Driven electron transfer in an environment with slow and fast degrees of freedom

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Driven electron transfer in a polar medium with slow and fast degrees of freedom is studied in the framework of a spin-boson Hamiltonian. Evolution dynamics is rigorously found when $\omega_c^s/(\Gamma(a))\sqrt{E_{rs}/kT} \ll 1$, where ω_c^s is the Debye cutoff frequency in the spectral function for the slow modes, E_{rs} is the reorganization energy of slow degrees of freedom, and $\Gamma^{-1}(a)$ is the reaction time dependent on the laser intensity parameter $a = \mu E_0/\hbar\omega$. Here ω and E_0 are the frequency and the amplitude of a cw electric field, and μ is the electron dipole moment difference between the initial and final states. The master equation is derived for an arbitrary driving force affecting both the transition matrix element and the potential energy. For a cw electric field, the time dependent probability of staying at the product state, $P_1(t)$, is shown to be strongly dependent on the field intensity parameter a: $P_1(a,t) \sim (\Gamma_{m_1,m_2}t)^{-E_{rf}/E_{rs}}$ or $P_1(a,t) \sim (\Gamma_{m_0}t)^{-E_{rf}/E_{rs}}$, double or single resonances, respectively. Here E_{rf} is the reorganization energy of fast degrees of freedom, $\Gamma_{m_1,m_2} \sim J_{m_1}^2(a) + J_{m_2}^2(a)$, and $\Gamma_{m_0} \sim J_{m_0}^2(a)$, where $J(a)$ is a Bessel function. By changing the parameter a, one is able to manipulate the rate and direction of the reaction. When $J_{m_0}^2(a)$ is close to zero the reaction is slow. Hence, slow modes turn out to be fast. This changes the character of the evolution dynamics from non- to mono- exponential decay, respectively. For the double resonance, the equilibrium constant is studied with the field intensity. It is shown that the reaction is almost insensitive to temperature. However, it strongly depends on the reaction heat, which provides a condition for the resonance.

I. INTRODUCTION

Recent experimental studies of electron transfer dynamics in solution [1–13] and proteins [14–20] established ultrafast time scales in the region <100 fs. For such fast reactions, one expects that nuclear relaxation processes become essential. An ordinary description based on the transition state theory [21–24], the variational transition state theory [25–27], the Kramers-Grote-Hynes approach [28–32], or nonadiabatic transition described by the Golden Rule [33–35] is questionable [36–38] in the non-equilibrium environment. Relaxation dynamics of the bath modes should be taken into account. The bath relaxation can be considered by a few different approaches. Marcus and co-workers [39,40] proposed a phenomenological picture of slow mode dynamics. The Markovian description of the dynamical system relaxation is valid for times longer than the correlation time of the bath. For shorter times a microscopic approach is necessary. Hornbach *et al.* [41] employed a description based on a microscopic spin-boson Hamiltonian for electron transfer in slow solvents. For some solvents, both slow and fast modes affect the electron transfer [42]. Consequently, dynamics becomes essentially non-exponential [43] under the following assumptions:

$$\frac{\omega_c^s}{\Gamma}\sqrt{\frac{E_{rs}}{kT}} \ll 1, \tag{1}$$

where ω_c^s is the Debye cutoff frequency in the spectral function for the slow degrees of freedom, E_{rs} is the reorganization energy of the slow degrees of freedom, and Γ^{-1} is the typical reaction time. It has been assumed that clear separation between slow and fast degrees of freedom takes place. However, this is not always so. There exists a coupling between slow and fast modes. Such a coupling is not considered in this work. In general, slow bath dynamics was studied by many authors: Chandler and Wolynes [44,45], Carmeli and Chandler [46], and Coalson [47] were mostly interested in thermodynamic properties. Coalson [48,49] considered a spectroscopic form of a spin-boson Hamiltonian. Evans *et al.* [50] numerically analyzed spectroscopic data [5–11] of electron transfer in mixed-valence compounds. As shown in Ref. [43], at longer times the transition probability, $P(t)$, for the activationless reaction can be described by the power law evolution:

$$P(t) \sim t^{-E_{rf}/E_{rs}}, \tag{2}$$

where E_{rf} is the reorganization energy of the fast modes. Such a dependence is essentially non-exponential. Hence, the dynamics cannot be presented as a two exponential process either.

Recent theoretical studies of long-range electron transfer driven by a laser present opportunities to manipulate a reaction—accelerating, decelarating, or even changing a direction of the transfer process. Indeed, as shown in Ref. [51], the reaction rate exhibits giant resonances depending upon the laser intensity. Different types of manipulation by a driving force were demonstrated in Refs. [52–54]. Driven ET in

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a stochastic medium was investigated in Refs. [55,56]. Numerical methods were developed in Refs. [57–59]. Recently, electric field modulation of the transition matrix element has also been considered [60,61]. In this work, we continue to study the effect of a strong time-dependent electric field on electron tunneling in a polar solvent. However, we extend the previous analysis to the case when both slow and fast degrees of freedom are presented in a solvent.

To describe microscopic the dynamics of the electron tunneling, we employ the approach based on the spin-boson Hamiltonian [62–64]:

$$\hat{H}_{SB} = -\frac{1}{2}\hbar\Delta\hat{\sigma}_x - \frac{1}{2}\epsilon\hat{\sigma}_z + \frac{1}{2}\sum_k \left(\frac{p_k^2}{m_k} + m_k\omega_k^2 q_k^2\right)$$

$$+ \frac{1}{2}\hat{\sigma}_z\sum_k g_k q_k, \qquad (3)$$

where the set of oscillators $\{k\}$ of mass $\{m_k\}$ and frequency $\{\omega_k\}$ represents the slow and fast environment, $\{g_k\}$ are coupling constants in the electron-boson interaction, and ϵ is the energy difference between the minima of the initial and final electronic states (the reaction heat). The electronic state associated with the $|+\rangle$ eigenstate of $\hat{\sigma}_z$ (with eigenvalue $+1$) shall be designated as the donor electronic state. The other electronic base state is then the acceptor state. A transition between two states is due to the first term in the Hamiltonian with the transition matrix element Δ. As usual [51,52,64], we introduce an electric field into the Hamiltonian with the following term:

$$\hat{H}_f = -\frac{1}{2}\mu E(t)\hat{\sigma}_z, \qquad (4)$$

where μ is the dipole moment difference between the donor and acceptor states, and $E(t)$ is the external electric (laser) field. Thus, the final Hamiltonian is given by

$$\hat{H} = \hat{H}_{SB} + \hat{H}_f. \qquad (5)$$

Experimentally, strong field effects can be observed in long range electron transfer. Larger tunneling distances become vitally important so that the breakdown threshold for the electric field in dielectrics is not exceeded. According to estimations made in Refs. [65–67], the breakdown threshold is about $10^6 - 10^7$ V/cm. Consequently, the electron tunneling range should be larger than $15-17$ Å [52,53]. Thus, primary long-range electron transfer in bacterial photosynthetic centers is a good candidate for the experimental observation of strong field effects in chemical dynamics. Indeed, the primary ET is rather fast in order to satisfy condition my (1), and the electron tunneling distance is larger than 15 -17 Å [68]. Interestingly, there are some other materials where an electron tunneling distance is even larger, $\propto 40$ Å [69]. We assume that the environment for these reactions contains slow modes. Thus, the incorporation of slow bath dynamics into the consideration of driven electron transfer becomes important. Here, one expects the electron transfer kinetics to be non-exponential. Slow and fast relaxation were

experimentally observed in some alcohols. For instance, according to Huppert and co-workers [42], solvation relaxation in *hexanol* can be approximated by two exponents with the Debye relaxation times $\tau_f = 2$ ps and $\tau_{sl} = 33.3$ ps.

As mentioned above, the electric field can decelerate the reaction. If the reaction rate becomes much smaller than the Debye cutoff frequency, inequality (1) is no longer valid. Slow modes turn out to be fast. Consequently, the reaction reveals mono-exponential evolution.

In this work we consider how a time-dependent electric field changes the dynamics of electron transfer in a polar environment (e.g., solvent), which contains both slow and fast degrees of freedom. The paper is organized as follows: in Sec. II we present the theory which allows us to derive a master equation for the transition probability for the electron to be in the donor state. In Sec. III we study $P(t)$ for high temperatures and different values of the parameters. In Sec. IV we discuss and conclude.

II. A TIME-DEPENDENT PROBABILITY

The most rigorous approach used to describe non-adiabatic electron transfer is based on an analysis of the problem in the framework of spin-boson Hamiltonian Eq. (5). The transition probability can be found as an exact formal expansion with respect to the value of a transition matrix element Δ [62], which, in our case, is modified by the driving force (see function F_4 below) [64]

$$P(t) = \sum_{n=0}^{\infty}\left(-\frac{\Delta^2}{2}\right)^n \sum_{\{\eta_j = \pm 1\}} \int_0^t dt_{2n}\int_0^{t_{2n}} dt_{2n-1}\cdots\int_0^{t_2} dt_1$$

$$\times F(t_1, t_2, \ldots t_{2n}; \eta_1, \eta_2, \ldots \eta_n; \epsilon, E), \qquad (6)$$

where

$$F = F_1\cdot F_2\cdot F_3\cdot F_4, \qquad (7)$$

$$F_1 \equiv \exp\left[-\sum_{j=1}^n S_j\right],$$

$$F_2 \equiv \exp\left[-\sum_{k=1}^n\sum_{j=k+1}^n \eta_j\eta_k\Lambda_{jk}\right],$$

$$F_3 \equiv \prod_{k=1}^{n-1}\cos\left[\sum_{j=k+1}^n \eta_j X_{jk}\right],$$

$$F_4 \equiv \cos\left[\sum_{j=1}^n \eta_j((t_{2j}-t_{2j-1})\epsilon + V(t_{2j})-V(t_{2j-1})-X_{j0})\right], \qquad (8)$$

and

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

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

$$- Q_2(t_{2j-1}-t_{2k-1}),$$

$$X_{jk} \equiv Q_1(t_{2j} - t_{2k+1}) + Q_1(t_{2j-1} - t_{2k}) - Q_1(t_{2j} - t_{2k})$$
$$- Q_1(t_{2j-1} - t_{2k+1}). \tag{9}$$

Furthermore, $Q_1(t)$, $Q_2(t)$, and $V(t)$ are defined as follows:

$$Q_1(t) = \frac{1}{\hbar \pi} \int_0^\infty d\omega \frac{J^s(\omega) + J^f(\omega)}{\omega^2} \sin(\omega t), \tag{10}$$

$$Q_2(t) = \frac{1}{\hbar \pi} \int_0^\infty d\omega \frac{J^s(\omega) + J^f(\omega)}{\omega^2} [1 - \cos(\omega t)] \coth\left(\frac{\hbar \omega}{2kT}\right), \tag{11}$$

$$V(t) = \mu \int_0^t E(\tau) d\tau. \tag{12}$$

Here $J^s(\omega)$ and $J^f(\omega)$ are the spectral densities of the slow and fast degrees of freedom, respectively [62]:

$$J^{s,f}(\omega) = \frac{\pi}{2} \sum_k \frac{(g_k^{s,f})^2}{m_k^{s,f} \omega_k^{s,f}} \delta(\omega - \omega_k^{s,f}). \tag{13}$$

$J(\omega)$ can be expressed through the dielectric loss function of slow and fast polar modes (see, e.g., Refs. [51,70]):

$$J^{s,f}(\omega) = \frac{\pi E_{rs,f}}{2} \frac{\text{Im}\epsilon^{s,f}(\omega)/[\omega|\epsilon^{s,f}(\omega)|^2]}{\int_0^\infty d\omega \text{Im}\epsilon^{s,f}(\omega)/(\omega|\epsilon^{s,f}(\omega)|^2)}, \tag{14}$$

where the reorganization energy of the slow or fast modes is determined from the following equation [71]:

$$E_r^{s,f} = \frac{1}{4\pi^2} \int dv |\Delta \mathbf{D}^{s,f}(\mathbf{r})|^2 \cdot \int_0^\infty d\omega \frac{\text{Im}\epsilon^{s,f}(\mathbf{r},\omega)}{\omega|\epsilon^{s,f}(\mathbf{r},\omega)|^2}. \tag{15}$$

Here, $\text{Im}\epsilon^{s,f}(\mathbf{r},\omega)$ is the imaginary part of the dielectric function, $\epsilon^{s,f}(\mathbf{r},\omega)$ of the slow or fast modes, respectively.

$$\Delta \mathbf{D}^{s,f}(\mathbf{r}) \equiv \mathbf{D}_A^{s,f}(\mathbf{r}) - \mathbf{D}_D^{s,f}(\mathbf{r}) \tag{16}$$

is the difference between the induction vectors at the acceptor and donor sites [71]. For the Debye spectrum, the dielectric loss function takes the following form [71]:

$$\frac{\text{Im}\epsilon^{s,f}(\omega)}{|\epsilon^{s,f}(\omega)|^2} = \left(\frac{1}{\epsilon_0} - \frac{1}{\epsilon_\infty}\right) \cdot \frac{\omega/\omega_c^{s,f}}{1 + (\omega/\omega_c^{s,f})^2}. \tag{17}$$

ϵ_0 and ϵ_∞ stand for the optical and static dielectric constant, respectively; $\omega_c^{s,f} = 1/\tau_L^{s,f}$, where $\tau_L^{s,f}$ are the longitudinal Debye relaxation times of slow or fast polar dipoles. Slow and fast mode dynamics implies that

$$\frac{\omega_c^s}{\omega_c^f} \ll 1, \tag{18}$$

$$\frac{\Delta}{\omega_c^s} \gg 1, \tag{19}$$

and

$$\frac{\Delta}{\omega_c^f} \ll 1. \tag{20}$$

The experiments of Huppert and co-workers [42] indicate the existence of solvents with two relaxation times. Equations (19) and (20) allow one to compare the dynamics of the coherent electron motion with relaxation of the slow and fast degrees of freedom. In the former case, the electron coherence frequency is much faster than the Debye cutoff frequency of the slow motion. For the fast modes, the opposite condition takes place. According to [62], inequality (20) justifies the non-interacting blip approximation (NIBA), which results in exponential dynamics with the rate constant determined by the Golden Rule expression [62]. As in Ref. [23], we apply the NIBA only to the fast degrees of freedom. However, the slow bath approximation introduced in Ref. [41] is employed to the slow solvent modes. The NIBA assumes that the relaxation of the fast modes is so fast that the electron transitions (blips) between two electron levels are not correlated in time [62]. Consequently, only the first term contributes to the function Λ_{ij} in Eq. (9)

$$Q_2^{fast}(t_{2j} - t_{2j-1}) \equiv G_2(t_{2j} - t_{2j-1}). \tag{21}$$

The same is true for the term F_3 in Eq. (9):

$$Q_1^{fast}(t_{2j} - t_{2j-1}) \equiv G_1(t_{2j} - t_{2j-1}). \tag{22}$$

An analysis of the slow modes is different [41,72]. All terms with different time intervals must be included. If the time of observation is much smaller than the relaxation time of the slow modes and much longer than the reaction time (see inequality (1)), one can expand the functions $Q_1^{slow}(t)$ and $Q_2^{slow}(t)$ with respect to the small parameter $(t\omega_c^s)$. According to Refs. [41,70,72] one finds that

$$Q_1^s(t) = \frac{E_r^s}{\hbar \omega_c^s} [t\omega_c^s - \tfrac{1}{2}(t\omega_c^s)^2],$$

$$Q_2^s(t) = \frac{E_r^s kT t^2}{\hbar^2} = \left(\frac{t}{\tau_0}\right)^2, \tag{23}$$

where τ_0 is the blip relaxation time defined as follows:

$$\tau_0 \equiv \frac{\hbar}{\sqrt{E_r^s kT}}. \tag{24}$$

In the previous derivation, we have assumed that (a) the temperature is high

$$\omega_c^s \ll kT, \tag{25}$$

and (b) $J^s(\omega)$ is described by the Debye spectral function (17). In approximation (23) the functions S^s_j, Λ^s_{jk}, and X^s_{jk} (defined by Eqs. (9)) are now quadratic functions of time:

$$S^s_j = \frac{(t_{2j} - t_{2j-1})^2}{\tau_0^2} \equiv \frac{\tau_j^2}{\tau_0^2},$$

$$\Lambda^s_{jk} = \frac{2}{\tau_0^2}(t_{2j} - t_{2j-1})(t_{2k} - t_{2k-1}) \equiv \frac{\tau_j \tau_k}{\tau_0^2}, \quad (26)$$

$$X^s_{jk} = \frac{E^s_r \omega^s_c}{\hbar}(t_{2j} - t_{2j-1})(t_{2k+1} - t_{2k}) \equiv \frac{E^s_r \omega^s_c}{\hbar} \tau_j s_k, (j > k)$$

where

$$\tau_j \equiv t_{2j} - t_{2j-1},$$
$$s_k \equiv t_{2k+1} - t_{2k} \quad (27)$$

are the lengths of the jth blip and kth sojourn, respectively. Combining $Q^{s,f}_{1,2}$ from Eqs. (21), (22), and (26), and substituting them into the total expression for S_j, Λ_{jk}, and X_{jk}, one obtains the following expression for the time-dependent probability difference:

$$P(t) = \sum_{n=0}^{\infty}\left(-\frac{\Delta^2}{2}\right)^n \sum_{\{\eta_j = \pm 1\}} \int_0^t dt_{2n} \int_0^{t_{2n}} dt_{2n-1} \cdots \int_0^{t_2} dt_1$$

$$\times \exp\left(-\sum_{j=1}^{n} G_2(t_{2j} - t_{2j-1}) - \frac{\Lambda_1^2}{\tau_0^2}\right)$$

$$\times \cos[(\epsilon - E_r)\Lambda_1 - \eta_1 G_1(t_2 - t_1)]$$

$$\times \prod_{k=1}^{n-1} \cos\left[\omega_c E_r \Lambda_{k+1} s_k + \sum_{j=k+1}^{n} \eta_j G_1\right.$$

$$\left.\times (t_{2j} - t_{2j-1})\delta_{j-1,k}\right], \quad (28)$$

where Λ_k is defined as follows [72]:

$$\Lambda_k \equiv \sum_{j=k}^{n} \eta_j \tau_j.$$
$$(\{\eta_j = \pm 1\}). \quad (29)$$

For short times the following condition is valid:

$$\omega_c E_r \Lambda_{k+1} s_k \ll 1. \quad (30)$$

Equation (30) is equivalent to inequality (1) when the parameters Λ_{k+1} and s_k are estimated as follows:

$$\Lambda_{k+1} \approx \tau_0 = \frac{\hbar}{\sqrt{E^s_r kT}}, \quad (31)$$

$$s_k \lesssim (\Gamma)^{-1}. \quad (32)$$

Λ_{k+1} should be comparable to the typical length of the blip, τ_0, while s_k must be smaller than the reaction time. This time is rather short, since the reaction is considered to be fast relative to the relaxation time of the slow modes. Condition (30) essentially simplifies calculations of series (28).

To find the multiple sum over the Ising indices $\eta_j = \pm 1$ we exploit the following integral representation:

$$\exp\left[-\frac{(\Sigma_j \eta_j \tau_j)^2}{\tau_0^2}\right] = \frac{1}{\pi}\int_{-\infty}^{\infty} dx$$

$$\times \exp(-x^2)\cos\left(\frac{2x}{\tau_0}\sum_j \eta_j \tau_j\right).$$
$$(33)$$

This integral transformation allows one to substitute the Gaussian exponent by a linear one. The time dependent probability, $P(t)$, can be presented in the following form:

$$P(t) \equiv \frac{1}{\sqrt{\pi}}\int_{-\infty}^{\infty} dx \exp(-x^2) P(x,t), \quad (34)$$

where the partial probability, $P(x,t)$, is defined as follows:

$$P(x,t) = \sum_{n=0}^{\infty}\left(-\frac{\Delta^2}{2}\right)^n \sum_{\{\eta_j = \pm 1\}} \int_0^t dt_{2n} \int_0^{t_{2n}} dt_{2n-1} \cdots \int_0^{t_2} dt_1$$

$$\times \exp\left(-\sum_{j=1}^{n} G_2(t_{2j} - t_{2j-1})\right)$$

$$\times \cos\left[\left(\sum_{j=2}^{n} \eta_j \frac{\epsilon(x)}{\hbar}(t_{2j} - t_{2j-1}) + V(t_{2j})\right.\right.$$

$$\left.+ V(t_{2j-1})\right) + \eta_1\left(\frac{\epsilon(x)}{\hbar}(t_2 - t_1) + V(t_2) - V(t_1)\right)$$

$$\left.- G_1(t_2 - t_1)\right)\left]\prod_{k=1}^{n-1} \cos[\eta_k G_1(t_{2_k} - t_{2k-1})]. \quad (35)$$

Here the random reaction heat stands for

$$\epsilon(x) \equiv \frac{2\hbar x}{\tau_0} + \epsilon - E_{rs}. \quad (36)$$

In Eq. (35) we have used the parity of the Gaussian distribution. Thus, cosines with $+x$ and $-x$ contribute equally. In Eq. (35) we have chosen cosine with $+x$.

By making use of the following transformation

$$\sum_{\{\eta_j = \pm 1\}} \cos\left[A\sum_j \eta_j \tau_j\right] = \sum_{\{\eta_j \pm 1\}}\prod_{i=1}^{n} \cos[A \eta_j \tau_j]$$

$$= 2^n \prod_{i=1}^{n} \cos(A \tau_j), \quad (37)$$

one obtains the following series for $P(x,t)$:

$$P(x,t)=\sum_{n=0}^{\infty}\left(-\frac{\Delta^2}{2}\right)^n\int_0^t dt_{2n}\int_0^{t_{2n}}dt_{2n-1}\cdots\int_0^{t_2}dt_1$$

$$\times\left[\prod_{j=1}^n g(x;t_{2j},t_{2j-1})\right.$$

$$\left.+h(x;t_2,t_1)\prod_{j=2}^n g(x;t_{2j},t_{2j-1})\right], \qquad (38)$$

where the function $g(x;t_{2j},t_{2j-1})$ and $h(x;t_{2j},t_{2j-1})$ are defined as follows:

$$g(x;t_{2j},t_{2j-1})\equiv\exp[-G_2(t_{2j}-t_{2j-1})]$$

$$\times\cos\left[\frac{\epsilon(x)}{\hbar}(t_{2j}-t_{2j-1})+V(t_{2j}-V(t_{2j-1})]\right]$$

$$\times\cos[G_1(t_{2j}-t_{2j-1})], \qquad (39)$$

and

$$h(x;t_{2j},t_{2j-1})\equiv\exp[-G_2(t_{2j}-t_{2j-1})]$$

$$\times\sin\left[\frac{\epsilon(x)}{\hbar}(t_{2j}-t_{2j-1})+V(t_{2j}-V(t_{2j-1})]\right]$$

$$\times\sin[G_1(t_{2j}-t_{2j-1})]. \qquad (40)$$

Series (38) is equivalent to the solution of the following integro-differential equation for the partial probability density:

$$\frac{dP(x,t)}{dt}=-\Delta^2\int_0^t h(x;t,t_1)dt_1$$

$$-\Delta^2\int_0^t g(x;t,t_1)P(x,t_1)dt_1. \qquad (41)$$

As in Refs. [51–53], we only study a *cw* electric field:

$$E(t)=E_0\cos(\omega t). \qquad (42)$$

Thus, $V(t)$ defined by Eq. (12) is given by

$$V(t)=a\sin(\omega t), \qquad (43)$$

where the intensity parameter a is defined as follows:

$$a\equiv\frac{\mu E_0}{\hbar\omega}. \qquad (44)$$

To find the solution of Eq. (41) with field (42)–(43), one employs the following useful identity [73]:

$$\exp[a\sin(\omega t)]\equiv\sum_{m=\infty}^{\infty}J_m(a)\exp(im\omega t). \qquad (45)$$

We seek for the solution of Eq. (41) by making use of the Laplace transform:

$$P(x,\lambda)=\int_0^{\infty}dt\,\exp(-\lambda t)P(x,t). \qquad (46)$$

Hence the Laplace image, $P(x,\lambda)$, can be determined from the following equation:

$$\lambda P(x,\lambda)-1=-\frac{\Delta^2}{2i}\int_0^{\infty}dt_1\exp(-\lambda t_1)\int_0^{t_1}dt_2$$

$$\times\exp[-G_2(t_1-t_2)]\sin[G_1(t_1-t_2)]$$

$$\times\sum_{n,m=-\infty}^{\infty}J_n(a)J_{n+m}(a)\left[\exp\left(i\left(\frac{\epsilon(x)}{\hbar}+m\omega\right)\right.\right.$$

$$\left.\left.\times(t_1-t_2)+in\omega t_1\right)-\text{c.c.}\right]-\frac{\Delta^2}{2}\int_0^{\infty}dt_1$$

$$\times\exp(-\lambda t_1)\int_0^{t_1}dt_2\exp[-G_2(t_1-t_2)]$$

$$\times\cos[G_1(t_1-t_2)]\times\sum_{n,m=-\infty}^{\infty}J_n(a)J_{n+m}(a)$$

$$\times\left[\exp\left(i\left(\frac{\epsilon(x)}{\hbar}+m\omega\right)(t_1-t_2)+in\omega t_1\right)\right.$$

$$\left.+\text{c.c.}\right]P(x,t_2). \qquad (47)$$

The structure of integral (47) can be presented in the following way:

$$\int_0^{\infty}dt_1\exp(-\lambda t_1)\int_0^{t_1}dt_2F(t_1-t_2)=\frac{F(\lambda\pm in\omega)}{\lambda\pm in\omega}, \qquad (48)$$

or

$$\int_0^{\infty}dt_1\exp(-\lambda t_1)\int_0^{t_1}dt_2G(t_1-t_2)P(x,t_2)$$

$$=G(\lambda\pm in\omega)P(x,\lambda\pm in\omega). \qquad (49)$$

For $m\neq0$ and $\lambda\to0$ (a long time asymptotic), one can safely neglect λ. Indeed integral (48)

$$\int_0^{\infty}dt_1\exp(-\lambda t_1)\int_0^{t_1}dt_2F(t_1-t_2)=\frac{F(\pm in\omega)}{\pm in\omega} \qquad (50)$$

is finite. Being multiplied by the small factor

$$\left(\frac{\Delta}{\omega}\right)^2, \qquad (51)$$

the function in Eq. (50) provides a negligible contribution compared to unity in Eq. (47). Thus, the only term which is essential in this equation is the one with $m=0$. A similar analysis can be made for the second integral term in Eq. (47) (see also Eq. (49)). One can show, by employing iterations, that all terms with $P(x,\lambda\pm in\omega)$ are only corrections of or-

der $(\Delta/\omega)^2$ to $P(x,\lambda)$. Thus, keeping all the terms with $m = 0$, we obtain the following solution for $P(x,\lambda)$:

$$P(x,\lambda) = \frac{1 - h(x,\lambda)/\lambda}{\lambda + g(x,\lambda)}, \qquad (52)$$

where $h(x,\lambda)$ and $g(x,\lambda)$ are given by

$$h(x,\lambda) \equiv \Delta^2 \sum_{n,m=-\infty}^{\infty} J_n^2(a) \int_0^{\infty} dt \exp[-\lambda t - G_2(t)]$$

$$\times \sin\left[\frac{\epsilon(x)}{\hbar}t\right] \sin[G_1(t)] \sin(n\omega t), \qquad (53)$$

$$g(x,\lambda) \equiv \Delta^2 \sum_{n,m=-\infty}^{\infty} J_n^2(a) \int_0^{\infty} dt \exp[-\lambda t - G_2(t)]$$

$$\times \cos\left[\frac{\epsilon(x)}{\hbar}t\right] \cos[G_1(t)] \cos(n\omega t). \qquad (54)$$

For small λ (or long times)

$$h(x,\lambda \to 0) \equiv h_0(x),$$

$$g(x,\lambda \to 0) \equiv g_0(x). \qquad (55)$$

Consequently, $P(x,t)$ is found to be

$$P(x,t) = -\frac{h_0(x)}{g_0(x)} + \left[1 + \frac{h_0(x)}{g_0(x)}\right] \exp[-g_0(x)t]. \qquad (56)$$

Employing the identity [73]

$$\sum_{n,m=-\infty}^{\infty} J_n^2(a) \exp(in\omega) = J_0\left(2a \sin\frac{\omega t}{2}\right), \qquad (57)$$

one can collect series (53) and (54), resulting in the following equations for $h_0(x)$ and $g_0(x)$:

$$h(x,\lambda) = \Delta^2 \int_0^{\infty} dt\, J_0\left(2a \sin\frac{\omega t}{2}\right) \exp[-\lambda t - G_2(t)]$$

$$\times \sin\left[\frac{\epsilon(x)}{\hbar}t\right] \sin[G_1(t)] \sin(n\omega t); \qquad (58)$$

$$g(x,\lambda) = \Delta^2 \int_0^{\infty} dt\, J_0\left(2a \sin\frac{\omega t}{2}\right) \exp[-\lambda t - G_2(t)]$$

$$\times \cos\left[\frac{\epsilon(x)}{\hbar}t\right] \cos[G_1(t)] \cos(n\omega t). \qquad (59)$$

The final expression for the time-dependent probability of finding the electron at the donor state takes the following form:

$$P_1(t) = \frac{1}{2}[1 + P(t)] = \frac{1}{2\sqrt{\pi}} \int_{-\infty}^{\infty} dx \exp(-x^2)$$

$$\times \left[\frac{g_0(x) - h_0(x)}{g_0(x)} + \frac{g_0(x) + h_0(x)}{g_0(x)} \exp[-g_0(x)t]\right], \qquad (60)$$

where $\epsilon(x)$, $h_0(x)$, and $g_0(x)$ are determined by Eqs. (36), (58), and (59), respectively.

Equation (60) is the general solution for the transition probability when both slow and fast degrees of freedom are taken into consideration. In Sec. III we shall study particular solutions of Eq. (60) at high temperatures.

III. A HIGH TEMPERATURE LIMIT

In this section we shall analyze some important particular solutions of Eqs. (58)–(60), restricting ourselves to a high temperature limit for both degrees of freedom:

$$\hbar \omega_c^{s,f} \ll kT. \qquad (61)$$

As usual (see Refs. [41,70,72]), functions $G_1(t)$ and $G_2(t)$, defined by Eqs. (21) and (22), can be expanded into the Taylor series. Keeping only linear terms for $G_1(t)$ and quadratic terms for $G_2(t)$, one obtains

$$G_1(t) \simeq \frac{E_{rf}}{\hbar}t,$$

$$G_2(t) \simeq \frac{E_{rf}kT}{\hbar^2}t^2. \qquad (62)$$

Thus, the integrals in Eqs. (58) and (59) become Gaussian, and therefore can be calculated exactly:

$$h_0(x) = \frac{\hbar\Delta^2}{4} \sqrt{\frac{\pi}{E_{rf}kT}} \sum_{n,m=-\infty}^{\infty} J_n^2(a)$$

$$\times \left\{ \exp\left[-\frac{(\epsilon(x) - E_{rf} - n\hbar\omega)^2}{4E_{rf}kT}\right] \right.$$

$$\left. - \exp\left[-\frac{(\epsilon(x) + E_{rf} - n\hbar\omega)^2}{4E_{rf}kT}\right] \right\}, \qquad (63)$$

$$g_0(x) = \frac{\hbar\Delta^2}{4} \sqrt{\frac{\pi}{E_{rf}kT}} \sum_{n,m=-\infty}^{\infty} J_n^2(a)$$

$$\times \left\{ \exp\left[-\frac{(\epsilon(x) - E_{rf} - n\hbar\omega)^2}{4E_{rf}kT}\right] \right.$$

$$\left. + \exp\left[-\frac{(\epsilon(x) + E_{rf} - n\hbar\omega)^2}{4E_{rf}kT}\right] \right\}. \qquad (64)$$

The partial rate constant, $g_0(x)$, given by Eq. (64), is a sum of the infinite number of transitions with different activation energies in which the reaction heats are increased or decreased by an integer number of the photon energy $n\hbar\omega$. The

probability of each channel being turned on is determined by the factor $J_n^2(a)$. This coefficient is an oscillating function of a. The Bessel function, $J_n(a)$, can vanish at some particular values of the intensity parameter $a = \mu E_0/\hbar \omega$, the roots of the nth-order Bessel function (see Ref. [73]). The ability to change the channel probability becomes extremely important for manipulation, since the *effective channel* (the channel with the least activation energy) can be turned off. In this situation the partial rate constant is significantly decreased by many orders of magnitude (see Ref. [51]).

We consider the two particular cases of resonances when two or one exponents in series (63) and (64) vanish, resulting in the largest contribution to the series:

(a) Let the resonance condition for two exponents take place (i.e. there are simultaneous resonances for both forward and backward reactive channels):

$$\epsilon - E_{rs} - E_{rf} = m_1 \hbar \omega,$$
$$\epsilon - E_{rs} + E_{rf} = m_2 \hbar \omega. \qquad (65)$$

Conditions (65) select only two exponents from infinite series (63) and (64). Other exponents in this series are exponentially small. Thus, the partial probability $P_1(x,t)$ takes a simpler form:

$$P_1(x,t) = \frac{J_{m_2}^2(a)}{J_{m_1}^2(a) + J_{m_2}^2(a)} + \frac{J_{m_1}^2(a)}{J_{m_1}^2(a) + J_{m_2}^2(a)}$$
$$\times \exp\left[-t\Gamma_{m_1,m_2} \exp\left(-x^2 \frac{E_{rs}}{E_{rf}}\right)\right], \qquad (66)$$

where $\Gamma_{m_1,m_2}(a)$ is defined by the following equation:

$$\Gamma_{m_1,m_2} \equiv \Gamma_0 [J_{m_1}^2(a) + J_{m_2}^2(a)]$$
$$\equiv \frac{\hbar \Delta^2}{4} \sqrt{\frac{\pi}{E_{rf}kT}} [J_{m_1}^2(a) + J_{m_2}^2(a)]. \qquad (67)$$

Finally, in order to obtain the transition probability, integral (60) over x must be taken. However, since ϵ depends on x, resonance conditions (65) are not exact for different x. We assume that the mismatch due to the fluctuation of x is small compared to $\hbar \omega$, i.e.

$$\frac{\hbar \omega}{\sqrt{E_{rs}kT}} \gg 1. \qquad (68)$$

If condition (68) is satisfied, the resonances are still sharp. Thus, one can safely neglect other exponents in Eqs. (63) and (64), which results in the partial transition probability described by Eq. (66). To take Gaussian integral (60) over the variable x, we employ the saddle point approximation used in Ref. [43]:
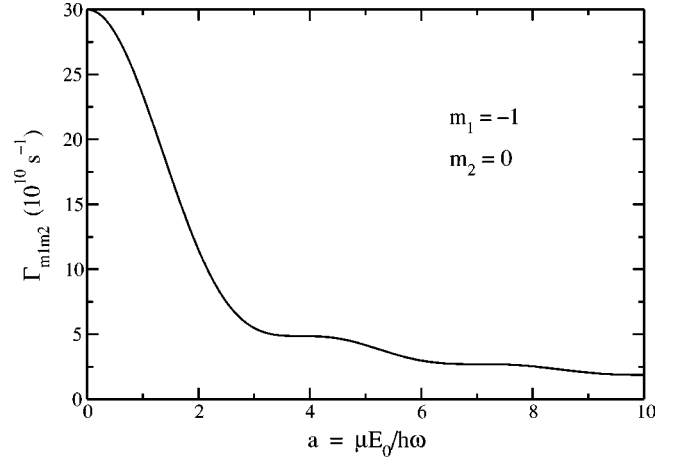

FIG. 1. Dependence of $\Gamma_{m_1 m_2}(a)$ upon the field intensity parameter a is given for $m_1 = -1$ and $m_2 = 0$.

$$P_1(t) \simeq \frac{J_{m_2}^2(a)}{J_{m_1}^2(a) + J_{m_2}^2(a) + J_{m_2}^2(a)}$$
$$+ \frac{J_{m_1}^2(a)}{J_{m_1}^2(a) + J_{m_2}^2(a)} \sqrt{2/\ln\left[\frac{E_{rs}}{E_{rf}}\Gamma_{m_1,m_2}t\right]}$$
$$\times \left(\frac{E_{rf}}{eE_{rs}}\right)^{E_{rf}/E_{rs}} (\Gamma_{m_1,m_2}t)^{-E_{rf}/E_{rs}}. \qquad (69)$$

This solution is valid provided [43]

$$\frac{E_{rs}}{E_{rf}}(\Gamma_{m_1,m_2}t) > 1. \qquad (70)$$

In accordance with Eq. (67), $\Gamma_{m_1,m_2}(a)$ is strongly affected by the field intensity. The dependence of $\Gamma_{m_1,m_2}(a)$ on a is shown in Fig. 1. $\Gamma_{m_1,m_2}(a)$ never vanishes, although it significantly decreases for $a > 2$. If $J_{m_1}^2(a) = 0$ (i.e., the backward reactive channel is turned off by the field), $P_1(t)$ becomes completely independent of time (see Fig. 2). When $J_{m_2}^2(a) = 0$ (for $m_2 = 0$, $a = 2.4$); (i.e., the forward reaction is switched off), the equilibrium distribution is shifted to the products. For $J_{m_1}^2(a) = 0$ ($m_1 = -1, a = 3.4$), the reaction is shifted to the reactants. At $a \simeq 1.45$ the forward and backward reactions contribute equally; i.e., the electron transition behaves like a symmetric reaction.

It is important to study the dependence of the equilibrium distribution upon the field intensity a. According to Eq. (69), the equilibrium rate constant is defined in the following way [74,75]:

$$\Gamma_{eq} \equiv \frac{P_2(a)}{P_1(a)}\bigg|_{t \to \infty} = \frac{J_{m_1}^2(a)}{J_{m_2}^2(a)}. \qquad (71)$$

According to Eq. (71), Γ_{eq} varies from 0 to ∞, depending on the values of the parameter a. As shown in Fig. 3, when
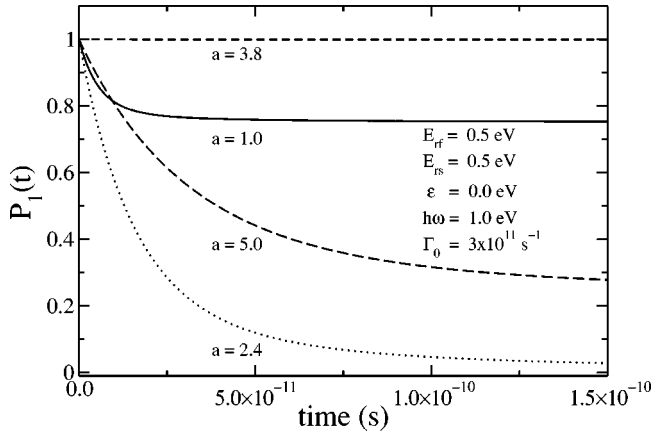
FIG. 2. Time dependence of the probability $P_1(t)$ of an electron remaining at the donor state is presented for different values of the field intensity. For $E_{rf} = E_{rs} = 0.5$ eV, $\epsilon = 0$, $T = 300$ K, $\hbar\omega = 1$ eV, and $\Gamma_0 = 3 \times 10^{11}$ s^{-1}, the reaction dynamics is sensitive to the field intensity.

$J_{m_1}^2(a) = 0$, the reaction is shifted to the reactants. If $J_{m_2}^2(a) = 0$, the reaction is shifted to the products.

It is always useful to compare analytical solution (69) with numerical calculations of integral (60), with $h_0(x)$ and $g_0(x)$ determined by Eqs. (63) and (64). The results are depicted in Fig. 4. It is clearly shown that a perfect match occurs at $t \geq 2 \times 10^{-11}$ s. As expected, the asymptotic analytical solution fails at earlier times.

(b) Now we consider the single resonance case when resonances occur only for the forward reaction, while the backward reaction is suppressed by a small activation exponent:

$$\epsilon - E_{rs} - E_{rf} = m_0 \hbar\omega,$$
$$(72)$$
$$|\epsilon - E_{rs} + E_{rf} - m_1 \hbar\omega| \gg \sqrt{E_{rf}kT} \cdot (m_0 \neq m_1).$$
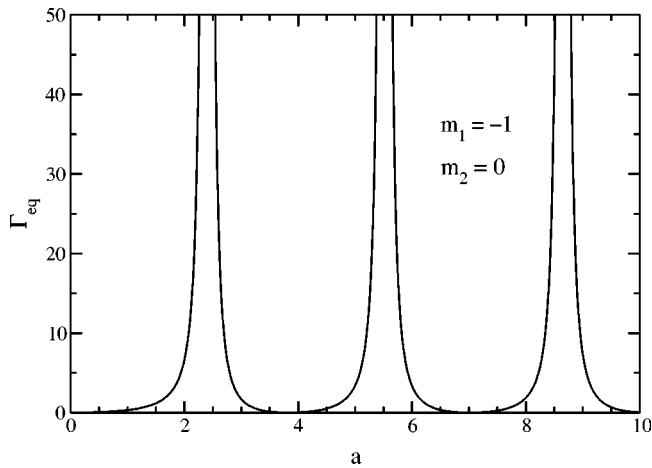

FIG. 3. Dependence of $\Gamma_{eq}(a)$ upon the field intensity parameter a is given for $m_1 = -1$ and $m_2 = -0$. The equilibrium constant or the direction of the reaction can be manipulated by changing the amplitude of the driving force.
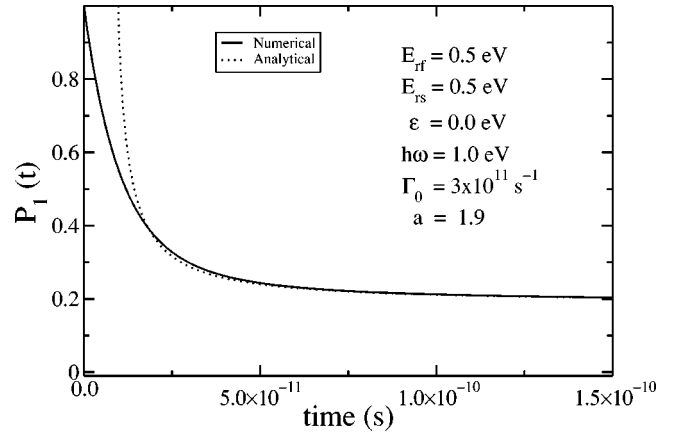

FIG. 4. Time-dependence of the transition probability for the reaction satisfying double resonance condition (65). The solid line is the numerical value of the integral in Eq. (60); the dashed line is the long time asymptotic described by Eq. (69). The parameters are chosen to be $E_{rf} = E_{rs} = 0.5$ eV, $a = 1.9$, $\epsilon = 0$, $T = 300$ K, $m_1 = -1$, $m_2 = 0$, $\hbar\omega = 1$ eV, and $\Gamma_0 = 3 \times 10^{11}$ s^{-1}.

Inequality (72) allows one to neglect all other exponents in series (63)–(64) except the resonance term. As in case (a), we exploit the saddle point method for the calculation of integral (60) over the auxiliary variable x [43]. As a result, the transition probability is given by [43]

$$P_1(t) \simeq \sqrt{2/\ln\left[\frac{E_{rs}}{E_{rf}}\Gamma_{m_0}(a)t\right]}$$
$$\times \left(\frac{E_{rf}}{eE_{rs}}\right)^{E_{rf}/E_{rs}} (\Gamma_{m_0}(a)t)^{-E_{rf}/E_{rs}}. \quad (73)$$

This solution is true provided [43]

$$\frac{E_{rs}}{E_{rf}}(\Gamma_{m_0}(a)t) > 1. \quad (74)$$

Here $\Gamma_{m_0}(a)$ stands for

$$\Gamma_{m_0}(a) \equiv \Gamma_0 J_{m_0}^2(a), \quad (75)$$

where Γ_0 is defined by Eq. (67). If $J_{m_0}^2(a) = 0$, then $\Gamma_{m_0}(a) = 0$. This might contradict inequality (74). Consequently, solution (73) is invalid. However, there is another reason for the theory presented above to be questionable at small $\Gamma_{m_0}(a)$. Validity condition (1) can be violated for small reaction rates. For this case, the inequality opposite to (1) takes place. The slow modes now become fast, relative to the reaction time. Consequently, the reaction is mono-exponential. The exponential evolution was previously studied in Refs. [51,52]. Thus, by changing the field intensity, we can even change the character of a time dependence. When the intensity parameter is far from a zero of the m_0th-order Bessel function, the dynamics is again non-exponential. If the intensity parameter is close to one of the zeroes of the m_0th-order Bessel function, the reaction dynamics becomes essentially mono-exponential. A 3D plot of $P_1(t)$ on time t
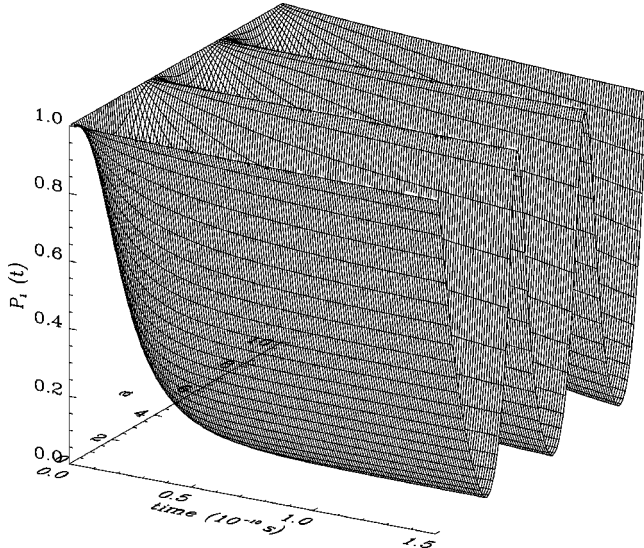
FIG. 5. 3D picture of evolution for the transition probability in the case of single resonance (72). The decay with time becomes extremely fast when the resonance Bessel functions ($m_0 = -1$) are rather close to the maxima ($a = 2.4, 5.5, 8.7 \ldots$). The reaction is terminated at zeroes of the resonance Bessel function. For $m_0 = -1$, $a = 3.8, 7.0, 10.2, \ldots$. The values of the parameters are chosen to be $\Gamma_0 = 3.7 \times 10^{11}$ s^{-1}, $\hbar\omega = 1$ eV, $T = 300$ K, $m_0 = -1$, $E_{rf} = 0.66$ eV, $E_{rs} = 0.33$ eV, and $\epsilon = 0$.

and the intensity parameter a is presented in Fig. 5. $P_1(t)$ is strongly dependent upon the intensity parameter. The time decay becomes extremely fast when the resonance Bessel function ($m_0 = -1$) is approximately close to the maxima of the Bessel function ($a = 2.4, 5.5, 8.7, \ldots$). The transfer is terminated at the zeroes of the resonance Bessel function. For $m_0 = -1$, the values of the intensity parameter are $a = 3.8, 7.0, 10.2, \ldots$.

The reaction probability is very sensitive to the reaction heat, ϵ. Figure 6 demonstrates such a dependence. Indeed, when resonance condition (72) is satisfied, the reaction is
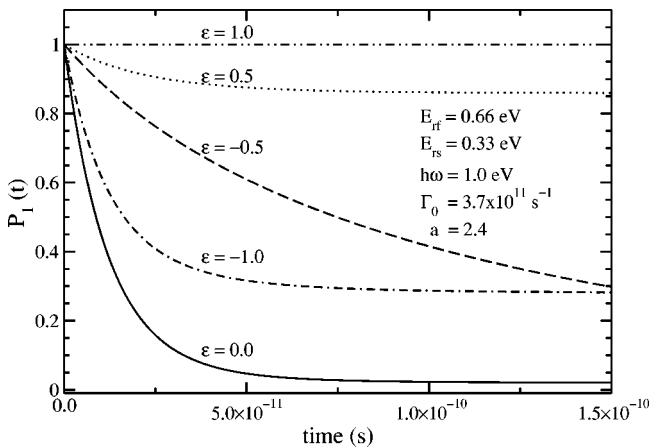

FIG. 6. Time dependence of the transition probability for the reaction for the case of single resonance (72) at the different values of the reaction heat ϵ. $a = 2.4$ while the values of the other parameters remain the same as in Fig. 5.
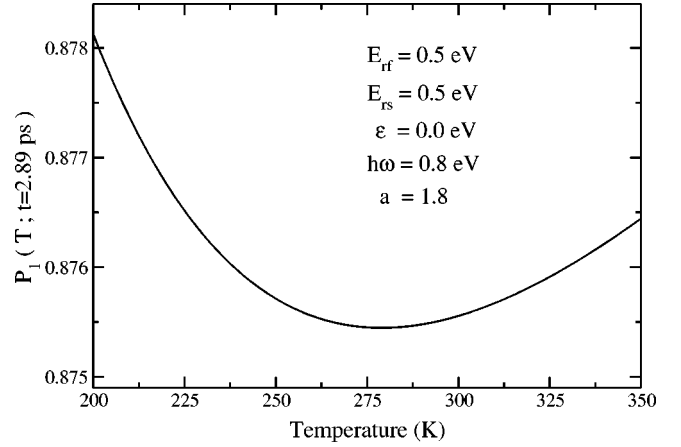

FIG. 7. Temperature dependence of the transition probability with the parameters close to the double resonance condition (see Eq. (65)). The values of the parameters are the same as in Fig. 2 except $a = 1.8$, $\hbar\omega = 0.8$ eV. The parameter Γ_0 varies with temperature in accordance with definitions (67) and (75).

fast at such a's when $J_{m_0}^2(a)$ is close to its maxima (here $m_0 = -1$). For $\epsilon = -1$, the resonance condition is satisfied again but now for $m_0 = 0(J_0(2.4) = 0)$. Consequently, the electron transfer is terminated.

The temperature dependence of the transition probability is one of the most important measurable characteristics. This dependence, shown in Fig. 7 at the fixed values of time ($t = 2.89$ ps), turns out to be very weak. For a broad range of temperatures, $P_1(t)$ changes by less than 1%. The minimum of $P_1(t)$ can be qualitatively explained in the following way: if the temperature is small, the fluctuations of x are less pronounced ($\tau/\hbar = 1/\sqrt{E_{rs}kT}$ in Eq. (36) is large). Therefore, the resonance discrepancy cannot be eliminated by small fluctuations of x. For a nonvanishing activation energy a direct temperature dependence is true. At higher temperatures, i.e. $T = 280$ K, it becomes possible to eliminate the activation mismatch. Hence, the resonance can be reached, and the reaction becomes activationless. For this type of reaction, the inverse temperature dependence is valid (the preexponential factor in $g_0(x)$).

Besides the time-dependent part of $P_1(t)$, we are interested in the equilibrium distribution of the reactants (see the first term in integrand (60)). Since the system is far from equilibrium it is apparent that $P_{eq}(\epsilon, a)$ should essentially differ from a Gibbs' distribution. There are two possible reasons: (a) non-equilibrium dynamics of slow modes, and (b) a time dependence of the driving force. Figure 8 demonstrates the dependence of P_{eq} on the reaction heat ϵ and the intensity parameter a. As expected, this dependence is essentially non-linear. The equilibrium distribution of reactants changes in the whole range of values from zero to one (i.e., products to reactants). At fixed values of ϵ, $P_{eq}(\epsilon, a)$ is an oscillating function of a.

IV. DISCUSSION AND CONCLUSIONS

In this work we have studied an effect of an intensive driving force on the transition probability of electron transfer
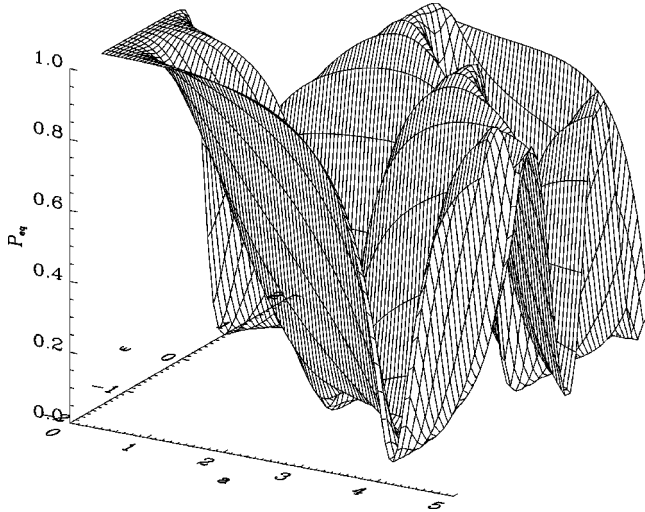
FIG. 8. 3D picture of the equilibrium distribution of reactants depending on the reaction heat, ϵ and the field intensity a. The value of the parameter are $\Gamma_0 = 3.7 \times 10^{11}$ s^{-1}, $\hbar\omega = 1$ eV, $E_{rf} = 0.66$ eV, $E_{rs} = 0.33$ eV, and $T = 300$ K.

in a bath with well separated slow and fast degrees of freedom. Such separation can take place for some alcohols [42] (e.g., *hexanol*). The electron dynamics has been analyzed in the framework of spin-boson Hamiltonian (3), when condition (1) $\hbar\omega_c^s/(\Gamma(a))\sqrt{E_{rs}/kT} \ll 1$ is imposed. In fact, one implies that the reaction is rather fast, much faster than relaxation of slow degrees of freedom. The expression for the time-dependent probability of the electron staying at the initial state (see Eq. (60)) has been rigorously derived for an arbitrary electric field, reaction heat, and temperature. The time-dependent probability is asymmetric to the bare energy bias, ϵ. This effect is due to the fact that slow degrees of freedom are far from equilibrium. The expansion of $Q_1^{slow}(t)$ and $Q_2^{slow}(t)$ in Eq. (23) with respect to the small parameter $(t\omega_c^s)$ is the main assumption of the theory. Consequently, we have suggested that the relaxation time of slow degrees of freedom is much larger than the observation and reaction times. This approximation implies that slow degrees of freedom will never reach equilibrium during the time of observation; they are frozen. Even when the electron transfer is completed, the slow mode dipoles remain directed toward the initial position of the electron. Apparently, the effective initial energy should be corrected to the value of the solvation energy of the slow modes E_{rs}, while the energy of the acceptor state remains unchanged. Due to solvation effect [74–76], only for the initial electron state does the system become asymmetric to ϵ.

The main analysis has been made for high temperatures. In particular, we have studied two important cases of resonances: (a) the double resonance with condition (65); and (b) the single resonance described by condition (72). For both cases, the long-time asymptotic analytical solutions have been found. For case (a), the time dependent probability consists of the two parts; the equilibrium probability P_{eq} and the time-dependent part itself. The latter, according to Eq. (69), is proportional to $(\Gamma_{m_1 m_2}(a)t)^{-E_{rf}/E_{rs}}$, where $\Gamma_{m_1 m_2}(a)$

$= \Gamma_0 (J_{m_1}^2(a) + J_{m_2}^2(a))$ (see Eq. (67)). The dependence of $\Gamma_{-1,0}(a)$ on the intensity parameter a is presented in Fig. 1. The value of $\Gamma_{m_1 m_2}$ decreases at $a \gtrsim 2$. As shown in Fig. 2, $P(t)$ is very sensitive to the field intensity. When $a = 2.4$, the reaction is very fast. At the same time (see Eq. (66)), P_{eq} vanishes since $J_0(2.4) = 0$. At $a = 3.8$, the preexponential factor in the time-dependent part of the transition probability vanishes ($J_1(3.8) = 0$). Thus, the reaction is terminated. The equilibrium constant is depicted in Fig. 3. When $J_{m_1}(a) = 0$, the reaction is shifted to the reactants. If $J_{m_2}(a) = 0$, the reaction is shifted to the products. By changing the field intensity (the value of the parameter a), one is able to manipulate the direction of the reaction. Case (b) of the single resonance highlights one very important problem with the theory—the validity of the theory. According to analytical solution (73), the parameter Γ_0, defined by Eq. (75), oscillates with the field intensity. When J_{m_0} is rather small (i.e., the reaction is slow), condition (1) is no longer valid. Furthermore, the opposite inequality can occur. This means that slow modes appear to be fast. Thus, according to Refs. [51,52], the reaction becomes mono-exponential. The exponential evolution can be described by the rate constant given by the following equation [51,52]:

$$\Gamma = \frac{\hbar\Delta^2}{4} \sqrt{\frac{\pi}{(E_{rs} + E_{rf})kT}} \sum_{n=-\infty}^{\infty} J_n^2(a)$$

$$\times \left\{ \exp\left[-\frac{(\epsilon - E_{rs} - E_{rf} + n\hbar\omega)^2}{4(E_{rs} + E_{rf})kT} \right] \right.$$

$$\left. + \exp\left[-\frac{(\epsilon + E_{rs} + E_{rf} + n\hbar\omega)^2}{4(E_{rs} + E_{rf})kT} \right] \right\}. \qquad (76)$$

Hence, by changing the intensity of the field, one is able to change the character of the evolution of the reaction from the slow non-exponential to the faster mono-exponential dependence. The theory presented above is unable to describe the transition between these two limiting regimes.

For the single resonance case, the reaction is rather sensitive to the change of the reaction heat (see Fig. 6). According to Eq. (72), the reaction heat can fit the resonance condition and, therefore, make the reaction effectively activationless.

A dependence of the reaction on temperature is one of the most important characteristics in chemical dynamics. As demonstrated in Fig. 7, the transition probability is almost insensitive to temperature. Such a weak dependence can mislead an investigator who might interpret experimental data in accordance with a tunneling mechanism. Interestingly, a similar phenomenon of ''false tunneling'' was found for reactions in glasses [77].

The equilibrium distribution of reactants (or product) is an experimentally measurable quantity. As shown in Fig. 8, P_{eq} is extremely sensitive to the intensity of the field and the reaction heat. The latter can bring the system to resonance, while the former can change the direction of the reaction.

Experimental observation of strong field effects in chemi-

cal reactions of electron transfer can be an important step towards understanding of the physics of opto-electronic molecular devices. Perhaps, long range electron transfer in proteins is one of the most promising candidates for observation of such effects. Indeed long distances $(15-17$ Å$)$ for elec-

tron tunneling are necessary in order to apply electric fields with intensities below a breakdown threshold in dielectrics. We believe that a protein contains strong slow degrees of freedom. The theory presented above can be implemented for such systems.

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[1] A.H. Zewail and co-workers, J. Phys. Chem. A **103**, 7419 (1999).

[2] M. Chachivilis and A.H. Zewail, J. Phys. Chem. A **103**, 7408 (1999).

[3] K. Yoshihara, K. Tominaga, and Y. Nagasawa, Bull. Chem. Soc. Jpn. **68**, 696 (1995).

[4] P.F. Barbara, T.J. Meyer, and M.A. Ratner, J. Phys. Chem. **100**, 13 148 (1996).

[5] D.A. Kliner, K. Tominaga, G.C. Walker, and P.F. Barbara, J. Am. Chem. Soc. **114**, 8323 (1992).

[6] K. Tominaga, D.A. Kliner, A.E. Johnson, N.E. Levinger, and P.F. Barbara, J. Chem. Phys. **98**, 1228 (1993).

[7] N.E. Levinger, A.E. Johnson, G.C. Walker, and P.F. Barbara, Chem. Phys. Lett. **196**, 159 (1992).

[8] G.C. Walker, P.F. Barbara, S.K. Doorn, Y. Dong, and J.T. Hupp, J. Phys. Chem. **95**, 5712 (1991).

[9] H. Lu, V. Petrov, and J.T. Hupp, Chem. Phys. Lett. **235**, 521 (1995).

[10] L. Kakri, H. Lu, and J.T. Hupp, J. Phys. Chem. **100**, 15 637 (1996).

[11] H. Lu, J.N. Priescorn, and J.T. Hupp, J. Am. Chem. Soc. **115**, 4927 (1993).

[12] U. Banin and S. Ruhman, J. Chem. Phys. **99**, 4391 (1992).

[13] K. Wynne, G.D. Reid, and R.M. Hochstrasser, J. Chem. Phys. **105**, 2287 (1996).

[14] U. Lieble, G. Lipowski, M. Negrerie, J.-C. Lambry, J.-L. Martin, and M. Vos, Nature (London) **401**, 181 (1999).

[15] Q. Wang, R.W. Schoenlein, L.A. Peteanu, R.A. Mathies, and C.V. Shank, Science **266**, 422 (1994).

[16] M.H. Vos, J.C. Lambry, S.J. Robles, D.C. Youvan, J. Breton, and J.-L. Martin, Proc. Natl. Acad. Sci. U.S.A. **88**, 8885 (1991).

[17] L. Zhu, J.T. Sage, and P.M. Champion, Science **266**, 629 (1994).

[18] G.R. Fleming, J.L. Martin, and J. Breton, Nature (London) **333**, 190 (1988).

[19] J. Breton, J.-L. Martin, G.R. Fleming, and J.-C. Lambry, Biochemistry **27**, 9276 (1988).

[20] A.M. Streltsov, S.I.E. Vulto, A.Ya. Shkuropatov, A.J. Hoff, T.J. Aartsma, and V.A. Shuvalov, J. Phys. Chem. B **102**, 7293 (1998).

[21] R.A. Marcus, J. Chem. Phys. **24**, 966 (1957); *ibid.* **26**, 867, 872 (1957).

[22] Yu. Dakhnovskii and A.A. Ovchinnikov, Chem. Phys. **80**, 17 (1983).

[23] Yu. Dakhnovskii, J. Mol. Liq. **60**, 73 (1994).

[24] P.G. Wolynes, Phys. Rev. Lett. **47**, 968 (1981).

[25] G.A. Voth, D. Chandler, and W.H. Miller, J. Phys. Chem. **93**, 7009 (1989).

[26] G.A. Voth, D. Chandler, and W.H. Miller, J. Chem. Phys. **91**, 7749 (1989).

[27] G. A. Voth, D. Chandler, and W. H. Miller, ''A New Perspective on Quantum Mechanical Transition State Theory,'' in *Quantum Simulations of Condensed Matter Phenomena*, edited by J. D. Doll and J. E. Gubernatis (World Scientific, Singapore, 1990), pp. 391-400.

[28] R.F. Grote and J.T. Hynes, J. Chem. Phys. **73**, 2715 (1980).

[29] P. Hänggi and F. Mojtabai, Phys. Rev. A **26**, 1168 (1982).

[30] T. Fonseca and B.M. Ladanyi, J. Phys. Chem. **95**, 2116 (1991).

[31] M. Scaf, T. Fonseca, and B.M. Ladanyi, J. Chem. Phys. **98**, 8929 (1993).

[32] D.F. Calef and P.G. Wolynes, J. Phys. Chem. **87**, 3387 (1983).

[33] V. G. Levich, in *Physical Chemistry. An Advanced Treatise*, edited by H. Eyring (Academic, New York, 1970), Vol. 9, p. 169.

[34] R.A. Marcus and N. Sutin, Biochim. Biophys. Acta **811**, 265 (1985).

[35] N.R. Kestner, J. Logan, and J. Jortner, J. Phys. Chem. **78**, 2148 (1974).

[36] G.J. Small, J.H. Hayes, and R.J. Silbey, J. Phys. Chem. **96**, 7499 (1992).

[37] M. Bixon and J. Jortner, Chem. Phys. **176**, 467 (1993).

[38] M. Bixon and J. Jortner, in *Electron Transfer From Isolated Molecules and Biomolecules*, edited by J. Jortner and M. Bixon; Ser. Editors I. Prigogin and S. A. Rice (Wiley, New York, 1999) vol. **106**, p. 35.

[39] H. Sumi and R.A. Marcus, J. Chem. Phys. **84**, 4894 (1986).

[40] W. Nadler and R.A. Marcus, J. Chem. Phys. **86**, 3906 (1987); Chem. Phys. Lett. **144**, 24 (1988).

[41] M.J. Hornbach and Yu. Dakhnovskii, J. Chem. Phys. **111**, 5073 (1999).

[42] D. B. Feinberg and D. Huppert, in *Electron Transfer From Isolated Molecules and Biomolecules* [38], p. 191.

[43] Yu. Dakhnovskii, J. Chem. Phys. **111**, 5418 (1999).

[44] D. Chandler and P. Wolynes, J. Chem. Phys. **74**, 4078 (1981).

[45] K. Schweizer, R.M. Stratt, D. Chandler, and P. Wolynes, J. Chem. Phys. **75**, 1347 (1981).

[46] B. Carmeli and D. Chandler, J. Chem. Phys. **82**, 3400 (1984).

[47] R.D. Coalson, J. Chem. Phys. **92**, 4993 (1990).

[48] R.D. Coalson, Phys. Rev. B **39**, 12 052 (1989).

[49] R.D. Coalson, J. Chem. Phys. **94**, 1108 (1991).

[50] D.G. Evans, A. Nitzan, and M.A. Ratner, J. Chem. Phys. **108**, 6387 (1998).

[51] Yu. Dakhnovskii, J. Chem. Phys. **100**, 6492 (1994).

[52] Yu. Dakhnovskii and R.D. Coalson, J. Chem. Phys. **103**, 2908 (1995).

[53] Yu. Dakhnovskii, H. Kim, D. Evans, and R.D. Coalson, J. Chem. Phys. **103**, 5461 (1995).

[54] M. Grifoni, M. Sassetti, P. Hänggi, and U. Weiss, Phys. Rev. E **52**, 3596 (1995).

[55] M. Morillo and R.I. Cukier, J. Chem. Phys. **98**, 4548 (1993).

[56] R.I. Cukier and M. Morillo, Chem. Phys. **183**, 375 (1994).

[57] D.E. Makarov and N. Makri, Phys. Rev. B **52**, 2257 (1995).

[58] G. Taft and N. Makri, J. Phys. B **31**, 209 (1998).

[59] J.T. Stockbuürger, Phys. Rev. E **59**, R4709 (1999).

[60] M. Morillo and R. Cukier, J. Chem. Phys. **110**, 7966 (1999).

[61] I.M. Grifoni, Phys. Rev. E **54**, 3086 (1996); H. Adam *et al.*, Phys. Rev. Lett. **83**, 252 (1999).

[62] A.J. Leggett, S. Chakravarty, A.T. Dosey, M.P.A. Fisher, A. Garg, and W. Zwerger, Rev. Mod. Phys. **59**, 1 (1987).

[63] U. Weiss, *Quantum Dissipative Systems* (World Scientific, Singapore, 1993).

[64] M. Grifoni and P. Hänggi, Phys. Rep. **304**, 229 (1998).

[65] S. Franzen and S.G. Boxer, J. Phys. Chem. **97**, 6304 (1993); K. Lao, S. Franzen, R.J. Stanley, D.G. Lambright, and S.G. Boxer, *ibid.* **97**, 13 165 (1993).

[66] G. Feher, T. A. Arno, and M. Y. Okamura, in *The Photosynthetic Bacterial Reaction Center. Structure and Dynamics*, edited by J. Breton and A. Vermeglio (Plenum, New York, 1988) p. 271.

[67] G. Walker, private communication (1995).

[68] J.J. Hopfield, J.N. Onuchic, and D. Beratan, Science **241**, 817 (1988).

[69] M.Y. Ogawa, I. Moreira, J.F. Wishart, and S.S. Isied, Chem. Phys. **176**, 589 (1993).

[70] I. Rips and J. Jortner, J. Chem. Phys. **87**, 2090 (1987).

[71] A.A. Ovchinnikov and M.Ya. Ovchinnikova, Zh. Eksp. Teor. Fiz. **56**, 1278 (1969); [Sov. Phys. JETP **29**, 688 (1969)].

[72] A. Garg, J.N. Onuchic, and V. Ambegaokar, J. Chem. Phys. **83**, 4491 (1987).

[73] M. Abramowitz and I. Stegun, *Handbook of Mathematical Functions* (Dover, New York, 1972), p. 296.

[74] D. Chandler, *Introduction to Modern Statistical Mechanics* (Oxford U. P., New York, 1987).

[75] P. Atkins, *Physical Chemistry* (Freeman, New York, 1994), 5th ed., Ch. 25.

[76] D.V. Matyushov and B.M. Ladanyi, J. Chem. Phys. **110**, 994 (1999).

[77] Yu. Dakhnovskii, V. Lubchenko, and P. Wolynes, J. Chem. Phys. **104**, 1875 (1996).