Modeling and simulating excited-state dynamics of a system in condensed phases:
Machine Learning approach

Seiji Ueno*\dagger and Yoshitaka Tanimura*\ddagger
don
\daggerHPC Systems Inc., Japan
\ddaggerDepartment of Chemistry, Kyoto University, Kyoto, Japan

E-mail: se-ueno@hpc.co.jp \tanimura@kuchem.kyoto-u.ac.jp

Abstract

Simulating quantum irreversible dynamics of exciton and electron transfer problems possesses a non-trivial challenge. Because irreversibility of the system dynamics results from quantum thermal activation and dissipation caused by a surrounding environment, it is necessary to include infinite environmental degrees of freedom in the simulation. Because the capability of full quantum dynamics simulation that includes the surrounding molecular degrees of freedom is limited, a practical approach is to employ a system-bath model, in which dynamics of excitons or electrons are described by a system Hamiltonian, while the other degrees of freedom, arising from the environmental molecules, are described by a harmonic oscillator bath (HOB) plus a system-bath interaction. By extending a previous study of a machine-learning approach for molecular liquids [J. Chem. Theory Comput. 2020, 16, 2099], here we construct a system-bath model for exciton and electron transfer problems. We determine both the system and system-bath interaction parameters that include the bath spectral distribution, using
the electronic excitation energies obtained from Quantum Mechanics/Molecular Mechanics (QM/MM) simulations as a function of time. Using analytical expressions of optical response functions, we calculate linear and two-dimensional electronic (2DES) spectra for indocarbocyanine dimer in methanol. From these results, we demonstrate the capability of our approach to elucidate the non-equilibrium exciton dynamics of a quantum system in a non-intuitive manner.

1 INTRODUCTION

Quantum dynamics play a significant role in many chemical physics and biochemical physics problems. Frequently studied problems of this kind are exciton and electron transfer processes, those are involved in photosynthetic, electron transfer, DNA, and photovoltaic systems. In these problems, the environments (baths), for example, protein and solvation play a central role: These baths are complex and strongly coupled to a molecular system of interest at finite temperature. Recent theoretical works have demonstrated that the system and baths are quantum mechanically entangled (bathentanglement) that are essential to properly understand the quantum dynamics displayed by the system. For example, it has been shown that the optimal condition for excitation energy transfer in light-harvesting complexes is realized under the non-Markovian system-bath interactions in a strong coupling regime, in which the noise correlation time of the bath is comparable to the time scale of the system dynamics. To perform high accuracy simulations with reduced computational cost, some approaches have utilized machine learning methods to make models to reproduce open quantum dynamics, or estimate chemical properties for classical molecular dynamics. Although irreversibility of the system dynamics results from quantum thermal activation and dissipation caused by a surrounding environment, it is difficult to conduct the quantum molecular dynamics simulation that exhibits such a characteristic feature arising from the macroscopic degrees of freedom.

Thus we introduce a system-bath model in which dynamics of excitons or electrons are
described by a system Hamiltonian, while the other degrees of freedom, arising from the environmental molecules, are described by a harmonic oscillator bath (HOB). The HOB, whose distribution takes a Gaussian form, exhibits wide applicability to simulate bath effects, despite its simplicity. This is because the influence of the environment can in many cases be approximated by a Gaussian process, due to the cumulative effect of the large number of environmental interactions. In such a situation, the ordinary central limit theorem is applicable, and hence the Gaussian distribution function is appropriate.\textsuperscript{35,45} The distinctive features of the HOB model are determined by the spectral distribution function (SDF) of the coupling strength between the system and the bath oscillators for various values of frequency. By choosing the form of the SDF, the properties of the bath can be adjusted to represent various environments consisting of, for example, solid state materials\textsuperscript{46,47} and protein molecules.\textsuperscript{3–5} Because the SDF can be different for different form of a system-bath coupling, it is not easy to find an optimized Hamiltonian associated with optimized SDF, in particular for a bath describing a fluctuation of site-site interaction energy.

In the previous study,\textsuperscript{48} we employed a machine-learning approach to construct a system-bath model for intermolecular and intramolecular modes of molecular liquid using atomic trajectories obtained from molecular dynamics (MD) simulations. In this study, we extend the previous approach in order to investigate an exciton or electron transfer problem that is characterized by electronic states embedded in molecular environment using Quantum Mechanics/Molecular Mechanics (QM/MM) calculations for the atomic coordinates of molecules. In particular, we are aiming at the exciton transfer process of the photosynthesis antenna system to investigate how natural systems can realize such highly efficient yields, presumably by manipulating quantum mechanical processes. As a demonstration, we construct a model Hamiltonian of an indocarbocyanine dimer compound.\textsuperscript{49} The accuracy of a model is examined by calculating linear and two-dimensional electronic spectra.

This paper is organized as follows. In Sec. 2, we introduce an exciton or electron transfer model that is coupled to a harmonic heat-bath. We then describe the machine learning
approach that we use to determine the system parameters, the system-bath interaction, and the SDFs on the basis of QM/MM simulations. In Sec. 3, we present results for an indocarbocyanine dimer model constructed from the analysis of the QM/MD trajectories. Linear absorption and two-dimensional spectra are calculated from the analytical expressions of linear and nonlinear response functions. Section 6 is devoted to concluding remarks.

2 THEORY

2.1 Hamiltonian

We consider a situation in which an exciton or electron transfer system interacts with molecular environments that give rise to dissipation and fluctuation in the system. The Hamiltonian of the system is expressed as

\[ \hat{H}_S = \sum_j \hbar \omega_j |j\rangle \langle j| + \sum_{j \neq k} \hbar \Delta_{jk} |j\rangle \langle k|, \]  

(1)

where the \( j \)th exciton or electron states with energy \( \hbar \omega_j \) are represented by the bra and ket vectors as \( |j\rangle \) and \( \langle j| \). The interaction energy between the \( j \)th and \( k \)th states is described by \( \hbar \Delta_{jk} \). In our model, each state is coupled to a different molecular environment (labeled by \( a \)) that are treated as \( N_a \) harmonic oscillators. The total Hamiltonian is then given by

\[ H_{tot} = H_S - \sum_a \sum_{j=1}^{N_a} \alpha_j^a \hat{V}^a \hat{x}_j^a 
+ \sum_a \sum_{j=1}^{N_a} \left[ \frac{(\hat{\mathcal{P}}_j^a)^2}{2m_j^a} + \frac{1}{2} m_j^a (\omega_j^a)^2 (\hat{x}_j^a)^2 \right], \]

(2)

where the momentum, position, mass, and frequency of the \( j \)th oscillator in the \( a \)th bath are given by \( \hat{\mathcal{P}}_j^a, \hat{x}_j^a, m_j^a, \) and \( \omega_j^a \), respectively. The system part of the system-bath interacting is
expressed as
\[ \hat{V}^a = \sum_{j,k} V^a_{jk} |j\rangle \langle k|, \]
where \( V^a_{jk} \) is the coupling constant for the \( a \)th bath between the \( j \) and \( k \) states. The \( a \)th heat bath can be characterized by the spectral distribution function (SDF), defined by
\[ J_a(\omega) \equiv \sum_{j=1}^{N_a} \frac{\hbar (\alpha^a_j)^2}{2m^a_j \omega^a_j} \delta(\omega - \omega^a_j), \]
and the inverse temperature \( \beta \equiv 1/k_B T \), where \( k_B \) is the Boltzmann constant. Various environments, for example, those consisting of nanostructured materials, solvents, and protein molecules, can be modeled by adjusting the form of the SDF. For the heat bath to be an unlimited heat source possessing an infinite heat capacity, the number of heat bath oscillators \( N_a \) is effectively made infinitely large by replacing \( J_a(\omega) \) with a continuous distribution. The above model has been frequently used in the analysis of photosynthetic systems,\(^6\text{-}^{20}\) electron transfer,\(^21\text{-}^{25}\) DNA,\(^26\text{-}^{28}\) and solar battery systems.\(^29\text{-}^{34}\)

2.2 Learning data: QM/MM Simulations

We consider pigments in a molecular system, whose electric excitation or exciton states are described by Eq.(1). The electric states of the pigments depend on a configuration of the surrounding atoms at time \( t \). The time evolution of the excited states of the system and environmental molecules are described by QM/MM simulations. Because our aim of constructing the system-bath model is to perform full quantum simulation of the entire system, we should use quantum MD simulation to provide date on the basis of all atomic coordinates. In practice, however, it is impossible to treat large environmental degrees of freedom, quantum mechanically accurately. Fortunately, we are expected to have reasonable SDFs for quantum simulation even we evaluated them using the classical MD simulation, because we utilize the ensemble of the molecular trajectories, which exhibit Gaussian distribution where the difference between the quantum and classical trajectories is expected to be minor.
and because the dynamics of harmonic oscillators are identical in both classical and harmonic cases, as both classical and quantal Liouvillian for the \( j \)-th oscillator is expressed as 
\[
\hat{L}_j = -(p_j/m_j)(\partial/\partial x_j) - (m\omega^2)(\partial/\partial p_j)
\]
for the \( j \)-th oscillator. We thus use the classical MD simulation to acquire the atomic coordinates of the pigments and the molecular environment. We then conduct quantum chemistry calculations to obtain the desired electronic states, most typically the HOMO and LUMO states of the pigments as a function of time. The excited energy of the \( j \)-th pigment is denoted by \( \epsilon_{jj}(t) \) and the interaction energy between the \( j \)-th and \( k \)-th pigment that includes the bath induced fluctuation is denoted by \( \epsilon_{jk}(t) \). They are obtained using any kind of numerical programs for quantum chemistry calculations. In a case if the main system is too large to evaluate the entire electronic states, we evaluate the site energy \( \epsilon_{jj}(t) \) and the interaction energy \( \epsilon_{jk}(t) \) separately. From the calculated \( \epsilon_{jj}(t) \) and \( \epsilon_{jk}(t) \), we evaluate the system-bath coupling strength in \( \hat{V}_{jk}^a \) and its SDF, in addition to the excitation energy \( \hbar \omega_j \) and the interaction energy \( \Delta_{jk} \), on the basis of the machine learning approach.

While the SDFs evaluated from the MD simulation are temperature dependent, those for the HOB are temperature independent: We eliminate the temperature dependence of optimized parameters, assuming that the sampled MD trajectories exhibit canonical ensemble at finite temperature.

### 2.3 Machine Learning

For \( n \) exciton or electronic excitation sites, we express the simulated data in terms of \( \epsilon_{jk}(t) \) as describing the excited and site-site interaction energies of interest obtained from the QM/MM simulation. The learning Hamiltonian is then expressed as

\[
H(t) = \sum_{j,k=1}^{n} \epsilon_{jk}(t)\langle j \rangle \langle k |.
\]

(5)
We then attempt to reproduce the trajectories of $\epsilon_{jk}(t)$ for the total Hamiltonian Eq. (2) with Eqs. (1) and (3). Although the system-bath model considers an infinitely many degrees of freedom, here we employ a finite number of bath oscillators to estimate the SDFs. Then, sampling for the machine learning training is considered as the average of the classical bath oscillators for a choice of the system and system-bath parameters. The site energy and interaction energy can be expressed as

$$\epsilon_{jj}(t) = \hbar \omega_j - \delta_{jj}(t)$$

and

$$\epsilon_{jk}(t) = \hbar \Delta_{jk} - \delta_{jk}(t),$$

respectively, where $\delta_{jk}(t)$ is expressed in terms of the linear function of the bath coordinates as

$$\delta_{jk}(t) = \sum_a \alpha_{jk}^a x_{jk}^a(t).$$

Here the $a$th bath coordinate for the $jk$ site is described as a function of time as

$$x_{jk}^a(t) = A_{jk}^a \sin (\phi_{jk}^a + \omega_{jk}^a t),$$

where $A_{jk}^a$ and $\phi_{jk}^a$ are the amplitude and phase of the $jk$th bath oscillator. The phase $\phi_{jk}^a$ is randomly chosen to avoid recursive motion of the oscillator. Here, we assume that the influences of individual bath modes are all independent and that the correlations of the fluctuations among different modes can be ignored, although we can treat such correlated modes separately by introducing additional baths.

From Eqs. (8) and (9), $\delta_{jk}(t)$ can be expressed as

$$\delta_{jk}(t) = \sum_a c_{jk}^a \sin (\phi_{jk}^a + \omega_{jk}^a t),$$
where
\[ c_{jk}^a = \alpha_{jk}^a A_{jk}^a \tag{11} \]
and we treat the system-bath coupling parameters as the product of these two variables. The bath parameters and the system-bath interactions are expressed as a set of latent variables in the machine learning context, defined as
\[ \theta = (\{\omega_j\}, \{\Delta_{jk}\}, \{c_{jk}^a\}) \tag{12} \]
where \{\ldots\} is the set of system and bath parameters. The trajectories of \( \epsilon_{jj}(t) \) and \( \epsilon_{jk}(t) \), obtained from the QM/MM calculations, are described as the vibrational motions of the pigment molecular and the surrounding molecules. We then assume that the probability distribution of the pure state energy \( \lambda_i \) is determined from a Gaussian process and are described by the set of the bath parameters \( \alpha_{jk}^a \) and \( \phi_{jk}^a \), by optimizing the probability distribution given by
\[ P(\lambda_i | \theta) = \int \prod_{k,j,a} d\phi_{jk}^a P(\lambda_i | \theta; \phi_{jk}^a) P(\phi_{jk}^a), \tag{13} \]
which is marginalization of the phase of the oscillators \( \phi_{jk}^a \), where \( P(\phi_{jk}^a) \) is the uniform distribution of \([0, 2\pi)\). The marginalization is introduced in order to avoid a trapping in a local minimal state during the gradient method. The probability distribution is expressed in the normal form as
\[ P(\lambda_i|\theta; \phi_{jk}^a) \propto \exp \left[ -\sigma (\lambda_i - E_i)^2 \right], \tag{14} \]
where \( E_i \equiv E_i(\theta; \phi_{jk}^a) \) is the predicted energy as a function of the parameter set \( \theta \) and initial phase \( \phi_{jk}^a \) for the model Hamiltonian Eq. (5) and \( \sigma \) is the error width. Our purpose of employing a machine learning method is to choose the optimal parameter set in \( E_i(\theta; \phi_{jk}^a) \) that makes the probability distribution for given data \( \lambda_i \) maximize. Among several optimization methods, here we use the maximum likelihood method (MLE), where the loss function is
expressed in terms of the negative log of the probability as

\[ L = \sum_i (\lambda_i - E_i)^2. \]  

(15)

To find the maximum value of \( L \), we employ the Adam gradient method for optimization of the parameter set as

\[ \theta \leftarrow \theta + \gamma \frac{\partial L}{\partial \theta}, \]  

(16)

where \( \gamma \) is the learning rate. In this way, we obtain the \( J_{jk} \) element of the SDF for the state \( jk \). Because the energy distribution of each bath oscillator \( E_{jk}^a = \frac{1}{2} m_{jk}^a (\omega_{jk}^a)^2 \) is assumed to obey an canonical ensemble, the oscillator amplitude can be expressed as

\[ \langle A_{jk}^a \rangle = \frac{1}{\sqrt{\pi \beta m_{jk}^a (\omega_{jk}^a)^2}}. \]  

(17)

Using Eqs. (11) and (17) for Eq.(4), we obtain

\[ J_{jk}(\omega) = \sum_{a=1}^{N_a} \frac{1}{2} \pi \beta \hbar \omega_{jk}^a (c_{jk}^a)^2 \delta(\omega - \omega_{jk}^a). \]  

(18)

Because \( J_{jk}(\omega) \) rapidly changes in time in accordance with the structure change of the pigment molecules and environment, we evaluate \( J_{jk}(\omega) \) by averaging over the different sample trajectories. In the mathematical aspect, \( c_{jk} \) is the frequency domain expression of the time domain data and \( J_{jk}(\omega) \) can be obtained by averaging the power spectra \( c_{jk}^2 \) from the Wiener-Khinchin theorem.

It should be noted that the absolute intensity of \( J_{jk}(\omega) \) cannot be determined in the framework of this study, because we do not evaluate the dipole moment of this complex material for simplicity: We evaluate the intensity of \( J_{jk}(\omega) \) from the width of the experimentally obtained linear absorption spectrum.
3 Numerical demonstration

Figure 1: The molecule structure of indocarbocyanine dimer. Two pigments are connected by methylene chains. The gray/blue/white atoms represent the carbon/nitrogen/hydrogen, respectively. The red square represents the pigment 1, whereas the blue square represents the pigment 2.

3.1 Indocarbocyanine Dimer

We now demonstrate our approach for a dimer of identical indocarbocyanine molecules. Figure 1 displays the structure of the pigment molecule. The ground and the excited states of each pigment are expressed as $|0\rangle_j$ and $|1\rangle_j$ for $j = 1$ and 2, respectively. The ground state energies are chosen to be zero. The system Hamiltonian is then expressed as

$$
\hat{H} = \omega_0 (|1\rangle_{11}\langle 1| + |1\rangle_{22}\langle 1|) + \Delta (|0\rangle_{12}\langle 1| + |1\rangle_{12}\langle 0|),
$$

(19)

where $\omega_0$ is the excitation energy of a pigment and $\Delta$ is the interaction energy between the dimer. By diagonalizing $H$, we obtained the eigenvalues $\omega_k$ for the $k = +$ and $-$ eigenstates
$|1+\rangle = (|1\rangle_1|0\rangle_2 + |0\rangle_1|1\rangle_2)/\sqrt{2}$ and $|1-\rangle = (|1\rangle_1|0\rangle_2 - |0\rangle_1|1\rangle_2)/\sqrt{2}$, respectively, as

$$\omega_\pm = \omega_0 \pm \Delta. \quad (20)$$

The fluctuation of excitation energies and interaction energy as functions of time that arise from the intramolecular motions of the pigment and the intermolecular motions of surrounding molecules are expressed as $\delta\omega_\pm(t)$ and $\delta\Delta(t)$, respectively. They are evaluated from the quantum chemistry calculations for given atomic trajectories of the entire molecular system evaluated from a MD simulation.

In our model, because each exciton state is localized and the effects of the environmental modes are exciton site specific, we employ individual heat-bath for a description of energy fluctuation in each exciton state. Although it is possible to introduce a global heat-bath for low-frequency environmental modes coupled to multiple exciton states, here we ignore such effects. Then the fluctuation of the excitation energy and interaction energies are expressed as

$$\delta\omega_\pm(t) = \sum_{m}^{1,2} w_{\pm,m}(t) \sum_{a} c_{\omega_m}^a \sin(\omega_a^m t + \phi_{\omega_m}^a), \quad (21)$$

and

$$\delta\Delta(t) = w_{\Delta}(t) \sum_{a} c_{\Delta}^a \sin(\omega_a^\Delta t + \phi_{\Delta}^a), \quad (22)$$

where $c_{bm}^a$ is the amplitude (scaled by $\alpha$ as described in Eq. 11) and $\phi_{bm}^a$ is the initial phase of the $a$th oscillator for the state index $b = 11$ (or 22) and 12. We introduced the localization weight functions $w_{\pm,m}(t)$ and $w_{\Delta}(t)$ to describe the pigment specific effects of the environments in the delocalized exciton states representation that is obtained from the diagonalization of the pigment based Hamiltonian expressed as Eq. 19. They are evaluated from the electronic states of the pigment $m = 1$ and 2 on the basis of the atomic orbitals
Thus the targeting eigenenergies to be described by the system-bath model, $\lambda_\pm(t; \theta)$, are expressed as

$$\lambda_\pm(t; \theta) = \omega_0 + \delta \omega_\pm(t) \pm (\Delta + \delta \Delta(t)),$$

where $\theta$ is the set of parameters $\theta = (\omega_0, \{c_{\pm,m}^a\}, \Delta, \{c_\Delta^a\})$. As learning data, we compute the exciton energy $E_\pm(t)$, the molecular orbital (MO) coefficients for each exciton state, and wavefunctions (atomic orbital (AO) coefficients for each MO) from the quantum chemistry calculations for given atomic coordinates as a function of time, while the movements of all atoms in the system are evaluated from the classical MD simulation. Using these, we optimize the set of parameter $\theta$. In order to evaluate the weight function $w_{k,m}(t)$, we calculate the exciton and hole populations $p_{k,m}^{ex}(t)$ and $p_{k,m}^h(t)$ that are obtained as the summation of the absolute square of the AO coefficients, which are evaluated from the AO coefficients involved in the MO in the pigment $m$ for the excited state $k$. The weight function is then evaluated as $w_{k,m}(t) = p_{k,m}^{ex}(t)p_{k,m}^h(t)$ and $w(t) = \sum_{k=\pm} (p_{k,1}^h(t)p_{k,2}^{ex}(t) + p_{k,2}^h(t)p_{k,1}^{ex}(t))$. As the definitions indicated the exciton is localized when $w_{\pm,m}$ is close to 1, whereas the exciton states are mixed among the pigments when $w_\Delta$ is close to 1.

To optimize the system and bath parameter set, we minimize the loss function

$$L = \sum_n \sum_t L^n(t) = \sum_n \sum_t [\left(\lambda_-(t; \theta^n) - E^n_- (t)\right)^2 + \left(\lambda_+(t; \theta^n) - E^n_+ (t)\right)^2],$$

where $E^n_- (t)$ and $E^n_+ (t)$ are the lowest ($|1-\rangle$) and 2nd lowest ($|1+\rangle$) excitation energies, and the index $n$ indicates the $n$th sample. Using the MLE method, we optimize $c_{\omega_0m}^a$ and $c_\Delta^a$ for each time series as a sample set. In order to apply the machine learning algorithm, time series of the tuple $(E^n_- (t), E^n_+ (t), w^n_{k,m}(t))$ are regarded as the input feature variables.
In the indocarbocyanine case, the two pigments are symmetric, and the SDF of the bath for each pigment is considered to be identical. Therefore we use the averaged value $c_{\omega_0}^a = (c_{\omega_01}^a + c_{\omega_02}^a)/2$. We then evaluated $J_{jj}(\omega)(j = 1, 2)$ and $J_{12}(\omega)$, which are $J(\omega)$ for $\omega_0$ and $\Delta$, from $c_{\omega_0}^a$ and $c_{\Delta}^a$ using Eq. (18), respectively.

### 3.2 Fourier based approach versus Machine learning approach

Commonly used approach to evaluate the SDFs for $\epsilon_{ij}(t)$ utilizing the Fourier transformation of the auto-correlation function expressed as $\mathcal{F}[\langle \delta \epsilon_{ij}(0)\delta \epsilon_{ij}(t) \rangle]$, where $\delta \epsilon_{ij}(t) \equiv \epsilon_{ij}(t) - \langle \epsilon_{ij} \rangle$. In the actual calculation, the time series $\epsilon_{ij}^n(t)$, where $n$ is the index of a sample, are evaluated as the average of the auto-correlation function expressed as

$$C_{ij}(t) = \frac{1}{N} \sum_n \langle \delta \epsilon_{ij}^n(0)\delta \epsilon_{ij}^n(t) \rangle,$$

where $N$ is the number of the total sample. We then obtain the SDF as

$$J_{ij}(\omega) = \mathcal{F}[C_{ij}(t)].$$

Alternatively, using the Wiener-Khinchin’s theorem for stationary random processes, we can obtain the SDF as an average of power spectrum $P_{ij}^n(\omega) = \mathcal{F}[\epsilon_{ij}(t)]$ as

$$J_{ij}(\omega) = \frac{1}{N} \sum_n P_{ij}^n(\omega).$$

Although this Fourier based approach is simple and straightforward, the obtained SDFs are not necessary the optimal choice for the system-bath Hamiltonian to describe the QM/MM data, because the exciton and interaction energies are mutually depend on each other and thus $J_{ij}(\omega)$ and $J_{ik}(\omega)$ cannot be evaluated separately. In the machine learning approach, however, it is possible to optimize not only $J_{ij}(\omega)$ and $J_{ik}(\omega)$, but also $\omega_0$ and $\Delta$ without assuming the explicit relationships between the SDFs and system parameters. Moreover, if
necessary, we can introduce additional conditions for optimization of the SDFs and system parameters, as we employed \( w_{k,m}(t) \) to take into account the effects of the exciton localization for the indocarbocyanine dimer.

### 3.3 CALCULATION DETAILS

**Step 1: Classical MD**

We prepared a system consists of an indocarbocyanine dimer molecule with 1024 methanol molecules for solvent. The classical MD simulations were carried out with the GROMACS software package. The condition for preparation MD was set to be 1 atm at 300 K with the NPT ensemble. The equilibrium MD was carried out for 20 ps in the NVT ensemble followed by sampling MD with 5 ps in the NVE ensemble. These equilibrium MD and sampling MD were repeated 100 times. The entire MD simulation was done with the time step of 0.1 fs.

**Step 2: Quantum Chemistry Calculation**

To obtain the sample trajectories of the excitation energies, we conducted ZINDO calculation and natural transition orbital analysis for 1 femto-second period of one sample using the ORCA software package. We then obtained 100 samples of \((E_-(t), E_+(t), w(t))\) in 5 ps length.

**Step 3: Machine Learning**

We extracted 1000 points of data in the interval 2 fs. They were taken from the 5 ps length of data obtained from step 2 with shifting the starting time in each 1 step. We excluded a sample if \(E_+ - E_-\) is smaller than \(1 \times 10^{-3}\) eV. We then extracted the 721 series of ample in the 2 ps duration from the 100 samples in the 5 ps length of data. These sampling date was used as the input feature values in the machine learning calculations.
To perform learning calculations, we developed Python codes using the Tensorflow library.\(^{57}\) The training was performed until the value of the loss functions converges with the learning rate $\gamma = 1 \times 10^{-7}$. The initial values of the targeting optimize variables for the amplitudes of SDFs were set as $c_{\omega_0}^a = 1 \times 10^{-5}$ and $c_{\Delta}^a = 1 \times 10^{-5}$, and the exciton and interaction energies were set as $\omega_0 = (\langle E_+ \rangle + \langle E_- \rangle)/2$ and $\Delta = (\langle E_+ \rangle - \langle E_- \rangle)/2$. The initial phases $\phi_0^a$ were randomized 10 times for each series of sample. The loss functions were averaged for each 10 samples as a minibatch, while the parameters were optimized every minibatch. For 721 samples, each 1 epoch contained 73 iterations. To minimize the loss function, we employed the Adam algorithm.

**Step 4: Spectrum Calculation**

We assumed the dipole operator for the indocarbocyanine dimer was given by $\hat{\mu}_1 + \hat{\mu}_2 = \mu(|0\rangle_{11}\langle 1| + |1\rangle_{11}\langle 0| + |0\rangle_{22}\langle 1| + |1\rangle_{22}\langle 0|)$ creating the transition between the triplet state, $|00\rangle$, $|1+\rangle$, and $|11\rangle$, while the optical transitions from these states to the singlet state $|1-\rangle$ were forbidden. Thus the optical transitions in the present system were described by the three-level system with the eigenenergies 0, $\Omega_+$, and $2\omega_0$. This allowed us to employ the analytical expressions of the linear and nonlinear response functions, as presented in appendix A. We then calculated the linear absorption and 2D electronic spectroscopy signals using the line-shape functions.

### 3.4 RESULTS AND DISCUSSION

Representative examples of the prepared dataset are plotted in Fig. 2. The abrupt change of the exciton energies in Fig. 2(b) occurs due to the exciton transfer between the pigment 1 and 2 that takes place in the time duration of 10-100 fs. As illustrated in Fig. 2(c), the difference of the exciton energies $E_+ - E_-$ exhibits minima in accordance with the exciton transfer processes. As illustrated by the red-circles in Fig. 2(c), although such minimal point are significantly sharper than the minimal point arise from the fluctuation of energies, it is
Figure 2: Samples of data used for a learning calculation for (a) the excitation energy $E_k$ for $k = \pm$, (b) the weight functions $w_{k,m}(t)$ for the pigment $m = 1$ (blue) and $m = 2$ (orange) for $k = +$ (solid line) and $k = -$ (dotted line), respectively, and $w_\Delta$ (green dashed curve), and (c) the difference of the energy levels $E_\pm$. The panel (c) is plotted to illustrate the relationship between the energies and the weight functions.

Figure 3: The learning curve of the model.
Figure 4: The SDFs for the exciton energy $J_{11}(\omega) (= J_{22}(\omega))$ (blue) and the interaction energy $J_{12}(\omega)$ (orange) obtained from the machine learning approach.
Figure 5: Energy level diagram of a dimer system that undergoes the random fluctuations of the excited energy and coupling strength described by $\delta \omega(t)$ and $\delta \Delta(t)$, respectively. For the description of pure dephasing, only the difference of the energies involved in the optical excitation is important: The frequency fluctuation between $|00\rangle$ and $|1+\rangle$ is given by $\delta \omega(t) + \delta \Delta(t)$, whereas $|1+\rangle$ and $|11\rangle$ is given by $\delta \omega(t) - \delta \Delta(t)$. For perfectly uncorrelated fluctuations, we treat $\delta \omega(t)$ and $\delta \Delta(t)$ independently.
not easy to separate the effects of exciton transfer from the fluctuation of energies arises from the environmental motions. By introducing the localization weight functions \( w_{\pm,m}(t) \) and \( w_{\Delta}(t) \) in Eqs. \((21)\) and \((22)\) to eliminate the effects of non-environmental origin in the learning trajectories, we can stabilize and enhance the efficiency of the machine learning process.

In Fig. \(3\) we depict the learning curve of the loss function defined as Eq. \((24)\). After random samplings of \( \phi \), the loss function converged monotonically to a certain positive value, which demonstrated the efficiency of the present algorithm. The initial parameter values of the excitation energy and the interaction energy were set by \( \omega_0 = 17736 \text{ cm}^{-1} \) and \( \Delta = 1004 \text{ cm}^{-1} \), whereas the optimized values of the excitation energy and the interaction energy were given by \( \omega_0 = 18060 \text{ cm}^{-1} \) and \( \Delta = 845.0 \text{ cm}^{-1} \), which are closer to the experimental obtained values.

In Fig. \(4\) we display the results of the SDFs for the excitation energy \( J_{11}(\omega) (= J_{22}(\omega)) \) and the interaction energy \( J_{12}(\omega) \). Various intermolecular modes below 2000 cm\(^{-1}\) are observed as the prominent sharp peaks near 446, 562, 1530, 1790, 1840, and 1920 cm\(^{-1}\). In the region over 2000 cm\(^{-1}\), only two tiny peaks near 3000 cm\(^{-1}\) and 3840 cm\(^{-1}\) are observed. The normal mode analysis (B3LYP/def-SV(P)) indicates these peaks under 3300 \( \text{ cm}^{-1} \) arise from the intramolecular modes of the indocarbocyanine dimer, whereas the peak at 3850 cm\(^{-1}\) arises from a molecular vibration of solvent methanol molecules. We found that each sharp peak can be fitted by the Brownian spectral distribution\(^{24,25}\) whereas the broadened background peak in the range from 0 to 2000 cm\(^{-1}\) corresponding to the intramolecular modes is fitted by the Drude-Lorentz distribution\(^{55}\). The intensities of the peaks in \( J_{12}(\omega) \) are considerably weaker than those in \( J_{11}(\omega) \): Only the peaks near 456, 562, 1840 and 1920 cm\(^{-1}\) are identified. As we expected, the positions of intermolecular peaks are determined from the classical MD, whereas the heights of these are predominately determined from the quantum chemistry calculation.

To verify the description of obtained SDFs and system parameters, we computed lin-
ear absorption and two-dimensional electronic spectra (2DES), where the experimentally obtained spectra are available. In general, these spectra should be calculated in the framework of open quantum dynamics taking into account the complex interaction between the exciton sites. For a demonstration purpose, however, here we employ the analytical expressions of response functions ignoring the transition to the singlet state that is usually forbidden. The details of calculations are presented in Appendix A.

Linear absorption spectrum calculated from Eqs. (A.1) and (A.2) is presented in Fig. 6. Here, the Gaussian spectral peak, \( \lambda \exp \left[ -\left( \frac{(\omega - \omega_c)}{\gamma} \right)^2 \right] \), was fitted on the vicinity of the peak, where the amplitude, central frequency, and width were chosen as \( \lambda = 348.64 \), \( \omega_c = 18750 \text{cm}^{-1} \), and \( \gamma = 466 \text{cm}^{-1} \). Note that because we did not try to determined the amplitude of dipole operator for simplicity, we could not determine the intensities of SDFs: We scale the intensities of \( J_{11}(\omega) \) to fit the experimentally obtained signal. As presented in Fig. 6, we observe the single broadened absorption peak at \( \omega_0 + \Delta \) corresponding to the transition between \(|00\rangle\) and \(|1+\rangle\), while the transition between \(|00\rangle\) and \(|1-\rangle\) is forbidden. (see Fig. 5). Although the experimentally observed linear absorption spectrum exhibit 0–1 phonon sideband peak near \( \omega = 19500 \text{cm}^{-1} \), here we only observe it as the asymmetry of the Gaussian peak in the high frequency region.

The 2D correlation electronic spectra calculated using the analytical expressions of the response function (Eqs. (A.5)-(A.7)) are presented in Fig. 7. At \( t_2 = 0 \) fs only one peak stretched near the \( \omega_1 = \omega_3 \) line arising from the \(|00\rangle \rightarrow |1+\rangle \) transition is observed. At \( t_2 = 20 \) fs, then the peak is elongated to the low-frequency \( \omega_1 \) direction due to shift of the eigenenergy caused by the heat-bath induced exciton-exciton interaction described by \( J_{12}(\omega) \). Because the system-bath interaction here we considered is non-Markovian whose effects appear only after the period longer than the inverse correlation time of noise, we do not observe such heat-bath effects for small \( t_2 \). Then, around \( t_2 = 40 \) fs, the off-diagonal peak near \((\omega_1, \omega_3) = (17800, 20000)\) in units of cm\(^{-1}\) corresponding to the transition between \(|1+\rangle \rightarrow |11\rangle \) is observed, whereas the peak along the \( \omega_1 = \omega_3 \) line shifts to
Figure 6: Linear absorption spectrum calculated from Eqs. (A.1) and (A.2) with the line shape function Eq. (A.3) for the system parameters and SDFs obtained from the machine learning approach. The dotted line is the fitted Gaussian peak centered at 18750 cm\(^{-1}\), indicating that the calculated peak is asymmetric due to the 0 → 1 phonon transition near 19500 cm\(^{-1}\).

\((\omega_1, \omega_3) = (21000, 20000)\) due to the transition \(|00\rangle \rightarrow |1+\rangle\) arises from the exciton-exciton interaction described by \(\Delta\) and \(J_{12}(\omega)\). As \(t_2\) goes, the intensities of these two peaks change oscillatory, as the results of the population transition among \(|10\rangle, |1+\rangle, \text{ and } |11\rangle\) caused by \(\Delta\) and \(J_{12}(\omega)\). This phenomena was also observed experimentally.\(^{35}\) The appearance of this oscillatory feature at finite period in \(t_2\) indicates the importance of the off-diagonal heat-bath, whose modeling is not easy in the framework of the existing approach. At \(t_2 = 300\) fs the peak elongated in the \(\omega_1 = \omega_3\) direction due to the inhomogeneous broadening arises from the baths described as \(J_{11}(\omega)\) and \(J_{22}(\omega)\).\(^{35}\)

4 CONCLUSION

We introduced a machine leaning approach to constructing a model to analyze the dynamics of exciton or electron transfer processes in a complex environment on the basis of the energy eigenstates evaluated from QM/MM simulations as a function of time. The key feature of the present study is a system-bath model, in which the primary exciton/electron
Figure 7: 2DES calculated from Eqs. (A.5) - (A.7) with the line shape function Eq. (A.3) for the system parameters and SDFs obtained from the machine learning approach. The waiting time $t_2$ for each signal is displayed on the left top of each pane. The peak intensity of the signal was normalized for each $t_2$. 
dynamics are described by a system Hamiltonian expressed in terms of discretized energy states, while the other degrees of freedom are described by a harmonic heat-bath that is characterized by SDFs. An optimized system-bath Hamiltonian obtained from the machine learning approach allows us to conduct time-irreversible quantum simulations not feasible from a full quantum MD simulation approach.

Here, we demonstrated the above features by calculating linear and nonlinear optical spectra for the indocarbocyanine dimer system in the methanol environment, in which the quantum entanglement between the system and bath plays a central role. The calculated results explain the experimental results reasonably well: We found that the heat-bath for the exciton-exciton interaction plays a key role for describing exciton transfer process in this system. Here, we ignore the transition between the singlet and triple states due to an applicability of the analytical expression, if necessary, we can treat it explicitly using the HEOM formalism.

Finally, we briefly discuss some extensions of this study. As shown in the previous paper, the machine learning approach can be applied not only for a system described by electronic states but also a system described by reaction coordinates, which is useful for investigating chemical reaction processes characterized by potential energy surfaces. By combining the previous and present approaches, we can further investigate a system described as not only electronic states but also molecular configuration space in a framework of the system-bath model, for example, photoisomerization, molecular motor, and non-adiabatic transition problems. In this way, we may construct a system-bath model for entire photosynthesis reaction processes consisting of photoexcitation, exciton transfer, electron transfer, and proton transfer processes, including the conversion processes, such as exciton-coupled electron transfer and electron coupled proton transfer processes.

Further theoretical and computational efforts that include providing learning dates from accurate and large quantum simulations, improving learning algorithms, and developing accurate and efficient open quantum dynamics theory to treat a complex system-bath model
must be made. We leave such extensions to future studies, in accordance with progress in theoretical techniques.

Acknowledgement

The authors are thankful to professor Yuki Kurashige for helpful discussions concerning the QM/MM simulations for an indocarbocyanine dimer system. Financial support from HPC Systems Inc. is acknowledged.

A One-dimensional and two-dimensional spectra

Linear and nonlinear optical spectra can be expressed in the Fourier transformation form of the response functions. In the present dimer case, we can analytically express the response functions in terms of a line shape function including the contribution from an exciton-exciton interaction.

The linear absorption spectrum is given by

\[ S(\omega) = \int_0^\infty dt e^{i\omega t} R^{(1)}(t) - c.c., \quad (A.1) \]

where \( R^{(1)}(t) = \langle \mu(t), \mu(0) \rangle \) is the 1D response function expressed in terms of the transition dipole moment \( \mu(t) \). For a coupled dimer system, the analytical expression for the response function for Eq.\((A.1)\) is expressed as

\[ R^{(1)}(t_1) = \frac{i\mu}{\hbar} \exp[i\Omega t_1 - g^{11}(t_1) - g^{12}(t_1)] - c.c. \quad (A.2) \]
where the line shape function, $g_{\pm}^a(t)$, for the SDF, $J_a(\omega)$, with $a = 11$ and 12 is given by

$$g_{\pm}^a(t) \equiv \int_0^t dt' \int_0^{t'} dt \int \frac{d\omega}{2\pi} J_a(\omega) \left[ \coth\left( \frac{\beta \hbar \omega}{2} \right) \cos(\omega t) \pm i \sin(\omega t) \right],$$  \hspace{1cm} (A.3)

Figure A.0: Double-sided Feynman diagrams for the third-order response functions $R^{(3)}(t_3, t_2, t_1)$. In each diagram, time runs from bottom to top, and $t_i$ represents the time intervals for the $i$th sequence between successive laser–system interactions. The left line represents the time evolution of the ket, whereas the right line represents that of the bra. The black, red and blue lines represent that the system is in the $|00\rangle$, $|1+\rangle$, and $|11\rangle$ states, respectively. The complex conjugate paths of these, which can be obtained by interchanging the ket and bra diagrams, are not shown here.

For the coupled dimmer system, the third-order response function

$$R^{(3)}(t_3, t_2, t_1) = \langle [\mu(t_3), [\mu(t_2), [\mu(t_1), \mu(0)]]] \rangle$$  \hspace{1cm} (A.4)
is also evaluated in the analytical form as

$$R^{(3)}(t_3, t_2, t_1) \equiv \frac{i \hbar^4}{\hbar^3} \sum_{\alpha=1}^{8} \exp[Q_\alpha(t)] - c.c. \quad (A.5)$$

where

$$Q_1(t) = -i \Omega_+ t_1 - i \Omega_+ t_3$$

$$- f_1^1(t_1, t_2, t_3) - f_1^2(t_1, t_2, t_3),$$

$$Q_2(t) = i \Omega_+ t_1 - i \Omega_+ t_3$$

$$- f_2^1(t_1, t_2, t_3) - f_2^2(t_1, t_2, t_3),$$

$$Q_3(t) = i \Omega_+ t_1 - i \Omega_+ t_3$$

$$- f_3^1(t_1, t_2, t_3) - f_3^2(t_1, t_2, t_3),$$

$$Q_4(t) = -i \Omega_+ t_1 - i \Omega_+ t_3$$

$$- f_4^1(t_1, t_2, t_3) - f_4^2(t_1, t_2, t_3),$$

$$Q_5(t) = -i \Omega_+ t_1 + i \Omega_- t_3$$

$$- f_5^1(t_1, t_2, t_3) - f_5^2(t_1, t_2, t_3),$$

$$Q_6(t) = i \Omega_+ t_1 + i \Omega_- t_3$$

$$- f_6^1(t_1, t_2, t_3) - f_6^2(t_1, t_2, t_3),$$

$$Q_7(t) = i \Omega_+ t_1 + 2i \omega_0 t_2 + i \Omega_- t_3$$

$$- f_7^1(t_1, t_2, t_3) - f_7^2(t_1, t_2, t_3),$$

$$Q_8(t) = -i \Omega_+ t_1 - 2i \omega_0 t_2 - i \Omega_+ t_3$$

$$- f_8^1(t_1, t_2, t_3) - f_8^2(t_1, t_2, t_3)$$
with

\[
\begin{align*}
  f_1^a(t_1, t_2, t_3) &= -g_-^a(t_1) - g_+^a(t_3) \\
  &\quad - [g_+^a(t_2) - g_-^a(t_23) - g_+^a(t_{12}) + g_-^a(t_{123})], \\
  f_2^a(t_1, t_2, t_3) &= -g_+^a(t_1) - g_+^a(t_3) \\
  &\quad + [g_-^a(t_2) - g_-^a(t_23) - g_+^a(t_{12}) + g_-^a(t_{123})], \\
  f_3^a(t_1, t_2, t_3) &= -g_-^a(t_1) - g_-^a(t_3) \\
  &\quad + [g_+^a(t_2) - g_-^a(t_23) - g_+^a(t_{12}) + g_-^a(t_{123})], \\
  f_4^a(t_1, t_2, t_3) &= -g_-^a(t_1) - g_-^a(t_3) \\
  &\quad - [g_-^a(t_2) - g_-^a(t_23) - g_+^a(t_{12}) + g_-^a(t_{123})], \\
  f_5^a(t_1, t_2, t_3) &= -g_-^a(t_1) - g_-^a(t_3) \\
  &\quad - [g_-^a(t_2) - g_-^a(t_23) - g_+^a(t_{12}) + g_-^a(t_{123})], \\
  f_6^a(t_1, t_2, t_3) &= -g_+^a(t_1) - g_+^a(t_3) \\
  &\quad + [g_-^a(t_2) - g_-^a(t_23) - g_+^a(t_{12}) + g_-^a(t_{123})], \\
  f_7^a(t_1, t_2, t_3) &= -g_+^a(t_1) - g_+^a(t_3) \\
  &\quad + [g_-^a(t_2) - g_-^a(t_23) - g_+^a(t_{12}) + g_-^a(t_{123})], \\
  f_8^a(t_1, t_2, t_3) &= -g_-^a(t_1) - g_-^a(t_3) \\
  &\quad - [g_-^a(t_2) - g_-^a(t_23) - g_+^a(t_{12}) + g_-^a(t_{123})].
\end{align*}
\] (A.7)

Here, \( t_{12} \equiv t_1 + t_2, t_{23} \equiv t_2 + t_3, \) and \( t_{123} \equiv t_1 + t_2 + t_3. \) Because the fluctuation in the \(|1+\rangle\) and \(|11\rangle\) states are described by \( J_{11}(\omega) + J_{12}(\omega) \) and \( J_{11}(\omega) + J_{22}(\omega) = 2J_{11}(\omega), \) respectively, the line shape function \( g_\pm^a(t) \) in Eq. \[A.7\] is now expressed as \( g_\pm^a(t) = g_{1\pm}^a(t) + g_{12\pm}^a(t), \) and \( g_\pm^a(t) = 2g_{11\pm}^a(t). \) By using the third-order diagrams, the pump-probe spectrum and photon echo spectrum are, for example, calculated from the \( Q_1(t), Q_4(t), \) and \( Q_5(t) \) elements, and the \( Q_2(t), Q_3(t), \) and \( Q_6(t) \) elements, respectively.

Although the change of exciton population can be explored by pump-probe spectroscopy,
if we wish to investigate not only population dynamics but also the system-bath coherence, two-dimensional electronic correlation spectroscopy is a better choice. This spectrum can be calculated from

\[ I^{(\text{corr})}(\omega_3, t_2, \omega_1) = I^{(\text{NR})}(\omega_3, t_2, \omega_1) + I^{(R)}(\omega_3, t_2, \omega_1), \]  

(A.8)

where the non-rephasing and rephasing parts of the signal are defined by

\[ I^{(\text{NR})}(\omega_3, t_2, \omega_1) = \text{Im} \int_0^\infty dt_3 \int_0^\infty dt_1 e^{i\omega_3 t_3} e^{i\omega_1 t_1} R(3)(t_3, t_2, t_1), \]  

(A.9)

and

\[ I^{(R)}(\omega_3, t_2, \omega_1) = \text{Im} \int_0^\infty dt_3 \int_0^\infty dt_1 e^{i\omega_3 t_3} e^{-i\omega_1 t_1} R(3)(t_3, t_2, t_1). \]  

(A.10)
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