Supporting Information

Stochastic Adaptive Single-Site Time-Dependent Variational Principle

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1. Computational details

1.1 4-mode and 24-mode Pyrazine models

We first focus on the S_{1}/S_{2} interconversion of pyrazine through a conical intersection between the S_{1} and the S_{2} states after UV photoexcitation to the S_{2} state. This system is widely considered as an ideal model system for a rigorous test of the accuracy and capabilities of full quantum dynamics methods due to the strong vibronic couplings for both diagonal and off-diagonal terms. [S1] There are a widely used 24-mode model and a simplified 4-mode model for the pyrazine system. [S2, S3] Here, we present a brief introduction to them.

The equilibrium geometry of the ground-state pyrazine molecule conserves D_{2h} symmetry, and the S_{1} and S_{2} states have symmetry B_{3u} and B_{2u} symmetry, respectively. Therefore, the symmetry of vibration modes (for linear electron-vibration coupling) or the product of the symmetry of two modes (for bilinear coupling) should be B_{1g} to make corresponding off-diagonal vibronic couplings nonzero. For the on-site coupling terms, this symmetry should be A_{g}. Consequently, the 4- and 24-mode Hamiltonians can be generally expressed as,

\[ H = \begin{pmatrix} -\Delta & 0 \\ 0 & \Delta \end{pmatrix} + \sum_{I} \frac{\hbar \omega_{I}}{2} (\hat{b}_{I}^{\dagger} \hat{b}_{I} + \frac{1}{2}) + \sum_{i \in A_{g}} (\hat{g}_{i}^{1} \hat{g}_{i}^{1\dagger} + \hat{g}_{i}^{2} \hat{g}_{i}^{2\dagger}) + \sum_{i \in B_{1g}} (g_{i12} \hat{g}_{i12}^{1\dagger} \hat{g}_{i12}^{1\dagger} + g_{i12} \hat{g}_{i12}^{1\dagger} \hat{g}_{i12}^{1\dagger}) \]

(S1).

Here, \( \Delta \) is half the energy gap between S_{1} and S_{2} states. \( I \) and \( J \) are indices for vibration modes, and \( g \) are electron-vibration couplings.

For the simplified 4-mode model (\( A_{g} \) modes: \( v_{9a}, v_{1}, v_{9a}; \) \( B_{1g} \) mode: \( v_{10a} \)), the last two terms in the equation containing second-order vibronic couplings are absent, and the parameters are extracted from reference [S2].

For the 24-mode model, both first and second-order interaction terms are involved, and all parameters can be found in the reference [S3].

To build the matrix product state (MPS) structure for time-dependent variational principle (TDVP) simulations in this work, vibration modes are represented by independent sites, and one site at the end of the MPS represents all electronic states. Computational parameters such as time interval (\( \Delta t \)) and occupation number of each vibration mode (\( N_{\text{max}} \)) as well as the site ordering were tested for converging to the final dynamics/spectroscopy results in our previous work [S4], and we adopted these optimal parameters of \( \Delta t \) and \( N_{\text{max}} \) for TDVP calculations in this work. For the site ordering, here we used a slightly different ordering (in this work we put all the electronic states into one site and put this site onto the end of the chain).

In our zero-temperature TDVP simulations, we employ the projected-purification (PP) algorithm [S5] to reduce the computational cost. We set the initial state as the product of \( |S_{2}\rangle \) and all vibrational ground states. All TDVP simulations for the 4- and 24-mode pyrazine models are
The simulated absorption spectra signal \( I(\omega) \) can be written as the Fourier transform of the time autocorrelation function \( C(t) \) with a relaxation term:

\[
I(\omega) = \int_0^T C(\tau) e^{i\omega \tau - \tau} d\tau. \tag{S2}
\]

\( T \) is the relaxation time (\( T=200 \) fs in this section) and the time autocorrelation function \( C(t) \) is defined as:

\[
C(t) = \langle \psi(0) | \psi(t) \rangle. \tag{S3}
\]

\( |\psi(t)\rangle \) is the MPS at time \( t \).

**Figure S1.** Results for the 4-mode pyrazine model from 1TDVP and SA-1TDVP methods. (a) The absolute correlation function from 1TDVP and SA-1TDVP. (b) The error of correlation functions, measured by the absolute value of differences between them with those by exact 2TDVP. (c) The time cost of the 1TDVP and SA-1TDVP. (d) The increase of the maximum bond-dimension of 1TDVP and SA-1TDVP. For a convenient comparison with 1TDVP, here all TDVP simulations were performed without using the PP method.
Figure S2. Convergence of (a) time autocorrelation function and (b) simulated absorption spectra for the 24-mode pyrazine model by SA-1TDVP versus different threshold parameters.
1.2 Spin-1/2 Heisenberg model

The Hamiltonian for the Heisenberg spin-1/2 chain can be written as:

$$\hat{H} = \sum_{i=1}^{N-1} J \left( \hat{S}_{i}^{+} \hat{S}_{i+1}^{-} + \hat{S}_{i}^{-} \hat{S}_{i+1}^{+} \right) + J \hat{S}_{i}^{z} \hat{S}_{i+1}^{z}. \quad (S4)$$

Here $N$ is the number of sites of the chain and $J$ is the spin-coupling constant between neighboring sites. We choose $N = 24$ to perform 2TDVP for time length $10.0 \ J^{-1}$ (step $0.1 \ J^{-1}$) from a random initial state. We capture the singular value distributions on the bond 12-13 during time evolution. Note that the singular values we extracted only belong to states whose spin $z$-components are 0. Like in Figure 1 in the main text, we also show the singular value distribution in Figure S3 for the Heisenberg spin model.

From Figure S3 we can find that the small singular values deviate from the $\lambda_n \sim \exp(-\text{const} \times \ln^2 n)$ line like in the 4-mode pyrazine model. The distributions of second order differences are also fitted well by the exponential and quasi-Gaussian lines.

**Figure S3.** Singular value distribution versus $\log^2 n$ at (a) bond 12-13 time point $0.1 \ J^{-1}$ and (b) bond 12-13 at time point $3.0 \ J^{-1}$ in 24-site Heisenberg spin chain. The red line is fitted by $y = -\text{const} \times \log^{1+1/\alpha} n$ with $\alpha = 1$. (c) Distributions of second order differences at bond 12-13 at time point $0.1 \ J^{-1}$. (d) Distributions of all second order differences at bond 12-13 during time range $0-3.0 \ J^{-1}$.

Figure S4 shows the numerical performances of 2TDVP and SA-1TDVP. We use a 24-site Heisenberg chain with an initial Neel state to run dynamics simulation (total time $10.0 \ J^{-1}$, step $0.1 \ J^{-1}$, cutoff $10^{-6}$).
Figure S4. Results for a 24-site Heisenberg spin model from SA-1TDVP and conventional 2TDVP methods. (a) The absolute correlation function from conventional 2TDVP and SA-1TDVP. (b) The error of correlation vs exact 2TDVP. (c) The time cost of the SA-1TDVP and 2TDVP. (d) The increase of max bond dimension of SA-1TDVP and 2TDVP.
1.3 Spin-$1/2$ Fermi-Hubbard model

We consider a Fermi-Hubbard model with spin-$1/2$ particles whose Hamiltonian can be written as:

$$\hat{H} = -\sum_{i=1}^{N-1} t (\hat{c}_i^\dagger \hat{c}_{i+1}^\uparrow + \hat{c}_{i+1}^\uparrow \hat{c}_i^\dagger) + \sum_{i=1}^{N} U (\hat{c}_i^\dagger \hat{c}_i^\uparrow \hat{c}_i^\dagger \hat{c}_i^\downarrow).$$  \hfill (S5)

Here $N$ is the number of sites of the chain and $\hat{c}_i^\dagger, \hat{c}_i^\uparrow$ are creation and annihilation operators for particles with spin up on site $i$, respectively. Both the length of model and particle numbers are 12. We set the hopping integral $t=1.0$ and the repulsion term $U=3.0$. The total evolution time is 10.0 and step 0.1, starting from a random state. We extract the singular values in the central bond 6-7 and like the Heisenberg model mentioned above, we select those states with two conserved quantum numbers: the particle number 6 and total spin 0 in the blocks. Calculations in this section and data presented here were produced using the SyTen toolkit [S7], originally created by Claudius Hubig. The results are shown in Figure S5.

![Figure S5](image_url)

**Figure S5.** Singular value distribution versus $\log^2 n$ at the central bond (a) at time point 0.5 and (b) at time point 5.0. The red line is fitted by $y = -\text{const} \times \log^{1+1/\alpha} n$ with $\alpha = 1$. (c) Distributions of all second order differences during time range 0-0.5. (d) Distributions of all second order differences during time range 0-5.0.
1.4 PBI trimer model

The detailed Hamiltonian formula and its parameters in the J-aggregated PBI trimer model used for testing our method are extracted from ref. [S8]. We use a maximum occupation number of 10 for all the vibrational modes [S9] and a total evolution time 130 fs (step 0.13 fs). The trimer consists of three J-aggregated molecules. They have their own local S\(_1\) and S\(_2\) states. Here we consider two initial states: the superposition of three local S\(_1\) and S\(_2\) states, respectively. The relaxation time of the two kinds of states are different. Therefore, the resulting spectra can be written as:

\[
I(\omega) = \int_0^t d\tau \sum_{i=S_1,S_2} |d_i|^2 \left< i | e^{-iH\tau} e^{-\frac{\tau}{T_i}} | i \right>.
\]  

(S6)

Here the \(\hat{H}\) is the Hamiltonian and \(d_i\) is the transition dipole from S\(_0\) to state \(i\). We set the relaxation time to \(T_{S_1} = 30\) fs and \(T_{S_2} = 11\) fs and dipole strength to \(d_{S_1}/d_{S_2} = 1.86\).
2. Motivation of the Exponential Distribution

As shown in Figure S6, we can regard the distribution of the first-order differential ($\Delta s \equiv s_{n+1} - s_n$) of logarithmic singular value ($s_n \equiv \log(\lambda_n)$ with $\lambda_n$ being the n-th singular value) as a Poisson process, if we assume that the $s_n$ are uniformly distributed in the whole range, which corresponds to a homogeneous Poisson distribution.

\[ P(\Delta s_n) d(\Delta s_n) = \beta e^{-\beta \Delta s_n} d(\Delta s_n), \quad (S7) \]

with rate parameter $\beta$. Similarly, one has

\[ P(\Delta s_{n+1}) d(\Delta s_{n+1}) = \beta e^{-\beta \Delta s_{n+1}} d(\Delta s_{n+1}), \quad (S8) \]

and can define the second-order differential

\[ \Delta_2 s = \Delta s_{n+1} - \Delta s_n. \quad (S9) \]

The probability of finding $\Delta_2 s$ to be in the interval $[\Delta_2 s, \Delta_2 s + d(\Delta_2 s)]$ is therefore the product of probabilities for $\Delta s_n$ and $\Delta s_{n+1}$:

\[ P(\Delta_2 s) d(\Delta_2 s) = \int_{0}^{+\infty} d(\Delta s_n) \int_{0}^{+\infty} d(\Delta s_{n+1}) \beta^2 e^{-\beta \Delta s_n} e^{-\beta \Delta s_{n+1}}. \quad (S10) \]

The prime denotes the constraint of $\Delta s_{n+1} \in [\Delta_2 s + \Delta s_n - d(\Delta_2 s), \Delta_2 s + \Delta s_n]$ . To ensure $\Delta s_{n+1} (= \Delta s_n + \Delta_2 s)$ to be positive, the integral interval of $\Delta s_n$ is accordingly $[0, +\infty]$ for $\Delta_2 s \geq 0$ or $[-|\Delta_2 s|, +\infty]$ for $\Delta_2 s < 0$. Therefore, we have

\[ P(\Delta_2 s) d(\Delta_2 s) = \int_{0}^{+\infty} d(\Delta s_n) \beta^2 e^{-\beta \Delta s_n} e^{-\beta (\Delta_2 s + \Delta s_n)} d(\Delta_2 s) \]
\[ = \beta^2 e^{-\beta \Delta_2 s} \int_0^{+\infty} d(\Delta s_n) e^{-2\beta \Delta n} \]
\[ = \frac{\beta}{2} e^{-\beta \Delta_2 s} d(\Delta_2 s), \quad \text{(S11)} \]

for \( \Delta_2 s \geq 0 \), and

\[ P(\Delta_2 s) d(\Delta_2 s) = \int_{|\Delta_2 s|}^{+\infty} d(\Delta s_n) \beta^2 e^{-\beta \Delta s_n} e^{-\beta(\Delta_2 s + \Delta s_n)} d(\Delta_2 s) \]
\[ = \beta^2 e^{-\beta \Delta_2 s} \int_{|\Delta_2 s|}^{+\infty} d(\Delta s_n) e^{-2\beta \Delta s_n} \]
\[ = \frac{\beta}{2} e^{\beta \Delta_2 s} d(\Delta_2 s), \quad \text{(S12)} \]

for \( \Delta_2 s < 0 \). We can finally combine Equations S8 and S9 to have an exponential distribution of arbitrary \( \Delta_2 s \) as

\[ P(\Delta_2 s) d(\Delta_2 s) = \frac{\beta}{2} e^{\beta |\Delta_2 s|} d(\Delta_2 s). \quad \text{(S13)} \]

It is easy to prove that this probability function is normalized to 1, as

\[ \int_{-\infty}^{+\infty} \frac{\beta}{2} e^{\beta |\Delta_2 s|} d(\Delta_2 s) = 2 \int_0^{+\infty} \beta e^{-\beta \Delta_2 s} d(\Delta_2 s) = 1. \quad \text{(S14)} \]
3. Motivation of the Quasi-Gaussian Distribution

Besides the assumption of a Poisson distribution for $\Delta s$ in integrable systems, below we further consider the Wigner distribution for $\Delta s$ in non-integrable systems. More specifically, the probability for the next event $(s_{n+1})$ to happen in the interval $[\Delta s_n, \Delta s_n + d(\Delta s_n)]$ after the last event $(s_n)$ is

$$P(\Delta s_n) d(\Delta s_n) = \beta \Delta s_n e^{-\frac{\beta}{2}(\Delta s_n)^2} d(\Delta s_n), \quad (S15)$$

with rate parameter $\beta$.

Using the definition of the probability and integral interval in Equation S7, we have

$$P(\Delta_2 s) d(\Delta_2 s) = \beta^2 \int_0^{+\infty} d(\Delta s_n) \int_0^{+\infty} d(\Delta s_{n+1}) \Delta s_n \Delta s_{n+1} e^{-\frac{\beta}{2}(\Delta s_n)^2} e^{-\frac{\beta}{2}(\Delta s_{n+1})^2}$$

$$= \beta^2 d(\Delta_2 s) \int_0^{+\infty} d(\Delta s_n) \Delta s_n (\Delta s_n + \Delta_2 s) e^{-\frac{\beta}{2}(\Delta s_n)^2} e^{-\frac{\beta}{2}(\Delta s_n + \Delta_2 s)^2}$$

$$= \beta^2 d(\Delta_2 s) e^{-\frac{\beta}{4}(\Delta_2 s)^2} \int_0^{+\infty} d(\Delta_2 s_n) [\Delta s_n \Delta_2 s + (\Delta s_n)^2] e^{-\beta [\Delta s_n \Delta_2 s + (\Delta s_n)^2]}$$

$$= \beta^2 d(\Delta_2 s) e^{-\frac{\beta}{4}(\Delta_2 s)^2} \int_0^{+\infty} d(\Delta_2 s_n) \left[ (\Delta s_n + \frac{\Delta_2 s}{2})^2 - (\frac{\Delta_2 s}{2})^2 \right] e^{-\beta \left( \frac{\Delta_2 s}{2} \right)^2}$$

$$= \beta^2 d(\Delta_2 s) e^{-\frac{\beta}{4}(\Delta_2 s)^2} \int_{\frac{\Delta_2 s}{2}}^{+\infty} dy \left[ y^2 - (\frac{\Delta_2 s}{2})^2 \right] e^{-\beta y^2} \quad (S16)$$

for $\Delta_2 s \geq 0$. It is easy to generalize this quasi-Gaussian distribution to arbitrary $\Delta_2 s$:

$$P(\Delta_2 s) d(\Delta_2 s) = \beta^2 d(\Delta_2 s) e^{-\frac{\beta}{4}(\Delta_2 s)^2} \int_{\frac{\Delta_2 s}{2}}^{+\infty} dy \left[ y^2 - (\frac{\Delta_2 s}{2})^2 \right] e^{-\beta y^2}. \quad (S17)$$

Unfortunately, the resulting formula is not closed, but involves essentially the Gaussian error function. In practice, one can derive the parameter and apply this distribution by tabulating Equation S17.
4. Fitting parameter versus time evolution

**Figure S7.** Fitted parameter $\beta$ in the 4-mode pyrazine model for the exponential distribution from an exact 2TDVP simulation. The dimension of bond 1-2 is 2 all the time so we ignore it. $\bar{v}_n$ represents the auxiliary mode corresponding to $v_n$. 

5. Simulation of exciton diffusion in a monolayer molecular crystal

We build a $5 \times 5$ dimethyl-3,4,9,10-perylenetetracarboxilic diimide (Me-PTCDI) monolayer molecular aggregate, as shown in Figure S8a. To investigate the dynamics of the exciton diffusion in Me-PTCDI with SA-1TDVP, we use the exciton-vibration coupling model:

$$
\hat{H} = \varepsilon \sum_{n=1}^{25} |n\rangle \langle n| + J_{mn} \sum_{(mn)} (|m\rangle \langle n| + |n\rangle \langle m|) + \omega_{\text{vib}} \sum_{n=1}^{25} b_n^\dagger b_n + \lambda \sum_{n=1}^{25} |n\rangle \langle n| (b_n^\dagger + b_n). \quad (S18)
$$

Here $\varepsilon$ is the energy of the Frenkel exciton (FE) and $J_{mn}$ is the coupling between FE states on nearest-neighbor monomers $m,n$. Only one effective vibrational mode with frequency $\omega_{\text{vib}}$ is considered on each monomer and its coupling with FE is $\lambda$. $|m\rangle$ means one FE exciton is on the monomer $m$. All parameters are taken from ref.[S10]. We set the initial state as $|m = 13\rangle$, which is at the center of the whole aggregate. We then simulate the population dynamics of the system by using SA-1TDVP ($\varepsilon = 10^{-8}$), as shown in Figure S8. Here we use a time interval ($\Delta t$) of 0.2 eV$^{-1}$ and set the maximum occupation number of each vibration mode ($N_{\text{max}}$) as 10.

![Figure S8](image)

**Figure S8.** (a) Structure of ME-PCTDI for simulation. (b-d) population dynamics of selected sites.

We then calculate the correlation function and absorption spectra (See Equation S2 and Equation S3) as shown in Figure S9a and S9b. To characterize the delocalization of excitons, we extract the inverse participation ratio $P_R$ [S11] during time evolution:

$$
P_R = \frac{1}{\sum_m P_m^2}.
$$

Here $P_m$ is the population of the FE state on the monomer $m$. The time evolutions of the maximum bond dimension and of $P_R$ are shown in Figure S9c and S9d.
Figure S9. Results for the 25-molecule aggregate model from SA-1TDVP simulation. (a) The absolute time correlation function. (b) The absorption spectrum. (c) Time evolution of the maximum bond dimension. (d) Time evolution of inverse participation ratio.

We further analyze the phonon occupation. The populations of different occupation levels for all 25 vibrational modes are shown in Figure S10.

Figure S10. Calculated population of phonons on every occupation level on different vibrational modes at time point 10, 50, 100, 450 fs, respectively.
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