

Dynamics of the dimer-oscillator model with Fano damping

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The dynamical properties of an excitonic dimer coupled to a harmonic oscillator are analyzed as a simple model for the problem of self-localization of excitons in crystalline systems. If the oscillator is treated classically and a damping term is included in a phenomenological way, the system relaxes to its lowest-energy state, which is either a symmetrical or a site-trapped, symmetry-broken state depending on the values of the system parameters. When the system is treated quantum mechanically, and the accurate eigenstates of the system obtained in previous work are used, it is possible to establish a semiquantitative argument suggesting that this symmetry-breaking behavior is an artifact of the semiclassical approximation. [S0163-1829(97)02138-3]

I. INTRODUCTION

The present work is motivated by the background problem of the spatial self-localization of an initially delocalized electronic excitation in crystalline systems. From the observation of retarded luminescence in rare-gas crystals¹ and in alkali halides² we know that a free exciton generated by optical excitation can get self-trapped at two neighboring sites (dimerization) due to its interaction with the lattice vibrations. In this process energy is carried away from the excitonic system. This counteracts the excitonic transfer between lattice sites, which tends to delocalize the exciton.

The simplest archetypical model for studying this antagonism is a system with two exciton sites coupled to a harmonic oscillator. In addition to this, we will couple the oscillator to a Fano phonon bath representing the energy transport in the lattice. The aim of the present paper is to investigate the time evolution after an exciton has been created at one of the two sites.

We first employ a semiclassical approximation by treating the oscillator classically and simulating the Fano coupling with a classical damping term. The ground state of this system shows a pronounced bifurcation from a symmetrical to a pair of degenerate symmetry-broken states when the coupling between the exciton and the oscillator exceeds a critical value (Refs. 3 and 4). In the dynamical evolution there is a parameter range where the exciton in the beginning oscillates between the two sites, but after losing part of its energy due to the damping it gets site trapped into one of the symmetry-broken ground states.

In the second part of our paper the system is treated quantum mechanically. If the Fano coupling is absent, the occupation probability difference between the two sites shows sinusoidal oscillations. If the Fano coupling is included, a qualitative argument suggests that the amplitude of the occupational oscillations will decrease monotonously until the exciton has equal probabilities on both sites. So we can draw the conclusion that the symmetry-breaking behavior is an artifact of the semiclassical approximation.

In Sec. II we present our model and the basic analytical description of semiclassical dynamics if damping is absent. In Sec. III we introduce the coupling of the "singular" oscillator to a bath of other oscillators. This "indirect" cou-

pling is contrasted to the direct coupling of the exciton to the bath as it is usually employed in the literature (see, e.g., Ref. 5), and it is shown that our model corresponds to the situation known as the super-Ohmic case. In Sec. IV the numerical results for the semiclassical evolution without and with damping are given. In Sec. V we contrast the semiclassical description with the quantum-mechanical counterpart, exploiting the symmetry of the model. In Sec. VI we present our conclusions.

II. THE MODEL

A. The Hamiltonian of the system

We consider a symmetric dimer consisting of two excitonic sites, coupled to a harmonic oscillator. The Hamiltonian reads

$$\hat{H} = \hat{H}_{\text{exc}} + \hat{H}_{\text{osc}} + \hat{H}_{\text{int}}, \quad (1)$$

where

$$\hat{H}_{\text{exc}} = -\Omega_s T(|1\rangle\langle 2| + |2\rangle\langle 1|) = -\Omega_s T \hat{x}, \quad (2)$$

$$\hat{H}_{\text{osc}} = \frac{1}{2} (\hat{P}_s^2 + \Omega_s^2 \hat{Q}_s^2), \quad (3)$$

$$\hat{H}_{\text{int}} = \Omega_s^{3/2} D \hat{Q}_s (|1\rangle\langle 1| - |2\rangle\langle 2|) = \Omega_s^{3/2} D \hat{Q}_s \hat{z}, \quad (4)$$

respectively, are the Hamiltonians of the excitonic system, the oscillator, and the interaction between them. $|1\rangle$ and $|2\rangle$ are the site states of the exciton, \hat{P}_s and \hat{Q}_s the oscillatory coordinates, and \hat{x} , \hat{y} , \hat{z} are the pseudospin operators

$$\hat{x} = |1\rangle\langle 2| + |2\rangle\langle 1|, \quad (5)$$

$$\hat{y} = i(|2\rangle\langle 1| - |1\rangle\langle 2|), \quad (6)$$

$$\hat{z} = |1\rangle\langle 1| - |2\rangle\langle 2|. \quad (7)$$

Equation (1) is the two-site version of the Holstein Hamiltonian.⁶ The stationary states of this quantum-mechanical system were calculated by Shore and Sander,⁷ by

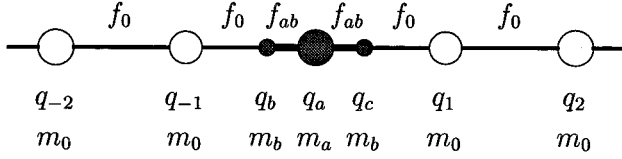


FIG. 1. A triatomic molecule embedded in a one-dimensional chain.

Wagner and Königter,⁸ and by Sonnek and co-workers.^{9,10} We will later return to specific properties of these states, since they imply a restrictive frame for the time evolution.

B. Time evolution (“semiclassical model”)

We consider the evolution in Heisenberg representation:

$$A(t) = \langle \Psi(0) | \hat{A}(t) | \Psi(0) \rangle \equiv \langle \hat{A}(t) \rangle = \langle \hat{A} \rangle_t, \quad (8)$$

$$i \frac{d}{dt} A(t) = \langle \Psi(0) | [\hat{A}(t), \hat{H}] | \Psi(0) \rangle. \quad (9)$$

Introducing the real Bloch variables

$$x(t) := \langle \hat{x} \rangle_t, \quad (10)$$

$$y(t) := \langle \hat{y} \rangle_t, \quad (11)$$

$$z(t) := \langle \hat{z} \rangle_t, \quad (12)$$

the basic equations of motion read

$$\dot{x} = -2\Omega_s^{3/2} D \langle \hat{Q}_s \hat{y} \rangle_t, \quad (13)$$

$$\dot{y} = 2(\Omega_s T z(t) + D \Omega_s^{3/2} \langle \hat{Q}_s \hat{x} \rangle_t), \quad (14)$$

$$\dot{z} = -2\Omega_s T y(t), \quad (15)$$

$$\dot{Q}_s = P_s(t), \quad (16)$$

$$\dot{P}_s = -[\Omega_s^2 Q_s(t) + \Omega_s^{3/2} D z(t)], \quad (17)$$

and the energy expectation value is

$$E(t) = \langle \hat{H} \rangle_t = \left[\frac{1}{2} \langle \hat{P}_s^2 + \Omega_s^2 \hat{Q}_s^2 \rangle_t - \Omega_s T x(t) + \Omega_s^{3/2} D \langle \hat{Q}_s \hat{z} \rangle_t \right]. \quad (18)$$

Normalization of $|\Psi(0)\rangle$ requires

$$x(t)^2 + y(t)^2 + z(t)^2 = 1 \quad (19)$$

for all times t .

The “semiclassical” approach of Holstein⁶ and of Kenkre and Campbell³ is found, if the following factorizations are made:

$$\langle \hat{Q}_s \hat{x} \rangle_t = Q_s(t) x(t), \quad \langle \hat{Q}_s \hat{y} \rangle_t = Q_s(t) y(t). \quad (20)$$

This assumption is tantamount to requiring a product form of the Schrödinger wave function at all times:

$$|\Psi(t)\rangle \equiv e^{-i\hat{H}t} |\Psi(0)\rangle \approx |\phi_{\text{exc}}(t)\rangle |\phi_{\text{osc}}(t)\rangle, \quad (21)$$

where

$$|\phi_{\text{exc}}(t)\rangle = g_1(t)|1\rangle + g_2(t)|2\rangle, \quad |g_1|^2 + |g_2|^2 = 1. \quad (22)$$

This simplifies the equations of motion to

$$\dot{x} = -2\Omega_s^{3/2} D Q_{s,y}, \quad (23)$$

$$\dot{y} = 2(\Omega_s T z + \Omega_s^{3/2} D Q_{s,x}), \quad (24)$$

$$\dot{z} = -2\Omega_s T y, \quad (25)$$

$$\dot{Q}_s = P_s, \quad (26)$$

$$\dot{P}_s = -(\Omega_s^2 Q_s + \Omega_s^{3/2} D z), \quad (27)$$

and establishes a nonlinear system of five coupled differential equations of first order. For later reference purposes we also note the stationary states of this system given by $\dot{x} = \dot{y} = \dot{z} = \dot{Q}_s = \dot{P}_s = 0$, which have been obtained by Esser and Schanz.⁴ For $D^2/T < 1$, there are only two solutions with

$$x^{(0)} = \pm 1, \quad z^{(0)} = Q_s^{(0)} = 0, \quad (28)$$

which preserve the symmetry of the system. For $D^2/T > 1$, two other solutions appear, with

$$x^{(0)} = \pm T/D^2, \quad z^{(0)} = \pm \sqrt{1 - (x^{(0)})^2}, \quad (29)$$

$$Q_s^{(0)} = -\Omega_s^{-1/2} D z^{(0)},$$

which break the symmetry of the system. These fixed points split off the lower of the two fixed points Eq. (28) at $D^2/T = 1$.

Equations (13)–(17) can be further simplified if the oscillator is “fast” compared to the excitonic system ($T \ll 1$). Then the oscillator coordinate Q_s is “slaved” by the excitonic system, i.e., the oscillator is always in its equilibrium position $Q_s = -\Omega_s^{3/2} D z$. This approximation leads to the so-called discrete self-trapping (DST) equation in the case of a dimer, which was solved analytically by Kenkre and Campbell.³ It should be noted, however, that the “slaving” assumption $Q_s = -\Omega_s^{3/2} D z$ imposes a severe restriction to the form of the initial conditions, i.e., $Q_s(0) = -\Omega_s^{3/2} D z(0)$, which experimentally cannot be verified easily.

III. FANO COUPLING TO A BATH

A. “Molecular” concept (“indirect” bath coupling)

So far, no mechanism for energy dissipation has been included. For atomistic definiteness we now introduce a coupling Hamiltonian $\hat{H}_{\text{osc,bath}}$ of the singular oscillator to the bath,

$$\hat{H}_{\text{osc,bath}} = \frac{1}{2} \hat{Q}_s \sum_k V_k \hat{Q}_k, \quad (30)$$

and a phonon-bath Hamiltonian

$$\hat{H}_{\text{bath}} = \frac{1}{2} \sum_k (\hat{P}_k^2 + \Omega_k^2 \hat{Q}_k^2), \quad (31)$$

which we add to our dimer-oscillator Hamiltonian (1), yielding the total Hamiltonian

$$\hat{H}_{\text{tot}} = \hat{H} + \hat{H}_{\text{bath}} + \hat{H}_{\text{osc,bath}}. \quad (32)$$

As an example for a physical system described by Hamiltonian (32) we consider a linear triatomic molecule embedded in a one-dimensional chain of atoms with nearest-neighbor coupling (see Fig. 1). The Hamiltonian of the oscillatory system is given by

$$\begin{aligned} \hat{H}_{\text{osc}} + \hat{H}_{\text{bath}} + \hat{H}_{\text{osc,bath}} = & \frac{1}{2m_0} (\cdots + \hat{p}_{-2}^2 + \hat{p}_{-1}^2 + \hat{p}_1^2 + \hat{p}_2^2 + \cdots) + \frac{1}{2m_a} \hat{p}_a^2 + \frac{1}{2m_b} (\hat{p}_b^2 + \hat{p}_c^2) + \frac{f_0}{2} [\cdots + (\hat{q}_{-1} - \hat{q}_{-2})^2 \\ & + (\hat{q}_b - \hat{q}_{-1})^2 + (\hat{q}_1 - \hat{q}_c)^2 + \cdots] + \frac{f_{ab}}{2} [(\hat{q}_b - \hat{q}_a)^2 + (\hat{q}_c - \hat{q}_a)^2] \end{aligned} \quad (33)$$

and the exciton-oscillator interaction Hamiltonian by

$$\hat{H}_{\text{int}} = \tilde{D} \hat{z} [(\hat{q}_a - \hat{q}_b) - (\hat{q}_c - \hat{q}_a)]. \quad (34)$$

If we introduce the normal coordinates in the triatomic molecule, neglecting the even vibrational mode

$$\hat{q}_a = \hat{q}_0 + \hat{q}_s, \quad \hat{q}_b = \hat{q}_c = \hat{q}_0 - \frac{m_a}{2m_b} \hat{q}_s, \quad (35)$$

$$\hat{p}_a = \frac{m_a}{m_a + 2m_b} \hat{p}_0 + \frac{2m_b}{m_a + 2m_b} \hat{p}_s, \quad (36)$$

$$\hat{p}_b = \hat{p}_c = \frac{m_b}{m_a + 2m_b} (\hat{p}_0 - \hat{p}_s),$$

and assume $m_0 = m_a + 2m_b$, Hamiltonian (33) takes the form

$$\begin{aligned} \hat{H}_{\text{osc}} + \hat{H}_{\text{bath}} + \hat{H}_{\text{osc,bath}} = & \frac{1}{2m_0} \sum_{\nu=-\infty}^{\infty} \hat{p}_{\nu}^2 \\ & + \frac{f_0}{2} \sum_{\nu=-\infty}^{\infty} (\hat{q}_{\nu} - \hat{q}_{\nu-1})^2 \\ & + \frac{1}{2m_a(1 + m_a/2m_b)} \hat{p}_s^2 \\ & + \left[\frac{m_a^2}{4m_b^2} f_0 + f_{ab} \left(1 + \frac{m_a}{2m_b} \right)^2 \right] \hat{q}_s^2 \\ & - \frac{m_a}{2m_b} f_0 (2\hat{q}_0 - \hat{q}_{-1} - \hat{q}_1) \hat{q}_s, \end{aligned} \quad (37)$$

from which we can identify

$$\hat{H}_{\text{bath}} = \frac{1}{2m_0} \sum_{\nu=-\infty}^{\infty} \hat{p}_{\nu}^2 + \frac{f_0}{2} \sum_{\nu=-\infty}^{\infty} (\hat{q}_{\nu} - \hat{q}_{\nu-1})^2, \quad (38)$$

$$\hat{H}_{\text{osc}} = \frac{1}{2m_s} \hat{p}_s^2 + m_s \Omega_s^2 \hat{q}_s^2, \quad (39)$$

$$\hat{H}_{\text{osc,bath}} = -\frac{m_a}{2m_b} f_0 (2\hat{q}_0 - \hat{q}_{-1} - \hat{q}_1) \hat{q}_s, \quad (40)$$

with

$$m_s = m_a \left(1 + \frac{m_a}{2m_b} \right), \quad (41)$$

$$m_s \Omega_s^2 = \frac{m_a^2}{4m_b^2} f_0 + f_{ab} \left(1 + \frac{m_a}{2m_b} \right)^2, \quad (42)$$

and the interaction Hamiltonian reads

$$\hat{H}_{\text{int}} = D \hat{z} \hat{q}_s \quad (43)$$

with

$$D = 2\tilde{D} \left(1 + \frac{m_a}{2m_b} \right). \quad (44)$$

If we introduce mass-reduced normal coordinates

$$\hat{q}_{\nu} = \frac{1}{\sqrt{m_0 N}} \sum_k e^{ik\nu} \hat{Q}_k, \quad (45)$$

$$\hat{q}_s = \frac{1}{\sqrt{m_s}} \hat{Q}_s, \quad (46)$$

we obtain \hat{H}_{bath} in the form (31) with

$$\Omega_k = \Omega_D |\sin(k/2)|, \quad \Omega_D = 2 \sqrt{\frac{f_0}{m_0}}, \quad (47)$$

\hat{H}_{osc} assumes the form (3), and the coefficients V_k in Eq. (30) are given by

$$V_k = V(\Omega_k) = \frac{4m_a f_0}{m_b \sqrt{m_0 m_s} \sqrt{N} \Omega_D^2} \Omega_k^2. \quad (48)$$

The last two parts of Hamiltonian (32), taken together with \hat{H}_{osc} , constitute an oscillatory Fano system, which both classically and quantum mechanically can be handled in an exact manner.^{11,12} This modifies the oscillatory equation of motion (17) to

$$\dot{P}_s = -\Omega_s (Q_s + Dz) - \frac{1}{2} \sum_k V_k Q_k, \quad (49)$$

the other equations (13)–(16) remaining unaltered.

B. General oscillatory system (“direct coupling”)

In this paper the dimer is coupled to a singular oscillator, which in turn is coupled to an oscillatory bath. This differs from the spin-boson model, which has been discussed extensively in the previous literature (e.g., Ref. 5). In the spin-boson model the exciton is coupled directly to the continuum degrees of freedom of the bath, the interaction Hamiltonian being

$$\hat{H}_{\text{int}} = \frac{1}{2} \hat{z} \sum_{\mu} D_{\mu} \hat{Q}'_{\mu}. \quad (50)$$

The exciton-bath interaction can be described by the strength function

$$S(\Omega) = \frac{1}{\Omega} \sum_{\mu} |D_{\mu}|^2 \delta(\Omega - \Omega_{\mu}) = \frac{1}{\Omega} |D_{\mu}|^2 \Big|_{\Omega_{\mu}=\Omega} \rho(\Omega), \quad (51)$$

where $\rho(\Omega)$ is the mode density of the bath. If we assume a power-law form for $S(\Omega)$

$$S(\Omega) = 4\alpha\Omega^s \quad \text{for } \Omega \ll \Omega_D \quad (\Omega_D: \text{Debye frequency}), \quad (52)$$

we can distinguish three main cases: super-Ohmic ($s > 1$), Ohmic ($s = 1$), and sub-Ohmic ($s < 1$) dissipation.

The “indirect” bath coupling considered in this paper can be mapped onto the spin-boson model with direct coupling to the bath (see, e.g., Refs. 5, 13) by diagonalizing the Hamiltonian (32) with respect to the oscillatory degrees of freedom. Then the singular oscillator together with the bath oscillators forms a new bath. If this bath is diagonalized, the coupling to the dimer assumes again the form (50).

This diagonalization has been carried out earlier by one of us.¹⁴ Since the eigenfrequencies Ω'_{μ} of the new bath are shifted from those of the original bath only by small amounts (smaller than the difference between adjacent eigenvalues), the mode density of the new bath equals that of the original bath. The original singular coordinate Q_s may be expressed in terms of the new bath coordinates Q'_{μ} by

$$Q_s = \sum_{\mu} \eta_s(\mu) Q'_{\mu}, \quad (53)$$

where $\eta_s(\mu)$ is given (for $N \gg 1$) by (see Ref. 14)

$$\eta_s(\mu)^2$$

$$= \frac{\pi V(\Omega_{\mu})^2}{[\Omega_{\mu}^2 - \Omega_s^2 - P(\Omega_{\mu})]^2 + [(\pi/2\Omega_{\mu})V(\Omega_{\mu})^2\rho(\Omega_{\mu})]^2}, \quad (54)$$

$$P(\Omega_{\mu}) = P \int_{\Omega_1}^{\Omega_N} \rho(\Omega) \frac{V(\Omega)^2}{\Omega_{\mu}^2 - \Omega^2} d\Omega. \quad (55)$$

The interaction Hamiltonian, expressed by the new coordinates, reads

$$\hat{H}_{\text{int}} = \frac{D}{\sqrt{m_s}} \hat{Q}_s \hat{z} = \hat{z} \sum_{\mu} \frac{D}{\sqrt{m_s}} \eta_s(\mu) \hat{Q}'_{\mu} \quad (56)$$

so we obtain $D_k = (D/\sqrt{m_s}) \eta_s(\mu)$ for the coefficients D_k and

$$S(\Omega) = \frac{1}{\Omega} \frac{D}{\sqrt{m_s}} \times \frac{\pi V(\Omega)^2}{[\Omega^2 - \Omega_s^2 - P(\Omega)]^2 + [(\pi/2\Omega)V(\Omega)^2\rho(\Omega)]^2} \times \rho(\Omega) \quad (57)$$

for the strength function. Since

$$P(\Omega_{\mu}) + \int_{\Omega_1}^{\Omega_N} \frac{\rho(\Omega)V(\Omega)^2}{\Omega^2} d\Omega = \Omega_{\mu}^2 P \int_{\Omega_1}^{\Omega_N} \frac{\rho(\Omega)V(\Omega)^2/\Omega^2}{\Omega_{\mu}^2 - \Omega^2} d\Omega \rightarrow 0 \quad \text{for } \Omega_{\mu} \rightarrow 0, \quad (58)$$

$P(\Omega_{\mu})$ approaches the finite negative value $-\int \rho(\Omega)V(\Omega)^2/\Omega^2$ for $\Omega_{\mu} \rightarrow 0$. Therefore the denominator in Eq. (57) remains finite and strictly positive for $\Omega_{\mu} \rightarrow 0$, and for small Ω we have

$$S(\Omega) \propto \frac{1}{\Omega} \rho(\Omega)V(\Omega)^2 \propto \Omega^3, \quad (59)$$

so our model corresponds to the super-Ohmic case ($s = 3$).

IV. NUMERICAL SOLUTIONS OF THE SEMICLASSICAL EQUATIONS OF MOTION

In the following we will discuss some numerical solutions of the system of Eqs. (23)–(27) with the initial condition that the exciton is on site 1 and the oscillator is resting in its unperturbed equilibrium position, i.e.,

$$x = y = 0, \quad (60)$$

$$z = 1, \quad (61)$$

$$Q_s = 0, \quad (62)$$

$$P_s = 0. \quad (63)$$

A. Behavior without damping

For comparison with the DST model (see Ref. 3), which is valid for $T \ll 1$, we first set $\gamma = 0$ and $D^2 = 0.045$, and vary T . The DST model predicts a transition from symmetry-broken to symmetric behavior at $T = 0.0225$. The numerical calculations of the occupation difference (Figs. 2 and 3, solid lines) show that the transition actually occurs between $T = 0.02263$ and $T = 0.02264$, and that the curves strongly resemble those obtained analytically for the DST model in Ref. 3. (The dashed lines in Figs. 2 and 3 show the quantum-mechanical behavior, which will be discussed below.) Note that for $T = 0.02264$ the evolution of the excitonic occupation is symmetric although the ground state is symmetry broken. This is because the energy of the exciton is too high.

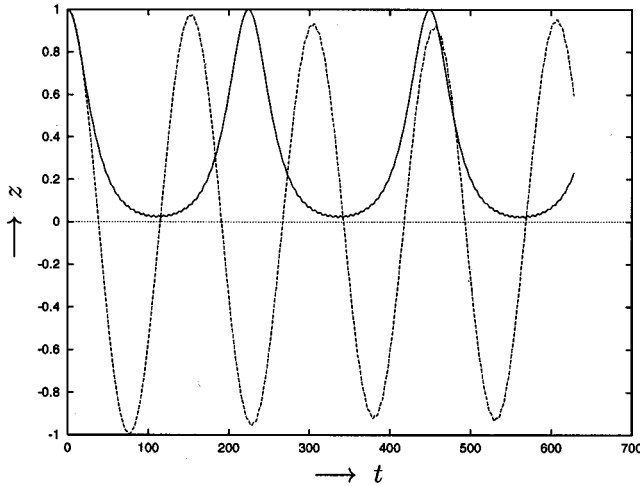


FIG. 2. The difference z of the occupation probabilities of the two sites in a dimer as a function of time t . Solid line: semiclassical approximation (compare Ref. 3). Dashed line: exact quantum-mechanical result. Parameter values: $\Omega_0=1$, $D^2=0.045$, $T=0.02263$, $\gamma=0$.

B. Behavior with damping

Instead of handling the dynamics of the full system, we now assume that the bath degrees of freedom Q_k carry away energy of the singular oscillator as if the exciton did not exist. This assumption certainly is not immediately evident in the case of a strong coupling to the bath. In this case the argument has to follow the lines described in Sec.V B 2, which now, however, has to be understood in a classical way (“coherent oscillatory state” \Rightarrow classical excitation), leading to classical Fano decay. Then, applying Green-function techniques,¹¹ we may replace the last term on the right-hand side of Eq. (49) by a damping term,

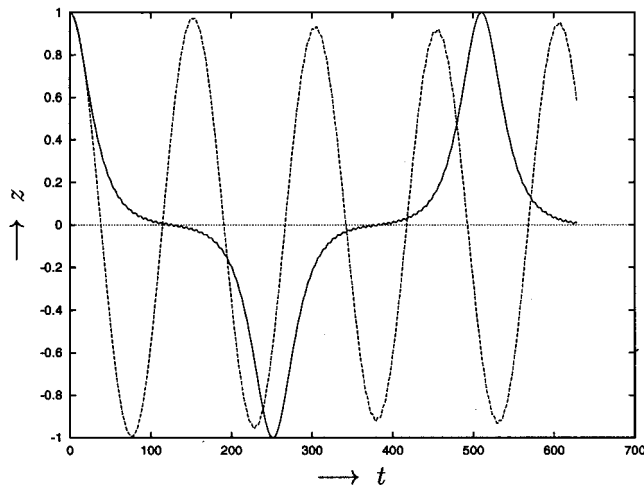


FIG. 3. The difference z of the occupation probabilities of the two sites in a dimer as a function of time t . Solid line: semiclassical approximation (compare Ref. 3). Dashed line: exact quantum-mechanical result. Parameter values: $\Omega_0=1$, $D^2=0.045$, $T=0.02264$, $\gamma=0$.

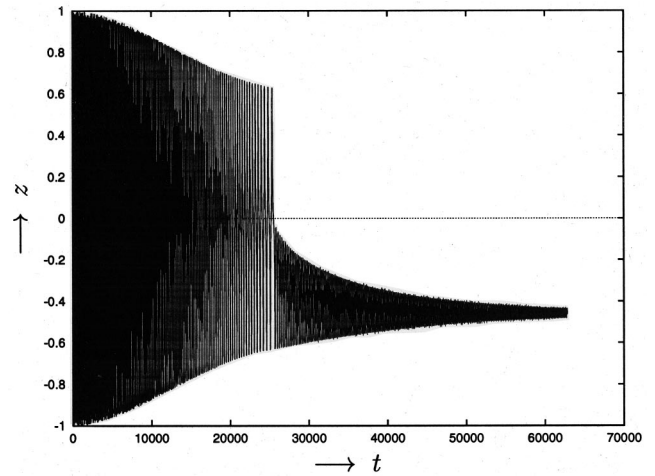


FIG. 4. The difference z of the occupation probabilities of the two sites in a dimer as a function of time t in the semiclassical approximation. Parameter values: $\Omega_0=1$, $D^2=0.045$, $T=0.02$, $\gamma=0.02$.

$$\frac{1}{2} \sum_k V_k Q_k \approx \gamma \Omega_0 P_s, \quad (64)$$

where the magnitude of γ depends on the distribution of coupling constants V_k and on the mode density in the bath. Hence, in the (classical part of the) further calculations we will replace Eqs. (17) and (27) by

$$\dot{P}_s = -\Omega_0(Q_s + Dz + \gamma P_s). \quad (65)$$

In contrast to Kenkre and Wu,¹⁵ who also modeled the oscillator-bath coupling by a damping term, we do not assume the damping to be so large ($\gamma \gg 1$) that \dot{P} can be approximately set to zero in Eq. (65).

1. Bifurcation for small coupling and small excitonic transfer

If damping is included, the system will lose energy and eventually settle down in a stable fixed point. If the critical parameter D^2/T is between 1 and 2, the exciton will first oscillate freely between the two sites; but after some time it will get trapped by either of the two sites (Fig. 4). For $D^2/T > 2$ the exciton is site trapped from the beginning, as it is the case for $\gamma=0$ (Fig. 5). For $D^2/T < 1$ there is no site trapping at all, and the exciton will end up in a state with equal occupation probabilities for both sites (Fig. 6).

2. Bifurcation for strong coupling

Increasing D and T further gives the results shown in Figs. 7 and 8, where D^2 was chosen as 4.5 and T was varied from 4 to 4.5. Since the fast motion of the exciton (compared to the oscillator) will produce only small oscillations and thus only a small energy loss of the oscillator, the damping term had to be drastically increased (to $\gamma=1$). In Fig. 7 we have $T=D^2=4.5$, so the final state of the exciton is not symmetry broken. In Fig. 8 ($T=4$), however, we have $T < D^2$ and the final state is a site-trapped state with broken symmetry. Contrary to the case of smaller values of D and T , the exciton will first relax to the symmetric state, which for $T \geq D^2$ is the ground state, and only then to the final state.

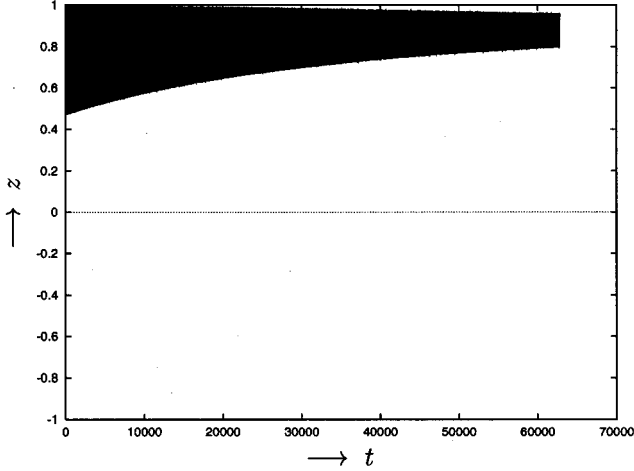


FIG. 5. The difference z of the occupation probabilities of the two sites in a dimer as a function of time t in the semiclassical approximation. Parameter values: $\Omega_0=1$, $D^2=0.045$, $T=0.04$, $\gamma=0.02$.

V. QUANTUM-MECHANICAL FRAME CONDITIONS AND REQUIREMENTS FROM SYMMETRY

In the numerical calculations, as represented in the preceding figures, several pronounced phenomena have been found, and it is highly desirable either to support these by rigorous quantum-mechanical requirements or to evince them as artifacts resulting from the basic approximation (20).

A. Stationary states of the dimer-oscillator subsystem and time evolution without damping

1. The Fulton-Gouterman Hamiltonian

We first disregard the coupling to the bath and consider the basic Hamiltonian (1). Application of group theory requires the eigenfunctions to be irreducible representations of the inversion group, whence they must display a definite parity p ($:=g,u$ or $:=\pm 1$),

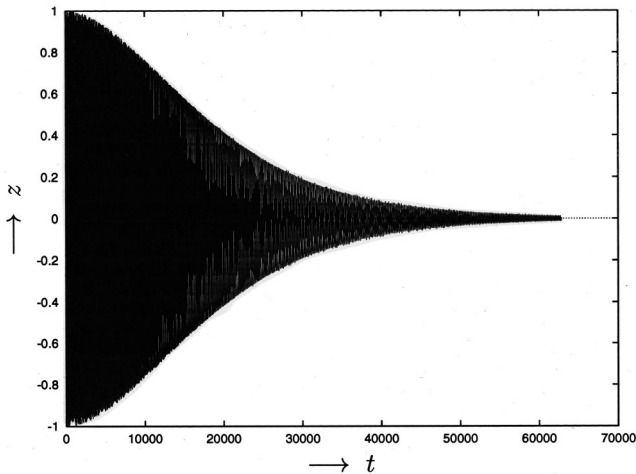


FIG. 6. The difference z of the occupation probabilities of the two sites in a dimer as a function of time t in the semiclassical approximation. Parameter values: $\Omega_0=1$, $D^2=0.045$, $T=0.05$, $\gamma=0.02$.

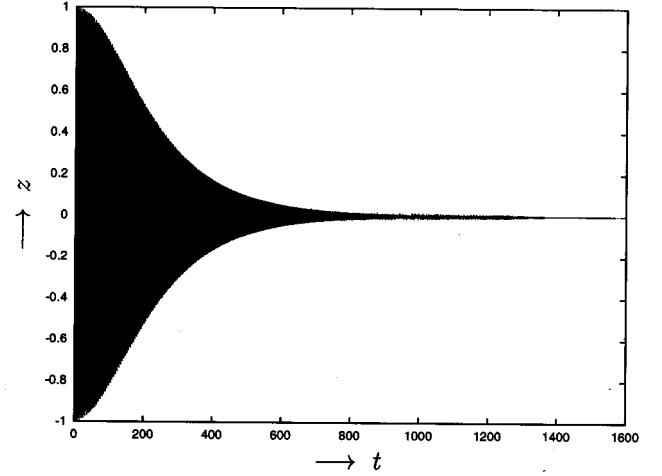


FIG. 7. The difference z of the occupation probabilities of the two sites in a dimer as a function of time t in the semiclassical approximation. Parameter values: $\Omega_0=1$, $D^2=4.5$, $T=4.5$, $\gamma=1$.

$$\hat{R}|\psi^{(p)}\rangle = p|\psi^{(p)}\rangle, \quad (66)$$

where \hat{R} is the inversion operator ($\hat{R}=\hat{R}_{\text{exc}}\hat{R}_{\text{osc}}$),

$$\hat{R}_{\text{exc}}|1\rangle = |2\rangle, \quad (67)$$

$$\hat{R}_{\text{osc}}\phi(Q_s) = \phi(-Q_s), \quad (68)$$

$$\hat{R}\hat{Q}_s = -\hat{Q}_s\hat{R}. \quad (69)$$

The eigenfunctions therefore must be of the general Wigner form

$$|\psi_n^{(p)}\rangle = \frac{1}{\sqrt{2}} (|1\rangle + p|2\rangle\hat{R}_{\text{osc}})\phi_n^{(p)}, \quad (70)$$

which for $\phi_n^{(p)}$ yields the Fulton-Gouterman (FG) equations

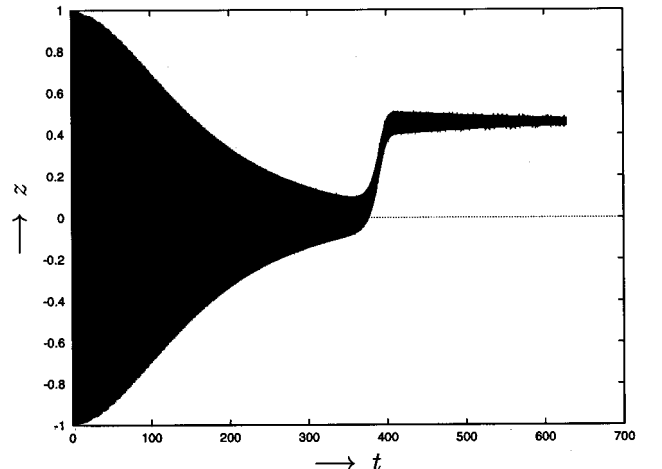


FIG. 8. The difference z of the occupation probabilities of the two sites in a dimer as a function of time t in the semiclassical approximation. Parameter values: $\Omega_0=1$, $D^2=4.5$, $T=4.0$, $\gamma=1$.

$$\begin{aligned} \hat{H}_{\text{FG}}^{(p)} \phi_n^{(p)} &\equiv \Omega_0 \left[\frac{1}{2} (\hat{P}_s^2 + \hat{Q}_s^2) + D \hat{Q}_s - p T \hat{R}_{\text{osc}} \right] \phi_n^{(p)} \\ &= E_n^{(p)} \phi_n^{(p)}. \end{aligned} \quad (71)$$

For details we refer to earlier work, see Refs. 6, 8, 9, 10, and 16.

2. Hierarchy $1 \gg D \gg T$

For the parameter hierarchy $1 \gg D \gg T$ the exact eigenvalues and eigenvectors of Eq. (71) read (viz. Ref. 17)

$$\begin{aligned} E_0^{(p)} &= \frac{1}{2} \Omega_0 (1 - D^2) - p \Omega_0 T e^{-D^2} - 2 \Omega_0 T^2 D^2 [1 + O(D^2)] \\ &\quad + O(T^3), \end{aligned} \quad (72)$$

$$\begin{aligned} \phi_0^{(p)} &= \Phi_0(Q_s + D) - p T D \sqrt{2} \Phi_1(Q_s + D) \\ &\quad - p T D^2 \frac{1}{\sqrt{2}} \Phi_2(Q_s + D) - p T O(D^3) + O(T^2), \end{aligned} \quad (73)$$

$$E_1^{(p)} = \frac{1}{2} \Omega_0 (3 - D^2) + p \Omega_0 T e^{-D^2} (1 - 2D^2) + O(T^2), \quad (74)$$

$$\phi_1^{(p)} = \Phi_1(Q_s + D) + O(T), \quad (75)$$

where $\Phi_n(Q_s)$ is the n th eigenstate of the unperturbed oscillator.

We now apply these results to the problem of the time evolution. The quantum-mechanical form of our initial state reads

$$\Psi(0) = |1\rangle \Phi_0(Q_s), \quad (76)$$

where

$$\Phi_0(Q_s) = \left(\frac{1}{\pi} \right)^{1/4} e^{-Q_s^2/2} \quad (77)$$

is the ground state of the unperturbed oscillator. This initial state (76) may be written as

$$\Psi(0) = \frac{1}{\sqrt{2}} [\Psi^{(+)}(0) + \Psi^{(-)}(0)], \quad (78)$$

$$\Psi^{(\pm)}(0) = \frac{1}{\sqrt{2}} [|1\rangle \pm |2\rangle] \Phi_0(Q_s). \quad (79)$$

Employing Eqs. (70) and (73) we observe that in the hierarchy $1 \gg D \gg T$ we have

$$\Psi(0) = \frac{1}{\sqrt{2}} [\psi_0^{(+)} + \psi_0^{(-)}] + O(D) \psi_1^{(\pm)} + O(D^2), \quad (80)$$

where $\psi_0^{(\pm)}, \psi_1^{(\pm)}$ are the exact eigenstates (70). We thus have the time evolution

$$\begin{aligned} \Psi(t) &= \frac{1}{\sqrt{2}} e^{-iE_0^+ t} \psi_0^{(+)} + \frac{1}{\sqrt{2}} e^{-iE_0^- t} \psi_0^{(-)} + O(D) \psi_1^{(\pm)} \\ &\quad + O(D^2). \end{aligned} \quad (81)$$

After some rearrangement this can be conveyed into the form

$$\begin{aligned} \Psi(t) &= \frac{1}{2} e^{-i(E_0^+ - E_0^-)t/2} \cos((E_0^+ - E_0^-)t/2) [|1\rangle (\phi_0^{(+)} + \phi_0^{(-)}) + |2\rangle \hat{R}(\phi_0^{(+)} - \phi_0^{(-)})] \\ &\quad + \frac{i}{2} e^{-i(E_0^+ - E_0^-)t/2} \sin((E_0^+ - E_0^-)t/2) [|2\rangle \hat{R}(\phi_0^{(+)} + \phi_0^{(-)}) + |1\rangle (\phi_0^{(+)} - \phi_0^{(-)})] + O(D) \psi_1^{(\pm)} + O(D^2). \end{aligned} \quad (82)$$

We note that

$$\begin{aligned} \phi_0^{(+)} + \phi_0^{(-)} &= 2 \Phi_0(Q_s + D) + O(T^2) \\ &= 2 \Phi_0(Q_s) + O(D) \Phi_1(Q_s) + O(D^2) + O(T^2), \end{aligned} \quad (83)$$

$$\phi_0^{(+)} - \phi_0^{(-)} = O(TD), \quad (84)$$

and

$$\phi_1^{(\pm)} = \Phi_1(Q_s) + O(D) + O(T). \quad (85)$$

Thus we finally end up with the evolution

$$\begin{aligned} \Psi(t) &= e^{-i(E_0^+ - E_0^-)t/2} [|1\rangle \cos \frac{1}{2} (E_0^+ - E_0^-)t \\ &\quad - i |2\rangle \sin \frac{1}{2} (E_0^+ - E_0^-)t] \Phi_0(Q_s) + O(D) \Phi_1(Q_s) \\ &\quad + O(D^2) + O(TD) + O(T^2), \end{aligned} \quad (86)$$

which would yield [see definition (12)]

$$z(t) = \cos(E_0^+ - E_0^-)t + O(D^2) + O(T^2)$$

$$\text{(for } 1 \gg D \gg T), \quad (87)$$

where in dominating order [see Eq. (72)]

$$E_0^{(-)} - E_0^{(+)} = 2 \Omega_0 T e^{-D^2}. \quad (88)$$

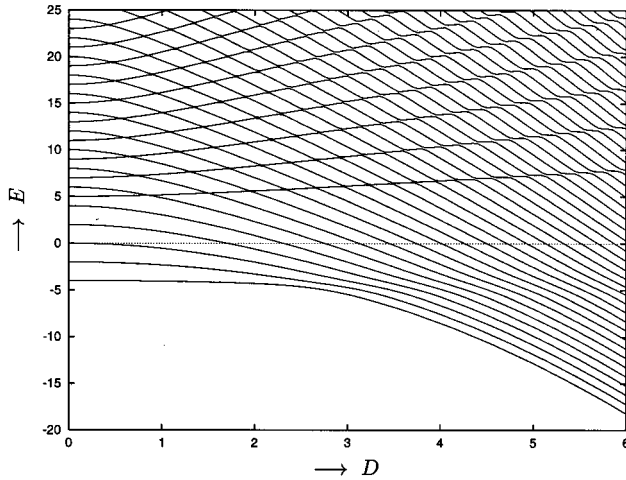


FIG. 9. Dependence of the energy eigenvalues on the coupling D for $\Omega_0=1$, $p=1$, $T=4$.

Since in both Figs. 2 and 3 the hierarchical supposition $1 \gg D \gg T$ is satisfied, we must conclude that the semiclassical time evolution in Fig. 2 contradicts quantal rigorosity. Thus, the persistent symmetry breaking of the excitonic occupation for $D=0.3$, $T \leq 0.02263$ must be considered as an artifact ensuing from the factorization (20). This result has also been obtained previously with different initial conditions by Vitali *et al.*¹⁸ and by Salkola *et al.*¹⁹ Also the semiclassical time evolution (Fig. 3) cannot be correct, since [viz. Eq. (87)] $z(t)$ should be dominantly a pure cosine function. This is confirmed by accurate numerical quantum-mechanical calculations, the results of which are shown in Figs. 2 and 3 with dashed lines.

3. The general case: Numerical calculations

If the hierarchical condition $1 \gg D \gg T$ is not fulfilled, we have to resort to numerical calculations of the exact eigenstates (70) of the dimer-oscillator subsystem. In Figs. 9 and 10 the eigenvalues of $\hat{H}_{FG}^{(p)}$ are shown as functions of the

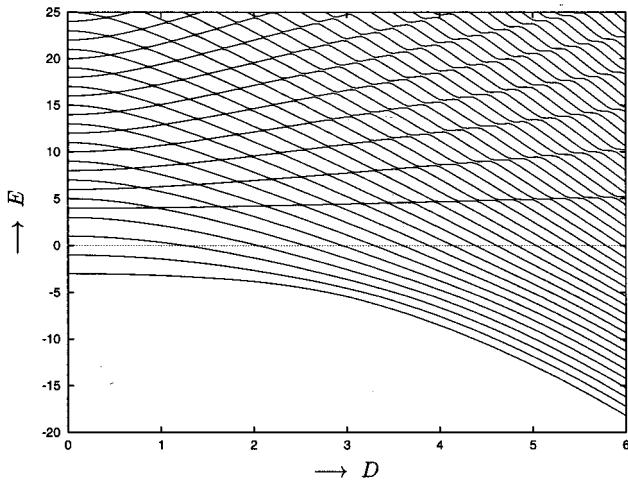


FIG. 10. Dependence of the energy eigenvalues on the coupling D for $\Omega_0=1$, $p=-1$, $T=4$.

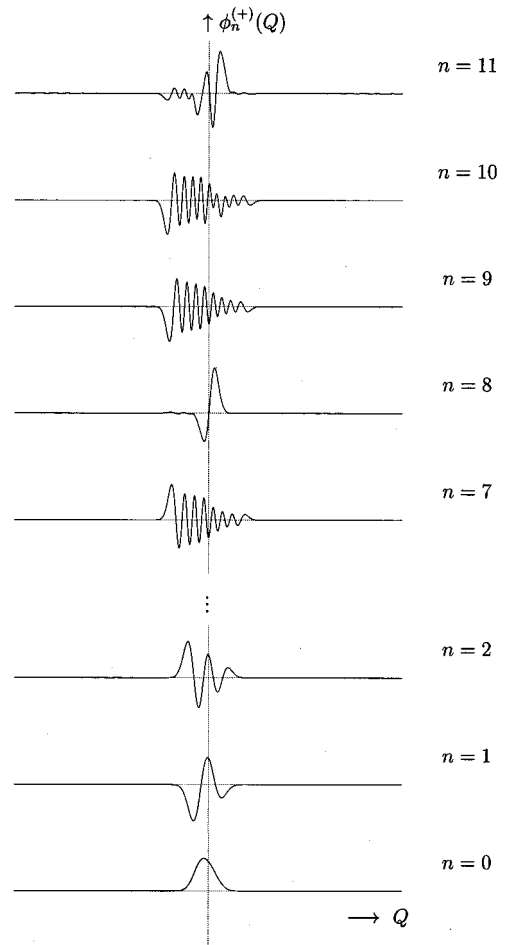


FIG. 11. Eigenfunctions of the FG Eq. (71) for $\Omega_0=1$, $p=+1$, $D=3/\sqrt{2}$, $T=3.9$.

excitonic transfer parameter T for $\Omega_0=1$, $D=4$, and $p=+1$ or $p=-1$, respectively. In these pictures we can distinguish two types of states: the so-called antisqueezed or conventional states, whose energy decreases with increasing coupling D , and the squeezed or exotic states, whose energy increases with increasing D (see Ref. 10). Wherever the energies of two states come close together, we observe an *avoided crossing*, making a clear distinction of the two types of states impossible. For large values of D the noncrossing is directly visible in Figs. 9 and 10. But even for lower values of D , where the noncrossing of the lines is visually not discernible, a closer examination with higher resolution reveals that the crossings are actually avoided.

In Figs. 11 and 12, which show the eigenfunctions of the FG equation (71) for $\Omega_0=1$, $D=3/\sqrt{2}$, $T=3.9$, and $p=+1$ or $p=-1$, the different shapes of conventional and exotic states are obvious. Note also that the FG wave functions of both the even-parity ground state ($\phi_0^{(+)}$, see Fig. 11) and the lowest odd-parity exotic state ($\phi_6^{(-)}$, see Fig. 12) strongly resemble the initial oscillatory wave function $\Phi_0(Q_s)$. Therefore, in our initial state (76) $\Phi_0(Q_s)$ projects onto $\phi_0^{(+)}$ and $\phi_6^{(-)}$, respectively, with approximate weight 1/2. From this we can conclude that the initial state is essentially a superposition of $\psi_0^{(+)}$ and $\psi_6^{(-)}$, respectively, multiplied by

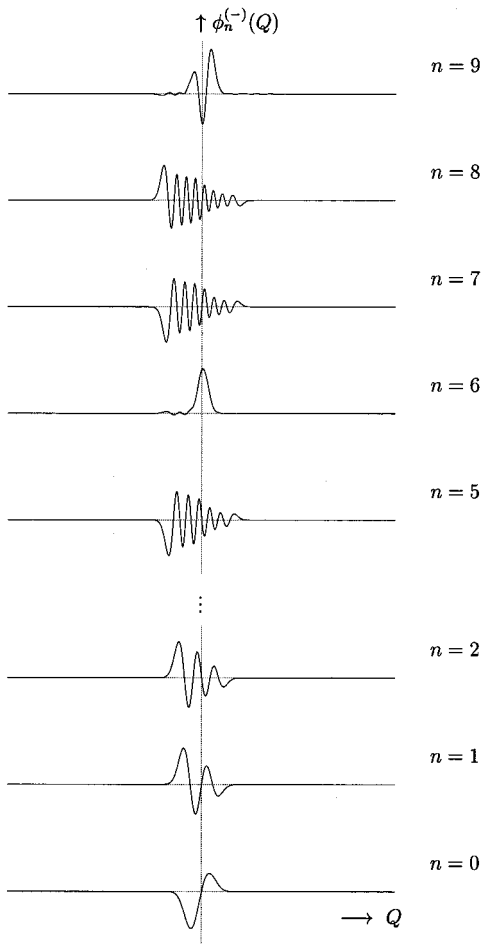


FIG. 12. Eigenfunctions of the FG Eq. (71) for $\Omega_0=1$, $p=-1$, $D=3/\sqrt{2}$, $T=3.9$.

the ground-state bath function $\Phi_0^{(\text{bath})}$. This can also be seen from Fig. 13, which shows the occupation probabilities $|\langle \phi_n^{(\pm)} | \Phi_0 \rangle|^2$ as a function of n .

A calculation of $z(t)$ similar to that given above for the case $1 \gg D \gg T$ yields

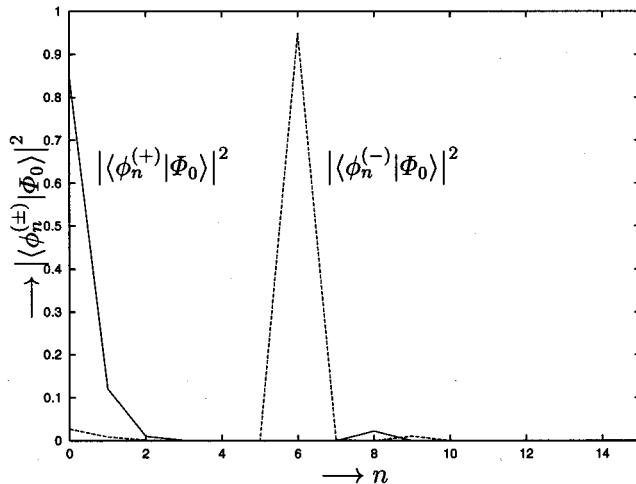


FIG. 13. Occupation probabilities $|\langle \phi_n^{(\pm)} | \Phi_0 \rangle|^2$ as a function of n for $\Omega_0=1$, $D=3/\sqrt{2}$, $T=3.9$.

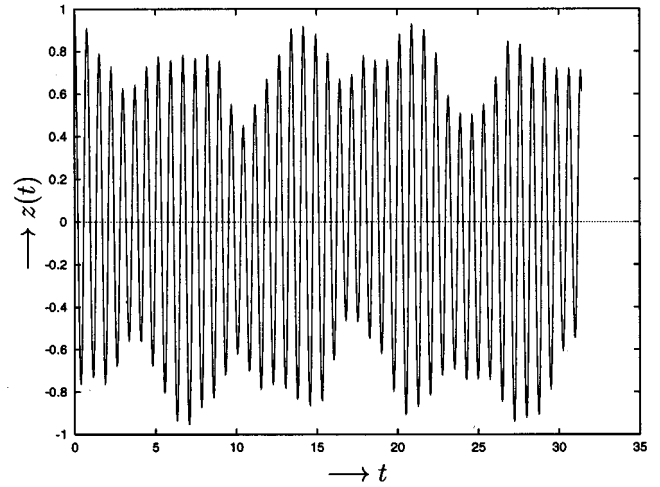


FIG. 14. Occupation probability difference $z(t)$ as a function of time for $\Omega_0=1$, $D=3/\sqrt{2}$, $T=3.9$.

$$z(t) = \sum_{m=0}^{\infty} \sum_{n=0}^{\infty} c_m^{(+)} c_n^{(-)} \langle \phi_n^{(-)} | \phi_m^{(+)} \rangle \cos[(E_n^{(-)} - E_m^{(+)})t], \quad (89)$$

where

$$c_n^{(\pm)} = \langle \phi_n^{(\pm)} | \Phi_0 \rangle = \langle \Phi_0 | \phi_n^{(\pm)} \rangle. \quad (90)$$

Since for $D=3/\sqrt{2}$ and $T=3.9$ the dominant term in sum (89) is given for $m=0$ and $n=6$, we expect $z(t)$ to show temporal oscillations with a frequency given by the energy difference $E_6^{(-)} - E_0^{(+)}$. This is confirmed in Fig. 14, which shows $z(t)$ calculated using Eq. (89). The amplitude fluctuations that can be seen in Fig. 14 are due to beats caused by the other terms in Eq. (89).

B. Quantum-mechanical description of the decay process

If we now include the coupling (30) to the bath, we have to consider state vectors in the product space of the dimer-oscillator subsystem and the bath. Consequently, we have to modify our initial state (76) to

$$\Psi(0) = |1\rangle \Phi_0(Q_s) \Phi_0^{(\text{bath})}(Q_k), \quad (91)$$

where $\Phi_0^{(\text{bath})}(Q_k)$ is the ground state of the bath Hamiltonian (31). Since the total Hamiltonian (32) commutes with the inversion operator, the parity of the total state is a conserved quantity. Our initial state is a superposition of an even and an odd state, $\Psi^{(+)}(0)$ and $\Psi^{(-)}(0)$, with equal weights of both parities [see Eqs. (78) and (79)]. Since in the time evolution $\Psi^{(+)}(0)$ and $\Psi^{(-)}(0)$ remain states of even and odd parities, respectively, i.e., since the two parities remain independent of each other, the equal weighting is conserved at all times. This does not mean, however, that the parity of the pure dimer-oscillator subsystem, respectively, is conserved too. Rather, since the parity of the phonon bath changes whenever a phonon is created, the parity of the dimer-oscillator subsystem itself must also change to preserve total parity. This has consequences for the decay process within the dimer-oscillator subsystem.

**1. Weak oscillator-bath coupling:
Fano (Fermi golden rule) decay**

If the coupling between the singular oscillator and the bath is sufficiently weak, the influence of the bath can be

$$\begin{aligned}\hat{Q}_s &= \sum_{p=\pm 1} \sum_{p'=\pm 1} |\psi_0^{(p)}\rangle\langle\psi_0^{(p)}|\hat{Q}_s|\psi_0^{(p')}\rangle\langle\psi_0^{(p')}| = |\psi_0^{(+)}\rangle\langle\psi_0^{(+)}|\hat{Q}_s|\psi_0^{(-)}\rangle\langle\psi_0^{(-)}| + \text{H.c.} \\ &= |\psi_0^{(+)}\rangle\langle\Phi_0(Q_s+D)|\hat{Q}_s|\Phi_0(Q_s+D)\rangle\langle\psi_0^{(-)}| + \text{H.c.} + O(T^2) \\ &= -D(|\psi_0^{(+)}\rangle\langle\psi_0^{(-)}| + |\psi_0^{(-)}\rangle\langle\psi_0^{(+)}|) + O(T^2)\end{aligned}\quad (92)$$

and

$$\hat{H}_{\text{tot}} = E_0^{(+)}|\psi_0^{(+)}\rangle\langle\psi_0^{(+)}| + E_0^{(-)}|\psi_0^{(-)}\rangle\langle\psi_0^{(-)}| \quad (93)$$

$$- \frac{1}{2} D(|\psi_0^{(+)}\rangle\langle\psi_0^{(-)}| + |\psi_0^{(-)}\rangle\langle\psi_0^{(+)}|) \sum_k V_k \hat{Q}_k + \hat{H}_{\text{bath}}.$$

If we now introduce the new Bloch operators in the two-state system

$$\hat{x}' = (|\psi_0^{(+)}\rangle\langle\psi_0^{(+)}| - |\psi_0^{(-)}\rangle\langle\psi_0^{(-)}|), \quad (94)$$

$$\hat{y}' = i(|\psi_0^{(-)}\rangle\langle\psi_0^{(+)}| - |\psi_0^{(+)}\rangle\langle\psi_0^{(-)}|), \quad (95)$$

$$\hat{z}' = -(|\psi_0^{(+)}\rangle\langle\psi_0^{(-)}| + |\psi_0^{(-)}\rangle\langle\psi_0^{(+)}|), \quad (96)$$

Eq. (93) can be written in the form

$$\hat{H}_{\text{tot}} = \bar{E}_0 - \frac{1}{2} \Delta E_0 \hat{x}' + \frac{1}{2} \hat{z}' \sum_k \tilde{D}_k \hat{Q}_k + \hat{H}_{\text{bath}}, \quad (97)$$

where $\bar{E}_0 = \frac{1}{2}(E_0^{(+)} + E_0^{(-)})$, $\Delta E_0 = E_0^{(-)} - E_0^{(+)}$ $= 2\Omega_0 T e^{-D^2}$, $\tilde{D}_k = D V_k$. This is nothing than the spin-boson Hamiltonian with direct coupling to the bath.

Therefore the results obtained by Leggett *et al.*⁵ for the weak-damping limit are applicable. The occupation probability difference shows damped oscillations with a damping time T given by

$$\begin{aligned}T^{-1} &= \frac{\pi}{4} D^2 \sum_k \frac{V_k^2}{\Omega_k} \delta(\Delta E_0 - \Omega_k) \\ &= \frac{\pi}{4} D^2 V(\Delta E_0)^2 \frac{\rho(\Delta E_0)}{\Delta E_0},\end{aligned}\quad (98)$$

and the condition for the validity of the approximation is $T^{-1} \ll \Delta E_0$.

The physical explanation of this damping is that the coupling of the dimer-oscillator subsystem to the bath leads to transitions from the (odd) excited state $|\psi_0^{(-)}\rangle$ to the (even) ground state $|\psi_0^{(+)}\rangle$ under emission of a phonon according to Fermi's golden rule. Since the oscillations of $z(t)$ are a result

treated as a perturbation of the dimer-oscillator subsystem.

a. Hierarchy $1 \gg D \gg T$: In the case $1 \gg D \gg T$ only the lowest two states of the subsystem are populated [see Eq. (80)], so it may be treated as a two-level system with states $|\psi_0^{(+)}\rangle$ and $|\psi_0^{(-)}\rangle$. In this two-state approximation we have

of the superposition of an even and an odd state, the decay of $|\psi_0^{(-)}\rangle$ to $|\psi_0^{(+)}\rangle$ will lead to a decay of the oscillations.

b. Case $D = 3\sqrt{2}$, $T = 3.9$: In this case, our initial state is essentially a superposition of $\psi_0^{(-)}$ and $\psi_6^{(-)}$. This superposition will lead to oscillations of $z(t)$ with a frequency given by the energy difference $E_6^{(-)} - E_0^{(+)}$. In the weak-damping limit we can again assume a golden-rule-type decay of the initial state. Since $\psi_0^{(+)}$ is the lowest state, it cannot decay to other states. $\psi_6^{(-)}$, on the other side, will decay exponentially by emitting phonons into the bath. With each emitted phonon the subsystem will change its parity; so it ‘‘cascades down’’ between the two parities, until it finally reaches the ground state $\psi_0^{(+)}$. Since for each step of this cascading process there are several target states into which the subsystem can decay by emitting a phonon, there are many possible routes for this decaying process. Two possibilities are shown in Fig. 15 with solid and dashed arrows.

Now it is important to note that after the first step of the cascading process the probability difference $z(t)$ remains zero. This can be seen by the following reasoning:

The state of the total system at time t can be written as

$$\begin{aligned}\psi(t) &= \frac{1}{\sqrt{2}} |\psi_0^{(+)}\rangle |\Phi_0^{(\text{phon})}\rangle e^{-iE_0^{(+)}t} + \frac{1}{\sqrt{2}} \left[c_6^{(-)}(t) \right. \\ &\quad \left. \times |\psi_6^{(-)}\rangle |\Phi_0^{(\text{phon})}\rangle + \sum_i c_i^{(-)}(t) |\psi_i^{(-)}\rangle |\phi_i^{(\text{phon})}\rangle \right]\end{aligned}$$

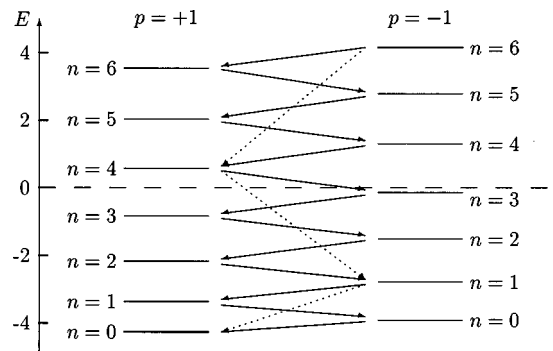


FIG. 15. Energy levels of the dimer-oscillator subsystem for the two parities, and two possible ‘‘cascading processes’’ for $\Omega_0 = 1$, $D = 3\sqrt{2}$, $T = 3.9$.

$$+ \sum_i c_i^{(+)}(t) |\psi_i^{(+)}\rangle |\phi_{i-}^{(\text{phon})}\rangle \Big], \quad (99)$$

where $|\Phi_0^{(\text{phon})}\rangle$ is the ground state of the bath, $|\phi_{i+}^{(\text{phon})}\rangle$ are even bath states with at least two phonons, and $|\phi_{i-}^{(\text{phon})}\rangle$ are odd bath states. If we now form the expectation value $z(t) = \langle \psi(t) | \hat{z} | \psi(t) \rangle$, terms connecting subsystem states of the same parity vanish, since \hat{z} is an odd operator in the subsystem space. Also, all terms of the form

$$\frac{1}{2} c_i^{(-)}(t) c_{i'}^{(+)}(t) \langle \psi_i^{(-)} | \langle \phi_{i+}^{(\text{phon})} | \hat{z} | \phi_{i-}^{(\text{phon})} | \psi_{i'}^{(+)} \rangle \rangle \quad (100)$$

and all terms of the form

$$\frac{1}{2} e^{iE_0^{(+)}t} c_i^{(-)}(t) \langle \psi_0^{(+)} | \langle 0^{(\text{phon})} | \hat{z} | \phi_{i+}^{(\text{phon})} | \psi_i^{(-)} \rangle \rangle, \quad i \neq 6 \quad (101)$$

vanish, because the bath states $|\phi_{i+}^{(\text{phon})}\rangle$ and $|\phi_{i'-}^{(\text{phon})}\rangle$ (opposite parity), or $|0^{(\text{phon})}\rangle$ and $|\phi_{i+}^{(\text{phon})}\rangle$ ($|\phi_{i+}^{(\text{phon})}\rangle$ has at least two phonons), are orthogonal to each other. So the only remaining term is

$$z(t) = \frac{1}{2} e^{iE_0^{(+)}t} c_6^{(-)}(t) \langle \psi_0^{(+)} | \hat{z} | \psi_6^{(-)} \rangle + \text{c.c.} \quad (102)$$

The amplitude of the oscillations of $z(t)$ is therefore determined only by the absolute value of $c_6(t)$, which decreases monotonously because of the decay of state $\psi_6^{(-)}$.

The reciprocal time constant T^{-1} of this decay is the sum of the reciprocal time constants for all possible decay channels, i.e.,

$$\begin{aligned} T^{-1} &= \frac{\pi}{2} \sum_{i=0}^6 \sum_k |\langle \psi_i^{(+)} | \Phi_k^{(\text{phon})} \rangle| \\ &\quad \times V_k Q_s Q_k |\psi_6^{(-)} | \Phi_0^{(\text{phon})} \rangle|^2 \delta(E_6^{(-)} - E_i^{(+)} - \Omega_k) \\ &= \frac{\pi}{4} \sum_{i=0}^6 |\langle \psi_i^{(+)} | Q_s | \psi_6^{(-)} \rangle|^2 V(E_6^{(-)} - E_i^{(+)})^2 \\ &\quad \times \frac{\rho(E_6^{(-)} - E_i^{(+)})}{E_6^{(-)} - E_i^{(+)}} \end{aligned} \quad (103)$$

and the condition for the validity of the weak-damping approximation is here $T^{-1} \ll \Omega_0$, since Ω_0 is the order of magnitude of the typical energy differences between the discrete states $|\psi_i^{\pm}\rangle$.

2. Strong oscillator-bath coupling

If the oscillator-bath coupling is strong compared to the excitonic transfer, the temporal evolution of the system can be separated into a short-time and a long-time regime.

For short times the excitonic transfer may be neglected so that the exciton is fixed in its initial site and therefore simply leads to a shift of the equilibrium positions of all oscillators, i.e., both the singular one and those of the bath. But, in fact, the displacement of the bath oscillators is of the order $1/N$ (N = number of the bath oscillators), whence we may neglect

it. Then the intrinsic oscillator initially is in a coherent state, which decays in a Fano manner.

After relaxation of the oscillatory subsystem, the system has reached a state corresponding to the initial state of Leggett *et al.*⁵ at zero temperature. Accordingly, for the long-time evolution caused by the excitonic transfer the results of Ref. 5 apply. Especially, in the super-Ohmic case the probability difference $z(t)$ shows damped oscillations. The frequency of these oscillations is reduced in comparison to its ‘‘bare’’ value $2\Omega_0 T$ by the Franck-Condon factor. For the Ohmic case Leggett *et al.* predict a transition to strict localization for sufficiently strong coupling. This is no contradiction to the result of Wagner and Vázquez-Márquez¹³ that even in the Ohmic case the ground state is never strictly degenerate. Yet it turns out that the splitting is exceedingly small, so that the transfer time becomes extremely long; and the results of Leggett *et al.* are restricted to times that are ‘‘not too long.’’⁵

VI. CONCLUSIONS

In this paper we have studied the dynamics of a dimer-oscillator model. We have contrasted a semiclassical and a full quantum-mechanical analysis. The term ‘‘semiclassical’’ signifies a classical handling of the oscillatory system. For the semiclassical initial condition we choose the state in which the exciton is located completely at one site and the oscillator is resting in its unperturbed equilibrium position. The corresponding quantum-mechanical initial condition is a product of a one-site exciton state and the unperturbed ground state of the oscillator. The semiclassical calculations without damping show a pronounced transition between a symmetric and a symmetry-broken dynamics, depending on the value of the parameter D^2/T . If the exciton-oscillator coupling $D\Omega_0$ and the transfer $T\Omega_0$ are small compared to the oscillator frequency Ω_0 , the so-called DST approximation applies³ and three cases can be distinguished: For $D^2/T < 1$ the ground state is a symmetric state with equally occupied dimer sites, and for the given initial conditions the excitonic occupation oscillates between the two sites. For $1 < D^2/T < 2$ the system would descend to a symmetry-broken state (‘‘left’’ or ‘‘right’’) if the kinetic energy were taken away. For the given initial state the excitonic occupation remains oscillating between the two sites. For $D^2/T > 2$ the exciton remains with a probability greater than 1/2 at the site where it is created.

If a classical damping term is added to the oscillator in a phenomenological way, the system will finally settle down in a stable stationary state. For $D^2/T < 1$ we have symmetric behavior at all times; for $D^2/T > 2$ the exciton is site-trapped from the beginning; and for $1 < D^2/T < 2$ the exciton shows symmetric behavior in the beginning, but later gets trapped at one of the two sites. If D and T are greater than 1, the DST approximation is no longer valid, but the system still shows a transition from a symmetric to a symmetry-broken final state at $D^2/T = 1$.

The quantum-mechanical calculations, on the other hand, show a completely different picture. In the absence of damping the occupational probability difference $z(t)$ shows sinusoidal oscillations. This can be derived analytically in the case $D, T \ll 1$; for $D, T > 1$ it is suggested by numerical calculation of the exact energy eigenstates of the system making

recourse to the Fulton-Gouterman transformation. If the oscillator is coupled to a Fano bath of other oscillators, the transitions induced by the bath between the states of the dimer-oscillator subsystem lead to a decay of the oscillations of $z(t)$ until the subsystem settles down in a state with equal probabilities at both sites.

The differences between semiclassical and quantum-mechanical behavior show that care must be taken when applying the semiclassical approximation. As has already been pointed out by Vitali *et al.*¹⁸ and by Salkola *et al.*,¹⁹ the quantum-mechanical fluctuations of the oscillator, which are neglected in the semiclassical approximation, lead to the possibility of polaron tunneling, tending to destroy the symmetry breaking. Only if the separation of the semiclassical equi-

librium positions Q_s of the oscillator [see Eq. (29)] is large compared to the quantum fluctuations of Q (i.e., $D \gg 1$), the polaron tunneling time increases exponentially.¹⁹ Especially in the validity range of the DST approximation ($D, T \ll 1$), the semiclassical approximation is unjustified; and from our numerical results we can conclude that this is the case even for $D = 3/\sqrt{2}$, $T = 3.9$.

Regarding our background problem of the spatial self-localization of an initially delocalized electronic excitation in crystalline systems, the findings presented in this paper show that the semiclassical approximation can give misleading results when applied to this problem, and that the results should be verified by means of a full quantum-mechanical calculation.

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