we rewrite Eqs. (11) and (12) in a more convenient form

$$P(t) = \sum_{n=0}^{\infty} \sum_{p_1=0}^{2n} \frac{(2n)! 2^{2p_1}}{(2n)! (2p_1)! p_2! 2^{p_2}} \left(-\frac{\Delta_0^2}{4}\right)^{p_1} \times \int_0^t dt_{2n} \int_0^{t_{2n}} dt_{2n-1} \cdots \int_0^{t_2} dt_1 \cdots \left[ -\frac{1}{\pi \hbar} M_2(t_{p_1} - t_{p_1}) \right] \cdots \left[ -\frac{1}{\pi \hbar} M_2(t_{p_{i_2}} - t_{p_{j_2}}) \right] \cdots. \quad (17)$$

The combinatorial multiplier requires some additional explanation. The term  $(2n)!$  in the denominator is due to the symmetrization of the multidimensional integral (the change of the upper limits from  $t_i$  to  $t$ ). The term  $(2n)!/(2p_1)!p_2!$  appears because of the combinatorial distribution in time of terms with  $\Delta_0$  and  $M_2$  in the integrand. Since all  $\Delta_0$  ( $2p_1$  terms) and  $M_2$  ( $p_2$  terms) contributions are distinguish-

able, the total number of permutations  $(2n)!$  should be divided by  $2^{p_1}!$  and  $p_2!$ , respectively. The term  $2^{2p_1}$  in the numerator is due to identical contributions from amplitudes  $\sigma_x$  and  $\tilde{\sigma}_x$ . Term  $2^{p_2}$  in the denominator appears due to the irrelevance of the time order for all  $M_2$  terms in the integrand of Eq. (17) where each  $M_2$  term should be divided by two.

The series (17) can be calculated exactly. Indeed, instead of the summation over  $n$  and  $p_1$ , we can change the parameters of the summation to  $p_1$  and  $p_2$ . Thus, the transition probability yields

$$P(t) = \sum_{p_1=0}^{\infty} \sum_{p_2=0}^{\infty} \frac{(-\Delta_0^2)^{p_1} t^{2p_1}}{(2p_1)!} \frac{1}{p_2!} \times \left( -\frac{1}{2\pi\hbar} \int_0^t dt_1 \int_0^t dt_2 M_2(t_2 - t_1) \right)^{p_2}. \quad (18)$$

After the summation, one obtains the following expression for the transition probability difference:

$$P(t) = \cos(\Delta_0 t) \exp[-\Gamma_m(t)], \quad (19)$$

where<sup>14,42,43</sup>

$$\Gamma_m(t) \equiv \frac{1}{2\pi\hbar} \int_0^t dt_1 \int_0^t dt_2 M_2(t_2 - t_1). \quad (20)$$

Equations (19) and (20) coincide with the expression for the transition probability obtained by two different methods:<sup>14</sup> (i) a canonical transformation method and (ii) a Keldysh function technique.

Another important particular case that will be considered here is the transition probability in the noninteracting blip approximation. In the noninteracting blip approximation for the solvation modes, we first symmetrize these equations and then demonstrate how to solve them to obtain exponential evolution with the golden rule expression for the rate constant.<sup>39,40</sup>

### III. METHOD OF ASYMPTOTIC SYMMETRIZATION

To find a solution of Eqs. (11)–(15), we employ the noninteracting blip approximation (NIBA). The validity condition for the NIBA was described by Leggett *et al.* in Ref. 39. The main assumption of the NIBA is that the ratio satisfies

$$\frac{\Delta_0}{\omega_c} \ll 1, \quad (21)$$

where  $\omega_c$  is a cut-off frequency for the relaxation of the solvation medium. This equation implies slow tunneling with respect to fast bath relaxation. Such an assumption enormously simplifies the solution of the problem resulting in the following expression for the transition probability difference:<sup>39,40,44</sup>

$$P(t) = \sum_{n=0}^{\infty} \sum_{p_1=0}^n (-\Delta_0^2)^{p_1} \int_0^t dt_{2n} \cdots \int_0^{t_2} dt_1 S_{p_2}(t_1, \dots, t_{2n}) \times \prod_{j=1}^n f(t_{2j} - t_{2j-1}), \quad (22)$$

where the function  $f(t_{2j} - t_{2j-1})$  stands for

$$f(t) = \cos \left[ \frac{1}{\pi\hbar} Q_1(t) \right] \exp \left[ -\frac{1}{\pi\hbar} Q_2(t) \right]. \quad (23)$$

In the absence of the modulation ( $S_{p_2}=0$ ), the standard approach for solution is to employ a Laplace transform.<sup>39</sup> This method becomes useless for the solution of Eq. (22) due to the symmetric function  $S_{p_2}$  modulating the integrand. To find a solution, we modify the product of  $f$  functions (23) in Eq. (22) by the complete symmetrization of this product with respect to the time differences, i.e., we introduce additional terms such as  $f(t_i - t_j)$  where  $i$  and  $j$  are arbitrary rather than  $t_{2j} - t_{2j-1}$ . According to the validity condition (21) for the NIBA, these additional terms in the symmetric sum of the different products do not essentially change the original product in Eq. (22) since these extra terms go to zero for larger time differences.<sup>44</sup> In accordance with Refs. 39 and 45, only the terms with the time difference of  $t_{2j} - t_{2j-1}$  (the blips) survive at longer times ( $\Delta_0 t \gg 1$ ). Thus, we follow the prescription that consists of (a) complete symmetrization of the integrand in Eq. (22) and (b) taking the limit  $t \rightarrow \infty$  in order to nullify the contribution of the additional terms artificially introduced into Eq. (22). Such a procedure is called *asymptotic symmetrization*.

To ensure that the *asymptotic symmetrization* works well, we rederive the golden-rule (NIBA) rate constant for the exponential evolution by using the method of *asymptotic symmetrization*. With no modulation (all the  $S_{p_2}$  equal zero), the symmetrized expression for the transition probability difference yields

$$P(t) = \sum_{n=0}^{\infty} (-\Delta_0^2)^n \int_0^t dt_{2n} \cdots \int_0^{t_2} dt_1 \tilde{F}_n(t_1, \dots, t_{2n}), \quad (24)$$

where the symmetric function  $\tilde{F}_n$  is defined in the following manner:

$$\tilde{F}_n(t_1, \dots, t_{2n}) \equiv \sum_{i,j\text{-perm}} f(t_{i_1} - t_{j_1}) \cdots f(t_{i_n} - t_{j_n}). \quad (25)$$

There are  $n$  terms in the product (25). Since the function  $\tilde{F}_n$  is symmetric with regard to variables  $t_1, \dots, t_{2n}$ , we present the multiintegral in a symmetric form where all of the upper limits in the integrals are the same and equal  $t$

$$\begin{aligned}
 P(t) &= \sum_{n=0}^{\infty} (-\Delta_0^2)^n \int_0^t dt_{2n} \cdots \int_0^{t_2} dt_1 \tilde{F}_n(t_1, \dots, t_{2n}) \\
 &= \sum_{n=0}^{\infty} \frac{1}{n!} (-\Delta_0^2)^n \int_0^t dt_{2n} \cdots \int_0^t dt_1 \tilde{F}_n(t_1, \dots, t_{2n}) \\
 &= \sum_{n=0}^{\infty} \frac{1}{n!} \left( -\frac{\Delta_0^2}{2} \int_0^t dt_2 \int_0^t dt_1 f(t_2 - t_1) \right)^n. \quad (26)
 \end{aligned}$$

Consequently, the series in Eq. (26) can readily be found

$$P(t) = \exp\left(-\frac{\Delta_0^2}{2} \int_0^t dt_2 \int_0^t dt_1 f(t_2 - t_1)\right), \quad (27)$$

where  $f(t)$  is defined by Eq. (23). In the limit of  $t \rightarrow \infty$ , the double integral can be asymptotically evaluated by parts. Indeed,

$$\begin{aligned}
 \frac{\Delta_0^2}{2} \int_0^t dt_2 \int_0^t dt_1 f(t_2 - t_1) &= \Delta_0^2 \int_0^t dt_2 \int_0^{t_2} dt_1 f(t_2 - t_1) \\
 &\simeq t \cdot \Delta_0^2 \int_0^{\infty} f(\tau) d\tau - \Delta_0^2 \int_0^{\infty} \tau \cdot f(\tau) d\tau. \quad (28)
 \end{aligned}$$

The latter integral is convergent and therefore, at a longer time it is much lesser than the former term. Moreover, it was proved by Leggett *et al.*<sup>45</sup> that the latter integral is much lesser than one. Hence, it can be safely neglected. Then the former term in Eq. (28) represents the exponent with the golden-rule rate constant.<sup>39</sup>

Thus, we have proved that the NIBA solution<sup>39</sup> can be obtained from Eq. (24) by applying the asymptotic symmetrization technique:

$$P_{\text{NIBA}}(t) = \exp(-\Gamma_{\text{NIBA}} t), \quad (29)$$

where

$$\begin{aligned}
 \Gamma_{\text{NIBA}} &= \Delta_0^2 \int_0^{\infty} f(\tau) d\tau \\
 &= \Delta_0^2 \int_0^{\infty} \cos\left[\frac{1}{\pi\hbar} Q_1(t)\right] \exp\left[\frac{1}{\pi\hbar} Q_2(t)\right] dt. \quad (30)
 \end{aligned}$$

Since the asymptotic symmetrization works well for the NIBA, we apply this method to find the solution of Eq. (22) with  $\tilde{F}_{p_2}$  instead of  $F_{p_2}$  in the integrand. In the same manner as in Ref. 14, we present the integral in the following form:

$$\begin{aligned}
 P(t) &= \sum_{n=0}^{\infty} \sum_{p_1=0}^{2n} \frac{(2n)! (-\Delta_0^2)^{p_1}}{(2n)! (2p_1)! p_2! 2^{p_2}} \int_0^t dt_{2n} \cdots \\
 &\times \int_0^t dt_1 \left[ -\frac{1}{\pi\hbar} M_2(t_{p_1} - t_{p_1}) \right] \cdots \\
 &\times \left[ -\frac{1}{\pi\hbar} M_2(t_{p_2} - t_{p_2}) \right] \cdots
 \end{aligned}$$

$$\times \sum_{i,j\text{-perm}} f(t_{i_1} - t_{j_1}) \cdots f(t_{i_n} - t_{j_n}). \quad (31)$$

The combinatorial multiplier requires some additional explanation. The term  $(2n)!$  in the denominator is due to the symmetrization of the multidimensional integral (the change of the upper limits from  $t_i$  to  $t$ ). The term  $(2n)!/(2p_1)!p_2!$  appears because of the combinatorial distribution in time of terms with  $\Delta_0$  and  $M_2$  in the integrand. Since all  $\Delta_0$  ( $2p_1$  terms) and  $M_2$  ( $p_2$  terms) contributions are distinguishable, the total number of permutations ( $(2n)!$  should be divided by  $2p_1!$  and  $p_2!$ , respectively. Term  $2^{p_2}$  in the denominator appears due to the irrelevance of the time order for all  $M_2$  terms in the integrand of Eq. (31) where each  $M_2$  term should be divided by two. Equation (31) can be rewritten in the same manner as Eq. (27)

$$\begin{aligned}
 P(t) &= \exp\left(-\frac{\Delta_0^2}{2} \int_0^t dt_2 \int_0^t dt_1 f(t_2 - t_1)\right) \\
 &\quad - \frac{1}{2\pi\hbar} \int_0^t dt_2 \int_0^t dt_1 M_2(t_2 - t_1) f(t_2 - t_1), \quad (32)
 \end{aligned}$$

At  $\Delta_0 t \gg 1$ , the former term results in the golden-rule expression described by Eqs. (29) and (30). Additionally, there is the second rate constant  $\Gamma_M$  that is due to the latter term in Eq. (32)

$$\begin{aligned}
 \Gamma_M &= \frac{1}{\pi\hbar} \int_0^{\infty} dt M_2(t) f(t) \\
 &= \frac{1}{2\hbar} \sum_i \frac{C_i^2}{M_i \Omega_i} \coth\left(\frac{\beta\Omega_i}{2}\right) \int_0^{\infty} dt \cos(\Omega_i t) \\
 &\quad \times \cos\left(\frac{1}{\pi\hbar} Q_1(t)\right) \exp\left(-\frac{1}{\pi\hbar} Q_2(t)\right). \quad (33)
 \end{aligned}$$

Hence, the evolution of the transition modulated for the electron by vibrations is given by

$$P(t) = \exp(-\Gamma_{\text{NIBA}} t) \exp(-\Gamma_M t) \quad (34)$$

where  $\Gamma_{\text{NIBA}}$  is given by Eq. (30). The integrand in the expression for  $\Gamma_M$  can be viewed as the partial rate constant with the bias (or reaction heat) equal to  $\hbar\Omega_i$ .

To analyze the result described by Eqs. (33) and (34), we assume that only a single mediation mode with the frequency  $\Omega_0$  modulates the electron transfer. Thus, the rate constant (33) becomes

$$\Gamma_M = \Delta_M^2 \int_0^{\infty} dt \cos(\Omega_0 t) \cos\left(\frac{1}{\pi\hbar} Q_1(t)\right) \exp\left(-\frac{1}{\pi\hbar} Q_2(t)\right), \quad (35)$$

where

$$\Delta_M^2 \equiv \frac{C_0^2}{2\hbar M_0 \Omega_0} \coth\left(\frac{\beta\Omega_0}{2}\right). \quad (36)$$

In this equation the modulation rate constant has the same form as the golden-rule rate constant with the bias  $\epsilon = \hbar\Omega_0$ .<sup>39,40</sup>

Following the standard procedure, the integral (35) can be performed in the saddle point approximation resulting in the effective golden-rule formula

$$\Gamma_M = \frac{\hbar \Delta_M^2(q)}{4} \sqrt{\frac{\pi}{E_r k_B T}} \left[ \exp\left(-\frac{(E_r - \hbar \Omega_0)^2}{4E_r k_B T}\right) + \exp\left(-\frac{(E_r + \hbar \Omega_0)^2}{4E_r k_B T}\right) \right]. \quad (37)$$

The expression for the rate constant in the non-Condon approximation was obtained by Medvedev and Stuchebrukhov,<sup>13</sup> Cukier,<sup>6</sup> Suarez and Silbey,<sup>4</sup> and Borgis and Hynes<sup>5</sup> where the interaction between the electron and modulating vibrations was chosen to be exponential. The latter interaction is valid when the electron modulation oscillator reservoir is strong. In this work the modulation bath however, has been presented by a set of oscillators  $\{q_j\}$  linearly interacting with the electron [see Eq. (1)]. The rate constant described by Eqs. (33) and (37) coincides with the expression obtained by Medvedev and Stuchebrukhov<sup>13</sup> and Cukier.<sup>6</sup> With the proper expansion of their results we arrive at the expression obtained in this work.

The direct averaging of the rate constant over modulation oscillators<sup>6,13</sup> requires an additional justification since in statistical mechanics only observables operators can be averaged. In this problem such an operator is the quantum transition probability  $\langle \psi(t) | \psi(t) \rangle_T$ , rather than the rate constant  $\Gamma$ . Thus, we have rigorously proved that the direct averaging of the rate constant is correct in the NIBA, and consequently, the Hamiltonian (1) can be generalized to an anharmonic bath as well.<sup>13</sup> It is not obvious that such an assumption is valid due to the strong correlations between the  $M$  terms (the modulation terms) and the  $F$  terms (the solvation terms) in the exact expression for the transition probability [see Eqs. (11)–(15)]. In the derivation described by Eqs. (31)–(36) it has been assumed that inequality (21) is valid, i.e., the dissipation  $\omega_c$  due to the interaction with vibrations is much faster than the electron shuttling frequency  $\Delta$ . This assumption allows us to neglect the correlations between different blips, or different tunneling events (see Leggett *et al.*<sup>39</sup>). In the NIBA each tunneling transition is treated independently, i.e., a short memory has been assumed due to the strong dissipation.<sup>39,40</sup>

#### IV. CONCLUSIONS

In this work we have found the exact expression for total time-dependent probability described by Eqs. (11)–(15). This allows us to analyze fast (with a nonequilibrium bath) electron transfer reactions where vibrational coherence was found.<sup>19,21–33</sup> The main feature of the experimental dependencies is strong coherent oscillations and nonexponential (slower) decay. Since this research is focused only on symmetric electron transfer we still are not able to provide a complete quantitative description of primary electron transfer in photosynthetic bacteria and fast nonequilibrium processes taking place in electron injection on TiO<sub>2</sub> nanoelectrodes in solar cells.<sup>46,47</sup> A generalization of the theory to biased tunneling is necessary.

The method we have used to derive the exact expression for the transition probability described by Eqs. (11)–(15), is the extension of the path-integral technique developed by Feynmann and Vernon<sup>41</sup> for a polaron problem and later employed by Leggett *et al.*<sup>39</sup> for electron tunneling between two states. As in the Feynman-Vernon approach we have integrated out the coordinates of oscillators for the two oscillator baths reducing the transition probability to a simpler expression that is described by a series of multidimensional integrals that excludes all the path integrals over oscillator trajectories [see Eqs. (11)–(15)]. For the future research such a representation can be useful for numerical calculations.

As a particular case of the absence of the solvation bath  $\{x_j\}$  we have demonstrated that the transition probability can be exactly derived exhibiting coherent oscillations and non-exponential decay [see Eqs. (19) and (20)]. Thus, for a weak solvation bath the transition probability cannot be simply described by exponential function with the rate constant.<sup>14</sup> The main difference between the results found in Ref. 14 and those of obtained in this work is that an additional (solvation) oscillator bath was introduced that provides more efficient relaxation for the electron dynamics. Indeed, in this case the electron evolution is exponential while in the absence of the solvation bath the relaxation is much slower.<sup>14</sup>

The rate constant in the non-Condon approximation was also studied by Medvedev and Stuchebrukhov,<sup>13</sup> Cukier,<sup>6</sup> Suarez and Silbey,<sup>4</sup> and Borgis and Hynes.<sup>5</sup> The modulation effect was introduced by the direct averaging of the rate constant over the modulation degrees of freedom.<sup>6,13</sup> Such an approximation requires an additional justification of their thermodynamic averaging procedure since in statistical mechanics only observables operators can be averaged. In this problem such an operator is the transition probability  $\langle \psi(t) | \psi(t) \rangle_T$  rather than the rate constant  $\Gamma$ . Thus, it is important to understand if the rate constant, obtained by Medvedev and Stuchebrukhov<sup>13</sup> provides the correct expression. However, there are some differences in the description for the electron-vibration interaction introduced in this research and in Ref. 13. In this work, the modulation bath has been chosen as a set of oscillators  $\{q_j\}$  linearly interacting with the electron [see Eq. (1)] rather than more general exponential interaction employed by Medvedev and Stuchebrukhov<sup>13,50</sup> and Cukier.<sup>6</sup> However, it is still possible to compare the results obtained by these authors with the rate constant described by Eqs. (33) and (37) after a proper expansion for small interaction coefficients  $C_i$  in the Hamiltonian (1). As a result of such comparison, we conclude that Eqs. (33) and (37) coincide with the expression obtained by Medvedev and Stuchebrukhov<sup>13</sup> where the interaction between the electron and modulating vibration was chosen to be both exponential (see also Cukier<sup>6</sup>) and linear. The former interaction is valid when the electron modulation oscillator reservoir is strong. Thus, we have rigorously proved that the direct averaging of the rate constant is correct in the NIBA. Moreover, Medvedev and Stuchebrukhov<sup>13</sup> used an anharmonic bath as a reservoir. This allows them to extend the Hamiltonian to anharmonic potential energy surfaces. In the beginning it is not obvious that a direct averaging of the rate constant by the modulation modes would provide the correct result. Such a procedure is only valid when inequality (21)

holds. In the NIBA the tunneling events (blips) are considered independent due to the fast and strong interaction of the electron with the bath modes.<sup>39,40</sup> If there are some slow degrees of freedom, the NIBA becomes unphysical. Indeed the reaction has already been over but some degrees of freedom are not in equilibrium. The details of electron transfer in a nonequilibrium bath were given by Hornbach and Dakhnovskii<sup>48</sup> and Dakhnovskii.<sup>49</sup>

Symmetric electron transfer studied in this work can be applied to electron transport in molecular wires. The symmetry of the donor and acceptor states implies that molecular bridges should be polyene chains. There is an important connection between the rate constant and electrical current found by Nitzan,<sup>37,38</sup> where incoherent electrical current can be expressed in terms of the rate constant calculated for a proper electron transfer reaction. This connection facilitates the calculations of a current for polyene molecular wires. Such systems were intensively studied theoretically<sup>51,52</sup> and experimentally.<sup>53</sup> In particular, the experimental current voltage characteristics for carotenoid polyene chains attached to gold electrodes were obtained by Lindsay and coworkers.<sup>53</sup> They used a conducting atomic force microscope to measure the electrical properties of carotenoid molecules attached to a gold electrode where thiolated carotene molecules were embedded in insulating *n*-alkanethiol self-assembled monolayers. The results of the present research indicate that the modulation of the electron transport by vibrations enhances the electron tunneling increasing the electrical current. However, a quantitative application of the present research to particular molecular wires requires quantum chemical calculations of the parameters for particular systems.

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#### APPENDIX: DOUBLE FLIPS

In this Appendix we discuss the reasons why  $M_1$  terms do not contribute to the integrand of Eq. (11) in contrast to  $M_2$ -terms contributions.

Indeed, the two transitions taking place at the times  $t_i$  and  $t_j$  ( $i > j$ ) can be due to the following terms:<sup>14</sup>(a)  $\sigma_x(t_i)\sigma_x(t_j)$ , (b)  $\sigma_x(t_i)\tilde{\sigma}_x(t_j)$ , (c)  $\tilde{\sigma}_x(t_i)\sigma_x(t_j)$ , and (d)  $\tilde{\sigma}_x(t_i)\tilde{\sigma}_x(t_j)$ . Case (a) can occur because of the transitions from bare amplitude,  $A$ ,  $M_1$ , and  $M_2$

$$\begin{aligned} & \left(1 - i\frac{\Delta_0}{2}dt_i\right)\left(1 - i\frac{\Delta_0}{2}dt_j\right), \\ & \left(1 + \frac{i}{\pi\hbar}M_1(t_i - t_j)dt_idt_j\right), \\ & \left(1 - \frac{1}{\pi\hbar}M_2(t_i - t_j)dt_idt_j\right). \end{aligned} \quad (\text{A1})$$

Case (b) can occur because of the following transitions:

$$\begin{aligned} & \left(1 - i\frac{\Delta_0}{2}dt_i\right)\left(1 + i\frac{\Delta_0}{2}dt_j\right), \\ & \left(1 + \frac{i}{\pi\hbar}M_1(t_i - t_j)dt_idt_j\right), \\ & \left(1 + \frac{1}{\pi\hbar}M_2(t_i - t_j)dt_idt_j\right). \end{aligned} \quad (\text{A2})$$

Case (c) can occur because of the following transitions:

$$\begin{aligned} & \left(1 + i\frac{\Delta_0}{2}dt_i\right)\left(1 - i\frac{\Delta_0}{2}dt_j\right), \\ & \left(1 - \frac{i}{\pi\hbar}M_1(t_i - t_j)dt_idt_j\right), \\ & \left(1 + \frac{1}{\pi\hbar}M_2(t_i - t_j)dt_idt_j\right). \end{aligned} \quad (\text{A3})$$

Finally, case (d) can occur because of the following transitions:

$$\begin{aligned} & \left(1 + i\frac{\Delta_0}{2}dt_i\right)\left(1 + i\frac{\Delta_0}{2}dt_j\right), \\ & \left(1 - \frac{i}{\pi\hbar}M_1(t_i - t_j)dt_idt_j\right), \\ & \left(1 - \frac{1}{\pi\hbar}M_2(t_i - t_j)dt_idt_j\right). \end{aligned} \quad (\text{A4})$$

Consider the flips due to  $M_1(t_i - t_j)$ . The flips with  $\sigma_x(t_i)\sigma_x(t_j)$  cancel out with the flips due to  $\tilde{\sigma}_x(t_i)\tilde{\sigma}_x(t_j)$  if all the remaining flips are unchanged. The sum is true for the flips due to  $\sigma_x(t_i)\tilde{\sigma}_x(t_j)$ , and  $\tilde{\sigma}_x(t_i)\sigma_x(t_j)$ . Consequently, all the flips due to the  $M_1(t_i - t_j)$  terms vanish.

Consider the  $M_2(t_i - t_j)$  terms. Such terms also have altering signs. We prove that the contribution from these terms does not vanish. The total number of  $\sigma_x$  (or  $\tilde{\sigma}_x$ ) is even since the trajectory begins at “++” and ends at the same state. The cases (a) and (d) contribute to the transitions with the minus sign “-” (we remember that the rest of the terms remain unchanged).

Analysis of the  $M_2$  contribution should be considered in conjunction with the  $\Delta_0$  terms. For the cases (b) and (c),  $M_2$  transitions should be complemented by the pair of  $\Delta_0$  transitions

$$\sigma_x(t_i)\tilde{\sigma}_x(t_j) \cdots \sigma_x(t_k)\tilde{\sigma}_x(t_l) \cdots. \quad (\text{A5})$$

The first two terms correspond to a  $M_2$  transition while the second two terms correspond to  $(-i\Delta_0/2)$  and  $(+i\Delta_0/2)$  for case (b). In case (c), the appropriate transition  $\sigma_x \leftrightarrow \tilde{\sigma}_x$  for these four transitions is

$$\tilde{\sigma}_x(t_i)\sigma_x(t_j) \cdots \tilde{\sigma}_x(t_k)\sigma_x(t_l) \cdots. \quad (\text{A6})$$

The total contribution from these two transitions does not vanish resulting in

$$+ \frac{1}{\pi\hbar} M_2(t_i - t_j) dt_i dt_j \cdots \left(-i \frac{\Delta_0}{2}\right) \left(+i \frac{\Delta_0}{2}\right) dt_k dt_l \quad (\text{A7})$$

for case (b) and

$$+ \frac{1}{\pi\hbar} M_2(t_i - t_j) dt_i dt_j \cdots \left(+i \frac{\Delta_0}{2}\right) \left(-i \frac{\Delta_0}{2}\right) dt_k dt_l \quad (\text{A8})$$

for case (c). Thus these two transitions doubly contribute. Similarly, the sign “+” appears for

$$\sigma_x(t_i) \sigma_x(t_j) \cdots \sigma_x(t_k) \sigma_x(t_l) \cdots \quad (\text{A9})$$

in case (a) and

$$\tilde{\sigma}_x(t_i) \tilde{\sigma}_x(t_j) \cdots \tilde{\sigma}_x(t_k) \tilde{\sigma}_x(t_l) \cdots \quad (\text{A10})$$

in case (d) corresponding to the following terms:

$$- \frac{1}{\pi\hbar} M_2(t_i - t_j) dt_i dt_j \cdots \left(-i \frac{\Delta_0}{2}\right) \left(-i \frac{\Delta_0}{2}\right) dt_k dt_l$$

(A11)

for case (a) and

$$- \frac{1}{\pi\hbar} M_2(t_i - t_j) dt_i dt_j \cdots \left(+i \frac{\Delta_0}{2}\right) \left(+i \frac{\Delta_0}{2}\right) dt_k dt_l$$

(A12)

for case (d). Hence, all four transitions make the same contribution independent of the sign for  $M_2$  (“+” or “-”). We adopt the sign “-” for  $M_2$  flips and the sign “-” for the  $\Delta_0$  double transition ( $-\Delta_0^2/4$ )—the same as in Eqs. (11) and (12).

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