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Nonradiative Electronic Relaxation Rate Constants from Approximations Based on Linearizing the Path-Integral Forward−Backward Action

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We consider two different semiclassical approximations for nonadiabatic quantum-mechanical correlation functions of the form $\mathrm{Tr}[\hat{A}\, e^{i\hat{H}_e t/\hbar}\hat{B}\, e^{-i\hat{H}_g t/\hbar}]$, where $\hat{H}_g \neq \hat{H}_e$ represent the nuclear Hamiltonians of two different electronic states. The first approximation is based on direct linearization (DL) of the forward−backward (FB) action in the *exact* path integral expression for this correlation function. The second approximation is based on linearizing the FB action in an *equivalent* quantum expression for this correlation function, which is given in terms of the Meyer−Miller mapping Hamiltonian (MML). The two approximations have several features in common, namely: (1) They are given in terms of an integral over a classical-like phase space; (2) The relevant operators are replaced by their Wigner transforms; (3) The dynamics is purely classical and governed by a Hamiltonian that represents an average over H_g and H_e; (4) The fact that $\hat{H}_g \neq \hat{H}_e$ gives rise to a phase factor of the form $e^{i\int_0^t d\tau U(\tau)/\hbar}\, d\tau$, where $U = H_e - H_g$. The main differences between the two approximations are: (1) The MML approximation involves an additional phase-space integral and Wigner transforms that correspond to the continuous variables representing the electronic degree of freedom; (2) The DL and MML approximations involve different averaged Hamiltonians, namely, $\hat{H}_{av} = (\hat{H}_g + \hat{H}_e)/2$ in the case of the DL approximation, as opposed to different relative weights of $\hat{H}_g$ and $\hat{H}_e$, which depend on the electronic degree of freedom, in the case of the MML approximation. The two approximations are tested within the framework of a nonradiative electronic relaxation (NRER) benchmark problem. Although the NRER rate constants are accurately reproduced by both methods, the DL approximation is consistently found to perform somewhat better. A discussion is provided of a feasible scheme for implementing those approximations in the case of anharmonic systems as well as the relationship to previous work.

I. Introduction

Most relevant measurable quantities pertaining to condensed-phase systems can be expressed in terms of real-time correlation functions.[1−6] In many cases, classical mechanics provide a reasonable approximation within which to calculate these correlation functions. However, there are many situations where this is not the case. An important class of such problems corresponds to cases that involve nonadiabatic dynamics, where the temporal behavior reflects the time evolution of an electronic superposition state and therefore lacks a well-defined classical limit.

The exact calculation of real-time quantum-mechanical correlation functions for general many-body systems remains far beyond the reach of currently available computer resources due to the exponential scaling of the computational effort with the number of degrees of freedom (DOF).[7] Hence, the development of effective, yet computationally feasible and versatile, approximate methods for calculating quantum-mechanical correlation functions is highly desirable. Several such methods have been proposed throughout the years, including mixed quantum-classical treatments,[8−13] analytical continuation,[14−23] centroid molecular dynamics (CMD),[24−41] quantum mode-coupling theory,[22,42−45] and the semiclassical (SC) approximation.[7,46−67] These methods have been applied, with relative success, to a rather extensive set of systems, including ones that involve nonadiabatic dynamics.

Nonradiative electron relaxation (NRER) represents an important example of a nonadiabatic process.[68−70] In this case, one is typically interested in the rate of transition from an excited electronic state to the ground electronic state, denoted by $|e\rangle$ and $|g\rangle$, respectively. This process, which involves the degradation of electronic energy into heat, can be described in terms of the following, *completely general*, overall Hamiltonian

$$\hat{H} = \hat{H}_g|g\rangle\langle g| + (\hbar\omega_{eg} + \hat{H}_e)|e\rangle\langle e| + \hat{V}_{ge}|g\rangle\langle e| + \hat{V}_{eg}|e\rangle\langle g| \tag{1}$$

Here, ω_{eg} is the electronic transition frequency in the absence of coupling to the nuclear DOF, $\hat{H}_g$ and $\hat{H}_e$ are the nuclear Hamiltonians that correspond to the ground and excited electronic states, respectively

$$\hat{H}_g = \sum_{k=1}^{N_n} \frac{(\hat{P}^{(k)})^2}{2M^{(k)}} + \hat{V}_g(\hat{\mathbf{Q}}) \tag{2a}$$

$$\hat{H}_e = \sum_{k=1}^{N_n} \frac{(\hat{P}^{(k)})^2}{2M^{(k)}} + \hat{V}_e(\hat{\mathbf{Q}}) \tag{2b}$$

and $\hat{V}_{ge}$ and $\hat{V}_{eg}$ are off-diagonal coupling operators which may be explicitly dependent on $\hat{\mathbf{Q}}$ and $\hat{\mathbf{P}}$ [$\hat{\mathbf{Q}} = (\hat{Q}^{(1)}, ..., \hat{Q}^{(N_n)})$, $\hat{\mathbf{P}} = (\hat{P}^{(1)}, ..., \hat{P}^{(N_n)})$, and $(M^{(1)}, ..., M^{(N_n)})$ are the coordinates, conjugate momenta, and masses that correspond to N_n nuclear DOF].

In a situation where the nuclear DOF reach thermal equilibrium on the excited surface prior to the NRER process, and the off-diagonal coupling term, $\hat{V}_{ge}|g\rangle\langle e| + \hat{V}_{eg}|e\rangle\langle g|$, can be treated

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as a small perturbation, one may use Fermi's golden rule in order to derive the following expression for the NRER rate constant[71]

$$k_{g\leftarrow e} = \frac{1}{\hbar^2}\int_{-\infty}^{\infty} dt e^{i\omega_{eg}t}\, C(t) \tag{3}$$

where

$$C(t) = Z_e^{\ -1}\mathrm{Tr}_n[e^{-\beta\hat{H}_e}\, e^{i\hat{H}_e t/\hbar}\hat{V}_{eg}\, e^{-i\hat{H}_g t/\hbar}\hat{V}_{ge}] \tag{4}$$

Here, $\beta = 1/k_BT$, Tr_n stands for the trace over the nuclear DOF, and $Z_e = \mathrm{Tr}_n[e^{-\beta\hat{H}_e}]$. Thus, the calculation of the NRER rate constant translates into that of calculating the correlation function $C(t)$ in eq 4.

Approximate schemes for calculating the correlation function in eq 4, as well as other related types of correlation functions, have been proposed by many authors in the past.[6,71-79] The main goal of the present paper is to consider an approach which is based on the linearization of the forward−backward (FB) action in the exact path integral expression for this correlation function. This work was particularly motivated by the recent finding that a similar approach is effective for calculating quantum mechanical adiabatic correlation functions which are relevant to vibrational energy relaxation.[80,81]

We note that approximations in a similar spirit were recently proposed by Egorov, Rabani, and Berne,[71,75,76] and derived by Miller and co-workers within the framework of the semiclassical initial-value-representation (SC-IVR) approach.[78,79] The present paper provides an alternative, and more general, derivation of some of the results obtained by those authors and sheds new light on several important aspects of the various possible approximations as well as the relationships between them. The analysis also leads to improved approximations that increase the accuracy without sacrificing the appealing cost effectiveness of the approach.

The plan of this papers is as follows. In section II, we derive one type of approximation, which is based on direct linearization of the FB action. In section III, we derive an alternative approximation, which is based on linearizing the FB action that corresponds to the same correlation function, within the framework on the Meyer−Miller mapping Hamiltonian. The two approximations are tested on a benchmark NRER problem in section IV. The results are summarized and discussed in section V.

II. Direct Linearization (DL) Approximation

Consider the following general nonadiabatic two-time correlation function

$$C_{AB}(t) = \mathrm{Tr}_n[\hat{A}\, e^{i\hat{H}_e t/\hbar}\hat{B}e^{\ -i\hat{H}_g t/\hbar}] \tag{5}$$

The correlation function in eq 4 is obviously of this type, with $\hat{A} = \hat{V}_{ge}\, e^{-\beta\hat{H}_e}/Z_e$ and $\hat{B} = \hat{V}_{eg}$. For the sake of simplicity, the direct linearization approximation will be derived below for the case of a single particle of mass m, which moves in 1D.

The *exact* path integral expression for $C_{AB}(t)$ is given by

$$C_{AB}(t) = \left(\frac{m}{2\pi\hbar\epsilon}\right)^N \int dx_0^+ \cdots \int dx_N^+ \int dx_0^- \cdots \int dx_N^-\, \langle x_0^+|\hat{A}|x_0^-\rangle\, \langle x_N^{\ -}|\hat{B}|x_N^+\rangle\, e^{i(S_N^{\ +}-S_N^{\ -})/\hbar} \tag{6}$$

Here

$$S_N^+ = \sum_{j=0}^{N-1}\epsilon\left[\frac{1}{2}m\left(\frac{x_{j+1}^+ - x_j^+}{\epsilon}\right)^2 - V_g(x_j^+)\right] \tag{7a}$$

$$S_N^- = \sum_{j=0}^{N-1}\epsilon\left[\frac{1}{2}m\left(\frac{x_{j+1}^- - x_j^-}{\epsilon}\right)^2 - V_e(x_j^-)\right] \tag{7b}$$

are the forward and backward actions, respectively, and $\{0, \epsilon, 2\epsilon, ..., N\epsilon = t\}$ corresponds to the discretized time (the limit $N \to \infty$ will be imposed at a later stage).

The linearization approximation is based on the assumption that the most important contributions to the path integral in eq 6 come from forward and backward trajectories, which are infinitesimally close to each other. Thus, one may expand the FB action, $S_N^+ - S_N^-$, to first order with respect to the difference between the forward and backward trajectories.[47,48,56,78,79,82-85] To this end, we change the integration variables in eq 6 from $x_0^+, ..., x_N^+, x_0^-, ..., x_N^-$ into $y_0, ..., y_N, z_0, ..., z_N$, such that

$$y_j = \frac{1}{2}(x_j^+ + x_j^-)$$

$$z_j = x_j^+ - x_j^- \tag{8}$$

The linearization approximation is then introduced by expanding the FB action, $S_N^+ - S_N^-$, to first order in $z_0, ..., z_N$. This yields

$$S_N^+ - S_N^{\ -} \approx \epsilon\sum_{j=0}^{N-1}\left[\frac{m}{\epsilon^2}(y_{j+1}-y_j)(z_{j+1}-z_j) - V'_{av}(y_j)z_j + U(y_j)\right] = \epsilon\sum_{j=1}^{N-1} z_j\left[\frac{m}{\epsilon^2}(2y_j - y_{j-1} - y_{j+1}) - V'_{av}(y_j) + U(y_j)\right] + \epsilon z_0\left[-\frac{m}{\epsilon^2}(y_1-y_0) - V'_{av}(y_0) + U(y_0)\right] + \epsilon z_N\frac{m}{\epsilon^2}(y_N - y_{N-1}) \tag{9}$$

where

$$V_{av}(y) = \frac{1}{2}[V_g(y) + V_e(y)] \tag{10}$$

is the arithmetic average of the ground and excited electronic potential surfaces, and

$$U(y) = V_e(y) - V_g(y) \tag{11}$$

is the difference between them.

Following the linearization, one can perform the integration over $z_1, ..., z_{N-1}$ explicitly by using the following identity

$$\int dz_j\, e^{-i\epsilon[(m/\epsilon^2)(y_{j+1}-2y_j+y_{j+1})+V_{av}'(y_j)]z_j/\hbar} = \frac{2\pi\hbar}{\epsilon}\,\delta\left[\frac{m}{\epsilon^2}(y_{j+1} - 2y_j + y_{j+1}) - V'_{av}(y_j)\right] \tag{12}$$

It should also be noted that in the limit $N \to \infty$ ($\epsilon \to 0$)

$$\epsilon z_0\left[-\frac{m}{\epsilon^2}(y_1 - y_0) - V'_{av}(y_0)\right] \to -z_0p_0$$

$$\epsilon z_N\frac{m}{\epsilon^2}(y_N - y_{N-1}) \to z_Np_N \tag{13}$$

where $p_0/m = \lim_{\epsilon\to 0}(y_1 - y_0)/\epsilon$ and $p_N/m = \lim_{\epsilon\to 0}(y_N -$

$y_{N-1})/\epsilon$. Changing the integration variables y_1 ..., y_{N-1} into f_1, ..., f_{N-1} such that

$$f_j = \frac{m}{\epsilon^2}(y_{j+1} - 2y_j + y_{j-1}) + V'_{\mathrm{av}}(y_j) \tag{14}$$

and explicitly integrating over f_1 ..., f_{N-1} then leads to the following approximation

$$C_{\mathrm{AB}}(t) \approx \frac{1}{2\pi\hbar}\int \mathrm{d}y_0 \int \mathrm{d}y_t \int \mathrm{d}z_0 \int \mathrm{d}z_t \left|\frac{\partial p_0}{\partial y_t}\right| \langle y_0 + z_0/2|\hat{A}|y_0 - z_0/2\rangle \, \langle y_t - z_t/2|\hat{B}|y_t + z/2\rangle \, \mathrm{e}^{-ip_0z_0/\hbar} e^{ip_tz_t/\hbar} \mathrm{e}^{i\int_0^t d\tau U(\tau)/\hbar} \tag{15}$$

It should be noted that, in arriving to eq 15, we have explicitly incorporated the limit $N \rightarrow \infty$ ($\epsilon \rightarrow 0$) such that $y_N \rightarrow y_t$, $z_N \rightarrow z_t$, and $\epsilon \sum_{j=0}^{N-1} U(y_j) \rightarrow \int_0^t \mathrm{d}\tau \; U(\tau)$ and made use of the following identity[86]

$$\lim_{N\rightarrow\infty} \frac{1}{\epsilon}\left(\frac{m}{\epsilon^2}\right)^{N-1} \left|\frac{\partial y}{\partial f}\right| = \frac{1}{m}\left|\frac{\partial p_0}{\partial y_t}\right| \tag{16}$$

($|\partial y/\partial f\,|$ is the determinant of the $(N - 1) \times (N - 1)$ matrix whose (i,j)th element is $\partial y_i/\partial f_j$). It should also be noted that $y_t = y_t(y_0,p_0)$ in eq 15 follows a classical trajectory which is dictated by the averaged potential (cf. eq 12)

$$f_j = \frac{m}{\epsilon^2}(y_{j+1} - 2y_j + y_{j+1}) + V'_{\mathrm{av}}(y_j) = 0 \xrightarrow{N\rightarrow\infty} m\frac{\mathrm{d}^2}{\mathrm{d}t^2}y(t) = -V'_{\mathrm{av}}[y(t)] \tag{17}$$

Finally, changing the integration variable y_t into p_0, we arrive at the following DL approximation

$$C_{\mathrm{AB}}(t) \approx C_{\mathrm{AB}}^{\mathrm{DL}}(t) = (2\pi\hbar)^{-1}\int \mathrm{d}y_0 \int \mathrm{d}p_0 \, A_{\mathrm{W}}(y_0,p_0) B_{\mathrm{W}}(y_t,p_t) \, \mathrm{e}^{i\int_0^t \mathrm{d}\tau U(\tau)/\hbar} \tag{18}$$

where

$$A_{\mathrm{W}}(q,p) = \int \mathrm{d}\Delta \, \mathrm{e}^{-ip\Delta/\hbar} \langle q + \Delta/2|\hat{A}|q - \Delta/2\rangle \tag{19}$$

is the Wigner transform and $y_t = y_t(y_0,p_0)$ and $p_t = p_t(y_0,p_0)$ follow a classical trajectory which is dictated by the averaged potential.

The DL approximation in eq 18 can be straightforwardly extended to the case of a multidimensional system

$$C_{\mathrm{AB}}(t) \approx C_{\mathrm{AB}}^{\mathrm{DL}}(t) = (2\pi\hbar)^{-N_n}\int \mathrm{d}\mathbf{Q}_0 \int \mathrm{d}\mathbf{P}_0 \, A_{\mathrm{W}}(\mathbf{Q}_0,\mathbf{P}_0) B_{\mathrm{W}}(\mathbf{Q}_t,\mathbf{P}_t) \, \mathrm{e}^{i\int_0^t \mathrm{d}\tau U(\tau)/\hbar} \tag{20}$$

Equation 20 represents the main result of this section. The following points should be noted in relation to it:

1. The dynamics in eq 20 takes place on a potential surface which corresponds to an arithmetic average of the ground and excited surfaces. Shemetulskis and Loring have previously obtained a similar result based on a somewhat different argument, which can be summarized as follows[72]

$$\mathrm{Tr}_n(\hat{A}\,\mathrm{e}^{i\hat{H}_\mathrm{e}t/\hbar}\hat{B}\,\mathrm{e}^{-i\hat{H}_\mathrm{g}t/\hbar}) = (2\pi\hbar)^{-N_n}\int \mathrm{d}\mathbf{Q}_0 \int \mathrm{d}\mathbf{P}_0 [\hat{A}]_{\mathrm{W}}(\mathbf{Q}_0,\mathbf{P}_0)[\mathrm{e}^{i\hat{H}_\mathrm{e}t/\hbar}\hat{B}\,\mathrm{e}^{-i\hat{H}_\mathrm{g}t/\hbar}]_{\mathrm{W}}(\mathbf{Q}_0,\mathbf{P}_0) \approx (2\pi\hbar)^{-N}\int \mathrm{d}\mathbf{Q}_0 \int \mathrm{d}\mathbf{P}_0 \, A_{\mathrm{W}}(\mathbf{Q}_0,\mathbf{P}_0) B_{\mathrm{W}}(\mathbf{Q}_t,\mathbf{P}_t)\,\mathrm{e}^{i\int_0^t \mathrm{d}\tau U(\tau)/\hbar} \tag{21}$$

The first equality in eq 21 is exact, and the second is based on the $\hbar \rightarrow 0$ limit of the equation of motion of $[\mathrm{e}^{i\hat{H}_e t/\hbar}\hat{B}\mathrm{e}^{-i\hat{H}_g t/\hbar}]_{\mathrm{W}}$. Under those conditions, the dynamics of $\mathbf{Q}_t$ and $\mathbf{P}_t$ is classical and dictated by the averaged Hamiltonian, H_{av}, which is identical to that in eq 20. Those two approximations are therefore completely equivalent.

2. Although eq 20 can also be obtained by direct linearization of the corresponding approximate SC-IVR expression for $C_{\mathrm{AB}}(t)$, invoking the SC-IVR approximation is not necessary for deriving this result.

3. When $V_{\mathrm{g}} = V_{\mathrm{e}}$, eq 20 reduces to the corresponding linearized approximation for a single surface, adiabatic, correlation function.[87] However, it should be noted that the second-order term in the expansion of the FB action vanishes in the adiabatic limit, which implies that the linearized approximation is in fact exact up to second order. This is no longer true in the nonadiabatic case, where the linearized approximation is exact to first-order only, unless $V''_{\mathrm{g}} = V''_{\mathrm{e}}$. This implies that the linearization approximation will not be exact, even when the potentials V_{e} and V_{g} are both harmonic, unless the ground and excited electronic surfaces can be described in terms of the same set of normal modes coordinates and frequencies.

4. The correlation function in eq 5 lacks a well-defined classical limit ($\hbar \rightarrow 0$). This is manifested by the fact that the DL approximation in eq 20 is not an analytical function of $\hbar$.

5. As for its adiabatic counterpart, eq 20 is exact at $t = 0$. This is particularly important when the desired quantity depends on high-frequency Fourier components of the correlation function, which is often rather sensitive to its behavior at short times.

Application of the DL approximation in eq 20 to the particular correlation function in eq 4 leads to the following approximation

$$C^{\mathrm{DL}}(t) = (2\pi\hbar)^{-N_n}\int \mathrm{d}\mathbf{Q}_0 \int \mathrm{d}\mathbf{P}_0 \, [\hat{V}_{\mathrm{ge}}\,\mathrm{e}^{-\beta\hat{H}_\mathrm{e}}/Z_\mathrm{e}]_{\mathrm{W}}(\mathbf{Q}_0,\mathbf{P}_0) [\hat{V}_{\mathrm{eg}}]_{\mathrm{W}}(\mathbf{Q}_t,\mathbf{P}_t)\,\mathrm{e}^{i\int_0^t \mathrm{d}\tau U(\tau)/\hbar} \tag{22}$$

It should be emphasized that, generally speaking, $[\hat{V}_{\mathrm{ge}}\,\mathrm{e}^{-\beta\hat{H}_\mathrm{e}}/Z_\mathrm{e}]_{\mathrm{W}} \neq [\hat{V}_{\mathrm{ge}}]_{\mathrm{W}}[\mathrm{e}^{-\beta\hat{H}_\mathrm{e}}/Z_\mathrm{e}]_{\mathrm{W}}$. This inequality reflects the fact that $\hat{V}_{\mathrm{ge}}$ may not commute with $\hat{H}_{\mathrm{e}}$. Egorov, Rabani, and Berne have recently proposed the Wigner averaged classical limit (WACL) approximation, which is equivalent to replacing $[\hat{V}_{\mathrm{ge}}\,\mathrm{e}^{-\beta\hat{H}_\mathrm{e}}/Z_\mathrm{e}]_{\mathrm{W}}$ by $[\hat{V}_{\mathrm{ge}}]_{\mathrm{W}}[\mathrm{e}^{-\beta\hat{H}_\mathrm{e}}/Z_\mathrm{e}]_{\mathrm{W}}$ in eq 22[71]

$$C^{\mathrm{WACL}}(t) = (2\pi\hbar)^{-N_n}\int \mathrm{d}\mathbf{Q}_0 \int \mathrm{d}\mathbf{P}_0 \, [\mathrm{e}^{-\beta\hat{H}_\mathrm{e}}/Z_\mathrm{e}]_{\mathrm{W}}(\mathbf{Q}_0,\mathbf{P}_0) [\hat{V}_{\mathrm{ge}}]_{\mathrm{W}}(\mathbf{Q}_0,\mathbf{P}_0)[\hat{V}_{\mathrm{ge}}]_{\mathrm{W}}(\mathbf{Q}_t,\mathbf{P}_t)\,\mathrm{e}^{i\int_0^t \mathrm{d}\tau U(\tau)/\hbar} \tag{23}$$

A similar approximation has also been proposed by Hernandez and Voth as a simplified version of the SC-IVR approximation for adiabatic correlation functions.[88] The WACL and DL approximations coincide when $\hat{V}_{\mathrm{ge}}$ and $\hat{V}_{\mathrm{eg}}$ are constants but will be different when $\hat{V}_{\mathrm{ge}}$ and $\hat{V}_{\mathrm{ge}}$ are explicitly dependent on the nuclear coordinates and momenta. Furthermore, we have recently shown that an approximation that is analogous to WACL fails to accurately account for high-frequency vibrational energy relaxation rate constants in condensed-phase hosts, where the quantities analogous to $\hat{V}_{\mathrm{ge}}$ and $\hat{V}_{\mathrm{eg}}$ are highly nonlinear functions of the nuclear coordinates and momenta.[80,81] By contrast, the corresponding DL approximation was found to be accurate under the same conditions.

III. Meyer−Miller Linearization (MML) Approximation

The correlation function in eq 5 can be rewritten in the following form

$$C_{\mathrm{AB}}(t) = \mathrm{Tr}[(\hat{A}|\mathrm{g}\rangle\langle\mathrm{e}|)\ \mathrm{e}^{i\hat{H}_0 t/\hbar}(\hat{B}|\mathrm{e}\rangle\langle\mathrm{g}|)\ \mathrm{e}^{-i\hat{H}_0 t/\hbar}] \qquad (24)$$

where $\mathrm{Tr} = \mathrm{Tr}_{\mathrm{n}}\mathrm{Tr}_{\mathrm{e}}$ stands for the trace over *both* electronic and nuclear DOF and

$$\hat{H}_0 = \hat{H}_{\mathrm{e}}|\mathrm{e}\rangle\langle\mathrm{e}| + \hat{H}_{\mathrm{g}}|\mathrm{g}\rangle\langle\mathrm{g}| = \sum_{k=1}^{N}\frac{(\hat{P}^{(k)})^2}{2M^{(k)}} + \hat{V}_{\mathrm{av}}(\hat{\mathbf{Q}}) + \frac{1}{2}(|\mathrm{e}\rangle\langle\mathrm{e}| - |\mathrm{g}\rangle\langle\mathrm{g}|)U(\hat{\mathbf{Q}}) \qquad (25)$$

At this point, one may employ the Meyer−Miller (MM) mapping in order to represent the electronic DOF in terms of classical-like variables.[63,78,82,89−93] More specifically, the electronic two-level system $\{|\mathrm{g}\rangle,|\mathrm{e}\rangle\}$ may be replaced by two harmonic modes with coordinates q_{g} and q_{e} and momenta p_{g} and p_{e}, respectively, ($[\hat{q}_k, \hat{p}_l] = i\hbar\delta(k,l)$). The state $|\mathrm{g}\rangle$ then corresponds to $|0,1\rangle$, where the e oscillator is in the ground state, $|0\rangle$, and the g oscillator is in the first excited state, $|1\rangle$ (we use the convention that the first and second indexes correspond to e and g, respectively). Similarly, the state $|\mathrm{e}\rangle$ corresponds to $|1,0\rangle$. Thus, the electronic operators can be expressed in terms of the harmonic oscillator coordinate and momenta operators

$$|\mathrm{g}\rangle\langle\mathrm{g}| \leftrightarrow \frac{1}{2\hbar}(\hat{q}_{\mathrm{g}}^2 + \hat{p}_{\mathrm{g}}^2 - \hbar)$$

$$|\mathrm{e}\rangle\langle\mathrm{e}| \leftrightarrow \frac{1}{2\hbar}(\hat{q}_{\mathrm{e}}^2 + \hat{p}_{\mathrm{e}}^2 - \hbar)$$

$$|\mathrm{g}\rangle\langle\mathrm{e}| \leftrightarrow \frac{1}{2\hbar}(\hat{q}_{\mathrm{g}}\hat{q}_{\mathrm{e}} + \hat{p}_{\mathrm{g}}\hat{p}_{\mathrm{e}} + i\hat{q}_{\mathrm{g}}\hat{p}_{\mathrm{e}} - i\hat{p}_{\mathrm{g}}\hat{q}_{\mathrm{e}})$$

$$|\mathrm{e}\rangle\langle\mathrm{g}| \leftrightarrow \frac{1}{2\hbar}(\hat{q}_{\mathrm{e}}\hat{q}_{\mathrm{g}} + \hat{p}_{\mathrm{e}}\hat{p}_{\mathrm{g}} + i\hat{q}_{\mathrm{e}}\hat{p}_{\mathrm{g}} - i\hat{p}_{\mathrm{e}}\hat{q}_{\mathrm{g}}) \qquad (26)$$

such that

$$C_{\mathrm{AB}}(t) = \mathrm{Tr}[(\hat{A}|0,1\rangle\langle 1,0|)\ \mathrm{e}^{i\hat{H}_0 t/\hbar}\hat{B}|1,0\rangle\langle 0,1|\mathrm{e}^{-i\hat{H}_0 t/\hbar}] \qquad (27)$$

with

$$\hat{H}_0 = \sum_{k=1}^{N_n}\frac{(\hat{P}^{(k)})^2}{2M^{(k)}} + \hat{V}_{\mathrm{av}}(\hat{\mathbf{Q}}) + \frac{1}{4\hbar}(\hat{q}_{\mathrm{e}}^2 + \hat{p}_{\mathrm{e}}^2 - \hat{q}_{\mathrm{g}}^2 - \hat{p}_{\mathrm{g}}^2)U(\hat{\mathbf{Q}}) \qquad (28)$$

It should be noted that eq 27 is exact and completely equivalent to eq 24 and that the trace in eq 27 corresponds to tracing over the nuclear DOF (the original Tr_n) *and* the DOF that correspond to the two harmonic modes representing the electronic DOF.

In the next step, we apply the linearization approximation to the correlation function in eq 27[87]

$$C_{\mathrm{AB}}(t) \approx C_{\mathrm{AB}}^{\mathrm{MML}}(t) = (2\pi\hbar)^{-(N_n+2)}\int \mathrm{d}\mathbf{q}_0 \int \mathrm{d}\mathbf{p}_0 \int \mathrm{d}\mathbf{Q}_0 \int \mathrm{d}\mathbf{P}_0\, A_{\mathrm{W}}(\mathbf{Q}_0,\mathbf{P}_0)[|0,1\rangle\langle 1,0|]_{\mathrm{W}}(\mathbf{q}_0,\mathbf{p}_0)B_{\mathrm{W}}(\mathbf{Q}_t,\mathbf{P}_t)[|1,0\rangle\langle 0,1|]_{\mathrm{W}}(\mathrm{q}_t,\mathrm{p}_t) \qquad (29)$$

where $\mathbf{q} = (q_{\mathrm{e}},q_{\mathrm{g}})$ and $\mathbf{p} = (p_{\mathrm{e}},p_{\mathrm{g}})$. The Wigner transforms that correspond to the electronic DOF can be evaluated analytically and are given by

$$[|1,0\rangle\langle 0,1|]_{\mathrm{W}}(\mathbf{q},\mathbf{p}) = \frac{2^3}{\hbar}(q_{\mathrm{g}} + ip_{\mathrm{g}})(q_{\mathrm{e}} - ip_{\mathrm{e}})\ \mathrm{e}^{-({q_{\mathrm{e}}}^2+{p_{\mathrm{e}}}^2+{q_{\mathrm{g}}}^2+{p_{\mathrm{g}}}^2)/\hbar}$$

$$[|0,1\rangle\langle 1,0|]_{\mathrm{W}}(\mathbf{q},\mathbf{p}) = \frac{2^3}{\hbar}(q_{\mathrm{g}} - ip_{\mathrm{g}})(q_{\mathrm{e}} + ip_{\mathrm{e}})\ \mathrm{e}^{-({q_{\mathrm{e}}}^2+{p_{\mathrm{e}}}^2+{q_{\mathrm{g}}}^2+{p_{\mathrm{g}}}^2)/\hbar} \qquad (30)$$

The variables $\mathbf{q}_{\mathrm{t}}$, $\mathbf{p}_t$, $\mathbf{Q}_t$, and $\mathbf{P}_t$ in eq 29 are propagated according to classical mechanics, subject to the Hamiltonian in eq 28. In practice, it is convenient to propagate the quantities $\sigma_+ = (q_{\mathrm{e}}q_{\mathrm{g}} + p_{\mathrm{e}}p_{\mathrm{g}} + iq_{\mathrm{e}}p_{\mathrm{g}} - ip_{\mathrm{e}}q_{\mathrm{g}})/2\hbar$, $\sigma_- = (q_{\mathrm{e}}q_{\mathrm{g}} + p_{\mathrm{e}}p_{\mathrm{g}} - iq_{\mathrm{e}}p_{\mathrm{g}} + ip_{\mathrm{e}}q_{\mathrm{g}})/2\hbar$, and $\sigma_z = (q_{\mathrm{e}}^2 + p_{\mathrm{e}}^2 - q_{\mathrm{g}}^2 - p_{\mathrm{g}}^2)/2\hbar$, which are the classical variables that correspond to the operators $|\mathrm{e}\rangle\langle\mathrm{g}|$, $|\mathrm{g}\rangle\langle\mathrm{e}|$, and $|\mathrm{e}\rangle\langle\mathrm{e}| - |\mathrm{g}\rangle\langle\mathrm{g}|$, respectively, within the MM mapping. The equations of motion for $\sigma_\pm$, σ_z, $\mathbf{Q}(t)$, and $\mathbf{P}(t)$ are given by

$$\dot{\sigma}_\pm = \pm\frac{i}{\hbar}U(\mathbf{Q})\sigma_\pm$$

$$\dot{\sigma}_z = 0$$

$$\dot{Q}^{(k)} = \frac{P^{(k)}}{M^{(k)}}$$

$$\dot{P}^{(k)} = -\frac{\partial V_{\mathrm{av}}}{\partial Q^{(k)}} - \frac{\sigma_z}{2}\frac{\partial U}{\partial Q^{(k)}} \qquad (31)$$

It should be noted that σ_z is a constant of the motion and that the equations of motion for $\sigma_\pm$ can be integrated explicitly to yield

$$\sigma_\pm(t) = \sigma_\pm(0)\ \mathrm{e}^{\pm i\int_0^t d\tau U(Q_\tau)/\hbar} \qquad (32)$$

It should also be noted that the nuclear dynamics is governed by an effective potential energy of the form

$$V_{\mathrm{eff}}(\mathbf{Q}) = V_{\mathrm{av}}(\mathbf{Q}) + \sigma_z U(\mathbf{Q})/2 \qquad (33)$$

rather than just $V_{\mathrm{av}}(\mathbf{Q})$, as in the DL approximation. Thus, the effective nuclear potential depends on the initially sampled values of $\mathbf{q}$ and $\mathbf{p}$, which dictate the value of σ_z.

Substituting eqs 30 and 32 back into eq 29 yields the final form of the MML approximation

$$C_{\mathrm{AB}}^{\mathrm{MML}}(t) = \frac{1}{(2\pi\hbar)^{N+2}}\frac{1}{\hbar^2}\int \mathrm{d}\mathbf{p}_0\,\mathrm{d}\mathbf{q}_0 \int \mathrm{d}\mathbf{P}_0\,\mathrm{d}\mathbf{Q}_0\ \mathrm{e}^{-(2/\hbar)({q_{\mathrm{g}}}^2+{p_{\mathrm{g}}}^2+{q_{\mathrm{e}}}^2+{p_{\mathrm{e}}}^2)}\sigma_-(\mathbf{q},\mathbf{p})\sigma_+(\mathbf{q},\mathbf{p})A_{\mathrm{W}}(\mathbf{Q},\mathbf{P})B_{\mathrm{W}}(\mathbf{Q}_t,\mathbf{P}_t)\ [\mathrm{e}^{i}\int_0^t \mathrm{d}\tau U[\mathbf{Q}_\tau]\mathrm{d}\tau/\hbar] \qquad (34)$$

The MML approximation in eq 34 has a few features in common with the DL approximation of eq 23, namely: (1) The nuclear dynamics in both cases is completely classical and governed by an effective potential surface that averages over the ground and excited electronic surfaces; (2) The same type of phase factor is accumulated along the classical trajectories; (3) The initial sampling of the nuclear coordinates and momenta is dictated by the same Wigner transform, $A_W(\mathbf{Q}_0,\mathbf{P}_0)$. At the same time, the two approximations differ in two important respects: (1) The MML approximation involves an additional average over the initial electronic state (within the MM representation); (2) The effective potential on which nuclear motion takes place within the MML approximation contains an additional term which depends on the initial electronic state.

IV. Illustrative Applications

In this section, we test the accuracy of the DL and MML approximations by applying them for calculating NRER rate constants. The specific model was adopted from the recent work of Egorov, Rabani, and Berne, who used it to test several mixed quantum-classical approximations, including the WACL approximation [cf. eq 23].[71,74,76,94] Within this model, both ground and excited electronic surfaces are assumed to be harmonic, which facilitates the analytical calculation of the *exact* correlation function in eq 4. More specifically, $\hat{H}_e$ and $\hat{H}_g$ are given in terms of mass-weighted normal-mode coordinates and momenta such that

$$\hat{H}_e = \frac{1}{2}\sum_{k=1}^{N_n}[(\hat{P}^{(k)})^2 + (\omega^{(k)})^2(\hat{Q}^{(k)})^2]$$

$$\hat{H}_g = \hat{H}_e - \hat{U}(\hat{\mathbf{Q}}) \tag{35}$$

with $\hat{U}$ either linear in $\hat{\mathbf{Q}}$ (linear diagonal coupling (LDC))

$$\hat{U}_{\mathrm{LDC}}(\hat{\mathbf{Q}}) = -\sum_{k=1}^{N_n}(\omega^{(k)})^2\delta^{(k)}[\hat{Q}^{(k)} + \delta^{(k)}/2] \tag{36}$$

or quadratic in $\hat{\mathbf{Q}}$ (quadratic diagonal coupling (QDC))

$$\hat{U}_{\mathrm{QDC}}(\hat{\mathbf{Q}}) = -\sum_{k=1}^{N_n}(\omega^{(k)})^2\delta^{(k)}[\hat{Q}^{(k)} + \delta^{(k)}/2] - \sum_{k,j=1}^{N_n} g_{j,k}\hat{Q}^{(j)}\hat{Q}^{(k)} \tag{37}$$

In the LDC case, the normal-mode frequencies are the same in the ground and excited electronic states, such that the DL approximation is formally exact (cf. section II). In the QDC case, the normal-mode coordinates and frequencies in the ground and exited electronic states are different and the DL approximation is no longer formally exact.

The operators $\hat{V}_{ge}$ and $\hat{V}_{eg}$ are assumed to be either *constant* (static off-diagonal coupling (SOC)), $\hat{V}_{eg} = \hat{V}_{ge} = V_0$, where V_0 is a real constant or linear in the nuclear momenta (Born−Oppenheimer off-diagonal coupling (BOC))

$$\hat{V}_{eg} = \sum_{k=1}^{N_n} S^{(k)}\hat{P}^{(k)} \tag{38}$$

where $\{S^{(k)}\}$ are real constants. The parameters used for each of those cases are provided in Appendix A, along with information regarding the exact results. It should be noted that the Wigner transforms in this case only involve Gaussian integrals and can be performed analytically.[71,80]

The results for each of the four possible scenarios, namely, SOC-LDC, SOC-QDC, BOC-LDC, and BOC-QDC, are presented in Figures 1−4, respectively. It should be noted that: (1) The WACL and DL approximations are equivalent when the off-diagonal coupling is static (SOC); (2) The DL approximation coincides with the exact result when the diagonal coupling is linear (LDC). Thus, only the MML approximation can be critically tested in the SOC-LDC case (Cf. Figure 1). Although the MML approximation is not formally exact, it performs quite well and particularly so at high frequencies. The main difference between the MML approximation and exact results is that the former exhibits weaker oscillations, which is particularly relevant at low frequencies and which can be traced

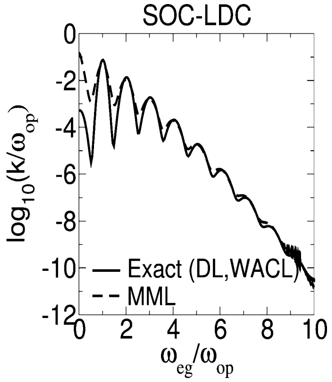

Figure 1. Semilog plots of the nonradiative electron relaxation rate constant as a function of ω_{eg} for SOC and LDC. Shown are the exact results, which coincide with those obtained via the DL and WACL approximations in this case, and the results obtained via the MML approximation.

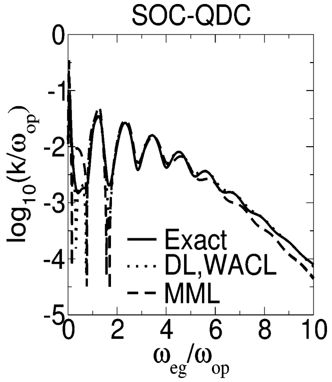

Figure 2. Semilog plots of the nonradiative electron relaxation rate constant as a function of ω_{eg} for SOC and QDC. Shown are the exact results and the results obtained via the DL, WACL, and MML approximations. Note that the DL and WACL approximations coincide in this case.

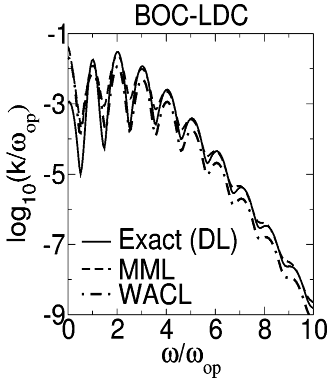

Figure 3. Semilog plots of the nonradiative electron relaxation rate constant as a function of ω_{eg} for BOC and LDC. Shown are the exact results, which coincides with those obtained via the DL approximation in this case, and the results obtained via the WACL and MML approximations.

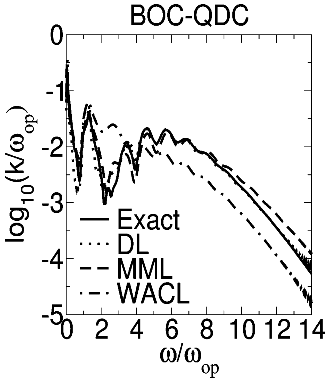

Figure 4. Semilog plots of the nonradiative electron relaxation rate constant as a function of ω_{eg} for BOC and QDC. Shown are the exact results and the results obtained via the DL, MML, and WACL approximations.

back to the additional averaging over the MM-mapped electronic DOF in eq 34.

We next consider the results obtained in the SOD-QDC case, where neither the DL approximation nor the MML approximation are formally exact (cf. Figure 2). Nevertheless, the DL approximation, which is also equivalent to the WACL approximation in this case, performs particularly well and practically coincides with the exact result beyond the low-frequency region. The agreement between the MML approximation and the exact result is also quite good, although larger errors are observed at high frequencies.

It should be noted that the observations regarding the MML approximation in Figures 1 and 2 are also consistent with those reported by Rabani, Egorov, and Berne in ref 75. Those authors proposed an approximation similar to our MML approximation for calculating the NRER rate constant within the framework of the reactive flux formalism and observed that, in the case of SOC, their approximation was in overall agreement with the exact result, except at very low and very high frequencies.

The DL approximation also coincides with the exact result, in the BOC-LDC case (cf. Figure 3). The MML approximation, although not formally exact, is also found to be in very good agreement with the exact result, except at very low frequencies. The WACL approximation is no longer equivalent to the DL approximation in this case. Although the agreement between the WACL approximation and the exact result is fairly good, it is clearly inferior in comparison to either the DL or MML approximations.

Both DL and MML approximations remain in very good overall agreement with the exact results in the BOC-QDC case (cf. Figure 4). The DL approximation, in particular, practically coincides with the exact result throughout the entire range of frequencies considered. The MML approximation exhibits a slight deviation from the exact result and particularly so at high frequencies. Finally, the WACL approximation is seen to be significantly inferior to both DL and MML approximations in this case. Thus, avoiding the approximation $[\hat{V}_{ge}\, e^{-\beta\hat{H}_e}Z_e]_W \approx [\hat{V}_{ge}]_W[e^{-\beta\hat{H}_e}Z_e]_W$ appears to be essential for obtaining an accurate result.

V. Discussion and Summary

The main result of this paper corresponds to the *derivation* of the DL and MML approximations, eqs 22 and 34, respectively, via linearization of the *exact* path integral expression for a nonadiabatic correlation function. Several related approximations have been derived and/or proposed by other authors in the past. More specifically:

- The technique used by Shemetulskis and Loring in the context of nonlinear response functions[72] can be used in order to provide an alternative route to the DL approximation.
- The WACL approximation proposed by Egorov, Rabani, and Berne[71] corresponds to a simplified version of the DL approximation.
- Miller and co-workers have employed the MM mapping in order to evaluate similar types of nonadiabatic correlation functions in the context of the SC-IVR methodology.[63] Furthermore, Rabani, Egorov, and Berne have also applied those techniques for calculating NRER rate constants, in the case of SOC, and within the framework of the reactive flux formalism.[75]

The present work provides the following new insights regarding such approximations:

- Although the DL and MML approximations can also be derived within the context of SC-IVR theory, we have shown that it is not necessary to invoke the SC-IVR approximation in order to derive them. This extends a similar earlier result pertaining to adiabatic correlation functions.[87]
- The rigorous derivation of the DL approximation clarifies and provides partial justification for the WACL approximation, which was originally suggested based on an intuitive argument.[71] Furthermore, it was shown that the DL approximation is exact for harmonic systems with the same normal-mode frequencies in the ground and excited electronic states, even when $\hat{V}_{eg}$ and $\hat{V}_{ge}$ are not constant and that a significant improvement can be obtained by avoiding the additional assumption, which is implicitly implied by the WACL approximation, according to which $[\hat{V}_{ge}\, e^{-\beta\hat{G}_e}Z_e]_W \approx [\hat{V}_{ge}]_W[e^{-\beta\hat{H}_e}Z_e]_W$.
- We have been able to put the MML approximation in a form which is particularly suitable for comparison with the DL approximation. More specifically, we have shown that, like the DL approximation, the MML approximation is based on classical propagation of the nuclear DOF on an *averaged* potential. However, the DL and MML approximations give rise to *different* averaged potentials, with the latter explicitly dependent on the initial electronic state.
- We performed a systematic comparison between the DL and MML approximations. Although both approximations performed rather well when tested on a benchmark problem, we have observed that the performance of the DL approximation was consistently better than that of the MML approximation in all of the situations considered.
- Despite the fact that the dynamics in both DL and MML approximations is purely classical, those approximations are still able to capture the resonances observed in the frequency dependence of the NRER rate constants (cf. Figures 1−4). Those resonances should therefore *not* be associated with quantum dynamics, as previously suggested.[75]

The very good agreement between the DL and MML approximations and the exact results should be attributed to the fact that those approximations are able to correctly capture the short-time quantum dynamics. Indeed, the most significant errors arise at small frequencies and reflect the fact that the long-time dynamics is treated by those approximations as purely classical. In this context, it is interesting to note that the same approximations should not be expected to do as well in capturing dynamical effects in the vibronic spectrum of a general system.[72,94] This is because the high-frequency tail corresponds to the relatively unimportant far wings of the vibronic spectrum or very short time behavior of the optical response functions. For the same reason, the DL and MML approximations should not be expected to be accurate when applied for simulating the nonequilibrium NRER dynamics. Such nonequilibrium simulations may be required in cases where the relaxation process does not follow simple rate kinetics. However, even in such cases, it is often possible to describe the influence of the environment in terms of a short-lived memory kernel, which may be accurately estimated via the DL and MML approximations.[95,96]

The major advantage of the DL and MML approximations over other approaches has to do with the fact that they provide a consistent strategy for calculating NRER rate constants, as well as other related quantities, in general *anharmonic* systems, where exact quantum results are not available. The major challenge involved in applications to anharmonic hosts has to do with the difficulty of computing the corresponding Wigner transforms. However, several strategies, which have been recently employed for computing such Wigner transforms in other contexts,[80,81,97] can be adopted for this purpose, thereby opening the door to such applications. The synthesis of those methods with the DL and MML approximations, and subsequent applications to nonradiative electron relaxation and related processes, in liquid solutions is the subject of ongoing work in our group and will be reported in a separate paper.

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Appendix A: Parameters and Exact Results for the Benchmark Problem

In this appendix, we provide a brief summary of the parameters and exact results that were used in order to generate Figures 1−4. The reader is referred to ref 71 for a more detailed discussion of the model.

In the SOC-LDC case, the exact correlation function in eq 4 is explicitly given by

$$C_{\mathrm{SOC-LDC}}(t) = |V_0|^2 \exp\left\{\frac{1}{2\hbar}\int_0^\infty d\omega\, J(\omega)\omega[\coth(\beta\hbar\omega/2) \times [\cos(\omega t) - 1] - i(\sin\omega t)]\right\} \tag{A1}$$

where

$$J(\omega) = \sum_k (\delta^{(k)})^2 \delta(\omega - \omega^{(k)}) \tag{A2}$$

is the spectral density. The spectral density used in the actual calculations is given by[71]

$$J(\omega) = \frac{\lambda}{(2\pi\sigma^2)^{1/2}} \exp[-(\omega - \omega_{\mathrm{op}})^2/2\sigma^2] \tag{A3}$$

with the following parameters: $\lambda = 1.0$, $\omega_{\mathrm{op}} = 1.0$, $\sigma = 0.1$, and $\hbar\beta = 4.0$. The off-diagonal coupling constant is given by $V_{\mathrm{ge}} = V_{\mathrm{eg}} = V_0 = 0.1$.

In the BOC-LDC case, the exact correlation function in eq 4 is explicitly given by

$$C_{\mathrm{BOC-LDC}}(t) = \exp\left\{\frac{1}{2\hbar}\int_0^\infty d\omega\, J(\omega)\omega[\coth(\beta\hbar\omega/2)[\cos(\omega t) - 1] - i\sin\omega t]\right\}\left\{\left[\frac{1}{2\hbar}\int_0^\infty d\omega\, J_{\delta\mathrm{S}}(\omega)\omega[\coth(\beta\hbar\omega/2)[\cos(\omega t) - 1] - i\sin(\omega t)]\right]^2 + \frac{1}{2\hbar}\int_0^\infty d\omega\, J_{\mathrm{S}}(\omega)\omega[\coth(\beta\hbar\omega/2)\cos(\omega t) - i\sin(\omega t)]\right\} \tag{A4}$$

where

$$J_{\mathrm{S}}(\omega) = \sum_k (S^{(k)})^2 \delta(\omega - \omega^{(k)}) \tag{A5}$$

and

$$J_{\delta\mathrm{S}}(\omega) = \sum_k S^{(k)}\delta^{(k)}\delta(\omega - \omega^{(k)}) \tag{A6}$$

It should be noted that the corresponding expression in eq 19 of ref 71 should be corrected by substituting $V_{10} = 1$ and replacing $|\cdots|^2$ by $[\cdots]^2$ on the right-hand side.[98] Following ref 71, we assume that $J_{\mathrm{S}}(\omega) = J_{\delta\mathrm{S}}(\omega) = J(\omega)$ (cf. eq A3), with the same parameters as for the SOC-LDC case.

In the SOC-QDC case, one has to determine the values of $\{\delta^{(k)}\}$ and$\{g_{j,k}\}$, which is done following a procedure similar to that reported in ref 71. More specifically, the electronic transition is assumed to be coupled to a single harmonic bath mode, $\tilde{Q}^{(1)}$, which is in turn bilinearly coupled to the remaining uncoupled harmonic bath modes $\{\tilde{Q}^{(2)}, ..., \tilde{Q}^{(N_n)}\}$. The corresponding coupling term is given by $\sum_{k=2}^{N_n} c^{(k)}\tilde{Q}^{(1)}\tilde{Q}^{(k)}$. The frequencies of the bath modes $\tilde{Q}^{(1)}, ..., \tilde{Q}^{(N_n)}$ are given by $\tilde{\omega}^{(1)}, ..., \tilde{\omega}^{(N_n)}$, respectively. The values of $\tilde{\omega}^{(1)}$ and the coupling coefficients, $\{c^{(k)}\}$, which correspond to the ground and excited electronic states, are assumed to be different. More specifically, it is assumed that $\sum_{k=2}^{N_n} (c^{(k)})^2\delta(\omega - \tilde{\omega}^{(k)})/2\omega^{(k)} = J(\omega)$, where $J(\omega)$ is as in eq (A3), with $\sigma = 0.2$, $\omega_{\mathrm{op}} = \tilde{\omega}^{(1)} = 1.1$ (1.0), and $\lambda = 0.05$ (0.125), in the ground (excited) electronic state. It is also assumed that the equilibrium displacement of the $\tilde{Q}^{(1)}$ mode in the ground state is shifted by the amount $d_0 = 2.0$ relative to the excited state. The resulting free bath Hamiltonian that corresponds to the excited electronic state is then numerically diagonalized, and the corresponding normal-mode frequencies, coordinates, and momenta are associated with those appearing in eq 37. The intermode coupling coefficients$\{g_{j,k}\}$ are obtained by rewriting the ground-state nuclear Hamiltonian in terms of the normal modes of the excited-state Hamiltonian. The temperature was given by $\hbar\beta = 4.0$, as in the SOC-LDC case. It was verified that the results are converged for $N_n = 60$ harmonic modes.

In the BOC-QDC case, the bath was treated in the same way as in the SOC-QDC case, with a direct coupling of the electronic DOF to a single primary bath mode, which is in turn coupled to the rest of the bath modes. The off-diagonal coupling between the nuclear and electronic DOF is given by $s_0\tilde{P}^{(1)}$, where $s_0 = 2.0$ and $\tilde{P}^{(1)}$ is the momentum of the primary bath mode. The resulting free bath Hamiltonian that corresponds to the excited electronic states is then numerically diagonalized, and the corresponding normal-mode frequencies, coordinates, and momenta are associated with those appearing in eq 37. The coefficients $\{g_{j,k}\}$ are obtained by rewriting the ground-state nuclear Hamiltonian in terms of the normal modes of the excited-state Hamiltonian, and the temperature is set to $\hbar\beta = 4.0$. It was verified that the results are converged for $N_n = 60$

harmonic modes. It should be noted that the results presented in Figure 4 are different in comparison to the corresponding Figure 4 of ref 71 due to a different choice of parameters.[98]

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