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Excited-state-induced subbarrier tunnelling in the double-well model

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Résumé. — Nous ajoutons un troisième état excité au modèle minimal standard d’un hamiltonien à deux états pour une particule dans un double puits symétrique interagissant avec un bain. Cet état est couplé dynamiquement (à travers le couplage au bain) avec les deux états les plus bas. Nous montrons qu’en plus du transfert habituel excité thermiquement 1 → 3 → 2 (qui peut être facilement supprimé en choisissant la température suffisamment basse), un effet tunnel est induit qui persiste même à $T = 0$. Cette nouvelle voie a tendance à provoquer des oscillations cohérentes si les voies habituelles (effet tunnel direct et transfert au-dessus de la barrière) sont supprimées. Ces conclusions contrastent avec la théorie admise de la symétrie de brisure asymptotique.

Abstract. — Standard minimal two-state Hamiltonian (spin-boson model) for a particle in a symmetric double-well potential, interacting with a bath, is complemented by a third particle-excited state. This state is dynamically coupled (via coupling to the bath) with the lowest two states. In addition to the standard over-barrier thermally-activated transfer $1 ↔ 3 ↔ 2$ (which might be easily suppressed by choosing a sufficiently low $T$), the third state is shown to cause excited-state-induced subbarrier tunnelling which persists even at $T = 0$. This new channel shows a tendency to coherent oscillations if standard (direct-tunnelling and over-barrier-transfer) channels get suppressed. These conclusions challenge the standard theory of the asymptotic symmetry breaking.

1. Introduction.

The double-well model for a quantum particle interacting with a bath is of increasing interest in several branches of physics (e.g. solid state, chemical physics and biophysics). For most applications, not only the static but also the dynamic properties of such a particle are needed. For these purposes, namely for far-from-equilibrium properties, knowledge of the ground-
and of a few excited state energies and corresponding wave functions is indispensable, though in general not yet sufficient. Unfortunately, the model is in general not exactly soluble.

Most treatments of the particle properties in the double-well (mostly symmetric) potential are connected with the minimal two-state Hamiltonian (spin-boson-model) [1-12]

\[
H = -\frac{1}{2} \hbar \omega_0 \sigma_x + \hbar \sum_{i=1}^{M} G_i \sigma_z (b_i + b_i^+) + \sum_{i=1}^{M} \hbar \omega_i b_i^+ b_i
= H_S + H_{SB} + H_B ,
\]

(1a)

Here, the reservoir is modelled by harmonic phonons (what we also shall do henceforth) with frequencies \( \omega_i \) and creation (annihilation) operators \( b_i^+ (b_i) \). The second term on the right hand side of (1a) is the simplest non-trivial form of the particle-phonon coupling (proportional to the lattice-point displacements \( \sim b_i + b_i^+ \)) for which, in combination with the first term \( H_S \), the solutions exist but are unknown. The latter term causes the direct hopping of the particle between the states \( |1\rangle = a_+ |0\rangle \) and \( |2\rangle = a_+ |0\rangle \). If the coupling constants \( G_i \) were zero, (1a) could be exactly diagonalized; \( \hbar \omega_0 \) would be then the energy splitting between the particle eigenstates

\[
|+\rangle = \frac{1}{\sqrt{2}} \left( |1\rangle + |2\rangle \right) , \quad |\rangle = \frac{1}{\sqrt{2}} \left( |1\rangle - |2\rangle \right).
\]

(2)

The most severe limitation connected with (1a) is that only the lowest two states of the particle are considered. This is usually believed to be justified provided that:

a) no external perturbations in the time-interval of interest are effectively able to excite the particle from the lowest two states to higher excited ones;

b) designating \( \Delta_0 \) the energy difference between the first omitted state and the higher of the states \( |+\rangle \) and \( |-\rangle \) (i.e. \( |-\rangle \) for \( \omega_0 \gg 0 \) as we shall assume henceforth),

\[
k_B T \ll \Delta_0 .
\]

(3a)

Here \( T \) is the initial temperature of the phonons. Sometimes, a more stringent condition is assumed

\[
k_B T \ll \hbar \omega_0
\]

(3b)

which means that the particle should mostly relax to the ground state \( |+\rangle \);

c) the initial condition assumed does not involve higher excited particle states.

In what follows, we shall also accept conditions a) and c). We shall not rely upon (3b) and in fact, our treatment as well as general conclusions apply irrespective of whether (3b) or the opposite condition \( (k_B T \gg \hbar \omega_0) \) applies. As far as (3a) is concerned, our theory does not rely upon this condition. Nevertheless, the new channel of the sub-barrier tunnelling \( 1 \leftrightarrow 2 \) which we should like to report here becomes most pronounced when (3a) applies. This then means that the standard over-barrier transfer via a thermal excitation to higher excited states becomes ineffective.

The aim of the present work is to argue that irrespective of the above mentioned conditions and in contrast with the usual opinion, higher particle-excited states cannot be fully omitted in dynamic treatments. In order to convince the reader, we first construct additional terms to
(1a), complementing the basic set \(|+\) and \(|-\rangle\) by the third state \(|3\rangle = a^+_3 |0\rangle\). This state is also an eigenstate of the particle-part of the Hamiltonian. We find that the simplest (but still realistic) generalization of (1a) may be well treated (as far as the kinetics is concerned) via the time-convolution as well as time-convolutionless Generalized Master Equations (TC-GME and TCL-GME) using a projector which suppresses all the physical information connected with the third state. In contrast to the standard GME treatment of the particle dynamics, we find a new channel of the transfer \(1 \leftrightarrow 2\) which critically depends on the existence of the third state but nevertheless, which does not necessarily involve the particle transfer via the state \(|3\rangle\). We find that this channel remains open at \(T = 0\). It competes with the direct-tunnelling channel (due to the first term \(H_S\) in (1a)), but it prevails once the barrier separating the left and right hand states \(|1\rangle\) and \(|2\rangle\) becomes sufficiently unpenetrable (i.e. for small enough \(\omega_0\)). The relative easiness with which the particle passes through this channel, and its tendency to coherent oscillations (when other channels become suppressed) question contemporary models of the asymptotic symmetry breaking and corresponding conclusions based on the Hamiltonian (1a).

2. Model.

It is worth noticing that in terms of the particle eigenstates \(|+\rangle\) and \(|-\rangle\), the interaction term in (1a) reads

\[
\begin{align*}
H_{S-B} &= \hbar \sum_{i=1}^{M} G_i [a^{(+)} + a^{(-)} + a^{(+)} + a^{(-)}](b_i + b_i^+), \\
(a^{(+)} &= \frac{1}{\sqrt{2}} (a_1 + a_2), \quad a^{(-)} = \frac{1}{\sqrt{2}} (a_1 - a_2). \tag{4a}
\end{align*}
\]

Hence, using the type of arguments leading to (1a), the additional term (to (1a)), owing to introduction of the third state, should be (in addition to a trivial term \(\varepsilon a_3^+ a_3\))

\[
\begin{align*}
\Delta H_{S-B} &= \hbar \sum_{i=1}^{M} \left\{ H_i^{(+)} a^{(+)} a^+_3 a^+_3 a^{(+)} + H_i^{(-)} a^{(-)} a^+_3 a^+_3 a^{(-)} \right\} \cdot (b_i + b_i^+) \\
&= \hbar \sum_{i=1}^{M} \left\{ \frac{1}{\sqrt{2}} (H_i^{(+)} + H_i^{(-)}) (a_{i}^+ a_3 + a^+_3 a_1) + \frac{1}{\sqrt{2}} (H_i^{(+)} - H_i^{(-)}) (a^+_2 a_3 + a^+_3 a_2) \right\} \times (b_i + b_i^+). \tag{5}
\end{align*}
\]

Therefore, the total Hamiltonian now reads

\[
\begin{align*}
H_{tot} &= H^{(0)} + H_{int} = H_0 + \Delta H_{S-B}, \\
H^{(0)} &= H_S + \varepsilon a_3^+ a_3 + H_B, \tag{6} \\
H_{int} &= H_{S-B} + \Delta H_{S-B} \equiv H_{S-B} + \mathcal{K}.
\end{align*}
\]

On grounds of symmetry arguments, one should ascribe certain parity to the third state. Consequently, we should choose \(H_i^{(+)} = 0\) or \(H_i^{(-)} = 0\) for the even or odd parity, respectively. For the sake of generality, however, we shall still keep the form of (5), keeping these two special cases in mind.

In order to make the correspondence with the standard treatment as close as possible, let us first of all perform the standard canonical transformation to the small-polaron basis. Taking

\[
U = \exp \left[ - \sum_{i=1}^{M} \left( G_i / \omega_i \right) (b_i - b_i^+) \sigma_z \right], \tag{7}
\]
we get

\[ \tilde{H}_{\text{tot}} = U H_{\text{tot}} U^{-1} = \tilde{H}_0 + \tilde{\kappa}, \] (8a)

\[ \tilde{H}_0 = - \sum_i \hbar (G_i^2/\omega_i) (a_i^+ a_i + a_i^+ a_i) + \varepsilon a_i^+ a_i + \sum_i \hbar \omega_i b_i^+ b_i, \] (8b)

\[
\tilde{\kappa} = \hbar \sum \left\{ \frac{1}{\sqrt{2}} \left( H_i^{(+)} + H_i^{(-)} \right) \left( a_i^+ \exp \left[ - \sum_j \frac{G_j}{\omega_j} (b_j - b_j^+) \right] a_i (b_i + b_i^+) + H.C. \right) + \\
+ \frac{1}{\sqrt{2}} \left( H_i^{(+)} - H_i^{(-)} \right) \left( a_i^+ \exp \left[ + \sum_j \frac{G_j}{\omega_j} (b_j - b_j^+) \right] a_i (b_i + b_i^+) + H.C. \right) \right\} + O(\omega_0), \quad \lim_{\omega_0 \to 0} O(\omega_0)/\omega_0 \neq 0. \] (8c)

The important point is that, due to a special form of (7), the diagonal elements of the particle density matrix

\[ \tilde{\rho}^R(t) = \text{Tr}_{ph}(\tilde{\rho}(t)), \] (9a)

\[ \tilde{\rho}(t) = U \rho(t) U^{-1} \] (9b)

preserve the meaning of probabilities. In (8c), we have not specified the form of the terms proportional to \( \omega_0 \) (term \( O(\omega_0) \)). The reader can find them elsewhere [8, 9]. As we are mainly interested in our new channel of the 1 \( \leftrightarrow \) 2 transfer, we shall anyway set finally \( \omega_0 = 0 \); this then suppresses the direct-hopping channel treated in other works, as well as possible interference terms.

Now, let us choose our projection superoperator to the relevant information. Preserving Latin (Greek) indices for designating particle (phonon) eigenstates of (8b), we make a non-standard choice (compare e.g. [13])

\[ D_{aa, b\beta, c\gamma, d\delta} = (1 - \delta_{a3})(1 - \delta_{b3}) \rho_{a\beta}^R \delta_{c\gamma} \delta_{d\delta}, \]

\[ \sum_a \rho_{aa}^R = 1. \] (10a)

So, for an arbitrary operator \( A \),

\[ (DA)_{aa, b\beta} = \sum_{c\gamma, d\delta} D_{aa, b\beta, c\gamma, d\delta} A_{c\gamma, d\delta} \]

\[ = (1 - \delta_{a3})(1 - \delta_{b3}) \rho_{a\beta}^R \text{Tr}_{ph} A_{ab}. \] (10b)

Hence, we are not interested in anything what is connected with our state 3, so that only the matrix elements

\[ P_1(t) = \tilde{\rho}_{11}^R(t), \quad P_2(t) = \tilde{\rho}_{22}^R(t), \quad \tilde{\rho}_{12}^R(t) \quad \text{and} \quad \tilde{\rho}_{21}^R(t) \] (11)

appear in our GME below. Nevertheless, we shall easily be able to check, if the particle appears at site 3 since

\[ P_3(t) = \tilde{\rho}_{33}^R(t) = 1 - P_1(t) - P_2(t). \] (12)

The last point to be now given is the choice of the initial conditions. We assume that

\[ (\tilde{\rho}(0))_{aa, b\beta} = (1 - \delta_{a3})(1 - \delta_{b3}) \rho_{a\beta}^R \tilde{\rho}_{ab}^R(0) \] (13a)
i.e.

\[(1 - D) \bar{\rho}(0) = 0.\]  \hspace{1cm} (13b)

(13a) means that initially, the probability of finding the particle in site 3 is zero. In addition to that, this means that phonons and the particle are initially statistically independent. With off-diagonal \(\rho_{\alpha\beta}^R\), we could model even the situation that the phonons are initially unrelaxed. For technical reasons, however, it is often useful to choose

\[\rho_{\alpha\beta}^R = \delta_{\alpha\beta} p_{\alpha}, \quad \sum_{\alpha} p_{\alpha} = 1\]  \hspace{1cm} (14)

which means initially relaxed phonons. In both cases, because of (13b), our GME will not contain any initial-condition term.

3. Time-convolution generalized master equations.

From the Liouville equation

\[i \frac{\partial}{\partial t} \rho(t) = \frac{1}{\hbar} [H, \rho(t)] = L \rho(t),\]  \hspace{1cm} (15)

using (9b) and the transformation to the interaction picture

\[\bar{\rho}(t) = \exp \left[ \frac{i}{\hbar} \hat{H}_{0} t \right] \tilde{\rho}(t) \exp \left[ -\frac{i}{\hbar} \hat{H}_{0} t \right] = e^{iL_{0} t} \bar{\rho}(t)\]

\[= U e^{\frac{i}{\hbar} H_{0} t} \rho(t) e^{-\frac{i}{\hbar} H_{0} t} U^{-1} = U(e^{iL_{0} t} \rho(t)) U^{-1},\]  \hspace{1cm} (16a)

\[\bar{\tilde{\rho}}(t) = e^{iL_{0} t} \bar{\tilde{\rho}} e^{-iL_{0} t},\]  \hspace{1cm} (16b)

with

\[\bar{L}_{0} = \frac{1}{\hbar} [\hat{H}_{0}, \ldots],\]  \hspace{1cm} (17a)

\[\bar{L} = \frac{1}{\hbar} [\bar{L}, \ldots],\]  \hspace{1cm} (17b)

one gets

\[i \frac{\partial}{\partial t} \bar{\rho}(t) = \frac{1}{\hbar} [\bar{L} \tilde{\rho}(t), \bar{\tilde{\rho}}(t)] = \bar{L}(t) \bar{\tilde{\rho}}(t).\]  \hspace{1cm} (18)

From (8b), it is clear that transferring to the interaction picture does not change the diagonal elements of \(\bar{\rho}^P(t)\) (i.e. \(\bar{\rho}^P(t)_{aa} = (\tilde{\rho}^P(t))_{aa}\)) and changes only the phase factor of the off-diagonal elements. Using a standard procedure for eliminating \((1 - D) \bar{\tilde{\rho}}(t)\) [14, 15], one gets from (18)

\[\frac{\partial}{\partial t} D\bar{\tilde{\rho}}(t) = -i D\bar{\tilde{\rho}}(t) D\bar{\tilde{\rho}}(t) - \]

\[- \int_{0}^{t} \bar{\tilde{\rho}}(t) \exp_{-} \left\{ -i (1 - D) \int_{\tau_{1}}^{t} \bar{\tilde{\rho}}(\tau_{2}) d\tau_{2} \right\} (1 - D) \bar{\tilde{\rho}}(\tau_{1}) D\bar{\tilde{\rho}}(\tau_{1}) d\tau_{1}\]

\[-i D\bar{\tilde{\rho}}(t) \exp_{-} \left\{ -i \int_{0}^{t} (1 - D) \bar{\tilde{\rho}}(\tau) d\tau \right\} (1 - D) \bar{\tilde{\rho}}(0).\]  \hspace{1cm} (19)
Because of (13b), the last term on the right hand side of (19) disappears. Taking the trace over phonons, (19) reduces to

\[
\frac{\partial}{\partial t} \bar{\Phi}^R_{a b}(t) = \sum_{c, d = 1}^2 \int_0^t w_{a b c d}(t, \tau) \rho^R_{c d}(\tau) \, d\tau, \quad a, b, c, d = 1, 2. \tag{20}
\]

Here, we have already set \( \omega_0 = 0 \); otherwise, the right hand side of (20) should be complemented by several terms which are (for the standard theory with \( H^{(2)} = 0 \)) known from previous treatments. The memory functions read to the lowest order in \( \tilde{c} \)

\[
w_{a b c d}(t, \tau) = - \sum_{\lambda, \gamma} (D e^{i L_0 t} \tilde{c} e^{-i L_0 t} (1 - D) \cdot e^{i L_0 \tau} \tilde{c} e^{-i L_0 \tau} D)_{a\lambda, b\lambda, c\gamma, d\delta} \rho^R_{\gamma\delta}. \tag{21}
\]

Now, we use the fact that due to (10a) and (8b),

\[
D \tilde{L}_0 = 0. \tag{22}
\]

Further, due to (10a) and (8c),

\[
D \tilde{c} D = 0. \tag{23}
\]

Consequently, (21) reduces to

\[
w_{a b c d}(t, \tau) = w_{a b, c d}(t - \tau) = - \sum_{\lambda, \gamma} (\tilde{c} e^{-i L_0 (t - \tau)} \tilde{c})_{a\lambda, b\lambda, c\gamma, d\delta} \rho^R_{\gamma\delta}. \tag{24}
\]

Introducing now (8c) (for \( \omega_0 = 0 \)) into (24) yields

\[
w_{11, 11}(\tau) = - \frac{2}{\hbar^2} \text{Re} \sum_{\lambda, \mu} \left\{ \tilde{c}_{1, \lambda, 3, \mu} \tilde{c}_{3, \mu, 1, \nu} \rho^{R}_{\mu, \nu} \exp \left[ - \frac{i}{\hbar} \epsilon_{\mu, \lambda} \tau \right] \right\}, \tag{25a}
\]

\[
w_{11, 12}(\tau) = w_{11, 21}(\tau)^* = w_{22, 12}(\tau)^* = w_{22, 21}(\tau) = w_{12, 11}(\tau)^* = w_{21, 11}(\tau) = w_{21, 22}(\tau) = \frac{1}{\hbar^2} \sum_{\lambda, \mu, \nu} \left\{ \tilde{c}_{2, \lambda, 3, \mu} \tilde{c}_{3, \mu, 1, \lambda} \rho^{R}_{\lambda, \nu} \exp \left[ \frac{i}{\hbar} \epsilon_{\mu, \lambda} \tau \right] \right\}, \tag{25b}
\]

\[
w_{22, 22}(\tau) = - \frac{2}{\hbar^2} \text{Re} \sum_{\lambda, \mu, \nu} \left\{ \tilde{c}_{2, \lambda, 3, \mu} \tilde{c}_{3, \mu, 2, \nu} \rho^{R}_{\nu, \lambda} \exp \left[ - \frac{i}{\hbar} \epsilon_{\mu, \lambda} \tau \right] \right\}, \tag{25c}
\]

\[
w_{12, 12}(\tau) = w_{21, 21}(\tau)^* = w_{21, 21}(\tau)^* = \frac{1}{\hbar^2} \sum_{\lambda, \mu, \nu} \left\{ \tilde{c}_{1, \lambda, 3, \mu} \tilde{c}_{3, \mu, 1, \nu} \rho^{R}_{\lambda, \nu} \exp \left[ - \frac{i}{\hbar} \epsilon_{\mu, \lambda} \tau \right] \right\} + \frac{1}{\hbar^2} \sum_{\lambda, \mu, \nu} \left\{ \tilde{c}_{2, 2, \mu} \tilde{c}_{2, \lambda, 2, \mu} \rho^{R}_{\lambda, \nu} \exp \left[ + \frac{i}{\hbar} \epsilon_{\mu, \lambda} \tau \right] \right\}, \tag{25d}
\]

with other memory functions being zero. Here, we used the notation

\[
\epsilon_{\mu, \lambda} = \epsilon + \hbar \sum_i \left( G_i^2/\omega_i \right) + \sum_i \hbar \omega_i (\mu_i - \lambda_i) \tag{26}
\]

for the energy difference in individual transitions.

It has a little sense to solve directly (20) since (25a-d) is correct only in the lowest order in \( \tilde{c} \). The error introduced by this approximation can be controlled in any finite interval of times.
just when \( \tilde{C} \) is sufficiently small. Then the Markov approximation becomes justified so that (20) turns to

\[
\frac{\partial}{\partial t} P_{ab}^P(t) = \sum_{c,d=-1}^2 W_{abcd} P_{cd}^P(t),
\]

(27a)

\[
W_{abcd} = \lim_{\delta \to 0^+} \int_{0}^{+\infty} w_{ab,cd}(\tau) e^{-\delta \tau} \, d\tau.
\]

(27b)

Using (25a-d), we obtain

\[
W_{1111} = -\frac{2}{\hbar} \sum_{\lambda \neq \mu} \tilde{\mathcal{K}}_{1\lambda,3\mu} \tilde{\mathcal{K}}_{3\mu,1\nu} \rho_{\nu\lambda}^R \delta(\epsilon_{\mu\lambda}),
\]

(28a)

\[
W_{2222} = -\frac{2}{\hbar} \sum_{\lambda \neq \mu} \tilde{\mathcal{K}}_{2\lambda,3\mu} \tilde{\mathcal{K}}_{3\mu,2\nu} \rho_{\nu\lambda}^R \delta(\epsilon_{\mu\lambda}),
\]

(28b)

\[
W_{1112} = W_{1212} = W_{2212} = W_{1122} = W_{1222} = W_{2122} = -\frac{i}{\hbar} \sum_{\lambda \neq \mu} \tilde{\mathcal{K}}_{2\lambda,3\mu} \tilde{\mathcal{K}}_{3\mu,1\lambda} \rho_{\nu\lambda}^R \frac{1}{\epsilon_{\mu\lambda} + i0^+} + \frac{1}{\epsilon_{\mu\lambda} + i0^+}.
\]

(28c)

\[
W_{1212} = W_{2122} = \frac{i}{\hbar} \sum_{\lambda \neq \mu} \left\{ \tilde{\mathcal{K}}_{1\lambda,3\mu} \tilde{\mathcal{K}}_{3\mu,1\nu} \rho_{\nu\lambda}^R \frac{1}{\epsilon_{\mu\lambda} - i0^+} - \tilde{\mathcal{K}}_{2\lambda,3\mu} \tilde{\mathcal{K}}_{3\mu,2\lambda} \rho_{\nu\lambda}^R \frac{1}{\epsilon_{\mu\lambda} + i0^+} \right\}.
\]

(28d)

When choosing (14) with \( p_a \) being the Boltzmann weighting factor, it is easy to recognize the Golden Rule hopping rates in (28) for transitions between relaxed-phonon states. On the other hand, for

\[
\rho_{\mu\nu}^R = 2(U e^{-\beta H(0)} U^{-1})_{\mu,1\nu} / \text{Tr} \left( e^{-\beta H(0)} \right)
\]

(29)

(28a-b) reduce to the Golden Rule hopping rates for transitions between unrelaxed states under the influence of \( \Delta H_{S-B} \).

Equations (27a) describe our particle hopping between the left and right states (sites) 1 and 2 though we set \( \omega_0 = 0 \). In general, because \( \sum_{a=1}^2 W_{aabc} \neq 0 \), the particle can be still transferred to site 3, provided that we accept e.g. (14) at a finite temperature \( T = (k_B \beta)^{-1} \). In order to show, however, that our 1 ↔ 2 transfer described by (27a) is not only the usual over-barrier hopping (though the standard mechanism of the over-barrier transfer is in general included), let us assume that the phonon spectrum is limited and that \( \epsilon \) is so large (i.e. the third state is so above the first two) that \( \epsilon_{\mu\lambda} \) in (26) is always positive. This means that there are no real transitions 1 ↔ 3 or 2 ↔ 3 possible, i.e. the standard over-barrier transfer gets (in our lowest-order theory) forbidden. (Similar effect may be achieved by choosing a sufficiently low
Then (27a) gives
\[
\frac{\partial}{\partial t} \begin{bmatrix} \tilde{\beta}_{11}^p(t) \\ \tilde{\beta}_{22}^p(t) \\ \tilde{\beta}_{12}^p(t) \\ \tilde{\beta}_{21}^p(t) \end{bmatrix} = \begin{bmatrix} 0 & 0 & -i \Omega & i \Omega \\ 0 & 0 & i \Omega & -i \Omega \\ -i \Omega & i \Omega & i \Gamma & 0 \\ i \Omega & -i \Omega & 0 & -i \Gamma \end{bmatrix} \begin{bmatrix} \tilde{\beta}_{11}^p(t) \\ \tilde{\beta}_{22}^p(t) \\ \tilde{\beta}_{12}^p(t) \\ \tilde{\beta}_{21}^p(t) \end{bmatrix}.
\] (30a)

With the initial condition \( \tilde{\beta}_{11}^p(0) = 1 \), the solution to (30a) reads
\[
\tilde{\beta}_{11}^p(t) = 1 - \tilde{\beta}_{22}^p(t) = \frac{1}{\omega^2} \left[ \Gamma^2 + 2 \Omega^2 (1 + \cos \omega t) \right],
\]
\[
\tilde{\beta}_{12}^p(t) = \frac{\tilde{\beta}_{21}^p(t)^*}{\omega^2} \left( 1 - \cos \omega t \right) - \frac{i \Omega}{\omega} \sin \omega t,
\]
\[
\omega = \sqrt{\left( \Gamma^2 + 4 \Omega^2 \right)}.
\] (31)

Consequently, the particle freely oscillates between states 1 \( \leftrightarrow \) 2. Because of (12) and (31), \( P_{3}(t) = 0 \), so that the particle never appears in state 3. Therefore, we got a pure coherent tunnelling. Formally, the tunnelling current \( I(t) \sim \frac{\partial}{\partial t} \tilde{\beta}_{11}^p(t) \sim \Omega^2 / \omega \), i.e. \( I(t) \) is of the second order in the particle-phonon coupling. In order to estimate its real value, (30b-c) must be made more explicit. We shall postpone this problem to section 5.

In connection with (31), it is yet worth mentioning that, due to formally asymmetric coupling to phonons in (5), our model has not the full symmetry 1 \( \leftrightarrow \) 2, unless we apply the symmetry arguments to \( \Delta H_{S - B} \). Therefore, it is not surprising that for the asymmetric initial condition used (\( \tilde{\beta}_{11}^p(0) = 1 \)), the dipole moment
\[
\langle \sigma_{z} \rangle (t) = \rho_{11}^p(t) - \rho_{22}^p(t) = \tilde{\beta}_{11}^p(t) - \tilde{\beta}_{22}^p(t) = \frac{1}{\omega^2} \left[ \Gamma^2 + 4 \Omega^2 \cos \omega t \right]
\] oscillates around a nonzero value for \( \Gamma \neq 0 \). Including the symmetry arguments leads to \( H_{i}^{(+)} = 0 \) or \( H_{i}^{(-)} = 0 \). Then \( \Gamma = 0 \) and \( \langle \sigma_{z} \rangle (t) \) oscillates between symmetric limits \( \pm 1 \).

4. Time-convolutionless generalized master equations.

As an exact consequence of (18), one can also write the exact identity [16, 17] (or [18] with [19])
\[
\frac{\partial}{\partial t} D\tilde{\sigma}(t) = -i D\tilde{\xi}(t) \left[ 1 + i \int_{t}^{t'} \exp_{-} \left\{ -i (1 - D) \int_{t_1}^{t} \tilde{\xi}(\tau_2) d\tau_2 \right\} \times \right.
\]
\[
\times \left( 1 - D \right) \tilde{\xi}(\tau_1) D \exp_{-} \left\{ i \int_{t_1}^{t} \tilde{\xi}(\tau_3) d\tau_3 \right\} d\tau_1 \right]^{-1}
\]
\[
\times \left[ D\tilde{\sigma}(t) + \exp_{-} \left\{ -i (1 - D) \int_{t}^{t'} \tilde{\xi}(\tau) d\tau \right\} (1 - D) \tilde{\sigma}(0) \right].
\] (33)
Because of (13b), the last term on the right hand side of (33) disappears. Taking the trace over phonons, (33) yields

$$\frac{\partial}{\partial t} \tilde{\rho}_{ab}(t) = \sum_{c, d = 1}^{2} V_{abcd}(t) \tilde{\rho}_{cd}^{P}(t), \ a, b = 1, 2,$$

$$V_{abcd}(t) = -i \sum_{\lambda, \gamma, \delta} \left( D \tilde{\xi}(t) \left[ 1 + i \int_{0}^{t} \exp \left\{ -i (1 - D) \int_{\tau_{1}}^{t} \tilde{\xi}(\tau_{2}) d\tau_{2} \right\} \times \right. \right.$$  

$$\left. \times (1 - D) \tilde{\xi}(\tau_{1}) \right) D \exp \left\{ i \int_{\tau_{1}}^{t} \tilde{\xi}(\tau_{3}) d\tau_{3} \right\} \left( D \right)_{a \lambda, b \lambda, c \gamma, d \delta} \rho_{\gamma \delta}^{R}. \quad (34)$$

Formally, to the second order in $\tilde{\xi}$,

$$V_{abcd}(t) \approx -\int_{0}^{t} \sum_{\lambda, \gamma, \delta} (D \exp \left\{ \int_{\tau_{1}}^{t} \tilde{\xi}(\tau_{3}) d\tau_{3} \right\} \left( D \right)_{a \lambda, b \lambda, c \gamma, d \delta} \rho_{\gamma \delta}^{R} d\tau \rightarrow W_{abcd}, \ t \rightarrow +\infty. \quad (35)$$

Therefore, to this order in $\tilde{\xi}$, (34) reduces to (27a) except for a short initial interval of times ($t \leq \tau_{p} = $ phonon dephasing time). Therefore, the conclusions of the last section are fully reproduced.

5. Discussion and interpretation.

Effectiveness of our new channel critically depends on the values of $\Omega$ in (30b) since our theory (as well as any other theory which is based on a finite order expansion) is reliable just for a finite time interval. For simplicity, let us assume e.g. $H_{i}^{(-)} = 0$, i.e. $\Gamma = 0$ in (30c) and (31). Assume now that $\varepsilon + \hbar (G_{i}^{2}/\omega_{i}) \equiv \bar{\varepsilon}$ is much greater than the typical (cut-off) or a maximum phonon frequency $\omega_{c}$. To the lowest order in $\hbar \omega_{c}/\varepsilon$, (30b) reduces to

$$\Omega \approx \frac{1}{\hbar \varepsilon} \sum_{\lambda, \mu} \tilde{\xi}_{2, \mu, 3, 3, \mu} \tilde{\xi}_{3, 1, 1, \lambda} \rho_{\lambda \varepsilon}^{R} = \frac{1}{\hbar \varepsilon} \sum_{\lambda, \mu} \tilde{\xi}_{1, \mu, 3, 3, \mu} \tilde{\xi}_{3, 2, 1, \lambda} \rho_{\lambda \varepsilon}^{R}. \quad (36)$$

This has a form of a trace over phonons which might be calculated in any phonon basis.

First, let us assume initially unrelaxed phonons with thermal distribution given by a canonical distribution without any particle-phonon coupling. This means that we assume (29). Then (36) yields

$$\Omega \approx \frac{1}{\hbar \varepsilon} \frac{\hbar^{2}}{2} \sum_{i = 1}^{M} \left| H_{i}^{(+)} \right|^{2} \left[ 1 + 2 \eta_{B}(\hbar \omega_{i}) \right]$$

$$= \frac{\hbar}{2 \varepsilon} \int_{0}^{\infty} \left| H_{i}^{(+)}(\omega) \right|^{2} \rho(\omega) \coth \left( \frac{1}{2} \beta \hbar \omega \right) d\omega, \quad (37a)$$

$$n_{B}(z) = \frac{1}{e^{\beta z} - 1}, \quad \beta = \frac{1}{k_{B} T}. \quad (37b)$$

Here, $\rho(\omega)$ is the density of the phonon modes

$$\rho(\omega) = \frac{1}{M} \sum_{i = 1}^{M} \delta(\omega - \omega_{i}), \ M \rightarrow +\infty \quad (38a)$$
\[ |H^{(+)}(\omega)|^2 \rho(\omega) \approx M \sum_{i=1}^{M} |H_i^{(+)}|^2 \delta(\omega - \omega_i), \quad M \to +\infty \]  

(38b)

is the strength function for \( \Delta H_{S-B} \) (still for \( H^{(-)} = 0 \)). Clearly, for \( T = 0 \) and \( r' > -1 \), one needs \( r' > 0 \). It is worth mentioning that we have ignored any possible role of \( H_{S-B} \) in the initial condition (i.e. we set \( G_i = 0 \) in (29)), but not in the dynamic treatment (e.g. in (7), (16) etc.). Still, the result (37) applies for any form of \( H_{S-B} \). This clearly challenges the contemporary theory of the asymptotic symmetry breaking. As we have \( \Omega \neq 0 \) even for \( \omega_0 = 0 \) and \( T = 0 \), we have really got a new channel of subbarrier transfer \( 1 \to 2 \). The fact that \( \Omega \neq 0 \) for any \( H_{S-B} \), \( r' > 0 \) may be found for any initial condition with essentially off-diagonal form of \( \rho^R_{\mu \nu} \) in (13a). The situation is, however, different in the special case when \( \rho^R_{\mu \nu} \) is diagonal. Let us assume for example (14) with

\[ P_\alpha = \prod_{i=1}^{M} \left[ e^{-\beta \hbar \omega_i} \alpha_i (1 - e^{-\beta \hbar \omega_i}) \right]. \]  

(40)

Then

\[ \Omega \approx \frac{\hbar}{2 \varepsilon} \int_{0}^{+\infty} |H^{(+)}(\omega)|^2 \rho(\omega) \coth \left( \frac{1}{2} \beta \hbar \omega \right) d\omega e^{-W} \]  

(41a)

with

\[ W = 2 \int_{0}^{+\infty} \frac{d\omega}{\omega^2} |G(\omega)|^2 \rho(\omega) \coth \left( \frac{1}{2} \beta \hbar \omega \right) d\omega \]  

(41b)

and

\[ |G(\omega)|^2 \rho(\omega) \approx M \sum_{i=1}^{M} G_i^2 \delta(\omega - \omega_i), \quad M \to +\infty. \]  

(41c)

Assuming that

\[ |G(\omega)|^2 \rho(\omega) \sim \omega', \quad \omega \to 0 \]  

(42)

we obtain that \( W \) is finite (i.e. \( \Omega \neq 0 \) in (41a)) just for \( r > 1 \) (for \( T = 0 \)) or \( r > 2 \) (for \( T \neq 0 \)). This result for the diagonal form of \( \rho^R_{\mu \nu} \) corresponds to singular properties of \( H_0 \) when \( \omega_0 = 0 \) [20]; for arbitrarily small but nonzero \( \omega_0 \), these singular properties disappear. Nevertheless, a higher order generalization of our approach including positive powers of \( \omega_0 \) is needed.

The question now arises whether one may really neglect the standard tunnelling channel which is due to the term \( H_5 \) in (1a). It is interesting to observe that increasing e.g. the barrier width separating our two wells, \( \omega_0 \) decreases exponentially. On the other hand, as the third state added here may be an arbitrary excited state above the barrier, the decrease of efficiency (frequency factor \( \Omega \)) of our new channel may be much slower. From that, one can easily infer that our excited-state-induced subbarrier tunnelling channel may easily become dominating even in standard situations.
The final point to be solved here is the physical interpretation of our new channel. Let us designate the collection of nuclear coordinates as \( R \) and let \( R_0 \) be the set of corresponding equilibrium values. Clearly \( R - R_0 \sim b_i + b_i^\dagger \). Designating \( \psi (r, R) \) the initial wave function for the particle localized in e.g. the left (or right) well, we may set

\[
\psi (r, R_0) \sim \langle r | 1 \rangle \quad \text{(or} \quad \langle r | 2 \rangle \text{)}.
\]

(43)

This means that \( \psi (r, R_0) \) is an eigenstate of \( H_{\text{tot}} \) for \( \omega_0 = 0 \) and, formally, \( R = R_0 \). For \( R \neq R_0 \) and total Hamiltonian (6), \( \psi (r, R) \) will, however, always (due to (5)) contain an admixture of the third state \( \langle r | 3 \rangle = \langle r | a_3 \rangle = 0 \). Averaging formally over \( R \) and in the lowest order in \( R - R_0 \), this admixture disappears as \( \langle R - R_0 \rangle = R_0 - R_0 = 0 \). However, averaging pair combinations of the wave functions yields a finite contribution even at \( T = 0 \) since \( \langle (R - R_0^2) \rangle \neq 0 \). This is the channel which yields the transfer \( 1 \leftrightarrow 2 \) even at \( \omega_0 = 0 \).

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References


Note added during the referee procedure

The author is grateful to an anonymous referee for drawing his attention to an interesting paper [21]. This work aims at presenting a systematic framework for reducing a double-well problem to an equivalent two-level one — the possibility of such a reduction would contradict
conclusions of the present work. As a matter of fact, in [21], mainly the renormalization of the bare tunnelling parameter (i.e. splitting of two lowest particle levels) in the double-well model due to high-frequency reservoir modes with frequencies $\approx \omega_c$ is treated. Higher particle states are then omitted without any further justification on grounds of the low-temperature assumption ($k_B T \ll \hbar \omega_c \leq$ distance to higher excited states) declaring that at these conditions, « ...the excited states will not be appreciably populated and can be ignored » (p. 1118 of [21]). The first part of this statement is correct; the second one is a standard and seemingly natural assumption which has never been questioned before. The present work shows that exactly this assumption is not correct. In other words, we prove that, though these states are really not populated under above conditions, they still cannot in general be ignored in dynamic treatments due to their dynamic coupling to the low-lying states. Yet in other words, our new channel is due to virtual transitions to higher states; these virtual (not real) transitions do persist even at $T = 0$ but are fully ignored in the spin-boson model as well as theories like [21].