

Density-matrix theory of charge transfer

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A dynamic theory is presented for the description of dissipative charge transfer in molecular systems. The quantum dynamics of the coupled electron-vibration motion are described in the framework of the density-matrix theory. The equations of motion of the density matrix are given in a representation that uses the Born-Oppenheimer states of the different localization centers of the electron together with the vibrational modes coupling to the electron. A dissipative environment is introduced by separating all molecular vibrations which do not couple to the transferred electron and providing thermal equilibrium for them. The description allows (a) the introduction of any type of potential surfaces, (b) the description of any microscopic model for the coupling between the vibrational modes and the dissipative environment, and (c) the consideration of any strength of electronic intercenter coupling. Therefore the approach allows one to study the transition from the wavelike to the hoppinglike electron motion between the centers as well as nonadiabatic transfer, adiabatic transfer, and any intermediate type. Besides the derivation of the basic density-matrix theory, the numerical solution of the density-matrix equations is presented for the model of a two-center single-vibrational-mode system. The exact results of the density-matrix equations are compared with those of approximate rate equations.

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I. INTRODUCTION

The theoretical concepts of charge-transfer reactions in molecular systems have been utilized in different disciplines extending from molecular physics and chemistry up to molecular biology. The present state of the art is well documented in numerous review articles, e.g., [1–3]. It can be characterized briefly as a description which considers the charge-transfer events as sequences of hopping processes between appropriately chosen electronic states. In the case of adiabatic transfer these states are electronic states extending over the molecular sites taking part in the reaction. The electronic states of isolated molecular sites are used in the case of nonadiabatic reactions. As is usual for hopping processes the transfer appears as an incoherent quantum-particle motion, i.e., any phase coherence of the electronic wave function has been destroyed. The characteristic time of such a dephasing process is determined by the relaxation of the nuclear degrees of freedom of the molecule and any type of surroundings (e.g., the solvent) and lies in the picosecond and subpicosecond regime.

With the utilization of femtosecond spectroscopic techniques the interest has been directed towards transfer reactions that are not of the incoherent type. These coherent (wavelike) or partly coherent reactions are characterized by transfer times comparable to the corresponding intramolecular relaxation time.

In the past few years different authors have put em-

phasis on such types of reactions (for a review, see [4]). Calculations have been published, e.g., for the charge-transfer dynamics in a benzene-radical complex [5], the nuclear dynamics on vibronically coupled potential-energy surfaces of ethylene, cation pyrazine, and NO_2 [6], and the exciton motion in molecular dimers and chains (e.g., [7,8]).

Most of the approaches are based on the solution of the time-dependent Schrödinger equation, thus being in the limit of coherent transfer (describing the quantum dynamics of a closed system). The Schrödinger equation has been treated by introducing an appropriate ansatz for the time-dependent wave function or by using numerical methods for a strict solution. Sometimes it can be argued that the dynamic regime of interest appears short compared to characteristic dephasing times. Otherwise the description remains incomplete.

From the theory of femtosecond optical spectra of molecules it is known how to handle the dissipative dynamics of coupled electron-vibration systems. Usually, one takes the Born-Oppenheimer states of the electron-vibration system to realize an appropriate representation of the density-matrix equations (see, e.g., the recently published paper [9]). Vibrational modes that are not involved in the electronic transition as well as those of the surroundings or a nonpolar solvent form a dissipative environment. Its basic effect is to produce finite lifetimes of the vibrational modes coupling to the electronic transition. An alternative approach is to consider a sufficiently large number of

vibrational modes—three or four—coupling to the electron. Then, intramolecular relaxation appears as a redistribution of excitation energy among the different modes [6].

The aim of the present paper is to translate the above-mentioned idea to the description of charge-transfer dynamics in molecular complexes with emphasis on partly incoherent transfer which has been extensively discussed for molecular crystals, e.g., in [10,11]. Our approach starts with a general model of molecular complexes dividing them into localization centers of the transferred electron—an externally given electron in the present case (an excess electron)—together with the nuclear modes coupling to that electron. The remaining nuclear degrees of freedom form a thermal environment in which the coupled electron-vibration states are embedded. To describe the quantum dynamics of the charge transfer, density-matrix theory has been applied in a representation of these coupled electron-vibration states (Born-Oppenheimer states). Although such a representation is not necessary, it allows one to simply derive the standard hopping rates of nonadiabatic transfer.

Corresponding equations of motion for the density matrix have been derived in applying the technique of nonequilibrium Green's functions. The environmental degrees of freedom appear via relaxation terms which are defined by corresponding thermally averaged correlation functions.

The density-matrix approach given in a representation of the coupled electron-vibration states has some advantages to standard Liouville-space methods (see, e.g., [12–15]). The whole set of density-matrix equations, which contains off-diagonal contributions with respect to the center index as well as the vibrational quantum number, allows one to account for the electronic intercenter coupling in any order of perturbation theory. Liouville-space methods end up with non-Markovian rate equations (generalized master equations) with a power expansion for the memory kernel with respect to the electronic intercenter coupling. Besides its practicability for numerical calculations, this property of the density-matrix equations given below makes them most appropriate to study the change from coherent to incoherent transfer.

To carry out the numerical solution of the density-matrix equations, first we have to reduce the infinite system of equations of motion to a finite system in defining a maximum vibrational quantum number taken into account. Since the size of the density matrix depends on the electronic quantum number and the quantum number of the vibrational state quadratically, the dimension of the dynamic system related to the equations of motion expands rapidly with the number of vibrational modes. Therefore the numerical practicability of the approach is restricted to a low number of vibrational modes.

To demonstrate how the given method works, as well as to discuss in detail the influence of the increasing coupling to the environmental degrees of freedom on the transfer dynamics, we restrict ourselves to a simple model system. Therefore we consider the case of a system of two localization centers for the transferred electron and of a single vibrational mode with linear coupling to the

environmental degrees of freedom (see also [2,16]).

Extending the approach of the previous papers [17,18] we take into account Pauli statistics corresponding to operators creating and destroying the Born-Oppenheimer reference states. Additionally, we improve the Markov approximation that must be made in the derivation of the density-matrix equations in order to drop memory effects originating from the coupling to the environmental degrees of freedom. This second improvement slightly changes the corresponding equations of motion for the density matrix and results in a somewhat different dynamic behavior. Quadratic contributions with respect to the density matrix are also discussed. These terms stem from the final-state occupation occurring in the scattering processes with the environmental quanta.

The presented method of a density-matrix description for charge-transfer dynamics in molecular systems comprises a considerable number of theoretical problems and allows description of different physical systems. Therefore the present paper has to be considered, on the one hand side, as a comprehensive presentation of the general theory, and, on the other hand, as a demonstration of the numerical practicability of the approach. (Different aspects of the theoretical approach and the corresponding results have already been published in [17,18].)

In the following section we briefly review the derivation of the Hamiltonian of the molecular system in a representation using Pauli operators for the coupled electron-vibration states. Such a representation is appropriate to apply the method of nonequilibrium Green's functions to derive the equations of motion for the density matrix. The details of the corresponding derivation are presented in Sec. III. In Sec. IV we specialize the general results to the model of a dimer with a single vibrational mode and a linear coupling of that mode to the environmental degrees of freedom. Section V is devoted to a detailed discussion of the results of the numerical calculations which have been performed for the model introduced in Sec. IV. After some concluding remarks, in the Appendix we present the derivation of an equation of motion for the single vibrational mode of the dimer model of Sec. IV as a further illustration of the method.

II. HAMILTONIAN OF THE MOLECULAR COMPLEX

To define a sufficiently general model for our further purposes we present a brief derivation of a Hamiltonian for the electron-vibration system of an electron-transferring molecular complex (donor-acceptor complex with intermediate spacer molecules). Therefore let us make the following assumptions.

(a) We consider the motion of a single external (excess) electron with coordinates comprised by x . It may be injected into the molecular complex from the surroundings. Eventually, we change to the picture of an electron which has been optically excited into the empty donor state from a lower occupied molecular orbit.

(b) The molecular complex considered contains localization centers for the transferred electron which are the

lowest-unoccupied-molecular-orbital (LUMO) states of the excess electron in the isolated donor, acceptor, or spacer molecule.

(c) These localization centers $m=1,2,3,\dots$ are described by respective pseudopotentials $V_e^{(m)}$ for the single excess electron which can be attributed to the total electronic system of the neutral molecular complex.

(d) The whole set of nuclear coordinates will be divided into two subsets. The first subset contains those coordinates which couple to the excess electron via the pseudopotentials. They will be denoted X and are usually named interaction coordinates. The set of interaction coordinates plus the transferred electron form the relevant system of the molecular complex. The second subset of nuclear coordinates does not appear in the pseudopotentials. These coordinates are denoted Y and define the (dissipative) environment for the relevant system.

Therefore our Hamiltonian reads

$$H = T_e(x) + T_v(X, Y) + \sum_m V_e^{(m)}(x, X) + V_v. \quad (2.1)$$

The T s are the operators of the kinetic energy of the electronic and nuclear (vibrational) system. The nuclear contribution V_v to the total potential energy splits into three parts corresponding to the system of interaction coordinates, the system of the coordinates of the environment, and to the contribution which couples both systems, respectively,

$$V_v(X, Y) = V_v^{(I)}(X) + V_v^{(E)}(Y) + V_v^{(I-E)}(X, Y). \quad (2.2)$$

For the density-matrix description of the transfer dynamics we change to a representation of the total Hamiltonian in the eigenstates of the single localization centers of the relevant system (single-center Born-Oppenheimer states). The nuclear modes of the environment will be handled separately. Such a treatment is necessary to avoid any perturbation theory with respect to the strong electron-vibration coupling within the relevant system. Furthermore, providing weak or intermediate coupling to the environment this interaction can be taken into account in the lowest (second) order. Within the adiabatic approximation the eigenvalue problem of the single localization centers splits into that of the electronic part

$$[T_e(x) + V_e^{(m)}(x, X)]\varphi_m(x; X) = \varepsilon_m(X)\varphi_m(x; X) \quad (2.3)$$

and the nuclear part

$$[T_v(X) + \varepsilon_m(X) + V_v^{(I)}(X)]\chi_{m,M}(X) = E_{m,M}\chi_{m,M}(X). \quad (2.4)$$

With respect to the electronic spectrum we have restricted ourselves to the lowest excess electron state which corresponds to the LUMO state of the neutral molecule. Therefore a further electronic quantum number does not appear. The $\varepsilon_m + V_v^{(I)}$ are the corresponding vibrational surfaces. The whole set of vibrational quantum numbers has been denoted M for short. The energies $E_{m,M}$ define the spectrum of the coupled electron-vibration states.

To give the representation of the Hamiltonian (2.1) with respect to these states we have to calculate the following matrix elements:

$$\begin{aligned} \langle m, M | H | n, N \rangle &= \int dx dX \varphi_m^*(x; X) \chi_{m,M}^*(X) H \varphi_n(x; X) \chi_{n,N}(X) \\ &= \delta_{mM, nN} E_{nN} + \int dx dX \varphi_m^* \chi_{m,M}^* \sum_{k \neq n} V_e^{(k)} \varphi_n \chi_{n,N} \\ &\quad + \delta_{m,n} \int dX \chi_{m,M}^*(X) V_v^{(I-E)}(X, Y) \chi_{m,N}(X) + \delta_{mM, nN} H_v^{(E)}. \end{aligned} \quad (2.5)$$

The first contribution on the right-hand side (rhs) follows from the solution of the eigenvalue problem of the relevant system, Eqs. (2.3) and (2.4). The second contribution can be simplified applying a Condon-type approximation which results in

$$\begin{aligned} \int dx dX \varphi_m^* \chi_{m,M}^* V_e^{(k \neq n)} \varphi_n \chi_{n,N} &\approx \int dx dX \varphi_m^*(x; X_0) \chi_{m,M}^*(X) V_e^{(k \neq n)}(x, X_0) \varphi_n(x; X_0) \chi_{n,N}(X) \\ &= \delta_{mM, nN} \Delta \varepsilon_m^{(k \neq n)} + (1 - \delta_{m,n}) V_{mn}^{(k \neq n)} F_{FC}(mM, nN) \end{aligned} \quad (2.6)$$

where X_0 indicates a set of equilibrium positions of the interaction coordinates and $\Delta \varepsilon_m^{(k)}$ denotes the shift of the electronic level of center m due to the action of the potential field of center k . Here, we have neglected electronic overlap integrals. $V_{mn}^{(k)}$ is the overlap integral of the potential of center k and of the electronic wave functions of centers m and n . The Franck-Condon factor F_{FC} reads

$$F_{FC}(mM, nN) = \int dX \chi_{m,M}^*(X) \chi_{n,N}(X). \quad (2.7)$$

The coupling of the interaction coordinate to the environment [the third contribution to the matrix element

(2.5)] will be denoted

$$K_{mM, nN}(Y) = \int dX \chi_{m,M}^*(X) V_v^{(I-E)}(X, Y) \chi_{m,N}(X). \quad (2.8)$$

Due to the neglected electronic overlap, off-diagonal contributions with respect to the center index do not appear.

The fourth contribution in the matrix element (2.5) contains the Hamiltonian of the vibrational degrees of freedom of the environment:

$$H_v^{(E)} = T_v(Y) + V_v^{(E)}(Y). \quad (2.9)$$

Introducing bra and ket vectors for the electron-vibration states of the relevant system the desired representation of

the Hamiltonian (2.1) reads

$$\begin{aligned} H &= \sum_{m,M;n,N} \langle m,M | H | n,N \rangle |m,M\rangle \langle n,N| \\ &= \sum_{\mu,\nu} H_{\mu,\nu} A_{\mu}^{\dagger} A_{\nu} . \end{aligned} \quad (2.10)$$

Note the introduction of the indices μ and ν which comprise mM and nN , respectively, and the replacement of the matrix element by $H_{\mu,\nu}$. The projector $|m,M\rangle \langle n,N|$ has been expressed by level operators A_{μ}^{\dagger} and A_{ν} with commutation relations of Pauli operators:

$$(A_{\mu}, A_{\nu}^{\dagger})_{+} = \delta_{\mu,\nu} + 2(1 - \delta_{m,n}) A_{\nu}^{\dagger} A_{\mu} . \quad (2.11)$$

The introduction of level operators is appropriate for applying the Green's-function technique for the derivation of equations of motion for the density-matrix elements. According to Eq. (2.5) it is useful to divide the matrix elements $H_{\mu,\nu}$ into the following parts:

$$H_{\mu,\nu} = H_{\mu,\nu}^{(0)} + \delta_{m,n} K_{M,N}(Y) + \delta_{\mu,\nu} H_{\nu}^{(E)} , \quad (2.12)$$

where the first contribution is that of the relevant system

$$\begin{aligned} H_{\mu,\nu}^{(0)} &= \delta_{mM,nN} E_{nN} + \delta_{mM,nN} \sum_{k(\neq n)} \Delta \epsilon_n^{(k)} \\ &+ (1 - \delta_{m,n}) \sum_{k(\neq n)} V_{mn}^{(k)} F_{\text{FC}}(mM, nN) . \end{aligned} \quad (2.13)$$

To simplify this formula we include the quantities $\Delta \epsilon_n^{(k)}$ into the definition of E_{nN} . Of course, the representation of the Hamiltonian is an approximate one since we only took into account the LUMO state of the single localization centers. Therefore excited vibrational states have to be restricted to energies below the next electronic level.

The given representation of the Hamiltonian (2.10) allows us to define the reduced (one-particle) density matrix (RDM) which is of basic interest for the discussion of the charge-transfer dynamics:

$$\rho_{\mu\nu}(t) = \text{tr}[\hat{W}(t) A_{\mu}^{\dagger} A_{\nu}] . \quad (2.14)$$

The employed statistical operator $\hat{W}(t)$ is defined by the relevant system plus the environment.

If the RDM is known all expectation values of interest can be calculated. To characterize the transfer dynamics it is useful to depict the diagonal elements of the RDM,

$$P_{\mu}(t) = \rho_{\mu\mu}(t) . \quad (2.15)$$

These quantities represent the occupation probability for the vibrational levels M at center m . If the number of interaction coordinates is larger than three or four it is more appropriate to consider the total electronic occupation probability of center m (the trace of the RDM with respect to the vibrational quantum numbers),

$$P_m(t) = \sum_M P_{\mu}(t) . \quad (2.16)$$

The expectation value of the single interaction coordinate X_a follows as

$$\langle X_a \rangle = \sum_{\mu,\nu} \langle \mu | X_a | \nu \rangle \rho_{\mu\nu}(t) \quad (2.17)$$

with

$$\langle \mu | X_a | \nu \rangle = \delta_{m,n} \int dX \chi_{m,M}^*(X) X_a \chi_{m,N}(X) . \quad (2.18)$$

The neglected electronic overlap results in $\delta_{m,n}$. The explicit values of this matrix element are well known for the case of harmonic oscillator functions and can be found in Sec. IV A.

III. NONEQUILIBRIUM GREEN'S-FUNCTION TECHNIQUE

A. Definition of the nonequilibrium Green's function

In the following we apply the nonequilibrium Green's-function (NGF) technique to derive equations of motion for the (one-particle) reduced density matrix defined in Eq. (2.14). This method of nonequilibrium quantum statistics and quantum dynamics is originally due to Keldysh [19] and has been extensively reviewed in recent years [20–23]. The derivation given below follows that of Ref. [24]. The presented approach has two important advantages with respect to other techniques.

(i) In contrast to common methods it avoids dealing with the complete statistical information contained in the statistical operator $\hat{W}(t)$. Instead, one only considers from the very beginning a reduced quantity in taking a generalization of the RDM. Especially, one directly obtains equations of motion for all elements of the RDM.

(ii) The formal similarity of the NGF technique with equilibrium Green's-function approaches makes it possible to translate directly the different perturbation techniques.

Of course, one has to pay for these advantages by some technical difficulties. As already mentioned we provide a sufficiently weak coupling of the relevant system to the environmental degrees of freedom. Such an assumption allows us to restrict the RDM equations to the second order with respect to this coupling. Therefore, following the treatment of [24], we have to introduce an additional interaction of the environmental degrees of freedom to a time-dependent external field $u(\mu, \nu; t)$

$$H_{\text{ext}}(t) = \sum_{\mu,\nu} K_{\mu,\nu}(Y(t)) u(\mu, \nu; t) . \quad (3.1)$$

This expression has only formal character and will be used to formulate the perturbation theory with respect to the system environment coupling (2.8). For that reason we provide that the time dependence of the statistical operator $\hat{W}(t)$ is given by the system Hamiltonian (2.10) supplemented by H_{ext} .

To derive the NGF we shift the time dependence of $\hat{W}(t)$ in the RDM (2.14) to the level operators, and then split the time-evolution operator into a part depending on the system Hamiltonian (2.10) alone and a remaining part. We obtain

$$\rho_{\mu\nu}(t) = \text{tr}[\hat{W}(-\infty) S^{\dagger} T S A_{\mu}^{\dagger}(t) A_{\nu}(t)] \quad (3.2)$$

with $\hat{W}(-\infty)$ as the statistical operator at minus infinity. T is the usual time-ordering operator and the operator S reads

$$S = S(\infty, -\infty) = T \exp \left[-\frac{i}{\hbar} \int_{-\infty}^{\infty} dt H_{\text{ext}}(t) \right]. \quad (3.3)$$

Expanding expression (3.3) for the RDM with respect to H_{ext} there appear time-ordered as well as anti-time-ordered contributions, originating from the nonequilibrium situation in which S and its Hermitian conjugate occur simultaneously under the trace.

To avoid this complication the NGF technique formally enlarges the time region [19–23]. Therefore we introduce Keldysh's time contour $C = C_+ + C_-$. It extends from $-\infty$ to $+\infty$ (C_+) and back from $+\infty$ to $-\infty$ (C_-). If time runs along this contour we use the argument τ instead of t . Furthermore, we assume that the external field u introduced in Eq. (3.1) differs depending on which part of the time contour (C_+ or C_-) is considered. S and S^\dagger in Eq. (3.2) are consolidated into a single S operator defined on C and we obtain the NGF as the two-time generalization of the RDM (see also [24]):

$$G(1, 1') = -\frac{i}{\hbar} \frac{\text{tr}[\hat{W}(-\infty) T_C S_C A(1) A^\dagger(1')]}{\text{tr}[\hat{W}(-\infty) S_C]} \\ = -\frac{i}{\hbar} \langle\langle A(1) A^\dagger(1') \rangle\rangle. \quad (3.4)$$

Here, 1 ($1'$) abbreviates μ_1, τ_1 (μ_1', τ_1'). T_C is the generalization of the usual time-ordering operator to C and the new S operator reads

$$S_C = T_C \exp \left[-\frac{i}{\hbar} \int_C d\tau H_{\text{ext}}(\tau) \right]. \quad (3.5)$$

The time integration has to be taken with respect to the whole contour C .

The artificial assumption that u and hence H_{ext} are different on C_+ and C_- guarantees $S_C \neq 1$. The limit in which this difference is removed combined with the restriction of the time argument to the branch from $-\infty$ to $+\infty$ has been named the physical limit [23]. Taking this limit, the NGF splits into four different functions depending on which part of the contour the time arguments are positioned. Taking τ_1 and $\tau_1' \in C_+$ the causal function follows, for τ_1 and $\tau_1' \in C_-$ we obtain the anticausal function. In the remaining cases the correlation functions

$$G(1, 1')|_{\tau_1 \in C_-; \tau_1' \in C_+} = G^>(\mu_1, t_1; \mu_1', t_1') \\ = -\frac{i}{\hbar} \text{tr}[\hat{W}(-\infty) \tilde{A}_{\mu_1}(t_1) \tilde{A}_{\mu_1'}^\dagger(t_1')], \quad (3.6a)$$

$$G(1, 1')|_{\tau_1 \in C_+; \tau_1' \in C_-} = G^<(\mu_1, t_1; \mu_1', t_1') \\ = -\frac{i}{\hbar} \eta_{m_1, m_1'} \\ \times \text{tr}[\hat{W}(-\infty) \tilde{A}_{\mu_1'}^\dagger(t_1') \tilde{A}_{\mu_1}(t_1)] \quad (3.6b)$$

follow. The tilde on the level operators indicates that the time dependence is given by the system Hamiltonian plus H_{ext} . To account for the Pauli-commutation relation of the level operators, Eq. (2.11), we have introduced the prefactor $\eta_{m,n}$. η equals -1 for $m=n$ and 1 for $m \neq n$.

In the limit $t_1 = t_1' = t$ the correlation function $G^<$ reproduces the RDM,

$$i\hbar G^<(\mu t, \nu t) = \eta_{m,n} \rho_{\nu,\mu}(t). \quad (3.7)$$

Only two of the four functions contained in the NGF are independent from one another. As in the equilibrium case the causal function, e.g., can be expressed by $G^>$ and $G^<$ as

$$G(1, 1')|_{\tau_1, \tau_1' \in C_+} = G^C(\mu_1, t_1; \mu_1', t_1') \\ = \Xi(t_1 - t_1') G^>(\mu_1, t_1; \mu_1', t_1') \\ + \Xi(t_1' - t_1) G^<(\mu_1, t_1; \mu_1', t_1') \quad (3.8)$$

where Ξ is the unit step function. It is the aim of the following calculations to derive an equation of motion for the RDM, i.e., the equal-time case of $G^<$ starting from a general equation for the NGF.

B. Equations of motion

If one derives equations of motion for the NGF there occurs a new type of Green's function. This new type can be expressed by a functional derivative of G with respect to the external field u [23,24] in the following way:

$$-\frac{i}{\hbar} \langle\langle K_{\mu,\nu}(Y(\tau)) A(1) A^\dagger(1') \rangle\rangle \\ = \left[\langle\langle K_{\mu,\nu}(Y(\tau)) \rangle\rangle + i\hbar \frac{\delta}{\delta u(\mu, \nu; \tau)} \right] G(1, 1'). \quad (3.9a)$$

We introduce the abbreviation

$$\Phi(\mu, \nu; \tau) = \langle\langle K_{\mu,\nu}(Y(\tau)) \rangle\rangle \quad (3.9b)$$

and obtain the following equation of motion for the NGF:

$$\sum_{\nu} \left[i\hbar \frac{\partial}{\partial \tau_1} \delta_{\mu_1, \nu} - H_{\mu_1, \nu}^{(0)} - \Phi(\mu_1, \nu; \tau_1) \right] G(\nu, \tau_1, 1') = \delta(1 - 1') + i\hbar \sum_{\nu} \frac{\delta G(\nu, \tau_1, 1')}{\delta u(\mu_1, \nu; \tau_1^+)}$$

$$[\tau_1^+ = \tau_1 + \varepsilon; \varepsilon \Rightarrow 0 + (0-) \text{ for } \tau_1 \in C_+ (C_-)] . \quad (3.10)$$

The formal δ function on the rhs comprises $\delta_{\mu_1, \mu_{1'}}$ and the δ function with time arguments from the contour C . Such a function equals the usual δ function if τ_1 and $\tau_{1'}$ are from the same branch of C . Otherwise it is zero.

It is convenient to shorten the term in parentheses on the left-hand side (lhs) of Eq. (3.10) by the inverse of the zero-order NGF [24]:

$$G_0^{-1}(1, 1') = \left[i\hbar \frac{\partial}{\partial \tau_1} \delta_{\mu_1, \mu_{1'}} - H_{\mu_1 \mu_{1'}}^{(0)} - \Phi(\mu_1, \mu_{1'}; \tau_1) \right] \times \delta(\tau_1 - \tau_{1'}). \quad (3.11)$$

Moreover, let us rewrite the second term from the rhs of Eq. (3.10) by introducing the nonequilibrium self-energy by

$$i\hbar \sum_{\nu} \frac{\delta G(\nu, \tau_1, 1')}{\delta u(\mu_1, \nu; \tau_1^+)} = \int d2 \Sigma(1, 2) G(2, 1'), \quad (3.12a)$$

$$\int d2 = \sum_{\mu_2} \int_C d\tau_2.$$

The self-energy reads

$$\Theta(\mu_1 \nu_1 \tau_1; \nu_1 \mu_1 \tau_{1'}) = -\frac{i}{\hbar} [\langle \langle K_{\mu_1 \nu_1}(Y(\tau_1)) K_{\mu_1 \nu_1}(Y(\tau_{1'})) \rangle \rangle - \Phi(\mu_1, \nu_1; \tau_1) \Phi(\mu_1, \nu_1; \tau_{1'})]. \quad (3.15)$$

Note that the functional derivative automatically produces the correlated part of the environmental NGF.

With the above-given expression for the self-energy the equation of motion for the NGF is closed provided we take the propagator Θ as a given quantity. According to the assumption of weak coupling between the relevant system and the environment the environmental degrees of freedom are not disturbed in their stochastic motion by the relevant system. Therefore we handle the environment as a heat bath and take the statistical average contained in Θ as that with respect to thermal equilibrium.

To derive an equation of motion for the RDM from the nonequilibrium Dyson equation we have to carry out the physical limit. The single equation for the NGF splits into four different equations for the causal, the anticausal, and the correlation functions $G^<$ and $G^>$. Since the causal and anticausal function are determined by $G^<$ and $G^>$ it suffices to take the equations for $G^<$ and $G^>$ (for more details see [24]). These equations read (note the change from τ_1 and $\tau_{1'}$ to t_1 and $t_{1'}$)

$$\sum_{\nu} \left[i\hbar \frac{\partial}{\partial t_1} - H_{\mu_1 \nu}^{(\text{ren})}(t_1) \right] G^{\geq}(\nu, t_1; \mu_1, t_{1'}) = \sum_{\nu} \int_{-\infty}^{\infty} d\bar{t} [\Sigma^{(\text{ret})}(\mu_1, t_1; \nu, \bar{t}) G^{\geq}(\nu, \bar{t}; \mu_1, t_{1'}) + \Sigma^{\geq}(\mu_1, t_1; \nu, \bar{t}) G^{(\text{adv})}(\nu, \bar{t}; \mu_1, t_{1'})]. \quad (3.16)$$

The conjugated equation is obtained if one takes the time derivative with respect to $t_{1'}$. The renormalized matrix elements of the system Hamiltonian contain the contribution from the environmental coordinates

$$H_{\mu\nu}^{(\text{ren})}(t) = H_{\mu\nu}^{(0)} + \Phi(\mu, \nu; t). \quad (3.17)$$

The retarded and advanced NGF's of Eq. (3.16) are defined according to

$$G^{(\text{ret})}(\mu_1, t_1; \mu_1, t_{1'}) = \Xi(t_1 - t_{1'}) \hat{G}(\mu_1, t_1; \mu_1, t_{1'}), \quad (3.18)$$

$$G^{(\text{adv})}(\mu_1, t_1; \mu_1, t_{1'}) = -\Xi(t_{1'} - t_1) \hat{G}(\mu_1, t_1; \mu_1, t_{1'}) \quad (3.19)$$

where the so-called spectral function \hat{G} is given by [23,24]

$$\hat{G}(\mu_1, t_1; \mu_1, t_{1'}) = G^>(\mu_1, t_1; \mu_1, t_{1'}) - G^<(\mu_1, t_1; \mu_1, t_{1'}). \quad (3.20)$$

$$\Sigma(1, 1') = i\hbar \sum_{\nu} \int d2 \frac{\delta G(\nu, \tau_1, 2)}{\delta u(\mu_1, \nu; \tau_1^+)} G^{-1}(2, 1') \quad (3.12b)$$

and the inverse of the NGF has been defined according to

$$\int d2 G^{-1}(1, 2) G(2, 1') = \delta(1 - 1'). \quad (3.13)$$

Comparing Eq. (3.13) with Eq. (3.10) we can identify G^{-1} with $G_0^{-1} - \Sigma$. Therefore Eq. (3.13) is the nonequilibrium version of the Dyson equation.

With this equation the functional derivative in Eq. (3.12a) can be shifted from G to G^{-1} . If one replaces the derivative of G^{-1} by the derivative of the zero-order function (3.11) one obtains the self-energy in the second order with respect to the system-environment coupling (2.8):

$$\Sigma(1, 1') = i\hbar \sum_{\nu_1, \nu_{1'}} G(\nu_1 \tau_1; \nu_{1'} \tau_{1'}) \Theta(\mu_1 \nu_1 \tau_1; \nu_{1'} \mu_1 \tau_{1'}). \quad (3.14)$$

This expression contains the NGF of the environmental degrees of freedom

The relations are the same for the nonequilibrium self-energy. The respective correlation parts follow as

$$\Sigma^{\geq}(\mu_1, t_1; \mu_1, t_{1'}) = i\hbar \sum_{\nu_1, \nu_{1'}} G^{\geq}(\nu_1, t_1; \nu_{1'}, t_{1'}) \times \Theta^{\geq}(\mu_1 \nu_1 t_1; \nu_{1'} \mu_1 t_{1'}) \quad (3.21)$$

where $\Theta^>$ ($\Theta^<$) is defined in the same way as $G^>$ ($G^<$).

C. Density-matrix equations

In the next step on the way to the RDM equations one has to reduce Eq. (3.16) to an equation containing a single time argument only. For that reason one introduces sum and difference times $t = (t_1 + t_{1'})/2$ and $\Delta t = t_1 - t_{1'}$, respectively, and carries out a Fourier transformation with respect to Δt .

Using this mixed time-frequency representation the RDM can be obtained as

$$\tilde{\rho}_{\mu\nu}(t) = \eta_{m,n} \rho_{\mu\nu}(t) = \frac{i\hbar}{2\pi} \int_{-\infty}^{\infty} d\omega G^<(\nu, \mu; \omega, t). \quad (3.22)$$

Note the definition of $\tilde{\rho}_{\mu\nu}$ and the arrangement of the arguments of $G^<$ in a somewhat different manner.

As can be seen from this relation we are able to obtain the RDM equations in carrying out the following manip-

ulations with respect to Eq. (3.16) (and its conjugated version): (i) Introduction of sum and difference time, (ii) Fourier transformation of the whole equation with respect to the difference time and replacement of all functions by their mixed time-frequency representation, (iii) frequency integration of the resulting equation. However, before doing that it becomes necessary to take the difference of the direct equation and the conjugated equation to remove terms proportional to ω .

We obtain (for details, see [24])

$$\begin{aligned} \frac{\partial}{\partial t} \tilde{\rho}_{\mu\nu}(t) = & -\frac{i}{\hbar} \sum_{\kappa} H_{\nu\kappa}^{(\text{ren})}(t) \tilde{\rho}_{\mu\kappa}(t) \\ & + \sum_{\kappa} \int_{-\infty}^t d\bar{t} \int_{-\infty}^{\infty} \frac{d\omega d\bar{\omega}}{2\pi^2} e^{-2i(\omega - \bar{\omega})(t - \bar{t})} [\Sigma^>(\nu, \kappa; \omega, \bar{t}) - \Sigma^<(\nu, \kappa; \omega, \bar{t}) G^<(\kappa, \mu; \bar{\omega}, \bar{t})] \\ & + (\text{c. c.}; \mu \rightleftharpoons \nu). \end{aligned} \quad (3.23)$$

The abbreviation at the end of this expression indicates that the rhs has been completed by adding the complex-conjugated version of the terms shown with interchanged μ and ν .

The structure of the rhs of Eq. (3.23) is well known from the NGF technique [20–23], in which the self-energy contributions reflect the scattering with respect to the environmental degrees of freedom. The non-Markovian character of these expressions accounts for the retardation of the scattering processes.

Since the rhs contains the correlation functions $G^>$ and $G^<$ this equation is not closed with respect to the RDM. To end up with a closed equation we have to express the correlation functions by the RDM. For the present reasoning it is sufficient to take the following zeroth-order expressions [24]:

$$G^>(\mu, \nu; \omega, t) = -2\pi i \delta(\hbar\omega - (E_{\mu} + E_{\nu})/2) (\delta_{\mu, \nu} + \tilde{\rho}_{\nu, \mu}), \quad (3.24)$$

$$G^<(\mu, \nu; \omega, t) = -2\pi i \delta(\hbar\omega - (E_{\mu} + E_{\nu})/2) \tilde{\rho}_{\nu, \mu}. \quad (3.25)$$

These expressions guarantee the relation (3.22) and obey the sum rule for the spectral function

$$\frac{i\hbar}{2\pi} \int_{-\infty}^{\infty} d\omega \hat{G}(\mu, \nu; \omega, t) = \delta_{\mu, \nu}. \quad (3.26)$$

Taking the expressions (3.24) and (3.25), Eq. (3.23) for the RDM changes to

$$\begin{aligned} \frac{\partial}{\partial t} \tilde{\rho}_{\mu\nu}(t) = & -\frac{i}{\hbar} \sum_{\kappa} H_{\nu\kappa}^{(\text{ren})}(t) \tilde{\rho}_{\mu\kappa}(t) \\ & -\frac{i}{\hbar} \sum_{\kappa} \int_{-\infty}^t d\bar{t} \int_{-\infty}^{\infty} \frac{d\omega}{\pi} e^{-i[2\omega - (E_{\mu} + E_{\kappa})/\hbar](t - \bar{t})} \{ \Sigma^>(\nu, \kappa; \omega, \bar{t}) \tilde{\rho}_{\mu\kappa}(\bar{t}) - \Sigma^<(\nu, \kappa; \omega, \bar{t}) [\delta_{\mu, \kappa} + \tilde{\rho}_{\mu\kappa}(\bar{t})] \} \\ & + (\text{c. c.}; \mu \rightleftharpoons \nu). \end{aligned} \quad (3.27)$$

For further calculations we need a definite expression of the self-energy parts $\Sigma^>$ and $\Sigma^<$. Equation (3.21) together with the expressions (3.24) and (3.25) for the correlation functions yield

$$\Sigma^{\lessgtr}(\mu_1, \mu_1'; \omega, t) = \sum_{\nu_1, \nu_1'} \Theta^{\lessgtr}(\mu_1 \nu_1; \nu_1' \mu_1'; \omega - (E_{\nu_1} + E_{\nu_1'})/2\hbar, t) \times \begin{cases} [\delta_{\nu_1, \nu_1'} + \tilde{\rho}_{\nu_1, \nu_1'}(t)] & (\text{for } \Sigma^>) \\ \tilde{\rho}_{\nu_1, \nu_1'}(t) & (\text{for } \Sigma^<) \end{cases}. \quad (3.28)$$

The non-Markovian contributions in Eq. (3.27) will be taken into account by a procedure carried out in [24]. For this purpose we separate the lowest-order time dependence of the RDM which is given by the exponential factor $\exp[(i/\hbar)(E_{\mu} - E_{\nu})t]$ [compare Eq. (3.27)]:

$$\tilde{\rho}_{\mu\nu}(t) = \exp\left\{\frac{i}{\hbar}(E_{\mu} - E_{\nu})t\right\} \hat{\rho}_{\mu\nu}(t). \quad (3.29)$$

Provided that the remaining time dependence of the RDM is slow compared to the oscillating contribution we can take $\hat{\rho}_{\mu\nu}$ out of the time integration. This procedure has not been applied consistently in the previous papers [17,18]. But there appear only differences of minor importance.

The time dependence of the environmental correlation functions disappears because of thermal equilibrium conditions, and we can carry out the remaining time integration. For that end one has to replace $t - \bar{t}$ by t' and to take notice of the well-known formula

$$\int_0^\infty dt e^{i\omega t} = i/(\omega + i\varepsilon); \quad \varepsilon \Rightarrow 0+ . \quad (3.30)$$

The RDM $\tilde{\rho}_{\mu\nu}$ is reconstructed according to Eq. (3.29) and we obtain

$$\begin{aligned} \frac{\partial}{\partial t} \tilde{\rho}_{\mu\nu}(t) = & -\frac{i}{\hbar} E_\nu \tilde{\rho}_{\mu\nu} - i \sum_\kappa \left[V_{\nu,\kappa} \tilde{\rho}_{\mu,\kappa} + \frac{1}{\hbar} \delta_{n,\kappa} \Phi(n, N, K; t) \tilde{\rho}_{\mu,\kappa} \right] \\ & - \sum_{K,L} \frac{1}{2\pi\hbar} \int_{-\infty}^\infty d\omega [\Theta^>(nNL, nLK; \omega) \tilde{\rho}_{\mu,nK} / (\omega - \omega_{nKL} - i\varepsilon) \\ & \quad - \Theta^<(nNK, nLM; \omega) \tilde{\rho}_{mL,nK} / (\omega - \omega_{mML} - i\varepsilon)] \\ & + \sum_\kappa \sum_{L,L'} \frac{1}{2\pi\hbar} \int_{-\infty}^\infty d\omega \hat{\Theta}(nNL, kL'K; \omega) \tilde{\rho}_{kL',nL} \tilde{\rho}_{\mu\kappa} / (\omega - \omega_{kKL'} - i\varepsilon) + (\text{c.c.}; \mu \Leftrightarrow \nu) . \end{aligned} \quad (3.31)$$

Here, we took into account that $K_{\mu\nu}$ [compare Eq. (2.8)] and thus $\Phi(\mu, \nu; t)$ are proportional to $\delta_{m,n}$. Furthermore, we have introduced the abbreviation

$$\omega_{mMN} = (E_{mM} - E_{mN}) / \hbar . \quad (3.32)$$

The derived equations of motion (3.31) for the RDM are of a very general type. They only contain the restriction to a second-order system-environment interaction and the assumption of thermal equilibrium conditions for the environment. The functional type of the system-environment interaction has not yet been specified.

The first and the second term on the rhs of Eq. (3.31) describe the internal dynamics of the relevant system, here transitions between the different centers are realized by the second contribution. The corresponding inter-center coupling has already been reduced by the Franck-Condon factor.

The remaining contributions to the rhs of Eq. (3.31) follow from the coupling to the environment and describe the dissipation of vibrational energy of the relevant system. Note that the approximation used for the system-environment coupling separates the processes of inter-center transfer and the dissipation of energy into the environment.

Expressions for the coupling to the environmental degrees of freedom similar to those contained in Eq. (3.31) have also been obtained in Ref. [15], in which time-resolved light scattering at a two-level system has been considered. The coupling of the single vibrational mode to the environment used there is nearly identical to Eq. (2.8).

The quadratic contributions with respect to the RDM [see the last term of Eq. (3.31)] follow from those parts of Eq. (3.27) which contain the RDM together with the δ symbol [compare the upper row in Eq. (3.28)]. Hence these contributions perceive the final-state occupation in the transition processes. However, if the occupation probability is distributed among different levels these terms are of minor importance.

IV. THE TWO-CENTER SINGLE-INTERACTION-COORDINATE SYSTEM

A. Density-matrix equations

To carry out numerical calculations we restrict ourselves in the present paper to the minimal system (a molecular dimer) of two electronic centers and a single interaction coordinate $X (=Q)$. The coupling between the interaction coordinate and the set of environmental degrees of freedom $\{Y\}$ [$=q_\xi$, compare Eq. (2.8)] will be taken in the lowest order of a power expansion. The corresponding coefficients [the first derivatives with respect to Q and q_ξ of the potential $V_v^{(I-E)}$ introduced in Eq. (2.2)] are given by K_ξ . More complicated cases are planned to be published elsewhere.

The resulting two-center one-interaction-coordinate problem will be further simplified by assuming that the two vibrational surfaces are parabolas of the same curvature which are shifted with respect to the origin of Q by the amount $-2g_m$. The constants g_m represent the dimensionless electron-vibration coupling constants. Furthermore, the eigenvalue problem of the interaction coordinate is that of a harmonic oscillator with frequency ω_v . The set of vibrational quantum numbers M is reduced to a single integer. The energy E_{mM} of the diabatic states can be written as

$$E_{mM} = \varepsilon_m - \hbar\omega_v g_m^2 + \hbar\omega_v (M + \frac{1}{2}) , \quad (4.1)$$

ε_m is the electronic energy at $Q=0$ and $-\hbar\omega_v g_m^2$ gives the so-called polaron shift. The Franck-Condon factors (2.7) reduce to a single integral. Here we give the corresponding Hilbert space expression

$$\begin{aligned} F_{\text{FC}}(mM, nN) |_{m \neq n} &= F_{\text{FC}}(M, N; g_m - g_n) \\ &= \langle M | S(g_m) S^\dagger(g_n) | N \rangle \end{aligned} \quad (4.2)$$

with

$$|M\rangle = \frac{C^{\dagger M}}{\sqrt{M!}} |0\rangle . \quad (4.3)$$

The phonon operators are related to the dimensionless interaction coordinate according to

$$Q = C + C^\dagger. \quad (4.4)$$

The shift operator S^\dagger reads

$$S^\dagger(g_m) = \exp[g_m(C - C^\dagger)]. \quad (4.5)$$

From the above representation of the Franck-Condon factor we can deduce two useful relations needed later, namely,

$$F_{FC}^*(M, N; g) = F_{FC}(N, M; -g) \quad (4.6a)$$

and

$$\begin{aligned} \sqrt{M+1}F_{FC}(M+1, N; g) &= gF_{FC}(M, N; g) \\ &+ \sqrt{N}F_{FC}(M, N-1; g). \end{aligned} \quad (4.6b)$$

For the numerical calculation we use the following expansion:

$$\Theta^{\gtrless}(\mu_1\nu_1; \nu_1\mu_1; \omega, t) = \delta_{m_1 n_1} \delta_{m_1' n_1'} \sum_{\xi} g_{\xi}(m_1; M_1, N_1) g_{\xi}(m_1'; M_1', N_1') D^{\gtrless}(\xi, \xi'; \omega, t). \quad (4.10a)$$

The NGF with respect to the coordinates q_{ξ} is generally defined as [remember Eq. (3.4)]

$$D(\xi_1, \tau_1; \xi_1', \tau_1') = -\frac{i}{\hbar} (\langle\langle \hat{q}(\xi_1, \tau_1) \hat{q}(\xi_1', \tau_1') \rangle\rangle - \langle\langle \hat{q}(\xi_1, \tau_1) \rangle\rangle \langle\langle \hat{q}(\xi_1', \tau_1') \rangle\rangle). \quad (4.10b)$$

Since we take the environment as a large collection of harmonic oscillators with frequency ω_{ξ} staying in thermal equilibrium the explicit time dependence of the correlation functions D^{\gtrless} vanishes, and they become diagonal with respect to the mode index ξ . Therefore the mixed time-frequency representation needed in the RDM equations reads

$$D^{\gtrless}(\xi, \omega) = -\frac{2\pi i}{\hbar} \{ \delta(\omega \mp \omega_{\xi}) [1 + n(\omega_{\xi})] + \delta(\omega \pm \omega_{\xi}) n(\omega_{\xi}) \}, \quad n(\omega) = [\exp(\beta\hbar\omega) - 1]^{-1}. \quad (4.11)$$

> (<) corresponds to the upper (lower) sign in the argument of the δ functions. The expressions for D^{\gtrless} simplify the RDM equations (3.31) to

$$\begin{aligned} \frac{\partial}{\partial t} \rho_{\mu\nu}(t) &= -\frac{i}{\hbar} E_{\nu} \rho_{\mu\nu} + \frac{i}{\hbar} \sum_K V_{\nu, \hbar K} \rho_{\mu, \hbar K} \\ &- \sum_{\xi} K_{\xi}^2 \int_{-\infty}^{\infty} \frac{d\omega}{2\pi\hbar} D^{>}(\xi, \omega) \{ (N+1) \rho_{\mu, \nu} / (\omega + \omega_{\nu} - i\varepsilon) + \sqrt{(N+1)(N+2)} \rho_{\mu, \nu+2} / (\omega - \omega_{\nu} - i\varepsilon) \\ &+ \sqrt{(N-1)N} \rho_{\mu, \nu-2} / (\omega + \omega_{\nu} - i\varepsilon) + N \rho_{\mu, \nu} / (\omega - \omega_{\nu} - i\varepsilon) \\ &- 2g_n [\sqrt{N+1} \rho_{\mu, \nu+1} / (\omega - \omega_{\nu} - i\varepsilon) + \sqrt{N} \rho_{\mu, \nu-1} / (\omega + \omega_{\nu} - i\varepsilon)] \} \\ &+ \sum_{\xi} K_{\xi}^2 \int_{-\infty}^{\infty} \frac{d\omega}{2\pi\hbar} D^{<}(\xi, \omega) \{ \sqrt{(M+1)(N+1)} \rho_{\mu+1, \nu+1} / (\omega + \omega_{\nu} - i\varepsilon) + \sqrt{(M+1)N} \rho_{\mu+1, \nu-1} / (\omega + \omega_{\nu} - i\varepsilon) \\ &+ \sqrt{M(N+1)} \rho_{\mu-1, \nu+1} / (\omega - \omega_{\nu} - i\varepsilon) + \sqrt{MN} \rho_{\mu-1, \nu-1} / (\omega - \omega_{\nu} - i\varepsilon) \\ &- 2g_n [\sqrt{M+1} \rho_{\mu+1, \nu} / (\omega - \omega_{\nu} - i\varepsilon) + \sqrt{M} \rho_{\mu-1, \nu} / (\omega + \omega_{\nu} - i\varepsilon)] \} \\ &+ \sum_{\xi} K_{\xi}^2 \int_{-\infty}^{\infty} \frac{d\omega}{2\pi\hbar} \hat{D}(\xi, \omega) \sum_{\kappa} \rho_{\mu, \kappa} \{ \sqrt{(K+1)(N+1)} \rho_{\kappa+1, \nu+1} / (\omega + \omega_{\nu} - i\varepsilon) \} \end{aligned}$$

$$\begin{aligned} F_{FC}(M, N; g) &= \sqrt{M!N!} g^{M+N} e^{-g^2/2} \\ &\times \sum_{n=0}^{\min(M, N)} \frac{(-1)^{N+n}}{g^{2n} n! (M-n)! (N-n)!}. \end{aligned} \quad (4.7)$$

Within the same notation the linearized coupling of the interaction coordinate to the environment can be expressed by the following matrix element:

$$\begin{aligned} K_{m; M, N}(q) &= \langle M | S(g_m) \sum_{\xi} K_{\xi} q_{\xi} Q S^{\dagger}(g_m) | N \rangle \\ &= \sum_{\xi} g_{\xi}(m; M, N) q_{\xi} \end{aligned} \quad (4.8)$$

with

$$\begin{aligned} g_{\xi}(m; M, N) &= (\sqrt{M+1} \delta_{M+1, N} + \sqrt{M} \delta_{M-1, N} \\ &- \delta_{M, N} 2g_m) K_{\xi}. \end{aligned} \quad (4.9)$$

Inserting this expression into the general formula (3.15) for the NGF of the environmental degrees of freedom one can deduce the correlation functions

$$\begin{aligned}
& +\sqrt{(K+1)N}\rho_{\kappa+1,\nu-1}/(\omega+\omega_\nu-i\epsilon) \\
& +\sqrt{K(N+1)}\rho_{\kappa-1,\nu+1}/(\omega-\omega_\nu-i\epsilon)+\sqrt{KN}\rho_{\kappa-1,\nu-1}/(\omega-\omega_\nu-i\epsilon) \\
& -2g_n[\sqrt{K+1}\rho_{\kappa+1,\nu}/(\omega+\omega_\nu-i\epsilon)+\sqrt{K}\rho_{\kappa-1,\nu}/(\omega-\omega_\nu-i\epsilon)] \\
& +(\text{c.c.};\mu\rightleftharpoons\nu)
\end{aligned}$$

$$(\hat{n}=2,1 \text{ if } n=1,2 \text{ and } \mu\pm 1=m,M\pm 1). \quad (4.12)$$

Note that those contributions which contain frequency denominators of the type $\omega-i\epsilon$ have already been neglected. Furthermore, we took into account the prefactors $\eta_{m,n}$ [see Eq. (3.6b)] following from the Pauli statistics of the level operators.

To arrive at the final form of the equations appropriate for a numerical solution we drop the real part of the frequency denominators, thus neglecting a spectral renormalization of the electron interaction-coordinate system due to the coupling to the environment. The frequency integration results in environmental correlation functions with frequency arguments ω_ν and $-\omega_\nu$. These expressions together with the sum taken over the mode index of the environmental degrees of freedom can be comprised defining the frequency-dependent damping rate of the interaction-coordinate quanta

$$\gamma(\omega)=2\pi a(\omega)[1+n(\omega)]. \quad (4.13)$$

The spectral density of the environmental degrees of freedom reads

$$a(\omega)=\frac{1}{\hbar^2}\sum_{\xi}K_{\xi}^2[\delta(\omega-\omega_{\xi})-\delta(\omega+\omega_{\xi})]. \quad (4.14)$$

The damping rate at frequency ω_ν ($-\omega_\nu$) determines the lifetime of the coupled electron-vibration state due to the emission (absorption) of a single environmental quantum.

If we use the relations

$$\sum_{\xi}K_{\xi}^2D^{>}(\xi,\pm\omega_\nu)=-i\hbar\gamma(\pm\omega_\nu) \quad (4.15a)$$

and

$$\sum_{\xi}K_{\xi}^2D^{<}(\xi,\pm\omega_\nu)=-i\hbar\gamma(\mp\omega_\nu) \quad (4.15b)$$

we obtain the final form of the RDM equations ($v_{\mu,\nu}=V_{\mu,\nu}/\hbar$):

$$\begin{aligned}
\frac{\partial}{\partial t}\rho_{\mu\nu}(t)=& i\tilde{\omega}_{\mu\nu}\rho_{\mu\nu}+i\sum_K(v_{\nu,\hat{n}K}\rho_{\mu,\hat{n}K}-v_{\hat{n}K,\mu}\rho_{\hat{n}K,\nu})-\frac{1}{2}\sqrt{(M+1)(M+2)}\gamma(\omega_\nu)\rho_{\mu+2,\nu} \\
& -\frac{1}{2}\sqrt{(M-1)M}\gamma(-\omega_\nu)\rho_{\mu-2,\nu}-\frac{1}{2}\sqrt{(N+1)(N+2)}\gamma(\omega_\nu)\rho_{\mu,\nu+2}-\frac{1}{2}\sqrt{(N-1)N}\gamma(-\omega_\nu)\rho_{\mu,\nu-2} \\
& +\sqrt{(M+1)(N+1)}\gamma(\omega_\nu)\rho_{\mu+1,\nu+1}+\sqrt{MN}\gamma(-\omega_\nu)\rho_{\mu-1,\nu-1} \\
& +\frac{1}{2}\sqrt{(M+1)N}[\gamma(\omega_\nu)+\gamma(-\omega_\nu)]\rho_{\mu+1,\nu-1}+\frac{1}{2}\sqrt{M(N+1)}[\gamma(\omega_\nu)+\gamma(-\omega_\nu)]\rho_{\mu-1,\nu+1} \\
& +(g_m-g_n)[\sqrt{M+1}\gamma(\omega_\nu)\rho_{\mu+1,\nu}+\sqrt{M}\gamma(-\omega_\nu)\rho_{\mu-1,\nu}-\sqrt{N+1}\gamma(\omega_\nu)\rho_{\mu,\nu+1}-\sqrt{N}\gamma(-\omega_\nu)\rho_{\mu,\nu-1}] \\
& +\frac{1}{2}[\gamma(\omega_\nu)-\gamma(-\omega_\nu)]\sum_{\kappa}\sqrt{K+1}[\sqrt{M+1}(\rho_{\mu+1,\kappa}\rho_{\kappa+1,\nu}-\rho_{\mu+1,\kappa+1}\rho_{\kappa,\nu})+\sqrt{M}(\rho_{\mu-1,\kappa}\rho_{\kappa+1,\nu}-\rho_{\mu-1,\kappa+1}\rho_{\kappa,\nu}) \\
& +\sqrt{N+1}(\rho_{\mu,\kappa+1}\rho_{\kappa,\nu+1}-\rho_{\mu,\kappa}\rho_{\kappa+1,\nu+1})+\sqrt{N}(\rho_{\mu,\kappa+1}\rho_{\kappa,\nu-1}-\rho_{\mu,\kappa}\rho_{\kappa+1,\nu-1}) \\
& +2(g_m-g_n)(\rho_{\mu,\kappa+1}\rho_{\kappa,\nu}-\rho_{\mu,\kappa}\rho_{\kappa+1,\nu})]. \quad (4.16)
\end{aligned}$$

Here, we have introduced the complex transition frequencies

$$\begin{aligned}
\tilde{\omega}_{\mu\nu}=& (E_{\mu}-E_{\nu})/\hbar \\
& +i\{\frac{1}{2}(M+N)[\gamma(\omega_\nu)+\gamma(-\omega_\nu)]+\gamma(-\omega_\nu)\}. \quad (4.17)
\end{aligned}$$

They contain the transition frequency between diabatic

levels μ and ν and the finite lifetime of these levels due to the coupling to the environment.

The above equations of motion of the RDM differ in three aspects from those used in the previous paper [18]. First, we have considered here the full linearized version of the interaction-coordinate environment coupling instead rescaling Q to the quantity $\delta Q=Q-2\sum_m g_m P_m$. It yields the additional terms proportional to g_m . However,

the numerical results are only slightly changed compared with those of [18]. Second, the RDM equations have been derived taking into account the non-Markovian contributions from the coupling to the environment (see Sec. III C). This improvement avoids the occurrence of the damping functions (4.13) with frequency arguments others than $\pm\omega_v$. And third, we have specified here the quadratic terms with respect to the RDM.

It can be proven simply that the above RDM equations conserve the total probability $\sum_\mu \rho_{\mu\mu}$. Furthermore, as one expects, the effect of the coupling to the environment is twofold. On the one hand this coupling produces the dephasing rates

$$\Gamma_M = \frac{1}{2}[(M+1)\gamma(-\omega_v) + M\gamma(\omega_v)] \quad (4.18)$$

of the vibrational level M . This quantity is contained in the transition frequencies (4.17). On the other hand real transitions occur accompanied by the emission and absorption of environmental quanta described by the third up to the last term of the rhs of Eq. (4.16). (This will become more obvious below when we derive an equation for the diagonal elements of the RDM.)

If the vibrational quantum number in the RDM is increased $\gamma(\omega_v)$ occurs as a prefactor, and if the quantum number is decreased the prefactor is given by $\gamma(-\omega_v)$. In the mixed case the prefactor contains $\gamma(\omega_v)$ as well as $\gamma(-\omega_v)$.

Finally, it is interesting to note that the linearized version of the RDM equations (4.16) leads to a simple damped-harmonic-oscillator equation for the interaction coordinate Q . However, the oscillatory motion is disturbed by an "external" force proportional to $\sum_m g_m P_m$. This distortion comprises the complicated dynamics of Q

(see Sec. V). Details of the derivation of the equation mentioned can be found in the appendix.

B. Generalized master equation

To gain a deeper understanding of the underlying physics of the RDM equations (4.16) we indicate the approximations necessary to change to the generalized master equations (GME) and afterwards to rate equations of the nonadiabatic electron transfer. The GME's represent non-Markovian equations of motion for the diagonal elements of the RDM. Although of approximate type such GME's have the advantage of characterizing the transfer dynamics in a configuration space with a considerably reduced dimension compared to the case of the RDM equations. First, we change from the complete RDM $\rho_{\mu,\nu}$ to its diagonal elements $P_\mu = \rho_{\mu,\mu}$, the occupation probabilities of the Born-Oppenheimer states. Afterwards, one can derive non-Markovian as well as Markovian rate equations for the total electronic site-occupation probabilities $P_m = \sum_M P_\mu$.

The physical background allowing such a reduced description consists in a decreasing lifetime of excited vibrational states compared to the intercenter transfer time. If the vibrational lifetime becomes short enough the electron quickly relaxes at the given center before any transfer can happen. In that limit the transfer dynamics can be described by simple rate equations.

To end up with the standard (linear) rate equations we neglect the nonlinear contributions in the RDM equations (4.16). The diagonal set of the remaining equations reads

$$\begin{aligned} \frac{\partial}{\partial t} P_\mu = & -[M\gamma(\omega_v) + (M+1)\gamma(-\omega_v)]P_\mu + (M+1)\gamma(\omega_v)P_{\mu+1} + M\gamma(-\omega_v)P_{\mu-1} - 2 \sum_N \text{Im}(v_{\mu,\hat{m}N} \rho_{\mu,\hat{m}N}) \\ & - \sqrt{(M+1)(M+2)}\gamma(\omega_v)\text{Re}\rho_{\mu+2,\mu} - \sqrt{(M-1)M}\gamma(-\omega_v)\text{Re}\rho_{\mu-2,\mu} \\ & + \sqrt{M(M+1)}[\gamma(\omega_v) + \gamma(-\omega_v)]\text{Re}\rho_{\mu+1,\mu-1}. \end{aligned} \quad (4.19)$$

The GME's will be obtained if we succeed in replacing the terms containing off-diagonal elements of the RDM by diagonal ones. There occur two different types, namely, those being off diagonal with respect to the center index and the vibrational quantum number ($\rho_{\mu,\hat{m}N}$) and those being diagonal with respect to the center index ($\rho_{\mu+K,\mu+L}$; $K,L = -2, \dots, +2$). To replace both types it is necessary to write down the corresponding equations of motion. If we solve these equations we can insert the solutions into the original equation (4.19). Once again, there appear off-diagonal parts of the RDM. Thus we can repeat this procedure, resulting in a perturbation expansion for the memory kernels of the GME's.

We start by determining an approximation for the first type of the RDM elements, namely $\rho_{\mu,\hat{m}N}$. In the lowest-order approximation with respect to the memory kernel we obtain

$$\frac{\partial}{\partial t} \rho_{\mu,\hat{m}N} = i\bar{\omega}_{\mu,\hat{m}N} \rho_{\mu,\hat{m}N} + iv_{\hat{m}N,\mu} (P_\mu - P_{\hat{m}N}) \quad (4.20)$$

with the solution

$$\begin{aligned} \rho_{\mu,\hat{m}N}(t) = & \rho_{\mu,\hat{m}N}(0) e^{i\bar{\omega}_{\mu,\hat{m}N}t} \\ & + iv_{\hat{m}N,\mu} \int_0^t d\bar{t} e^{i\bar{\omega}_{\mu,\hat{m}N}\bar{t}} \\ & \times [P_\mu(t-\bar{t}) - P_{\hat{m}N}(t-\bar{t})]. \end{aligned} \quad (4.21)$$

Taking the Markov limit of this expression [$P_\mu(t-\bar{t}) \simeq P_\mu(t)$] we realize that the given approximation can be characterized by the perturbation-expansion contribution $v_{\hat{m}N,\mu}/\bar{\omega}_{\mu,\hat{m}N}$.

To take into account off-diagonal elements of the

RDM in Eq. (4.20) other than $\rho_{\mu, \hat{m}N}$ requires the solution of the corresponding equations of motion. This solution would also give powers of the basic contributions $v_{\mu\nu}/\tilde{\omega}_{\mu, \nu}$ and $\gamma/\tilde{\omega}_{\mu, \nu}$. For example, the lowest-order solution for the above-mentioned second type of off-diagonal parts of the RDM $\rho_{\mu+K, \mu+L}$ would contribute terms of the order $\gamma/\tilde{\omega}_{\mu, \nu}$.

In the following we restrict ourselves to a memory kernel for the GME's of the order $|v_{\hat{m}N, \mu}|^2/|\tilde{\omega}_{\mu, \hat{m}N}|$ in inserting the expression (4.21) into Eq. (4.19). Therefore we have to drop all off-diagonal functions of the type $\rho_{\mu+K, \mu+L}$. Those would contribute the order $\gamma^2/|\tilde{\omega}_{\mu, \nu}|$. The resulting GME's read

$$\begin{aligned} \frac{\partial}{\partial t} P_{\mu} = & -[M\gamma(\omega_{\nu}) + (M+1)\gamma(-\omega_{\nu})]P_{\mu} \\ & + (M+1)\gamma(\omega_{\nu})P_{\mu+1} + M\gamma(-\omega_{\nu})P_{\mu-1} \\ & - \sum_N \int_0^t d\bar{t} K_{\mu, \hat{m}N}(t-\bar{t})[P_{\mu}(\bar{t}) - P_{\hat{m}N}(\bar{t})] \\ & + 2 \sum_N \text{Im}[v_{\mu, \hat{m}N} \rho_{\mu, \hat{m}N}(0) e^{i\tilde{\omega}_{\mu, \hat{m}N}t}]. \end{aligned} \quad (4.22)$$

The first term describes the decrease of the occupation probability of the level μ resulting from intracenter transitions to the neighboring levels $M+1$ and $M-1$ with rates $\gamma(-\omega_{\nu})$ and $\gamma(\omega_{\nu})$, respectively. The reverse of these processes leads to an increase of probability as represented by the second and the third term.

The integral term describes intercenter transitions. As a consequence of the time integration (memory effect) and oscillating parts in the kernel, the integral term may create oscillating contributions to the occupation probabilities. The kernel itself reads

$$K_{\mu, \hat{m}N}(t) = 2|v_{\mu, \hat{m}N}|^2 e^{i\tilde{\omega}_{\mu, \hat{m}N}t}. \quad (4.23)$$

It oscillates with the frequency $\omega_{\mu, \hat{m}N} = (E_{\mu} - E_{\hat{m}N})/\hbar$ and disappears in a time given by the inverse rate of the intercenter dephasing

$$\tau_{M, N} = 1/(\Gamma_M + \Gamma_N). \quad (4.24)$$

The last contribution in Eq. (4.22) stems from the initial value term in Eq. (4.21).

To discuss the dynamics described by the GME's it is useful to assume that the level N_0 at center 1 is initially occupied with probability one, and to discriminate three different processes.

As the first process we introduce the intracenter relaxation indicated by the first three terms of the GME's. The characteristic time of this process is the inverse of $\gamma(\omega_{\nu})$. The second process is the dephasing of the wave function at center 1 with respect to center 2. Its characteristic time is given by $2/\gamma(\omega_{\nu})$. The third process is the electron transfer without any coupling to the environment, the coherent transfer. The electron moves from level N_0 at center 1 to the levels at center 2. If the state N_0 at center 1 is degenerate with state N at center 2 one expects an oscillatory behavior with frequency $2|v_{1N_0, 2N}|$ in the beginning of that motion. Later, this will be super-

imposed by transitions to neighboring levels $N\pm 1$, $N\pm 2$, and so on. If there is no degeneracy with level N at center 2 one can expect an oscillatory behavior with frequency $\omega_{1N_0, 2N}^2 + 4|v_{1N_0, 2N}|^2)^{1/2}$, where N is the level nearest to N_0 .

If the damping rate $\gamma(\omega_{\nu})$ is small compared to $|v_{1N_0, 2N}|$ the electron oscillates between the two centers. In that case the memory kernel $K_{\mu, \hat{m}N}(t-\bar{t})$ remains large for all \bar{t} . In the contrasting case $\gamma(\omega_{\nu}) > |v_{1N_0, 2N}|$ transfer dynamics are dominated by intracenter relaxation at first. If this process is finished the transfer to the neighboring center becomes significant. Since oscillating contributions to the memory kernel have been damped out, the occupation probabilities themselves do not show any oscillating behavior.

C. Rate equations

If one concentrates on the system dynamics on a time scale larger than the intracenter relaxation it is possible to formulate rate equations in carrying out three different approximations. First, one can introduce the separation ansatz for the occupation probabilities

$$P_{\mu}(t) = f(M)P_m \quad (4.25)$$

which takes into account the finished intracenter relaxation by providing a thermal distribution over the vibrational levels

$$f(M) = (1 - e^{-\beta\hbar\omega_{\nu}})e^{-\beta M\hbar\omega_{\nu}}. \quad (4.26)$$

This ansatz leads to a mutual compensation of the intracenter relaxation terms in the GME's. The remaining total occupation probability P_m of center m has to be determined separately. As a second approximation one can take the Markov limit of the GME's since the memory kernel extends over times [the intercenter dephasing time (4.24)] small compared with the time region of interest. Since the last term of the GME's (4.22) vanishes in the same time region we can drop this contribution.

A summation with respect to M gives the following rate equation:

$$\frac{\partial}{\partial t} P_m(t) = -\tilde{k}_{\hat{m}m}(t)P_m(t) + \tilde{k}_{m\hat{m}}(t)P_{\hat{m}}(t) \quad (4.27)$$

with time-dependent rate coefficients for the transition between center m and center \hat{m}

$$\begin{aligned} \tilde{k}_{m\hat{m}}(t) = & 2 \sum_{M, N} |v_{mM, \hat{m}N}|^2 f(N) \\ & \times \text{Im}[(e^{i\tilde{\omega}_{mM, \hat{m}N}t} - 1)/\tilde{\omega}_{mM, \hat{m}N}]. \end{aligned} \quad (4.28)$$

For $t \gg \max(\tau_{MN})$ this expression approaches the standard rate coefficient $k_{m\hat{m}}$ of nonadiabatic electron transfer. Taking into account the time dependence of the rate coefficients one can hope to extend the range of validity of the rate equation into the transition regime from the coherent to the incoherent transfer. (The numerical results given below justify this reasoning.) Therefore we split the total time-dependent coefficient

$$\tilde{k}_{m\hat{m}}(t) = k_{m\hat{m}} + \Delta k_{m\hat{m}}(t) \quad (4.29)$$

into the standard rate coefficient of nonadiabatic electron transfer (see, e.g., [2])

$$k_{m\hat{m}} = \sum_{M,N} |v_{mM, \hat{m}N}|^2 f(N) \frac{2(\Gamma_M + \Gamma_N)}{\omega_{mM, \hat{m}N}^2 + (\Gamma_M + \Gamma_N)^2} \quad (4.30)$$

and the time-dependent correction

$$\begin{aligned} \Delta k_{m\hat{m}}(t) = & 2 \sum_{M,N} |v_{mM, \hat{m}N}|^2 f(N) \frac{e^{-(\Gamma_M + \Gamma_N)t}}{\omega_{mM, \hat{m}N}^2 + (\Gamma_M + \Gamma_N)^2} \\ & \times [\omega_{mM, \hat{m}N} \sin(\omega_{mM, \hat{m}N} t) \\ & - (\Gamma_M + \Gamma_N) \cos(\omega_{mM, \hat{m}N} t)]. \quad (4.31) \end{aligned}$$

This last expression shows that the most important contribution originates from the vibrational ground state with exponential time dependence according to $\exp[-\gamma(-\omega_v)t]$. If the absorption processes of environmental quanta are improbable ($k_B T \ll \hbar\omega_v$) this term gives a significant correction to the standard rate expression.

The solution of Eq. (4.27) can be cast into analytical form

$$P_1(t) = \frac{1}{2}[1 + D(t)], \quad (4.32)$$

$$P_2(t) = \frac{1}{2}[1 - D(t)], \quad (4.33)$$

with

$$\begin{aligned} D(t) &= P_1(t) - P_2(t) \\ &= D(0)e^{-A(t,0)} \\ &+ \int_0^t d\bar{t} e^{-A(t,\bar{t})} [\tilde{k}_{12}(\bar{t}) - \tilde{k}_{21}(\bar{t})] \quad (4.34) \end{aligned}$$

and

$$A(t, \bar{t}) = \int_{\bar{t}}^t dt' [\tilde{k}_{12}(t') + \tilde{k}_{21}(t')]. \quad (4.35)$$

These equations will be used in the following section for a comparison with exact solutions of the RDM equations.

We also note that the terms in Eq. (4.19) proportional to $\rho_{\mu+K, \mu+L}$, which give contributions to the GME's of the order $\gamma^2/\bar{\omega}_{\mu+K, \mu+L}$, describe intracenter relaxation processes accompanied by the emission and absorption of two environmental quanta. Using the separation ansatz (4.25) to derive the corresponding rate equation these contributions also vanish like the single-quantum processes.

Now, let us consider the simplest correction to the GME's following from the quadratic contributions in the RDM equations (4.16). The lowest-order contribution to the GME's is obtained if we neglect all off-diagonal elements of the RDM in the κ summation in Eq. (4.16). This approximation has to be carried out after changing to the diagonal elements of Eq. (4.16). We get

$$\begin{aligned} \left[\frac{\partial}{\partial t} P_\mu \right]_{\text{quadr}} &\approx -\frac{1}{2}[\gamma(\omega_v) - \gamma(-\omega_v)] \\ &\times [(M+1)P_{\mu+1}P_\mu - MP_{\mu-1}P_\mu]. \quad (4.36) \end{aligned}$$

Employing the separation ansatz (4.25) and carrying out the summation with respect to the vibrational quantum numbers this expression vanishes. Therefore we can conclude that the quadratic contributions may be of minor importance in the regime of incoherent transfer. Non-vanishing contributions are of the order $\gamma v_{\mu\nu}/\bar{\omega}_{\mu,\nu}$ and $\gamma\gamma/\bar{\omega}_{\mu,\nu}$ with respect to the resulting memory kernel. The conclusion about the minor importance of the quadratic terms will be further justified by numerical calculations published elsewhere.

V. NUMERICAL RESULTS

The results given below of the numerical solution of the RDM equations extend earlier studies of the same dimer model. In Ref. [25] the limiting case of the coherent charge motion has been extensively discussed. The numerical calculations have been based on the solution of the time-dependent Schrödinger equation for the isolated dimer (the relevant system without any coupling to the environment).

Expanding the time-dependent wave function with respect to the single-center Born-Oppenheimer states defined in Eqs. (2.3) and (2.4) one obtains for the expansion coefficients f_μ

$$i\hbar \frac{\partial}{\partial t} f_\mu = \sum_\nu H_{\mu\nu}^{(0)} f_\nu \quad (5.1)$$

or, considering the simple structure of $H_{\mu\nu}^{(0)}$ for the present case,

$$\frac{\partial}{\partial t} f_\mu = -i\omega_\mu f_\mu - i \sum_N v_{\mu, \hat{m}N} f_{\hat{m}N}. \quad (5.2)$$

The solution of these equations is equivalent to the solution of the RDM equations in the limiting case of infinite lifetime of the vibrational quanta. Therefore the results of the foregoing paper can be used to corroborate the validity of the present calculation in the case of small vibrational damping rates.

In [25] we introduced reduced quantities in scaling all energies with respect to the energy of a vibrational quantum $\hbar\omega_v$ and in renormalizing the time with respect to the vibrational period $1/\omega_v$. The same reduced quantities will be used here. The system is characterized by the parameters $\alpha = v/\omega_v$ and the electron-vibration coupling constants which will be taken symmetrically as $-g_1 = g_2 = g > 0$. The electronic energy levels of the two centers are set equal ($\varepsilon_1 = \varepsilon_2$) in correspondence to Ref. [25].

Although only two parameters (α and g) remain a rich scenario of charge motion can be studied by varying the type of initial state. A pronounced transition from charge localization at the initially occupied center to

charge oscillation between the two centers appears in the intermediate case $\alpha=1$ for the coupling $g=2$.

Using the well-known localization parameter $v/2g^2\omega_v$ for the characterization of the system one expects strong localization for the above-mentioned parameter values because $v/2g^2\omega_v = \frac{1}{8}$. Localizing the electron initially at center 1 without any vibrational quantum we are in the region of nuclear tunneling. Because of weak tunneling in the present case the electron remains localized up to $t \cong 190/\omega_v$. Exciting two or three vibrational quanta one enters the region of activated transfer where the activation energy $N_0\hbar\omega_v$ (N_0 is the number of initially excited vibrational quanta) becomes comparable to the so-called polaron shift $\hbar\omega_v g^2$. Now, the electron oscillates between the two centers with a frequency roughly given by the Franck-Condon factor (4.2) for a horizontal transition $F_{FC}(N_0, N_0; 2g)$. This oscillation is usually called coherent charge motion.

Increasing the coupling to the environment (decreasing the vibrational lifetimes) these oscillations are masked by the intracenter relaxation down the ladder of vibrational states. Such a relaxation destroys the phase coherence of the electronic motion between the two centers. The transfer dynamics changes to the incoherent type (hopping motion) for which one expects an exponential time dependence of the occupation probabilities P_m .

For a numerical integration of the equations of motion (4.16) one has to reduce the infinite set of equations to a finite number. Therefore we introduce an upper limit for the number of vibrational states N_{\max} . The remaining contributions to the equations of motion will be dropped. We choose $N_{\max}=20$. A dynamic system with $(2^*N_{\max})^2=1600$ degrees of freedom results. This number follows if one takes into account that the RDM splits into a real and an imaginary part and has the property $\rho_{\mu,\nu}^* = \rho_{\nu,\mu}$.

The chosen number for N_{\max} is sufficient to allow a stable solution of the equations of motion with a standard Runge-Kutta method of fourth order up to times of $t=200/\omega_v$. The stability has been proven by checking the conservation of the total probability $\sum_{\mu} \rho_{\mu\mu} = P_1 + P_2 = 1$. This equation could be fulfilled with an accuracy of 10^{-5} .

As demonstrated during the derivation of the rate equations in Secs. IV B and IV C one can drop the quadratic contribution to the equations of motion (4.16) in a first approximation. The resulting linearized RDM equations will be used throughout the present analysis. A detailed discussion of the quadratic terms with respect to the RDM will be given elsewhere.

For all calculations discussed in the following the initial state has been prepared as an eigenstate of center 1 with N_0 excited vibrational quanta

$$|\Psi(t=0)\rangle = S^\dagger(g_1)|N_0\rangle|g_1\rangle. \quad (5.3)$$

The corresponding initial values of the RDM read

$$\rho_{\mu\nu}(0) = \delta_{\mu,\nu} \delta_{m,1} \delta_{M,N_0}. \quad (5.4)$$

In the numerical calculations we have investigated three

different types of quantities, the electronic occupation probabilities (2.16), the expectation value Q of the interaction coordinate (2.17)

$$\begin{aligned} Q &= 2 \sum_{\mu} (\sqrt{M+1} \text{Re} \rho_{\mu+1,\mu} - g_m \rho_{\mu,\mu}) \\ &= 2 \sum_{\mu} \sqrt{M+1} \text{Re} \rho_{\mu+1,\mu} + 2g(2P_1 - 1), \end{aligned} \quad (5.5)$$

and the mean number of vibrational quanta

$$\begin{aligned} W &= \langle C^\dagger C \rangle \\ &= \sum_{\mu} [(M + g_m^2) \rho_{\mu,\mu} - 2g_m \sqrt{M+1} \text{Re} \rho_{\mu+1,\mu}]. \end{aligned} \quad (5.6)$$

The time dependence of Q completes the description of the transfer dynamics by P_1 and P_2 . Moreover, the quantity W indicates the exchange of energy between the dimer and the environment. The initial values of Q and W are given according to the initial values (5.4) of the RDM as

$$Q(0) = -2g_1 = 4 \quad (5.7)$$

and

$$W(0) = N_0 + g_1^2 = N_0 + 4. \quad (5.8)$$

$Q(0)$ is the equilibrium position of the interaction coordinate in the isolated monomer 1. The appearance of g_1^2 indicates that W has been defined with respect to the vibrational quanta of the dimer without the excess electron, i.e., the basis of the oscillatory states corresponding to the harmonic potential centered at $Q=0$. The temperature of the environment has been taken as $k_B T = 0.1\hbar\omega_v$ reflecting a high-frequency vibration in the dimer.

The results are ordered with respect to N_0 and the coupling strength to the environment. In Fig. 1 we present the occupation probability of center 1 for different values of the scaled spectral density $a(\omega_v)/\omega_v$ [see Eq. (4.14)]. The considered time region extends up to $t_{\max} = 50/\omega_v$. This range is sufficient to display the different dynamic behavior in the following cases.

For $N_0=0$ and in the weak-dephasing limit $a/\omega_v = 10^{-3}$ [full curve in Fig. 1(a)] the electron remains localized at center 1 during the time interval considered. Such a localization appears because the Franck-Condon factor of the vibrational ground states $F_{FC}(0,0;2g)$ is small for the actual values of the electron-vibration coupling. Increasing the coupling to the environment the localization is removed. In the case of three initially excited vibrational quanta ($N_0=3$) we reach the region of activated transfer: the occupation probability oscillates with a frequency of about $F_{FC}(3,3;2g)\omega_v$ as shown in Fig. 1(b) (see also [25]). The damping of the oscillations is of minor importance in the time region considered.

Taking a value of a/ω_v below 10^{-3} one can definitely reproduce the results of the solution of the time-dependent Schrödinger equation (5.2) in [25]. As expected, the time dependence of P_m becomes independent of the initial state in the case of large damping rates [com-

pare the dashed and dash-dotted curves in Figs. 1(a) and 1(b)]. For these examples the characteristic time of intracenter relaxation $\tau_{\text{rel}}=1/\gamma(\omega_v)$ amounts to $\omega_v t \simeq 2\omega_v/2\pi a \simeq 1.59$ and 0.159 , respectively. Since we consider a symmetric model for the dimer the electronic occupation probability becomes distributed uniformly over both centers with the asymptotic values $P_m(\infty)=\frac{1}{2}$.

The above-discussed low-temperature examples display charge-transfer dynamics accompanied by relaxation processes dominated by emission processes of environmental quanta. Considering temperatures of $k_B T \approx \hbar\omega_v$ with pronounced absorption processes the time dependence of P_m does not change significantly. Furthermore, one can also notice only minor differences if one compares the results of Fig. 1 with the corresponding results of the foregoing paper [18] in which we used a somewhat different type of RDM equations and a reduced interaction-coordinate environment coupling (see also the discussion in Sec. IV).

To complete the results of Fig. 1 we display in Figs.

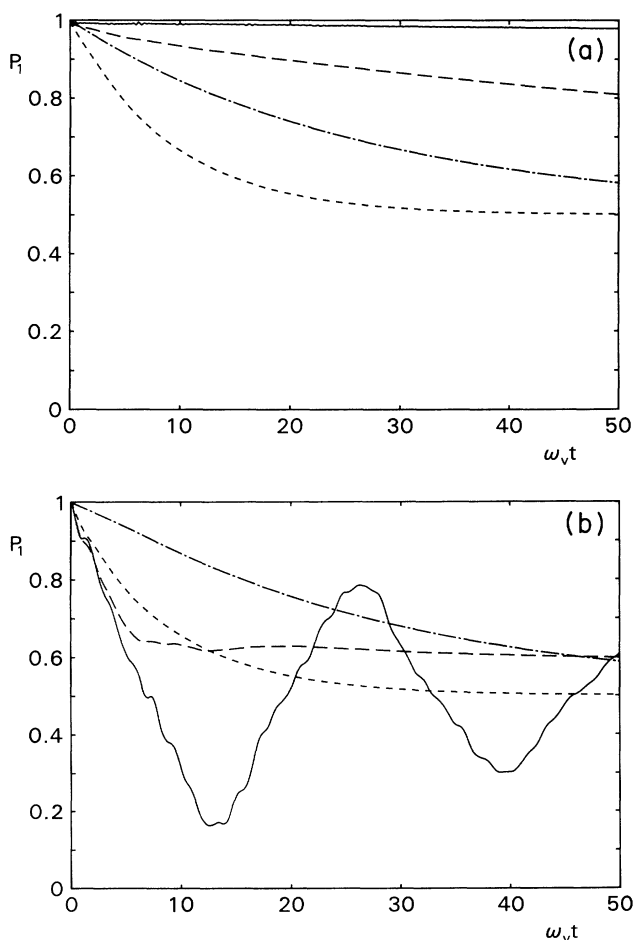


FIG. 1. Electronic occupation probability at center 1 vs scaled time $\omega_v t$ for $k_B T = 0.1\hbar\omega_v$, $a/\omega_v = 10^{-3}$ (full line), 10^{-2} (long-dashed line), 0.1 (dashed line), and 1 (dash-dotted line); the number of initially excited vibrational quanta is (a) $N_0 = 0$, (b) $N_0 = 3$.

2(a) and 2(b) the corresponding time dependence of the interaction coordinate. Using the initial condition $N_0 = 0$ the already discussed localization behavior of the charge for large vibrational lifetimes can be observed as weak oscillations of Q around the initial value of 4. Increasing a/ω_v this behavior changes to a diffusive one with the asymptotic value $Q(\infty) = 0$ corresponding to the symmetric dimer model.

Contrarily, for $N_0 = 3$ we observe large oscillations of Q for $a/\omega_v = 10^{-3}$ [full curve of Fig. 2(b)]. These oscillations are in phase with the corresponding oscillations of P_m . For larger values of the electronic intercenter coupling (approaching the case of adiabatic electron transfer) the electron motion will become faster compared to the oscillations of Q , so that P_m will be out of phase with the oscillations of Q .

Increasing a/ω_v above the value of 0.01 the motion of Q becomes diffusivelike. The time dependence of Q (like that of P_1) is independent of the initial condition for the two smallest values of the vibrational lifetimes.

If one carefully compares the curves of P_1 and Q one can notice the importance of the off-diagonal elements of the RDM. In Eq. (5.5) Q was defined by means of the RDM. If the off-diagonal elements $\text{Re}\rho_{\mu+1,\mu}$ are of minor importance the time dependence of Q follows that of P_1 scaled by the factor $4g$ [second contribution in Eq. (5.5)]. This can be seen for $a/\omega_v = 0.01$ and 0.1 for both cases $N_0 = 0$ and 3 . In contrast, for the case $a/\omega_v = 1$

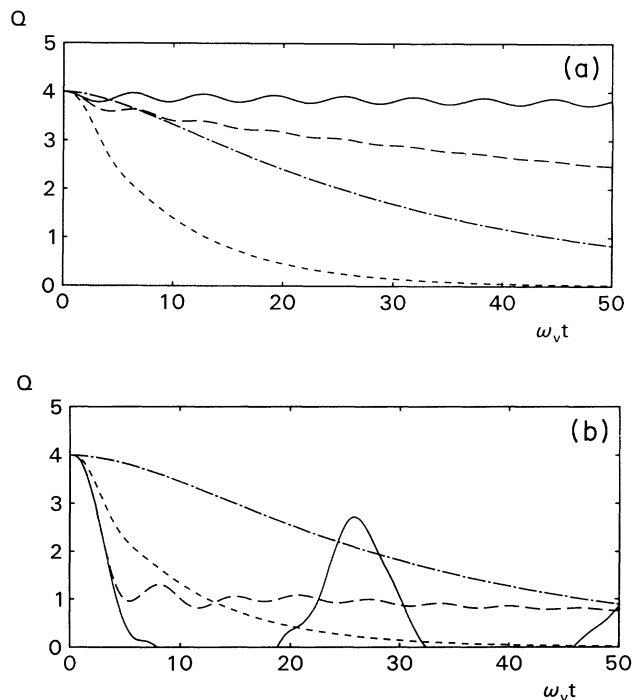


FIG. 2. Expectation value Q of the interaction coordinate vs scaled time $\omega_v t$ for $k_B T = 0.1\hbar\omega_v$, $a/\omega_v = 10^{-3}$ (full line), 10^{-2} (long-dashed line), 0.1 (dashed line), and 1 (dash-dotted line); the number of initially excited vibrational quanta is (a) $N_0 = 0$, (b) $N_0 = 3$.

there are systematic deviations.

A further noticeable result is the behavior of P_1 and Q in the case $N_0=3$ and $a/\omega_v=0.01$. Both quantities reach a plateau value in the considered time region. If one extends the calculations to larger times ($t=200/\omega_v$, not shown here) one observes a very slow relaxation [compared to $1/\gamma(\omega_v)=15.9/\omega_v$] to the asymptotic values $P_1(\infty)=\frac{1}{2}$ and $Q(\infty)=0$. Such a slowing down indicates the existence of a critical region of the intracenter relaxation processes.

The relaxation processes as well as the energy exchange with the environment are also reflected in the time dependence of the mean number of vibrational quanta W (see Fig. 3). For the case $N_0=3$ one can notice the relaxation behavior starting from the initial value 7 according to Eq. (5.8). The relaxation becomes faster as a/ω_v is increased.

However, the asymptotic values of W depend on the magnitude of a/ω_v , in contrast to first expectations. Irrespective of the contribution g^2 , W should reach a thermal occupation $n(\omega_v)$. Due to the low value of the temperature in the present case this would mean $W(\infty)=4$.

For $N_0=3$, however, $W(\infty)$ decreases with increasing a/ω_v . Furthermore, W rises in time for $N_0=0$, except in the case of $a/\omega_v=1$. The values of $W(\infty)$ coincide for the two different initial conditions as they should, but this cannot yet be seen for the smaller damping rates in the time interval presented in Fig. 3. The dependence of $W(\infty)$ on a/ω_v is shown in Fig. 4. The curve levels off

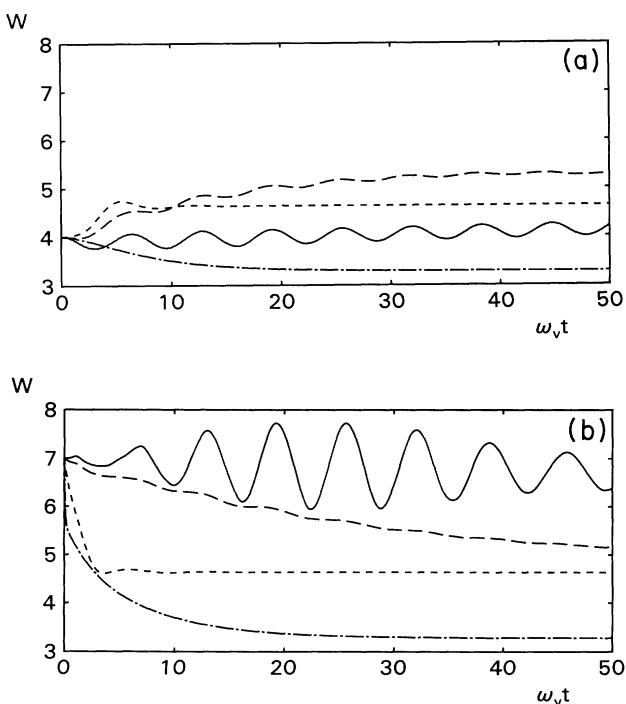


FIG. 3. Expectation value W of the number of vibrational quanta vs scaled time $\omega_v t$ for $k_B T=0.1\hbar\omega_v$, $a/\omega_v=10^{-3}$ (full line), 10^{-2} (long-dashed line), 0.1 (dashed line), and 1 (dash-dotted line); the number of initially excited vibrational quanta is (a) $N_0=0$, (b) $N_0=3$.

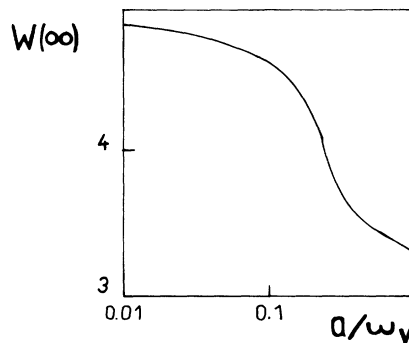


FIG. 4. Asymptotic expectation value $W(t \rightarrow \infty)$ of the number of vibrational quanta vs a/ω_v for $k_B T=0.1\hbar\omega_v$.

for low values of a/ω_v . In conclusion, $W(\infty)$ becomes independent of a/ω_v for very low damping rates. To understand this behavior it is useful to discuss the transfer dynamics presuming that the eigenvalue problem of the electron-vibration system of the dimer

$$E f_\mu = \sum_\nu H_{\mu\nu}^{(0)} f_\nu \quad (5.9)$$

has been solved. In the case of weak coupling to the environment the time dependence of P_m , Q , and W can be interpreted by taking into account that the system has been initially prepared in a monomer state which is not identical with the eigenstates of the coupled monomers in the dimer.

This becomes obvious for the time dependence of P_1 in the case $N_0=3$. In the energy range in which the vibrational states of the two monomers overlap strongly, the spectrum of the coupled system is very different from the monomer spectra; hence large oscillations occur. (The localization behavior of P_1 for $N_0=0$ indicates that the reconstruction of the vibrational ground states of the monomer in the coupled system is of minor importance.) Similar oscillations can be observed for the corresponding time development of Q and W .

However, if a/ω_v is increased these oscillations are damped out. Now, the dynamic behavior of the system features a relaxation of the different quantities from their initial values to the values corresponding to the lowest eigenstate of the coupled system. This value is larger than 4 in the case of W . Accordingly, W relaxes to this value in the case of an intermediate coupling to the environment for $N_0=3$. A respective increase of W occurs for $N_0=0$.

If such a reasoning is true the asymptotic values of W should coincide with $g^2 + n(\omega_v)$ for weak electronic intercenter coupling. Figure 5 shows $W(t)$ for the same values of a/ω_v as in Fig. 3 but for the intercenter coupling $\alpha=0.1$. Now, the usual relaxation behavior towards $W(\infty) \approx 4$ is obtained.

Let us return to the original case of $\alpha=1$. If we further increase the coupling to the environment the quantity a/ω_v not only determines the swiftness of the relaxation but also influences the spectrum of the coupled sys-

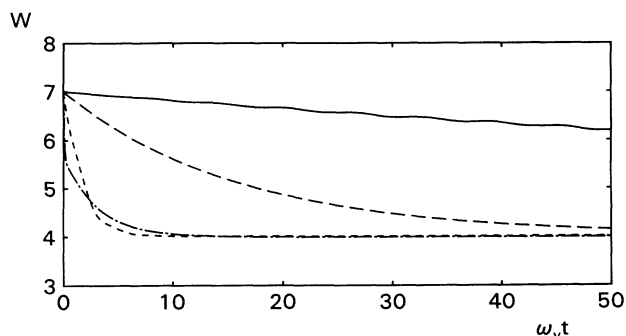


FIG. 5. Expectation value W of the number of vibrational quanta vs scaled time $\omega_v t$ for $k_B T = 0.1 \hbar \omega_v$ and intercenter coupling $\alpha = 0.1$; $a/\omega_v = 10^{-3}$ (full line), 10^{-2} (long-dashed line), 0.1 (dashed line), and 1 (dash-dotted line); the number of initially excited vibrational quanta is $N_0 = 3$.

tem of monomers in the dimer. This combined influence of the intermediate value of the electronic intercenter coupling and the large value of the coupling to the environment determines the further decrease of $W(\infty)$ with increasing a/ω_v . We note that in the case $a/\omega_v = 1$ the linewidth of the vibrational states amounts to $2\pi\omega_v$ overcoming the energetic separation of the vibrational levels.

The obtained characteristics of the transfer dynamics in the case of a large coupling to the environment coincide with the deviation of the time dependence of P_1 from that given by the rate equation (4.27). Such a deviation should be expected if one remembers that the derivation of the "golden-rule" rate coefficients (4.30) requires $\gamma/\omega_v \ll 1$.

For a detailed comparison we return to the data in Fig. 1(a). Since the solution of the rate equation results in an exponential time dependence we have plotted $\ln[P_1 - P_1(\infty)]$ versus time [remember $P_1(\infty) = \frac{1}{2}$] in Fig. 6. One notes the overall exponential decrease of P_1 . Figure 7 displays the derivatives of these curves which

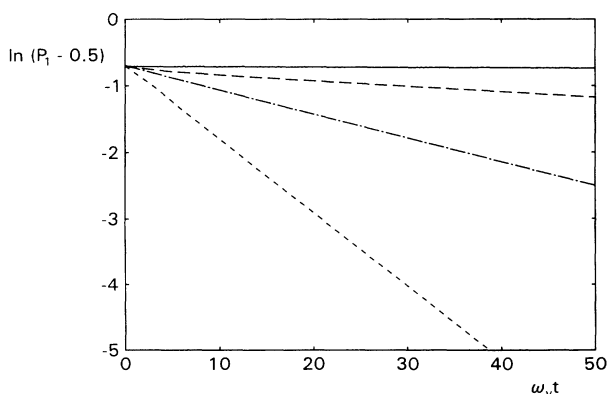


FIG. 6. Logarithmic plot of the electronic occupation probability at center 1 determined from the density-matrix equations (4.16) vs scaled time $\omega_v t$ for $k_B T = 0.1 \hbar \omega_v$; $a/\omega_v = 10^{-3}$ (full line), 10^{-2} (long-dashed line), 0.1 (dashed line), and 1 (dash-dotted line); the number of initially excited vibrational quanta is $N_0 = 0$.

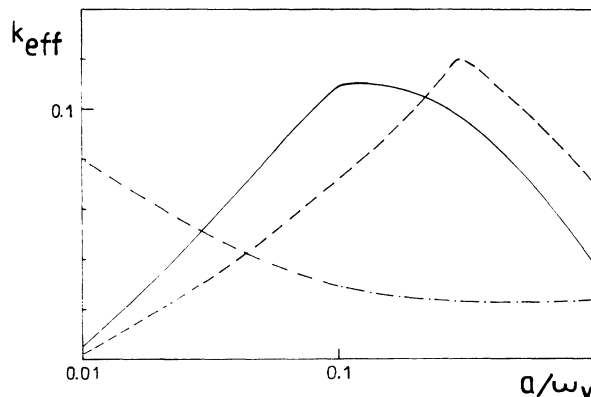


FIG. 7. Effective rate coefficients vs a/ω_v given by the derivatives of the curves in Fig. 6 (full line), the derivatives of P_1 in Eq. (4.32) (dashed line), and the "golden rule" (4.30) (dash-dotted line).

are nothing but effective rate coefficients k_{eff} versus a/ω_v . The respective coefficients for P_1 obtained from Eq. (4.32) and the standard rate coefficients (4.30) are shown for comparison. It is obvious that the "golden-rule" rate coefficients provide an incorrect description in the considered case of intermediate electronic intercenter coupling.

VI. CONCLUSIONS

A general approach to study the charge-transfer dynamics in molecular complexes has been presented. We started with the formulation of a general model of molecular complexes which comprises (a) different localization centers for the excess electrons, (b) molecular vibrations (along so-called interaction coordinates) coupling to the transferred electron, and (c) environmental degrees of freedom (further molecular vibrations) which only couple to the interaction coordinates and provide dissipative surroundings for the charge transfer.

Using a special method of quantum statistics (the nonequilibrium Green's-function technique) equations of motion for the density matrix of coupled electron-vibration states (the Born-Oppenheimer states of the electronic localization centers) could be derived. The environment has been taken into account via correlation functions. The corresponding expressions are valid for any type of interaction-coordinate environment coupling.

The obtained type of density-matrix equations is appropriate for further analytical studies as well as for numerical computations. The equations allow the consideration of any strength of the electronic intercenter coupling and any strength of electron-vibration coupling. Therefore nonadiabatic electron transfer, adiabatic transfer, and the intermediate transfer regime can be described.

Numerical calculations for the charge-transfer dynamics have been presented for the minimal model of a dimer with a single molecular vibration and a linear interaction between this vibration and the environmental degrees of freedom. The necessary restriction to a finite number of excited vibrational states maps the infinite number of

density-matrix equations onto a linear dynamic system with 1600 degrees of freedom in the present case.

Using an intermediate value of the electronic intercenter coupling (i.e., of the transfer integral) the change from the coherent, wavelike motion to the incoherent, hoppinglike motion upon increasing coupling to the environment has been demonstrated in detail. The relatively large value of the intercenter coupling strongly influences the details of the dynamics. For large values of the coupling to the environment the asymptotically approached states of the dimer strongly depend on the magnitude of this coupling.

The description of the charge transfer in using standard "golden-rule" rate expressions fails for the value of the electronic intercenter coupling used.

It should be noted here that the investigations are not primarily devoted to explaining experimental results, but to demonstrating how the density-matrix equations work in the simplest conceivable case, and to clarifying details of the already complicated dynamics. More complex systems, e.g., those with two or three interaction coordinates and a nonlinear coupling to the environment, will be discussed in the near future.

Nevertheless, the investigation of the simple dimer case has to be continued, too. We plan further investigations concerning the solution of the eigenvalue problem of the dimer and the quadratic contributions in the density-matrix equations.

APPENDIX: EQUATION OF MOTION FOR THE INTERACTION COORDINATE

To obtain a deeper understanding of the RDM equations it is instructive to employ them to derive equations

$$\left[\frac{\partial}{\partial t} - i\omega_v \right] \sum_{\mu} \sqrt{M+1} \rho_{\mu+1,\mu} = -i \sum_{\mu,N} (v_{\mu,\hat{m}N} \rho_{\mu+1,\hat{m}N} - v_{\hat{m}N,\mu+1} \rho_{\hat{m}N,\mu}) - \frac{1}{2} [\gamma(\omega_v) - \gamma(-\omega_v)] \sum_{\mu} \sqrt{M+1} (\rho_{\mu+1,\mu} - \rho_{\mu,\mu+1}) \quad (\text{A6})$$

and

$$\frac{\partial}{\partial t} \sum_M \rho_{\mu,\mu} = 2 \sum_{M,N} \text{Im}(v_{\mu,\hat{m}N} \rho_{\mu,\hat{m}N}) \quad (\text{A7})$$

Combining Eqs. (A6) and (A7) leads to

$$\frac{\partial}{\partial t} z = i\omega_v (z + \sum_{m=1,2} g_m P_m) - \frac{1}{2} [\gamma(\omega_v) - \gamma(-\omega_v)] (z - z^*) \quad (\text{A8})$$

Note that the terms proportional to the Franck-Condon renormalized intercenter coupling compensate each other as can be seen using the relation (4.6b). Recalling the relations (A5) one reproduces Eq. (A2) for Q .

of motion for the expectation value of the interaction coordinate Q . As a reference let us first consider the equations for Q which follow from Heisenberg's equations of motion. According to the definition of the dimensionless interaction coordinate (4.4) the corresponding momentum operator reads

$$\Pi = -\frac{i\hbar}{2} (C - C^\dagger) \quad (\text{A1})$$

From Heisenberg's equations we obtain for the expectation values

$$\frac{d}{dt} Q = \frac{2\omega_v}{\hbar} \Pi \quad (\text{A2})$$

and

$$\frac{d}{dt} \Pi = -\frac{\hbar\omega_v}{2} Q - \hbar\omega_v \sum_{m(=1,2)} g_m P_m - \sum_{\xi} k_{\xi} q_{\xi} \quad (\text{A3})$$

It is the aim of the following derivation to show how the RDM equations reproduce these relations and how the contribution of the environment [the last term in Eq. (A3)] is reformulated.

For the present purposes it is convenient to start with the expectation value of the interaction coordinate operator C^\dagger ,

$$\langle C^\dagger \rangle = z(t) = \sum_{\mu} (\sqrt{M+1} \rho_{\mu+1,\mu} - g_m \rho_{\mu,\mu}) \quad (\text{A4})$$

Q and Π are obtained as

$$Q = z + z^*, \quad \Pi = \frac{i\hbar}{2} (z - z^*) \quad (\text{A5})$$

Using the RDM equations (4.16) in their linearized version we get

The contribution of the environment in Eq. (A3) for the momentum is replaced by the frictionlike term $-[\gamma(\omega_v) - \gamma(-\omega_v)]\Pi$. Alternatively, one can construct a second-order differential equation for Q ,

$$\left[\frac{\partial^2}{\partial t^2} + [\gamma(\omega_v) - \gamma(-\omega_v)] \frac{\partial}{\partial t} + \omega_v^2 \right] Q = -2\omega_v^2 \sum_{m=1,2} g_m P_m \quad (\text{A9})$$

This equation with the temperature-independent friction term looks very simple. However, the complicated dynamics displayed by the RDM equations (4.16) are now contained in the inhomogeneity of Eq. (A9).

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