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Rate concept and retarded master equations for dissipative tight-binding models

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Employing a "noninteracting-cluster approximation," the dynamics of multistate dissipative tight-binding models has been formulated in terms of a set of generalized retarded master equations. The rates for the various pathways are expressed as power series in the intersite couplings. We apply this to the superexchange mechanism, which is relevant for bacterial photosynthesis and bridged electron transfer systems. This approach provides a general and unified description of both incoherent and coherent transport.

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The problem of a tight-binding (TB) particle coupled to a thermal bath has attracted a lot of recent attention. It is of relevance for a great variety of transport processes in chemistry and physics. The simplest case of two states (popularized as the spin-boson model) has been studied exhaustively, both analytically [1] and numerically [2]. Of particular conceptual importance was the development of a simple and powerful approximation, the "noninteracting-blip approximation" (NIBA) by Leggett *et al.* [1]. In this Rapid Communication, we present a generalization of this idea for the case of a dissipative system with N arbitrary tight-binding sites, based on a "noninteracting-cluster approximation" (NICA).

A multistate system with three states ($N=3$) is of special interest for an understanding of the ultrafast primary electron transfer (ET) in bacterial photosynthesis [3]. Nature designs the photosynthetic reaction center with a bridging electronic state between the donor and the acceptor chromophores and optimizes the energetics and the influence of the surrounding protein environment to produce a remarkable quantum yield near unity. Describing the reaction center by a dissipative three-state model, one may then ask for possible transfer mechanisms between the relevant chromophores. Similarly, in bridged ET reactions [4], the transfer of an electron from a donor to an acceptor state occurs via a bridge. The bridge may consist of one or several molecular units, and inclusion of the solvent environment leads to a dissipative N-state system [5]. Such systems are important in molecular electronics [6], where one is interested in transferring electrons from donor to acceptor under controlled conditions; e.g., by applying an external signal to the bridge. Our method allows for a classification and calculation of possible transfer rates and their bridge-length dependence [7]. Finally, multistate dissipative TB models have also been used widely to study quantum diffusion and other quantum transport processes in condensed phase systems [8].

For a qualitative understanding of the environmental effects on the TB dynamics, we study the Hamiltonian $H=H_0+H_1$ (we put $\hbar=1$) with

$$H_0=\begin{pmatrix} E_1 & -K_{12} & \vdots & 0 & 0 \\ -K_{12} & E_2 & \vdots & 0 & 0 \\ \vdots & \vdots & & \vdots & \vdots \\ 0 & 0 & \vdots & E_{N-1} & -K_{N-1,N} \\ 0 & 0 & \vdots & -K_{N-1,N} & E_N \end{pmatrix}, \tag{1}$$

where the matrix elements $K_{j,j+1}$ describe tunneling between successive wells, and E_j are the binding energies. The dissipative environment is modeled by a term H_1 describing a harmonic oscillator bath and a bilinear coupling in the coordinates of the bath and of the TB particle [8,9]. All environmental effects are captured by the (twice-integrated) bath correlation function [1]

$$Q(t)=\frac{a^2}{\pi}\int_0^\infty d\omega \frac{J(\omega)}{\omega^2}\frac{\cosh[\omega\beta/2]-\cosh[\omega(\beta/2-it)]}{\sinh[\omega\beta/2]},$$

where $\beta=1/k_BT$, a is the intersite distance, and $J(\omega)$ is the spectral density. In the classical limit ($\beta\to 0$), the bath is completely described by one single parameter,

$$\Lambda=(a^2/\pi)\int_0^\infty d\omega\ \omega^{-1}J(\omega),$$

which in the context of conventional electron transfer theory is known as the bath reorganization energy [5]. The short-time behavior for $Q(t)$ is $Q(t)\approx(\Lambda/\beta)t^2+i\Lambda t$, whereas at long times and for Ohmic damping, the typical behavior is

$$S(t)\equiv \mathrm{Re}Q(t)\sim t, \quad R(t)\equiv \mathrm{Im}Q(t)\sim \mathrm{const} \tag{2}$$

for finite temperatures [1,8].

Suppose that at all times $t<0$ the particle is held at the site k with the bath having a thermal distribution. We then wish to compute the probability $P(n,t;k)$ for finding the particle at site n as a function of time $t>0$ for this factorizing initial condition. In order to eliminate the bath degrees of freedom, we employ Feynman-Vernon theory [10] which represents the diagonal elements of the reduced density matrix by the double path integral

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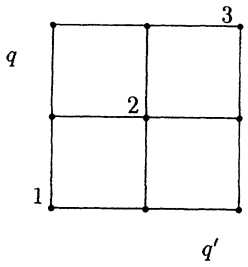

FIG. 1. The $N\times N$ states of the reduced density matrix in the q-q' plane for $N=3$. The diagonal states are labeled $1,\ldots,N$.

$$P(n,t;k)=\int \mathscr{D}q \int \mathscr{D}q' \exp(S_0[q,q']+\Phi[q,q']), \quad (3)$$

with S_0 being the bare action and Φ the influence functional. All paths contributing to Eq. (3) are subject to the constraints at the end points: $q(0)=q'(0)=ka$, $q(t)=q'(t)=na$.

The path integration in Eq. (3) can now be visualized as a summation over all pairs of discrete paths on the q-q' plane shown in Fig. 1. It is convenient to introduce sum and difference coordinates,

$$x(t')\equiv[q(t')+q'(t')]/a, \quad y(t')\equiv[q(t')-q'(t')]/a.$$

The diagonal states of the reduced density matrix are characterized by $y=0$, and we label them as "states" 1 through N (these should not be confused with the original sites of the TB model). All paths contributing to Eq. (3) start in diagonal state k and end in diagonal state n, making transitions along the lattice in Fig. 1. The total number of transitions is necessarily even; hence a path with $2m$ transitions at times $t_1, t_2, \ldots, t_{2m}$ can be parametrized by two sets of "charges" $\{\chi_1,\chi_2,\ldots,\chi_{2m}\}$ and $\{\xi_1,\xi_2,\ldots,\xi_{2m}\}$, each of which can take two possible values ± 1,

$$\dot{x}(t')=\sum_{j=1}^{2m} \chi_j\, \delta(t'-t_j), \quad \dot{y}(t')=\sum_{j=1}^{2m} \xi_j\, \delta(t'-t_j),$$

in such a way that the path is confined to the $N\times N$ lattice in Fig. 1 and has the end points fixed in the diagonal states k and n.

For each transition from site j to $j+1$ on the path q (q'), the bare action contributes a factor $+$ ($-$) $iK_{j,j+1}$. This results in a factor $A_m[\{\chi_j,\xi_j\}]$, which is essentially a product of $2m$ matrix elements $K_{j,j+1}$. The bare action also gives a bias factor of

$$B_m[\{\chi_j,\xi_j\}]=\exp\left(-i\sum_j \tau_j\,(E_{q_j}-E_{q_j'})\right)$$

for any duration τ_j the system spends in the (q_j,q_j') off-diagonal state along the path. Furthermore, the influence functional takes the form [1]

$$\Phi m[\{\chi_j,\xi_j\}]=\sum_{l=2}^{2m}\sum_{j=1}^{l-1} \xi_l S(t_l-t_j)\xi_j+i\xi_l R(t_l-t_j)\chi_j.$$

Summing over all orders m and all possible arrangements of charges subject to the constraint that the path remain on the $N\times N$ lattice, we finally obtain the exact formal expression

$$P(n,t;k)=\sum_{m=|n-k|}^{\infty}\int \mathscr{S}_{2m}\{t_j\}\sum_{\{\chi_j,\xi_j\}} A_m[\{\chi_j,\xi_j\}] \times B_m[\{\chi_j,\xi_j\}]\exp\Phi_m[\{\chi_j,\xi_j\}], \quad (4)$$

with the time-ordered integrations over the $2m$ flip times defined as

$$\int \mathscr{S}_{2m}\{t_j\}\equiv\int_0^t dt_{2m}\int_0^{t_{2m}} dt_{2m-1}\cdots\int_0^{t_2} dt_1.$$

This expression is of formidable appearance and in general does not allow for an exact evaluation.

To develop a useful approximation for the cumbersome expression (4), we first introduce some terminology. The ξ-charge configuration can be divided into subsets, each of which we call a *cluster*. Each cluster is a neutral sequence of contiguous ξ charges which sum to zero. In the path picture, a cluster corresponds to a segment of the path between two successive visits of any diagonal states. Two consecutive clusters are separated by a *sojourn*, which is the time the system spends in a diagonal state. In this language, any path is just a sequence of sojourns and clusters, where the ξ charges within each cluster sum to zero.

In general, the influence functional Φ_m couples the χ charges in each cluster with the ξ charges in all other clusters, and similarly the ξ clusters are coupled to each other. These interactions render the path summation intractable. To simplify (4), we introduce an approximation which we call the "noninteracting-cluster approximation." Within the NICA, *all intercluster interactions are neglected.* Then the integrations over the sojourn times in Eq. (4) appear as convolutions. Switching now to the Laplace transform $P(n,\lambda;k)$, we find that each sojourn simply contributes a factor of λ^{-1}, while each cluster gives a factor whose precise value depends on the number of charges and their configuration inside that particular cluster according to Eq. (4). The sum of all clusters that begin in diagonal state i and end in state j will then result in a *cluster function* $h_{ij}(\lambda)$.

Similar to the NIBA, the NICA can be justified in several physically distinct limits, and is expected to give accurate results in most of the rest [1]. The NICA reduces to the NIBA in the case $N=2$, as we shall show shortly. The central argument for the neglect of the intercluster interactions comes from the short-range character of the interactions between neutral objects like the clusters defined above. From the typical long-time behavior (2), one can verify that the intercluster interactions would indeed vanish because $\Sigma\xi_j=0$ within each cluster. Consequently, the NICA is expected to be an excellent approximation for the important case of Ohmic damping. This has been confirmed for the three-state problem by numerically exact quantum Monte Carlo simulations [11].

The NICA is able to describe quantum coherence as well as relaxational behaviors, thus providing a framework of

general applicability to open quantum systems. In addition, the Fermi distribution can be described by the Fourier transform of $\exp[-Q(t)]$ with $Q(t)$ in the Ohmic form as it results from the choice $J(\omega)=(\pi/a^2)\omega$ [8]. Hence, systems coupled to fermionic baths, such as single electron tunneling between nonsuperconducting leads, can also be treated by this formalism [12].

In practical calculations, one can obtain expressions for the cluster functions $h_{ij}(\lambda)$ by expanding Eq. (4) in the tunneling matrix elements. This yields the power series

$$h_{ij}(\lambda)=2\,\mathrm{Re}\sum_{m=|i-j|}^{\infty}\int_0^\infty d\tau_1\cdots\int_0^\infty d\tau_{2m-1}\times\exp[-\lambda(\tau_1+\cdots+\tau_{2m-1})]\sum_{\{\chi_j,\xi_j\}}\times A_m[\{\chi_j,\xi_j\}]B_m[\{\chi_j,\xi_j\}]\,\exp\Phi_m[\{\chi_j,\xi_j\}] \tag{5}$$

with the difference times $\tau_j\equiv t_{j+1}-t_j$. The sum over the charge configurations can be restricted to all paths in the upper diagonal of the lattice, since the corresponding mirror paths obtained by reflection across the diagonal are simply their complex conjugates.

By virtue of the NICA, every path can be topologically reduced to a sequence of clusters punctuated by sojourns. In terms of the cluster functions defined previously, the sum of all p-cluster diagrams contributing to $P(n,\lambda;k)$ is then given by

$$P^{(p)}(n,\lambda;k)=\sum_{s_1,s_2,\ldots,s_p}\frac{1}{\lambda}h_{k,s_1}\frac{1}{\lambda}h_{s_1,s_2}\cdots h_{s_p,n}\frac{1}{\lambda}, \tag{6}$$

where the sums run over all possible intermediate states $s=1,\ldots,N$. Defining the *cluster matrix* $\mathrm{H}(\lambda)$ with matrix elements $h_{ij}(\lambda)$, we can rewrite Eq. (6) as a matrix product

$$P^{(p)}(n,\lambda;k)=\frac{1}{\lambda}\{[\lambda^{-1}\mathrm{H}(\lambda)]^p\}_{nk}.$$

Summing finally over all p yields

$$P(n,\lambda;k)=\left(\frac{1}{\lambda-\Gamma(\lambda)}\right)_{nk}, \tag{7}$$

which can be inverse transformed to give a set of *generalized (retarded) master equations*

$$\frac{dP(n,t;k)}{dt}=\sum_{j=1}^{N}\int_0^t dt'\tilde{\Gamma}_{jn}(t-t')P(j,t';k), \tag{8}$$

where $\tilde{\Gamma}(t)$ is the inverse transform of the *rate matrix* $\Gamma(\lambda)$, whose elements are given by the cluster functions

$$\Gamma_{ij}(\lambda)=h_{ij}(\lambda), \tag{9}$$

and the initial conditions for (8) are $P(n,t=0;k)=\delta_{nk}$. Based on a projection operator formalism, a similar set of nonlocal master equations has been derived previously by Hu and Mukamel [13].

From the formal series (5) for the cluster functions, we observe that a symmetry relation holds for the cluster functions, $\Sigma_{j=1}^{N}h_{ji}(\lambda)=0$ for all i. This sum rule is valid *order by order* in Eq. (5). Consequently, the diagonal rates can be computed alternatively from $\Gamma_{ii}(\lambda)=-\Sigma_{j\neq i}\Gamma_{ji}(\lambda)$, and conservation of probability is fulfilled for Eq. (8) even when only lowest-order rates are used.

For the spin-boson model, $N=2$, and the relevant rates Γ_{12} and Γ_{21} consist of terms of order K_{12}^2 only,

$$\Gamma_{12}(\lambda)=2K_{12}^2\mathrm{Re}\int_0^\infty d\tau\, e^{-\lambda\tau+i(E_1-E_2)\tau-Q(\tau)},$$

since for $N=2$, the system necessarily returns to a diagonal state after every two transitions. One can easily check that this golden rule expression leads directly to the familiar noninteracting-blip approximation [1]. For $N>2$, terms of higher orders in K_{12} become important, because the system is no longer required to return to a diagonal state after every two transitions. For high enough temperatures or sufficiently strong system-bath coupling, the relaxation is frequency-independent, and Eq. (8) leads to the conventional local master equations with rate matrix $\Gamma(\lambda\to 0^+)$. In addition to the usual stepwise rates, Γ may contain important contributions from non-nearest-neighbor rates due to nonvanishing higher-order cluster matrix elements.

Now we apply this formalism to the dissipative three-state problem in Fig. 1. If the system starts in site $k=1$ at $t=0$, the efficiency of the transport is measured by $P(3,t;1)$. It is clear from our analysis that there are two types of cluster functions: (1) *incoherent (sequential) clusters* — these are Γ_{12} and Γ_{23} which describe stepwise transport via site 2, and (2) *a coherent (superexchange) cluster* — Γ_{13} which describes a direct transfer without any real population on the intermediate state [14].

The quantum-mechanical superexchange rate Γ_{13} can now be expanded in orders of the tunneling matrix elements. To lowest order, only four transitions are possible, with charge configurations,

$$\{\xi_j\}=(+,+,-,-),\quad \{\chi_j\}=(+,+,+,+),$$

plus its complex conjugate. This corresponds to the path that travels along the outer edges of the lattice from state 1 to state 3. We obtain from Eq. (5)

$$\Gamma_{13}(\lambda)=2K_{12}^2K_{23}^2\mathrm{Re}\int_0^\infty d\tau_1 d\tau_2 d\tau_3 e^{-\lambda(\tau_1+\tau_2+\tau_3)}\times\exp[Q^*(\tau_3)-Q(\tau_2+\tau_3)-Q(\tau_1+\tau_2+\tau_3)-Q(\tau_2)-Q(\tau_1+\tau_2)+Q(\tau_1)]\,\exp[-i(E_2-E_1)\times(\tau_1-\tau_3)-i(E_3-E_1)(\tau_2+\tau_3)]. \tag{10}$$

In the high-temperature limit, one can take the short-time expression for $Q(t)$ given earlier, yielding the *classical* superexchange rate $(\lambda\to 0^+)$

$$\Gamma_{13}=\tilde{K}_{13}^2\sqrt{\frac{\pi\beta}{4\Lambda}}\left(e^{-\beta F_{13}^*}-\frac{1}{2}\left[e^{-\beta F_+}+e^{-\beta F_-}\right]\right). \quad (11)$$

The effective superexchange coupling $\tilde{K}_{13}$ coincides with the matrix element given by Marcus [14]

$$\tilde{K}_{13}=K_{12}K_{23}/\delta E, \quad (12)$$

where $\delta E=E_2-(E_1+E_3)/2-\Lambda$. The classical activation free energy for the $1\to3$ step is [5]

$$F_{13}^*=[E_3-E_1+4\Lambda]^2/16\Lambda,$$

and the energies $F_\pm$ are defined by

$$F_\pm=[\delta E\pm(E_3-E_1+4\Lambda)/2]^2/4\Lambda.$$

The rate (11) is well defined for $\delta E\to0$, although the effective coupling $\tilde{K}_{13}$ is not; the superexchange rate has a maximum for this resonant situation. However, in that case the incoherent channel will cause an extremely efficient transfer as well, albeit with large population buildup in state 2. Therefore, the coherent contribution will only be important for a high-lying bridge for which the incoherent channel is energetically forbidden.

The above suggests that as long as the intermediate state is not accessible by thermal or quantal fluctuations, the superexchange rate (10) can be written in the form of the golden rule rate for an *effective two-state system* spanned by states 1 and 3. The effective superexchange rate would then be $(\lambda\to0^+)$

$$\Gamma_{13}^{\rm eff}=\tilde{K}_{13}^2\int_{-\infty}^{\infty}d\tau\,\exp[i(E_1-E_3)\tau-4Q(\tau)]. \quad (13)$$

For a high-lying intermediate state, the dominant contributions to the triple integral (10) come from $\tau_1,\tau_3\ll\tau_2$. Linearizing in τ_1 and τ_3, we then obtain directly Eq. (13) with the effective two-state coupling matrix element (12). The truncation of the dissipative three-state to a two-state system becomes more accurate at lower temperatures due to the absence of thermal fluctuations populating the intermediate state.

Finally, we stress that the retarded master equations (8) provide a unified treatment of the various competing pathways for coherent and incoherent tunneling in open quantum systems. This allows for a proper description of the turnover between sequential and superexchange behavior.

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