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Quantum Brownian motion on potential surfaces coupled via tunneling in an external electric field

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Abstract. The present paper deals with the motion of a Brownian particle on two identical but shifted potential surfaces, coupled *via* a tunneling matrix element in an external electric field. Dissipation is induced by a heat bath represented by an infinite set of harmonic oscillators with a continuum range of frequencies. We derive a perturbative solution for the quantum coherence term of the particle system after performing a small-polaron-like transformation. This is subsequently necessary for the extraction of an equation that describes the reduced dynamics and the minimal action path of the Brownian particle. Finally we extract expressions for the population relaxation rate and the pure quantum-dephasing rate of the two-level system.

PACS. 73.40.Gk Tunneling – 31.70.Hq Time-dependent phenomena: excitation and relaxation processes, and reaction rates – 05.40.-a Fluctuation phenomena, random processes, noise, and Brownian motion

1 Introduction

The modelling of Brownian motion and reaction dynamics as a system coupled to a bath of harmonic oscillators with a continuous range of frequencies is ubiquitous in physics and chemistry. The approach is common place in statistical mechanics.

In the present case we consider a two-potential-surface system coupled *via* a tunneling matrix element [1–8] with a particle moving on the surfaces. An external field [14] is applied as well as the heat bath. The bath in the case of Brownian motion [9–13] represents the environment, while in reaction dynamics it describes the possible excited states of a molecule or condensed medium [15,16].

We note that on the one hand systems coupled *via* tunneling have been studied extensively [12]. On the other hand there exist much discussion on the Brownian motion on an actual spatial coordinate of a particle. We suppose that an electric field, being either external or arising from the structure of the environment, acts on that coordinate.

One possible application of the present model is to describe electron transfer on macromolecules in a solution, the action of which is represented as a bath of harmonic oscillators.

The paper proceeds in the following order. In Section 2 we present the model Hamiltonian and perform a small-polaron-like transformation on it. This brings us to a stage from which we can proceed to apply a perturbative expansion to the terms related with the two-surface system. In Section 3, using the results of Section 2, we study the two-level dynamic state transitions. We obtain perturbative terms for the quantum coherence and the population difference of the two-surface system, and make calculations up to second order. In Section 4 we study the motion of a particle on a system coupled *via* tunneling potential surfaces. The additional, two-surface, modelled component of the motion induces an additional effective force in the quasiclassical equation of the motion. There is also a shift in the form of the potential in the effective action. This probably arises from the polarization of the two-surface system itself under the action of the external field in the fully quantum mechanical treatment. Formally the effect of this extra component appears with the introduction of the quantum coherence term of the two-surface system in all the terms of Section 4. The results of this section resemble those derived in the pioneering work of Caldeira and Leggett [9,17], but they differ considerably because of the presence of the two-surface system. In Section 5 we derive analytical expressions for the population relaxation rate and the pure quantum-dephasing rate, using the small polaron representation. As an effect of the coupling of the two-surface system with the spatial coordinate, the population relaxation rate involves explicitly the time dependent spatial coordinate. Finally in Section 6 we present our conclusions.

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$$\tilde{H} = U^{+}HU = \begin{pmatrix} \dfrac{p_{\mathrm{s}}^2}{2} + V_0(s) + \varDelta_0 \cos\left(2\sum_i \dfrac{c_i s}{\omega_i^2}P_i\right) & \mathrm{i}\varDelta_0 \sin\left(2\sum_i \dfrac{c_i s}{\omega_i^2}P_i\right) \\ -\mathrm{i}\varDelta_0 \sin\left(2\sum_i \dfrac{c_i s}{\omega_i^2}P_i\right) & \dfrac{p_{\mathrm{s}}^2}{2} + V_0(s) - \varDelta_0 \cos\left(2\sum_i \dfrac{c_i s}{\omega_i^2}P_i\right) \end{pmatrix} + \tilde{J}\sigma_x + H_{\mathrm{b}} \tag{3a}$$

$$\tilde{H} = \begin{pmatrix} \dfrac{p_{\mathrm{s}}^2}{2} + V_0(s) + \varDelta_0 \cos\left(2\sum_{i,j} A_{ji}\dfrac{c_i s}{\omega_i^2}D_j\right) & \mathrm{i}\varDelta_0 \sin\left(2\sum_i A_{ji}\dfrac{c_i s}{\omega_i^2}D_j\right) \\ -\mathrm{i}\varDelta_0 \sin\left(2\sum_i A_{ji}\dfrac{c_i s}{\omega_i^2}D_j\right) & \dfrac{p_{\mathrm{s}}^2}{2} + V_0(s) - \varDelta_0 \cos\left(2\sum_{i,j} A_{ji}\dfrac{c_i s}{\omega_i^2}D_j\right) \end{pmatrix} + \tilde{J}\sigma_x + H_{\mathrm{b}} \tag{3a*}$$

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2 The model Hamiltonian and small-polaron-like transformation

The present model Hamiltonian can be written as

$$H = H_{\mathrm{s}} + H_{\mathrm{t}} + H_{\mathrm{b}} + H_{\mathrm{I}}. \tag{1a}$$

The first term H_{s} describes the system motion in space and is given

$$H_{\mathrm{s}} = \begin{pmatrix} \dfrac{p_{\mathrm{s}}^2}{2} + V_0(s) + \varDelta_0 & 0 \\ 0 & \dfrac{p_{\mathrm{s}}^2}{2} + V_0(s) - \varDelta_0 \end{pmatrix}. \tag{1b}$$

The tunneling term between the two surfaces is described by the term H_{t} where

$$H_{\mathrm{t}} = J\sigma_x. \tag{1c}$$

We stress that the coupling matrix element is J. $\varDelta_0$ is just a shifting term.

The harmonic oscillator bath is given by the term H_{b} where

$$H_{\mathrm{b}} = \frac{1}{2}\sum_{i=1}^{N}(P_i^2 + \omega_i^2 Q_i^2). \tag{1d}$$

Finally the interaction term is

$$H_{\mathrm{I}} = \sum_{i=1}^{N} c_i s Q_i \sigma_x + \sum_{i=1}^{N} \frac{c_i^2 s^2}{2\omega_i^2}\,. \tag{1e}$$

The last term in (1e) is present in order to renormalize the potential [12].

The present case applies in the case of an electric field on the reaction coordinate. We suppose that both this field and the harmonic oscillator bath act on the system. This interaction comes out in the first term in (1e). The constant c_i is proportional to the electric-dipole matrix element between the two states of the two-level system.

$V_0(s)$ is the potential due to the presence of the electric field on the spatial coordinate. $2\varDelta_0$ is the energy difference between the two identical potential surfaces and J is the tunneling matrix element.

On performing on H a small-polaron-like unitary transformation using the following operator

$$U = \exp\left\{\mathrm{i}\sum_{j=1}^{N} \frac{c_j s P_j}{\omega_j^2}\sigma_\chi\right\} \tag{2}$$

we obtain the following expression

see equation (3a) above

where

$$\tilde{J} = J - \frac{1}{2}p_{\mathrm{s}}\left(\sum_{i=1}^{N}\frac{c_i}{\omega_i^2}P_i\right) - \frac{1}{2}\left(\sum_{i=1}^{N}\frac{c_i}{\omega_i^2}P_i\right)p_{\mathrm{s}} \tag{3b}$$

$$H_{\mathrm{b}} = \frac{1}{2}\sum_{i,j}F_{ij}P_iP_j + \frac{1}{2}\sum_i \omega_i^2 Q_i^2 \tag{3c}$$

$$F_{ij} = \delta_{ij} + \frac{c_i}{\omega_i^2}\frac{c_j}{\omega_j^2} \tag{3d}$$

$$[Q_i, P_j] = \mathrm{i}\delta_{ij}. \tag{3e}$$

Expressing the bath in terms of its normal modes we obtain

$$H_{\mathrm{b}} = \sum_{i=1}^{N}\frac{1}{2}(d_i^2 D_i^2 + \omega_i^2 Q_i^2) \tag{4a}$$

$$d^2 = A^{-1}FA \tag{4b}$$

$$d = diag(d_i) \tag{4c}$$

$$A^T = A^{-1} \quad \text{(orthogonal matrix)} \tag{4d}$$

$$P_i = \sum_j A_{ji}D_j \tag{4e}$$

$$[Q_j, D_k] = \mathrm{i}A_{kj}. \tag{4f}$$

Consequently (3a, b) can be written

see equation (3a) above*

and

$$\tilde{J} = J - \frac{1}{2}p_{\mathrm{s}}\left(\sum_{i=1}^{N}A_{ji}\frac{c_i}{\omega_i^2}D_j\right) - \frac{1}{2}\left(\sum_{i=1}^{N}A_{ji}\frac{c_i}{\omega_i^2}D_j\right)p_{\mathrm{s}}. \tag{3b*}$$

In the second quantization form, (4a) can be written as

$$H_{\mathrm{b}} = \sum_{i=1}^{N} \omega_i d_i \left(a_i^+ a_i + \frac{A_{ii}}{2} \right) \tag{5a}$$

where

$$a_i = \sqrt{\frac{d_i}{2\omega_i}} \left(\frac{\omega_i}{d_i} Q_i + \mathrm{i} D_i \right) \tag{6a}$$

$$a_i^+ = \sqrt{\frac{d_i}{2\omega_i}} \left(\frac{\omega_i}{d_i} Q_i - \mathrm{i} D_i \right). \tag{6b}$$

Now we split (3a) into three parts

$$H_{\mathrm{A}} = J\sigma_X \tag{7a}$$

$$H_{\mathrm{B}} = \frac{p_{\mathrm{s}}^2}{2} + V_0(s) + H_{\mathrm{b}} \tag{7b}$$

$$V_{\mathrm{AB}} = \mathit{\Delta}_0 \cos\eta\sigma_z - \mathit{\Delta}_0 \sin\eta\sigma_y + (\tilde{J} - J)\sigma_x \tag{7c}$$

where

$$\eta = 2\sum_{i,j} A_{ji} \frac{c_i s}{\omega_i^2} D_j. \tag{7d}$$

We observe that under the small polaron transformation we have arrived to a form from which a perturbation expansion is possible.

3 Two-surface system population dynamics

The quantum coherence of the two surface system is expressed by the matrix elements

$$\mathit{\Theta}_{+-}(t) = \langle + | \rho(t) | - \rangle \tag{8a}$$

$$\mathit{\Theta}_{-+}(t) = \langle - | \rho(t) | + \rangle \tag{8b}$$

while the population difference is given by

$$P(t) = \langle + | \rho | + \rangle - \langle - | \rho | - \rangle \tag{8c}$$

where $|+\rangle$, $|-\rangle$ are the two local eigenstates of the two level system and $\rho(t)$ is the reduced density matrix of the two level system

$$\rho(t) = \mathrm{Tr}_{\mathrm{B}}[\rho_{\mathrm{t}}(t)]. \tag{9}$$

$\mathrm{Tr}_{\mathrm{B}}[\ ]$ represents the trace over the environment (the bath and the reaction path) and $\rho_{\mathrm{t}}(t)$ is the total density matrix.

Our intention is to derive an expansion with respect to V_{AB} for the quantum coherence term, which will be used in a subsequent section.

The total density matrix obeys the Liouville equation

$$\mathrm{i}\frac{\mathrm{d}\rho_{\mathrm{t}}(t)}{\mathrm{d}t} = [H_{\mathrm{A}} + H_{\mathrm{B}} + V_{\mathrm{AB}}, \rho_{\mathrm{t}}(t)]. \tag{10}$$

We deal with V_{AB} term using the method of perturbation theory.

Finally we have the following expression for the expansion of the reduced density matrix of the two-level system $\rho(t) = \mathrm{Tr}_{\mathrm{B}}[\rho_{\mathrm{t}}(t)]$, in orders of the interaction V_{AB}

$$\rho(t) = \sum_{n=0}^{\infty} \int_0^t \mathrm{d}\tau_n \int_0^{\tau_n} \mathrm{d}\tau_{n-1} \cdots \int_0^{\tau_2} \mathrm{d}\tau_1 \rho^{(n)} \times (t, \tau_n, \tau_{n-1}, \ldots, \tau_1) \tag{11}$$

where

$$\begin{aligned} \rho^{(n)}(t, \tau_n, \tau_{n-1}, \ldots, \tau_1) = \\ [-\mathrm{i}]^n \mathrm{Tr}_{\mathrm{B}} \Big[\exp(-\mathrm{i}(t - \tau_n)(H_{\mathrm{A}} + H_{\mathrm{B}})^X) V_{\mathrm{AB}}^X \\ \times \exp\left[-\mathrm{i}(\tau_n - \tau_{n-1})(H_{\mathrm{A}} + H_{\mathrm{B}})^X\right] V_{\mathrm{AB}}^X \ldots V_{\mathrm{AB}}^X \\ \times \exp\left[-\mathrm{i}(\tau_2 - \tau_1)(H_{\mathrm{A}} + H_{\mathrm{B}})^X\right] V_{\mathrm{AB}}^X \rho(0) \Big]. \end{aligned} \tag{12}$$

In the above expression we used the super operator notation X defined by

$$S^X R = SR - RS$$

$$S^X R^X T = S(RT - TR) - (RT - TR)S$$

and so on. S, R and T are ordinary operators.

$\rho(0)$ corresponds to an initial equilibrium state density matrix of the two-level system plus the environment (consisting of the bath and the reaction path).

We assume that this term factorizes according to

$$\rho(0) = |g\rangle\langle g| \rho_{\mathrm{B}} \tag{13}$$

where $|g\rangle$ is the initial state of the two-level system. At this point we note that $|g\rangle$ can be written in the form $|g\rangle = a|+\rangle + b|-\rangle$, $|a|^2 + |b|^2 = 1$. The expression for ρ_{B} is given in the next section.

Since V_{AB}^X acts either from the left or from the right and $\rho^{(n)}$ contains nV_{AB} factors, (12) can be separated into $M = 2^n$ terms denoted as Liouville-space paths. It is necessary to evaluate half of these terms, since they come in Hermitian conjugate pairs and $\rho^{(n)}$ are Hermitian. Consequently

$$\rho^{(n)}(t, \tau_n, \tau_{n-1}, \ldots, \tau_1) = \sum_{k=1}^{M/2} \rho_k^{(n)}(t) + \mathrm{h.c.} \tag{14}$$

where k denotes the paths.

For an initial $\frac{1}{\sqrt{2}}(|+\rangle + |-\rangle)$ state the quantum coherence is finally reduced to the following expressions

$$\begin{aligned} \mathit{\Theta}_{+-}(t) = \langle + | \rho | - \rangle = \\ \frac{1}{2} + \mathrm{Tr}\left(I_{+-}^2 - I_{+-} I_{+-}^+ - \frac{1}{2} I_{++}^2 - \frac{1}{2} I_{--}^2 + I_{++} I_{--} \right) \rho_{\mathrm{B}} \end{aligned} \tag{15a}$$

$$\begin{aligned} \mathit{\Theta}_{-+}(t) = \langle - | \rho | + \rangle = \\ \frac{1}{2} + \mathrm{Tr}\left(I_{-+}^2 - I_{-+} I_{-+}^+ + \frac{1}{2} I_{++}^2 - \frac{1}{2} I_{--}^2 + I_{++} I_{--} \right) \rho_{\mathrm{B}}, \end{aligned} \tag{15b}$$

while for an initial $|+\rangle$ state the population difference is

$$P(t) = 1 - 2\,\mathrm{Tr}(I_{+-} I_{+-}^+) \rho_{\mathrm{B}}. \tag{15c}$$

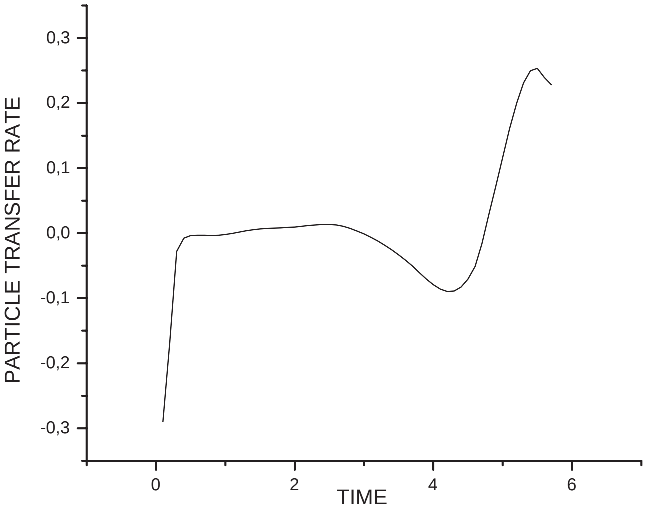

Fig. 1. Particle transfer rate *versus* time with parameters: $\Delta_0 = 0.02$, $c_i = 3.0 \times 10^{-5}$, $\omega_i = 0.1$, $\beta = 0.1$, $w_{\mathrm{s}} = 0.1$, $J = 1.0$. Three harmonic oscillators have been used.

From this expression the particle transfer rate between the potential surfaces follows directly *via* differentiation. In Figure 1 we plot the rate *versus* time. We observe a plateau at a zero value of the rate corresponding to a temporary population trapping, followed by a dip corresponding to an increase and a subsequent decrease of the population of the initial state. Similar results can be obtained for other initial states.

ρ_{B} is the B system density matrix and I_{++}, I_{--}, I_{+-}, I_{-+} are given by the expressions

$$I_{++} = \int_0^t \mathrm{d}t_1 U_0^{\mathrm{B}^+}(t_1)\langle +|V_{\mathrm{AB}}|+\rangle U_0^{\mathrm{B}}(t_1) \tag{16a}$$

$$I_{--} = \int_0^t \mathrm{d}t_1 U_0^{\mathrm{B}^+}(t_1)\langle -|V_{\mathrm{AB}}|-\rangle U_0^{\mathrm{B}}(t_1) \tag{16b}$$

$$I_{+-} = \int_0^t \mathrm{d}t_1 \mathrm{e}^{-2\mathrm{i}Jt_1} U_0^{\mathrm{B}^+}(t_1)\langle +|V_{\mathrm{AB}}|-\rangle U_0^{\mathrm{B}}(t_1) \tag{16c}$$

$$I_{-+} = \int_0^t \mathrm{d}t_1 \mathrm{e}^{-2\mathrm{i}Jt_1} U_0^{\mathrm{B}^+}(t_1)\langle -|V_{\mathrm{AB}}|+\rangle U_0^{\mathrm{B}}(t_1) \tag{16d}$$

where

$$U_0^{\mathrm{B}}(t) = \exp(-\mathrm{i}H_{\mathrm{B}}t). \tag{16e}$$

Explicit expressions are given in Appendix A.

In the next section we are going to use for $\Theta(t)$ the value

$$\Theta(t) = \Theta_{+-}(t) + \Theta_{-+}(t). \tag{17}$$

We use both the present form and a Wick-rotated form.

Additionally we have assumed that an inverted parabolic potential is added to the two level system due to the presence of the electric field. Here $V_0(s)$ is given by the expression

$$V_0(s) = -\frac{1}{2} w_{\mathrm{s}}^2 s^2. \tag{18}$$

This form is the result after a Taylor expansion of the potential of the electric field of the environment near a saddle point. *I.e.* under this assumption we have restricted ourselves to a transition state theory.

4 Reduced dynamics and minimal action path

We easily obtain the reduce Hamiltonian of (1a) by taking a trace over the two surface system. This results in the expression

$$H_{\mathrm{red}} = F(t) + \frac{p_{\mathrm{s}}^2}{2} + V_0(s) + \frac{1}{2}\sum_{\alpha=1}^{N}(P_\alpha^2 + \omega_\alpha^2 Q_\alpha^2) + \Theta(t)\sum_{\alpha=1}^{N} c_\alpha s Q_\alpha + \sum_{\alpha=1}^{N}\frac{c_\alpha^2 s^2}{2\omega_\alpha^2} \tag{19}$$

where $F(t)$ is a term coming from the rest terms of the initial Hamiltonian (1), and depends on time and some constants. We note that $F(t)$ does not appear in most of our final expressions. $\Theta(t)$ has been obtained in the previous section.

The corresponding Lagrangian is the following

$$L(s(t),\{Q_\alpha(t)\}) = -F(t) + \frac{1}{2}\dot{s}^2 - V_0(s) + \frac{1}{2}\sum_{\alpha=1}^{N}(\dot{Q}_\alpha^2 - \omega_\alpha^2 Q_\alpha^2) - \Theta(t)\sum_{\alpha=1}^{N} c_\alpha s Q_\alpha - \sum_{\alpha=1}^{N}\frac{c_\alpha^2 s^2}{2\omega_\alpha^2}\,. \tag{20}$$

Let $K(s_f,\{Q_{\alpha f}\};s_i,\{Q_{\alpha i}\};T)$ be the quantum propagator for the universe (system plus environment), which goes from coordinates $(s_i,\{Q_{\alpha i}\})$ at time zero to $(s_f\{Q_{\alpha f}\})$ at time T. It is given by the expression

$$K(s_f,\{Q_{\alpha f}\};s_i,\{Q_{\alpha i}\};T) = \sum_n \psi_n^*(s_i,\{Q_{\alpha i}\})\psi_n(s_f,\{Q_{\alpha f}\})\exp(-\mathrm{i}E_n T). \tag{21}$$

In the Feynman path integral form the propagator can be written as

$$K(s_f,\{Q_{\alpha f}\};s_i,\{Q_{\alpha i}\};T) = \int_{s(0)=s_i}^{s(T)=s_f}\mathrm{D}s(t) \times \int_{\{Q_\alpha(0)\}=\{Q_{\alpha i}\}}^{\{Q_\alpha(T)\}=\{Q_{\alpha f}\}}\prod_\alpha \mathrm{D}Q_\alpha(t) \times \exp\left(\mathrm{i}\int_0^T L(s(t),\{Q_\alpha(t)\})\mathrm{d}t\right). \tag{22}$$

By integrating out the normal modes Q_α, we can eliminate the degrees of freedom of the bath and the influence function, which involves an effective action, drops out. This can be written as [18,19]

$$\begin{aligned}\tilde{K}(s_f, s_i; T) = \int \prod_\alpha \mathrm{d}Q_{\alpha f} K(s_f, \{Q_{\alpha f}\}; s_i, \{Q_{\alpha i}\}; T) \\ \times K^*(s_f, \{Q_{\alpha f}\}; s_i, \{Q'_{\alpha i}\}; T) \\ \times \prod_\alpha \left(\sum_j \phi_j(Q_{\alpha i}) \phi_j^*(Q'_{\alpha i}) \mathrm{e}^{-j\omega_\alpha \beta}(1 - \mathrm{e}^{-\omega_\alpha \beta}) \right) \\ \times \prod_\alpha \mathrm{d}Q_{\alpha i} \mathrm{d}Q'_{\alpha i}. \quad (23)\end{aligned}$$

We assume that we have decoupled forced harmonic oscillators at temperature β at the initial time. $\phi_j(Q_\alpha)$ is the j eigenfunction of the α harmonic oscillator.

We observe that the Lagrangian (20), with respect to Q_α, is that of the sum of forced oscillators, plus some other terms. Consequently for these oscillators we can write the path integral expression

$$\begin{aligned}\int_{Q(0)=Q_i}^{Q(T)=Q_f} \mathrm{D}Q(t) \\ \times \exp\left\{ \mathrm{i} \int_0^T \left[\frac{1}{2}(\dot{Q}^2 - \omega_\alpha^2 Q^2) - \Theta(t) s(t) Q \right] \mathrm{d}t \right\} \\ = \left(\frac{\omega_\alpha}{2\pi \mathrm{i} \sin(\omega_\alpha t)} \right)^{1/2} \exp(\mathrm{i}\Phi_\alpha) \quad (24)\end{aligned}$$

where

$$\begin{aligned}\Phi_\alpha = \frac{\omega_\alpha}{2\sin(\omega_\alpha T)} \left\{ (Q_{\alpha i}^2 + Q_{\alpha f}^2) \cos(\omega_\alpha T) - 2 Q_{\alpha i} Q_{\alpha f} \right\} \\ + \frac{Q_{\alpha i} c_\alpha}{\sin(\omega_\alpha T)} \int_0^T \mathrm{d}u \sin(\omega_\alpha (T-u)) \Theta(u) s(u) \\ + \frac{Q_{\alpha f} c_\alpha}{\sin(\omega_\alpha T)} \int_0^T \mathrm{d}u \sin(\omega_\alpha u) \Theta(u) s(u) \\ - \frac{c_\alpha^2}{\omega_\alpha \sin(\omega_\alpha T)} \int_0^T \mathrm{d}u \int_0^u \mathrm{d}w \\ \times \sin(\omega_\alpha (T-u)) \sin(\omega_\alpha w) \Theta(u) s(u) \Theta(w) s(w). \quad (25)\end{aligned}$$

On using the identity

$$\begin{aligned}\sum_j \phi_j(Q_{\alpha i}) \phi_j^*(Q'_{\alpha i}) \mathrm{e}^{-j\omega_\alpha \beta}(1 - \mathrm{e}^{-\omega_\alpha \beta}) = \left(\frac{\omega_\alpha}{\pi \coth(\omega_\alpha \beta/2)} \right)^{1/2} \\ \times \exp\left\{ -\frac{\omega_\alpha}{2\sinh(\omega_\alpha \beta)} \left[(Q_{\alpha i}^2 + Q_{\alpha i}^{\prime 2}) \cosh(\omega_\alpha \beta) - 2 Q_{\alpha i} Q'_{\alpha i} \right] \right\} \\ (26)\end{aligned}$$

and performing the Gaussian integrations we finally get the influence phase [18,19]

$$\begin{aligned}\Phi(s, s') = -\int_0^T \int_0^t [(s(t) - s'(t))(\alpha(t,t') s(t') \\ - \alpha^*(t,t') s'(t'))] \mathrm{d}t \mathrm{d}t' \quad (27\mathrm{a})\end{aligned}$$

where

$$\begin{aligned}\alpha(t,t') = \sum_i \Theta(t)\Theta(t') \frac{c_i^2}{2\omega_i} \left\{ [1 + N(\omega_i)] \mathrm{e}^{\mathrm{i}\omega_i (t-t')} \right. \\ \left. + N(\omega_i) \mathrm{e}^{-\mathrm{i}\omega_i (t-t')} \right\}. \quad (27\mathrm{b})\end{aligned}$$

$N(\omega)$ is the Bose-Einstein distribution function

$$N(\omega) = \frac{1}{\mathrm{e}^{\beta\omega} - 1} \cdot \quad (28)$$

Finally (23) can be written as

$$\begin{aligned}\tilde{K}(s_f, s_i, T) = \iint \mathrm{D}s(t) D s'(t) \exp(\mathrm{i} S[s(t)] \\ - \mathrm{i} S[s'(t)] + \Phi(s, s')) \quad (29)\end{aligned}$$

where

$$S[s(t)] = \int_0^T \mathrm{d}t \left[\frac{1}{2}\dot{s}^2(t) - V_0(s(t)) - F(t) - s^2(t) \sum_{\alpha=1}^N \frac{c_\alpha^2}{2\omega_\alpha^2} \right]. \quad (30)$$

The Lagrangian can be simplified by analytically continuing T to imaginary times iθ. Since the resulting $\alpha(\tau)$ is periodic with period β we can continue the imaginary time outside the range $0 \leq \tau \leq \theta$, using the periodic boundary conditions $s(\beta + \tau) = s(\tau)$, $\Theta(\beta + \tau) = \Theta(\tau)$. Finally using in addition the following expansion

$$\frac{1}{1 - \mathrm{e}^{-\beta\omega}} = \sum_{n=0}^\infty \mathrm{e}^{-n\beta\omega} \quad (31)$$

we obtain the Euclidean terms

$$\begin{aligned}\Phi_{\mathrm{E}}(s, s') = -\frac{1}{2} \int_0^\theta \int_{-\infty}^\infty \alpha(\tau, \tau') \\ \times [(s(\tau) - s'(\tau))(s(\tau') - s'(\tau'))] \mathrm{d}\tau \mathrm{d}\tau' \quad (32)\end{aligned}$$

$$S_{\mathrm{E}}[s(\tau)] = \int_0^\theta \mathrm{d}\tau \left[\frac{1}{2}\dot{s}^2(\tau) + V_0(s(\tau)) + F(\tau) \right] \quad (33)$$

where

$$\alpha(\tau, \tau') = \Theta(\tau)\Theta(\tau') \sum_i \frac{c_i^2}{2\omega_i} \mathrm{e}^{-\omega_i |\tau - \tau'|}. \quad (34)$$

The last term in (30) has been incorporated into the potential $V_0(s)$.

Now we make the crucial assumption that for all values of ω of interest for the present problem the spectrum of the environmental oscillators may be treated as continuous. Then the generalized spectral density of the problem has the following form

$$J(\omega,t,t')=\frac{\pi}{2}\Theta(t)\Theta(t')\sum_{i=1}^{N}\frac{c_i^2}{\omega_i}\delta(\omega-\omega_i). \qquad (35)$$

Continuing our study under this assumption. Then (27b) can be rewritten as

$$\alpha(t,t')=\int_0^{+\infty}\frac{\mathrm{d}\omega}{\pi}J(\omega,t,t')$$
$$\times\left\{[1+N(\omega)]\mathrm{e}^{\mathrm{i}\omega(t-t')}+N(\omega)\mathrm{e}^{\mathrm{i}\omega(t-t')}\right\}, \qquad (36)$$

while (34) is given as

$$\alpha(\tau,\tau')=\int_0^{\infty}\frac{\mathrm{d}\omega}{\pi}J(\omega,\tau,\tau')\exp(-\omega|\tau-\tau'|). \qquad (37)$$

Variation with respect to $s(\tau)$ with fixed endpoints (see (39) bellow) leads to the equation obeyed by the minimal action path

$$\ddot{s}_\mathrm{c}=\frac{\partial V_0'}{\partial s_\mathrm{c}}+\int_{-\infty}^{+\infty}\mathrm{d}\tau'\alpha(\tau,\tau')s_\mathrm{c}(\tau') \qquad (38)$$

$$s(0)=s_i,\quad s(\theta)=s_f. \qquad (39)$$

Now we study the Ohmic case in which the spectral density has the form

$$J(\omega,\tau,\tau')=\Theta(\tau)\Theta(\tau')\eta\omega. \qquad (40)$$

With this choice (37) yields

$$\alpha(\tau,\tau')=\Theta(\tau)\Theta(\tau')\frac{\eta}{2\pi}\frac{1}{(\tau-\tau')^2}\cdot \qquad (41)$$

By choosing the potential $V_0(s)$ as in Section 3 and using (41, 38) yields

$$\ddot{s}_\mathrm{c}=-w_\mathrm{s}^2 s_\mathrm{c}+\frac{\eta}{\pi}\int_{-\infty}^{+\infty}\mathrm{d}\tau'\Theta(\tau)\Theta(\tau')\frac{1}{(\tau-\tau')^2}s_\mathrm{c}\tau \qquad (42)$$

$$s(0)=s_i,\quad s(\theta)=s_f. \qquad (43)$$

(42) is an integro-differential equation, which can be solved numerically.

5 The small polaron representation, population relaxation rate and pure dephasing rate

The thermal average of $\varDelta_\mathrm{s}$ over the bath is given by the expression

$$\langle\varDelta_\mathrm{s}\rangle_\mathrm{b}=\varDelta_0\langle\cos\eta\rangle$$
$$=\varDelta_0\exp\left\{-\sum_{i,j}A_{ji}^2\frac{c_i^2s^2}{\omega_i^4}A_{jj}\frac{\omega_j}{d_j}\coth\frac{\beta\omega_j d_j}{2}\right\} \qquad (44)$$

where

$$\eta=2\sum_{i,j}A_{ji}\frac{c_i s}{\omega_i^2}D_j \qquad (45)$$

as given in Section 2.

Adding and subtracting $\langle\varDelta_\mathrm{s}\rangle_\mathrm{b}\sigma_z$ in the Hamiltonian (7) and splitting it into two parts with the criterion that the dynamics generated by the one part, here $\tilde{H}_0$, should be close to those generated by the full Hamiltonian, we obtain in the so called small polaron representation

$$\tilde{H}=\tilde{H}_0+\varDelta\tilde{H} \qquad (46a)$$

$$\tilde{H}_0=J\sigma_\chi-\langle\varDelta_\mathrm{s}\rangle_\mathrm{b}\sigma_z+H_\mathrm{b}+\frac{1}{2}p_\mathrm{s}^2+V_0(s) \qquad (46b)$$

$$\varDelta\tilde{H}=(\tilde{J}-J)\sigma_\chi-\varDelta_0(\cos\eta-\langle\cos\eta\rangle)\sigma_z-\varDelta_0\sin\eta\sigma_y. \qquad (46c)$$

Adopting the present second order perturbation description, the population relaxation rate is given by the expression [21]

$$\varGamma=\int_{-\infty}^{+\infty}\mathrm{d}t\mathrm{e}^{2\mathrm{i}Jt}\langle\varDelta\tilde{H}_{-+}(t)\varDelta\tilde{H}_{+-}\rangle_{\mathrm{b,s}}. \qquad (47)$$

We have assumed that the tunneling constant is dominant in comparison to the well's splitting. Additionally we note that the statistical average is taken over both the thermal bath of harmonic oscillators and the initial and final quantum distribution of position, described by a density matrix. A path integral as presented in the previous section can evaluate this density matrix. We note that $F(t)$ does not appear in the final expression of the density matrix as can easily be observed.

It is not difficult to extract that

$$\varDelta\tilde{H}_{+-}(t)=\varDelta(t)+\mathrm{i}\varDelta_0\sin\eta \qquad (48a)$$

$$\varDelta\tilde{H}_{-+}(t)=\varDelta(t)-\mathrm{i}\varDelta_0\sin\eta \qquad (48b)$$

where

$$\varDelta(t)=\frac{1}{2}p_\mathrm{s}(t)\left(\sum_{i,j}A_{ji}\frac{c_i}{\omega_i^2}D_j(t)\right)$$
$$+\frac{1}{2}\left(\sum_{i,j}A_{ji}\frac{c_i}{\omega_i^2}D_j(t)\right)p_\mathrm{s}(t). \qquad (49)$$

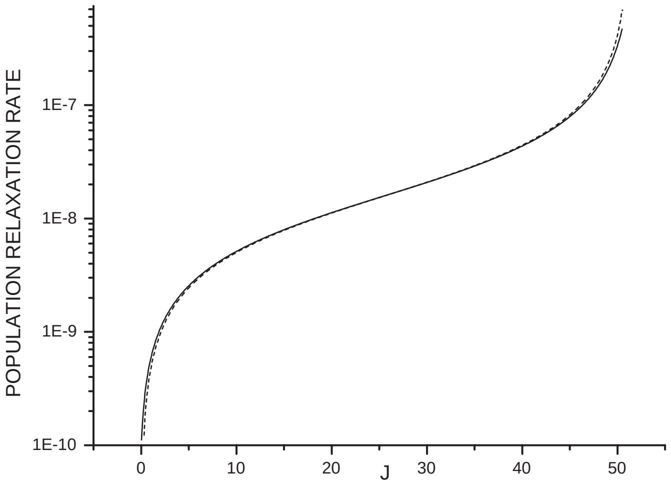

Fig. 2. Population relaxation rate *versus* tunneling coupling constant for various temperatures. Solid curve: $\beta = 0.1$. Dashed curve: $\beta = 50.0$. The rest of the parameters are: $c_i = 3.0 \times 10^{-5}$, $\omega_i = 0.1$, $w_\mathrm{s} = 0.1$. Three harmonic oscillators have been used.

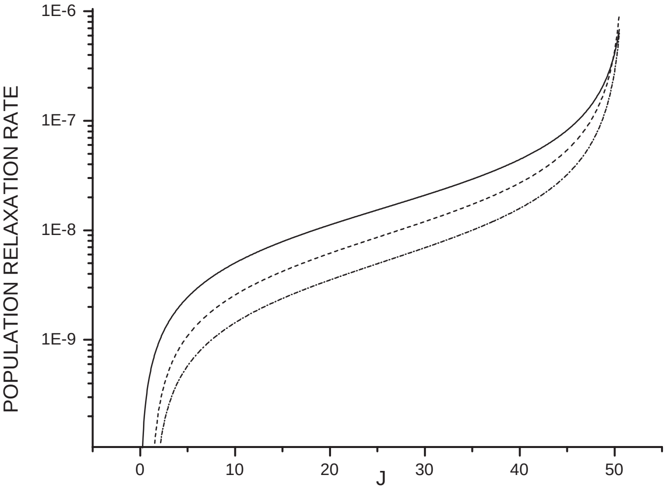

Fig. 3. Population relaxation rate *versus* tunneling coupling constant for various w_s. Solid curve: $w_\mathrm{s} = 0.1$. Dashed curve: $w_\mathrm{s} = 0.6$. Dashed-dotted curve: $w_\mathrm{s} = 1.0$. The rest of the parameters are: $c_i = 3.0 \times 10^{-5}$, $\omega_i = 0.1$, $\beta = 2.0$. Three harmonic oscillators have been used.

The average over the bath can be evaluated *via* standard theorems of statistical mechanics [20]. The average over the system is obtained by using a density matrix as described above.

Thus (47) can be written as

$$\Gamma = \sum_{i,l,j} A_{ji} A_{jl} \frac{c_i}{\omega_i^2} \frac{c_l}{\omega_l^2} \frac{\omega_j}{d_j} \int_{-\infty}^{\infty} \mathrm{d}t \mathrm{e}^{2\mathrm{i}Jt} \langle p_\mathrm{s}(t) p_\mathrm{s} \rangle_\mathrm{s} \times (\overline{n}_j \exp(\mathrm{i}\omega_j d_j t) + (1 + \overline{n}_j) \exp(-\mathrm{i}\omega_j d_j t)). \tag{50}$$

$\overline{n}_j$ is given by the expression

$$\overline{n}_j = \frac{1}{\mathrm{e}^{\beta \omega_j d_j} - 1} \cdot \tag{51}$$

We have plotted the population relaxation rate *versus* J for different temperatures in Figure 2 and for different w_s in Figure 3. We observe an increase in the population relaxation rate with increased J as expected, since stronger tunneling coupling assists population transfer and consequently population relaxation rate.

The pure dephasing rate is given as [21]

$$\Gamma_\mathrm{PD} = \frac{1}{2} \int_{-\infty}^{+\infty} \mathrm{d}t \left\langle \left(\Delta\tilde{H}_{--}(t) - \Delta\tilde{H}_{++}(t) \right) \times \left(\Delta\tilde{H}_{--} - \Delta\tilde{H}_{++} \right) \right\rangle_{\mathrm{b,s}} \cdot \tag{52}$$

On setting

$$S = \Delta_0 \exp\left\{ -2\mathrm{i} \sum_{i,j} A_{ji} \frac{c_i s}{\omega_i^2} D_j \right\}, \tag{53}$$

we can write

$$\left\langle \left(\Delta\tilde{H}_{--}(t) - \Delta\tilde{H}_{++}(t) \right) \left(\Delta\tilde{H}_{--} - \Delta\tilde{H}_{++} \right) \right\rangle_{\mathrm{b,s}} = \left\langle \begin{matrix} \langle S(t) S \rangle_\mathrm{b} + \langle S(t) S^+ \rangle_\mathrm{b} + \\ + \langle S^+(t) S \rangle_\mathrm{b} + \langle S^+(t) S^+ \rangle_\mathrm{b} \end{matrix} \right\rangle_\mathrm{s} \cdot \tag{54}$$

As far as the bath averages are concerned we give the value of one of them. Similar expressions are valid for the others:

$$\langle S(t) S^+ \rangle_\mathrm{b} = \Delta_0^2 \times \exp\left\{ -\sum_{i,j} \left(A_{ji}^2 \frac{c_i^2}{\omega_i^4} A_{jj} \frac{\omega_j}{d_j} (s_t^2 + s^2) \right) \coth \frac{\beta \omega_j d_j}{2} \right\} \times \exp\left\{ 2 \sum_{i,j} A_{ji}^2 A_{jj} \frac{\omega_j}{d_j} \frac{c_i^2}{\omega_i^4} s_t s \begin{pmatrix} \coth \frac{\beta \omega_j d_j}{2} \cos(\omega_j d_j t) \\ -\mathrm{i} \sin(\omega_j d_j t) \end{pmatrix} \right\} \tag{55}$$

where s_t is a shortening for $s(t)$.

As discussed above the average over the spatial coordinate can be performed using the results of the previous section.

In Figure 4 we plot the pure dephasing rate *versus* w_s for different Δ_0. We observe an increase of the pure dephasing rate with increasing Δ_0, since dephasing is proportional to Δ_0^2.

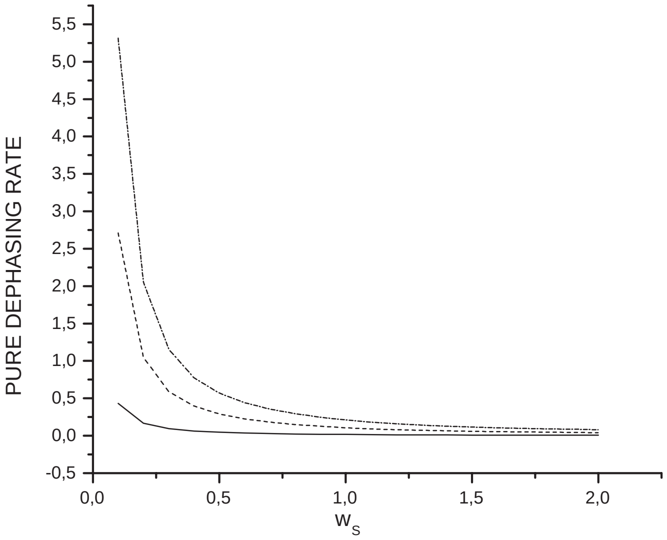

Fig. 4. Pure dephasing rate *versus* w_s. Solid curve: $\Delta_0 = 0.02$. Dashed curve: $\Delta_0 = 0.05$. Dashed-dotted curve: $\Delta_0 = 0.07$. The other parameters are: $c_i = 3.0 \times 10^{-5}$, $\omega_i = 0.1$, $\beta = 50.0$. Three harmonic oscillators have been used.

6 Conclusions

In the present study we investigated the solution of a problem described by the Hamiltonian (1), *i.e.* the dynamics of a system with components represented by motion on two surfaces coupled *via* tunneling in both an electric field and a harmonic bath with a continuous range of frequencies. To achieve that, we used the Hamiltonian (1) in three different, either partitioned or reduced forms, depending on the quantity we wish to calculate.

Firstly we used a small polaron transformation to extract dynamical information of the two-surface system, *i.e.* the quantum coherence term. Then we used a reduced form to obtain information concerning the spatial motion. Finally we used a small polaron representation to obtain statistical information for the two-surface system.

The new point of the present model is the combination of the spatial Brownian motion with a two level system. Independently these systems have already been studied extensively [1–17]. On comparing our results with the independent cases we see that the other component induces new factors into the equations describing the combined system. In many aspects the means of treating the specific component remains, in principle the same. For example we use the formalism developed originally by Caldeira and Leggett to integrating out the heat bath degrees of freedom acting on the system.

Despite its simplicity, our model is able to produce accurate and tractable expressions. In addition the application to electron transfer in macromolecules in solutions, as discussed in the introduction, appears quite promising. We are going to use it in future calculations.

Appendix A

After (17) we can write (16a, b, c, d) as

$$I_{++} = -\Delta_0 \int_0^t \mathrm{d}t_1 \cos\eta = -\frac{\Delta_0}{2} \int_0^t \mathrm{d}t_1 [L(t_1) + L^{+}(t_1)] \tag{A.1a}$$

$$I_{--} = -I_{++} \tag{A.1b}$$

$$\begin{aligned} I_{+-} &= \int_0^t \mathrm{d}t_1 \mathrm{e}^{-2\mathrm{i}Jt_1} (\tilde{J} - J - \mathrm{i}\Delta_0 \sin\eta) \\ &= -\int_0^t \mathrm{d}t_1 \mathrm{e}^{-2\mathrm{i}Jt_1} \left[T(t_1) + \frac{\Delta_0}{2} \left(L^{+}(t_1) - L(t_1) \right) \right] \end{aligned} \tag{A.1c}$$

$$\begin{aligned} I_{-+} &= \int_0^t \mathrm{d}t_1 \mathrm{e}^{-2\mathrm{i}Jt_1} (\tilde{J} - J + \mathrm{i}\Delta_0 \sin\eta) \\ &= -\int_0^t \mathrm{d}t_1 \mathrm{e}^{-2\mathrm{i}Jt_1} \left[T(t_1) - \frac{\Delta_0}{2} \left(L^{+}(t_1) - L(t_1) \right) \right] \end{aligned} \tag{A.1d}$$

where

$$L(t_1) = \exp\left[-2\mathrm{i}s(t_1) \sum_{i,j} A_{ji} \frac{c_i}{\omega_i^2} D_j(t_1) \right] \tag{A.2a}$$

$$T(t_1) = p_\mathrm{s}(t_1) \sum_{i,j} A_{ji} \frac{c_i}{\omega_i^2} D_j(t_1) \tag{A.2b}$$

and

$$s(t_1) = \frac{s_f \sinh(w_\mathrm{s} t_1) + s_i \sinh(w_\mathrm{s}(t - t_1))}{\sinh(w_\mathrm{s} t)} \tag{A.3a}$$

$$p_\mathrm{s}(t_1) = \frac{w_\mathrm{s} s_f \cosh(w_\mathrm{s} t_1) - w_\mathrm{s} s_i \cosh(w_\mathrm{s}(t - t_1))}{\sinh(w_\mathrm{s} t)} \tag{A.3b}$$

$$D_i(t_1) = \frac{\omega_i}{d_i} \frac{R_i \cos(\omega_i d_i t_1) - Q_i \cos(\omega_i d_i (t - t_1))}{\sin(\omega_i d_i t)} \cdot \tag{A.3c}$$

The initial time density matrix is given by the expression

$$\rho_\mathrm{B} = \rho_\mathrm{s}(s_f, s_i) \prod_k \rho_\mathrm{B}^{(k)}(R_k, Q_k) \tag{A.4}$$

$$\begin{aligned} \rho_\mathrm{B}^{(k)}(R_k, Q_k) &= \left(\frac{\omega_k d_k}{2\pi \sinh(\beta\omega_k d_k)} \right)^{1/2} \\ &\times \exp\left\{ -\frac{\omega_k d_k}{2\sinh(\beta\omega_k d_k)} \left[(R_k^2 + Q_k^2)\cosh(\beta\omega_k d_k) - 2R_k Q_k \right] \right\} \end{aligned} \tag{A.5a}$$

$$\rho_{\mathrm{s}}(s_f, s_i) = \left(\frac{w_{\mathrm{s}}}{2\pi\sin(\beta w_{\mathrm{s}})}\right)^{1/2} \times \exp\left\{-\frac{w_{\mathrm{s}}}{2\sin(\beta w_{\mathrm{s}})}\left[(s_i^2+s_f^2)\cos(\beta w_{\mathrm{s}}) - 2s_i s_f\right]\right\}. \tag{A.5b}$$

(A.5a) represents the density matrix of a harmonic oscillator.

The following expressions are defined in terms of certain traces that have been calculated in closed form by the author [22]:

$$S(t) = \int_0^t \int_0^t \mathrm{d}t_1 \mathrm{d}t_2 \mathrm{e}^{-2\mathrm{i}J(t_1-t_2)} \mathrm{Tr}(T(t_1)T^+(t_2)\rho_{\mathrm{B}}) \tag{A.6}$$

$$W(t) = \int_0^t \int_0^t \mathrm{d}t_1 \mathrm{d}t_2 \mathrm{e}^{-2\mathrm{i}J(t_1-t_2)} \times \left[\begin{array}{l} \mathrm{Tr}(T(t_1)L(t_2)\rho_{\mathrm{B}}) - \mathrm{Tr}(T(t_2)L(t_1)\rho_{\mathrm{B}}) - \\ -\mathrm{Tr}(T(t_1)L^+(t_2)\rho_{\mathrm{B}}) + \mathrm{Tr}(T(t_2)L^+(t_1)\rho_{\mathrm{B}}) \end{array}\right] \tag{A.7}$$

$$U(t) = \int_0^t \int_0^t \mathrm{d}t_1 \mathrm{d}t_2 \mathrm{e}^{-2\mathrm{i}J(t_1-t_2)} \times \left[\begin{array}{l} \mathrm{Tr}(L^+(t_1)L^+(t_2)\rho_{\mathrm{B}}) + \mathrm{Tr}(L(t_1)L(t_2)\rho_{\mathrm{B}}) - \\ -\mathrm{Tr}(L(t_1)L^+(t_2)\rho_{\mathrm{B}}) - \mathrm{Tr}(L^+(t_1)L(t_2)\rho_{\mathrm{B}}) \end{array}\right] \tag{A.8}$$

$$V(t) = \int_0^t \int_0^t \mathrm{d}t_1 \mathrm{d}t_2 \mathrm{e}^{-2\mathrm{i}J(t_1+t_2)} \times \left[\begin{array}{l} \mathrm{Tr}(L^+(t_1)L^+(t_2)\rho_{\mathrm{B}}) + \mathrm{Tr}(L(t_1)L(t_2)\rho_{\mathrm{B}}) - \\ -\mathrm{Tr}(L(t_1)L^+(t_2)\rho_{\mathrm{B}}) - \mathrm{Tr}(L^+(t_1)L(t_2)\rho_{\mathrm{B}}) \end{array}\right] \tag{A.9}$$

$$C(t) = \int_0^t \int_0^t \mathrm{d}t_1 \mathrm{d}t_2 \times \left[\begin{array}{l} \mathrm{Tr}(L^+(t_1)L^+(t_2)\rho_{\mathrm{B}}) + \mathrm{Tr}(L(t_1)L(t_2)\rho_{\mathrm{B}}) + \\ +\mathrm{Tr}(L(t_1)L^+(t_2)\rho_{\mathrm{B}}) + \mathrm{Tr}(L^+(t_1)L(t_2)\rho_{\mathrm{B}}) \end{array}\right]. \tag{A.10}$$

The quantum coherence terms are given by the following expressions, for the initial state $\frac{1}{\sqrt{2}}(|+\rangle + |-\rangle)$

$$\Theta_{+-}(t) = \frac{\Delta_0^2}{4}V(t) - \frac{\Delta_0^2}{4}U(t) - \frac{\Delta_0^2}{2}C(t) + \frac{1}{2} - \frac{\Delta_0}{2}W(t) \tag{A.11}$$

$$\Theta_{+-}(t) = \frac{\Delta_0^2}{4}V(t) - \frac{\Delta_0^2}{4}U(t) - \frac{\Delta_0^2}{2}C(t) + \frac{1}{2} + \frac{\Delta_0}{2}W(t). \tag{A.12}$$

Similarly for the initial state $|+\rangle$ the population difference is given by

$$P(t) = 1 - 2S(t) - \frac{\Delta_0^2}{2}U(t) - \Delta_0 W(t). \tag{A.13}$$

In the same way we can obtain the quantum coherence terms and the population difference as a function of time, for any initial state of the two level system.

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