Quantum heat transfer: A Born Oppenheimer method

Lian-Ao Wu\textsuperscript{1} and Dvira Segal\textsuperscript{2}
\textsuperscript{1}\textit{Department of Theoretical Physics and History of Science, The Basque Country University (EHU/UPV) and IKERBASQUE – Basque Foundation for Science, 48011, Bilbao, Spain}
\textsuperscript{2}\textit{Chemical Physics Group, Department of Chemistry and Center for Quantum Information and Quantum Control, University of Toronto, 80 St. George street, Toronto, Ontario, M5S 3H6, Canada}

We develop a Born-Oppenheimer type formalism for the description of quantum thermal transport along 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 isolated 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, while in the presence of nonlinearity multiphonon tunneling effects are realized.

PACS numbers: 63.22.-m, 44.10.+i, 05.60.Gg, 66.70.-f

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure1.png}
\caption{A Scheme of our setup (top), including a subsystem, e.g., a molecular chain, connecting two solids. The bottom panel exemplifies the vibrational spectra \( \rho(\omega) \) of the isolated solids and molecule.}
\end{figure}

Introduction.— Thermal transport in molecular objects has recently become a topic of major interest, relevant for designing electronic and mechanical nanoscale devices \cite{1}, and for resolving mechanisms and pathways of energy flow in biomolecules \cite{2}. In modelling such systems we typically consider an impurity object, a subsystem, e.g., an alkane molecule \cite{3}, bridging two thermal reservoirs, representing solids or large residues in a protein, maintained each at a fixed temperature. Various treatments have been developed for simulating the thermal conduction properties of such structures, either classically \cite{4}, or in the quantum regime \cite{5,6}. Among these treatments are the generalized Langevin equation method \cite{7,8}, the Kinetic-Boltzmann theory \cite{9}, mode coupling theory \cite{10}, the non-equilibrium Green’s function technique \cite{6,11}, classical \cite{4} and mixed classical-quantum \cite{6,12} molecular dynamics simulations, and exact quantum simulations on simplified models \cite{13}.

The master equation technique at weak system-bath coupling is of particular interest \cite{14}, allowing to obtain simple analytical results in interesting limits \cite{15}, guiding experimentalists and motivating theoreticians in developing more detailed treatments \cite{13}. In this approach the heat current is described by sequential \textit{incoherent} emission and absorption processes, relaying on a resonance condition. Thus, a finite conductance exists only when the frequencies of the two thermal reservoirs match the subsystem characteristic frequency. Nevertheless, in many systems the characteristic frequencies of the impurity object are high relative to the cutoff frequencies of the reservoirs. 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 \cite{16}. Developing a general formalism that can treat such scenarios, providing simple analytical results and bringing in physical insight, is of a great importance.

Here we describe a new formalism for treating quantum thermal transport in such \textit{non-resonant} systems, where subsystem’s frequencies, relevant for thermal transfer, are \textit{above} the reservoirs spectral window, or the baths temperatures are low, below the subsystem energy spacing \cite{17}. Using a Born-Oppenheimer (BO) type approximation we develop a compact expression for the heat current in the form of a generalized Landauer formula \cite{18}. For harmonic systems we recover the elastic Landauer formula. When nonlinear interactions persist multiphonon processes contribute to the thermal current.

Model.— Consider a small subsystem, representing e.g., a molecule, placed in between two thermal reservoirs (e.g., solids) maintained each at a fixed temperatures \( T_{\nu} (\nu = L, R) \), see Fig. \textsuperscript{1}. The total Hamiltonian is given by

\begin{equation}
H = H_{S} + H_{L} + H_{R} + V_{L} + V_{R},
\end{equation}

where \( H_{S} \) is the Hamiltonian of the subsystem and \( H_{\nu} \) stands for the \( \nu \) heat bath. \( V_{L} (V_{R}) \) couples separately the subsystem and the left (right) reservoir. The subsystem and the two reservoirs’ Hamiltonians assume diagonal forms, and we consider a bipartite form, \( V_{\nu} = S B_{\nu} \). Here \( S \) is a subsystem operator and \( B_{\nu} \) is an operator in terms of the \( \nu \) bath degrees of freedom. In particular, it is useful to study two extreme realizations for the subsystem. In the first case nonlinear interactions are incorporated by adopting a two-level system (TLS) model \cite{13}, \( S = \sigma_{x} \), \( H_{S} = \frac{1}{2} \sigma_{z} \). In the second model the subsystem is represented by a single harmonic mode linearly coupled to
the baths, $S = b + b^\dagger$, $H_S = \Omega b^\dagger b$. Here $b^\dagger (b)$ is the bosonic creation (annihilation) operator.

**Adiabatic evolution and the Born-Oppenheimer approximation.** — Consider the nonresonant case where the subsystem characteristic frequencies are high relative to the frequencies of the reservoirs. This implies a timescale 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 $B_L$. In the second step we assume that the baths dynamics evolves on the ground potential surface, and solve the vibrational heat transfer problem, form $L$ to $R$. Next we follow this procedure using the generic Hamiltonian. Beginning with the fast contribution, we diagonalize

$$H_g = H_S + S B; \quad (B = B_L + B_R), \quad (2)$$

and acquire the potential surface $W$. For example, for a TLS subsystem we resolve $|g(B_L)\rangle = c_0|0\rangle + c_1|1\rangle$ as the ground state of $H_g$; $c_{0,1}$ are the superposition coefficients, functions of $B$ and $\epsilon$, with the eigenenergy $W = -\sqrt{|\epsilon/2|^2 + B^2} = -\epsilon/2 - B^2/4 + O(\epsilon^3/4^3)$. For an harmonic oscillator model we exactly obtain $W = \frac{\Omega^2}{\pi} - \frac{B^2}{2\pi}$, including the zero-point motion. We assume next that the total density matrix is initially factorized,

$$\rho(0) = |g(B_0)\rangle \langle g(B_0)|, \quad (3)$$

where $\rho_B(0) = \rho_L \times \rho_R$; $\rho_0 = e^{-\frac{W_0}{\beta}}/\text{Tr}_\nu[e^{-\frac{W_0}{\beta}}]$ is the equilibrium-canonical distribution function of the $\nu$ bath. Time evolution is dictated by the Liouville equation

$$\rho(t) = e^{-iHt} \rho(0) e^{iHt} \approx |g(B_t)\rangle e^{-iH_{BO}t} \rho_B(0) e^{iH_{BO}t} \langle g(B_t)|, \quad (4)$$

where the second step is justified under the BO approximation with the effective Hamiltonian

$$H_{BO} = H_L + H_R + W. \quad (5)$$

Thus, the reduced density matrix of the reservoirs, $\rho_B(t) = \text{Tr}_S \rho(t)$, where the trace is performed over the subsystem degrees of freedom, evolves as

$$\rho_B(t) = e^{-iH_{BO}t} \rho_B(0) e^{iH_{BO}t}. \quad (6)$$

In the present scheme we thus propagate the bath coordinates along the subsystem potential energy surface $W$, and an explicit study of the subsystem motion is not required, unlike the typical situation in other approaches. We identify the operator $W$ as an interaction term directly connecting the two reservoirs. Note that in the original model, Eq. 1, $W$ is linear in $B$, additive in the $L$ and $R$ coordinates. In contrast, under the approximation we obtain a potential energy surface $W$ which is often nonlinear in $B$, mixing the left and right reservoirs’ coordinates in a nontrivial way.

**Heat current.** — The heat current operator, between the two reservoirs, can be defined as

$$\hat{J}_L = i[H_L, W]/2. \quad (7)$$

For example, for a harmonic subsystem we recover $\hat{J}_L = -\frac{1}{\Omega}(BP_L + P_L B)$, while for a TLS subsystem $\hat{J}_L \approx -\frac{1}{\Omega}(BP_L + P_L B)$ when $B/\epsilon \ll 1$; $P_L = i[H_L, B_L]$. The current operator in both cases is identical in the first order of $B/\epsilon$. Generally, the expectation value of the current is

$$J_L(t) = \text{Tr}[[\hat{J}_L(t), W] \rho_B(0)]/\text{d}t, \quad (8)$$

where 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.

**First Order Current.** — When system-baths couplings, absorbed in $W$, are weak, the time evolution operator can be approximated by the first order term

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

and the current reduces to

$$J_L(t) = -i \int_0^t \text{Tr}[[\hat{J}_L(\tau), W] \rho_B(0)] d\tau, \quad (10)$$

where $W(\tau)$ and $\hat{J}_L(\tau)$ are interaction picture operators, $A(t) = e^{iH_{BO}t} A e^{-iH_{BO}t}$ with $H_B = H_L + H_R$. We are mostly interested in steady state quantities, $J = J_L(t \to \infty)$, if the limit exists. This expression can be further customized by using a diagonal form for the reservoirs, e.g., for the $L$ bath we write, $H_L = \sum E_k |k\rangle \langle k|$, and by expanding the potential surface in the left bath $(L)$ and right $(R)$ bath operators, functions of $B_L$, $W = \sum \sum L^a \otimes R^b = \sum \sum \sum \sum L^a_{k,m} R^b_{k,m,p,s} |kp\rangle \langle m|s|. \quad (11)$

$|k\rangle$ and $|m\rangle$ are the many body states of the left reservoir with energies $E_k$ and $E_m$; $|p\rangle$ and $|s\rangle$ are the many body states of the right reservoir with energies $E_p$ and $E_s$. The interaction $W$ sums (nonseparable) contributions from the two reservoirs, $a$ and $b$ are integers. For example, for the harmonic subsystem with bilinear coupling $W = -B^2/\Omega = -(B_L^2 + B_R^2 + 2B_L B_R)/\Omega$. It can be shown that terms containing either $L$ or $R$ operators do not add to the current, as only mixed terms account. Therefore, in the case of a harmonic subsystem a single term contributes to (11) with $L^1 = iB_L \sqrt{2/\Omega}$ and $R^1 = iB_R \sqrt{2/\Omega}$. Back to (10), employing (11), we accede to the steady state heat current

$$J = \frac{2\pi}{Z_L Z_R} \sum \sum \sum E_{km} \left| L^a_{km} \right|^2 \left| R^b_{ps} \right|^2 \times \delta(E_{km} + E_{ps}) e^{-\beta L E_k - \beta R E_p}$$

$$= \frac{2\pi}{Z_L Z_R} \sum \sum \sum \left( \left| L^a_{km} \right|^2 \left| R^b_{ps} \right|^2 - \left| L^{-a}_{km} \right|^2 \left| R^{+b}_{ps} \right|^2 \right) \times \delta(E_{km} - E_{ps}) e^{-\beta L E_k - \beta R E_p}, \quad (12)$$
where $E_{km} = E_k - E_m$ and, e.g., $Z_L = \sum_k e^{-\beta L E_k}$ is the L bath partition function. Here $L^{\pm}\alpha = (L^\pm)^*\alpha$ denotes matrix elements when $E_k > E_m$ ($E_k < E_m$). We identify next the Fermi-like golden rule excitation (+) and relaxation (–) rates, e.g., at the L contact, by

$$ k^\pm_{L,a}(\omega) = 2\pi \sum_{l,m} |L^\pm a_{l,m}|^2 \delta(E_k - E_m \mp \omega) e^{-\beta L E_k} Z_L, \quad (13) $$

satisfying detailed balance, $k^+_L(a)(\omega) = k^-_L(a) e^{-\beta L \omega}$. We can therefore reduce Eq. (12) into the compact form

$$ J = \frac{1}{2\pi} \sum_{a,b} \int_0^\infty \omega d\omega k^-_L(\omega) k^-_R(\omega)(e^{-\beta L \omega} - e^{-\beta R \omega})(14) $$

where the sum over $a$ and $b$ is determined given a particular $W$. This is the main result of our paper. We refer to this expression as the "generalized Landauer formula" \cite{18}, as the net heat current is given by the difference between left-moving and right-moving excitations. Nevertheless, our formula can incorporate anharmonic interactions, absorbed in the rates $k^\pm_{L,a}(\omega)$ unlike the original treatment \cite{18}. We emphasize the broad status of Eq. (14). It was derived without specifying the subsystem Hamiltonian or the system-bath interaction form, both contained in $W$. It is valid as long as (i) there exists a timescale separation between the subsystem motion (fast) and the reservoirs dynamics (slow), and (ii) system-bath interaction is weak, see Eq. (9). In what follows we apply Eq. (14) on some models of particular interest: a fully harmonic model, a nonlinear model with strong system-bath interactions, and utilizing a spin subsystem, representing a nonlinear impurity.

**Harmonic model.**— We consider first a harmonic model, $H = H_L + H_R + V_L + V_R + H_S$, with

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

and show that Eq. (14) reduces to the standard elastic limit \cite{7,18}. Here the subsystem comprises a single mode of frequency $\Omega$. $b^\dagger_{\nu,j}$ ($b_{\nu,j}$) are the creation (annihilation) operators of the mode $j$ in the $\nu$ bath, $b^\dagger$ and $b$ are the respective subsystem operators. $\lambda_{\nu,j}$ are system-bath interaction energies, $S$ is a subsystem operator. The expectation value of the current can be calculated either by following Eq. (10) in the long time limit, or by directly applying Eq. (14), as we do next. In the occupation number representation the many body states of the L reservoir are $|m\rangle = |m_1, m_2, \ldots, m_L\rangle$ with $m_l$ excitations for the $l$ mode. Since $W = -B^2/\Omega$, the relevant matrix elements in (11) are

$$ |L^\pm_{1m}| = \sqrt{\frac{2\pi}{\Omega}} \sum_l \lambda_{1,l} \sqrt{m_l + 1} \delta_{k_l, m_l+1} + \sqrt{m_l} \delta_{k_l, m_l-1}. $$

An analogous expression exists for $R^1_L$. We thus identify the excitation and relaxation rates in Eq. (13) by

$$ \Omega \Gamma_\nu(\omega) n_\nu(\omega) $$

and

$$ k^-_\nu(\omega) = \frac{\Omega}{\pi} \Gamma_\nu(\omega) n_\nu(\omega) + 1, $$

respectively, where $n_\nu(\omega) = [e^{\nu / T_\nu} - 1]^{-1}$ is the Bose-Einstein distribution function and $\Gamma_\nu(\omega) = 2\pi \sum_{j \in \nu, k} \lambda^2_{\nu,j} \delta(\omega - \omega_j)$. Using these rates the current (14) reduces to

$$ J = \frac{2}{\pi} \int_0^\infty \frac{\Gamma_L(\omega) \Gamma_R(\omega)}{\Omega^2} [n_L(\omega) - n_R(\omega)] \omega d\omega, \quad (16) $$

This is the Landauer’s formula for heat conduction \cite{18} in the BO limit; assuming the system frequency is above the baths spectral window, further utilizing the weak-coupling approximation [Eq. 9]. Beyond this limit, the heat current for the harmonic model (15) is exactly given by

$$ J = \frac{2}{\pi} \int \mathcal{T}(\omega) [n_L(\omega) - n_R(\omega)] \omega d\omega, \quad (17) $$

with the transmission coefficient $\mathcal{T}(\omega) = \frac{\pi^2 \Gamma_L(\omega) \Gamma_R(\omega)}{\Omega^2}$. The rate $\Gamma_\nu$ has been defined above Eq. (16); for convenience we discard the direct reference to frequency. In the weak coupling limit, $\Gamma_\nu < \Omega$, the transmission coefficient is sharply peaked around $\Omega$. In the nonresonant case $\Omega \gg \omega_\nu$, where $\omega_\nu$ is the reservoirs cutoff frequency, $\mathcal{T}(\omega) \sim \frac{\Gamma_L(\omega) \Gamma_R(\omega)}{\Omega^2}$ and Eq. (16) is recovered. In the opposite limit, when the baths spectral window overlap with the molecular vibrations, $\omega_\nu \gg \Omega$, Eq. (17) reduces into a resonant energy transfer expression, $J = \Omega \frac{\Gamma_L(\omega) \Gamma_R(\omega)}{\Omega^2} [n_L(\Omega) - n_R(\Omega)]$. Here $\Gamma_L$ is calculated 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 $J \propto 1/\Omega^2$.

**Anharmonic models.**— We generalize next the harmonic result by modifying the model (15), adopting an exponentially repulsive interaction,

$$ B_\nu = e^{-\sum \lambda_\nu (b^\dagger_{\nu,j} + b_{\nu,j})}, \quad (18) $$

appropriate for the relevant nonresonant case \cite{20}. As before, diagonalizing $H_g = H_S + V_L + V_R$, we obtain the potential surface $W = -B^2/\Omega$; $B = B_L + B_R$, controlled by the bipartite term $2B_L B_R/\Omega$. 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 excitation/relaxation rates [Eq. (13)] are given by

$$ \Omega \Gamma_\nu(\omega) n_\nu(\omega) $$

and

$$ k^-_\nu(\omega) = \frac{2}{\pi} \sum_{l=0}^{\infty} \frac{\lambda^2_{\nu,l} \sum_{s=0}^{l} \frac{l!}{(l-s)!}[n_\nu(\omega_B) + 1]^s}{l + 1} \times \left[ n_\nu(\omega_B) + 1 \right]^{l-s} \delta(\omega - (2s - l)\omega_B). \quad (19) $$

Assuming $\lambda$ is small, we enclose only single-phonon and two-phonon contributions in (14), yielding the heat current

$$ J = \frac{8\pi}{\Omega^2} \left\{ \omega_B^2 \lambda^2_L \lambda^2_R [n_L(n_L + 1) - n_R(n_R + 1)] + \frac{(2\omega_B)\lambda^4_L \lambda^4_R}{4} [n_L^2(n_L + 1)^2 - n_R^2(n_R + 1)^2] \right\}. \quad (20) $$
The Bose-Einstein functions are evaluated at the frequency \( \omega_B \). This expression presents a generalization to the harmonic result \( \sigma_0 \), accommodating multiphonon processes; the second term describes tunneling of a two-phonon combination.

The starting point of our next anharmonic model is again Eq. (15), utilizing a two-level subsystem, \( H_S = \frac{1}{2} \sigma_{x} \), representing a nonlinear impurity bilinearly coupled to bath phonons. In this case we resolve \( W = -\sqrt{B^2 + \epsilon^2} \), thus the first order current is identical to the harmonic result \( \sigma_0 \), with \( \Omega \) replaced by \( \epsilon \). Incorporating the next term in the expansion, \( W \sim \epsilon/2 - B^2/\epsilon + B^4/\epsilon^3 \), we get

\[
J = \frac{1}{2\pi} \int_0^\infty \omega d\omega (e^{-\beta_L \omega} - e^{-\beta_R \omega}) \left[ k_L^{-1}(\omega)k_R^{-1}(\omega) + \right. \\
\left. k_L^{-2}(\omega)k_R^{-2}(\omega) + k_L^{-1}(\omega)k_R^{-1}(\omega) + k_L^{-1}(\omega)k_R^{-3}(\omega) \right] (21)
\]

The first term in the square brackets describes a single phonon (harmonic) process, proportional to \( 1/\epsilon^2 \). The other terms collect contributions from multiphonon processes. For example, the second element accounts for the absorption of two phonons in the left bath, followed by an emission of these phonons at the other end, with, e.g.,

\[
k_L^{-2}(\omega) \propto \frac{1}{\epsilon^2} \sum_{l,l'} (1 + n_l)(1 + n_{l'}) \delta(\omega - \omega_l - \omega_{l'}),
\]

\[
+ \frac{1}{\epsilon^3} \sum_{l,l'} 2(1 + n_l)n_{l'} \delta(\omega - \omega_l + \omega_{l'}).
\]

The last two contributions in (21) convene three-phonon processes, where, e.g., a single mode from the left bath decays into three excitations at the right side. Fig. 2 presents the frequency components of the heat current (the integrand of Eq. (21)), where for simplicity we assume a spectral density \( S(\omega) = \sum_{j} \chi_{j}^{2} \delta(\omega - \omega_j) \) peaked around a specific bath frequency \( \omega_B = 2 \) with a hard cutoff at \( \omega = 3 \), see panel (a).

We identify three contributions to the current: A dominant, single-phonon element at \( \omega \sim \omega_B \), a weaker two-phonon contribution, and a rudimentary three-phonon current, see panel (b). In the presence of a spatial asymmetry these high order terms are responsible for the thermal rectification effect \( \sigma_0 \). Note that in the resonant regime, when a hopping mechanism dominates, the heat current across harmonic junctions is higher than its anharmonic counterpart \( \sigma_0 \) due to a saturation effect. In contrast, in the nonresonant case anharmonicity enhances the thermal current due to the participation of multiphonon processes. Similar observations were obtained in a study of classical heat flow in molecular junctions \( \sigma_0 \).

Summary.— We have presented here a generally applicable Born-Oppenheimer type formalism for describing thermal energy transfer in the off-resonant case, where an impurity object has a characteristic frequency above the (populated) bath modes. In this limit energy propagates across the structure in a tunneling-like motion, keeping the subsystem population intact. In the weak coupling limit we derived a compact expression for the thermal current, bearing the structure of a generalized Landauer relation, yet incorporating multiphonon effects.

In the harmonic limit our formula reduces to known results. We have also applied it onto nonlinear models: Incorporating molecular anharmonicity or assuming short range interactions we reach simple analytic expressions for the heat current, reflecting the underlying transport mechanism. The new method described here is complementary to kinetic approaches that are typically valid in the resonant case. By incorporating quantum effects and nonlinearity it opens new ways for describing vibrational or electronic energy dynamics in organic materials \( \sigma_0 \), biomolecules \( \sigma_0 \) and superconductors \( \sigma_0 \).

L. -A. Wu has been supported by the Ikerbasque Foundation Start-up, the CQIQC grant and the Spanish MEC (Project No. FIS2009-12773-C02-02). DS was supported by NSERC.

[1] E. Pop, Nano Research 3, 147 (2010).
[2] "Proteins: Energy, heat and signal flow", (2009), D. Leitner and J. Straub, editors. CRC Press.
[3] R. Y. Wang, R. A. Segalman, and A. Majumdar, App. Phys. Lett. 89, 173113 (2006).
[4] S. Lepri, R. Livi, and A. Politi, Phys. Rep. 377, 1 (2003).
[5] A. Dhar, Adv. in Phys. 57, 457 (2008).
[6] J.-S. Wang, J. Wang, and J. T. Lü, Euro. Phys. J. B 62, 381 (2008).
[7] D. Segal, A. Nitzan, P. Hänggi, J. Chem. Phys. 119, 6840 (2003).
[8] A. Dhar and D. Roy, J. Stat. Phys. 125, 801 (2006).
[9] H. Spohn, J. Stat. Phys. 124, 1041 (2006).
[10] L. Delfini, S. Lepri, R. Livi, and A. Politi, Phys. Rev. E 73, 060201(R) (2006); J. Stat. Mech. P02007 (2007).
[11] N. Mingo, Thermal nanosystems and nanomaterials 118, 63 (2009).
[12] J.-S. Wang, Phys. Rev. Lett. 99, 160601 (2007).
[13] K. A. Velizhanin, H. Wang, and M. Thoss, Chem. Phys. Lett. 460, 325 (2008); J. Chem Phys. 133 (2010).
[14] D. Segal and A. Nitzan, Phys. Rev. Lett. 94, 034301 (2005), D. Segal, Phys. Rev. B 73, 205415 (2006).
[15] J. Ren, P. Hänggi, and B. Li, Phys. Rev. Lett. 104, 170601.
[16] M. Schade, et al., J. Phys. Chem. B, 113 13393 (2009).
[17] Our scheme is valid for Ohmic baths, if their temperatures are low, below the subsystem energy spacing. In such cases bath modes overlapping with subsystem vibrations are not populated and the dynamics is controlled by off-resonance bath modes.
[18] L. G. C. Rego, G. Kirczenow, Phys. Rev. Lett. 81, 232 (1998).
[19] L.-A. Wu and D. Segal, J. Phys. A: Math. Theor. 42, 025302 (2009).
[20] A. Nitzan Chemical Dynamics in Condensed Phases, Oxford University Press, 2006.
[21] L.-A. Wu and D. Segal, Phys. Rev. Lett. 102, 095503 (2009).
[22] Y. Zhou and D. Segal, J. Chem. Phys 133, 094101 (2010).
[23] G. D. Scholes, Ann. Rev. Phys. Chem., 54, 57 (2003).
[24] F. Giazotto, et al., Rev. Mod. Phys. 78, 217 (2006).