Supplemental Information: *Phase-Space Wavepacket Dynamics of Internal Conversion via Conical Intersection: Multi-State Quantum Fokker-Planck Equation Approach*

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Abstract

This is supplemental information concerning the paper "Phase-Space Wavepacket Dynamics of Internal Conversion via Conical Intersection: Multi-State Quantum Fokker-Planck Equation Approach".

S1. Quantum Liouvillian in the Wigner-Moyal Expression Form

S1.1. The Liouville Von-Neumann equation

We consider a system described by the Hamiltonian, Eq. (1). By adapting the canonical quantization of dimensionless coordinates

$$\hat{p}_s \to \frac{1}{i}\frac{\partial}{\partial z_s} \qquad \text{and} \qquad q_s \to z_s, \tag{S1}$$

we have the Schrödinger equation for the wavefunction $\Psi^j(\vec{z})$ expressed as

$$\begin{aligned}\frac{d}{dt}\Psi^j(\vec{z},t) = i\sum_s \frac{\omega_s}{2}\frac{\partial^2}{\partial z_s^2}\Psi^j(\vec{z},t) \\ - \frac{i}{\hbar}\sum_k U^{jk}(\vec{z})\Psi^k(\vec{z},t).\end{aligned} \tag{S2}$$

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Accordingly, the Liouville von-Neumann equation for the density matrix $\rho^{jk}(\vec{z},\vec{z}\,') = \Psi^j(\vec{z})\Psi^{k*}(\vec{z}\,')$ is written as

$$\begin{aligned}\frac{d}{dt}\rho^{jk}(\vec{z},\vec{z}\,',t) = i\sum_s \frac{\omega_s}{2}\left(\frac{\partial^2}{\partial z_s^2} - \frac{\partial^2}{\partial z_s'^2}\right)\rho^{jk}(\vec{z},\vec{z}\,',t) \\ - \frac{i}{\hbar}\sum_l \Big[U^{jl}(\vec{z})\rho^{lk}(\vec{z},\vec{z}\,',t) \\ - \rho^{jl}(\vec{z},\vec{z}\,',t)U^{lk}(\vec{z}\,')\Big].\end{aligned} \tag{S3}$$

In the vector and matrix representations $\{\boldsymbol{\Psi}(\vec{z})\}_j \equiv \Psi^j(\vec{z})$ and $\{\boldsymbol{\rho}(\vec{z},\vec{z}\,')\}_{jk} \equiv \rho^{jk}(\vec{z},\vec{z}\,')$, Eqs. (S2) and (S3) are expressed as

$$\frac{d}{dt}\boldsymbol{\Psi}(\vec{z},t) = i\sum_s \frac{\omega_s}{2}\frac{\partial^2}{\partial z_s^2}\boldsymbol{\Psi}(\vec{z},t) - \frac{i}{\hbar}\boldsymbol{U}(\vec{z})\boldsymbol{\Psi}(\vec{z},t) \tag{S4}$$

and

$$\frac{d}{dt}\boldsymbol{\rho}(\vec{z},\vec{z}\,',t) = -\mathcal{L}(\vec{z},\vec{z}\,')\boldsymbol{\rho}(\vec{z},\vec{z}\,'), \tag{S5a}$$

where

$$\begin{aligned}\mathcal{L}(\vec{z},\vec{z}\,')\boldsymbol{\rho}(\vec{z},\vec{z}\,') \equiv -i\sum_s \frac{\omega_s}{2}\left(\frac{\partial^2}{\partial z_s^2} - \frac{\partial^2}{\partial z_s'^2}\right)\boldsymbol{\rho}(\vec{z},\vec{z}\,') \\ + \frac{i}{\hbar}\Big[\boldsymbol{U}(\vec{z})\boldsymbol{\rho}(\vec{z},\vec{z}\,') - \boldsymbol{\rho}(\vec{z},\vec{z}\,')\boldsymbol{U}(\vec{z}\,')\Big]\end{aligned} \tag{S5b}$$

is the quantum Liouvillian.

S1.2. Phase space representation

For the density matrix $\boldsymbol{\rho}(\vec{z},\vec{z}\,')$, the Wigner distribution is defined as

$$\boldsymbol{W}(\vec{p},\vec{q},t) \equiv \frac{1}{(2\pi)^N}\int d\vec{r}\, e^{-i\vec{p}\cdot\vec{r}}\boldsymbol{\rho}\left(\vec{q}+\frac{\vec{r}}{2},\vec{q}-\frac{\vec{r}}{2}\right), \tag{S6a}$$

whereas the inverse transformation is defined as

$$\boldsymbol{\rho}(\vec{z},\vec{z}\,') = \int d\vec{p}\, e^{+i\vec{p}\cdot(\vec{z}-\vec{z}\,')}\boldsymbol{W}\left(\vec{p},\frac{\vec{z}+\vec{z}\,'}{2},t\right). \tag{S6b}$$

For the mean coordinates $\vec{q} \equiv (\vec{z}+\vec{z}\,')/2$ and the differences $\vec{r} \equiv \vec{z}-\vec{z}\,'$, the chain rules are expressed as

$$\frac{\partial}{\partial z_s} = \frac{1}{2}\frac{\partial}{\partial q_s} + \frac{\partial}{\partial r_s} \qquad \text{and} \qquad \frac{\partial}{\partial z_s'} = \frac{1}{2}\frac{\partial}{\partial q_s} - \frac{\partial}{\partial r_s}. \tag{S7}$$

Then Eq. (S5a) can be rewritten as

$$\begin{aligned}
&\frac{d}{dt}\boldsymbol{\rho}\left(\vec{q}+\frac{\vec{r}}{2},\vec{q}-\frac{\vec{r}}{2},t\right)\\
&=i\sum_s \omega_s \frac{\partial^2}{\partial q_s \partial r_s}\boldsymbol{\rho}\left(\vec{q}+\frac{\vec{r}}{2},\vec{q}-\frac{\vec{r}}{2},t\right)\\
&\quad-\frac{i}{\hbar}\Bigg[\boldsymbol{U}\left(\vec{q}+\frac{\vec{r}}{2}\right)\boldsymbol{\rho}\left(\vec{q}+\frac{\vec{r}}{2},\vec{q}-\frac{\vec{r}}{2},t\right)\\
&\qquad-\boldsymbol{\rho}\left(\vec{q}+\frac{\vec{r}}{2},\vec{q}-\frac{\vec{r}}{2},t\right)\boldsymbol{U}\left(\vec{q}-\frac{\vec{r}}{2}\right)\Bigg].
\end{aligned} \tag{S8}$$

The time evolution of $\boldsymbol{W}(\vec{p},\vec{q})$ is now described by

$$\begin{aligned}
&\frac{d}{dt}\boldsymbol{W}\left(\vec{p},\vec{q},t\right)\\
&=-\sum_s \omega_s p_s \frac{\partial}{\partial q_s}\boldsymbol{W}\left(\vec{p},\vec{q},t\right)\\
&\quad-\frac{i}{\hbar}\int d\vec{p}'\Bigg[\frac{1}{(2\pi)^N}\int d\vec{r}\,e^{-i(\vec{p}-\vec{p}')\cdot\vec{r}}\boldsymbol{U}\left(\vec{q}+\frac{\vec{r}}{2}\right)\boldsymbol{W}\left(\vec{p}',\vec{q},t\right)\\
&\qquad-\boldsymbol{W}\left(\vec{p}',\vec{q},t\right)\int d\vec{r}\,\frac{1}{(2\pi)^N}e^{-i(\vec{p}-\vec{p}')\cdot\vec{r}}\boldsymbol{U}\left(\vec{q}-\frac{\vec{r}}{2}\right)\Bigg].
\end{aligned} \tag{S9}$$

The Fourier Expression

We introduce the Fourier transformed expression for $\boldsymbol{U}(\vec{q})$ defined as

$$\boldsymbol{U}_{\mathrm{w}}(\vec{p},\vec{q})\equiv\frac{1}{(2\pi)^N}\int d\vec{r}\,e^{-i\vec{p}\cdot\vec{r}}\boldsymbol{U}\left(\vec{q}+\frac{\vec{r}}{2}\right) \tag{S10}$$

and the convolution operator, $*$, expressed as

$$\boldsymbol{W}(\vec{p},\vec{q})*\boldsymbol{g}\left(\vec{p}\,',\vec{q}\right)\equiv\int d\vec{p}'\,\boldsymbol{W}(\vec{p}-\vec{p}\,',\vec{q})\boldsymbol{g}\left(\vec{p}\,',\vec{q}\right). \tag{S11}$$

The Liouville equation, Eq. (S9) can be rewritten as

$$\frac{d}{dt}\boldsymbol{W}\left(\vec{p},\vec{q},t\right)=-\mathcal{L}_W(\vec{p},\vec{q})\boldsymbol{W}(\vec{p},\vec{q}), \tag{S12}$$

where the quantum Liouvillian is expressed as

$$\begin{aligned}
\mathcal{L}_W(\vec{p},\vec{q})\boldsymbol{W}(\vec{p},\vec{q})=&\sum_s \omega_s p_s \frac{\partial}{\partial q_s}\boldsymbol{W}\left(\vec{p},\vec{q},t\right)\\
&+\frac{i}{\hbar}\Bigg[\boldsymbol{U}_{\mathrm{w}}(\vec{p},\vec{q})*\boldsymbol{W}\left(\vec{p},\vec{q},t\right)\\
&\qquad-\boldsymbol{W}\left(\vec{p},\vec{q},t\right)*\boldsymbol{U}_{\mathrm{w}}(\vec{p},\vec{q})^{\dagger}\Bigg].
\end{aligned} \tag{S13}$$

The Moyal Expression

The second and third terms of Eq. (S9) are expressed in the Taylor expansion form as

$$\begin{aligned}
&\int d\vec{p}'\,\frac{1}{(2\pi)^N}\int d\vec{r}\,e^{-i(\vec{p}-\vec{p}\,')\cdot\vec{r}}\boldsymbol{U}\left(\vec{q}+\frac{\vec{r}}{2}\right)\boldsymbol{W}\left(\vec{p}\,',\vec{q}\right)\\
&=\int d\vec{p}'\,\frac{1}{(2\pi)^N}\int d\vec{r}\,e^{-i(\vec{p}-\vec{p}\,')\cdot\vec{r}}\\
&\qquad\times\left[\sum_m\frac{1}{m!}\left(+\sum_s\frac{r_s}{2}\frac{\partial}{\partial q_s}\right)^m\boldsymbol{U}\left(\vec{q}\right)\right]\boldsymbol{W}\left(\vec{p}\,',\vec{q}\right)\\
&=\int d\vec{p}'\,\boldsymbol{U}\left(\vec{q}\right)\left[\sum_m\frac{1}{m!}\left(+\sum_s\frac{i}{2}\underleftarrow{\partial}_{q_s}\underrightarrow{\partial}_{p_s}\right)^m\right]\\
&\qquad\times\frac{1}{(2\pi)^N}\int d\vec{r}e^{-i(\vec{p}-\vec{p}\,')\cdot\vec{r}}\boldsymbol{W}\left(\vec{p}\,',\vec{q}\right)\\
&=\boldsymbol{U}\left(\vec{q}\right)e^{+\sum_s i\underleftarrow{\partial}_{q_s}\underrightarrow{\partial}_{p_s}/2}\boldsymbol{W}\left(\vec{p},\vec{q}\right)\\
&=\boldsymbol{U}\left(\vec{q}\right)\star\boldsymbol{W}\left(\vec{p},\vec{q}\right)
\end{aligned}\tag{S14}$$

and

$$\begin{aligned}
&\int d\vec{p}'\,\boldsymbol{W}\left(\vec{p}\,',\vec{q}\right)\int d\vec{r}\,\frac{1}{(2\pi)^N}e^{-i(\vec{p}-\vec{p}\,')\cdot\vec{r}}\boldsymbol{U}\left(\vec{q}-\frac{\vec{r}}{2}\right)\\
&=\boldsymbol{W}\left(\vec{p},\vec{q}\right)e^{-\sum_s i\underrightarrow{\partial}_{q_s}\underleftarrow{\partial}_{p_s}/2}\boldsymbol{U}\left(\vec{q}\right)\\
&=\boldsymbol{W}\left(\vec{p},\vec{q}\right)\star\boldsymbol{U}\left(\vec{q}\right),
\end{aligned}\tag{S15}$$

respectively, we have introduced the differentiation operations form the left and right, which are defined by

$$\underrightarrow{\partial}_x f(x)=f(x)\underleftarrow{\partial}_x\equiv\frac{\partial f(x)}{\partial x},\tag{S16}$$

and $\star$ is the Moyal product

$$\star\equiv\exp\left[+\sum_s i(\underleftarrow{\partial}_{q_s}\underrightarrow{\partial}_{p_s}-\underrightarrow{\partial}_{q_s}\underleftarrow{\partial}_{p_s})/2\right].\tag{S17}$$

The equation of motion, Eq. (S9), is expressed as

$$\frac{d}{dt}\boldsymbol{W}\left(\vec{p},\vec{q},t\right)=-\mathcal{L}_W\left(\vec{p},\vec{q}\right)\boldsymbol{W}\left(\vec{p},\vec{q}\right)\tag{S18}$$

where the quantum Liouvillian (S13) is defined as

$$\begin{aligned}
\mathcal{L}_W\left(\vec{p},\vec{q}\right)\boldsymbol{W}\left(\vec{p},\vec{q}\right)=&\sum_s\omega_s p_s\frac{\partial}{\partial q_s}\boldsymbol{W}\left(\vec{p},\vec{q}\right)\\
&+\frac{i}{\hbar}\Big[\boldsymbol{U}\left(\vec{q}\right)\star\boldsymbol{W}\left(\vec{p},\vec{q}\right)\\
&\qquad-\boldsymbol{W}\left(\vec{p},\vec{q}\right)\star\boldsymbol{U}\left(\vec{q}\right)\Big].
\end{aligned}\tag{S19}$$

This is the Wigner-Moyal expression of the Liouvillian, Eq. (7b).

S2. Adiabatic Representation of the Phase Space Distribution

By using the conversion matrix Eq. (17), the wavefunction $\boldsymbol{\Psi}(\vec{z})$ and the density matrix $\boldsymbol{\rho}(\vec{z},\vec{z}\,')$ in the electronic adiabatic basis are expressed as

$$\boldsymbol{\Psi}_{\mathrm{a}}(\vec{z}) \equiv \boldsymbol{Z}\left(\vec{z}\right)^{\dagger} \boldsymbol{\Psi}(\vec{z}) \tag{S20a}$$

and

$$\boldsymbol{\rho}_{\mathrm{a}}(\vec{z},\vec{z}\,') \equiv \boldsymbol{Z}\left(\vec{z}\right)^{\dagger} \boldsymbol{\rho}(\vec{z},\vec{z}\,')\boldsymbol{Z}\left(\vec{z}\,'\right). \tag{S20b}$$

In the adiabatic representation, $\boldsymbol{W}(\vec{p},\vec{q})$ is expressed as

$$\boldsymbol{W}_{\mathrm{a}}(\vec{p},\vec{q},t) \equiv \frac{1}{(2\pi)^N}\int d\vec{r}\, e^{-i\vec{p}\cdot\vec{r}}\boldsymbol{\rho}_{\mathrm{a}}\left(\vec{q}+\frac{\vec{r}}{2},\vec{q}-\frac{\vec{r}}{2}\right) \tag{S21a}$$

$$\begin{aligned} &= \frac{1}{(2\pi)^N}\int d\vec{p}\,'\int d\vec{r}\, e^{-i(\vec{p}-\vec{p}\,')\cdot\vec{r}} \\ &\quad\times \boldsymbol{Z}\left(\vec{q}+\frac{\vec{r}}{2}\right)^{\dagger}\boldsymbol{W}\left(\vec{p}\,',\vec{q},t\right)\boldsymbol{Z}\left(\vec{q}-\frac{\vec{r}}{2}\right). \end{aligned} \tag{S21b}$$

The inverse transform is expressed as

$$\begin{aligned} \boldsymbol{W}(\vec{p},\vec{q},t) &= \frac{1}{(2\pi)^N}\int d\vec{p}\,'\int d\vec{r}\, e^{-i(\vec{p}-\vec{p}\,')\cdot\vec{r}} \\ &\quad\times \boldsymbol{Z}\left(\vec{q}+\frac{\vec{r}}{2}\right)\boldsymbol{W}_{\mathrm{a}}\left(\vec{p}\,',\vec{q},t\right)\boldsymbol{Z}\left(\vec{q}-\frac{\vec{r}}{2}\right)^{\dagger}. \end{aligned} \tag{S21c}$$

Therefore, Eqs. (S21b) and (S21c) are expressed in the Taylor expansion form of $\boldsymbol{Z}(\vec{q})$ as

$$
\begin{aligned}
&\boldsymbol{W}_{\mathrm{a}}(\vec{p},\vec{q}) \\
&= \frac{1}{(2\pi)^N}\int dp' \int dr e^{-i(p-p')r}\boldsymbol{Z}\left(q+\frac{r}{2}\right)^{\dagger}\boldsymbol{W}(\vec{p}\,',\vec{q})\boldsymbol{Z}\left(q-\frac{r}{2}\right) \\
&= \int dp' \left[\sum_m \frac{1}{m!}\left(\sum_s \frac{i}{2}\frac{\partial}{\partial p_s}\frac{\partial}{\partial q_s}\right)^m \boldsymbol{Z}\left(\vec{q}\right)^{\dagger}\right] \\
&\qquad \times \boldsymbol{W}(\vec{p}\,',\vec{q})\left[\sum_{m'}\frac{1}{m'!}\left(-\sum_s \frac{i}{2}\frac{\partial}{\partial p_s}\frac{\partial}{\partial q_s}\right)^{m'}\boldsymbol{Z}\left(\vec{q}\right)\right] \\
&\qquad \times \delta(\vec{p}-\vec{p}\,') \\
&= \boldsymbol{Z}\left(\vec{q}\right)^{\dagger}\exp\left(\sum_s \frac{i}{2}\overrightarrow{\partial_{p_s}}\overleftarrow{\partial_{q_s}}\right) \\
&\qquad \times \boldsymbol{W}(\vec{p}\,',\vec{q})\exp\left(-\sum_s \frac{i}{2}\overleftarrow{\partial_{p_s}}\overrightarrow{\partial_{q_s}}\right)\boldsymbol{Z}\left(\vec{q}\right) \\
&= \boldsymbol{Z}\left(\vec{q}\right)^{\dagger}\star\boldsymbol{W}(\vec{p},\vec{q})\star\boldsymbol{Z}\left(\vec{q}\right),
\end{aligned}
\tag{S22}
$$

and

$$
\boldsymbol{W}(\vec{p},\vec{q}) = \boldsymbol{Z}\left(\vec{q}\right)\star\boldsymbol{W}_{\mathrm{a}}(\vec{p},\vec{q})\star\boldsymbol{Z}\left(\vec{q}\right)^{\dagger}, \tag{S23}
$$

respectively.

S3. The Brinkman Hierarchy Expression for The Multi-State Quantum Fokker-Planck Equation

In this section, we present a derivation of the Brinkman hierarchy expression for the MSQFPE (15).

S3.1. The creation and annihilation operators

In order to simplify the calculations, we introduce the creation and annihilation operators for Hermite function $\psi_{n_s}^{(s)}(p_s)$ defined as

$$
a_s^{\pm} = \frac{1}{\sqrt{2}}\left(\frac{1}{\alpha_s}p_s \mp \alpha_s\frac{\partial}{\partial p_s}\right). \tag{S24}
$$

For $\psi_{n_s}^{(s)}(p_s)$, they operate as

$$
\begin{cases}
a_s^{+}\psi_{n_s}^{(s)}(p_s) = \sqrt{n+1}\,\psi_{n_s+1}^{(s)}(p_s) \\
a_s^{-}\psi_{n_s}^{(s)}(p_s) = \sqrt{n}\;\psi_{n_s-1}^{(s)}(p_s),
\end{cases}
\tag{S25}
$$

while, for $\psi_{\vec{n}}(\vec{p})$, as

$$\begin{cases} a_s^+ \psi_{\vec{n}}(\vec{p}) = \sqrt{n_s+1}\psi_{\vec{n}+\vec{e}_s}(\vec{p}) \\ a_s^- \psi_{\vec{n}}(\vec{p}) = \sqrt{n_s}\ \psi_{\vec{n}-\vec{e}_s}(\vec{p}). \end{cases} \tag{S26}$$

The operators p_s and $\partial/\partial p_s$ are expressed as

$$p_s = \frac{\alpha_s}{\sqrt{2}}(a_s^+ + a_s^-) \tag{S27a}$$

and

$$\frac{\partial}{\partial p_s} = -\frac{1}{\sqrt{2}\alpha_s}(a_s^+ - a_s^-). \tag{S27b}$$

For the Brinkman hierarchy expression, we introduce the transformation from a superoperator $\mathcal{O}^W(\vec{p},\vec{q})$ that acts on $\boldsymbol{W}(\vec{p},\vec{q})$ to the superoperator $\mathcal{O}^c(\vec{n},\vec{q})$ on $\boldsymbol{c}_{\vec{n}}(\vec{q})$ as

$$\begin{aligned} &\mathcal{O}^c(\vec{n},\vec{q})\boldsymbol{c}_{\vec{n}}(\vec{q}) \\ &= \int d\vec{p}\,\psi_{\vec{n}}(\vec{p})\psi_{\vec{0}}(\vec{p})^{-1} e^{\varepsilon\beta \boldsymbol{U}_0(\vec{q})/2} \\ &\quad \times \left(\mathcal{O}^W(\vec{p},\vec{q}) \left\{ \sum_{\vec{n}'} e^{-\varepsilon\beta \boldsymbol{U}_0(\vec{q})/2} \boldsymbol{c}_{\vec{n}\,'}(\vec{q}) e^{-\varepsilon\beta \boldsymbol{U}_0(\vec{q})/2} \right.\right. \\ &\qquad\qquad \left.\left. \times\, \psi_{\vec{0}}(\vec{p})\psi_{\vec{n}\,'}(\vec{p}) \right\} \right) e^{\varepsilon\beta \boldsymbol{U}_0(\vec{q})/2}. \end{aligned} \tag{S28}$$

We also employ the following relations

$$\begin{aligned} &p_s \boldsymbol{W}(\vec{p},\vec{q}) \\ &\to \int d\vec{p}\,\psi_{\vec{n}}(\vec{p})\psi(\vec{0},\vec{p})^{-1} \\ &\qquad \times p_s \sum_{\vec{n}\,'} \boldsymbol{c}_{\vec{n}\,'}(\vec{q})\psi(\vec{0},\vec{p})\psi_{\vec{n}\,'}(\vec{p}) \\ &= \sum_{\vec{n}\,'} \boldsymbol{c}_{\vec{n}\,'}(\vec{q}) \int d\vec{p}\,\psi_{\vec{n}}(\vec{p}) \frac{\alpha_s}{\sqrt{2}}(a_s^+ + a_s^-)\psi_{\vec{n}\,'}(\vec{p}) \\ &= \sum_{\vec{n}\,'} \boldsymbol{c}_{\vec{n}\,'}(\vec{q}) \int d\vec{p} \left[\frac{\alpha_s}{\sqrt{2}}(a_s^- + a_s^+)\psi_{\vec{n}}(\vec{p}) \right] \psi_{\vec{n}\,'}(\vec{p}) \\ &= \frac{\alpha_s}{\sqrt{2}}(b_s^- + b_s^+)\boldsymbol{c}_{\vec{n}}(\vec{q}) \end{aligned} \tag{S29a}$$

and

$$
\begin{aligned}
&\frac{\partial}{\partial p_s}\boldsymbol{W}(\vec{p},\vec{q}) \\
&\to \int d\vec{p}\,\psi_{\vec{n}}(\vec{p})\psi(\vec{0},\vec{p})^{-1} \\
&\qquad\qquad \times \frac{\partial}{\partial p_s}\sum_{\vec{n}\,'}\boldsymbol{c}_{\vec{n}\,'}(\vec{q})\psi(\vec{0},\vec{p})\psi_{\vec{n}\,'}(\vec{p}) \\
&= -\sum_{\vec{n}\,'}\boldsymbol{c}_{\vec{n}\,'}(\vec{q})\int d\vec{p}\,\psi_{\vec{n}}(\vec{p})\frac{\sqrt{2}}{\alpha_s}a_s^{+}\psi_{\vec{n}\,'}(\vec{p}) \\
&= -\sum_{\vec{n}\,'}\boldsymbol{c}_{\vec{n}\,'}(\vec{q})\int d\vec{p}\,\left[\frac{\sqrt{2}}{\alpha_s}a_s^{-}\psi_{\vec{n}}(\vec{p})\right]\psi_{\vec{n}\,'}(\vec{p}) \\
&= -\frac{\sqrt{2}}{\alpha_s}b_s^{-}\boldsymbol{c}_{\vec{n}}(\vec{q}),
\end{aligned}
\tag{S29b}
$$

where we have formally introduced the creation and annihilation operators for $\boldsymbol{c}_{\vec{n}}(\vec{q})$ as

$$
\begin{cases}
b_s^{+}\boldsymbol{c}_{\vec{n}}(\vec{q}) = \boldsymbol{c}_{\vec{n}}(\vec{q})b_s^{-} = \sqrt{n_s+1}\,\boldsymbol{c}_{\vec{n}+\vec{e}_s}(\vec{q}) \\
b_s^{-}\boldsymbol{c}_{\vec{n}}(\vec{q}) = \boldsymbol{c}_{\vec{n}}(\vec{q})b_s^{+} = \sqrt{n_s}\;\boldsymbol{c}_{\vec{n}-\vec{e}_s}(\vec{q}).
\end{cases}
\tag{S30}
$$

Thus we can perform the transformation (S28) by merely replacing as

$$
p_s \to \frac{\alpha_s}{\sqrt{2}}(b_s^{-}+b_s^{+}), \tag{S31a}
$$

$$
\underset{\rightarrow}{\partial}_{p_s} \to -\frac{\sqrt{2}}{\alpha_s}b_s^{-}, \tag{S31b}
$$

and

$$
\underset{\leftarrow}{\partial}_{p_s} \to -\frac{\sqrt{2}}{\alpha_s}b_s^{+}, \tag{S31c}
$$

respectively. Note that the order of the operators a_s^{+} and a_s^{-} are inversed in Eq. (S29).

All of the terms in Eq. (7b) and the last term of Eq. (15) are then transformed as follows,

The first term of Eq. (7b)*:*

$$
\begin{aligned}
&\sum_s \omega_s p_s \frac{\partial}{\partial q_s} \boldsymbol{W}\left(\vec{p}, \vec{q}, t\right) \\
&\to e^{\varepsilon\beta \boldsymbol{U}_0(\vec{q})/2} \Bigg[\sum_s \frac{\omega_s \alpha_s}{\sqrt{2}} (b_s^- + b_s^+) \\
&\qquad\qquad \times \frac{\partial}{\partial q_s} e^{-\varepsilon\beta \boldsymbol{U}_0(\vec{q})/2} \boldsymbol{c}_{\vec{n}}(\vec{q}) e^{-\varepsilon\beta \boldsymbol{U}_0(\vec{q})/2} \Bigg] e^{\varepsilon\beta \boldsymbol{U}_0(\vec{q})/2} \\
&= \sum_s (b_s^- + b_s^+) \Bigg\{ \frac{\omega_s \alpha_s}{\sqrt{2}} \frac{\partial \boldsymbol{c}_{\vec{n}}(\vec{q})}{\partial q_s} \\
&\qquad\qquad - \frac{\varepsilon}{\sqrt{2}\alpha_s} \left[\frac{\partial \boldsymbol{U}_0(\vec{q})}{\partial q_s} \boldsymbol{c}_{\vec{n}}(\vec{q}) + \boldsymbol{c}_{\vec{n}}(\vec{q}) \frac{\partial \boldsymbol{U}_0(\vec{q})}{\partial q_s} \right] \Bigg\} \\
&\equiv \mathcal{A}_b(\vec{b}^+, \vec{q}) \boldsymbol{c}_{\vec{n}}(\vec{q}) + \mathcal{A}_b(\vec{b}^-, \vec{q}) \boldsymbol{c}_{\vec{n}}(\vec{q})
\end{aligned}
\tag{S32}
$$

The second term of Eq. (7b)*:*

$$
\begin{aligned}
&\boldsymbol{U}\left(\vec{q}\right) \star \boldsymbol{W}\left(\vec{p}, \vec{q}\right) \\
&= \boldsymbol{U}\left(\vec{q}\right) e^{+\sum_s i \overleftarrow{\partial}_{q_s} \overrightarrow{\partial}_{p_s}/2} \boldsymbol{W}\left(\vec{p}, \vec{q}\right) \\
&\to e^{\varepsilon\beta \boldsymbol{U}_0(\vec{q})/2} \Bigg[\boldsymbol{U}\left(\vec{q}\right) e^{-\sum_s i \overleftarrow{\partial}_{q_s} \sqrt{2} b_s^-/2\alpha_s} \\
&\qquad\qquad \times e^{-\varepsilon\beta \boldsymbol{U}_0(\vec{q})/2} \boldsymbol{c}_{\vec{n}}(\vec{q}) e^{-\varepsilon\beta \boldsymbol{U}_0(\vec{q})/2} \Bigg] e^{\varepsilon\beta \boldsymbol{U}_0(\vec{q})/2} \\
&= e^{+\varepsilon\beta \boldsymbol{U}_0(\vec{q})/2} \left[\boldsymbol{U}\left(\vec{q}\right) e^{-\sum_s i \overleftarrow{\partial}_{q_s} b_s^-/\sqrt{2}\alpha_s} \right] e^{-\varepsilon\beta \boldsymbol{U}_0(\vec{q})/2} \boldsymbol{c}_{\vec{n}}(\vec{q}) \\
&\equiv \mathcal{B}_b^+(\vec{b}^-, \vec{q}) \boldsymbol{c}_{\vec{n}}(\vec{q})
\end{aligned}
\tag{S33}
$$

The third term of Eq. (7b)*:*

$$
\begin{aligned}
&\boldsymbol{W}\left(\vec{p}, \vec{q}\right) \star \boldsymbol{U}\left(\vec{q}\right) \\
&= \boldsymbol{W}\left(\vec{p}, \vec{q}\right) e^{-\sum_s i \overrightarrow{\partial}_{q_s} \overleftarrow{\partial}_{p_s}/2} \boldsymbol{U}\left(\vec{q}\right) \\
&\to e^{\varepsilon\beta \boldsymbol{U}_0(\vec{q})/2} \Bigg[e^{-\varepsilon\beta \boldsymbol{U}_0(\vec{q})/2} \boldsymbol{c}_{\vec{n}}(\vec{q}) e^{-\varepsilon\beta \boldsymbol{U}_0(\vec{q})/2} \\
&\qquad\qquad \times e^{\sum_s i \overrightarrow{\partial}_{q_s} \sqrt{2} b_s^+/2\alpha_s} \boldsymbol{U}\left(\vec{q}\right) \Bigg] e^{\varepsilon\beta \boldsymbol{U}_0(\vec{q})/2} \\
&= \boldsymbol{c}_{\vec{n}}(\vec{q}) e^{-\varepsilon\beta \boldsymbol{U}_0(\vec{q})/2} \left[e^{-\sum_s i \overrightarrow{\partial}_{q_s} b_s^+/\sqrt{2}\alpha_s} \boldsymbol{U}\left(\vec{q}\right) \right] e^{+\varepsilon\beta \boldsymbol{U}_0(\vec{q})/2} \\
&\equiv \mathcal{B}_b^-(\vec{b}^+, \vec{q}) \boldsymbol{c}_{\vec{n}}(\vec{q})
\end{aligned}
\tag{S34}
$$

The last term of Eq. (15)*:*

$$
\begin{aligned}
&\zeta_s \frac{\partial}{\partial p_s}\left(p_s + \frac{1}{\beta\omega_s}\frac{\partial}{\partial p_s}\right)\boldsymbol{W}(\vec{p},\vec{q},t) \\
&\to \left(-\zeta_s\left(\frac{\alpha_s}{\sqrt{2}}(b_s^- + b_s^+) - \frac{1}{\beta\omega_s}\frac{\sqrt{2}}{\alpha_s}b_s^-\right)\frac{\sqrt{2}}{\alpha_s}b_s^-\boldsymbol{c}_{\vec{n}}(\vec{q})\right) \\
&= -\zeta_s b_s^+ b_s^- \boldsymbol{c}_{\vec{n}}(\vec{q})
\end{aligned}
\tag{S35}
$$

Note that the differential operators $\underset{\leftarrow}{\partial}_{q_s}$ and $\underset{\rightarrow}{\partial}_{q_s}$, in Eqs. (S33) and (S34) act on the square brackets $[\dots]$. Hence, the MSQFPE for the coefficients $\boldsymbol{c}_{\vec{n}}(\vec{q})$ is expressed as

$$
\begin{aligned}
\frac{d}{dt}\boldsymbol{c}_{\vec{n}}(\vec{q},t) = &-\mathcal{A}_b(\vec{b}^+,\vec{q})\boldsymbol{c}_{\vec{n}}(\vec{q},t) - \mathcal{A}_b(\vec{b}^-,\vec{q})\boldsymbol{c}_{\vec{n}}(\vec{q},t) \\
&- \frac{i}{\hbar}\left[\mathcal{B}_b^+(\vec{b}^-,\vec{q})\boldsymbol{c}_{\vec{n}}(\vec{q},t) - \mathcal{B}_b^-(\vec{b}^+,\vec{q})\boldsymbol{c}_{\vec{n}}(\vec{q},t)\right] \\
&- \sum_s \zeta_s b_s^+ b_s^- \boldsymbol{c}_{\vec{n}}(\vec{q})
\end{aligned}
\tag{S36}
$$

S3.2. The multi-index notation

Hereafter, we employ the multi-index notation Table 1. Using the multinomial expansion

$$
\begin{aligned}
\left(\sum_s x_s\right)^M &= \sum_{m_0+m_1+\cdots=M} \frac{M!}{m_0!m_1!\dots}\prod_s x_s^{m_s} \\
&= \sum_{|\vec{m}|=M} \frac{|\vec{m}|!}{\vec{m}!}\vec{x}^{\,\vec{m}},
\end{aligned}
\tag{S37a}
$$

We can expand the exponential function as

$$
\begin{aligned}
e^{\sum_s x_s} &= \sum_M \frac{1}{M!}\left(\sum_s x_s\right)^M \\
&= \sum_M \frac{1}{M!}\sum_{|\vec{m}|=M}\frac{|\vec{m}|!}{\vec{m}!}\vec{x}^{\,\vec{m}} \\
&= \sum_{\vec{m}\geq\vec{0}} \frac{1}{\vec{m}!}\vec{x}^{\,\vec{m}}.
\end{aligned}
\tag{S37b}
$$

By using Eq. (S37b), Eqs. (S33) and (S34) are evaluated as

$$
\begin{aligned}
&\mathcal{B}_b^+(\vec{b}^-,\vec{q})\boldsymbol{c}_{\vec{n}}(\vec{q}) \\
&= e^{\varepsilon\beta\boldsymbol{U}_0(\vec{q})/2}\left[\boldsymbol{U}(\vec{q})\sum_{0\le\vec{m}}\frac{1}{\vec{m}!}\prod_s\left(-\frac{i}{\sqrt{2}\alpha_s}\underleftarrow{\partial}_{q_s}b_s^-\right)^{m_s}\right] \\
&\qquad\times e^{-\varepsilon\beta\boldsymbol{U}_0(\vec{q})/2}\boldsymbol{c}_{\vec{n}}(\vec{q}) \\
&= \sum_{\vec{0}\le\vec{m}\le\vec{n}}\sqrt{\frac{\vec{n}!}{(\vec{n}-\vec{m})!}}\frac{(-i/\sqrt{2})^{|\vec{m}|}}{\vec{\alpha}^{\,\vec{m}}\vec{m}!} \\
&\qquad\times e^{\varepsilon\beta\boldsymbol{U}_0(\vec{q})/2}\frac{\partial^{|\vec{m}|}\boldsymbol{U}(\vec{q})}{\partial\vec{q}^{\,\vec{m}}}e^{-\varepsilon\beta\boldsymbol{U}_0(\vec{q})/2}\boldsymbol{c}_{\vec{n}-\vec{m}}(\vec{q}) \\
&= \sum_{\vec{0}\le\vec{m}\le\vec{n}}\sqrt{\frac{\vec{n}!}{(\vec{n}-\vec{m})!}}(-i)^{|\vec{m}|}\boldsymbol{B}_{\vec{m}}(\vec{q})\boldsymbol{c}_{\vec{n}-\vec{m}}(\vec{q})
\end{aligned}
\tag{S38}
$$

and

$$
\begin{aligned}
&\mathcal{B}_b^-(\vec{b}^+,\vec{q})\boldsymbol{c}_{\vec{n}}(\vec{q}) \\
&= \boldsymbol{c}_{\vec{n}}(\vec{q})e^{-\varepsilon\beta\boldsymbol{U}_0(\vec{q})/2} \\
&\qquad\times\left[\sum_{0\le\vec{m}}\frac{1}{\vec{m}!}\prod_s\left(+\frac{i}{\sqrt{2}\alpha_s}\underrightarrow{\partial}_{q_s}b_s^+\right)\boldsymbol{U}(\vec{q})\right]e^{\varepsilon\beta\boldsymbol{U}_0(\vec{q})/2} \\
&= \sum_{0\le\vec{m}\le\vec{n}}^{\vec{n}}\sqrt{\frac{\vec{n}!}{(\vec{n}-\vec{m})!}}\frac{(+i/\sqrt{2})^{|\vec{m}|}}{\vec{\alpha}^{\,\vec{m}}\vec{m}!} \\
&\qquad\times\boldsymbol{c}_{\vec{n}-\vec{m}}(\vec{q})e^{-\varepsilon\beta\boldsymbol{U}_0(\vec{q})/2}\frac{\partial^{|\vec{m}|}\boldsymbol{U}(\vec{q})}{\partial\vec{q}^{\,\vec{m}}}e^{\varepsilon\beta\boldsymbol{U}_0(\vec{q})/2} \\
&= \sum_{\vec{0}\le\vec{m}\le\vec{n}}\sqrt{\frac{\vec{n}!}{(\vec{n}-\vec{m})!}}\boldsymbol{c}_{\vec{n}-\vec{m}}(\vec{q})(+i)^{|\vec{m}|}\boldsymbol{B}_{\vec{m}}(\vec{q})^\dagger,
\end{aligned}
\tag{S39}
$$

where

$$
\boldsymbol{B}_{\vec{m}}(\vec{q}) \equiv \frac{1}{\sqrt{2}^{|\vec{m}|}\vec{\alpha}^{\,\vec{m}}\vec{m}\,!}e^{+\varepsilon\beta\boldsymbol{U}_0(\vec{q})/2}\frac{\partial^{|\vec{m}|}\boldsymbol{U}(\vec{q})}{\partial\vec{q}^{\,\vec{m}}}e^{-\varepsilon\beta\boldsymbol{U}_0(\vec{q})/2}. \tag{S40}
$$

Here,

$$
\begin{aligned}
b_s^{-m_s}\boldsymbol{c}_{\vec{n}}(\vec{q}) &= \boldsymbol{c}_{\vec{n}}(\vec{q})b_s^{+m_s} \\
&= \begin{cases}\sqrt{\dfrac{n_s!}{(n_s-m_s)!}}\boldsymbol{c}_{\vec{n}-m_s\vec{e}_s}(\vec{q}), & \text{if } m_s\le n_s \\ 0. & \text{otherwise}\end{cases}
\end{aligned}
\tag{S41}
$$

Therefore, Eq. (S36) is written as

$$\begin{aligned}\frac{d}{dt}\boldsymbol{c}_{\vec{n}}(\vec{q},t) = &-\sum_s \mathcal{A}_s(\vec{q})\Big[\sqrt{n_s+1}\boldsymbol{c}(\vec{n}+\vec{e}_s,\vec{q},t) \\ &\qquad + \sqrt{n_s}\boldsymbol{c}(\vec{n}-\vec{e}_s,\vec{q},t)\Big] \\ &- \sum_{0\le\vec{m}\le\vec{n}} \mathcal{B}_{\vec{m}}(\vec{q})\sqrt{\frac{\vec{n}!}{(\vec{n}-\vec{m})!}}\boldsymbol{c}_{\vec{n}-\vec{m}}(\vec{q},t) \\ &- \sum_s \zeta_s n_s \boldsymbol{c}_{\vec{n}}(\vec{q},t),\end{aligned} \tag{S42}$$

where

$$\begin{aligned}\mathcal{A}_s(\vec{q})\boldsymbol{c}_{\vec{n}}(\vec{q}) \equiv &\frac{\alpha_s\omega_s}{\sqrt{2}}\frac{\partial \boldsymbol{c}_{\vec{n}}(\vec{q})}{\partial q_s} \\ &- \frac{1}{\hbar}\left[\boldsymbol{A}_s(\vec{q})\boldsymbol{c}_{\vec{n}}(\vec{q}) + \boldsymbol{c}_{\vec{n}}(\vec{q})\boldsymbol{A}_s(\vec{q})\right]\end{aligned} \tag{S43a}$$

and

$$\begin{aligned}\mathcal{B}_{\vec{m}}(\vec{q})\boldsymbol{c}_{\vec{n}}(\vec{q}) \equiv &\frac{i}{\hbar}\Big[(-i)^{|\vec{m}|}\boldsymbol{B}_{\vec{m}}(\vec{q})\boldsymbol{c}_{\vec{n}}(\vec{q}) \\ &- \boldsymbol{c}_{\vec{n}}(\vec{q})(+i)^{|\vec{m}|}\boldsymbol{B}_{\vec{m}}(\vec{q})^\dagger\Big]\end{aligned} \tag{S43b}$$

and we introduce the auxiliary matrices

$$\boldsymbol{A}_s(\vec{q}) \equiv \frac{\varepsilon}{\sqrt{2}\alpha_s}\frac{\partial \boldsymbol{U}_0(\vec{q})}{\partial q_s}. \tag{S44}$$

S4. Adiabatic transformation matrix for a two-state system

In this section, we introduce the transformation matrix, Eq. (32), that diagonalize the potential matrix of a two-state system. The potential matrix is expressed as

$$\boldsymbol{U}(\vec{q}) = \begin{pmatrix} U^{00}(\vec{q}) & U^{01}(\vec{q}) \\ U^{10}(\vec{q}) & U^{11}(\vec{q}) \end{pmatrix}. \tag{S45}$$

Then, Eq. (18) is expressed as

$$\begin{aligned}&\begin{pmatrix} Z^{0g*}(\vec{q}) & Z^{1g*}(\vec{q}) \\ Z^{0e*}(\vec{q}) & Z^{1e*}(\vec{q}) \end{pmatrix}\begin{pmatrix} U^{00}(\vec{q}) & U^{01}(\vec{q}) \\ U^{10}(\vec{q}) & U^{11}(\vec{q}) \end{pmatrix}\begin{pmatrix} Z^{0g}(\vec{q}) & Z^{0e}(\vec{q}) \\ Z^{1g}(\vec{q}) & Z^{1e}(\vec{q}) \end{pmatrix} \\ &= \begin{pmatrix} U_{\mathrm{a}}^{gg}(\vec{q}) & U_{\mathrm{a}}^{ge}(\vec{q}) \\ U_{\mathrm{a}}^{eg}(\vec{q}) & U_{\mathrm{a}}^{ee}(\vec{q}) \end{pmatrix},\end{aligned} \tag{S46}$$

where

$$U_{\mathrm{a}}^{gg}(\vec{q}) = Z^{0g*}(\vec{q})[U^{00}(\vec{q})Z^{0g}(\vec{q}) + U^{01}(\vec{q})Z^{1g}(\vec{q})] + Z^{1g*}(\vec{q})[U^{10}(\vec{q})Z^{0g}(\vec{q}) + U^{11}(\vec{q})Z^{1g}(\vec{q})], \tag{S47a}$$

$$U_{\mathrm{a}}^{ge}(\vec{q}) = Z^{0g*}(\vec{q})[U^{00}(\vec{q})Z^{0e}(\vec{q}) + U^{01}(\vec{q})Z^{1e}(\vec{q})] + Z^{1g*}(\vec{q})[U^{10}(\vec{q})Z^{0e}(\vec{q}) + U^{11}(\vec{q})Z^{1e}(\vec{q})], \tag{S47b}$$

$$U_{\mathrm{a}}^{eg}(\vec{q}) = Z^{0e*}(\vec{q})[U^{00}(\vec{q})Z^{0g}(\vec{q}) + U^{01}(\vec{q})Z^{1g}(\vec{q})] + Z^{1e*}(\vec{q})[U^{10}(\vec{q})Z^{0g}(\vec{q}) + U^{11}(\vec{q})Z^{1g}(\vec{q})], \tag{S47c}$$

and

$$U_{\mathrm{a}}^{ee}(\vec{q}) = Z^{0e*}(\vec{q})[U^{00}(\vec{q})Z^{0e}(\vec{q}) + U^{01}(\vec{q})Z^{1e}(\vec{q})] + Z^{1e*}(\vec{q})[U^{10}(\vec{q})Z^{0e}(\vec{q}) + U^{11}(\vec{q})Z^{1e}(\vec{q})]. \tag{S47d}$$

By inserting Eq. (32), these functions are evaluated as

$$U_{\mathrm{a}}^{gg}(\vec{q}) = \frac{U^{00}(\vec{q})\chi(\vec{q})^2 + U^{11}(\vec{q})\sigma(\vec{q})^2 - (U^{01}(\vec{q}) + U^{10}(\vec{q}))\chi(\vec{q})\sigma(\vec{q})}{\chi(\vec{q})^2 + \sigma(\vec{q})^2}, \tag{S48a}$$

$$U_{\mathrm{a}}^{ge}(\vec{q}) = \frac{(U^{00}(\vec{q}) - U^{11}(\vec{q}))\sigma(\vec{q})\chi(\vec{q}) + U^{01}(\vec{q})\chi(\vec{q})^2 - U^{10}(\vec{q})\sigma(\vec{q})^2}{\chi(\vec{q})^2 + \sigma(\vec{q})^2}, \tag{S48b}$$

$$U_{\mathrm{a}}^{eg}(\vec{q}) = \frac{(U^{00}(\vec{q}) + U^{11}(\vec{q}))\chi(\vec{q})\sigma(\vec{q}) - U^{01}(\vec{q})\sigma(\vec{q})^2 + U^{10}(\vec{q})\chi(\vec{q})^2}{\chi(\vec{q})^2 + \sigma(\vec{q})^2}, \tag{S48c}$$

and

$$U_{\mathrm{a}}^{ee}(\vec{q}) = \frac{U^{00}(\vec{q})\sigma(\vec{q})^2 + U^{11}(\vec{q})\chi(\vec{q})^2 + (U^{01}(\vec{q}) + U^{10}(\vec{q}))\chi(\vec{q})\sigma(\vec{q})}{\chi(\vec{q})^2 + \sigma(\vec{q})^2}. \tag{S48d}$$

Using the relations

$$U_{10}(\vec{q}) = U_{01}(\vec{q}) = \sigma(\vec{q}) \tag{S49}$$

and

$$\chi(\vec{q})^2 - \sigma(\vec{q})^2 = [U^{11}(\vec{q}) - U^{00}(\vec{q})]\chi(\vec{q}), \tag{S50}$$

we obtain

$$U_{\mathrm{a}}^{gg}(\vec{q}) = U^{11}(\vec{q}) - \chi(\vec{q}), \tag{S51a}$$

$$U_{\mathrm{a}}^{ge}(\vec{q}) = 0, \tag{S51b}$$

$$U_{\mathrm{a}}^{eg}(\vec{q}) = 0, \tag{S51c}$$

and

$$U_{\mathrm{a}}^{ee}(\vec{q}) = U^{00}(\vec{q}) + \chi(\vec{q}). \tag{S51d}$$

Hence, the potential matrix is diagonalized and the adiabatic BO PES of the ground and excited states are expressed as Eqs. (30a) and (30b), respectively.

S5. Formulas for the Coefficients of the Brinkman Hierarchy

S5.1. Adiabatic transformation

We introduce the Brinkman hierarchy in terms of $\boldsymbol{c}_{\mathrm{a},\vec{n}}(\vec{q})$ for adiabatic distribution $\boldsymbol{W}_{\mathrm{a}}(\vec{p},\vec{q})$ as

$$\begin{aligned}\boldsymbol{c}_{\mathrm{a},\vec{n}}(\vec{q}) \equiv \int d\vec{p}\,\psi_{\vec{n}}(\vec{p})\psi_{\vec{0}}(\vec{p})^{-1} \\ \times e^{\varepsilon\beta\boldsymbol{U}_0(\vec{q})/2}\boldsymbol{W}_{\mathrm{a}}(\vec{p},\vec{q})e^{\varepsilon\beta\boldsymbol{U}_0(\vec{q})/2}.\end{aligned} \tag{S52}$$

Using Eq. (S30), Eq. (S22), we have

$$\begin{aligned}\boldsymbol{c}_{\mathrm{a},\vec{n}}(\vec{q}) = e^{\varepsilon\beta\boldsymbol{U}_0(\vec{q})/2}\left[\boldsymbol{Z}\left(\vec{q}\right)^{\dagger} e^{-\sum_s i\underleftarrow{\partial}_{q_s} b_s^-/\sqrt{2}\alpha_s}\right]e^{-\varepsilon\beta\boldsymbol{U}_0(\vec{q})/2} \\ \times \boldsymbol{c}_{\vec{n}}(\vec{q}) \\ \times e^{-\varepsilon\beta\boldsymbol{U}_0(\vec{q})/2}\left[e^{+\sum_s i\underrightarrow{\partial}_{q_s} b_s^+/\sqrt{2}\alpha_s}\boldsymbol{Z}\left(\vec{q}\right)\right]e^{\varepsilon\beta\boldsymbol{U}_0(\vec{q})/2}\end{aligned} \tag{S53}$$

In the multi-index notation presented in Table 1, this is written as

$$\begin{aligned}&\boldsymbol{c}_{\mathrm{a},\vec{n}}(\vec{q}) \\ &= \sum_{\vec{m}\geq 0,\vec{m}'\geq 0}^{\vec{m}+\vec{m}'\leq\vec{n}} e^{\varepsilon\beta\boldsymbol{U}_0(\vec{q})/2}\left[\frac{(-i/\sqrt{2})^{|\vec{m}|}}{\vec{m}!\vec{\alpha}^{\,\vec{m}}}\frac{\partial^{|\vec{m}|}\boldsymbol{Z}\left(\vec{q}\right)^{\dagger}}{\partial\vec{q}^{\,\vec{m}}}\right]e^{-\varepsilon\beta\boldsymbol{U}_0(\vec{q})/2} \\ &\quad\times\sqrt{\frac{\vec{n}!}{(\vec{n}-\vec{m}-\vec{m}')!}}\boldsymbol{c}_{\vec{n}-\vec{m}-\vec{m}'}(\vec{q}) \\ &\quad\times e^{-\varepsilon\beta\boldsymbol{U}_0(\vec{q})/2}\left[\frac{(+i/\sqrt{2})^{|\vec{m}'|}}{\vec{m}'!\vec{\alpha}^{\,\vec{m}'}}\frac{\partial^{|\vec{m}'|}\boldsymbol{Z}\left(\vec{q}\right)}{\partial\vec{q}^{\,\vec{m}'}}\right]e^{\varepsilon\beta\boldsymbol{U}_0(\vec{q})/2} \\ &= \sum_{\vec{m}\geq 0,\vec{m}'\geq 0}^{\vec{m}+\vec{m}'\leq\vec{n}}\sqrt{\frac{\vec{n}!}{(\vec{n}-\vec{m}-\vec{m}')!}}(-i)^{|\vec{m}|}(+i)^{|\vec{m}'|} \\ &\quad\times\boldsymbol{Z}^{-}_{\vec{m}}(\vec{q})^{\dagger}\boldsymbol{c}_{\vec{n}-\vec{m}-\vec{m}'}(\vec{q})\boldsymbol{Z}^{-}_{\vec{m}'}(\vec{q}),\end{aligned} \tag{S54}$$

where

$$\boldsymbol{Z}^{\pm}_{\vec{m}}(\vec{q}) \equiv \frac{1}{\sqrt{2}^{|\vec{m}|}\vec{\alpha}^{\,\vec{m}}\vec{m}!}e^{\pm\varepsilon\beta\boldsymbol{U}_0(\vec{q})/2}\frac{\partial^{|\vec{m}|}\boldsymbol{Z}\left(\vec{q}\right)}{\partial\vec{q}^{\,\vec{m}}}e^{\mp\varepsilon\beta\boldsymbol{U}_0(\vec{q})/2}. \tag{S55}$$

The inverse transformation can be expressed as

$$\begin{aligned}\boldsymbol{c}_{\vec{n}}(\vec{q}) = \sum_{\vec{m}\geq 0,\vec{m}'\geq 0}^{\vec{m}+\vec{m}\leq\vec{n}}\sqrt{\frac{\vec{n}!}{(\vec{n}-\vec{m}-\vec{m}')!}}(-i)^{|\vec{m}|}(+i)^{|\vec{m}'|} \\ \times\boldsymbol{Z}^{+}_{\vec{m}}(\vec{q})\boldsymbol{c}_{\mathrm{a},\vec{n}-\vec{m}-\vec{m}'}(\vec{q})\boldsymbol{Z}^{+}_{\vec{m}'}(\vec{q})^{\dagger}\end{aligned} \tag{S56}$$

Then the relation among $\boldsymbol{W}_{\mathrm{a}}(\vec{p},\vec{q})$, $\boldsymbol{F}_{\mathrm{a}}(\vec{q})$ and $\boldsymbol{c}_{\vec{n}}(\vec{q})$ are given by

$$\begin{aligned}
&\boldsymbol{W}_{\mathrm{a}}(\vec{p},\vec{q}) \\
&= e^{-\varepsilon\beta\boldsymbol{U}_0(\vec{q})/2}\sum_{\vec{n}}\sum_{\vec{m}\geq 0,\vec{m}'\geq 0}^{\vec{m}+\vec{m}'\leq\vec{n}}\sqrt{\frac{\vec{n}!}{(\vec{n}-\vec{m}-\vec{m}')!}}(-i)^{|\vec{m}|}(+i)^{|\vec{m}'|} \\
&\quad\times \boldsymbol{Z}^{-}_{\vec{m}}(\vec{q})^{\dagger}\boldsymbol{c}_{\vec{n}-\vec{m}-\vec{m}'}(\vec{q})\boldsymbol{Z}^{-}_{\vec{m}'}(\vec{q})e^{-\varepsilon\beta\boldsymbol{U}_0(\vec{q})/2} \\
&\quad\times \psi(\vec{0},\vec{p})\psi(\vec{n},\vec{p}),
\end{aligned} \tag{S57}$$

$$\begin{aligned}
&\boldsymbol{F}_{\mathrm{a}}(\vec{q}) \\
&= \boldsymbol{Z}^{\dagger}(\vec{q})e^{-\varepsilon\beta\boldsymbol{U}_0(\vec{q})/2}\boldsymbol{c}(\vec{0},\vec{q})e^{-\varepsilon\beta\boldsymbol{U}_0(\vec{q})/2}\boldsymbol{Z}(\vec{q}),
\end{aligned} \tag{S58}$$

and

$$\begin{aligned}
&\boldsymbol{c}_{\vec{n}}(\vec{q}) \\
&= \sum_{\vec{m}\geq 0,\vec{m}'\geq 0}^{\vec{m}+\vec{m}\leq\vec{n}}\sqrt{\frac{\vec{n}!}{(\vec{n}-\vec{m}-\vec{m}')!}}(-i)^{|\vec{m}|}(+i)^{|\vec{m}'|} \\
&\quad\times \boldsymbol{Z}^{+}_{\vec{m}}(\vec{q})\int d\vec{p}\,\psi_{\vec{n}-\vec{m}-\vec{m}'}(\vec{p})\psi_{\vec{0}}(\vec{p})^{-1} \\
&\quad\times e^{\varepsilon\beta\boldsymbol{U}_0(\vec{q})/2}\boldsymbol{W}_{\mathrm{a}}(\vec{p},\vec{q})e^{\varepsilon\beta\boldsymbol{U}_0(\vec{q})/2}\boldsymbol{Z}^{+}_{\vec{m}'}(\vec{q})^{\dagger}.
\end{aligned} \tag{S59}$$

S5.2. Temporary initial conditions

Using ${\psi_0}^{(s)}(p_s) = \exp(-\beta\omega_s p_s^2/4)/\sqrt{\alpha_s\sqrt{\pi}}$, the temporary initial distribution can be written as

$$\begin{aligned}
W^{\mathrm{a}}_{ab}(\vec{p},\vec{q},-t_{\mathrm{eq}}) = \delta_{ag}\delta_{bg}F^{\mathrm{a}}_{g}(\vec{q},-t_{\mathrm{eq}}) \\
\times {\psi_0^{(\mathrm{t})}(p_{\mathrm{t}})}^2{\psi_0^{(\mathrm{c})}(p_{\mathrm{c}})}^2,
\end{aligned} \tag{S60}$$

where δ_{ab} is the Kronecker delta and $F^{\mathrm{a}}_{g}(\vec{q},-t_{\mathrm{eq}})$ is the initial distribution of the coordinate space set as

$$F^{\mathrm{a}}_{g}(\vec{q},-t_{\mathrm{eq}}) = \frac{1}{\mathcal{Z}_{\vec{q}}}\exp\left[-\beta U^{\mathrm{a}}_{g}(\vec{q})\right]. \tag{S61}$$

The constants $\mathcal{Z}_{\vec{q}}$ are the coordinate part of the partial function $\mathcal{Z}$. Then the coefficients $\vec{c}_{\vec{n}}(\vec{q},0)$ describing Eq. (S60) are calculated using Eqs. (22b) and (21b), and are evaluated as

$$\begin{aligned}
&\boldsymbol{c}_{\vec{n}}(\vec{q},-t_{\mathrm{eq}}) \\
&= \sum_{\vec{m},\vec{m}':\vec{m}+\vec{m}=\vec{n}}\sqrt{\vec{n}!}(-i)^{|\vec{m}|}(+i)^{|\vec{m}'|} \\
&\quad\times \boldsymbol{Z}^{+}_{\vec{m}}(\vec{q})e^{\varepsilon\beta\boldsymbol{U}_0(\vec{q})/2}\boldsymbol{F}_{\mathrm{a}}(\vec{q},-t_{\mathrm{eq}})e^{\varepsilon\beta\boldsymbol{U}_0(\vec{q})/2}\boldsymbol{Z}^{+}_{\vec{m}'}(\vec{q})^{\dagger}.
\end{aligned} \tag{S62}$$

S5.3. The expectation value of kinetic energy

We define the expectation value of the kinetic energy of the sth mode as

$$E_s^{\mathrm{K}}(t) \equiv \int d\vec{p} \int d\vec{q} \frac{\hbar\omega_s p_s^2}{2} \sum_j W_{jj}(\vec{p},\vec{q},t). \tag{S63}$$

This is expressed by using $\vec{c}_{\vec{n}}(\vec{q},t)$ as

$$\begin{aligned} E_s^{\mathrm{K}}(t) &= \int d\vec{p} \int d\vec{q} \sum_j \sum_{\vec{n}\geq\vec{0}} e^{-\varepsilon\beta U_{jj}(\vec{q})} c_{jj,\vec{n}}(\vec{q},t) \\ &\quad \times \frac{\hbar\omega_s}{2} \psi_{\vec{0}}(\vec{p}) \frac{\alpha_s^2}{2} (b_s^+ + b_s^-)^2 \psi_{\vec{n}}(\vec{p}) \\ &= \frac{1}{2\beta} \int d\vec{q} \sum_j e^{-\varepsilon\beta U_{jj}(\vec{q})} [c_{jj}(\vec{0},\vec{q},t) + \sqrt{2} c_{jj}(2\vec{e}_s,\vec{q},t)]. \end{aligned} \tag{S64}$$

Under the temporary initial distribution,

$$E_s^{\mathrm{K}}(0) = \frac{1}{2\beta} = \frac{k_{\mathrm{B}}T}{2}. \tag{S65}$$

S6. Finite Difference and Artificial Viscosity

S6.1. Upwind difference and artificial viscosity for the phase space

In a phase space representation, the derivative $\partial \boldsymbol{W}(\vec{p},\vec{q})/\partial \vec{q}_s$ is often approximated by the first-order difference expression: The first-order upwind difference with the $(2N-1)$th-order accuracy is expressed as [1–5]

$$\frac{\Delta \boldsymbol{W}(\vec{p},\vec{q})}{\Delta q_s} = \begin{cases} \delta^{(1)}_{s;[-N+1,N]} \boldsymbol{W}(\vec{p},\vec{q}), & \text{if } p_s < 0 \\ \delta^{(1)}_{s;[-N,N-1]} \boldsymbol{W}(\vec{p},\vec{q}). & \text{otherwise} \end{cases} \tag{S66}$$

Here we introduce the finite difference symbol

$$\delta^{(L)}_{s;[a,b]} \boldsymbol{W}(\vec{p},\vec{q}) \equiv \sum_{m=a}^{b} \delta^{(L)}_{[a,b],m} \boldsymbol{W}(\vec{p},\vec{q} + m\Delta q_s \vec{e}_s), \tag{S67}$$

where Δq_s is the mesh width in the q_s direction and $\delta^{(L)}_{[a,b],m}$ represents the coefficients of the Lth order differences at $m = 0$ for the mth point that are evaluated from the mesh points in the q_s direction expressed as$\{a\Delta q_s, (a+1)\Delta q_s, \ldots, (b-1)\Delta q_s, b\Delta q_s\}$ [6]. Equation (S66) can be rewritten using the sign function $\mathrm{sgn}(x)$ as

$$\frac{\Delta \boldsymbol{W}(\vec{p},\vec{q})}{\Delta q_s} = \left[\delta^{(1)}_{s;[-N,N]} + \mathrm{sgn}(p_s)\delta^{(\mathrm{visc})}_{s;[-N,N]}\right] \boldsymbol{W}(\vec{p},\vec{q}), \tag{S68}$$

where $\delta^{(\mathrm{visc})}_{s;[-N,N]}$ is defined as

$$\delta^{(\mathrm{visc})}_{[-N,N],m} \equiv \delta^{(2N)}_{[-N,N],m} \Delta q_s^{(2N)} \times \delta^{(1)}_{[-N,N],-N} \tag{S69}$$

and Eq. (S67). This term is $\mathcal{O}(\Delta q_s^{(2N)})$ and gives Eq. (S66) the artificial viscosity. Table S1 lists these coefficients for $N = 1$—5.

Table S1: The coefficients of the finite difference calculations at $m = 0$ point for Eq. (S67).

N	$m =$	-5	-4	-3	-2	-1	± 0	$+1$	$+2$	$+3$	$+4$	$+5$
$N = 1$ (1st)	$\delta^{(1)}_{[0,1],m}\Delta q_s$						-1	$+1$				
	$\delta^{(1)}_{[-1,0],m}\Delta q_s$					-1	$+1$					
	$\delta^{(1)}_{[-1,1],m}\Delta q_s$					$-1/2$	$+0$	$+1/2$				
	$\delta^{(\text{visc})}_{[-1,1],m}\Delta q_s$					$-1/2$	$+1$	$-1/2$				
$N = 2$ (3rd)	$\delta^{(1)}_{[-1,2],m}\Delta q_s$					$-1/3$	$-1/2$	$+1$	$-1/6$			
	$\delta^{(1)}_{[-2,1],m}\Delta q_s$				$+1/6$	-1	$+1/2$	$+1/3$				
	$\delta^{(1)}_{[-2,2],m}\Delta q_s$				$+1/12$	$-2/3$	$+0$	$+2/3$	$-1/12$			
	$\delta^{(\text{visc})}_{[-2,2],m}\Delta q_s$				$+1/12$	$-1/3$	$+1/2$	$-1/3$	$+1/12$			
$N = 3$ (5th)	$\delta^{(1)}_{[-2,3],m}\Delta q_s$				$+1/20$	$-1/2$	$-1/3$	$+1$	$-1/4$	$+1/30$		
	$\delta^{(1)}_{[-3,2],m}\Delta q_s$			$-1/30$	$+1/4$	-1	$+1/3$	$+1/2$	$-1/20$			
	$\delta^{(1)}_{[-3,3],m}\Delta q_s$			$-1/60$	$+3/20$	$-3/4$	$+0$	$+3/4$	$-3/20$	$+1/60$		
	$\delta^{(\text{visc})}_{[-3,3],m}\Delta q_s$			$-1/60$	$+1/10$	$-1/4$	$+1/3$	$-1/4$	$+1/10$	$-1/60$		
$N = 4$ (7th)	$\delta^{(1)}_{[-3,4],m}\Delta q_s$			$-1/105$	$+1/10$	$-3/5$	$-1/4$	$+1$	$-3/10$	$+1/15$	$-1/140$	
	$\delta^{(1)}_{[-4,3],m}\Delta q_s$		$+1/140$	$-1/15$	$+3/10$	-1	$+1/4$	$+3/5$	$-1/10$	$+1/105$		
	$\delta^{(1)}_{[-4,4],m}\Delta q_s$		$+1/280$	$-4/105$	$+1/5$	$-4/5$	$+0$	$+4/5$	$-1/5$	$+4/105$	$-1/280$	
	$\delta^{(\text{visc})}_{[-4,4],m}\Delta q_s$		$+1/280$	$-1/35$	$+1/10$	$-1/5$	$+1/4$	$-1/5$	$+1/10$	$-1/35$	$+1/280$	
$N = 5$ (9th)	$\delta^{(1)}_{[-4,5],m}\Delta q_s$		$+1/504$	$-1/42$	$+1/7$	$-2/3$	$-1/5$	$+1$	$-1/3$	$+2/21$	$-1/56$	$+1/630$
	$\delta^{(1)}_{[-5,4],m}\Delta q_s$	$-1/630$	$+1/56$	$-2/21$	$+1/3$	-1	$+1/5$	$+2/3$	$-1/7$	$+1/42$	$-1/504$	
	$\delta^{(1)}_{[-5,5],m}\Delta q_s$	$-1/1260$	$+5/504$	$-5/84$	$+5/21$	$-5/6$	$+0$	$+5/6$	$-5/21$	$+5/84$	$-5/504$	$+1/1260$
	$\delta^{(\text{visc})}_{[-5,5],m}\Delta q_s$	$-1/1260$	$+1/126$	$-1/28$	$+2/21$	$-1/6$	$+1/5$	$-1/6$	$+2/21$	$-1/28$	$+1/126$	$-1/1260$

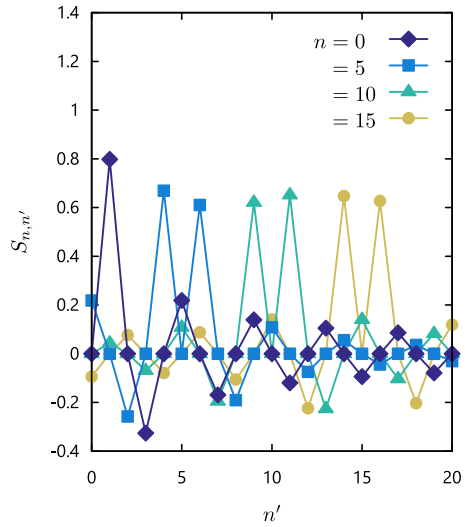

Figure S1: The overlap matrix with the sign function (S71) for the case $\alpha_s = 1$.

S6.2. Artificial viscosity for the coefficients of the Hermite expansion

The upwind difference (S68) is transformed in the Hermite expansion form as

$$\begin{aligned}\frac{\Delta \boldsymbol{c}_{\vec{n}}(\vec{q})}{\Delta q_s} &= \delta^{(1)}_{s;[-N,N]} \boldsymbol{c}_{\vec{n}}(\vec{q}) \\ &\quad + \delta^{(\mathrm{visc})}_{s;[-N,N]} \sum_{n'_s} S_{n_s,n'_s} \boldsymbol{c}_{\vec{n}+(n'_s-n_s)\vec{e}}(\vec{q}),\end{aligned} \tag{S70}$$

where we introduce the overlap matrix with the sign function as

$$S_{n_s,n'_s} \equiv \int dp_s\, \psi_{n_s}(p_s) \mathrm{sgn}(p_s) \psi_{n'_s}(p_s). \tag{S71}$$

Figure S1 plots S_{n_s,n'_s} for the case $\alpha_s = 1$. Because $\mathrm{sgn}(p_s)$ is an odd function, S_{n_s,n'_s} has non-zero value only in the case that $n_s + n'_s$ is odd.

Although we can add the artificial viscosity to Eq. (25) using Eq. (S70), the summation of n'_s in Eq. (S70) increases the numerical cost. To improve the efficiency, we used the fact that the two points $n'_s = n_s \pm 1$ have larger contributions to Eq. (S70) than other points, and found either this two points make our calculations sufficiently stable. Therefore, we employed the finite

difference form of Eq. (25) as

$$
\begin{aligned}
&\frac{d}{dt}\boldsymbol{c}_{\vec{n}}\left(\vec{q},t\right)\\
&=-\sum_{s}\Big\{\sqrt{n_s+1}\frac{\alpha_s\omega_s}{\sqrt{2}}\left[\delta^{(1)}_{s;[-N,N]}\boldsymbol{c}_{\vec{n}+\vec{e}_s}(\vec{q})+\delta^{(\mathrm{visc})}_{s;[-N,N]}\boldsymbol{c}_{\vec{n}}(\vec{q})\right]\\
&\qquad-\sqrt{n_s+1}\frac{1}{\hbar}\left[\boldsymbol{A}_s(\vec{q})\boldsymbol{c}_{\vec{n}+\vec{e}_s}(\vec{q})+\boldsymbol{c}_{\vec{n}+\vec{e}_s}(\vec{q})\boldsymbol{A}_s(\vec{q})\right]\\
&\qquad+\sqrt{n_s}\frac{\alpha_s\omega_s}{\sqrt{2}}\left[\delta^{(1)}_{s;[-N,N]}\boldsymbol{c}_{\vec{n}-\vec{e}_s}(\vec{q})+\delta^{(\mathrm{visc})}_{s;[-N,N]}\boldsymbol{c}_{\vec{n}}(\vec{q})\right]\\
&\qquad-\sqrt{n_s}\frac{1}{\hbar}\left[\boldsymbol{A}_s(\vec{q})\boldsymbol{c}_{\vec{n}-\vec{e}_s}(\vec{q})+\boldsymbol{c}_{\vec{n}-\vec{e}_s}(\vec{q})\boldsymbol{A}_s(\vec{q})\right]\Big\}\\
&-\sum_{\vec{0}\leq\vec{m}\leq\vec{n}}\mathcal{B}_{\vec{m}}(\vec{q})\sqrt{\frac{\vec{n}\,!}{(\vec{n}-\vec{m})!}}\boldsymbol{c}_{\vec{n}-\vec{m}}(\vec{q})\\
&-\sum_{s}\zeta_s n_s\boldsymbol{c}_{\vec{n}}(\vec{q},t).
\end{aligned}
\tag{S72}
$$

Here, we employed an approximation, $S_{n_s,n_s-1}\sim S_{n_s,n_s+1}\sim 1$, at the order in $\mathcal{O}(\Delta q_s^{(2N)})$, because accurate values of them are not important to describe the time evolution.

Figure S2 shows that relations between the accuracy of the the finite difference expressions and time evolution of the excited wavepacket using Eq. (S72) with and without the artificial viscosity terms. The model and parameters of the calculations are the same as Sec. 4.1 and the order of the truncated Moyal product and the equilibration time are $\mathcal{M}=3$ and $t_{\mathrm{eq}}=2,000$ fs, respectively. Note that the finite difference expressions given in Table S1 are the $(2N)$th-order accuracy for N without the artificial viscosity terms. The calculation with second-order accuracy with mesh size $N_{\mathrm{t}}=128$ exhibit unphysical oscillating distribution (Fig. S2(a-i)). The more accurate differencial calculations we employ, the worse ossillations appear (Figs. S2(a-ii) and S2(a-iii)). In the case that we would like to improve the stability of the calculations without the artificial viscosity terms, we need to employ very fine grid (Fig. S2(b)).

Contrastingly, the calculations with the artificial viscosity terms exhibit good stability with the same mesh size $N_{\mathrm{t}}=128$ (Figs. S2(c-ii) and S2(c-iii)). Figure S2(c-i) indicates the initial distribution different from other calculations. This is because the equilibration is also not accurate because of the finite difference expression with the first-order accuracy.

Figure S3 shows that the accuracy of the kineticy energy of the tuning mode $K_{\mathrm{t}}(t)$. The calculations with the artificial viscosity terms (Fig. S3(c)) exhibit almost the same as the calculation with fine mesh (Fig. S3(b)). Note that, although the calculations without the artificial viscosity terms display divergent behavior in their distributions (Fig. S2(a)), the kinetic energy calculations are correct (Fig. S3(a)), because the oscillating behavior is averaged out for the caluculations of the kinetic energy. Therefore, to enhance the stability of the

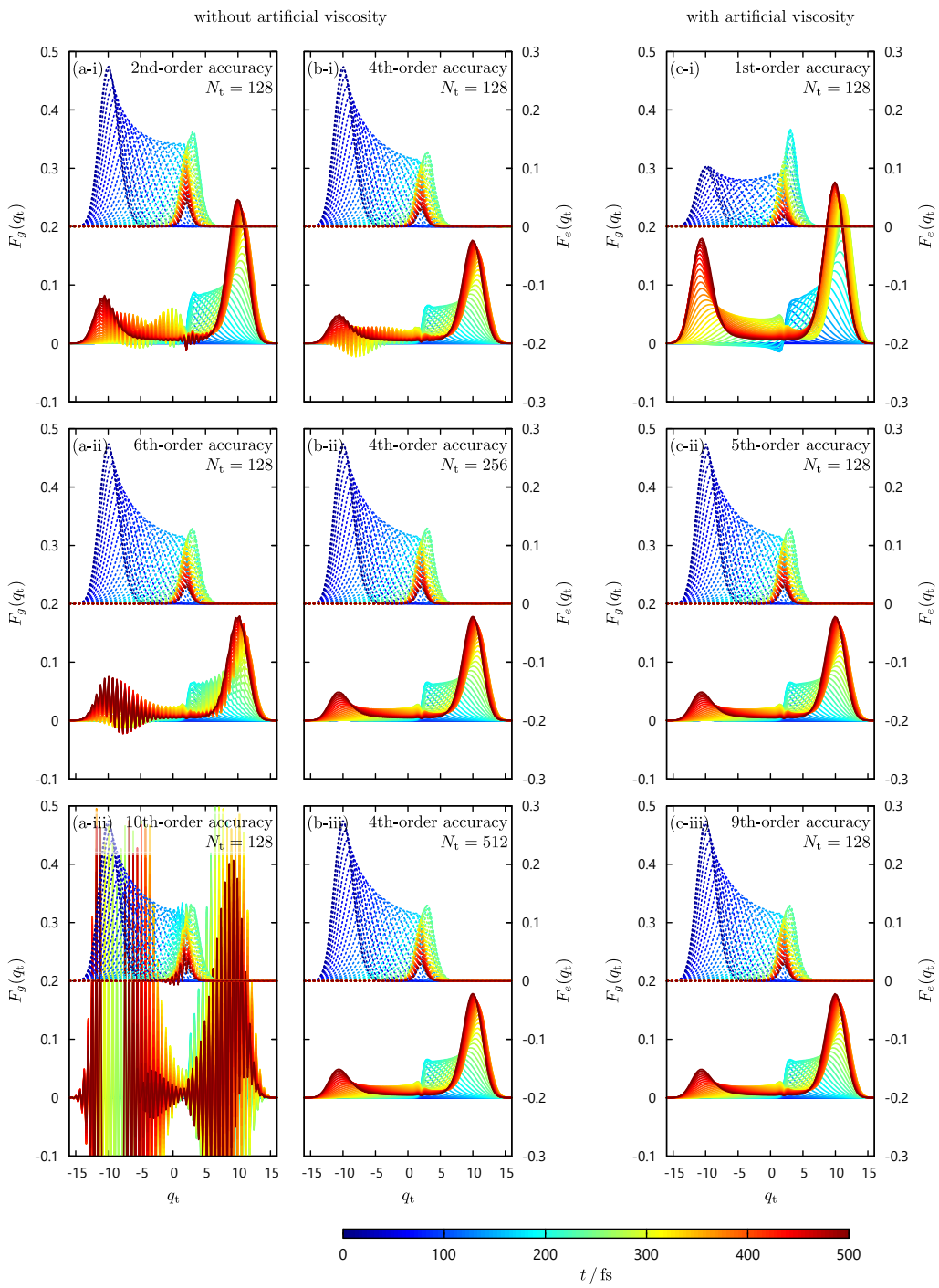

Figure S2: (Continued on the following page.)

Figure S2: Wavepacket dynamics of the AC0 model for different finite difference expressions. The solid and dashed curves represent the wavepacket in the adiabatic ground and excited states, respectively. The colors of the curves represent different time at t. (a) The results obtained from the finite difference expressions with the (i) second-, (ii) sixth-, and (iii) tenth-order accuracy without the artificial viscosity terms. The mesh sizes are $N_{\rm t} = 128$. (b) The results obtained from the finite difference expressions with the fourth-order accuracy. The mesh sizes are (i) $N_{\rm t} = 128$, (ii) 256, and (iii) 512, respectively. (c) The results obtained from the finite difference expressions with the (i) first-, (ii) fifth-, and (iii) ninth-order accuracy with the artificial viscosity terms.

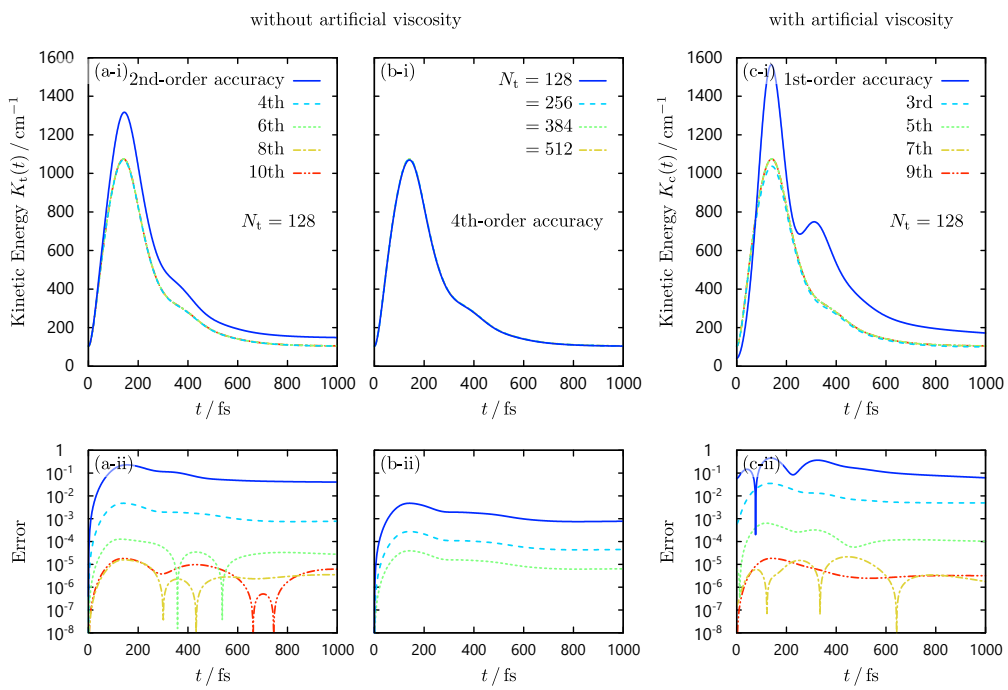

Figure S3: (i) The kinetic energy of the tuning mode $K_{\rm t}(t)$ for the AC0 model are plotted as a function of time for different finite difference calculations. (a) The calculations performed with the finite difference calculations with different accuracy without the artificial viscosity terms. The mesh sizes are $N_{\rm t} = 128$. (b) The calculations performed with the finite difference calculations with the fourth-order accuracy. The mesh sizes are changed within $N_{\rm t} = 128$, 256, 384 and 512. (c) The calculations performed with the finite difference calculations with different accuracy with the artificial viscosity terms. (ii) The relative errors defined as $\left|K_{\rm t}(t) - K_{\rm t}^{\rm 4th\text{-}order, N_t=512}(t)\right| / \left|\max_{t'}\left\{K_{\rm t}^{\rm 4th\text{-}order, N_t=512}(t')\right\}\right|$ for the calculations in Fig. S3(i).

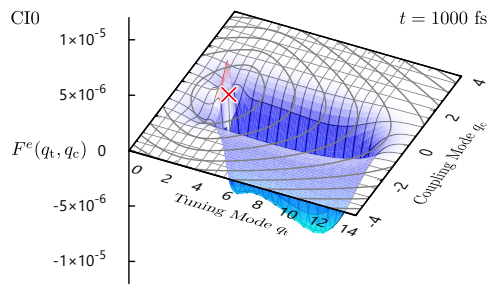

Figure S4: A snapshot of the wavepacket in the adiabatic excited state $F^e(\vec{q}, t)$ in the CI0 model with $d = 0$ at $t = 1,000$ fs. The contours of the adiabatic excited BO PES for every $1,000$ cm^{-1} are expressed as the gray curves on the two-dimensional plate. The mark $\times$ represents the CI point.

finite difference expression, we have to test not only the averaged values of the observable but also the distribution function of the system.

Note that, if we employ different parameters, for example weak system-bath tuning constants or PESs having significantly tilted points, the artificial viscosity based on rough estimations, Eq. (S72), may not work. In such cases, we need to use Eq. (S70).

S7. Breakdown of the positivity condition from the high-temperature approximation

In this paper, we employed the high-temperature approximation $\coth(\beta\hbar\omega_0/2) \sim 2/\beta\hbar\omega_0$, where ω_0 is the effective characteristic frequency of the entire dynamics. Although the vibrational frequency of the tuning mode is slow ($\omega_t = 100$ cm^{-1}), that of the coupling mode is not slow in comparison with the room temperature ($\omega_c = 500$ cm^{-1} and $2/\beta = 417.02$ cm^{-1}). Moreover, the electronic resonant frequency between the adiabatic ground and excited states is fast outside of the crossing region, and this also affects the effective characteristic frequency ω_0. As a result, slight negative probability distributions appear in the calculations as presented in Fig. S4. Because these negative values are small, we concluded that this approximation did not change our results. However, when we employ different parameters and we consider more sensitive quantities, this approximation may cause more unphysical behavior. In such cases, we need to avoid the approximation using the hierarchical techniques. [3, 4, 7, 8]

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