Phase-space wavepacket dynamics of internal conversion via conical intersection: Multi-state quantum Fokker-Planck equation approach

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A B S T R A C T

We theoretically investigate internal conversion processes of a photoexcited molecule in a condensed phase. The molecular system is described by two-dimensional adiabatic ground and excited potential energy surfaces that are coupled to heat baths. We quantify the role of conical intersection (CI) and avoided crossing (AC) in the PESs in dissipative environments by simulating the time evolution of wavepackets to compute the lifetime of the excited wavepacket, yield of the product, and adiabatic electronic coherence. For this purpose, we employ the multi-state quantum Fokker-Planck equation (MSQFPE) for a two-dimensional Wigner space utilizing the Wigner-Moyal expansion for the potential term and the Brinkman hierarchy expression for the momentum. We find that the calculated results are significantly different between the CI and AC cases due to the transition in the tuning mode and vibrational motion in the coupling mode.

1. Introduction

Internal conversion (IC) of a photoexcited molecule through conical intersection (CI) points plays an important role in photochemical processes, such as ultrafast electronic and vibrational transitions [1–16]. Such systems are characterized by adiabatic ground and excited potential energy surfaces (PESs) that are functions of multi-dimensional reaction coordinates. Conical intersections arise at the intersections of the PESs, where the Born-Oppenheimer (BO) approximation breaks down. As a result, efficient non-adiabatic transitions occur through CIs. Experimentally, the roles of CIs are not easy to explore, because excited wavepackets at the CI points are in transition states exhibiting very short lifetimes. For this reason, theoretical input regarding de-excitation processes via CIs are important for analyzing such experimental results.

Theoretically, investigations of this kind are carried out by obtaining the profiles of the multi-dimensional PESs and then performing quantum kinetic simulations running the wavepackets in the PESs. However, the existence of singular points at CI points make it difficult to obtain accurate static structures of the PESs and to carry out reliable kinetic simulations. For kinetic simulations, because the momentum and lifetime of the wavepackets in excited states are also determined by thermal activation and relaxation processes, environmental effects must be described in terms of open quantum dynamics; quantum mechanically consistent treatments of the system and environment are essential to obtain reliable results. The excited state dynamics of such systems that explicitly take into account nuclear degrees of freedom and electronic states have been investigated using approaches that employ equations of motion for the density matrices or phase space distributions [13–24], mixed quantum-classical trajectories [25–30], and Gaussian quantum wavepackets [31–33]. Many of these approaches, however, involve non-trivial assumptions, in particular, those regarding the quantum dynamical treatment of the couplings between electronic states and reaction coordinates, without careful verification of their validity.

In this paper, we investigate the role of CI and avoided crossing (AC) in dissipative environments. Although the qualitative analysis has been done from a perturbative approach [34], here we carry out a quantitative analysis using a numerically accurate approach with systematically changing diabatic coupling parameters. For this purpose, we employ the multi-state quantum Fokker-Planck equation (MSQFPE) approach, which is an extension of the quantum Fokker-Planck equation for a Wigner distribution function (WDF) to a multi-state system [18–21]. While this technique allows us to treat systems with arbitrary PESs by taking into account the electric coherence explicitly, solving the MSQFPE is numerically demanding, in particular, in the case of multi-dimensional PESs. For this reason, we apply the Wigner-Moyal expansion to a multi-state Wigner distribution function (MSWDF) in order to evaluate the quantum Liouvillian for the multi-state system and the Brinkman hierarchy for the momentum space of the MSWDF.
We consider a molecular system with multiple electronic states \(|j\rangle\) coupled to \(N\) dimensionless reaction coordinates \(\vec{q} = (\ldots q_a, \ldots)\), where \(j\) represents the electronic diabatic states and \(s\) is the index for the reaction coordinates. Here and hereafter, we employ dimensionless coordinates and momentum \(\vec{q}_s\) and \(\vec{p}_s\), as \(q_s = \sqrt{m_s\omega_s/\hbar}\) and \(p_s = \sqrt{m_s\omega_s/\hbar}\), where \(\omega_s\) is the characteristic frequency and \(m_s\) is the effective mass of the \(s\)th mode. The system Hamiltonian is expressed as \([18–21]\)

\[
\hat{H}(\vec{q}, \vec{p}) = \sum_s \frac{\hbar\omega_s}{2} \hat{\vec{p}}_s^2 + \sum_{j,k} \langle j| U^{jk}(\vec{q}) |k\rangle,
\]

where \(\vec{p} = (\ldots \vec{p}_1, \ldots)\) represents the momentum conjugate to the coordinates. Here, the nuclear and electronic operators are denoted by hats, and we omit direct products with the identity, \(\hat{1}\), in the kinetic term. The electronic potential is also expressed in matrix form as \(|U^{jk}(\vec{q})|_{jk} = U^{jk}(\vec{q})\), where the diagonal element \(U^{jj}(\vec{q})\) and the off-diagonal element \(U^{jk}(\vec{q})\) \((j \neq k)\) represent the diabatic PES of the \(j\)th electronic state and the diabatic coupling between the \(j\)th and \(k\)th states, respectively. Note that the frequency \(\omega_s\) is determined by the curvature of the potential \(U(\vec{q})\) as

\[
\hbar\omega_s \approx \frac{\partial^2}{\partial \vec{q}_s^2} U^{00}(\vec{q})|_{\vec{q}=\vec{q}_s^{(0)}}
\]

where \(\vec{q}_s^{(0)}\) is a local minimum of the primary PES.

### 2.2. Quantum Liouvillian and Wigner distribution functions

Under the canonical quantization of the dimensionless momentum and coordinates, given by

\[
\hat{p}_s = -\frac{\hbar}{i} \frac{\partial}{\partial q_s} \quad \text{and} \quad q_s \rightarrow z_s,
\]

the state of the system at time \(t\) is described using the density matrix \(\rho(\vec{z}, \vec{z}', t)\), where \(\rho^0(\vec{z}, \vec{z}')\) and \(\rho^k(\vec{z}, \vec{z}')\) \((j \neq k)\) represent the population of \(|j\rangle\) and the coherence between \(|j\rangle\) and \(|k\rangle\), respectively. The time evolution of the system is described by the Liouville-von Neumann equation as

\[
\frac{d}{dt} \rho(\vec{z}, \vec{z}', t) = -\mathcal{L}(\vec{z}, \vec{z}') \rho(\vec{z}, \vec{z}', t),
\]

(4a)

where \(\mathcal{L}(\vec{z}, \vec{z}')\) is the quantum Liouvillian defined as

\[
\mathcal{L}(\vec{z}, \vec{z}') \rho(\vec{z}, \vec{z}') \equiv -i \sum_s \omega_s \left( \frac{\partial}{\partial z_s} - \frac{\partial}{\partial z_s'} \right) \rho(\vec{z}, \vec{z}') + \frac{i}{\hbar} \left[ U(\vec{z}) \rho(\vec{z}, \vec{z}') - \rho(\vec{z}', \vec{z}) U(\vec{z}') \right].
\]

(4b)

We now introduce the multi-state Wigner distribution function (MSWDF) for a multi-electronic state system \([18]\):

\[
W(\vec{p}, \vec{q}, t) \equiv \frac{1}{(2\pi\hbar)^N} \int d^2\vec{r} e^{-\vec{r}^2/2} \rho(\vec{q} + \frac{\vec{r}}{2}, \vec{q} - \frac{\vec{r}}{2}, t).
\]

(5)

where \(\vec{q} \equiv (\vec{z} + \vec{z}')/2\) and \(\vec{r} \equiv \vec{z} - \vec{z}'\). Both \(\vec{p}\) and \(\vec{q}\) are now \(N\)-dimensional vectors in this phase space representation. The distribution \(W(\vec{p}, \vec{q}, t)\) always satisfies the normalization condition

\[
\sum_j \int d\vec{p} \int d\vec{q} W^{jk}(\vec{p}, \vec{q}, t) = 1.
\]

(6)

The MSWDF is ideal for studying quantum transport systems, because it allows for the treatment of continuous systems, utilizing open boundary conditions and periodic boundary conditions. In addition, the formalism can accommodate the inclusion of an arbitrary time-dependent external field \([19,20]\). Moreover, because we can compare quantum results with classical results obtained in the classical limit of the equation of motion for the WDF, this approach is effective for identifying purely quantum effects \([35–38]\).

Using \(W(\vec{p}, \vec{q}, t)\), the equation of motion (4) can be expressed in the Wigner–Moyal expansion form as

\[
\frac{\partial}{\partial t} \mathcal{W}(\vec{p}, \vec{q}, t) = -\mathcal{L}_W(\vec{p}, \vec{q}) \mathcal{W}(\vec{p}, \vec{q}, t),
\]

(7a)
where $\mathcal{L}(\vec{p}, \vec{q})$ is the quantum Liouvillian for the MSWDF, defined as

$$
\mathcal{L}_{ij}(\vec{p}, \vec{q}) W(\vec{p}, \vec{q}) 
\equiv \sum_j \omega_j \rho_{j, i} \mathcal{W}(\vec{p}, \vec{q}) 
+ \frac{i}{\hbar} [U(\vec{q}) \star W(\vec{p}, \vec{q}) - W(\vec{p}, \vec{q}) \star U(\vec{q})],
$$

(7b)

where the star operator, $\star$, represents the population of $\rho_{j, i}$ and $\rho_{i, j}$ are the vibrational frequency and dimensionless co-efficient, respectively. The condition $\omega_j > 2\omega_0$, where $\omega_0$ is the harmonic PES with frequency $\omega_0$, and $\omega_j > 2\omega_0$, for the $j$th mode correspond to the underdamped, critically damped, and overdamped cases, respectively.

The total system is described by $W_{\text{tot}}(\vec{p}, \vec{q}, \vec{F}, \vec{X}, t)$, where $X = (\cdots X_{i, f}, \cdots)$ and $F = (\cdots F_{i, f}, \cdots)$. The reduced MSWDF is then given by

$$
W(\vec{p}, \vec{q}, t) \equiv \int d\vec{F} \int d\vec{X} W_{\text{tot}}(\vec{p}, \vec{q}, \vec{F}, \vec{X}, t).
$$

(14)

In general, the equations of motion for the reduced system are expressed in the hierarchical form [19–21, 24–22, 24]. The equations of motion of the quantum Fokker-Planck equation [41]. In the present case, this is expressed as [18]

$$
\frac{\partial}{\partial t} W(\vec{p}, \vec{q}, t) = -\mathcal{L}(\vec{p}, \vec{q}) W(\vec{p}, \vec{q}, t)
+ \sum_j \frac{\partial}{\partial p_j} \left( \frac{1}{\beta \hbar \omega_0} \frac{\partial}{\partial p_j} \right) W(\vec{p}, \vec{q}, t).
$$

(15)

The above equation is the MSQFPE, which is a generalization of the quantum Fokker-Planck equation for multiple modes and multiple electronic states.

### 2.4. The adiabatic representation

We now introduce electronic adiabatic states, $|\Phi^a(\vec{q})\rangle$. In the following, $a$, $b$, and $c$ refer to electronic adiabatic states and $j$, $k$, and $l$ refer to electronic diabatic states. The electronic adiabatic state is an eigenfunction of the time-independent Schrödinger equation

$$
\hat{H}(\vec{q}) |\Phi^a(\vec{q})\rangle = U^a_j |\Phi^a(\vec{q})\rangle,
$$

(16)

where $U^a_j(\vec{q}) \equiv \sum_{k, l} |j\rangle U^{bl}(\vec{q}) |k\rangle$, and $U^{bl}(\vec{q})$ is the $a$th adiabatic BO PES. The diabatic and adiabatic states are related through the transformation matrix expressed as

$$
Z^a(\vec{q}) \equiv \langle j | \Phi^a(\vec{q})\rangle.
$$

(17)

Using the matrix $\langle Z(\vec{q}) \rangle_{ab} = Z^a(\vec{q})$, Eq. (16) can be written in the form of a diagonal matrix as

$$
\mathcal{H}(\vec{q}) U(\vec{q}) Z(\vec{q}) = U^a_j(\vec{q}),
$$

(18)

where $U(\vec{q}) \equiv \sum_{a, b} \langle j | U^{bl}(\vec{q}) |k\rangle$, and $U^{bl}(\vec{q})$ is the $a$th adiabatic BO PES. The adiabatic representation of the (reduced) density matrix, $\rho_{\vec{z}, \vec{z}'}$, is defined through application of the transformation matrix $Z(\vec{q})$ to $\rho(\vec{z}, \vec{z}')$ as

$$
\rho_{\vec{z}, \vec{z}'}(\vec{q}) \equiv Z(\vec{q}) \rho(\vec{z}, \vec{z}') Z(\vec{q}^\dagger).
$$

(19)

The adiabatic representation of the MSWDF, $W_{\text{tot}}(\vec{p}, \vec{q}, t)$, is defined as

$$
W_{\text{tot}}(\vec{p}, \vec{q}, t) \equiv \frac{1}{(2\pi)^N} \int d\vec{r} e^{i\vec{r} \cdot \vec{p}} F_{\vec{z}, \vec{z}'}(\vec{q} + \frac{\vec{r}}{2}, \vec{q} - \frac{\vec{r}}{2}) t.
$$

(20)

The inverse transformation is expressed as

$$
W(\vec{p}, \vec{q}, t) = Z(\vec{q})^\dagger \mathcal{W}(\vec{p}, \vec{q}, t) Z(\vec{q}).
$$

(21a)
\[ W(\vec{p}', \vec{q}', t) = W(\vec{p}, \vec{q}, t) \star Z(\vec{q}, t) \star W(\vec{p}', \vec{q}', t) \star Z(\vec{q}', t). \]  

(21b)

Details regarding Eqs. (17), (19), (21a), and (21b) are presented in Supplemental Information S2 (Available at: http://dx.doi.org/10.17632/w9k8xh3d4t.2).

Integrating Eq. (15) with the Liouvillean Eq. (7), we obtain the MSQDF in the diabolic representation, \( W(\vec{p}, \vec{q}, t) \). Then, using the transformation \( (21a) \), we obtain the MSQDF in the adiabatic representation, \( W(\vec{p}, \vec{q}, t) \). Although we can construct the MSQFPE for \( W(\vec{p}, \vec{q}, t) \), numerical integration of this equation is difficult, because the present PESs in the diabolic basis \( \Phi(\vec{q}') \) have a singularity at the CI point. For this reason, in the present work, we solve Eq. (15) for \( W(\vec{p}, \vec{q}, t) \) to obtain \( W(\vec{p}, \vec{q}, t) \).

### 2.5. Brinkman hierarchy

While the quantum dynamics for an N-dimensional system can be studied by solving the Schrödinger equation for N-dimensional wave functions, we must treat 2N-dimensional reduced density matrices or Wigner functions in the study of open quantum dynamics evolving toward the thermal equilibrium state. Although the present approach allows us to obtain accurate results, solving the MSQDF is numerically demanding, in particular for multi-dimensional PESs. Thus, to reduce the numerical cost, here we describe the momentum space of \( W(\vec{p}, \vec{q}, t) \) using a series expansion in terms of Hermite functions expressed as

\[ W(\vec{p}, \vec{q}, t) = \sum_{\vec{p}, \vec{q}} e^{-\frac{i}{\hbar}U(\vec{q}, t)} e^{-\frac{1}{2}\sum_{i,j}p_iq_j} e^{-\frac{1}{2}\sum_{i,j}p_iq_j} \psi_{\vec{p}, \vec{q}}(\vec{p}, \vec{q}, t), \]

(22a

where the function of the coordinates in matrix form, \( \{ \epsilon(\vec{q}, t) \} \), is defined as

\[ \epsilon(\vec{q}, t) = \int d\vec{p} \epsilon(\vec{q}, t) e^{-\frac{i}{\hbar}U(\vec{q}, t)} e^{-\frac{1}{2}\sum_{i,j}p_iq_j} \psi_{\vec{p}, \vec{q}}(\vec{p}, \vec{q}, t). \]

(22b

Here, the vector \( \vec{m} \equiv (\ldots, m_n, \ldots) \) represents the momentum state of the Hermite function \( \psi_{\vec{p}}(\vec{p}, \vec{q}, t) \), where \( \psi_{\vec{p}}(\vec{p}, \vec{q}, t) \equiv \prod_i \psi_{\vec{p}}(p_i), \) with

\[ \psi_{\vec{p}}(p_i) = \frac{1}{\sqrt{2^n n! \sqrt{\alpha s}}} H_n \left( \frac{p_i}{\sqrt{\alpha s}} \right) \exp \left( - \frac{p_i^2}{2\alpha s} \right). \]

(23

Here, \( \alpha_s \equiv \frac{\sqrt{2} \hbar \omega_0}{m} \) and the \( m \)th Hermite polynomial is defined as \( H_m(x) \equiv (-1)^m e^{x^2} (d^m e^{-x^2}) \). In Eqs. (22a) and (22b), \( U(\vec{q}, t) \) is the diagonal matrix whose diagonal elements are identical to those of \( U(\vec{q}, t) \), and \( \alpha_s \) is an arbitrary constant. Because of Eq. (6), \( \epsilon(\vec{q}, t) \) always satisfies

\[ \sum \int d\vec{q} e^{-\frac{i}{\hbar}U(\vec{q}, t)} \psi_{\vec{p}, \vec{q}}(\vec{p}, \vec{q}, t) = 1. \]

(24

The notation employed here is defined in Table 1. Note that the zeroth order expansion term is proportional to the classical Boltzmann distribution: \( \psi_{\vec{p}}(p_i, t) \propto e^{-\hbar \omega_0 p_i^2 / 2m}. \)

The MSQFPE (15) for \( \epsilon(\vec{q}, t) \) can be expressed in the form of simultaneous differential equations as

\[ \frac{d}{dt} \epsilon(\vec{q}, t) = -\sum_i \alpha_s \epsilon(i, \vec{q}, t) + \sum_{m \neq n} \omega_{mn} \epsilon(m, \vec{n}, t) - \sum_i \omega_{i1} \epsilon(i, \vec{q}, t), \]

(25

where \( \vec{n} \) is the sth unit vector and \( \vec{m} \equiv (\ldots, m_n, \ldots) \) is the multi-index for the Moyal product (8). Here, we have introduced the superoperators \( \alpha_s(\vec{q}) \) and \( \omega_{mn}(\vec{q}) \) defined as

### Table 1

<table>
<thead>
<tr>
<th>Notation Meaning</th>
<th>Notation Meaning</th>
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<tbody>
<tr>
<td>( \vec{n} \equiv \vec{m} \equiv (\ldots, m_n, \ldots) )</td>
<td>( \vec{n} \equiv (\ldots, n_m, \ldots) )</td>
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<tr>
<td></td>
<td>( \sum n_i )</td>
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<tr>
<td>( \vec{p} \equiv (\ldots, p_m, \ldots) )</td>
<td>( \prod_i \alpha_s )</td>
</tr>
<tr>
<td></td>
<td>( \delta(\vec{q}, \vec{q}') \prod_i \delta(q_i, q'_i) )</td>
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Details regarding the derivation of Eq. (25) are presented in Supplemental Information S3 (Available at: http://dx.doi.org/10.17632/w9k8xh3d4t.2).

We note that Eq. (25) has been employed as the equations of motion for the Brinkman hierarchy to describe a classical Fokker-Planck equation [45–47]. The first and second terms in Eq. (25) are the kinetic and potential terms. The potential term involves the higher-order Moyal expansion terms. The last term in Eq. (25) describes the fluctuation and dissipation that arise from the heat baths. While \( t \) is an arbitrary constant, we found that the best choice to enhance the numerical stability of Eq. (25) is \( t = 1/2, \) as in a case of the single PES [45]. Note that the Brinkman hierarchy representation is suitable for the case that the force described by the PESs is not strong, i.e., the case in which wavepackets in the momentum space is close to the thermal equilibrium state and the wavepackets can be described by a small number of coefficients \( \epsilon(\vec{q}, t) \).

### 3. Models

#### 3.1. Potential energy surfaces and diabatic coupling

We consider an IC system with two diabatic states, \( |0\rangle \) and \( |1\rangle \), the reactant and product states, respectively. These states are strongly coupled to two reaction coordinates, \( q_i \) and \( q_j \), corresponding to the tuning and coupling modes, respectively. The tuning mode tunes the energy gap between two electronic states, while the coupling mode couples two electronic diabatic states in the CI case [3,4]. The diabatic PESs are described by the following combinations of the Morse and harmonic potential curves:

\[ U^{00}(q_i) = D^0 \left( 1 - e^{-\sqrt{\hbar \omega_0 / 2m}(q_i - q_i^0)^2} \right) + \frac{h_{\omega_0}}{2}(q_i - q_i^0)^2 + E^0, \]

(28a

and

\[ U^{01}(q_i) = D^1 \left( 1 - e^{-\sqrt{\hbar \omega_0 / 2m}(q_i - q_i^0)^2} \right) + \frac{h_{\omega_0}}{2}(q_i - q_i^0)^2 + E^1, \]

(28b

where \( D^j \) is the dissociation energy, \( E^j \), and \( q_i^j \) are the equilibrium minima and displacements of the diabatic PES for \( j = 0 \) and \( 1 \), respectively, and \( \omega_0 \) and \( \omega_1 \) are the vibrational frequencies at the minimum of
the PESs in the \( q_i \) and \( q_j \) directions. Note that when a molecule we consider obeys a certain point-group symmetry, we can clearly separate the vibrational modes into the tuning and coupling modes [3,4]. In our model, this condition is expressed as \( q_i^0 = q_i^1 \). When the molecule is non-symmetric, however, the mixing of the tuning and coupling modes occurs. In our model, this condition is expressed as \( q_i^0 \neq q_i^1 \), which implies that the coupling mode \( q_i \) also tunes the energy gap, and the position of the stable points in the \( q_i \) direction change during the reaction processes.

For the case \( q_i^0 < q_i^1 \), the crossing curve of the diabatic PESs is defined as \( \mathbf{q}^0 \equiv (q_i^0, q_j^1) \), where \( q_i^0 \) and \( q_i^1 \) satisfy \( U^{00}(q_i^0) = U^{11}(q_i^1) \) and \( q_i^0 < q_i^1 \). We chose the parameter values of the PESs such that this crossing curve exists. Then, we define the reactant and product regions, \( s \) and \( p \), as \( q_i < q_i^* \) and \( q_i > q_i^* \), respectively, under the condition \( q_i = q_i^0 \).

We introduce the diabatic coupling function as 
\[
U^{01}(q_i) = U^{11}(q_i) \equiv \sigma(q_i^0),
\]
and consider the CI and AC models in which \( |\psi\rangle^c = \psi(q_i^0) \) and \( |\psi\rangle^d = \psi(q_i^1) \) (29a).

When we introduce the CI-minimum distance defined as
\[
d = r^c - r^{c,\text{min}},
\]
(37)
where \( r^c \) and \( r^{c,\text{min}} \) are the CI point and the minimum of the adiabatic excited PES. The parameter values for the system and the heat baths are listed in Table 2.

Numerical calculations were carried out to integrate Eq. (25) using the fourth-order low-storage Runge-Kutta method with a time step \( \delta t = 0.2 \text{ fs} \) [48,49]. The finite difference calculations for the \( \frac{\partial}{\partial t} \) derivatives in Eq. (25) were performed using the first-order difference method with ninth-order accuracy [50]. The numerical integrations of the MSWDF in \( \mathbf{q} \) space were performed using the trapezoidal rule. The mesh size in \( \mathbf{q} \) space was \( N_q \times N_q = 128 \times 48 \) with mesh ranges \(-20 \leq \psi_i, j \leq +20 \) and \(-8 \leq \psi_i, j \leq +8 \). The depth of the Brinkman hierarchy was 40 and 32 for \( n_r \) and \( n_s \), respectively. We introduced artificial viscosity terms in Eq. (25) to enhance the stability of the numerical integrations. The details regarding the finite differences and artificial viscosity terms are explained in Supplemental Information S6 (Available at: http://dx.doi.org/10.17632/w9k8hx3d4t.2).

It has been shown that a GPGPU, which utilizes fast access memory and super parallel architecture, is a powerful device to integrate simultaneous differential equations for systems with many degrees of freedom, as Eq. (25). We carried out the time integration of Eq. (25) using the first-order form of Eq. (7b) given in Eq. (10) for 1000 fs employing C++/CUDA codes with an NVIDIA Tesla P100 and employing single thread C++ codes with an Intel Xeon CPU E5-2667. The computation times were approximately 15 min for the former and 16 h for the latter.

### 4. Numerical results

We carried out numerical simulations for the system described by the diabatic PESs, Eqs. (28a) and (28b). Next, we introduce the CI and AC models described by the diabatic coupling given in Eqs. (29a) and (29b). For each model, we consider the case with and without displacements in the tuning mode \( q_i \). Thus, we have four models, which we call CI0, CI1, AC0, and AC1, where 0 and 1 correspond to the cases \( q_i^0 = 0 \) and \( q_i^1 = 0 \). For \( q_i^0, q_i^1 \neq 0 \), the coupling mode also tunes the energy gap. To investigate the efficiency of the IC process, we introduce the CI-minimum distance defined as
\[
d = r^c - r^{c,\text{min}},
\]
(37)
where \( r^c \) and \( r^{c,\text{min}} \) are the CI point and the minimum of the adiabatic excited PES. The parameter values for the system and the heat baths are listed in Table 2.

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### 4.1. Verification of the truncated Moyal expansion

We introduce the truncated Moyal product defined as
\[
\mathbf{M} \equiv \sum_{m=0}^{M} \frac{1}{m!} \sum_i \left( \frac{\partial}{\partial q_i} \delta_{\phi_{\mathbf{q}}^m} \right)^m,
\]
(38)
where \( M \) is the order of the truncation. Then Eqs. (7b) and (21) can be written as
\[
\mathbf{F}(\mathbf{q}) = \mathbf{W}(\mathbf{q}) \mathbf{W}(\mathbf{q}),
\]
(39a)
and
\[
\mathbf{F}(\mathbf{q}) \equiv \int d\mathbf{q}' F^\phi(\mathbf{q}', t),
\]
(35)
where \( u^\phi(t) = u^\psi(t) + u^\omega(t) \) and \( u^\psi(t) + u^\omega(t) = 1 \). Then the expectation value of \( q^c_i \) at time \( t \) is defined as
\[
\langle q^c_i(t) \rangle^\phi \equiv \int d\mathbf{q}' q^c_i F^\phi(\mathbf{q}', t)/u^\phi(t).
\]
(36)
second-order term \([51]\). For the elements \(W^{jk} \equiv W^{jk}(p, q)\) with \(\tilde{\beta} = \mu/(0)(11 + 11)(0)\), \(W(p, q, 0)\) is given in matrix form as

\[
W(p, q, 0) = \begin{pmatrix}
\| 0 \|
\| 1 \|
\end{pmatrix}
+ A \begin{pmatrix}
\| 0 \|
\| 1 \|
\end{pmatrix}
+ A \begin{pmatrix}
\| 0 \|
\| 1 \|
\end{pmatrix}
+ A \begin{pmatrix}
\| 0 \|
\| 1 \|
\end{pmatrix}
+ A \begin{pmatrix}
\| 0 \|
\| 1 \|
\end{pmatrix}
\]

(39b)

where \(A \equiv \{E\mu\alpha\gamma\}/\hbar^2\). Thus, when we choose the dimensionless constant \(A\) to be \(A = 1\), the excitation pulses cause the populations of \(0\) and \(1\) states to be exchanged.

In Fig. 2, we depict the kinetic energy of the tuning mode \(K(t)\) for fixed \(q = 200\) cm\(^{-1}\) from \(M = 1\) to 5. As seen there, the results obtained with the first-order truncation \(\beta = 1\) are very similar to those from \(\beta = 5\). This is because the damping operators in the MSFPE cause the profile of the wavepackets to be Gaussian-like and because the anharmonicity of the Morse potential is not strong.

We have examined the numerical accuracy for the AC0 case, but the same argument can be applied to the CI0, CI1, and AC1 case, because the diabatic PESs in the \(q\) direction are harmonic, and as a result the truncation for \(\beta = 1\) is analytically exact. Hence, hereafter we employ \(\beta = 1\).

4.2. Wavepacket dynamics

In the previous subsection, we demonstrated the accuracy of the numerical calculations starting from the true thermal equilibrium state. For the case \(\beta = 1\), however, the difference between the classical Boltzmann equilibrium state and the true thermal equilibrium state described by the MSQFPE is minor, as shown in the case for \(t_{eq} = 0\) fs in Fig. 2. For this reason, we use the classical Boltzmann distribution of

\[
\begin{align*}
W(p, q, t) &= \int Z(q) \star W(p, q) Z(q) \, dq, \\
W(p, q, t) &= \sum_{M=M-d=1} Z(q) \star W(p, q, t) \star Z(q).
\end{align*}
\]

respectively, where \(d \geq 1\). Before carrying out the full analysis, we examine the accuracy of the above expressions. For this purpose, we consider the AC0 case, in which the coupling mode, \(q\), decouples from the tuning mode, \(q\), and the electronic states. For this reason, we can ignore the dynamics in the \(q\) direction and regard the AC0 model as a one-dimensional system.

To obtain a proper initial distribution that is consistent with the truncation Eq. (38) and the high-temperature approximation, we first set the initial distribution as the classical Boltzmann distribution of the reactant adiabatic ground state, which is approximated as

\[
W(p, q, -t_{eq}) = W(p, q, -t_{eq}) = W(p, q, -t_{eq}) = \text{for } q_i\text{ in}
\]

(39a)

the region \(\beta\), and as \(W(p, q, -t_{eq}) = 0\) otherwise, where \(\beta\) is the partition function. Then we integrate Eq. (15) for a sufficiently long time \(t_{eq}\) to obtain a stationary distribution, expressed as \(W(p, q)\).

We assume that the reaction process is initiated by photostimulation created by a pair of impulsive pulses at \(t = 0\) described by the dipole moment \(\mu(\beta) \equiv \mu(\beta/k)\) for \(k = 0, 1\) as

\[
W(p, q, 0) = W(p, q) + (E\Delta t)^2 \sum_{jk} [\mu, \mu, W(p, q)]
\]

(40)

where \(E\) and \(\Delta t\) are the electric field amplitude and pulse duration of the two pulses, and the square brackets represent the ordinary commutator, defined as \([A, B] \equiv AB - BA\). Eq. (40) consists of the zeroth- and second-order perturbative expansion terms of the electric field, and the excited wavepacket dynamics measured in impulsive pump–probe spectroscopy can be simulated from the

\[
\begin{align*}
\text{Table 2} \quad & \text{The parameter values for the CI and AC models.} \\
\hline
\text{Model} & \text{Symbol} & \text{Value} \\
\hline
\text{CI} & c & 200 \text{ cm}^{-1} \\
& d & -2.5 \pm 2.5 \\
0 & q_0^0 & 0 \\
& q_1^0 & 0 \\
1 & q_0^1 & -0.5 \\
& q_1^1 & +0.5 \\
\text{AC} & a & 50-500 \text{ cm}^{-1} \\
0 & q_0^a & 0 \\
& q_1^a & 0 \\
1 & q_0^1 & -0.5 \\
& q_1^1 & +0.5 \\
\hline
\end{align*}
\]
the adiabatic ground state as the initial state. We thus set the initial
distribution for $\vec{q}$ in the region $\mathfrak{F}$ as

$$W_{\mathfrak{F}}^{eq}(\vec{q}, \vec{q}, 0) = \frac{1}{\mathfrak{F}} \exp(-\hbar a q^2/2 + \hbar u q^2/2 + U_{eq}(\vec{q})),$$

(42)

and as $W_{\mathfrak{F}}(\vec{q}, \vec{q}, 0) = 0$ otherwise.

Fig. 3 illustrates the time evolution of the populations in the excited,
ground reactant, and ground product states, $u^e(t)$, $u^r(t)$, and $u^p(t)$, with
the CI-minimum distance $d = 1.5$. For the excited state, the excited
wavepacket is initially in the reactant region on the excited state, and
then the wavepacket arrives at the crossing region at approximately
$t = 100$ fs. Because the excited wavepacket has kinetic energy obtained
from the potential in the direction of the product region at the CI point,
most of the population quickly transfers to the product region in the
ground state.

For the time evolution of $u^e(t)$, we observe slight oscillatory beha-
viour at approximately $t = 200$ fs, when the wavepackets are in the
crossing region. To analyze this point more closely, we display snap-
shots of wavepackets in the ground and excited adiabatic states,
$F^s(\vec{q}, \vec{q}, t)$ and $F^e(\vec{q}, \vec{q}, t)$, in Fig. 4. Due to the difference between
the stable points for the adiabatic ground and excited states in the
direction of $q$, the wavepacket exhibits vibrational motion in the direc-
tion of the coupling mode, $q$. As depicted in Fig. 4(ii), the wavepacket
cannot be centered at the CI point because of this vibrational motion. As
a result, the population of the reactant also exhibits oscillatory motion,
as observed in Fig. 3. Note that the vibrational motions in the coupling
mode induce non-adiabatic transitions for the case $q^0 \neq q^1$, because
the coupling mode also couples to the electronic states. After the os-
cillatory motion of the excited state wavepacket in the $q$ direction and
the motion in the $q$ direction relax, a small portion of the wavepacket is
trapped at the local minimum in the crossing region. This wavepacket
slowly relaxes to both the reactant and product regions in the ground
state. By $t = 500$ fs, illustrated in Fig. 4(iii), has excited wavepacket is
relaxed and has mostly transferred to the product states.

4.3. The lifetime of the adiabatic excited state

We next investigate the lifetime of the adiabatic excited state for the
CI and AC models with various values of the diabatic coupling pa-
rameters. We define the lifetime $\tau^e$ as

$$\tau^e \equiv \int_0^{t_e} dt \frac{u^e(t) - u^e(t)}{u^e(0) - u^e(t)}$$

(43)

where $t_e$ is a sufficiently long time to evaluate the entire de-excitation.

![Fig. 3. The time evolution of the population in the CI1 model with $d = 1.5$. The red,
green, and purple curves represent the populations for the excited, ground
reactant, and ground product states, $u^e(t)$, $u^r(t)$, and $u^p(t)$, respectively. Here,
the lifetime of the excited population, given in Eq. (43), and the yield, given in
Eq. (44), are evaluated as $\tau^e = 235$ fs and $\eta^e = 0.788$, respectively. (For inter-
pretation of the references to colour in this figure legend, the reader is referred to
the web version of this article.)](image1)

![Fig. 4. Snapshots of excited wavepackets in CI1 model with waiting times (i)
$t = 0$ fs, (ii) 250 fs, and (iii) 500 fs. The CI-minimum distance is $d = 1.5$. The red,
green, and purple curves represent the mean coordinates for the excited, ground
reactant, and ground product states, $(\vec{q}(t))^e$, $(\vec{q}(t))^r$, and $(\vec{q}(t))^p$, respectively.
The contours of the adiabatic BO PESs for every $1000$ cm$^{-1}$ are represented by
the black curves in the two-dimensional plates. The symbols $\times$ and $\triangle$ represent
the CI point and the minimum of $U_{eq}(\vec{q})$, respectively. Videos of excited wa-
vepackets in CI1($d = 1.5$), CI1($d = -1.5$) and AC1($a = 300$ cm$^{-1}$) models are
presented in Supplemental Information (Available at: http://dx.doi.org/10.17632/v9k8hxd34t.2). (For interpretation of the references to colour in this
figure legend, the reader is referred to the web version of this article.)](image2)
are the CI point curve in the CI1 case exhibits a bifurcation and increases monotonically as a function of the lifetime as a function of the diabatic coupling $a$ in the AC0 (the dashed curve) and AC1 (the solid curve) cases.

We observe large yields in the CI0, AC0, and AC1 cases for larger $d$. In the CI0 and AC1 cases, the yield $y^p$ as a function of the diabatic coupling $a$ is not symmetric as a function of $a$. (44)

Fig. 5(i) depicts $\tau^e$ as a function of the CI-minimum distance $d \equiv q^{e,\text{CI}}_\text{min} - q^{e,\text{CI}}_\text{max}$ for the CI model, where $q^{e,\text{CI}}$ and $q^{e,\text{CI}}_{\text{min}}$ are the CI point and the minimum of the adiabatic excited PES. The lifetime $\tau^d$ is shortest at $d = 0$, while it increases with the absolute value of $d$, because the center of the excited wavepackets is away from the CI point for larger $d$. In the CI1 case, $\tau^e$ is not symmetric as a function of $d$, because the diabatic PESs are not symmetric in the $q_e$ direction for $q_e^{0} \neq q_e^{1}$. Fig. 5(ii) depicts $\tau^e$ as a function of the diabatic coupling $a$ in the AC model. Because the energy gap between the adiabatic ground and excited PESs increases as the diabatic coupling increases, the lifetime $\tau^e$ increases monotonically as $a$ increases. In the case $q_e^{0} \neq q_e^{1}$, the motion of the coupling mode is excited in the $q_e$ direction due to the difference between the stable points of the PESs. Because of this motion, the BO approximation breaks down. As a result, the lifetimes are shorter in the CI1 and AC1 cases than in the CI0 and AC0 cases.

4.4. The yield

In Fig. 6, we illustrate the relationship between the lifetime $\tau^e$ and the yields at the final time, $t_i$, defined as

$$y^p \equiv \frac{u^1(t_i)u^0(t_i)}{u^0(t_i)}$$

using the same parameter values as in the calculations considered in Fig. 5.

We observe large yields in the CI0, AC0, and AC1 cases, in accordance with their lifetimes $\tau^e$. Note that a short $\tau^e$ implies that the excited wavepackets move smoothly across the crossing region while maintaining a large momentum in the direction of the product region, as explained in Section 4.2. The yields $y^p$ in the CI0 and AC1 cases are smaller than in the AC0 case due to the contributions from non-adiabatic transitions in the coupling mode. The similarity between the CI0 and AC0 cases indicates that when the adiabatic excited PESs are smooth and there is no displacement in the coupling mode, and hence $q_e^{0} = q_e^{1}$, the CI does not play an important role. In such cases, the results of the IC processes via the CI are described by an AC model that is characterized by an effectively weak diabatic coupling constant, $a$.

Contrastingly, the $\tau^e$-$y^p$ curve in the CI1 case exhibits a bifurcation for negative and positive $d$. The yields $y^p$ in the case of negative $d$ are smaller than in the other three cases, while the lifetimes $\tau^e$ are short. This is because, for negative $d$, the excited wavepackets first pass through the crossing region away from the CI point. Then, after bouncing off of the barrier of the excited PES in the product region and losing energy due to dissipation, the wavepacket encounters the CI point on the way back from the reactant region. Therefore, although the lifetimes for $d = \pm 1.5$ in the CI1 case are similar, $\tau^e \sim 250$ fs, the yield in the negative $d$ case is much lower. This indicates that the photo-isomerization process is sensitive to the profiles of the PESs, in particular when the CI plays a significant role.

4.5. Kinetic energy and momentum distribution of the coupling mode

In Fig. 7, we plot the kinetic energy of the coupling mode, $K_c(t_i)$, as a function of time for the CI and AC models. In these calculations, we adjusted the diabatic coupling parameters so as to have lifetimes $\tau^e \sim 200$ fs and 300 fs. The parameter sets we used are listed in Table 3.
In the CI0 cases, the excitation energy and the kinetic energy $K_e(t)$ are coupled to $K_c(t)$ during the non-adiabatic transition process, and $K_c(t)$ reaches the equilibrium value $k_B T/2 = 104 \text{ cm}^{-1}$ due to thermal relaxation. In the AC0 cases, in which the coupling mode $q_c$ is independent of the tuning mode $q_t$ and the electronic states, $K_c(t)$ does not change during the non-adiabatic transition process. In the CI1 and AC1 cases, vibrational motion in the coupling mode arises due to the coupling between the adiabatic ground and excited PESs, $q_c^e - q_c^g = 1$. Because $K_c(t)$ is proportional to $p_c^2$, we observe the vibrational peaks with frequency $\omega_c = 1000 \text{ cm}^{-1}$ that corresponds to the period of 33.4 fs. Then the vibrational peaks become larger as a function of time due to the non-adiabatic transitions, and subsequently decreases due to the relaxation induced by the environments. The maximum value of $K_c(t)$ is large for the long lifetime cases in Fig. 7(iii), because the wavepackets are trapped in the crossing region and the kinetic energy of the excited state converts to the vibrational energy of the tuning mode, while the wavepackets pass through the crossing region without exciting the coupling mode for the short lifetime cases in Fig. 7(i). These results indicate that, the vibrational dynamics of the coupling mode through the non-adiabatic transition processes are different even when the lifetimes of the excited population are similar.

### Table 3

<table>
<thead>
<tr>
<th>Lifetime $\tau^*$</th>
<th>CI0</th>
<th>CI1</th>
<th>AC0</th>
<th>AC1</th>
</tr>
</thead>
<tbody>
<tr>
<td>~ 200 fs</td>
<td>$d=0$</td>
<td>0.0</td>
<td>0.0</td>
<td>100</td>
</tr>
<tr>
<td>~ 300 fs</td>
<td>$d=1.5$</td>
<td>2.0</td>
<td>200</td>
<td>350</td>
</tr>
</tbody>
</table>

In the CI0 cases, the excitation energy and the kinetic energy $K_e(t)$ are coupled to $K_c(t)$ during the non-adiabatic transition process, and $K_c(t)$ reaches the equilibrium value $k_B T/2 = 104 \text{ cm}^{-1}$ due to thermal relaxation. In the AC0 cases, in which the coupling mode $q_c$ is independent of the tuning mode $q_t$ and the electronic states, $K_c(t)$ does not change during the non-adiabatic transition process. In the CI1 and AC1 cases, vibrational motion in the coupling mode arises due to the coupling between the adiabatic ground and excited PESs, $q_c^e - q_c^g = 1$. Because $K_c(t)$ is proportional to $p_c^2$, we observe the vibrational peaks with frequency $\omega_c = 1000 \text{ cm}^{-1}$ that corresponds to the period of 33.4 fs. Then the vibrational peaks become larger as a function of time due to the non-adiabatic transitions, and subsequently decreases due to the relaxation induced by the environments. The maximum value of $K_c(t)$ is large for the long lifetime cases in Fig. 7(iii), because the wavepackets are trapped in the crossing region and the kinetic energy of the excited state converts to the vibrational energy of the tuning mode, while the wavepackets pass through the crossing region without exciting the coupling mode for the short lifetime cases in Fig. 7(i). These results indicate that, the vibrational dynamics of the coupling mode through the non-adiabatic transition processes are different even when the lifetimes of the excited population are similar.

![Fig. 7. The kinetic energy of the coupling mode $K_c(t)$ as a function of $t$ for (i) $\tau^* \sim 200$ fs and (ii) $\tau^* \sim 300$ fs in the CI0 (the red dashed curve), CI1 (the orange solid curve), AC0 (the blue dashed curve), and AC1 (the cyan solid curve) cases. In each case, the lifetime was controlled by adjusting the diabatic coupling parameters.](image)

![Fig. 8. Snapshots of momentum distributions of the coupling mode as functions of $p_c$ and $q_c$ in the excited adiabatic state, $f^e(p_c, q_c, t)$, for (i) the CI0 case and (ii) the AC0 case at $t = 200$ fs.](image)

To analyze this point more closely, in Fig. 8, we present snapshots of the momentum distributions of the coupling mode as functions of $p_c$ and $q_c$ in the excited adiabatic state, defined as $f^e(p_c, q_c, t) \equiv \int dp_t \int dq_t W^e(p_t, q_t, t)$. In the CI0 and AC0 cases at $t = 200$ fs for $\tau^* \sim 200$ fs. In the AC0 case, because the coupling mode $q_c$ is independent of the electronic states as well as the tuning mode $q_t$, $f^e(p_c, q_c, t)$ exhibits a simple Gaussian-like shape in the $p_c$ direction. Contrastingly, in the CI0 case, $f^e(p_c, q_c, t)$ has two peaks in the positive and negative regions of $p_c$ near the crossing region, due to the role of the CI.

### 4.6. Electronic coherence

Finally, we investigate the electronic coherence between the adiabatic ground and excited states for the CI and AC models, defined as $C_{ei}(q_t, t) \equiv \int d\vec{p}_c \int d\vec{q}_c W^e(\vec{p}_c, \vec{q}_c, t)$. In order to illustrate the details of the coherent elements of the wavepackets, here we employed a fine mesh, with $N_t \times N_e = 256 \times 128$, although we had to use a smaller timestep $\delta t$ for this smaller mesh, because the information representing the wavepacket propagates faster as the grid becomes finer. We employed $\delta t = 0.1$ fs for these calculations.

In Figs. 9(i) and 9(ii), we display the real parts of the electronic coherence $C_{ei}(q_t, t)$ for the CI0 and AC0 cases at $t = 200$ fs. The lifetime in each case was adjusted to be $\tau^* \sim 200$ fs using the values of the diabatic coupling parameters listed in Table 3. In the AC0 case, in which the coupling mode $q_c$ is independent of the electronic states as well as the tuning mode $q_t$ and $C_{ei}(q_t, t)$, we observe characteristic features only in the $q_t$ direction. Contrastingly, in the CI0 case, $C_{ei}(q_t, t)$ exhibits nodes at $q_t = 0$, which arise from the $q_c$-dependence of the diabatic coupling. These clear differences between the CI and AC models, however, become blurred by the vibrational dynamics in the
coupling mode and the structure of the PESs, as seen in Figs. 9(iii) and 9(iv) for \( \tau \sim 300 \text{fs} \).

5. Conclusion

We employed a two-dimensional, two-state system coupled to baths in order to analyze the role of the CI in dissipative environments. The MSQFPE for two-dimensional PESs were employed to rigorously study the dynamics of the system quantum mechanically. To numerically integrate the MSQFPE efficiently, we employed the Moyal expansion for the potential term and the Brinkman hierarchy for the momentum space of the equation of motion. We studied wavepacket dynamics and the efficiency of the IC process for the CI and AC models both symmetric and non-symmetric configurations. Our results are summarized as follows:

1. In terms of lifetime of the excited wavepacket and yield of the product, both CI and AC models exhibit similar results when the effectively diabatic coupling is weak. In the CI case with large PESs asymmetry (the CI1 model with \( d \neq 0 \)), however, the yields of the non-adiabatic transitions are sensitive to the configuration of the adiabatic excited PES. This behavior cannot be reproduced from AC models.

2. The vibrational dynamics of the coupling mode \( q_c \) through non-adiabatic transition processes strongly depend on the structure of diabatic coupling, even when the lifetimes of the excited wavepacket are almost the same.

3. Nodal structures in adiabatic electronic coherences during non-adiabatic transition processes is observed around the CI point, in particular when the PESs have symmetric structure.

While yields and kinetic energy are not direct experimental observables, we can extract these kinds of information by means of non-linear optical spectroscopies, such as femtosecond stimulated Raman spectroscopy \([52–54]\) and two-dimensional electronic-vibrational spectroscopy \([55,56]\). Using the MSQFPE, it is possible to calculate such advanced optical spectra. This is left to future investigations.

In our calculations, the most significant difference between the AC and CI models appears in adiabatic electronic coherence. These phase structures in electronic coherence may be due to a geometric phase (the Berry’s phase) effects \([2,57]\), but further investigations are necessary to verify this hypothesis.

In this paper, we restricted our analysis to the Markovian case described by Ohmic spectral distributions with the high-temperature approximation. We note that when we study the low temperature case within the framework of the Markovian MSQFPE, we encounter a positivity problem involving the reduced density matrix elements. (See related discussion in Supplemental Information S7 (Available at: http://dx.doi.org/10.17632/w9k8hxd34t.2)) Although it is computationally demanding, we often have to study the non-Markovian case at low temperature, where the quantum effects of the electronic subspace and the reaction coordinate space become important, using the hierarchical equations of motion (HEOM) approach \([15,19–21,42–44,36,37,58,59]\). We leave such extensions to future studies.

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