Supporting Information: Variational Squeezed Davydov Ansatz for Realistic Chemical Systems with Nonlinear Vibronic Coupling

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Contents

Time evolution of the squeezing parameters of the full-modes pyrazine model

Figure S1 to S4 plot the time evolution of each squeezing parameter, in which the multiplicities used are $M = 128/192$ for the QVC model, and $M = 48/64$ for the LVC model. For the QVC model, the indices are the same as the Table 1 in ref 1. For the LVC model, the former four indices correspond to the vibrational modes of the system and are the same as the Table 1 in ref 2. Other twenty modes correspond to the bath oscillators whose indices are the same as the Table 2 in ref 2. Corresponding vibrational modes of the indices are also shown in Table S1.

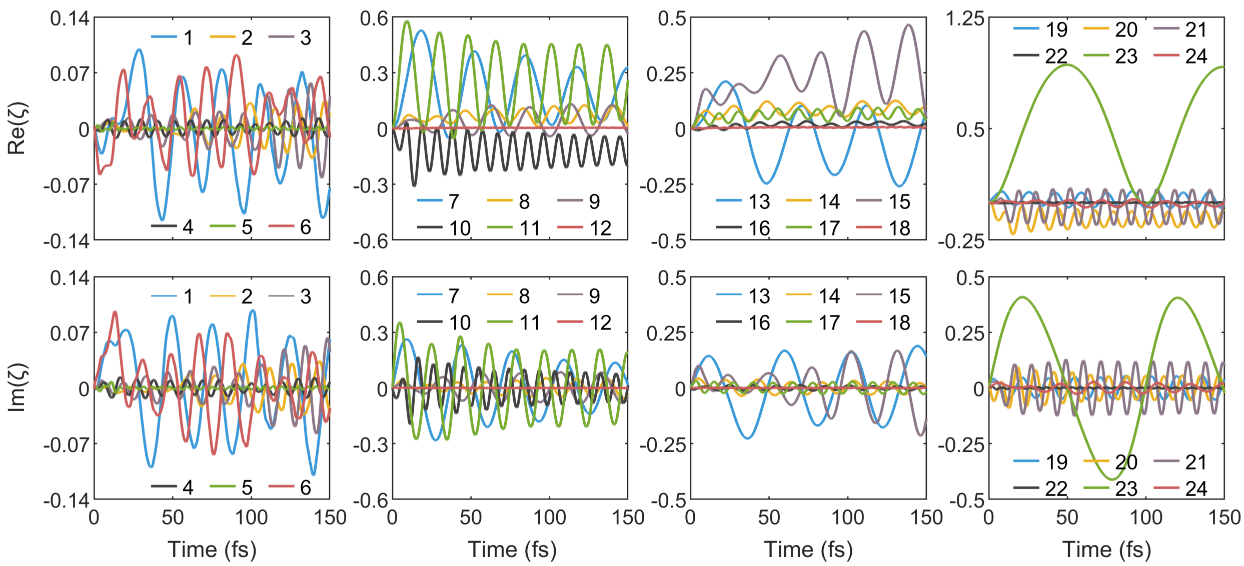

Figure S1: Time evolution of the squeezing parameters for the full-modes QVC model, using the multi-S_2 ansatz with $M = 128$. The bilinear parameter $b_{18b,19b}$ is adjusted to the CASSCF value. The upper row is the real part and the lower row is the imaginary part of the parameters.

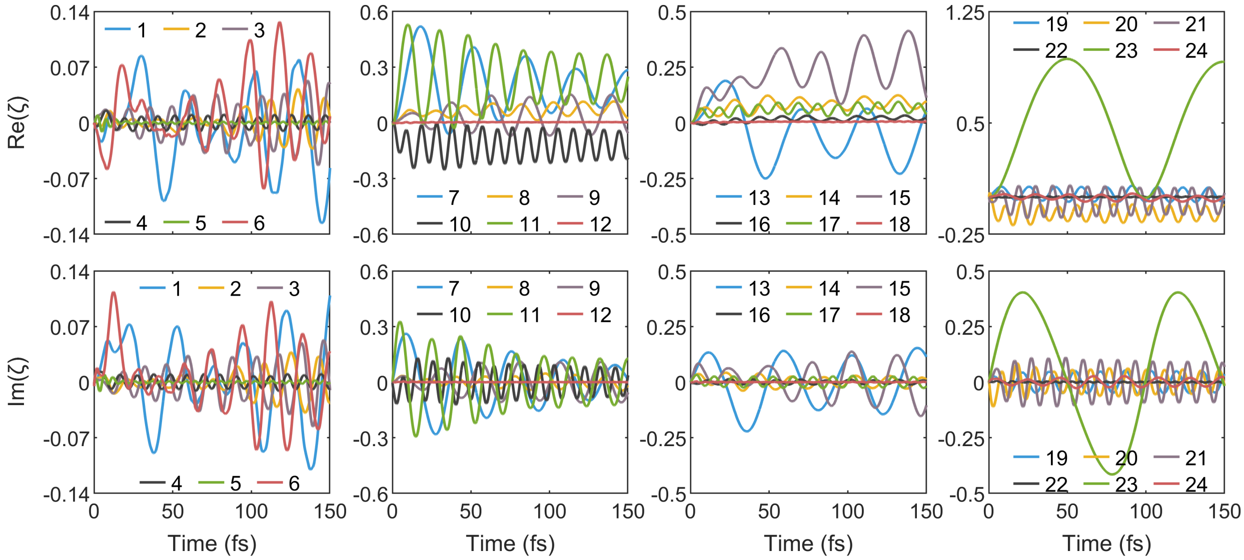

Figure S2: Time evolution of the squeezing parameters for the full-modes QVC model, using the multi-S_2 ansatz with $M = 192$. The bilinear parameter $b_{18b,19b}$ is adjusted to the CASSCF value. The upper row is the real part and the lower row is the imaginary part of the parameters.

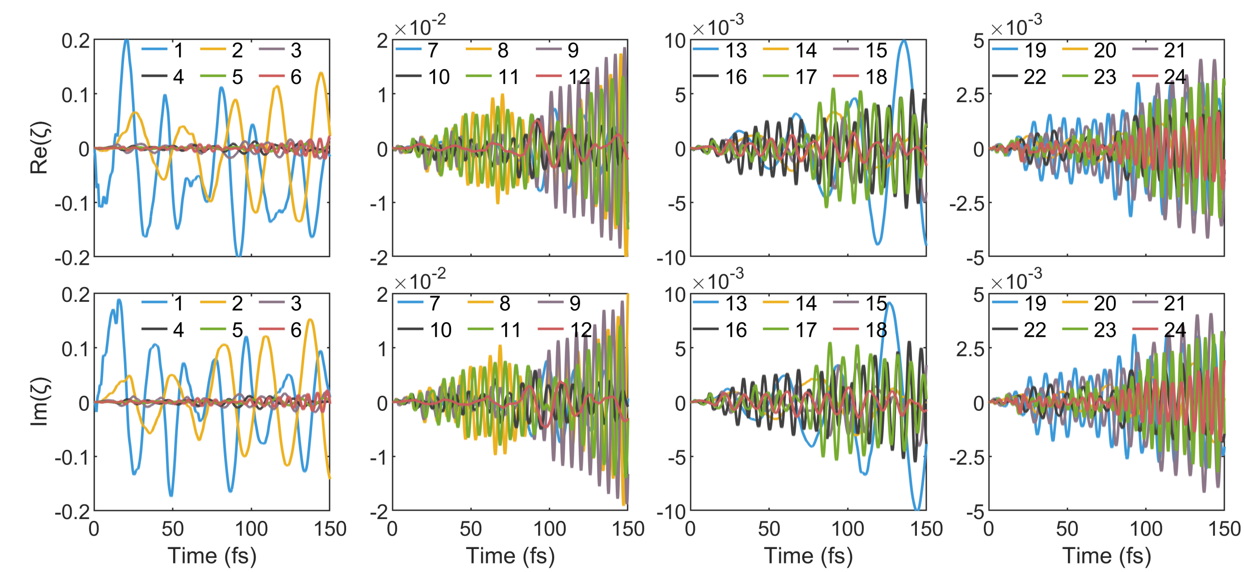

Figure S3: Time evolution of the squeezing parameters for the full-modes LVC model, using the multi-S_2 ansatz with $M = 48$. The upper row is the real part and the lower row is the imaginary part of the parameters.

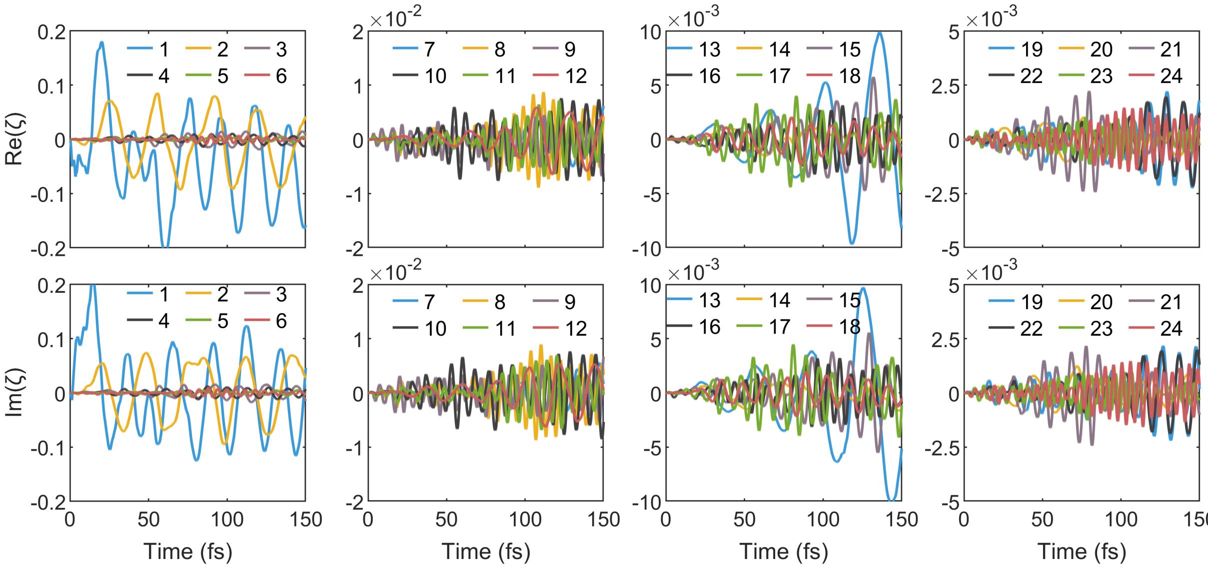

Figure S4: Time evolution of the squeezing parameters for the full-modes LVC model, using the multi-S_2 ansatz with $M = 64$. The upper row is the real part and the lower row is the imaginary part of the parameters.

Table S1: Corresponding vibrational modes of the indices in Figure 3 and Figure S1-S4.

	1	2	3	4	5	6	7	8	9	10	11	12
QVC	ν_{6a}	ν_1	ν_{9a}	ν_{8a}	ν_2	ν_{10a}	ν_4	ν_5	ν_{6b}	ν_3	ν_{8b}	ν_{7b}
LVC	ν_{10a}	ν_{6a}	ν_1	ν_{9a}	bath oscillators							
	13	14	15	16	17	18	19	20	21	22	23	24
QVC	ν_{16a}	ν_{17a}	ν_{12}	ν_{18a}	ν_{19a}	ν_{13}	ν_{18b}	ν_{14}	ν_{19b}	ν_{20b}	ν_{16b}	ν_{11}
LVC	bath oscillators											

Equations of motion of multi-S_2 ansatz

The general vibronic coupling Hamiltonian can be written as following:

$$\begin{aligned}\hat{H} &= \hat{H}_{\mathrm{e}} + \hat{H}_{\mathrm{vib}} + \hat{H}_1 + \hat{H}_2 \\ &= \sum_{m,n} \epsilon_{mn}|m\rangle\langle n| + \sum_q \omega_q b_q^\dagger b_q + \sum_{m,n,q} \kappa_{mnq}|m\rangle\langle n| \left(b_q^\dagger + b_q\right) \\ &\quad + \sum_{m,n,p,q} \gamma_{mnpq}|m\rangle\langle n| \left(b_p^\dagger + b_p\right)\left(b_q^\dagger + b_q\right)\end{aligned} \tag{1}$$

Herein, some of the symbols which are different in the manuscript are combined for convenience. The first term represents diabatic electronic states with energies ϵ_{nn} and couplings ϵ_{mn} $(m \neq n)$. $b_q^\dagger$ (b_q) is the creation (annihilation) operator of the qth vibrational mode with a frequency of ω_q. The third and last terms are truncations of the vibronic couplings in a Taylor series, leading to the linear vibronic couplings and quadratic/bilinear vibronic couplings, respectively.

The multi-S_2 ansatz reads

$$\begin{aligned}|S_2\rangle &= \sum_{i,n} \alpha_{in}|n\rangle \hat{S}\hat{D}_i|0\rangle_{\mathrm{ph}} \\ &= \sum_{i,n} \alpha_{in}|n\rangle \exp\left(\frac{1}{2}\sum_q \zeta_q b_q^{\dagger 2} - \bar{\zeta}_q b_q^2\right) \exp\left(\sum_q \beta_{iq} b_q^\dagger - \bar{\beta}_{iq} b_q\right)|0\rangle_{\mathrm{ph}}\end{aligned} \tag{2}$$

where $\hat{D}_i$ is the displacement operator which can act on the creation and annihilation operators and yield

$$\hat{D}_i^\dagger b_q \hat{D}_i = b_q + \beta_{iq} \tag{3}$$

$$\hat{D}_i^\dagger b_q^\dagger \hat{D}_i = b_q^\dagger + \bar{\beta}_{iq} \tag{4}$$

and $\hat{S}$ is the squeezing operator having the properties as

$$\hat{S}^\dagger b_q \hat{S} = b_q \cosh|\zeta_q| + b_q^\dagger e^{i\theta_q} \sinh|\zeta_q| \tag{5}$$

$$\hat{S}^\dagger b_q^\dagger \hat{S} = b_q^\dagger \cosh|\zeta_q| + b_q e^{-i\theta_q} \sinh|\zeta_q| \tag{6}$$

with $\zeta_q = |\zeta_q| e^{i\theta_q}$.

Then we obtain the Lagrangian written as ($\hbar = 1$):

$$\begin{aligned} L = & \sum_{j,i,m,n} \langle 0|\hat{D}_j^\dagger \hat{S}^\dagger \langle m|\bar{\alpha}_{jm} \left(\frac{i}{2}\frac{\overrightarrow{\partial}}{\partial t} - \frac{i}{2}\frac{\overleftarrow{\partial}}{\partial t} - \hat{H} \right) \alpha_{in}|n\rangle \hat{S}\hat{D}_i|0\rangle \\ = & \frac{i}{2}\sum_{j,i,n} \left[\bar{\alpha}_{jn}\alpha_{in}\langle 0| \left(\hat{D}_j^\dagger \frac{\partial \hat{D}_i}{\partial t} + \hat{D}_j^\dagger S^\dagger \frac{\partial S}{\partial t}\hat{D}_i - \frac{\partial \hat{D}_j^\dagger}{\partial t}\hat{D}_i - \hat{D}_j^\dagger \frac{\partial S^\dagger}{\partial t} S\hat{D}_i \right) |0\rangle \right. \\ & \left. + \bar{\alpha}_{jn}\dot{\alpha}_{in}R_{ji} - \dot{\bar{\alpha}}_{jn}\alpha_{in}R_{ji} \right] - \langle S_2|\hat{H}|S_2\rangle \end{aligned} \tag{7}$$

where

$$\langle 0|\hat{D}_j^\dagger \frac{\partial \hat{D}_i}{\partial t}|0\rangle = \sum_q \left(\bar{\beta}_{jq}\dot{\beta}_{iq} - \frac{\dot{\bar{\beta}}_{iq}\beta_{iq} + \bar{\beta}_{iq}\dot{\beta}_{iq}}{2} \right) R_{ji} \tag{8}$$

$$\langle 0|\frac{\partial \hat{D}_j^\dagger}{\partial t}\hat{D}_i|0\rangle = \sum_q \left(\dot{\bar{\beta}}_{jq}\beta_{iq} - \frac{\dot{\bar{\beta}}_{jq}\beta_{jq} + \bar{\beta}_{jq}\dot{\beta}_{jq}}{2} \right) R_{ji} \tag{9}$$

and

$$\begin{aligned} \langle 0|\hat{D}_j^\dagger S^\dagger \frac{\partial S}{\partial t}\hat{D}_i|0\rangle = & \sum_q \left\{ \frac{i\dot{\theta}_q}{2} \left[\sinh^2|\zeta_q| \left(2\bar{\beta}_{jq}\beta_{iq} + 1 \right) + \frac{1}{2}\sinh 2|\zeta_q| \right. \right. \\ & \left. \left. \times \left(e^{i\theta_q}\bar{\beta}_{jq}^2 + e^{-i\theta_q}\beta_{iq}^2 \right) \right] + \frac{|\dot{\zeta_q}|}{2} \left(e^{i\theta_q}\bar{\beta}_{jq}^2 - e^{-i\theta_q}\beta_{iq}^2 \right) \right\} R_{ji} \end{aligned} \tag{10}$$

$$\begin{aligned} \langle 0|\hat{D}_j^\dagger \frac{\partial S^\dagger}{\partial t} S\hat{D}_i|0\rangle = & -\sum_q \left\{ \frac{i\dot{\theta}_q}{2} \left[\sinh^2|\zeta_q| \left(2\bar{\beta}_{jq}\beta_{iq} + 1 \right) + \frac{1}{2}\sinh 2|\zeta_q| \right. \right. \\ & \left. \left. \times \left(e^{i\theta_q}\bar{\beta}_{jq}^2 + e^{-i\theta_q}\beta_{iq}^2 \right) \right] + \frac{|\dot{\zeta_q}|}{2} \left(e^{i\theta_q}\bar{\beta}_{jq}^2 - e^{-i\theta_q}\beta_{iq}^2 \right) \right\} R_{ji} \end{aligned} \tag{11}$$

with the Debye-Waller factor

$$R_{ji} = \langle 0|\hat{D}_j^\dagger \hat{D}_i|0\rangle = \exp\left(\sum_q \bar{\beta}_{jq}\beta_{iq} - \frac{|\beta_{jq}|^2}{2} - \frac{|\beta_{iq}|^2}{2} \right) \tag{12}$$

The final term in the eq 7 is the energy of the system with $E = E_{\mathrm{e}} + E_{\mathrm{vib}} + E_1 + E_2$ and calculated as

$$E_{\mathrm{e}} = \langle S_2|\hat{H}_{\mathrm{e}}|S_2\rangle = \sum_{j,i,m,n} \varepsilon_{mn}\bar{\alpha}_{jm}\alpha_{in}R_{ji} \tag{13}$$

$$\begin{aligned} E_{\mathrm{vib}} = \langle S_2|\hat{H}_{\mathrm{vib}}|S_2\rangle &= \sum_{j,i,n,q} \bar{\alpha}_{jn}\alpha_{in}\omega_q\Big(\bar{\beta}_{jq}\beta_{iq}\cosh 2|\zeta_q| + \bar{\beta}_{jq}^2\frac{e^{i\theta_q}\sinh 2|\zeta_q|}{2} \\ &\quad + \beta_{iq}^2\frac{e^{-i\theta_q}\sinh 2|\zeta_q|}{2} + \sinh^2|\zeta_q|\Big)R_{ji} \\ &= \sum_{j,i,n,q} \bar{\alpha}_{jn}\alpha_{in}\omega_q\Big(A_q\bar{\beta}_{jq}\beta_{iq} + B_q\bar{\beta}_{jq}^2 + \bar{B}_q\beta_{iq}^2 + C_q\Big)R_{ji} \end{aligned} \tag{14}$$

$$E_1 = \langle S_2|\hat{H}_1|S_2\rangle = \sum_{j,i,m,n,q} \bar{\alpha}_{jm}\alpha_{in}\kappa_{mnq}\Big(I_q\bar{\beta}_{jq} + \bar{I}_q\beta_{iq}\Big)R_{ji} \tag{15}$$

$$\begin{aligned} E_2 = \langle S_2|\hat{H}_2|S_2\rangle &= \sum_{j,i,m,n,p,q} \bar{\alpha}_{jm}\alpha_{in}\gamma_{mnpq}\Big(I_p\bar{\beta}_{jp} + \bar{I}_p\beta_{ip}\Big)\Big(I_q\bar{\beta}_{jq} + \bar{I}_q\beta_{iq}\Big)R_{ji} \\ &\quad + \sum_{j,i,m,n,q} \bar{\alpha}_{jm}\alpha_{in}\gamma_{mnqq}|I_q|^2R_{ji} \end{aligned} \tag{16}$$

where $I_q = \cosh|\zeta_q| + e^{i\theta_q}\sinh|\zeta_q|$. Then the equations of motion for the parameter α is

$$\begin{aligned} & -\frac{d}{dt}\frac{\partial L}{\partial\dot{\bar{\alpha}}_{jm}} + \frac{\partial L}{\partial\bar{\alpha}_{jm}} \\ &= i\sum_i \dot{\alpha}_{im}R_{ji} + \frac{i}{2}\sum_{iq}\alpha_{im}R_{ji} \times \Bigg\{\dot{\beta}_{iq}\Big(2\bar{\beta}_{jq} - \bar{\beta}_{iq}\Big) - \dot{\bar{\beta}}_{iq}\beta_{iq} \\ &\quad + \frac{\dot{\zeta}_q}{2\zeta_q}\Bigg[\sinh^2|\zeta_q|\Big(2\bar{\beta}_{jq}\beta_{iq} + 1\Big) + \frac{\sinh 2|\zeta_q| + 2|\zeta_q|}{2}e^{i\theta_q}\bar{\beta}_{jq}^2 + \frac{\sinh 2|\zeta_q| - 2|\zeta_q|}{2}e^{-i\theta_q}\beta_{iq}^2\Bigg] \\ &\quad - \frac{\dot{\bar{\zeta}}_q}{2\bar{\zeta}_q}\Bigg[\sinh^2|\zeta_q|\Big(2\bar{\beta}_{jq}\beta_{iq} + 1\Big) + \frac{\sinh 2|\zeta_q| - 2|\zeta_q|}{2}e^{i\theta_q}\bar{\beta}_{jq}^2 + \frac{\sinh 2|\zeta_q| + 2|\zeta_q|}{2}e^{-i\theta_q}\beta_{iq}^2\Bigg]\Bigg\} \\ &\quad - \sum_{i,n}\varepsilon_{mn}\alpha_{in}R_{ji} - \sum_{i,q}\alpha_{im}\omega_q\Big(A_q\bar{\beta}_{jq}\beta_{iq} + B_q\bar{\beta}_{jq}^2 + \bar{B}_q\beta_{iq}^2 + C_q\Big)R_{ji} \\ &\quad - \sum_{i,n,q}\alpha_{in}\kappa_{mnq}\Big(I_q\bar{\beta}_{jq} + \bar{I}_q\beta_{iq}\Big)R_{ji} - \sum_{i,n,p,q}\alpha_{in}\gamma_{mnpq}\Big(I_p\bar{\beta}_{jp} + \bar{I}_p\beta_{ip}\Big)\Big(I_q\bar{\beta}_{jq} + \bar{I}_q\beta_{iq}\Big)R_{ji} \\ &\quad - \sum_{i,n,q}\alpha_{in}\gamma_{mnqq}|I_q|^2R_{ji} \end{aligned} \tag{17}$$

For the parameter β, it reads

$$
\begin{aligned}
&-\frac{d}{dt}\frac{\partial L}{\partial\dot{\bar{\beta}}_{j\ell}}+\frac{\partial L}{\partial\bar{\beta}_{j\ell}} \qquad (18)\\
&=i\sum_{i,n}\dot{\alpha}_{in}\bar{\alpha}_{jn}\beta_{i\ell}R_{ji}+i\sum_{i,n}\bar{\alpha}_{jn}\alpha_{in}R_{ji}\times\Bigg\{\dot{\beta}_{i\ell}+\frac{\dot{\zeta}_\ell}{2\zeta_\ell}\Bigg[\sinh^2|\zeta_\ell|\beta_{i\ell}\\
&\quad+\frac{\sinh 2|\zeta_\ell|+2|\zeta_\ell|}{2}e^{i\theta_\ell}\bar{\beta}_{j\ell}\Bigg]-\frac{\dot{\bar{\zeta}}_\ell}{2\bar{\zeta}_\ell}\Bigg[\sinh^2|\zeta_\ell|\beta_{i\ell}+\frac{\sinh 2|\zeta_\ell|-2|\zeta_\ell|}{2}e^{i\theta_\ell}\bar{\beta}_{j\ell}\Bigg]\Bigg\}\\
&\quad+\frac{i}{2}\sum_{i,q}\bar{\alpha}_{jm}\alpha_{im}\beta_{i\ell}R_{ji}\times\Bigg\{\dot{\beta}_{iq}\Big(2\bar{\beta}_{jq}-\bar{\beta}_{iq}\Big)-\dot{\bar{\beta}}_{iq}\beta_{iq}\\
&\quad+\frac{\dot{\zeta}_q}{2\zeta_q}\Bigg[\sinh^2|\zeta_q|\Big(2\bar{\beta}_{jq}\beta_{iq}+1\Big)+\frac{\sinh 2|\zeta_q|+2|\zeta_q|}{2}e^{i\theta_q}\bar{\beta}_{jq}^2+\frac{\sinh 2|\zeta_q|-2|\zeta_q|}{2}e^{-i\theta_q}\beta_{iq}^2\Bigg]\\
&\quad-\frac{\dot{\bar{\zeta}}_q}{2\bar{\zeta}_q}\Bigg[\sinh^2|\zeta_q|\Big(2\bar{\beta}_{jq}\beta_{iq}+1\Big)+\frac{\sinh 2|\zeta_q|-2|\zeta_q|}{2}e^{i\theta_q}\bar{\beta}_{jq}^2+\frac{\sinh 2|\zeta_q|+2|\zeta_q|}{2}e^{-i\theta_q}\beta_{iq}^2\Bigg]\Bigg\}\\
&\quad-\sum_{i,m,n}\bar{\alpha}_{jm}\alpha_{in}\varepsilon_{mn}\beta_{i\ell}R_{ji}-\sum_{i,n}\bar{\alpha}_{jn}\alpha_{in}\omega_\ell\Big(A_\ell\beta_{i\ell}+2B_\ell\bar{\beta}_{j\ell}\Big)R_{ji}\\
&\quad-\sum_{i,n,q}\bar{\alpha}_{jn}\alpha_{in}\omega_q\Big(A_q\bar{\beta}_{jq}\beta_{iq}+B_q\bar{\beta}_{jq}^2+\bar{B}_q\beta_{iq}^2+C_q\Big)\beta_{i\ell}R_{ji}\\
&\quad-\sum_{i,m,n}\bar{\alpha}_{jm}\alpha_{in}\kappa_{mn\ell}I_\ell R_{ji}-\sum_{i,m,n,q}\bar{\alpha}_{jm}\alpha_{in}\kappa_{mnq}\Big(I_q\bar{\beta}_{jq}+\bar{I}_q\beta_{iq}\Big)\beta_{i\ell}R_{ji}\\
&\quad-\sum_{i,m,n}\bar{\alpha}_{jm}\alpha_{in}\Bigg[\sum_p\gamma_{mnp\ell}\Big(I_p\bar{\beta}_{jp}+\bar{I}_p\beta_{ip}\Big)+\sum_q\gamma_{mn\ell q}\Big(I_q\bar{\beta}_{jq}+\bar{I}_q\beta_{iq}\Big)\Bigg]I_\ell R_{ji}\\
&\quad-\sum_{i,m,n}\bar{\alpha}_{jm}\alpha_{in}\Bigg[\sum_{p,q}\gamma_{mnpq}\Big(I_p\bar{\beta}_{jp}+\bar{I}_p\beta_{ip}\Big)\Big(I_q\bar{\beta}_{jq}+\bar{I}_q\beta_{iq}\Big)+\sum_q\gamma_{mnqq}|I_q|^2\Bigg]\beta_{i\ell}R_{ji}
\end{aligned}
$$

Finally, for the variational paratmer ζ, the differential equation is

$$\begin{aligned}
&-\frac{d}{dt}\frac{\partial L}{\partial \dot{\bar{\zeta}}_\ell}+\frac{\partial L}{\partial \bar{\zeta}_\ell} \qquad (19)\\
=\ &\frac{i}{2}\sum_{j,i,n}\Big(\dot{\bar{\alpha}}_{jn}\alpha_{in}+\dot{\alpha}_{in}\bar{\alpha}_{jn}\Big)\tilde{S}_{jin\ell}R_{ji}+\frac{i}{2}\sum_{j,i,n}\bar{\alpha}_{jn}\alpha_{in}\Big\{\dot{\bar{\beta}}_{j\ell}\Big[2\sinh^2|\zeta_\ell|\beta_{i\ell}\\
&+\big(\sinh 2|\zeta_\ell|-2|\zeta_\ell|\big)e^{i\theta_\ell}\bar{\beta}_{j\ell}\Big]+\dot{\beta}_{i\ell}\Big[2\sinh^2|\zeta_\ell|\bar{\beta}_{j\ell}+\big(\sinh 2|\zeta_\ell|+2|\zeta_\ell|\big)e^{-i\theta_\ell}\beta_{i\ell}\Big]\\
&+\dot{\zeta}_\ell e^{-i\theta_\ell}\Big[\sinh 2|\zeta_\ell|\Big(2\bar{\beta}_{j\ell}\beta_{i\ell}+1\Big)+2\sinh^2|\zeta_\ell|\Big(e^{i\theta_\ell}\bar{\beta}_{j\ell}^2+e^{-i\theta_\ell}\beta_{i\ell}^2\Big)\Big]\Big\}R_{ji}\\
&+\frac{i}{2}\sum_{j,i,n,q}\bar{\alpha}_{jn}\alpha_{in}\Big[\dot{\bar{\beta}}_{jq}\Big(\beta_{iq}-\frac{\beta_{jq}}{2}\Big)-\dot{\beta}_{jq}\frac{\bar{\beta}_{jq}}{2}-\dot{\bar{\beta}}_{iq}\frac{\beta_{iq}}{2}+\dot{\beta}_{iq}\Big(\bar{\beta}_{jq}-\frac{\bar{\beta}_{iq}}{2}\Big)\Big]\Big\}\tilde{S}_{jin\ell}R_{ji}\\
&-\omega_\ell\sum_{j,i,n}\bar{\alpha}_{jn}\alpha_{in}\Big[\tilde{A}_\ell\Big(2\bar{\beta}_{j\ell}\beta_{i\ell}+1\Big)+\tilde{B}_\ell^+\bar{\beta}_{j\ell}^2+\tilde{B}_\ell^-\beta_{i\ell}^2\Big]R_{ji}\\
&-\sum_{j,i,m,n}\bar{\alpha}_{jm}\alpha_{in}\kappa_{mn\ell}\Big(\tilde{I}_\ell^+\bar{\beta}_{j\ell}+\tilde{I}_\ell^-\beta_{i\ell}\Big)R_{ji}\\
&-\sum_{j,i,m,n}\bar{\alpha}_{jm}\alpha_{in}\Bigg[\sum_p\kappa_{mnp\ell}\Big(I_p\bar{\beta}_{jp}+\bar{I}_p\beta_{ip}\Big)\Big(\tilde{I}_\ell^+\bar{\beta}_{j\ell}+\tilde{I}_\ell^-\beta_{i\ell}\Big)\\
&+\sum_q\kappa_{mn\ell q}\Big(\tilde{I}_\ell^+\bar{\beta}_{j\ell}+\tilde{I}_\ell^-\beta_{i\ell}\Big)\Big(I_q\bar{\beta}_{jq}+\bar{I}_q\beta_{iq}\Big)+\kappa_{mn\ell\ell}\Big(\tilde{I}_\ell^+\bar{I}_\ell+\tilde{I}_\ell^-I_\ell\Big)\Bigg]R_{ji}
\end{aligned}$$

where

$$\tilde{S}_{jin\ell}=\sinh^2|\zeta_\ell|\left(2\bar{\beta}_{j\ell}\beta_{j\ell}+1\right)+\frac{\sinh 2|\zeta_\ell|-2|\zeta_\ell|}{2}e^{i\theta_\ell}\bar{\beta}_{j\ell}^2+\frac{\sinh 2|\zeta_\ell|+2|\zeta_\ell|}{2}e^{-i\theta_\ell}\beta_{i\ell}^2 \qquad (20)$$

and

$$\tilde{A}_\ell=|\zeta_\ell|\sinh 2|\zeta_\ell| \qquad (21)$$

$$\tilde{B}_\ell^+=e^{i\theta_\ell}\left(|\zeta_q|\cosh 2|\zeta_q|-\frac{\sinh 2|\zeta_q|}{2}\right) \qquad (22)$$

$$\tilde{B}_\ell^-=e^{-i\theta_\ell}\left(|\zeta_q|\cosh 2|\zeta_q|+\frac{\sinh 2|\zeta_q|}{2}\right) \qquad (23)$$

$$\tilde{I}_\ell^+=|\zeta_\ell|\sinh|\zeta_\ell|+e^{i\theta_\ell}\left(|\zeta_\ell|\cosh|\zeta_\ell|-\sinh|\zeta_\ell|\right) \qquad (24)$$

$$\tilde{I}_\ell^-=e^{-i\theta_\ell}\left(|\zeta_\ell|\cosh|\zeta_\ell|+\sinh|\zeta_\ell|\right)+|\zeta_\ell|\sinh|\zeta_\ell| \qquad (25)$$

Expressions of the calculated observables

Observables of interest in simulations are diabatic population, spectrum intensity and autocorrelation function. The first physical quantity is written as

$$P_n(t) = \langle S_2|n\rangle\langle n|S_2\rangle = \sum_{ji} \bar{\alpha}_{jn}\alpha_{in}R_{ji} \tag{26}$$

The spectrum intensity can be calculated by the Fourier transformation of the autocorrelation function as following

$$I(\omega) = \int C(t)e^{i\omega t}dt \tag{27}$$

with

$$C(t) = \langle S_2(0)|S_2(t)\rangle \tag{28}$$

$$= \langle S_2^*(t/2)|S_2(t/2)\rangle \tag{29}$$

$C(t)$ is called the autocorrelation function which is the overlap between the initial and final state, leading to eq 28. Ignoring the initial random noise, we assume the system is factorized and propagated from the nth electronic state. Then the variational parameters are initially equal to zero except $\alpha_{1,n}(t=0) = 1$ and the autocorrelation function can be simplified as

$$C(t) = \sum_i \alpha_{in} \prod_q \exp\left(-\frac{|\beta_{iq}|^2}{2} - \frac{\beta_{iq}^2}{2}e^{-i\theta_q}\tanh|\zeta_q|\right)\sqrt{\operatorname{sech}|\zeta_q|} \tag{30}$$

A more useful way is to calculate the $C(t)$ with the wavefunction at time $t/2$, namely eq 29.[2] It allows to obtain a more accurate result than eq 28. With $B_{iq} = \beta_{iq}\cosh|\zeta_q| +$

$\bar{\beta}_{iq} \sinh|\zeta_q| e^{i\theta_q}$ and $Z_q = \tanh|\zeta_q| e^{i\theta_q}/2$, we have

$$C(t) = \sum_{j,i,n} \alpha_{jn}\alpha_{in} \prod_q \sum_{u,v=0}^{\infty} \frac{(2u)! Z_q^{u+v}}{u!v!} \frac{\left[\left(B_{iq} - \bar{B}_{jq}\right) - 2Z_q\left(\bar{B}_{iq} - B_{jq}\right)\right]^{2(u-v)}}{(2u-2v)!} \times \exp\left[Z_q\left(\bar{B}_{iq} - B_{jq}\right)^2 + B_{jq}B_{iq} - \frac{|B_{jq}|^2 + |B_{iq}|^2}{2}\right] \operatorname{sech}|\zeta_q| \tag{31}$$

where u and v are indices of the Taylor series. In practical calculations, we restrict them with $u, v \leq 4$.

References

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