Coherent and incoherent photon-assisted electron tunneling in optoelectronic molecular devices in soft solids

Joshua D. Bodyfelt¹ and Yuri Dahnovsky^{2,*}

¹Department of Physics and Astronomy, University of Wyoming, P.O. Box 3905, Laramie, Wyoming 82071 ²Department of Chemistry, University of Wyoming, P.O. Box 3905, Laramie, Wyoming 82071

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An electron in a bath with slow degrees of freedom (such as soft solids, e.g., proteins) is driven by a strong time-dependent electric field. In this molecular device, the electron dynamics are characterized by quasicoherent oscillations with slow square-root decay even at room temperatures. The frequency of the oscillations and the equilibrium distribution are found essentially to depend on the field intensity and the medium parameters. The applied field effectively changes the relaxation time of the environment from fast to slow and vice versa. The quasicoherence allows for the prevention of overheating in the microdevice. It is also shown that the applied field is capable of changing the character of the electron dynamics from quasicoherence to incoherent decay. The electron transition probability strongly depends upon the applied voltage (bias) and at some values of the field parameters, this voltage can quickly switch the coherent transfer over to incoherent transfer and *vice versa*. Despite the slow electron transfer in the incoherence region, the equilibrium distribution can favor either products or reactants, depending upon the field intensity. In the incoherent regime, the electron localization is possible. All these features can be exploited in microcomputers or quantum computers.

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I. INTRODUCTION

The design and production of energy efficient, state-ofthe-art electronic devices depend on the ability to produce ever-higher densities of circuit elements within integrated circuits. Indeed, the electronics industry is driven by this very necessity. In order to achieve these goals, the use of molecular devices in these applications has been suggested. These molecular devices involve a long-range electrontransfer process in which the electron movements occur according to binary logic. For this reason, these types of electron transfer can be exploited in switchers or elementary cells in microcomputers or quantum computers.^{1–7}

There are many advantages in using molecular devices for these types of information-processing applications. For example, the use of molecules for these purposes would allow for high component density, increased response speeds, and very high energy efficiency. Because of their small size, there have been many discussions regarding the possibility of increasing data-storage density to as much as 10¹⁸ bits per square centimeter with the use in molecular switchers.² Also, since electron transfer occurs within the molecules on picosecond or even femtosecond time scale, it should be possible to produce devices that respond extremely rapidly.

A specific feature of molecular devices is that the electron transfer takes place in an environment in which many polar modes are strongly coupled to the electron. A promising system for experimental observation is primary long-range electron transfer (longer than 17 Å) in photosynthetic bacteria. Recent experiments on such electron transfer reveal new properties in electron dynamics and one particular interesting phenomenon is nonexponential decay of the electron density.^{8–14}

The normal approach to the description of electron tunneling is based on the noninteracting blip approximation (NIBA) or the same as the "Golden rule." As found by Leggett *et al.*⁵ (see also Ref. 16) for the NIBA, a polar medium (a solvent or protein) should have rather fast relaxation in order to satisfy the following validity condition:

$$\left(\frac{\Delta}{\omega_c}\right)^2 \ll 1,\tag{1}$$

where Δ is the transition matrix element and ω_c is the relaxation frequency of the medium modes. As demonstrated in Refs. 15–19, the simplest microscopic model, which is capable of describing electron transfer in the most rigorous way, is based on the spin-boson Hamiltonian:^{15,19}

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

where the set of oscillators $\{k\}$ of mass $\{m_k\}$ and frequency $\{\omega_k\}$ represents the slow 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 bias or applied voltage). The electronic state associated with the $|+\rangle$ eigenstate of $\hat{\sigma}_z$ (with eigenvalue +1) shall be designated as the initial electronic state. The other electronic base state is then the final state. A transition between two states is due to the first term in the Hamiltonian. Δ is the transition matrix element.

In proteins, however, a physical picture is rather different. For example, in a protein called *ubiquitin* it was found²⁰ that the cutoff frequency for the relaxation slow modes is

$$\omega_c = 2 \times 10^{-2} \text{ cm}^{-1} . \tag{3}$$

For the primary electron transfer in photosynthetic bacteria $\Delta = 25 \text{ cm}^{-1}$.^{21,22} Apparently, the ratio

$$\left(\frac{\Delta}{\omega_c}\right)^2 \simeq 1.4 \times 10^6 \gg 1 \tag{4}$$

becomes extremely large, and the NIBA [see Eq. (1)], therefore, cannot be used to describe the electron transfer in proteins.

Since the NIBA is not valid for use in proteins, a new solution of the problem is necessary. We have, therefore, constructed in the framework of spin-boson Hamiltonian (2), a solution for electron transfer in slow relaxation environment. As shown in Ref. 17 condition (4) is more complicated and should be corrected in the following way:

$$\left(\frac{\Delta}{\omega_c}\right)^2 \left(\frac{kT}{E_r}\right) \gg 1.$$
(5)

Here the reorganization energy E_r is defined as follows:

$$E_r = \frac{1}{2} \sum_k \frac{g_k^2}{m_k \omega_k^2}.$$

This slow bath approximation was widely exploited in statistical physics, $^{23-25}$ spectroscopy, $^{26-28}$ instanton tunneling, 29,30 spin glasses, $^{31-33}$ and glasses³⁴ by many authors. We will use this approximation for the dynamic problem of electron transfer.

Transfer of an undriven electron in a slow relaxation bath was analyzed in Ref. 17 where it was shown that the timedependent electron density exhibits quasicoherent oscillations with slow decay $\sim \sqrt{t}$. The physical picture of electron transfer changes dramatically, however, when a laser field is applied. Long-range electron transfer can be manipulated by a time-dependent electric field encoded with a high density of information. Many different authors have investigated the unusual properties of electron tunneling in a strong electric field. Hänggi and co-workers^{35–38} (see also review Ref. 39) discovered that tunneling can be suppressed by a timedependent electric field. Cukier and Morillo^{40,41} emphasized that interaction of an electron with a stochastic environment can essentially affect the tunneling transition rate. Giant resonances in the rate constant with respect to the field intensity indicate that the electron transition can be practically terminated (or greatly accelerated) by a small change of the field amplitude.⁴²⁻⁴⁵ Theoretical predictions were numerically verified in Refs. 46-48. The excellent agreement was found in Ref. 47.

An applied electric field also has the ability to reverse the direction of the electron transfer from an initial to final well and *vice versa*.⁴⁵ If an applied electric field has a pulsed structure, the electron density coherently oscillates between two states, despite the strong dissipative interaction of an electron with a polar environment.^{49–51} The capability of changing the direction of the electron transfer in quantum heterostructures was theoretically examined in Refs. 52–54 and experimentally discovered in Refs. 55,56.

In this paper, we are interested in dynamics of an electron driven by an external time-dependent electric field. This allows for manipulation of the electron motion⁴²⁻⁴⁵ in optoelectronic molecular devices. A new term of electron-field interaction should be introduced into the Hamiltonian

$$\hat{H} = \hat{H}_{\rm SB} - \frac{1}{2}\mu E(t)\hat{\sigma}_z, \qquad (6)$$

where μ is the dipole-moment difference between the donor and acceptor states, E(t) is the external arbitrary electric (laser) field.

As it will be shown later [see Eq. (18)], the applied electric field essentially changes the whole physical picture. Inequalities (1) and (4) with Eq. (3), therefore, become

$$\left(\frac{\Delta J_{m_0}(a)}{\omega_c}\right)^2 = \left(\frac{\Delta}{\omega_{\text{eff}}(a)}\right)^2 \gg 1 \,(\ll 1). \tag{7}$$

Here $J_{m_0}(a)$ is the m_0 th order Bessel function. The laser intensity parameter is defined in the following way:

$$a = \frac{\mu E_0}{\hbar \,\omega_0},\tag{8}$$

where a cw electric field is defined as

$$E(t) = E_0 \cos(\omega_0 t). \tag{9}$$

The effective relaxation time in Eq. (7) can be written in the following way:

$$\omega_{\text{eff}} = \frac{\omega_c}{|J_{m_0}(a)|}.$$
 (10)

Thus, the relaxation time of the medium becomes affected by the electric field. When $|J_{m_0}(a)|$ is close to its maximum the medium is still slow in accordance with Eq. (5). At $J_{m_0}(a) \rightarrow 0, \omega_{\text{eff}} \gg \omega_c$; therefore, the protein relaxation becomes extremely fast. Consequently, inequality (1) is valid, and the NIBA should be used. Hence, a time-dependent field is able to change the relaxation time of a protein through driving the electron. We will study the main interesting properties of a driven electron in proteins and consider possible applications for electron molecular devices.

The outline of this paper is as follows. In Sec. II we present the derivation of the transition probability for a driven electron motion in a slow relaxation environment. The analysis of the results and its properties relevant to electronic molecular devices are given in Sec. III. The significance of this work is discussed in Sec. IV. The rigorous derivation of the master equation and different expressions for the transition probability are presented in Appendices A and B.

II. THE TIME-DEPENDENT PROBABILITY: MAIN RESULTS

A time-dependent probability for driven electron transfer is rigorously derived in Appendix A in the framework of spin-boson Hamiltonian (2) and (6) and given by the following equation [see Eqs. (A1) and (A6)]:

$$P(t) \equiv \frac{1}{\sqrt{\pi}} \int_{-\infty}^{\infty} dx \exp(-x^2) P(x,t), \qquad (11)$$

where P(x,t) satisfies the following integro-differential equation:

$$\frac{dP(x,t)}{dt} = -\Delta^2 \int_0^t \cos\left[\frac{\epsilon(x)}{\hbar}(t-t_1) + V(t) - V(t_1)\right] P(t_1) dt_1.$$
(12)

V(t) is defined as follows [see Eq. (A7)]:

$$V(t) = \mu \int_0^t E(\tau) d\tau.$$
(13)

Here the electric field has an arbitrary shape. For cw electric field (9), V(t) is equal to

$$V(t) = a \sin(\omega_0 t). \tag{14}$$

The bias $\epsilon(x)$ depends on temperature, the parameter of integration *x*, and the reorganization energy E_r in the following way:

$$\boldsymbol{\epsilon}(x) = 2x\sqrt{E_r kT} + \boldsymbol{\epsilon} - E_r. \tag{15}$$

The simplest solution of Eqs. (11) and (12) can be presented in resonance approximation (B2) as follows [see Eq. (B9)] $(t \rightarrow \infty)$:

$$P_{1}(t) = 1 - \frac{\Delta_{m_{0}}}{2\sqrt{E_{r}kT/\hbar^{2} + \Delta_{m_{0}}^{2}}} + \frac{\hbar\Delta_{m_{0}}}{\sqrt{E_{r}kT}} \frac{\cos(\Delta_{m_{0}}t + \pi/4)}{\sqrt{\Delta_{m_{0}}t}},$$
(16)

where

$$P_1(t) = \frac{1 + P(t)}{2} \tag{17}$$

is the decay probability of the electron density in the initial state. The effective transition matrix element is given by Eq. (A21),

$$\Delta_{m_0} \equiv \Delta |J_{m_0}(a)|. \tag{18}$$

Here m_0 stands for a resonance number defined as follows [Eq. (A14)]:

$$\boldsymbol{\epsilon}(\boldsymbol{x})/\hbar + \boldsymbol{m}_0\boldsymbol{\omega} = 0, \tag{19}$$

where ϵ is the bias [see Hamiltonian (2)]. A more general solution is presented in Appendices A and B.

As seen from Eq. (16), the electron density reveals quasicoherent oscillations with weak square-root decay ($\sim \sqrt{t}$) at room temperatures despite the strong interaction between the electron and polar modes of the protein. As shown in Fig. 1, the decay is very slow with respect to the period of oscillations. The numerical solution described by Eq. (B7) and analytical Eq. (16) are very close.



FIG. 1. Comparison of the transition probability calculated numerically by employing Eq. (B5) and analytically by making use of Eq. (B7). Here a time is normalized to $\tau_0 \equiv \hbar/\sqrt{E_r kT}$. The resonance condition is taken at $m_0 = 0$. The intensity of the field is $a = \mu E_0/\hbar \omega = 0$ and $\hbar \Delta/\sqrt{E_r kT} = 5.0$.

III. APPLICATION TO ELECTRONIC MOLECULAR DEVICES

Conventional quantum wells of GaAs/Al_xGa_{1-x}As are usually studied at low temperatures with no interaction between an electron and its environment. An electron-transfer system in proteins can also be considered as a quantum well or microelectronic molecular device. The important difference between GaAs/Al_xGa_{1-x}As double-well heterostructures and molecular devices is that, in molecular devices, the interaction with the protein environment is crucial ($E_r \approx 0.3-1.0$ eV). The other essential feature of molecular quantum wells, which is important from a technological point of view, is the ability to operate at room temperatures. The electron-transfer complex can also be considered as an elementary cell for a microcomputer or quantum computer.

The applied time-dependent electric field drastically changes the properties of the molecular device. There are a few features that attribute to the unusual device properties. First, according to Eq. (16), the electron transport is quasicoherent at room temperatures despite the strong coupling to the polar protein environment. This property should not be mixed with a pure coherent motion in conventional quantum wells where the interaction with a medium is excluded from a Hamiltonian. Second, in molecular devices, the reorganization energy appears in the frequency of the quasicoherent oscillations [see Eq. (15)]. The slow square-root decay indicates that there is still weak dissipation into the environment. The quasicoherence, therefore, becomes a very important property for microdevices since a small amount of heat is transferred to the medium. This will allow the device to operate without overheating, a common problem in circuits. The third important property is the electron localization in the initial well. This feature can be used in quantum computers.

As mentioned in the Introduction, the photon assistance can effectively change the relaxation of the protein environment through driving the electron [see Eq. (10)],

$$\omega_{\text{eff}} = \frac{\omega_c}{|J_{m_0}(a)|}$$



FIG. 2. Time-dependent transition probability for two different values of the field intensity. When the intensity parameter a = 2.3 is taken within the *incoherence* region, the evolution is exponential. For a = 3.8, the dynamics is oscillative. The values of the parameters are $m_0 = 0$ and $\hbar \Delta / \sqrt{E_r kT} = 5.0$.

When J_{m_0} is far away from the zeros of the m_0 th order Bessel function, the medium is slow. Consequently, the electron dynamics exhibits quasicoherent properties. If $J_{m_0}(a)$ $\rightarrow 0$, $\omega_{\text{eff}} = \omega_c / |J_{m_0}(a)|$ becomes extremely large, and inequality (5) takes the opposite sign. The approach described in Sec. II, Appendices A and B, therefore, is invalid, and one should use the traditional NIBA.

The transition probability for the transfer of an electron driven by a cw electric field is well known in the noninteracting blip approximation.^{42,45} For high temperatures ($\hbar \omega_c \ll kT$), $P_1(t)$ is equal to

$$P_1(t) = \frac{\Gamma_2 + \Gamma_1 \exp[-(\Gamma_1 + \Gamma_2)t]}{\Gamma_1 + \Gamma_2},$$
(20)

where Γ_1 and Γ_2 are the forward and backward reaction rates, respectively,

$$\Gamma_{1,2} = \frac{\hbar \Delta^2}{4} \left(\frac{\pi}{E_r k T} \right)^{1/2} \sum_{n=-\infty}^{\infty} J_n^2(a) \exp\left[-\frac{(\epsilon - E_r \pm \hbar \omega_0)^2}{4E_r k T} \right].$$
(21)

Equation (21) was derived in a high-temperature limit. In accordance with Eq. (20), the equilibrium electron density at the donor state is described by the following equation:

$$P_{\rm eq} = \frac{1}{1 + \Gamma_1 / \Gamma_2}.$$
 (22)

The time-dependent probability, $P_1(t)$, is exponential and essentially different from the quasicoherent oscillations described by Eq. (16). The quasicoherent and incoherent regimes are shown in Fig. 2. The dashed line represents the fast exponential decay at $J_0(2.3)=0.055$. For a=3.8, the zeroth order Bessel function has the maximum. Hence, the electron transfer is quasicoherent $[|J_0(3.8)| \approx 0.4]$. As demonstrated in Fig. 2, the coherence decay is much slower than that for the exponential regime.

Another important feature of the system is the dependence on the applied voltage, or ϵ (see Fig. 3). Since we consider only the resonance transitions satisfying Eq. (19), the dependence of the transition probability on the Bessel index m_0 is



FIG. 3. Applied voltage or bias dependence of the transition probability. The different resonance numbers m_0 correspond to different values of the voltage satisfying resonance condition (19). The value of the parameter $\hbar \Delta / \sqrt{E_r kT} = 5.0$. The intensity parameter a = 1.8 is chosen to be within the *coherence* region. The dramatic change in the transition probability is demonstrated.

given. According to Fig. 3, $P_1(t)$ is rather sensitive to the applied voltage. For $m_0=0$ the transition probability has the maximum, while for $m_0=1$, $P_1(t)$ has the minimum.

IV. CONCLUSIONS

In this work we have found some unusual features for driven electron transfer in proteins at room temperatures. These characteristics can be very useful for electronic molecular devices or elementary cells in microcomputers or quantum computers. The investigated properties are (a) the electron exhibits quasicoherent oscillations with slow square-root decay at room temperatures despite strong coupling to a bath; (b) the relaxation time of the environment can effectively be changed from slow to fast and *vice versa* by tuning the laser intensity; (c) the electron can be quickly localized in the initial state; (d) the quasicoherent oscillations can be changed to exponential evolutions by choosing the appropriate intensity of the time-dependent electric field.

Property (a) is important in microdevices since quasicoherent current does not overheat the device at room temperatures. On the contrary, the reaction with exponential evolution supplies the reaction heat into the environment that does lead to overheating. Properties (b), (c), and (d) allow the electron to quickly relax to the localized state without transferring the reaction heat into the environment. This localization can become the main feature in quantum computers and switchers.

All of the characteristics mentioned above have been rigorously derived on the basis of spin-boson Hamiltonian (2). The validity condition is given by Eq. (5). Quasicoherent features appear in a slow relaxation bath even at room temperatures. For the driven electron the effective relaxation time of the protein environment can be shortened by the time-dependent electric field in such a way that the quasicoherence is changed to exponential evolution. Only in the exponential regime can an electron can be localized in the initial well.

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APPENDIX A: THE MASTER EQUATION

We study dynamics of driven long-range electron transfer in the framework of the spin-boson Hamiltonian [see Eqs. (1) and (6)]. In general, the transition probability can be found as an exact formal expansion relative to the value of a transition matrix element Δ ,¹⁵ which, in our case, is modified by the driving force.^{16,58} In this Appendix we follow the derivation presented in Ref. 17.

First, we assume that the observation time is much smaller than the relaxation time of the slow modes, i.e., $t \omega_c^s \leq 1$. Second, the next assumption is inequality (5) (see the derivation in Ref. 17). It means that the relaxation of the environment is much slower than the shuttling of the electron between the wells (Δ^{-1}). Under these assumptions¹⁷ we can present the time-dependent probability in the following way [see Eq. (11)]:

$$P(t) \equiv \frac{1}{\sqrt{\pi}} \int_{-\infty}^{\infty} dx \exp(-x^2) P(x,t), \qquad (A1)$$

where the partial transition probability is defined as follows:

$$P(x,t) = \sum_{n=0}^{\infty} (-\Delta^2)^n \int_0^t dt_{2n} \int_0^{t_{2n}} dt_{2n-1} \cdots \int_0^{t_2} dt_1$$
$$\times \prod_{j=1}^n \cos \left[\frac{\epsilon(x)}{\hbar} (t_{2j} - t_{2j-1}) + V(t_{2j}) - V(t_{2j-1}) \right].$$
(A2)

Here the reaction heat $\epsilon(x)$ stands for

$$\boldsymbol{\epsilon}(x) \equiv \frac{2\hbar x}{\tau_0} + \boldsymbol{\epsilon} - \boldsymbol{E}_r. \tag{A3}$$

 τ_0 is the blip relaxation time defined in the following way:

$$\tau_0 \equiv \frac{\hbar}{\sqrt{E_* kT}}.\tag{A4}$$

In the previous derivation we have assumed that the temperature is high, i.e.,

$$\hbar \,\omega_c^s \leq kT. \tag{A5}$$

The high-temperature approximation becomes essential for devices working at room temperatures.

Series (A2) can be obtained as a formal expansion of the following integrodifferential master equation for the partial probability P(x,t),

$$\frac{dP(x,t)}{dt} = -\Delta^2 \int_0^t \cos\left[\frac{\epsilon(x)}{\hbar}(t-t_1) + V(t) - V(t_1)\right] P(t_1)dt_1$$
(A6)

with the initial condition P(t=0)=1. Here V(t) is defined as follows:

$$V(t) = \mu \int_0^t E(\tau) d\tau.$$
 (A7)

Equation (A6) is valid for an arbitrary bias and driving force. In this work, we restrict ourselves to a cw electric field given by the following equation:

$$V(t) = a\sin(\omega t) \equiv \frac{\mu E_0}{\hbar \omega} \sin(\omega t), \qquad (A8)$$

where μ is the electron dipole-moment difference, and E_0 and ω are the amplitude and the frequency of the electric field, respectively. Taking into consideration Eq. (A8), Eq. (A6) yields

$$\frac{dP(x,t)}{dt} = -\Delta^2 \int_0^t \cos\left[\frac{\epsilon(x)}{\hbar}(t-t_1) + a\sin(\omega t) - a\sin(\omega t_1)\right] P(t_1)dt_1.$$
(A9)

In order to solve Eq. (A9) one employs the following useful identity:⁵⁷

$$\exp[a\sin(\omega t)] \equiv \sum_{m=\infty}^{\infty} J_m(a) \exp(im\,\omega t).$$
 (A10)

By making use of the Laplace transform,

$$P(x,\lambda) = \int_0^\infty dt \exp(-\lambda t) P(x,t), \qquad (A11)$$

one can obtain the following equation for the Laplace image of the partial probability $P(x,\lambda)$:

$$\lambda P(x,\lambda) - 1 = -\frac{\Delta^2}{2} \int_0^\infty dt_1 \exp(-\lambda t_2) \int_0^{t_1} dt_2$$
$$\times \sum_{n,m=-\infty}^\infty J_n(a) J_{n+m}(a) \left(\exp\left\{ i \left[\frac{(x)}{\hbar} + m_\omega \right] \right. \right. \right.$$
$$\times (t_1 - t_2) + in \, \omega t_1 \left. \right\} + \text{c.c.} \left. \right) P(x, t_2).$$
(A12)

The direct integration over t_1 and t_2 yields the following equation for $P(x,\lambda)$:

$$\lambda P(x,\lambda) - 1 = -\frac{\Delta^2}{2} \sum_{n,m=-\infty}^{\infty} J_n(a) J_{n+m}(a)$$

$$\times \left[\frac{P(\lambda - in\omega)}{\lambda - i[\epsilon(x)\hbar + (n+m)\omega]} + \frac{P(\lambda + in\omega)}{\lambda + i[\epsilon(x)/\hbar + (n+m)\omega]} \right]. \quad (A13)$$

The terms, which mainly contribute to the series, are terms either in the exact resonance or close to resonance. The resonance is defined by the following condition:

$$\boldsymbol{\epsilon}(\boldsymbol{x})/\hbar + (n+m)\boldsymbol{\omega} = 0 \tag{A14}$$

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or

$$\Delta \epsilon_{m_0} \equiv |\epsilon(x) + (n+m)\hbar \omega| \ll \hbar \omega. \tag{A15}$$

The latter condition assumes that the mismatch is very small. These resonance conditions were widely used for driven electron transfer without⁵⁹ and with dissipation.⁶⁰

We denote the resonance value of the integer as follows:

$$m_0 \equiv m + n. \tag{A16}$$

The double sum in Eq. (A13) becomes single with resonance condition (A14) or (A15). Thus, for long times or small λ 's, Eq. (A13) can be transformed into the following equation:

$$\lambda P(x,\lambda) - 1 = -\frac{\Delta^2}{2} J_{m_0}(a) \sum_{n=-\infty}^{\infty} J_{m_0 - n}(a) \left[\frac{P(\lambda - in\omega)}{\lambda - i\Delta\epsilon_{m_0}\hbar} + \frac{P(\lambda + in\omega)}{\lambda + i\Delta\epsilon_{m_0}/\hbar} \right].$$
(A17)

For $n \neq 0$, one can neglect small λ in $P(\lambda \pm in\omega)$, since all terms become the small corrections of the order $(\Delta/\omega)^2$ with respect to unity in Eq. (A17). Therefore, one should keep the term with n=0. This condition essentially simplifies Eq. (A17),

$$\lambda P(x,\lambda) - 1 = -\Delta^2 \frac{\lambda J_{m_0}^2(a) P(x)}{\lambda^2 + (\Delta \epsilon_{m_0}/\hbar)^2}.$$
 (A18)

The solution of this equation is straightforward,

$$P(x,\lambda) = \frac{1}{\lambda} \frac{\lambda^2 + (\Delta \epsilon_{m_0}/\hbar)^2}{\lambda^2 + \Omega_{m_0}^2},$$
 (A19)

where the Rabi frequency Ω_{m_0} is defined in the usual way,

$$\Omega_{m_0}^2 \equiv \Delta_{m_0}^2 + (\Delta \epsilon_{m_0} / \hbar)^2 .$$
 (A20)

 Δ_{m_0} stands for

$$\Delta_{m_0} \equiv \Delta \left| J_{m_0}(a) \right| \,. \tag{A21}$$

Finally the time-dependent probability difference can be found with the inverse Laplace transform of Eq. (A19), yielding the following solution:

$$P_{m_0}(x,t) = \frac{(\Delta \epsilon_{m_0}/\hbar)^2}{\Omega_{m_0}^2} + \frac{\Delta_{m_0}^2}{\Omega_{m_0}^2} \cos(\Omega_{m_0} t). \quad (A22)$$

The final expression for the transition probability difference is determined by Eq. (A1)

$$P(t) = \frac{1}{\sqrt{\pi}} \int_{-\infty}^{\infty} dx \exp(-x^2) P_{m_0}(x,t), \qquad (A23)$$

with P_{m_0} defined by Eq. (A22).

APPENDIX B: A HIGH FREQUENCY ELECTRIC FIELD

As seen from Eqs. (A3) and (A15), $\Delta \epsilon_{m_0}$ depends on the parameter *x*. Therefore, resonance condition (A14) or (A15)

is smeared by the distribution of *x*. Consequently, many resonances (actually an infinite number) occur. We consider fields with high frequencies in order to study a single, well-defined resonance, assuming that the following condition is satisfied:

$$\hbar \omega \gg \sqrt{E_r kT}.$$
 (B1)

The contribution of the term, where $m + n = m_0$ in Eq. (A13), dominates. Here m_0 is determined from the following equation:

$$\boldsymbol{\epsilon} - \boldsymbol{E}_r + \boldsymbol{m}_0 \hbar \,\boldsymbol{\omega} = \boldsymbol{0}. \tag{B2}$$

For a small mismatch, the following inequality takes place:

$$|\epsilon - E_r + m_0 \hbar \omega| \ll 2\sqrt{E_r kT}.$$
(B3)

In an experiment one measures an electron density at a donor site rather than the probability difference P(t). Hence the probability for the electron density to be at the donor level $P_1(t)$ can be merely defined through P(t),

$$P_1(t) = \frac{1 + P(t)}{2}.$$
 (B4)

Consequently, Eq. (A23) is transformed to the following equation for $P_1(t)$:

$$P_{1}(t) = 1 - \frac{\Delta_{m_{0}}^{2}}{2\sqrt{\pi}} \int_{-\infty}^{\infty} dx \exp(-x^{2}) \frac{1 - \cos[\Omega_{m_{0}}(x)t]}{\Omega_{m_{0}}^{2}(x)}.$$
(B5)

Here the frequency $\Omega_{m_0}^2(x)$ stands for

$$\Omega_{m_0}^2(x) = \Delta^2 J_{m_0}^2(a) + \left(\frac{2x}{\tau_0} + \frac{\epsilon - E_r + m_0 \hbar \omega}{\hbar}\right)^2. \quad (B6)$$

Integral (B5) with $\Omega_{m_0}^2(x)$ defined by Eq. (B4) with resonance condition (B2), can be performed using the saddle-point approximation and results in the following expression for $P_1(t)$:

$$P_{1}(t) = 1 - \frac{\Delta_{m_{0}}}{2\sqrt{E_{r}kT/\hbar^{2} + \Delta_{m_{0}}^{2}}} + \frac{\Delta_{m_{0}}\cos[\Delta_{m_{0}}t + \phi(t)/2]}{2\sqrt[4]{(E_{r}kT/\hbar^{2} + \Delta_{m_{0}}^{2})^{2} + t^{2}\Delta_{m_{0}}^{2}(E_{r}kT/2\hbar^{2})^{2}}},$$
(B7)

where $\phi(t)$ is defined by

$$\cos[\phi(t)] = \frac{E_r k t/\hbar^2 + \Delta_{m_0}^2}{\sqrt{(E_r k T/\hbar^2 + \Delta_{m_0}^2)^2 + t^2 \Delta_{m_0}^2 (E_r k T/2\hbar^2)^2}},$$

$$\sin[\phi(t)] = \frac{\Delta_{m_0} t/2}{\sqrt{(E_r k T/\hbar^2 + \Delta_{m_0}^2)^2 + t^2 \Delta_{m_0}^2 (E_r k T/2\hbar^2)^2}}$$
(B8)

 $\phi \to 0$ when $t \to 0$ and $\phi \to \pi/2$ when $t \to \infty$. Solution (B7) is valid when condition (B8) is satisfied, i.e., $\Delta \epsilon(x) \ll 2\sqrt{E_r kT}$.

At long t,

$$P_{1}(t) = 1 - \frac{\Delta_{m_{0}}}{2\sqrt{E_{r}kT/\hbar^{2} + \Delta_{m_{0}}^{2}}} + \frac{\hbar\Delta_{m_{0}}\cos(\Delta_{m_{0}}t + \pi/4)}{\sqrt{E_{r}kT}}.$$
(B9)

Thus, at $t \to \infty$ the coherent oscillations slowly decay in time as $1/\sqrt{t}$. This dependence is much slower than exponential

*Electronic mail: yurid@uwyo.edu

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fast relaxation. In the derivation of Eq. (B7) or (B9) we have not specified the value of Δ_{m_0} . It can be larger or smaller than $\sqrt{E_r kT/\hbar^2}$. At the small ratio of the following parameter:

$$\frac{\Delta_{m_0}}{\sqrt{E_r kT/\hbar^2}},$$

a time dependence becomes insignificant.

The other important characteristic that should be analyzed is the equilibrium distribution P_{eq} determined from the following equation:

$$P_{\rm eq} = 1 - \frac{\Delta_{m_0}}{2\sqrt{(E_r k T/\hbar)^2 + \Delta_{m_0}^2}} \,. \tag{B10}$$

Equation (B10) determines the current in a circuit.

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