

# Quantum heat transfer: A Born-Oppenheimer method

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We develop a Born-Oppenheimer-type formalism for the description of quantum thermal transport across hybrid nanoscale objects. Our formalism is suitable for treating heat transfer in the off-resonant regime, where, e.g., the relevant vibrational modes of the interlocated molecule are high relative to typical bath frequencies, and at low temperatures when tunneling effects dominate. A general expression for the thermal energy current is accomplished in the form of a generalized Landauer formula. In the harmonic limit this expression reduces to the standard Landauer result for heat transfer. In the presence of nonlinearities, multiphonon effects are realized.

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## I. INTRODUCTION

Describing nonequilibrium transport in quantum models, incorporating many-body interactions, is a challenging problem. Theoretical treatments and numerical tools have been traditionally developed for examining the *charge transfer* scenario [1]. However, in recent years *thermal transport* in nanoscale objects has become a topic of major fundamental and practical interest, relevant, e.g., for realizing electronic and mechanical molecular devices [2], and for resolving mechanisms and pathways of energy flow in biomolecules [3]. In modeling such systems one typically considers an impurity object, a subsystem, e.g., a molecule, bridging two thermal reservoirs, representing solids or large residues in a protein, each maintained at a fixed temperature.

What tools are available for studying quantum heat transfer in interacting systems? While classical molecular dynamics simulations can incorporate anharmonic interactions to all orders [4,5], they are restricted to high temperatures. The alternative Green's function technique [6,7] describes quantum effects, however, anharmonicity is only perturbatively included. Mixed quantum-classical simulations [8,9] are valid only at high temperatures or at weak interactions. Furthermore, utilizing these approaches one typically gains only *numerical* results, impeding a clear resolution of transport mechanisms. Other tools of limited applicability are the generalized Langevin equation method [10,11], restricted to harmonic models, Schrödinger equation dynamics [12], suitable for a class of simple models, the master equation technique at weak [13] and intermediate [14] system-bath interactions, and exact quantum simulations on simplified models [15].

The Born-Oppenheimer (BO) approximation [16], recognizing time scale separation in molecular systems, is a cornerstone in quantum chemistry, allowing one to calculate molecular structure and dynamics. In this paper we adopt this principle and develop a general framework treating *quantum thermal transport* in (potentially strong) interacting systems driven to a steady state by a temperature bias. The method is applicable in the *off-resonant* regime, where the characteristic frequencies of the impurity object are high relative to the cutoff frequencies of the reservoirs, or the baths' temperatures are low, below the subsystem energy spacing [17]. For instance,

consider an electronic spin surrounded by nuclear spins subjected to an external field, a molecule of high vibrational frequency coupled to solids with low Debye frequencies, or a high-frequency heat source inside a protein with low-frequency bonds as thermometers [18]. Our method provides transparent analytical results, allowing a clear resolution of transport mechanisms: For weakly coupled (subsystem-bath) setups we develop a compact expression for the heat current in the form of the generalized Landauer formula. For harmonic models this expression reduces to the elastic Landauer's result [19]. In the presence of nonlinear interactions contributions of multiphonon processes are clearly identified.

## II. MODEL AND METHOD

Consider a small subsystem placed in between two thermal reservoirs with each maintained at a fixed temperature  $T_\nu$  ( $\nu = L, R$ ) (see Fig. 1). The total Hamiltonian is given by

$$H = H_S(q) + H_L(Q_L) + H_R(Q_R) + V_L(q, Q_L) + V_R(q, Q_R), \quad (1)$$

where  $H_S(q)$  is a subsystem Hamiltonian,  $H_\nu(Q_\nu)$  stands for the  $\nu$  heat bath, and  $V_\nu(q, Q_\nu)$  separately couples the subsystem and the  $\nu$  reservoir. The coordinates  $Q_L$  and  $Q_R$  are vectors, consisting of many environmental degrees of freedom (DOF). Similarly,  $q$  may enclose several subsystem DOF. Note that  $q$  and  $Q$  both include displacements and momenta. In particular, a bipartite interaction model is assumed,  $V_\nu(q, Q_\nu) = S(q)B_\nu(Q_\nu)$ , with  $S$  as a subsystem operator and  $B_\nu$  an operator in terms of the reservoirs' coordinates.

### A. Adiabatic evolution and the Born-Oppenheimer approximation

In isolated molecules, the "traditional" BO approximation relies on the mass separation of electrons and atomic nuclei. In this context, one assumes that the electron cloud instantly adjusts to changes in the nuclear configuration, and that the nuclei propagate on a single potential energy surface associated with a single electronic quantum state.

Here we utilize this principle in the context of nonequilibrium nanoscale energy transfer. Consider the Hamiltonian

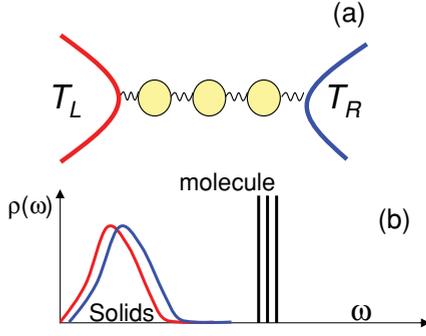


FIG. 1. (Color online) (a) A scheme of our setup (top), including a subsystem, e.g., a molecular chain, connecting two solids. Panel (b) exemplifies the vibrational spectra  $\rho(\omega)$  of the isolated solids and molecule, demonstrating that the characteristic frequencies of the impurity object are high relative to the cutoff frequencies of the reservoirs.

(1) in an off-resonance limit, where the subsystem characteristic frequencies are *high* relative to the frequencies of the reservoirs [17]. This implies a time scale separation, as the subsystem dynamics is fast, while the bath motion is slow. A BO-type approximation can thus be employed following two consecutive steps. First, the fast variable is considered: We solve the subsystem eigenproblem fixing the reservoirs configuration, acquiring a set of potential energy surfaces which parametrically depend on bath coordinates. In the second step we adopt the adiabatic approximation and assume that the baths' coordinates, the slow variables, evolve without changes on the subsystem state. We then solve the vibrational heat transfer problem from  $L$  to  $R$ , on a fixed potential surface. We now follow this procedure using the generic Hamiltonian (1). Fixing the bath coordinates, we define the “fast” Hamiltonian ( $Q$  counts DOF from both reservoirs)

$$H_f(q, Q) = H_S(q) + \sum_{\nu} V_{\nu}(q, Q_{\nu}), \quad (2)$$

and solve the time-independent Schrödinger equation

$$H_f(q, Q)|g_n(q, Q)\rangle = W_n(Q)|g_n(q, Q)\rangle, \quad (3)$$

to acquire a set of “potential energy surfaces”  $W_n$ , and states  $|g_n(q, Q)\rangle$ . As we exemplify below,  $W_n$  mixes the left and right system-bath interaction terms in a nontrivial way. Assuming that the surfaces are well separated, we make the adiabatic ansatz and write the total density matrix as

$$\rho(t) = |g_n(q, Q)\rangle \rho_B^n(Q, t) \langle g_n(q, Q)|, \quad (4)$$

where the bath density matrix obeys the Liouville equation

$$\rho_B^n(Q, t) = e^{-iH_{\text{Bo}}^n t} \rho_B(0) e^{iH_{\text{Bo}}^n t}, \quad (5)$$

$\hbar \equiv 1$ , with the effective Hamiltonian

$$H_{\text{Bo}}^n = H_L(Q_L) + H_R(Q_R) + W_n(Q_L, Q_R). \quad (6)$$

Here  $\rho_B(0) = \rho_L \times \rho_R$  is a factorized initial condition with  $\rho_{\nu} = e^{-H_{\nu}/T_{\nu}} / \text{Tr}_{\nu}[e^{-H_{\nu}/T_{\nu}}]$ , the equilibrium-canonical distribution function of the  $\nu$  bath. Thus, in our scheme, as we propagate the *baths'* density matrix on a particular potential energy surface  $W_n$ , an explicit study of the subsystem motion is not required, unlike standard master equation methods

[13–15,20]. Equation (5) dictates a correlated dynamics for the reservoirs, leading to the generation of quantum entanglement. In what follows, we assume that the baths evolve on the ground potential surface, thus we discard the index  $n$  in Eqs. (4)–(6). For brevity, we also omit references to coordinates.

## B. Heat current

We now study the heat transfer dynamics within the effective Hamiltonian (6). In steady state, the heat current operator, e.g., at the  $L$  contact, can be defined as [21]

$$\hat{J}_L = i[H_L, W], \quad (7)$$

with the expectation value

$$J_L(t) = \text{Tr}[\hat{J}_L \rho_B(t)] = \text{Tr}[e^{iH_{\text{Bo}} t} \hat{J}_L e^{-iH_{\text{Bo}} t} \rho_B(0)]. \quad (8)$$

The left expression is written in the Schrödinger picture; the second is in the Heisenberg representation. The trace is performed over the two baths' degrees of freedom. When system-bath couplings, absorbed into  $W$ , are weak, the time evolution operator can be approximated by the first order term

$$e^{-iH_{\text{Bo}} t} = e^{-i(H_L + H_R)t} \left( 1 - i \int_0^t W(\tau) d\tau \right), \quad (9)$$

and the current (8) reduces to

$$J_L(t) = -i \int_0^t \text{Tr}[\{\hat{J}_L(\tau), W\} \rho_L \rho_R] d\tau. \quad (10)$$

Here  $W(\tau)$  and  $\hat{J}_L(\tau)$  are interaction picture operators,  $O(t) = e^{iH_B t} O e^{-iH_B t}$  with  $H_B = H_L + H_R$ . We are interested in steady state quantities,  $J = J_L(t \rightarrow \infty)$ , if the limit exists. Expression (10) can be further customized, recalling the bipartite interaction model for the original Hamiltonian (1), by formally expanding  $W$ , the eigensolution in Eq. (3), in terms of  $B_{\nu}$ ,

$$\begin{aligned} W &= \sum_{a,b} \alpha_{L,a} \alpha_{R,b} B_L^a \otimes B_R^b \\ &= \sum_{a,b} \sum_{k,m} \sum_{p,s} \alpha_{L,a} \alpha_{R,b} (B_L^a)_{km} (B_R^b)_{ps} |kp\rangle \langle ms|. \end{aligned} \quad (11)$$

The coefficients  $\alpha_{L,a}$  and  $\alpha_{R,b}$  absorb the subsystem parameters. The powers  $a$  and  $b$  are integers.  $|k\rangle$  and  $|m\rangle$  are the many-body states of the left reservoir with energies  $E_k$  and  $E_m$  (i.e.,  $H_L = \sum E_k |k\rangle \langle k|$ ). Similarly,  $|p\rangle$  and  $|s\rangle$  are the many-body states of the right reservoir with energies  $E_p$  and  $E_s$ . It can be shown that terms containing contributions of either  $B_L$  or  $B_R$  do not add to the current, thus only compound terms are taken into account. Returning to Eq. (10), and employing Eq. (11), we obtain

$$\begin{aligned} J &= \frac{1}{Z_L Z_R} \sum_{a,b} \sum_{a',b'} \int_0^{\infty} dt \left[ \sum_{k,m} E_{km} e^{iE_{km}t} \alpha_{L,a} \alpha_{L,a'} (B_L^a)_{km} \right. \\ &\quad \times (B_L^{a'})_{mk} e^{-\beta_L E_k} \sum_{p,s} \alpha_{R,b} \alpha_{R,b'} (B_R^b)_{ps} \\ &\quad \left. \times (B_R^{b'})_{s,p} e^{iE_{ps}t} e^{-\beta_R E_p} + \text{c.c.} \right], \end{aligned} \quad (12)$$

where, e.g.,  $Z_L = \sum_k e^{-\beta_L E_k}$  is the  $L$  bath partition function;  $\beta_\nu = 1/T_\nu$ ,  $k_B \equiv 1$ , and  $E_{km} = E_k - E_m$ . Time integration can be readily performed, leading to the steady state heat current

$$J = \frac{1}{2\pi} \sum_{a,b} \sum_{a',b'} \int_0^\infty \omega d\omega [k_{L+}^{(a,a')}(\omega) k_{R-}^{(b,b')}(\omega) - k_{L-}^{(a,a')}(\omega) k_{R+}^{(b,b')}(\omega)], \quad (13)$$

where the sum over the pairs  $(a,b)$  and  $(a',b')$  is determined by the particular expansion (11). The excitation (+) and relaxation (−) rates are given by

$$k_{L\pm}^{(a,a')}(\omega) = 2\pi \sum_{k,m} \alpha_{L,a} \alpha_{L,a'} [(B_L^a)_{km} (B_L^{a'})_{mk}]^\pm \times \delta(E_k - E_m \mp \omega) \frac{e^{-\beta_L E_k}}{Z_L}, \quad (14)$$

satisfying detailed balance,  $k_{L+}^{(a,a')}(\omega) = k_{L-}^{(a',a)}(\omega) e^{-\beta_L \omega}$ . We have introduced here the short notation  $[(B_L^a)_{km} (B_L^{a'})_{mk}]^+$  to denote matrix elements when  $E_k > E_m$ . Similarly,  $[(B_L^a)_{km} (B_L^{a'})_{mk}]^-$  describes the  $E_k < E_m$  case. Analogous expressions hold for the  $R$  rates.

Equation (13), a “generalized Landauer formula” [19], is the main result of our paper. The net heat current is given as the difference between left-moving and right-moving excitations; nevertheless, unlike the original treatment [19], this formula can incorporate *anharmonic interactions* absorbed inside the rates  $k_{v\pm}(\omega)$  in a *nonperturbative way*. We emphasize the broad status of Eq. (13): It does not assume a particular subsystem or a specific system-bath interaction form,  $B_\nu$ , both contained in  $W$ . It is valid as long as (i) there exists a time scale separation between the subsystem motion (fast) and the reservoirs dynamics (slow), and (ii) system-bath interactions, given in a bipartite form, are weak [see Eq. (9), [22]].

### III. EXAMPLES

We apply our general result (13) on several models of particular interest: (a) a fully harmonic model, (b) adopting nonlinear system-bath interactions, and (c) assuming a spin subsystem, representing an anharmonic impurity.

#### A. Harmonic model

We show that Eq. (13) reduces into the standard Landauer’s result for harmonic systems [10,19]. In second quantization, the elements of Eq. (1) take the form

$$H_\nu = \sum_{j \in \nu} \omega_j b_{\nu,j}^\dagger b_{\nu,j}, \quad H_S = \Omega b^\dagger b, \quad V_\nu = S B_\nu, \quad (15)$$

$$S = (b^\dagger + b), \quad B_\nu = \sum_{j \in \nu} \lambda_{\nu,j} (b_{\nu,j} + b_{\nu,j}^\dagger).$$

The subsystem comprises a single mode of frequency  $\Omega$ ,  $b_{\nu,j}^\dagger$  ( $b_{\nu,j}$ ) are the creation (annihilation) operators of the mode  $j$  in the  $\nu$  bath, and  $b^\dagger$  and  $b$  are the respective subsystem operators.  $\lambda_{\nu,j}$  are system-bath interaction energies. Solving

the eigenproblem (3), we obtain the ground-state potential surface

$$W = \frac{\Omega}{2} - \frac{B_\Sigma^2}{\Omega}, \quad B_\Sigma = B_L + B_R, \quad (16)$$

including the zero-point motion. In practice, only terms melding the  $L$  and  $R$  baths’ DOF contribute to the current. The mixed term here is  $-2B_L B_R / \Omega$ , thus the expansion (11) comprises a single element, with  $\alpha_{L,1} = \alpha_{R,1} = i\sqrt{\frac{2}{\Omega}}$  and  $a = b = 1$ . This leads to the transition rates [Eq. (14)],

$$k_{v+}^{(1,1)}(\omega) = \frac{2}{\Omega} \Gamma_\nu(\omega) n_\nu(\omega), \quad (17)$$

$$k_{v-}^{(1,1)}(\omega) = \frac{2}{\Omega} \Gamma_\nu(\omega) [n_\nu(\omega) + 1],$$

where  $n_\nu(\omega) = [e^{\omega/T_\nu} - 1]^{-1}$  is the Bose-Einstein distribution function and  $\Gamma_\nu(\omega) = 2\pi \sum_{j \in \nu} \lambda_{\nu,j}^2 \delta(\omega - \omega_j)$  encloses the interaction strength. Using these rates, the expectation value of the current [Eq. (13)] reduces to

$$J = \frac{2}{\pi} \int_0^\infty \frac{\Gamma_L(\omega) \Gamma_R(\omega)}{\Omega^2} [n_L(\omega) - n_R(\omega)] \omega d\omega. \quad (18)$$

This is the celebrated Landauer formula for heat conduction [19] in the BO limit, assuming the relevant subsystem’s frequency is above the populated baths’ modes, further utilizing the weak-coupling approximation [Eq. (9)]. It can be obtained from the exact result

$$J = \frac{2}{\pi} \int \mathcal{T}(\omega) [n_L(\omega) - n_R(\omega)] \omega d\omega, \quad (19)$$

with  $\mathcal{T}(\omega) = \frac{\omega^2 \Gamma_L \Gamma_R}{[(\omega^2 - \Omega^2)^2 + (\Gamma_L + \Gamma_R)^2 \omega^2]}$  [10], when (i)  $\Gamma_\nu < \Omega$  (weak coupling) and (ii)  $\Omega \gg \omega_c$  (off-resonance condition). Here  $\omega_c$  is the reservoirs’ cutoff frequency [17]. For convenience, we omit the reference to frequency in  $\Gamma_\nu(\omega)$ . Note that in the opposite limit, when the baths’ spectral window extends the molecular vibrations,  $\omega_c \gg \Omega$ , the exact result (19) reduces to a resonant energy transfer expression,  $J = \Omega \frac{\Gamma_L \Gamma_R}{\Gamma_L + \Gamma_R} [n_L(\Omega) - n_R(\Omega)]$ ; here  $\Gamma_\nu$  is evaluated at the (local oscillator) frequency  $\Omega$ . This expression describes a *hopping motion*, with energy flowing sequentially from the  $L$  bath into the subsystem, then into the  $R$  contact. This process is dictated by the subsystem energetic window, yielding  $J \propto \Omega$ . In contrast, Eq. (18) accounts for a *coherent*, deep tunneling energy transfer mechanism and the current decays with the energetic barrier as  $J \propto 1/\Omega^2$ .

#### B. Nonlinear system-bath interactions

We next generalize the harmonic result by modifying the model (15), replacing the interaction operator  $B$  by an exponentially repulsive form

$$B_\nu = e^{-\sum_j \lambda_{\nu,j} (b_{\nu,j}^\dagger + b_{\nu,j})}, \quad (20)$$

appropriate for the relevant off-resonance case [23]. Formally, the ground state potential surface is still given by Eq. (16), with the newly defined  $B_\nu$ . For simplicity, we assume an (identical) Einstein-type model for the reservoirs spectra, represented by

a single frequency  $\omega_B$ . Under this assumption, the relevant rates [Eq. (14)] are given by [23]

$$k_{v\pm}^{(1,1)}(\omega) = \frac{2}{\Omega} \sum_{p=0}^{\infty} 2\pi \frac{\lambda_v^{2p}}{p!} \sum_{s=0}^p \frac{p!}{(p-s)!s!} [n_v(\omega_B) + 1]^s \times n_v(\omega_B)^{p-s} \delta(\mp\omega - (2s-p)\omega_B). \quad (21)$$

Assuming that  $\lambda$  is small, we maintain only single-phonon and two-phonon contributions, resulting in the heat current

$$J = \frac{8\pi}{\Omega^2} \left\{ \omega_B \lambda_L^2 \lambda_R^2 (n_L - n_R) + \frac{(2\omega_B)\lambda_L^4 \lambda_R^4}{4} \times [n_L^2 (n_R + 1)^2 - n_R^2 (n_L + 1)^2] \right\}. \quad (22)$$

The Bose-Einstein functions are evaluated at frequency  $\omega_B$ . This expression generalizes the harmonic result (18), accommodating multiphonon processes; the second term describes tunneling of a two-phonon combination.

### C. Anharmonic subsystem

We next investigate the heat current behavior in the eminent spin-boson model. We modify Eq. (15) by using  $H_S = \frac{\epsilon}{2}\sigma_z$ ,  $S = \sigma_x$ , representing a nonlinear impurity bilinearly coupled to two phonon baths. Recent studies have analyzed this model perturbatively [13,14] and have simulated it exactly [15]. Solving Eq. (3), the lowest potential surface is given by ( $B_\Sigma = B_L + B_R$ )

$$W = -\sqrt{B_\Sigma^2 + \epsilon^2/4} = -\epsilon/2 - B_\Sigma^2/\epsilon + B_\Sigma^4/\epsilon^3 + \dots, \quad (23)$$

thus, to first order, the heat current is identical to the harmonic result [Eq. (18)], with  $\epsilon$  replacing  $\Omega$ . Incorporating the next term,  $\propto B_\Sigma^4/\epsilon^3$ , the current (13) includes, besides single-phonon effects, contributions from multiphonon processes. For example, the product  $k_{L-}^{(2,2)}(\omega)k_{R-}^{(2,2)}(\omega)$  is responsible for the absorption or scattering of two phonons in the left bath,

$$k_{L-}^{(2,2)}(\omega) \propto \frac{1}{\epsilon^3} \sum_{l,l'} [1 + n_L(\omega_l)][1 + n_L(\omega_{l'})] \delta(\omega - \omega_l - \omega_{l'}) + \frac{1}{\epsilon^3} \sum_{l,l'} 2[1 + n_L(\omega_l)]n_L(\omega_{l'}) \delta(\omega - \omega_l + \omega_{l'}), \quad (24)$$

followed by a two-phonon emission process at the right end. Figure 2 presents the frequency components of the heat current [the integrand of Eq. (13)], where we assume a spectral density,  $S(\omega) = \sum_j \lambda_{v,j}^2 \delta(\omega - \omega_j)$ , peaked around a specific bath frequency,  $\omega_B = 2$ , with a hard cutoff at  $\omega = 3$  [see panel (a)]. We identify three contributions in  $J(\omega)$ : A dominant, single-phonon element at  $\omega \sim \omega_B$ , a weak two-phonon contribution at  $\omega \sim 2\omega_B$ , and a rudimentary three-phonon current [see panel (b)]. Weaker system-bath interactions, reflected in smaller  $S(\omega)$  values, will further minimize the contribution of multiphonon processes. We note that in the resonant regime, when a hopping mechanism dominates, the heat current across harmonic junctions is *higher*

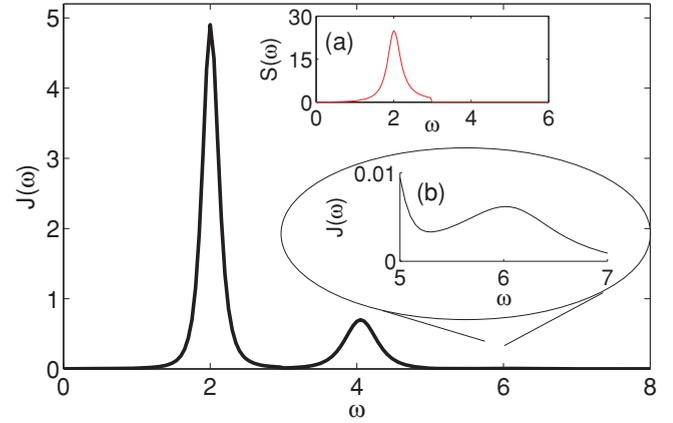


FIG. 2. (Color online) Frequency components of the heat current  $J(\omega)$ , for a spin subsystem bilinearly coupled to heat baths. Multiphonon processes are observed [see also panel (b)]. The parameters  $\epsilon = 6$ ,  $T_L = 1$ , and  $T_R = 0.5$  were used with the bath spectral function  $S(\omega)$ , depicted in panel (a), identical at the two ends.

than its anharmonic counterpart due to a saturation effect [13]. In contrast, in the off-resonance case anharmonicity *enhances* the current allowing for multiphonon processes. Similar conclusions were drawn in a classical heat transfer study [24].

### IV. SUMMARY

We have presented here a general BO-type formalism for describing heat transfer in nonequilibrium interacting quantum systems. In the applicable nonresonant limit energy propagates across the structure in a tunnelinglike motion, keeping the subsystem population intact. In the weak-coupling limit a compact expression for the thermal current has been accomplished, bearing the structure of a generalized Landauer relation, yet incorporating multiphonon effects. In the harmonic limit our formula reduces to known results. Admitting anharmonic effects, we have reached simple analytic expressions, reflecting the underlying transport mechanisms. For molecular chains, the scaling of the thermal conductance with length and internal interactions could be readily determined, reflected in the potential energy surface  $W$ . The inclusion of nonadiabatic effects by utilizing a surface hopping approach [25] will be the subject of future studies. The method described here is complementary to existing techniques, which are treating anharmonicity perturbatively [6] or enforcing a Markovian approximation [13]. By incorporating quantum effects and nonlinearities it opens new ways for describing vibrational or electronic energy dynamics in organic materials [26], biomolecules [3], and superconductors [27].

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