

Development of An Exciton Model of Light-Harvesting Antenna LH2 Considering Charge Transfer States and Their Fluctuations

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Abstract

The light-harvesting complex 2 (LH2) of the purple bacteria absorbs sunlight and transfers energy to the RC with high efficiency. To achieve a microscopic understanding of the energy transfer process, theoretical analysis of the excited states of the bacteriochlorophyll *a* pigment aggregates is effective. In particular, not only the locally excited (LE) states of pigments but also the charge transfer (CT) states between pigments play a significant role in the excited states of the B850 ring where the pigments are in close proximity to each other. We developed a new method to incorporate the fluctuations of such CT states into the exciton model of LH2, based on quantum chemical calculations and molecular dynamics simulations with the aid of a machine learning model. The excitation energies to LE and CT states and the electronic couplings between these states were calculated from the MD trajectory with low computational

cost to obtain time-dependent exciton Hamiltonian. The calculated absorption spectra of LH2 using the exciton Hamiltonian revealed that the fluctuations of the CT states have an important role in the broadening of the B850 absorption band.

1 Introduction

The photosynthetic system is a natural organism that converts solar energy into storable chemical energy. In the initial process of photosynthesis, the light-harvesting antenna absorbs sunlight and transfers the energy to the reaction center, where the primary charge separation takes place, followed by the light-dependent reaction. The photosynthetic system exhibits a very high quantum yield of the excitation energy transfer process,¹ and has been intensively studied both experimentally²⁻¹³ and theoretically.^{2,14-24} The light-harvesting antenna is composed of pigments and environmental protein moiety (pigment-protein complex, PPC). The pigments in the PPC can absorb a wide range of light energy because the interaction between pigments and protein environment tunes the light absorption properties of pigments. Therefore, studies on the spectroscopic properties of PPCs are effective in elucidating the detailed mechanism of highly efficient energy transfer in the photosynthetic system.

However, theoretical studies on the spectroscopic properties of PPC suffer from a huge computational burden, which mainly arises from two reasons. First, quantum mechanical (QM) treatment of the overall pigment aggregate in PPC is required, even if the anisotropic protein environment is considered using the combined quantum mechanical and molecular mechanical (QM/MM) methods. The photosynthetic PPCs generally have a large number of pigments. For example, both the light-harvesting complex (LH2) in purple bacteria *Rsp. Molischianum*²⁵ and the Fenna-Mathews-Olson (FMO) complex in green sulfur bacteria²⁶ have 24 bacteriochlorophyll *a* (BChl) pigments, and the light-harvesting complex II (LHCII) of photosystem II (PSII) in photosynthetic system of higher plants has 24 chlorophyll *a* and 18 chlorophyll *b*.²⁷ The total size of these pigment aggregates can exceed 1,000 atoms,

making it difficult to calculate the excited states by standard QM methods. To overcome this problem, several exciton models have been developed. The Frenkel model²⁸ is the most popular simple exciton model of PPC. The Frenkel model approximately describes the overall excited states as a linear combination of the locally excited (LE) states of each pigment. This approximation assumes that the excited electron and hole exist within the same pigment. The Frenkel Hamiltonian consists of two terms: the excitation energy of LE state, i.e., the site energy, and the electronic coupling between LE states. When the pigments are spatially separated, the electronic coupling can be calculated by the interaction between transition densities of two pigments, which can be further approximated by the point dipole approximation or the transition charges from electrostatic potential (TrESP) method.²⁹ Due to these simplified treatments, only QM calculations of single pigments are required.

The second reason is that structural fluctuation by thermal motion should be sufficiently considered for spectral calculations. The electronic states of pigment aggregates fluctuate from moment to moment due to the thermal motion of pigment and protein environment. All-atom molecular dynamics (MD) simulations have often been used in previous studies to sample the thermal fluctuation.^{14,15,30,31} If QM calculations are used to evaluate forces during MD simulations, this approach requires a huge computational cost. Therefore, MD simulations with a conventional MM force field have generally been performed. However, it becomes problematic that the potential energy surface used in MD simulations is different from that of QM calculations. It has been reported that the excitation energy fluctuations of photosynthetic pigments are sensitive to the MM force field in MD simulations.³² To overcome these problems, interpolation-based MM force fields have been developed. The interpolation-based method spans semiglobal QM/MM level potential energy function around the reference structures.^{33,34} Higashi and Saito developed molecular mechanics with Shepard interpolation correction (MMSIC) method.³⁵ The MMSIC method roughly describes the semiglobal QM/MM potential energy function by an MM force field at first, and then the correction term is created from a few reference structures. They applied the MMSIC method to BChl

pigments in the FMO complex and successfully analyzed the excitation energy transfer by accelerating the site energy calculations of thermally fluctuating pigments.^{35,36} Recently, the MMSIC method was also applied to the analysis of optical spectra of LHCII.³⁷

As shown above, the approaches based on the Frenkel model have been successfully applied to the analysis of spectroscopic properties of several light-harvesting antennas. However, another problem arises when pigments are close to each other. One typical example is the LH2, the peripheral light-harvesting antenna of purple bacteria. Before introducing the problem, the detailed structure of LH2 is presented. Figure 1(a) shows the atomistic structure of LH2 of *Rsp. Molischianum* revealed by X-ray crystallography.²⁵ One subunit is composed of two helices, three BChls, and one lycopene. The inner and outer helices, called α -apoprotein and β -apoprotein, respectively, traverse the lipid bilayer membrane. The α -apoprotein and β -apoprotein have α -BChl and β -BChl, respectively, bound by a coordination bond at the Mg center and a hydrogen bond at the acetyl group. In addition, the α -apoprotein also contains a short helix that runs almost parallel to the lipid bilayer, and make a non-covalent bond with the third BChl called γ -BChl. The eight subunits are arranged in circular symmetry to form cylindrical structure: The eight pairs of α -BChl and β -BChl aggregate and overlap in close proximity to form the B850 pigment ring, whereas the eight γ -BChls are arranged isolated from each other to form the B800 pigment ring (see Figure 1). The B800 has absorption band at about 800 nm, whereas the B850 has absorption band at lower energy side (about 850 nm) because the B850 can form delocalized exciton states owing to overlapped structure of pigments.

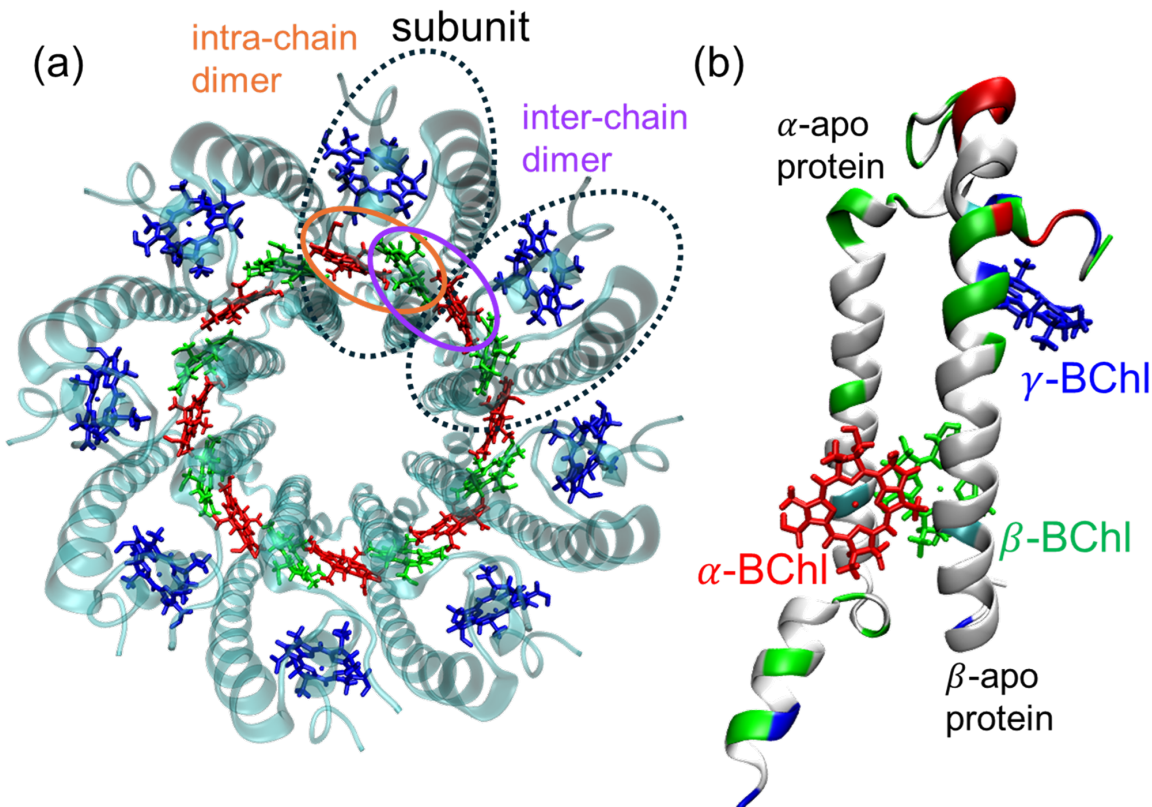


Figure 1: (a) The structure of LH2 from X-ray crystallography.²⁵ (b) The structure of a non-equivalent subunit in LH2. The color of protein helix shows the basic (blue), acidic (red), non-polar (white), and polar (green) residues.

Some previous theoretical studies reproduced the experimental spectra of LH2 using the Frenkel Hamiltonian.^{14,15} However, in these studies, the LE-LE coupling was evaluated by the point dipole approximation, which is known to overestimate the electronic coupling.²⁹ Otherwise, scaling parameters were used to adjust the LE-LE coupling.²³ On the other hand, in recent years, the importance of considering the CT state between adjacent pigments in the exciton Hamiltonian has been emphasized. Adjacent pigments in B850 are arranged almost parallel to each other (Figure 1(a)), and charge transfer (CT) states between them have been experimentally observed.³⁸ Mennucci group modeled the excited state of LH2 as the linear combination of the LE states of individual pigments and the CT state of adjacent pigment dimers to calculate the exciton states and absorption spectra.^{39–41} In their stud-

ies, the multi-FED-FCD diabaticization method,³⁹ which combines the Fragment-Excitation-Difference (FED) method⁴² and the Fragment-Charge-Difference (FCD) method,^{43,44} was used for the evaluation of CT state energies and LE-CT couplings. However, due to the high computational cost of the multi-FED-FCD method, the effect of fluctuations in the CT states was investigated only limitedly. As with the acceleration schemes for calculating the site energy and LE-LE couplings described above, those efficient enough to evaluate the CT energies and LE-CT couplings at each MD step are desirable.

This study aims to develop such acceleration schemes for calculating thermally fluctuating CT states, and clarify the effect of fluctuating CT states on absorption spectra of LH2. To accomplish this, the LE-CT couplings are evaluated using a machine learning model. This article is structured as follows. Section 2 describes the theory used in this study. The computational details are shown in Section 3. In Section 4, we present and discuss the calculated results. Section 5 summarizes the conclusions.

2 Methods

2.1. Model Hamiltonian. We considered coupled two-level quantum systems and described them by the exciton Hamiltonian with couplings between LE states and CT states.³⁹

$$\begin{aligned}
H(t) = & \sum_{m \in \text{B800, B850}} \epsilon_m(t) |m\rangle \langle m| \\
& + \sum_{m, n \in \text{B800, B850}} V_{mn}(t) |m\rangle \langle n| \\
& + \sum_{m \in \text{B850}} \sum_{n \in \text{adjacent}} \epsilon_{m \rightarrow n}^{\text{CT}}(t) |m \rightarrow n\rangle \langle m \rightarrow n| \\
& + \sum_{m \in \text{B850}} \sum_{n \in \text{adjacent}} V_{m, m \rightarrow n}^{\text{LE-CT}}(t) (|m\rangle \langle m \rightarrow n| + |m \rightarrow n\rangle \langle m|)
\end{aligned} \tag{1}$$

The first and second terms represent the Frenkel exciton Hamiltonian, where the indices m and n run on the all pigments in B800 and B850. $|m\rangle$ represents the LE state of m -th

pigment with site energy ϵ_m . V_{mn} represents the LE-LE coupling between the excited state of m -th pigment and that of n -th pigment. The third and fourth terms incorporate the CT effects on adjacent pigment dimers, where the index m refers to B850 pigments, and the index n means the two adjacent pigments of m . Namely, the summation symbol indices in the third and fourth terms enumerate all the adjacent pigment pairs of B850 ring in LH2. $|m \rightarrow n\rangle$ represents the CT state where an electron of m -th pigment moves to n -th pigment. $\epsilon_{m \rightarrow n}^{\text{CT}}$ represents the CT energy of $|m \rightarrow n\rangle$ state. The fourth term represents the couplings between the LE and CT states; $V_{m,m \rightarrow n}^{\text{LE-CT}}$ represents the electronic coupling between $|m\rangle$ state and $|m \rightarrow n\rangle$ state. CT states including B800 pigments are not considered in this model because B800 pigments are isolated from other pigments. From the next subsection, we explain the calculation methods for ϵ_m , V_{mn} , $\epsilon_{m \rightarrow n}^{\text{CT}}$, and $V_{m,m \rightarrow n}^{\text{LE-CT}}$.

2.2. Calculation of site energy. We used the MMSIC method to calculate the site energy ϵ_m . The details of the MMSIC method were described in the previous study.³⁵ Here we summarize them briefly. In QM/MM calculations, the total QM/MM energy of a system, $V^{\text{QM/MM}}$, can be expressed as

$$V^{\text{QM/MM}}(\mathbf{R}, \mathbf{R}^{\text{MM}}) = V^{\text{EEQM}}(\mathbf{R}, \mathbf{R}^{\text{MM}}) + V_{\text{non-ES}}^{\text{QM-MM}}(\mathbf{R}, \mathbf{R}^{\text{MM}}) + V^{\text{MM}}(\mathbf{R}^{\text{MM}}) \quad (2)$$

where $\mathbf{R}$ and $\mathbf{R}^{\text{MM}}$ are $3N^{\text{QM}}$ - and $3N^{\text{MM}}$ -dimensional vectors that contain coordinates of all QM and MM atoms, where N^{QM} and N^{MM} are the numbers of QM and MM atoms, respectively. $V_{\text{non-ES}}^{\text{QM-MM}}$ and V^{MM} are the non-electrostatic interaction energy between QM and MM subsystems, and the potential energy of MM subsystem, both of which are generally independent of the QM wave function and are expressed with MM force fields. The electrostatically embedded QM (EEQM) potential energy V^{EEQM} is defined as the sum of QM potential energy and QM-MM electrostatic (ES) interaction energy. We adopted the site-site representation for the ES interaction energy.³⁵ By introducing the ES potential at

atom a in the QM region from the MM region,

$$\Phi_a = \sum_{A=1} \frac{Q_A^{\text{MM}}}{|\mathbf{R}_a - \mathbf{R}_A^{\text{MM}}|} \quad (3)$$

where Q_A^{MM} is the effective charge of MM atom A . Note that atomic units are used through this article. The EEQM energy is described as

$$V^{\text{EEQM}}(\mathbf{R}, \Phi) = \langle \Psi | \hat{H}_0 + \hat{\mathbf{Q}}^T \Phi | \Psi \rangle \quad (4)$$

where $\hat{H}_0$ is the Hamiltonian of QM subsystem, $|\Psi\rangle$ is the wave function of QM subsystem, and $\hat{Q}_a$ is a population operator which generates the partial charge Q_a on the QM atom a .

In the MMSIC method, V^{EEQM} is approximately expressed by the sum of two terms

$$V^{\text{EEQM}}(\mathbf{R}, \Phi) \approx V^{\text{MM}}(\mathbf{R}) + V^{\text{SIC}}(\mathbf{R}, \Phi) \equiv V^{\text{MMSIC}}(\mathbf{R}, \Phi) \quad (5)$$

$V^{\text{SIC}}(\mathbf{R}, \Phi)$ evaluates the difference between V^{EEQM} and V^{MM} by the modified Shepard interpolation.

$$V^{\text{SIC}}(\mathbf{R}, \Phi) = \sum_{k=1}^{N^{\text{SIC}}} W_k(\mathbf{s}(\mathbf{R})) V_k^{\text{Taylor}}(\mathbf{s}(\mathbf{R}), \Phi) \quad (6)$$

where N^{SIC} is the number of reference structures called Shepard points. W_k is the normalized weight function of the Shepard point k . V_k^{Taylor} is evaluated by a second-order Taylor expansion around the k -th Shepard point in terms of internal coordinates of QM region $\mathbf{s}$ and ES potentials Φ .

Using the MMSIC potential function, we can obtain the site energy of m -th pigment as

$$\epsilon_m(t) = V_{m,\text{S1}}^{\text{MMSIC}}(\mathbf{R}_m(t), \Phi_m(t)) - V_{m,\text{S0}}^{\text{MMSIC}}(\mathbf{R}_m(t), \Phi_m(t)) \quad (7)$$

It is noted that Φ_m includes the ES potential from pigments other than m -th pigment.

2.3. Calculation of electronic coupling between LE states. We used the transition

charge response kernel (TrCRK) method³⁶ for the LE-LE coupling. The TrESP method²⁹ have been used for the LE-LE coupling calculation, which approximates V_{mn} by the interactions between transition charges

$$V_{mn} = \int \int \frac{\rho_m^{\text{Tr}}(\mathbf{r}_m) \rho_n^{\text{Tr}}(\mathbf{r}_n)}{|\mathbf{r}_m - \mathbf{r}_n|} d\mathbf{r}_m d\mathbf{r}_n \simeq \sum_{a \in m} \sum_{b \in n} \frac{Q_a^{\text{Tr}} Q_b^{\text{Tr}}}{|\mathbf{R}_a - \mathbf{R}_b|} \quad (8)$$

where $\rho_m^{\text{Tr}}(\mathbf{r}_m)$ is the transition density at position $\mathbf{r}_m$, and Q_a^{Tr} is the transition charge of atom a . As with the MMSIC method, the TrCRK method uses the Shepard interpolation for describing the transition charges of TrESP method,

$$Q^{\text{Tr}}(\mathbf{R}, \Phi) = \sum_{k=1}^{N^{\text{SIC}}} W_k(\mathbf{s}(\mathbf{R})) Q_k^{\text{Tr}}(\mathbf{s}(\mathbf{R}), \Phi) \quad (9)$$

where Q_k^{Tr} is the array of transition charges around the Shepard point k evaluated by the first order Taylor expansion with respect to the displacements of $\mathbf{s}$ and Φ . By introducing the fluctuations of Q_a^{Tr} , the TrCRK method can efficiently evaluate the fluctuation of V_{mn} .³⁶

2.4. Calculation of CT energy. We evaluated the CT energy of adjacent dimer using the MMSIC method as follows. The CT energy $\epsilon_{m \rightarrow n}^{\text{CT}}$ is the difference between the EEQM energy of m -th cationic pigment and n -th anionic pigment, and the EEQM energy of m -th and n -th neutral pigments at the same structure.

$$\epsilon_{m \rightarrow n}^{\text{CT}} = V_{m^+ n^-}^{\text{EEQM}} - V_{mn}^{\text{EEQM}} \quad (10)$$

We approximated $\epsilon_{m \rightarrow n}^{\text{CT}}$ as follows.

$$\epsilon_{m \rightarrow n}^{\text{CT}} = \epsilon_{m^+} + \epsilon_{n^-} + V_{m^+ n^-}^{\text{ES}} - V_{m^+ n}^{\text{ES}} - V_{m n^-}^{\text{ES}} + V_{mn}^{\text{ES}} \quad (11)$$

where ϵ_{m^+} is the site energy of cationic m -th pigment (anionic n -th pigment), and $V_{m^i n^j}^{\text{ES}}$ is the ES interaction between m -th pigment with electronic state i and n -th pigment with

electronic state j . The site energies can be calculated as Section 2.2.

$$\epsilon_{m+}(t) = V_{m,+}^{\text{MMSIC}}(\mathbf{R}_m(t), \mathbf{\Phi}_m(t)) - V_{m,S0}^{\text{MMSIC}}(\mathbf{R}_m(t), \mathbf{\Phi}_m(t)) \quad (12)$$

$$\epsilon_{n-}(t) = V_{n,-}^{\text{MMSIC}}(\mathbf{R}_n(t), \mathbf{\Phi}_n(t)) - V_{n,S0}^{\text{MMSIC}}(\mathbf{R}_n(t), \mathbf{\Phi}_n(t)) \quad (13)$$

$V_{m^i-n^j}^{\text{ES}}$ is calculated as

$$V_{m^i-n^j}^{\text{ES}}(t) = \sum_{a \in m} \sum_{b \in n} \frac{Q_a^i(t) Q_b^j(t)}{|\mathbf{R}_a(t) - \mathbf{R}_b(t)|} \quad (14)$$

where Q_a^i is the charge on atomic site a with electronic state i , which can be calculated from the MMSIC method.³⁵

2.5. Calculation of LE-CT coupling. We used the multi-FED-FCD method³⁹ as diabaticization scheme for calculation of the LE-CT couplings. The multi-FED-FCD method is the combination of the FED and FCD methods, and it generates Hamiltonian of a pigment dimer in diabatic expression by operating appropriate transformation matrix to the Hamiltonian in adiabatic expression. To incorporate the effect of thermal fluctuation into model Hamiltonian, we need information of the time evolution of LE-CT couplings. However, interpolation-based acceleration procedures such as the MMSIC and TrCRK methods is difficult to be combined with the multi-FED-FCD method because of high computational cost of the multi-FED-FCD method. Therefore, we adopted a kernel-ridge regression (KRR) model^{45,46} for the time evolution of $V_{m,m \rightarrow n}^{\text{LE-CT}}$ based on MD trajectory data. Notably, machine learning-based methods have been used to efficiently evaluate the thermal fluctuation of exciton Hamiltonian elements in previous studies.^{47,48} In the KRR model, the LE-CT couplings are described by using the structural information of intermolecular distances between pigments.

$$\mathbf{V}^{\text{LE-CT}}(t) = \sum_{i=1}^{N^{\text{train}}} \alpha_i K(\mathbf{P}_i^{\text{train}}, \mathbf{P}(t)) \quad (15)$$

where $\mathbf{V}^{\text{LE-CT}}(t)$ consists of 4 elements of LE-CT couplings included in one dimer of m -th

and n -th pigments.

$$\mathbf{V}^{\text{LE-CT}} \in \left\{ V_{m,m \rightarrow n}^{\text{LE-CT}}, V_{m,n \rightarrow m}^{\text{LE-CT}}, V_{n,m \rightarrow n}^{\text{LE-CT}}, V_{n,n \rightarrow m}^{\text{LE-CT}} \right\} \quad (16)$$

N^{train} is the number of training data, and $\mathbf{P}$ is a vector composed of a subset of the principal components of interatomic distances between m -th and n -th pigments. $K(\mathbf{P}_i, \mathbf{P}_j)$ is the radial basis function (RBF) kernel, which is expressed as

$$K(\mathbf{P}_i, \mathbf{P}_j) = \exp\left(-\gamma \|\mathbf{P}_i - \mathbf{P}_j\|^2\right) \quad (17)$$

where $\|\mathbf{P}_i - \mathbf{P}_j\|$ is the Euclidean norm. $\boldsymbol{\alpha}$ is a regression coefficient vector determined from training data $\{\mathbf{P}^{\text{train}}; \mathbf{V}^{\text{LE-CT,train}}\}$

$$\boldsymbol{\alpha} = \left(\mathbf{K}^{\text{train}} + \lambda \mathbf{I}\right)^{-1} \mathbf{V}^{\text{LE-CT,train}} \quad (18)$$

$$K_{ij}^{\text{train}} = \exp\left(-\gamma \|\mathbf{P}_i^{\text{train}} - \mathbf{P}_j^{\text{train}}\|^2\right) \quad (19)$$

where λ and γ are parameters. The computational details are explained in Section 3. Using the optimized KRR model, we generated the time evolution of $\mathbf{V}^{\text{LE-CT}}$ from $\mathbf{P}(t)$ based on MD trajectory.

2.6 Spectral density and absorption spectra.

We investigated the spectral densities of LE and CT energies and the absorption spectra of LH2. The spectra densities were calculated using

$$J(\omega) = \frac{\beta\omega}{\pi} \int_0^\infty dt C(t) \cos(\omega t) \quad (20)$$

The classical autocorrelation function $C(t)$ is computed as

$$C(t) = \langle \Delta\epsilon(t) \Delta\epsilon(0) \rangle \quad (21)$$

where $\Delta\epsilon(t) = \epsilon(t) - \langle\epsilon\rangle$. Here, a quantum correction prefactor $\beta\omega/\pi$ is employed to satisfy the detailed balance condition as in previous studies.^{35,49} The absorption spectra in site expression⁵⁰ was calculated using

$$I(\omega) = \omega \text{Re} \int_0^\infty dt e^{i\omega t} \text{Im} \langle \sum_{m,n} \mathbf{d}_m(t) U_{mn}(t) \mathbf{d}_n(0) \rangle \quad (22)$$

where $\mathbf{d}_m(t)$ is the transition dipole moment vector of m -th pigment, and $\mathbf{U}(t)$ is the time evolution operator matrix of exciton Hamiltonian from $t = 0$ to t .

$$\mathbf{U}(t) = \exp \left(-\frac{i}{\hbar} \int_0^t \mathbf{H}(\tau) d\tau \right) \quad (23)$$

where $\mathbf{H}$ is the exciton Hamiltonian, Eq. (1). $\mathbf{d}_m(t)$ is calculated as

$$\mathbf{d}_m(t) = \sum_{a \in m} Q_a^{\text{Tr}}(t) \mathbf{R}_a(t) \quad (24)$$

where $Q_a^{\text{Tr}}(t)$ is the transition charge on atomic site a calculated from Eq. (9).

3 Computational Details

3.1. Classical MD simulations. First, we prepared a simulation model from crystal structure of LH2 in *Rsp. Molischianum* (PDB code: 1LGH)²⁵ surrounded by the physiological environment with lipid bilayer and water molecules. This octameric form of LH2 has been investigated in several previous theoretical studies.^{6,14,23,51} The δ -positions of His 34 and His 89 were protonated to form the coordination bond between Mg center of BChl and histidine. Lipid bilayer was composed of 1-palmitoyl-2-oleoyl-sn-glycero-3-phosphocholine (POPC). Finally, 41 Na^+ and 49 Cl^- ions were added to ensure electroneutrality of the entire system of 104338 atoms. The ff19SB,⁵² lipid21,⁵³ and TIP3P⁵⁴ force fields were used for the protein, POPC lipid bilayer, and water, respectively. BChl and lycopene were treated with

the general Amber force field (GAFF).⁵⁵ In addition, Lennard-Jones parameters developed by Åqvist⁵⁶ were assigned to magnesium cations in BChl. Na^+ and Cl^- ions were treated as Lennard-Jones parameters developed by Joung and Cheatham.⁵⁷ We initially performed a 100-ns equilibration MD simulation of the prepared model at 300 K and 1 bar with the MM force field under the periodic boundary condition to bring the system to equilibrium state. Langevin thermostat with a collision frequency of 1.0 ps^{-1} and Berendsen barostat were used for temperature and pressure control. The simulation time step was set to 2 fs, and the bonds involving hydrogen atom were fixed by the SHAKE algorithm. The box size of obtained equilibrium system was $108.5 \text{ Å} \times 105.0 \text{ Å} \times 89.5 \text{ Å}$. These MD simulations were performed with the AMBER 11⁵⁸ program package.

3.2. QM/MM calculations. We performed QM/MM calculations to obtain reference QM results at Shepard points. The density functional theory (DFT) was used for the S_0 , cationic and anionic states of pigments, whereas the time-dependent DFT (TDDFT) was employed for the S_1 state. The CAM-B3LYP functional with range-separated parameter $\mu = 0.20$, which was tuned to reproduce the difference of the first excited Q_y absorption energies of BChl *a* in solutions,⁵⁹ was used with the 6-31G(d,p) basis set. The QM region consists of one BChl pigment, which includes only the methylene bridges of two long alkyl chains (Figure 2). The boundary of QM and MM region was treated by the link-atom method. As a result, the number of QM atoms is 73. The rest of long alkyl chains of BChl and surrounding molecules within a sphere with a radius of 35 Å centered at Mg atom of QM BChl were included in the MM region. The same force field as Section 3.1 was used for the MM region. Furthermore, we calculated the training data for LE-CT coupling using the multi-FED-FCD diabaticization scheme.³⁹ The adjacent BChl dimer in the B850 rings were treated as the QM region of the multi-FED-FCD method. Here we considered two types of BChl dimer (intra-chain α - β dimer and inter-chain α - β dimer). The MM region was assigned in the same way as above. We set the relative dielectric constant of the medium to 1 in all the calculations. All the QM/MM calculations were performed using our modified version

of GAMESS.⁶⁰

3.3. MD Simulations with MMSIC force field. After the equilibration in Section 3.1, we performed a production MD run with the MMSIC force field to calculate the excitonic properties. To construct the MMSIC force field, Shepard points were determined for three non-equivalent pigments (α -BChl, β -BChl, and γ -BChl). Using the procedure below, stable and important structures were specified for the Shepard points. The first Shepard point was created as a result of QM/MM-level geometry optimization from the last snapshot of equilibration MD simulation with the MM force field. The MMSIC force field was then updated by adding a SIC term (Eq. 6) centered at the Shepard point. MD simulations were performed using the updated MMSIC force field with a time step of 0.5 fs. The SHAKE method was applied to only the water molecules. The errors between the MMSIC energy and the QM/MM energy were calculated for the snapshots in the MD trajectory. The structure with the largest error was selected and optimized by the QM/MM method to create a new Shepard point. The above procedure was repeated until the mean unsigned error (MUE) in energy was below 2 kcal/mol. As a result, the numbers of Shepard points were 2, 3, and 2 for α -BChl, β -BChl, and γ -BChl, respectively.

From the equilibration run to the production run, we switched the potential energy functions of 24 BChl pigments from the MM force fields to the MMSIC potential force field of S_0 state. A 100-ps equilibration run was performed under the MMSIC force field with a weak harmonic restraint with a force constant of 1 kcal/(mol $\text{\AA}^2$) on proteins and pigments to avoid unwanted conformation changes. After a subsequent 100-ps equilibration run without any restraints, we performed a 1-ns production run. $\mathbf{R}_m(t)$ and $\mathbf{\Phi}_m(t)$ for all the BChls were saved every 0.5 fs time step and used for the analysis of exciton Hamiltonian, spectral density and absorption spectra. We calculated the absorption spectra from the time evolution of exciton Hamiltonian and transition dipole moments (Eq. (22)). The time evolution operator matrix of exciton Hamiltonian, Eq. (23), was calculated from the numerical integration of

Schrödinger equation,⁵⁰

$$\mathbf{U}(n\Delta t) = \prod_{k=0}^{n-1} \exp(-i\mathbf{H}(k\Delta t)\Delta t/\hbar) \quad (25)$$

The integration range in Eq. (22) was truncated at 10 ps, resulting in good convergence. All the MMSIC MD simulations were performed with the AMBERPLUS⁶¹ program package, combining the AMBER 11⁵⁸ and MCSI⁶² program packages.

The calculated site energy at each BChl in LH2 from Eq. (7) was red-shifted by 1720 cm^{-1} following the previous researches.^{35,36} This shift corrects the overestimation of the excitation energy of BChl due to the TDDFT. In addition, the calculated site energies were modified by quantum-chemical corrections on the ligand coordinated at the Mg atom and the hydrogen bond at the acetyl group.⁵⁹ The correction of site energy of m -th pigment is expressed as

$$\Delta\epsilon_m = \frac{1}{N_{\text{sample}}} \sum_l^{N_{\text{sample}}} \left[\epsilon_m^{\text{large}}(\mathbf{R}_l^{\text{large}}, \mathbf{R}_l^{\text{MM}}) - \epsilon_m(\mathbf{R}_l, \mathbf{R}_l^{\text{MM}}) \right] \quad (26)$$

where N_{sample} is the number of configurations extracted from MD trajectory and was set to 30. $\epsilon_m^{\text{large}}$ is the site energy calculated with the extended QM region, which is shown in Figure 2. Furthermore, we introduced a scaling factor of 0.803 for $\mathbf{Q}_k^{\text{Tr0}}$, as in the previous studies^{36,29} because it is known that the TDDFT calculation overestimates the transition dipole moment of BChl. It was also found that the CT energies calculated from Eq. (11) were larger than those calculated with the multi-FED-FCD method, probably due to the approximate treatment of cation and anion energies and their interactions. Therefore, to reproduce the mean CT energies (red-shifted by 1720 cm^{-1} as described above) obtained with the multi-FED-FCD method, the CT energies from Eq. (11) were red-shifted by 4404, 5263, 4216, and 5047 cm^{-1} for intra-chain $\epsilon_{\alpha \rightarrow \beta}^{\text{CT}}$, intra-chain $\epsilon_{\beta \rightarrow \alpha}^{\text{CT}}$, inter-chain $\epsilon_{\alpha \rightarrow \beta}^{\text{CT}}$, and inter-chain $\epsilon_{\beta \rightarrow \alpha}^{\text{CT}}$, respectively.

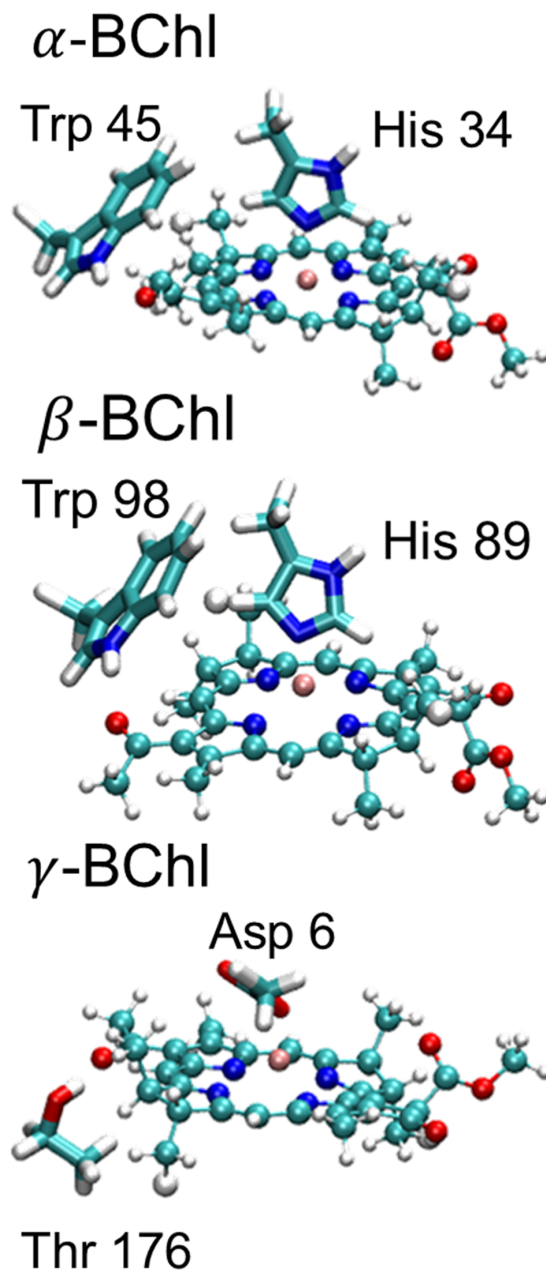


Figure 2: QM region (ball and stick) and the atoms included in the extended QM region for the site energy correction (thick line).

3.4. KRR modeling. We described the LE-CT couplings with the top eight principal components of interatomic distances of 196 atomic pairs between adjacent α -BChl and β -BChl. These atomic pair set is composed of the overall combination of 14 atoms of bacteriochlorin moiety of α -BChl with those of β -BChl (Figure S1 in Supporting Infor-

mation). The principal component analysis (PCA) was performed using 200,000 structures extracted from the production MD trajectory. The training data were obtained from the multi-FED-FCD diabaticization scheme at 50 structures extracted from the MD trajectory. We performed grid search to optimize parameters (λ, γ) in Eqs. (18) and (19). We screened 60,000 points of (λ, γ) in the region $[0, 0.1] \times [0, 0.01]$. For the parameter optimization, we divided 50 data points into 10 sets of 45 training data points and 5 test data points to perform the cross-validation test. We optimized the parameters to minimize the MUE between the original data and the predicted data across all 50 data points. We prepared two KRR models for intra-chain α - β dimer and inter-chain α - β dimer individually (see Figure 1). The optimized parameters were $(\lambda, \gamma) = (0.0575, 0.000533)$ for the intra-chain α - β dimer and $(\lambda, \gamma) = (0.0505, 0.000967)$ for the inter-chain α - β dimer. We examined the validity of selecting the top eight principal components (Figure S2). It was found that the top eight principal components adequately capture the thermal fluctuations (93% of the total variance) and that the MUEs of calculated LE-CT coupling converge well. In addition, we examined the potential overfitting of the KRR model. As shown in Table S1, both the training and test datasets exhibit similar MUEs between the original and predicted values in the cross-validation, indicating no overfitting.

4 Result and Discussion

4.1 Accuracy of MMSIC and KRR Modeling. We first checked the accuracy of MMSIC potential energy functions during the MD simulation. Figure 3(a) shows comparison of the MMSIC and EEQM energies of three BChls in the S_0 state at 300 configurations. The MUEs of MMSIC energies are remarkably small, ~ 1 kcal/mol for all the BChls. Comparison of the MM and EEQM energies are also shown in the lower panels of Figure 3(a). The MUEs of MM energies are more than 6 kcal/mol, which are much larger than those of MMSIC energies. Figure 3(b), (c), and (d) shows comparisons of the MMSIC and EEQM energies

as well as the MUEs of MMSIC energies in the S_1 , cationic, anionic states, which are also sufficiently small (~ 1 kcal/mol).

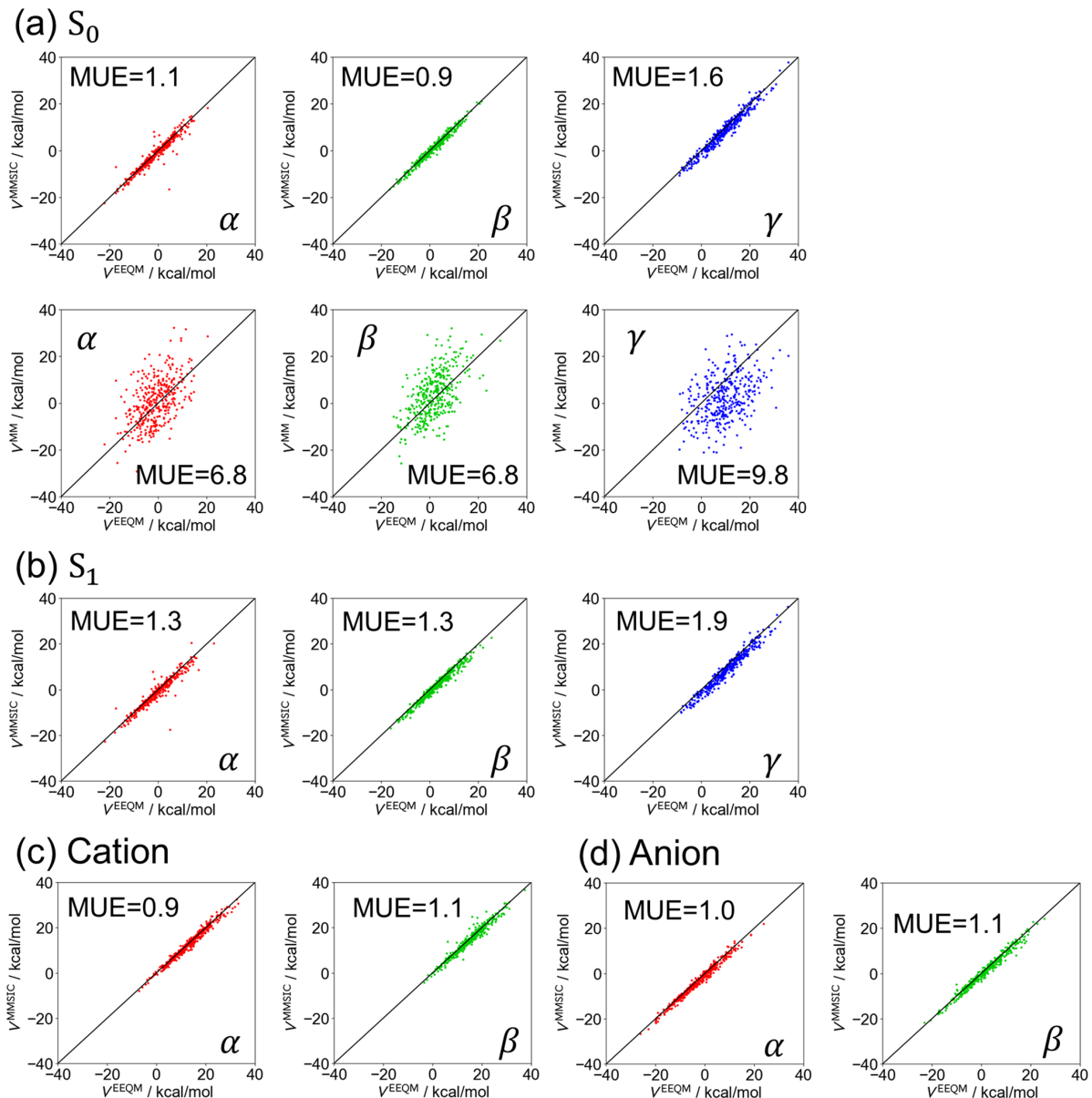


Figure 3: (a) Comparison of the MMSIC and EEQM energies (top) and the MM and EEQM energies (bottom) in the S_0 state at 300 configurations. (b), (c), (d) Comparison of the MMSIC and EEQM energies in the S_1 , cationic, anionic states at 300 configurations. Panels with red, green, and blue dots show the results of α -BChl, β -BChl, and γ -BChl, respectively.

Next, we investigated the accuracy of the LE-CT coupling calculated with the PCA and KRR model. Among the top eight principal components, the correlation coefficients

between principal components and the LE-CT couplings were from 0.2 to 0.8. The first principal components of both intra- and inter-chain dimers correspond to the motions of the two pigments approaching each other as a whole, whereas the remaining components represent motions orthogonal to the first principal components (Figures S3 and S4), which capture the thermal fluctuations.

Here we used the top eight principal components for the prediction of LE-CT couplings. Figure 4 shows comparison of the LE-CT couplings calculated using the KRR model from 50 training data with those from the reference multi-FED-FCD diabaticization scheme. For all the LE-CT coupling elements, the MUEs of KRR model were sufficiently small, $\sim 60 \text{ cm}^{-1}$. Figure S5 shows the correlation matrix between two CT energies, $\epsilon_{\alpha \rightarrow \beta}$ and $\epsilon_{\beta \rightarrow \alpha}$ calculated by the MMSIC method, and four LE-CT couplings, $V_{\alpha, \alpha \rightarrow \beta}^{\text{LE-CT}}$, $V_{\alpha, \beta \rightarrow \alpha}^{\text{LE-CT}}$, $V_{\beta, \alpha \rightarrow \beta}^{\text{LE-CT}}$, and $V_{\beta, \beta \rightarrow \alpha}^{\text{LE-CT}}$. The correlations within LE-CT couplings calculated with the multi-FED-FCD method are well reproduced with the KRR model. On the other hand, the correlation between CT energies and LE-CT couplings calculated with the MMSIC and KRR model are smaller than those with the multi-FED-FCD method. This underestimation could be due to the use of different methods for CT energies and LE-CT couplings. The MMSIC method accounts for the intra- and inter-molecular motions, whereas the KRR modeling is constructed based on the principal components obtained from the inter-molecular distances.

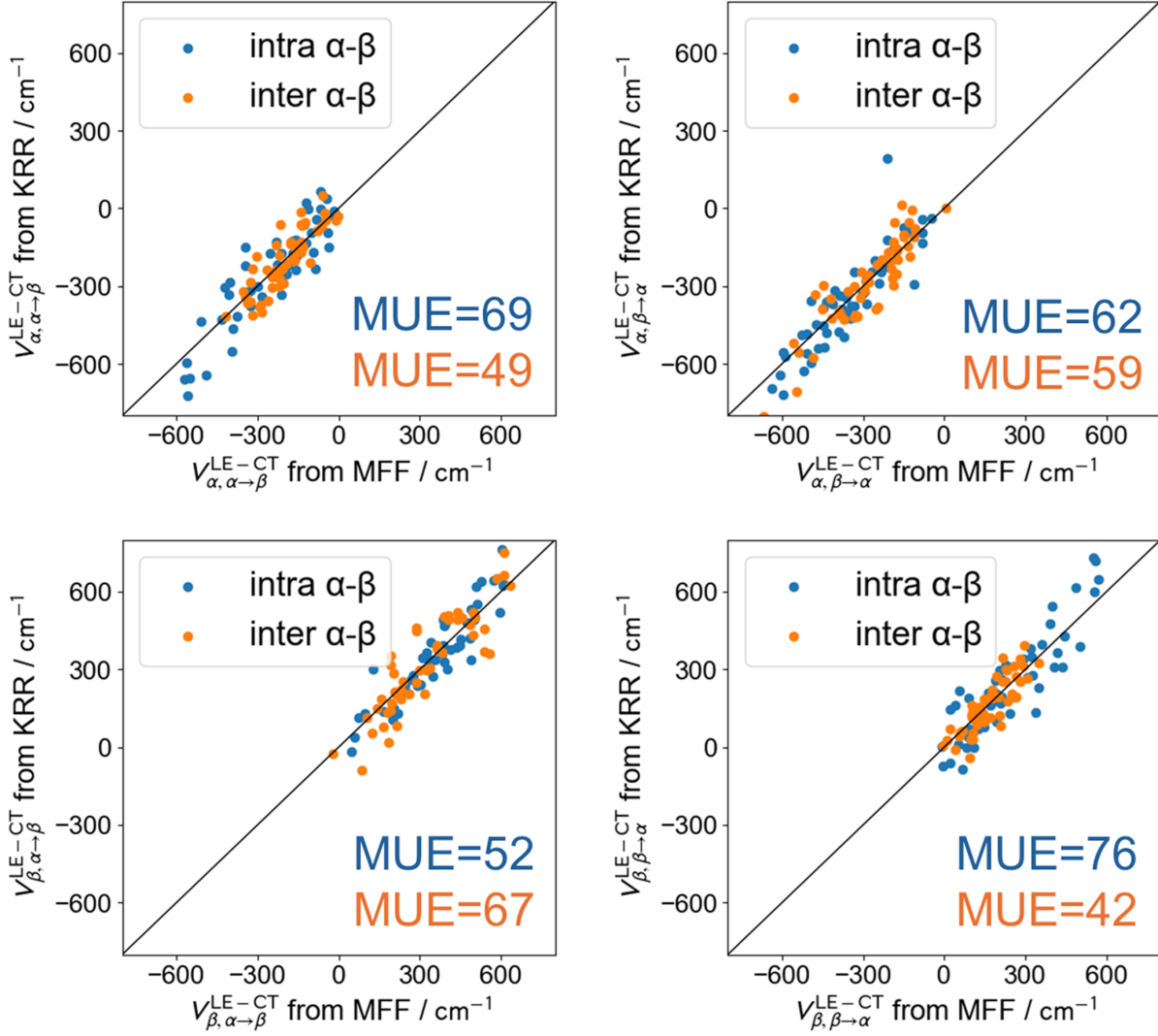


Figure 4: Comparison of the four elements of LE-CT couplings calculated with the KRR model (vertical axis) and multi-FED-FCD diabaticization scheme (horizontal axis) at 50 configurations of intra- and inter-chain dimer, respectively.

4.2 Site energy and LE-LE coupling. Figure 5(a) shows the calculated site energy distributions of three non-equivalent pigments obtained from the MD simulation with MM-SIC S_0 force field. Mean values and standard deviations of site energies are shown in Table 1. The mean value of site energy of β -BChl (12646 cm^{-1}) was higher than those of α - and γ -BChls (12617 cm^{-1} and 12507 cm^{-1}). The site energy fluctuation of β -BChl (514 cm^{-1}) was larger than those of α - and γ -BChls (411 cm^{-1} and 397 cm^{-1}). We compared the obtained site energies with the previous results in Figure 5(b). Our calculated results

were comparable to the previous studies and similar to those of Strümpfer and Shulten.⁶³ However, the site energy of γ -BChl seems underestimated because it was larger than those of α - and β -BChls in the previous studies. This underestimation could be due to an inadequate description of QM-MM interaction in the polar environment around γ -BChl. The calculated spectral densities of LE energies of α -, β -, and γ -BChls are shown in Figures S6(a) and (b). The spectral densities of α - and γ -BChls are similar to the experimental result of BChl in the FMO complex,⁶⁴ whereas that of β -BChl is larger, due to the broad distribution of site energy (Figure 5(a)).

Table 1: Mean values and standard deviations of calculated site energies (unit: cm^{-1}).

BChl	mean value	standard deviation
α	12617	411
β	12646	514
γ	12507	397

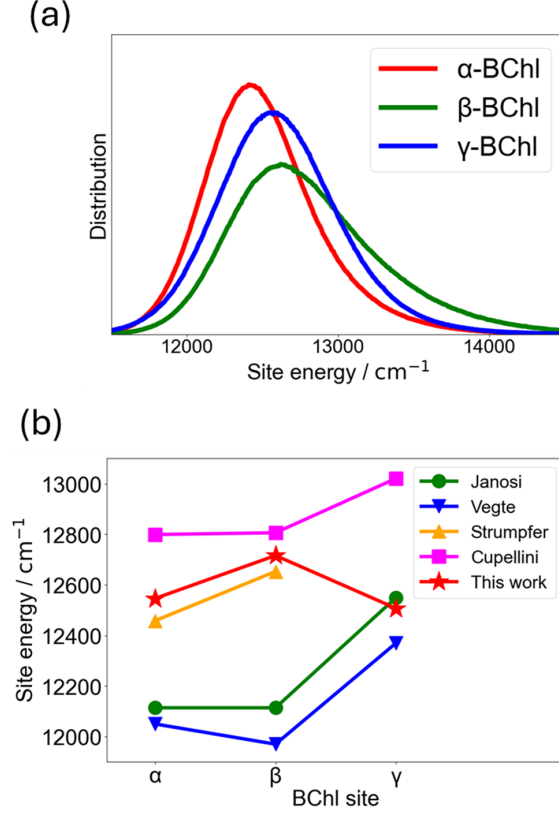


Figure 5: (a) Site energy distributions from 1-ns MMSIC MD calculation. Red, green, and blue lines show the results of α -BChl, β -BChl, and γ -BChl, respectively. (b) Comparison of the calculated site energies with the previous studies from Janosi et al.,¹⁴ Vegte et al.,²³ Cupellini et al.,⁴⁰ and Strümpfer and Schulten.⁶³

Next, we analyzed the transition dipole moments because the LE-LE coupling is approximately estimated by the interaction between transition dipole moments. The S_1 state of BChl is characterized as the Q_y state, where the orientation of transition dipole moment is almost parallel to the NB-ND y -axis (Figure S1). The average transition dipole strengths of α - and β -BChls were 6.0 D and 6.1 D, which are slightly smaller than that of γ -BChl, 6.3 D, reflecting from different protein environments. Figure 6(b) shows the distributions of calculated LE-LE couplings V_{mn} of representative BChl pairs in LH2, and their mean values and standard deviations are summarized in Table 2. The LE subblock of exciton Hamiltonian, including the mean values of all the LE-LE couplings, are shown in Figure S7. Adjacent BChl dimers, intra α - β and inter α - β , have large LE-LE couplings ($\sim 200 \text{ cm}^{-1}$) because of

the short distances between two pigments. The closest pairs of α - α and β - β pigments have almost the same intermolecular distance as the closest pairs of α - γ and β - γ pigments (~ 20 Å). However, the LE-LE couplings of α - α and β - β pigments are moderate ($30\sim 50$ cm $^{-1}$), whereas those of α - γ and β - γ pigments are weak ($0\sim 30$ cm $^{-1}$). The reason is the difference of relative orientation of two pigments; it is almost parallel in two $\alpha(\beta)$ pigments, whereas it is almost perpendicular in $\alpha(\beta)$ and γ pigments. We compared the obtained LE-LE couplings with the previous results in Figure 6(c). Our results are in good agreement with those of Vegte et al.²³ and Mallus et al.,⁵¹ where the TrESP method was used. Furthermore, our results are also in good agreement with those of Cupellini et al.,⁴⁰ where the multi-FED-FCD method was used to accurately consider the short range effect on LE-LE coupling. The LE-LE couplings of Sundström et al.⁶ were larger because the point dipole approximation scheme was used.

Table 2: Mean values and standard deviations of calculated LE-LE couplings of representative pigment pairs (unit: cm $^{-1}$).

pair	mean value	standard deviation
intra α - β	205	15
inter α - β	141	23
α - α	-54	3
β - β	-31	3
γ - γ	-16	3
α - γ	4	2
β - γ	18	2

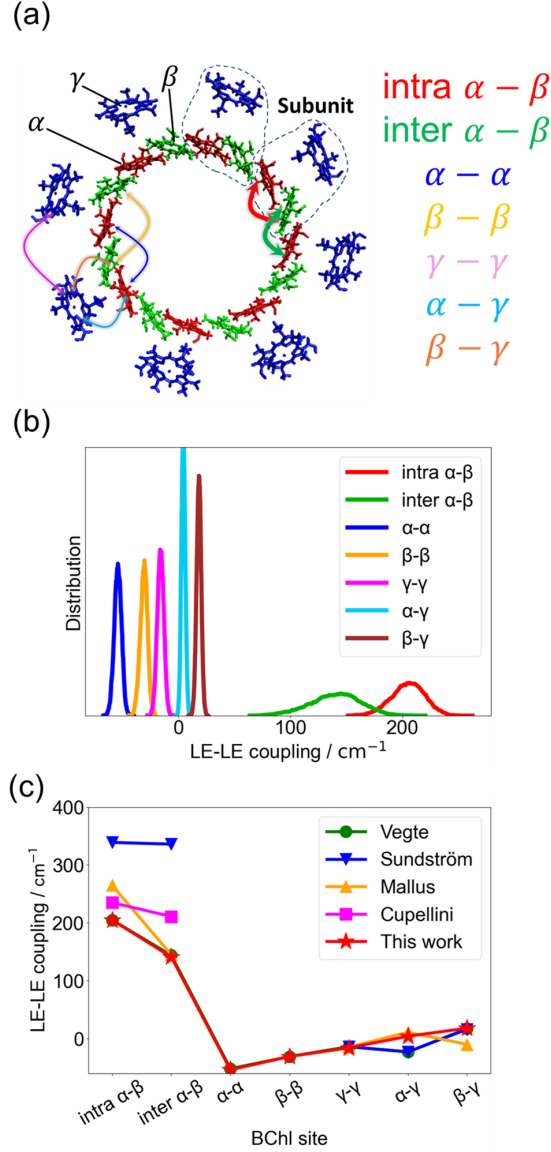


Figure 6: (a) Representative pairs of pigments in LH2. (b) Calculated LE-LE coupling distributions of representative pairs of pigments. (c) Comparison of the calculated LE-LE couplings with the previous studies from Vegte et al.,²³ Sundström et al.,⁶ Mallus et al.,⁵¹ and Cupellini et al.⁴⁰

4.3 CT energy and LE-CT coupling. Figure 7(a) shows the distributions of calculated CT excitation energies of pigment pairs of adjacent α -BChl and β -BChl in the B850 ring, which are the diagonal elements of CT submatrix of exciton Hamiltonian, Eq. (1). The mean values and standard deviations of CT energies are summarized in Table 3. The matrix form of CT energies are also shown in Figure S8. We calculated two CT states per

one pair; CT states from α -BChl to β -BChl ($\alpha \rightarrow \beta$) and from β -BChl to α -BChl ($\beta \rightarrow \alpha$). Further considering intra- and inter-dimers, four types of CT energies were obtained. The mean values of four CT energies differs from 15600 cm^{-1} to 17400 cm^{-1} , reflecting the non-equivalent protein environment. Notably, the distributions of CT energies are much broader than those of LE energies (Figure 5(a)). The standard deviations of CT energies are ~ 1500 cm^{-1} , whereas those of LE energies are ~ 400 cm^{-1} . The spectral densities of CT energies are also much larger than those of LE energies (Figure S6(a)). These results are because the CT states are sensitive to low-frequency vibrational modes such as intermolecular vibrational motions.⁴⁰

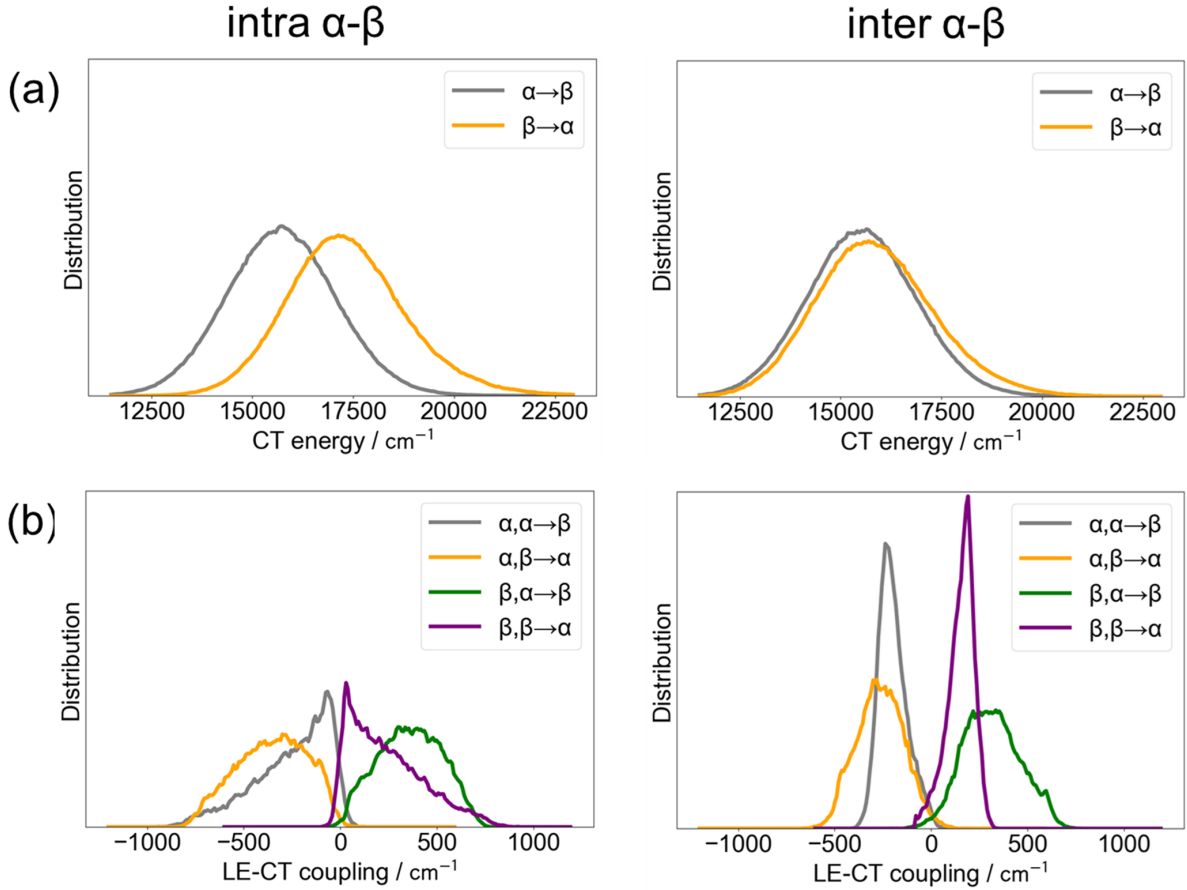


Figure 7: (a) CT energy distributions of BChl dimers in the B850 ring calculated from Eq. (11). (b) LE-CT coupling distributions of BChl dimers in the B850 ring from Eq. (15). The left and right panels show the results of intra-dimer and inter-dimer, respectively.

Table 3: Mean values (standard deviations) of CT energies and LE-CT couplings calculated from Eq. (11) and Eq. (15) (unit: cm^{-1}).

	intra-dimer	inter-dimer
$\epsilon_{\alpha \rightarrow \beta}^{\text{CT}}$	15752 (1381)	15572 (1373)
$\epsilon_{\beta \rightarrow \alpha}^{\text{CT}}$	17387 (1598)	15909 (1495)
$V_{\alpha, \alpha \rightarrow \beta}^{\text{LE-CT}}$	-247 (197)	-193 (74)
$V_{\alpha, \beta \rightarrow \alpha}^{\text{LE-CT}}$	-351 (182)	-259 (123)
$V_{\beta, \alpha \rightarrow \beta}^{\text{LE-CT}}$	365 (163)	319 (147)
$V_{\beta, \beta \rightarrow \alpha}^{\text{LE-CT}}$	245 (192)	158 (71)

Figure 7(b) and Table 3 show the distributions, mean values, and standard deviations of calculated LE-CT couplings in the B850 ring. The matrix form of LE-CT couplings are described in Figure S9. A intra/inter-dimer includes four types of LE-CT couplings, $V_{\alpha, \alpha \rightarrow \beta}^{\text{LE-CT}}$, $V_{\alpha, \beta \rightarrow \alpha}^{\text{LE-CT}}$, $V_{\beta, \alpha \rightarrow \beta}^{\text{LE-CT}}$, and $V_{\beta, \beta \rightarrow \alpha}^{\text{LE-CT}}$. For example, $V_{\alpha, \alpha \rightarrow \beta}^{\text{LE-CT}}$ represents the electronic coupling between LE state of α -BChl and CT state of cationic α -BChl and anionic β -BChl. The absolute values of LE-CT couplings (150~350 cm^{-1}) are larger than those of the LE-LE couplings (0~200 cm^{-1}). The LE-CT couplings also have broader distributions than the LE-LE couplings.

4.4 Absorption spectra. We constructed three types of exciton model to investigate the effects of the fluctuations of CT states. Table 4 summarizes the fluctuation properties in each model. The Frenkel model ignores the CT states and considers only the fluctuations of LE energies and LE-LE couplings. The constant CT model includes the CT states as well as the LE states, but $\epsilon_{m \rightarrow n}^{\text{CT}}$ and $V_{m, m \rightarrow n}^{\text{LE-CT}}$ are regarded as time-independent constants. The fluctuating CT model considers the fluctuations of CT energies and LE-CT couplings using the MMSIC and KRR modeling. Notably, the fluctuating CT model considers both the auto correlations and the mutual correlations of CT elements because these elements are generated based on structural data along the MD trajectory.

Table 4: Three exciton models used for absorption spectra calculations.

model	fluctuations of ϵ_m and V_{mn}	inclusions of $\epsilon_{m \rightarrow n}^{\text{CT}}$ and $V_{m,m \rightarrow n}^{\text{LE-CT}}$	fluctuations of $\epsilon_{m \rightarrow n}^{\text{CT}}$ and $V_{m,m \rightarrow n}^{\text{LE-CT}}$
Frenkel	YES	NO	NO
Constant CT	YES	YES	NO
Fluctuating CT	YES	YES	YES

Figure 8 shows the calculated absorption spectra using the three exciton models and the experimental spectra.² To clearly illustrate the effects of CT states on the B850 band, the absorption spectra are decomposed into B800 and B850 components according to

$$I(\omega) = I_{\text{B800}}(\omega) + I_{\text{B850}}(\omega) + I_{\text{cross}}(\omega) \quad (27)$$

where

$$\begin{aligned} I_{\text{B800(B850)}}(\omega) \\ = \omega \text{Re} \int_0^\infty dt e^{i\omega t} \text{Im} \langle \sum_{\substack{m,n \in \text{B800} \\ (m,n \in \text{B850})}} \mathbf{d}_m(t) U_{mn}(t) \mathbf{d}_n(0) \rangle \end{aligned} \quad (28)$$

and

$$\begin{aligned} I_{\text{cross}}(\omega) &= \omega \text{Re} \int_0^\infty dt e^{i\omega t} \text{Im} \langle \sum_{\substack{m \in \text{B800} \\ n \in \text{B850}}} \mathbf{d}_m(t) U_{mn}(t) \mathbf{d}_n(0) \rangle \\ &+ \omega \text{Re} \int_0^\infty dt e^{i\omega t} \text{Im} \langle \sum_{\substack{m \in \text{B850} \\ n \in \text{B800}}} \mathbf{d}_m(t) U_{mn}(t) \mathbf{d}_n(0) \rangle \end{aligned} \quad (29)$$

The decomposition results are shown in Figure S10. It was found that the cross term $I_{\text{cross}}(\omega)$ is small, and the total absorption spectra is almost equal to the sum of $I_{\text{B800}}(\omega)$ and $I_{\text{B850}}(\omega)$. It is also noted that the B800 bands obtained from the three models are nearly identical, and thus Figure 8 includes only the B800 band calculated with the Frenkel model. The calculated B800 band shape is close to the experimental one, although the calculated peak position is slightly red-shifted. The redshift could be due to the underestimation of site

energy of γ -BChl (Figure 5). Table 5 summarizes the peak position and half width at half maximum (HWHM) of the calculated B850 absorption band. The calculated spectra using Frenkel model has the B850 peak at 12124 cm^{-1} with the HWHM of 176 cm^{-1} . Compared to the experimental spectra² (11811 cm^{-1} and 238 cm^{-1} for the peak position and HWHM, respectively), the B850 peak position is in higher energy side, and the peak width is narrower. The absorption spectrum calculated using constant CT model, which considers the CT effects without fluctuations, showed a large redshift of the peak position of B850 (11991 cm^{-1}) from the results of Frenkel model. However, the peak width (166 cm^{-1}) was similar to that of Frenkel model and narrower than the experimental spectra. In the case of fluctuating CT model which considers the time correlation of CT energies and LE-CT couplings, the B850 peak position was further red-shifted to 11942 cm^{-1} . Especially, the fluctuating CT model increased the B850 peak width significantly to 242 cm^{-1} , which is in good agreement with the experimental width. Therefore, it was demonstrated that the fluctuations of CT energies and LE-CT couplings were important for the broad absorption of B850 band.

Our model with 1-ns sampling was able to reproduce the peak width of the B850 band; however, it did not accurately reproduce the peak shift. One possible reason for this discrepancy is the absence of large conformational changes from the X-ray crystal structure, which are not captured within the timescale of nanosecond-scale MD simulations. The atomic force microscope of the photosynthetic system of purple bacteria revealed that the size and shape of LH2 were distorted from the circular symmetry of crystal structure and were different from each other.⁶⁵ In addition, it was reported that the exciton band of the distorted ellipsoid structure of LH2 was different from that of the crystal structure.⁶⁶ These suggest that static disorder, such as a large-amplitude transformation into an ellipsoidal shape, may contribute to the peak shift. To treat such large conformational changes, further development of an efficient method could be required (see also below).

To investigate the reason why the fluctuations of CT energies and LE-CT couplings strongly affects the absorption spectra, we calculated the energy levels, expansion coefficients

and oscillator strengths of exciton states. The exciton states are eigenstates of exciton Hamiltonian Eq. (1)

$$|\mu\rangle = \sum_{m \in \text{B800, B850}} c_m^{(\mu)} |m\rangle + \sum_{m \in \text{B850}} \sum_{n \in \text{adjacent}} c_{m \rightarrow n}^{(\mu)} |m \rightarrow n\rangle \quad (30)$$

and the expansion coefficients of μ -th exciton state with the energy E_μ are partitioned into B800, B850, and CT components.

$$C_{\text{B800}}^{(\mu)} = \sum_{m \in \text{B800}} |c_m^{(\mu)}|^2 \quad (31)$$

$$C_{\text{B850}}^{(\mu)} = \sum_{m \in \text{B850}} |c_m^{(\mu)}|^2 \quad (32)$$

$$C_{\text{CT}}^{(\mu)} = \sum_{m \in \text{B850}} \sum_{n \in \text{adjacent}} |c_{m \rightarrow n}^{(\mu)}|^2 \quad (33)$$

Figure 9 shows the thermally averaged exciton energies and components of B800, B850, and CT states of the 24 lowest exciton states calculated with three models. Both the inclusions and fluctuations of CT energies and LE-CT couplings decrease the energy levels as expected from the calculated absorption spectra. The CT components are small for all the energy levels in constant CT model, but become somewhat larger in the fluctuating CT model. Figure 10 shows the thermally averaged oscillator strengths of exciton states. We found that the third and fourth exciton states has large oscillator strengths. Therefore, we focused on the difference between the exciton energies and components of the third and fourth exciton states among three models (Table 6). In the constant CT model, the small CT mixing was observed (0.023 and 0.019 for the third and fourth states). The small mixing of CT states results in the decrease in exciton energies (11913 cm^{-1} and 12011 cm^{-1}) from those in the Frenkel model (12001 cm^{-1} and 12087 cm^{-1}). Furthermore, the fluctuating CT model increases the CT components of the two states (0.065 and 0.059), which further decreases the exciton energies (11873 cm^{-1} and 11976 cm^{-1}). From these results, it was demonstrated that the fluctuation is important for CT mixing in exciton states. We emphasize that the

constant CT model is fictitious, whereas the fluctuating CT model is based on natural fluctuating motions sampled from the MD simulation. Therefore, it is considered that the fluctuation effects of CT states generated by natural protein environment finely tune the absorption band so that sunlight energy can be absorbed efficiently.

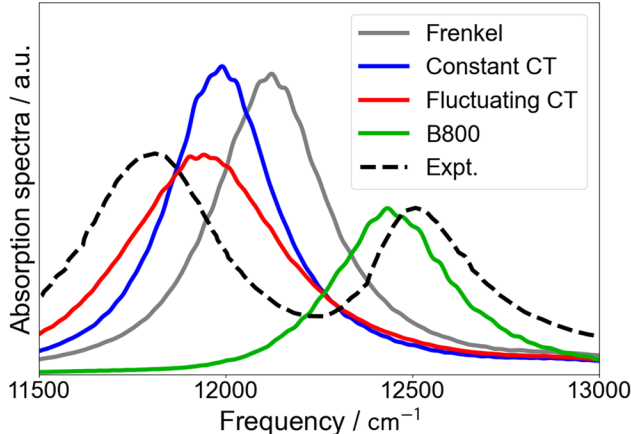


Figure 8: The absorption spectra calculated from three models. In the figure, components of B800 (green line) and B850 absorption bands are shown for clarity. The gray, blue, and red lines show the B850 bands of Frenkel, constant CT, and fluctuating CT models, respectively. As a reference, the experimental spectra² is shown in a black dashed line.

Table 5: Peak position and half width at half maximum (HWHM) of calculated B850 absorption band (unit: cm^{-1}).

	peak position	HWHM
Frenkel	12124	176
Constant CT	11991	166
Fluctuating CT	11942	242
Expt. ²	11811	238

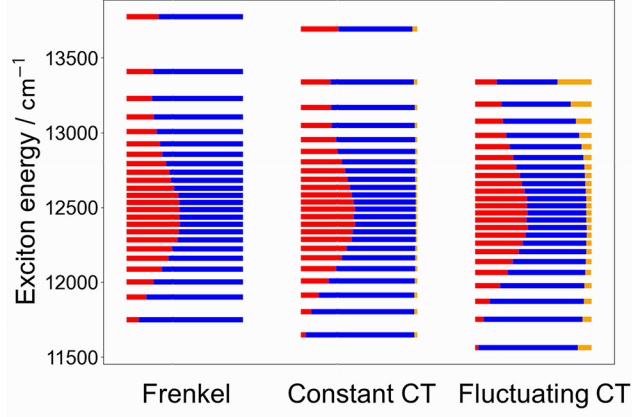


Figure 9: The thermally averaged energy levels and components of 24 lowest exciton states. The lengths of red, blue, orange lines in the energy level indicate the ratio of B800, B850, and CT components (Eqs. (31), (32), and (33)), respectively.

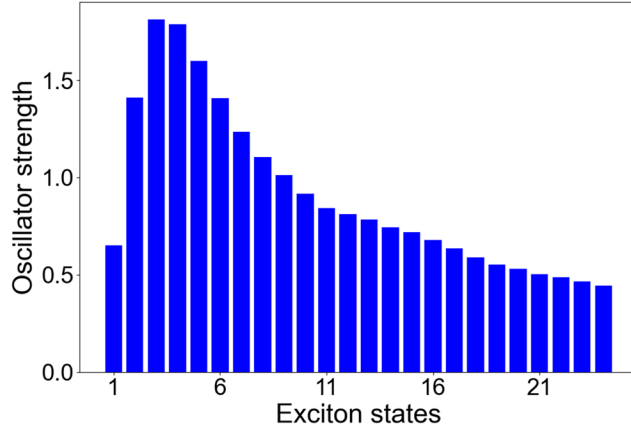


Figure 10: The thermally averaged oscillator strengths of 24 lowest exciton states calculated with fluctuating CT model.

Table 6: Comparisons of exciton energies and components of exciton states $\mu = 3, 4$ calculated with three models.

	E_3 / cm^{-1}	$C_{\text{B800}}^{(3)}$	$C_{\text{B850}}^{(3)}$	$C_{\text{CT}}^{(3)}$
Frenkel	12001	0.230	0.770	0.000
Constant CT	11913	0.154	0.823	0.023
Fluctuating CT	11873	0.127	0.808	0.065

	E_4 / cm^{-1}	$C_{\text{B800}}^{(4)}$	$C_{\text{B850}}^{(4)}$	$C_{\text{CT}}^{(4)}$
Frenkel	12087	0.301	0.699	0.000
Constant CT	12011	0.240	0.741	0.019
Fluctuating CT	11976	0.216	0.725	0.059

5 Summary

In this study, we developed the efficient calculation scheme for exciton Hamiltonian of LH2 which includes the LE and CT states. Using the MMSIC method and KRR model for the time evolution of CT energies and LE-CT couplings, we could obtain the fluctuating CT elements from the MD trajectory. The results calculated with the efficient calculation scheme were in agreement with those with the referenced method. This calculation scheme was applied to analyze the absorption spectra of LH2. We prepared the three exciton models to investigate the effects of CT elements and their fluctuations. The analysis revealed that the consideration of CT elements as constant is not sufficient, whereas MD-based fluctuations of CT effects is important for broad and red-shifted B850 absorption band.

As discussed above, large and slow conformational changes of overall proteins might need to be considered in the absorption spectra calculations to further improve the agreement with the experimental spectra. However, it is computationally difficult to access fluctuations on such large spatiotemporal scales by using structural sampling with all-atom MD simulations. Coarse-grained molecular dynamics (CGMD) simulations allow us to access to motions on spatiotemporal scales about 1000 times larger than all-atom MD simulations by approximating about 10 atoms to one bead. The combination of CGMD simulation with the MMSIC method and machine learning models is expected to account for the large-amplitude motions into optical phenomena of photosynthetic systems. Such a study is in progress.

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Supporting Information Available

- Figures for the 14 atoms that define the interatomic distances employed in the PCA; cumulative variance of principal components and the dependence of the number of principal components on MUEs of the LE-CT couplings; the atomic motions of the top eight principal components; assessment of potential overfitting in the KRR model; comparison of correlation matrices of the CT energies and the LE-CT couplings calculated with the MMSIC method and KRR model and those calculated with the multi-FED-FCD diabaticization scheme; the calculated spectral densities of LE and CT energies; LE subblock, CT subblock, and LE-CT subblock of the averaged exciton Hamiltonian; decompositions of the absorption spectra calculated with three models into B800, B850, and cross components.

References

- (1) Hogewoning, S. W.; Wientjes, E.; Douwstra, P.; Trouwborst, G.; van Ieperen, W.; Croce, R.; Harbinson, J. Photosynthetic Quantum Yield Dynamics: From Photosystems to Leaves. *The Plant Cell* **2012**, *24*, 1921–1935.
- (2) Ihalainen, J. A.; Myllyperkio, P.; van Stokkum, H. M.; Ucker, B.; Scheer, H.; Korppi-Tommola, J. E. I. Energy Transfer in LH2 of Rhodospirillum Rubrum, Studied by Subpicosecond Spectroscopy and Configuration Interaction Exciton Calculations. *Biophys. J.* **2001**, *80*, 2867–2877.
- (3) Harel, E.; Engel, G. S. Quantum Coherence Spectroscopy Reveals Complex Dynamics in Bacterial Light-Harvesting Complex 2 (LH2). *Proc. Natl. Acad. Sci.* **2012**, *109*, 706–711.
- (4) Bergstrom, H.; Sundstrom, V.; Vangrondelle, R.; Gillbro, T.; Cogdell, R. Energy-Transfer Dynamics of Isolated B800-850 and B800-820 Pigment-Protein Complexes

- of Rhodobacter- Sphaeroides and Rhodopseudomonas-Acidophila. *Biochim. Biophys. Acta.* **1988**, *936*, 90–98.
- (5) Beekman, L. M. P.; Frese, R. N.; Fowler, G. J. S.; Picorel, R.; Cogdell, R. J.; van Stokkum, I. H. M.; Hunter, C. N.; van Grondelle, R. Characterization of the Light-Harvesting Antennas of Photosynthetic Purple Bacteria by Stark Spectroscopy. 2. LH2 Complexes: Influence of the Protein Environment. *J. Phys. Chem. B* **1997**, *101*, 7293–7301.
- (6) Sundström, V.; Pullerits, T.; van Grondelle, R. Photosynthetic Light-Harvesting: Reconciling Dynamics and Structure of Purple Bacterial LH2 Reveals Function of Photosynthetic Unit. *J. Phys. Chem. B* **1999**, *103*, 2327–2346.
- (7) Yang, M.; Agarwal, R.; Fleming, G. R. The Mechanism of Energy Transfer in the Antenna of Photosynthetic Purple Bacteria. *J. Photochem. Photobiol.* **2001**, *142*, 107–119.
- (8) Pennoyer, J. D.; Kramer, H. J. M.; van Grondelle, R.; Westerhuis, W. H. J.; Ames, J.; Niederman, R. A. Excitation Energy Transfer in Rhodopseudomonas Sphaeroides Chromatophore Membranes Fused with Liposomes. *FEBS Lett.* **1985**, *182*, 145–150.
- (9) Trautman, J. K.; Shreve, A. P.; Violette, C. A.; Albrecht, A. C. Femtosecond Dynamics of Energy Transfer in B800-850 Light-Harvesting Complexes of Rhodobacter Sphaeroides. *Proc. Natl. Acad. Sci.* **1990**, *87*, 215–219.
- (10) Reddy, N. R. S.; Small, G. J.; Seibert, M.; Picorel, R. Energy-Transfer Dynamics of the B800-B850 Antenna Complex of Rhodobacter-Sphaeroides—a Hole Burning Study. *Chem. Phys. Lett.* **1991**, *181*, 391–399.
- (11) Hess, S.; Feldchtein, F.; Babin, A.; Nurgaleev, I.; Pullerits, T.; Sergeev, A.; Sundström, V. Femtosecond Energy Transfer within the LH2 Peripheral Antenna of the Pho-

- tosynthetic Purple Bacteria Rhodobacter Sphaeroides and Rhodopseudomonas Palustris LL. *Chem. Phys. Lett.* **1993**, *31*, 247–257.
- (12) Wu, H.-M.; Ratsep, M.; Jankowiak, R.; Cogdell, R. J.; Small, G. J. Comparison of the LH2 Antenna Complexes of Rhodopseudomonas acidophila (Strain 10050) and Rhodobacter sphaeroides by High-Pressure Absorption, High-Pressure Hole Burning, and Temperature-Dependent Absorption Spectroscopies. *J. Phys. Chem. B* **1997**, *101*, 7641–7653.
- (13) Georgakopoulou, S.; Frese, R. N.; Johnson, E.; Cogdell, R. J.; van Grondell, R.; van der Zwan, G. Absorption and CD Spectroscopy and Modeling of Various LH2 Complexes from Purple Bacteria. *Biophys. J* **2002**, *82*, 2184–2197.
- (14) Janosi, L.; Kosztin, I.; Damjanović, A. Theoretical Prediction of Spectral and Optical Properties of Bacteriochlorophylls in Thermally Disordered LH2 Antenna Complexes. *J. Chem. Phys.* **2006**, *125*, 014903–1–014903–11.
- (15) Damjanović, A.; Kosztin, I.; Kleinekathöfer, U.; Schulten, K. Excitations in a Photosynthetic Light-Harvesting System: A Combined Molecular Dynamics, Quantum Chemistry, and Polaron Model Study. *Phys. Rev. E* **2001**, *65*, 031919–1–031919–24.
- (16) He, Z.; Sundström, V.; Pullerits, T. Influence of the Protein Binding Site on the Excited States of Bacteriochlorophyll: DFT Calculations of B800 in LH2. *J. Phys. Chem. B* **2002**, *106*, 11606–11612.
- (17) Hu, X.; Ritz, T.; Damjanovic, A.; Autenrieth, F.; Schulten, K. Photosynthetic Apparatus of Purple Bacteria. *Q. Rev. Biophys.* **2002**, *35*, 5935.
- (18) Linnanto, J.; Korppi-Tommola, J. E. I.; Helenius, V. M. Electronic States, Absorption Spectrum and Circular Dichroism Spectrum of the Photosynthetic Bacterial LH2 Antenna of Rhodopseudomonas acidophila as Predicted by Exciton Theory and Semiempirical Calculations. *J. Phys. Chem. B* **1999**, *103*, 8739–8750.

- (19) Meier, T.; Zhao, Y.; Chernyak, V.; Mukamel, S. Polarons, Localization, and Excitonic Coherence in Superradiance of Biological Antenna Complexes. *J. Chem. Phys.* **1997**, *107*, 3876–3893.
- (20) Ray, J.; Makri, N. Short-Range Coherence in the Energy Transfer of Photosynthetic Light-Harvesting Systems. *J. Phys. Chem. A* **1999**, *103*, 9417–9422.
- (21) Mukai, K.; Abe, S.; Sumi, H. Theory of Rapid Excitation-Energy Transfer from B800 to Optically-Forbidden Exciton States of B850 in the Antenna System LH2 of Photosynthetic Purple Bacteria. *J. Phys. Chem. B* **1999**, *103*, 6096–6192.
- (22) Zhong, K.; Nguyen, H. L.; Do, T. N.; Tan, H.-S.; Knoester, J.; Jansen, T. L. C. Coarse-Grained Approach to Simulate Signatures of Excitation Energy Transfer in Two-Dimensional Electronic Spectroscopy of Large Molecular Systems. *J. Chem. Theory Comput.* **2024**, *20*, 6111–6124.
- (23) van der Vegte, C. P.; Prajapati, J. D.; Kleinekathöfer, U.; Knoester, J.; Jansen, T. L. C. Atomistic Modeling of Two-Dimensional Electronic Spectra and Excited-State Dynamics for a Light Harvesting 2 Complex. *J. Phys. Chem. B* **2015**, *119*, 1302–1313.
- (24) Sisto, A.; Stross, C.; van der Kamp, M. W.; O’Connor, M.; McIntosh-Smith, S.; Johnson, G. T.; Hohenstein, E. G.; Manby, F. R.; Glowacki, D. R.; Martinez, T. J. Atomistic Non-adiabatic Dynamics of the LH2 Complex with a GPU-accelerated *ab-initio* Exciton Model. *Phys. Chem. Chem. Phys.* **2017**, *19*, 14924–14936.
- (25) Koepke, J.; Hu, X.; Muenke, C.; Schulten, K.; Michel, H. The Crystal Structure of the Light-Harvesting Complex II (B800-850) from *Rhodospirillum Rubrum*. *Structure* **1996**, *4*, 581–597.
- (26) Fenna, R. E.; Matthews, B. W. Chlorophyll Arrangement in a Bacteriochlorophyll Protein from *Chlorobium limicola*. *Nature* **1975**, *258*, 573–577.

- (27) Standfuss, J.; van Scheltinga, A. C. T.; Lamborghini, M.; Kühlbrandt, W. Mechanisms of Photoprotection and Nonphotochemical Quenching in Pea Light-Harvesting Complex at 2.5 Å Resolution. **2005**, *24*, 919–928.
- (28) Davydov, A. S., Ed. *Theory of Molecular Excitons*; Springer New York: New York, 1971.
- (29) Madjet, M. E.; Abdurahman, A.; Renger, T. Intermolecular Coulomb Couplings from Ab Initio Electrostatic Potentials: Application to Optical Transitions of Strongly Coupled Pigments in Photosynthetic Antennae and Reaction Centers. *J. Phys. Chem. B* **2006**, *110*, 17268–17281.
- (30) Cupellini, L.; Jurinovich, S.; Campetella, M.; Guido, C. A.; Kelly, S. M.; Gardiner, A. T.; Cogdell, R.; Mennucci, B. An Ab Initio Description of the Excitonic Properties of LH2 and Their Temperature Dependence. *J. Phys. Chem. B* **2016**, *120*, 11348–11359.
- (31) Mallus, M. I.; Shakya, Y.; Prajapati, J. D.; Kleinekathöfer, U. Environmental Effects on the Dynamics in the Light-Harvesting Complexes LH2 and LH3 Based on Molecular Simulations. *Chem. Phys.* **2018**, *515*, 141–151.
- (32) Chandrasekaran, S.; Aghtar, M.; Valteau, S.; Aspuru-Guzik, A.; Kleinekathöfer, U. Influence of Force Fields and Quantum Chemistry Approach on Spectral Densities of BChl *a* in Solution and in FMO Proteins. *J. Phys. Chem. B* **2015**, *119*, 9995–10004.
- (33) Park, J. W.; Rhee, Y. M. Interpolated Mechanics-Molecular Mechanics Study of Internal Rotation Dynamics of the Chromophore Unit in Blue Fluorescent Protein and Its Variants. *J. Phys. Chem. B* **2012**, *116*, 11137–11147.
- (34) Cho, K. H.; Chung, S.; Rhee, Y. M. Efficiently Transplanting Potential Energy Interpolation Database between Two Systems: Bacteriochlorophyll Case with FMO and LH2 Complexes. *J. Chem. Inf. Model.* **2019**, *59*, 4228–4238.

- (35) Higashi, M.; Saito, S. Quantitative Evaluation of Site Energies and Their Fluctuations of Pigments in the Fenna-Matthews-Olson Complex with an Efficient Method for Generating a Potential Energy Surface. *J. Chem. Theory Comput.* **2016**, *12*, 4128–4137.
- (36) Saito, S.; Higashi, M.; Fleming, G. R. Site-Dependent Fluctuations Optimize Electronic Energy Transfer in the Fenna-Matthews-Olson Protein. *J. Phys. Chem. B* **2019**, *123*, 9762–9772.
- (37) Zhu, Z.; Higashi, M.; Saito, S. Development of Molecular Dynamics Parameters and Theoretical Analysis of Excitonic and Optical Properties in the Light-Harvesting Complex II. *J. Chem. Theory Comput.* **2025**, *21*, 413–427.
- (38) Rätsep, M.; Pajusalu, M.; Linnanto, J. M.; Freiberg, A. Subtle Spectral Effects Accompanying the Assembly of Bacteriochlorophylls into Cyclic Light Harvesting Complexes Revealed by High-Resolution Fluorescence Spectroscopy. *J. Chem. Phys.* **2014**, *141*, 155102–1–155102–10.
- (39) Nottoli, M.; Jurinovich, S.; Cupellini, L.; Gardiner, A. T.; Cogdell, R.; Mennucci, B. The Role of Charge-Transfer States in the Spectral Tuning of Antenna Complexes of Purple Bacteria. *Photosynth. Res.* **2018**, *137*, 215–226.
- (40) Cupellini, L.; Caprasecca, S.; Guido, C. A.; Müh, F.; Renger, T.; Mennucci, B. Coupling to Charge Transfer States in the Key to Modulate the Optical Bands for Efficient Light Harvesting in Purple Bacteria. *J. Phys. Chem. Lett* **2018**, *9*, 6892–6899.
- (41) Ramos, F. C.; Nottoli, M.; Cupellini, L.; Mennucci, B. The Molecular Mechanisms of Light Adaption in Light-Harvesting Complexes of Purple Bacteria Revealed by a Multiscale Modeling. *Chem. Sci.* **2019**, *10*, 9650–9662.
- (42) Hsu, C.-P.; You, Z.-Q.; Chen, H.-C. Characterization of the Short-Range Couplings in Excitation Energy Transfer. *J. Phys. Chem. C* **2008**, *112*, 1204–1212.

- (43) Voityuk, A. A.; Rösch, N. Fragment Charge Difference Method for Estimating Donor-Acceptor Electronic Coupling: Application to DNA π -stacks. *J. Chem. Phys.* **2002**, *117*, 5607–5616.
- (44) Yang, C.-H.; Hsu, C.-P. Multi-state Fragment Charge Difference Approach for Diabatic States in Electron Transfer: Extension and Automation. *J. Chem. Phys.* **2013**, *139*, 154104.
- (45) Hastie, T., Tibshirani, R., Friedman, J., Eds. *The Elements of Statistical Learning: Data Mining, Inference and Prediction*, 2nd ed.; Springer, 2009.
- (46) Murphy, K. P., Ed. *Machine Learning: A Probabilistic Perspective*; MIT Press: Cambridge, 2012.
- (47) Cignori, E.; Cupellini, L.; Mennucci, B. Machine Learning Exciton Hamiltonians in Light-Harvesting Complexes. *J. Chem. Theory Comput.* **2023**, *19*, 965–977.
- (48) Hoffmann, D. S.; Dohmen, P. M.; Sokolov, M.; Kleinekathöfer, U.; Elstner, M. Exciton Transfer Simulations in a Light-Harvesting 2 Complex Reveal the Transient Delocalization Mechanism. *J. Phys. Chem. B* **2025**, *13*, 3345–3365.
- (49) Valleau, S.; Eisfeld, A.; Aspuru-Guzik, A. On the Alternatives for Bath Correlators and Spectral Densities from Mixed Quantum-Classical Simulations. *J. Chem. Phys.* **2012**, *137*, 224103.
- (50) Jansen, T. I. C.; Knoester, J. Nonadiabatic Effects in the Two-Dimensional Infrared Spectra of Peptides: Application to Alanine Dipeptide. *J. Phys. Chem. B* **2006**, *110*, 22910–22916.
- (51) Mallus, M. I.; Shakya, Y.; Prajapati, J. D.; Kleinekathöfer, U. Environmental Effects on the Dynamics in the Light-Harvesting Complexes LH2 and LH3 Based on Molecular Simulations. *Chem. Phys.* **2018**, *515*, 141–151.

- (52) Tian, C.; Kasavajhala, K.; Belfon, K. A. A.; Raguetta, L.; Huang, H.; Miguels, A. N.; Bickel, J.; Wang, Y.; Pincay, J.; Wu, Q.; Simmering, C. ff19SB: Amino-Acid-Specific Protein Backbone Parameters Trained against Quantum Mechanics Energy Surfaces in Solution. *J. Chem. Theory Comput.* **2020**, *16*, 528–552.
- (53) Dickson, C. J.; Walker, R. C.; Gould, I. R. Lipid21: Complex Lipid Membrane Simulations with AMBER. *J. Chem. Theory Comput.* **2022**, *18*, 1726–1736.
- (54) Jorgensen, W. L.; Chandrasekhar, J.; Madura, J. D.; Impey, R. W.; Klein, M. L. Comparison of Simple Potential Functions for Simulating Liquid Water. *J. Chem. Phys.* **1983**, *79*, 926–935.
- (55) Wang, J.; Wolf, R. M.; Caldwell, J. W.; Kollman, P. A.; Case, D. A. Develop and Testing of a General Amber Force Field. *J. Comput. Chem.* **2004**, *25*, 1157–1174.
- (56) Åqvist, J. Ion-water Interaction Potentials Derived from Free Energy Perturbation Simulations. *J. Phys. Chem.* **1990**, *94*, 8021–8094.
- (57) Joung, I. S.; Cheatham III, T. E. Determination of Alkali and Halide Monovalent Ion Parameters for Use in Explicitly Solvated Biomolecular Simulations. *J. Phys. Chem. B* **2008**, *112*, 9020–9041.
- (58) Case, D. A.; Darden, T. A.; Cheatham, I., T. E.; Simmerling, C. L.; Wang, J.; Duke, R. E.; Luo, R.; Walker, R. C.; Zhang, W.; Merz, K. M.; Roberts, B.; Wang, B.; Hayik, S.; Roitberg, A.; Seabra, G.; Kolossváry, I.; Wong, K. F.; Paesani, F.; Vanicek, J.; Liu, J.; Wu, X.; Brozell, S. R.; Steinbrecher, T.; Gohlke, H.; Cai, Q.; Ye, X.; Wang, J.; Hsieh, M.-J.; Cui, G.; Roe, D. R.; Mathews, D. H.; Seetin, M. G.; Sagui, C.; Babin, V.; Luchko, T.; Gusarov, S.; Kovalenko, A.; Kollman, P. A. AMBER 11, University of California, San Francisco. 2010.
- (59) Higashi, M.; Kosugi, T.; Hayashi, S.; Saito, S. Theoretical Study on Excited States of

- Bacteriochlorophyll *a* in Solutions with Density Functional Assessment. *J. Phys. Chem. B* **2014**, *118*, 10906–10918.
- (60) Schmidt, M. W.; Baldrige, K. K.; Boatz, J. A.; Elbert, S. T.; Gordon, M. S.; Jensen, J. H.; Koseki, S.; Matsunaga, N.; Nguyen, K. A.; Su, S. J.; Windus, T. L.; Dupuis, M.; Montgomery, J. A. General Atomic and Molecular Electronic Structure System. *J. Comput. Chem.* **1993**, *14*, 1347–1363.
- (61) Higashi, M.; Truhlar, D. G. AMBERPLUS 2010, University of Minnesota, Minneapolis. 2010.
- (62) Tishchenko, O.; Higashi, M.; Albu, T. V.; Corchado, J. C.; Kim, Y.; Villá, J.; Xing, J.; Lin, H.; Truhlar, D. G. MCSI 2010, University of Minnesota, Minneapolis. 2010.
- (63) Strümpfer, J.; Schulten, K. Light Harvesting Complex II B850 Excitation Dynamics. *J. Chem. Phys.* **2009**, *131*, 225101–1–225101–9.
- (64) Wendling, M.; Przyjalowski, M. A.; Gülen, D.; Vulto, S. I. E.; Aartsma, T. J.; van Grondelle, R.; van Amerongen, H. The Quantitative Relationship between Structure and Polarized Spectroscopy in the FMO Complex of *Prosthecochloris aestuarii*: Refining Experiments and Simulations. *Photosynth. Res.* **2002**, *71*, 99–123.
- (65) Brotosudarmo, T. H. P.; Limantara, L.; Heriyanto; Prihastyanti, M. N. U. Adaptation of the Photosynthetic Unit of Purple Bacteria to Changes of Light Illumination Intensities. *Procedia Chemistry* **2015**, *14*, 414–421.
- (66) Matsushita, M.; Ketelaars, M.; van Oijen, A. M.; Köhler, J.; Aartsma, T. J.; Schmidt, J. Spectroscopy on the B850 Band of Individual Light-Harvesting 2 Complexes of *Rhodospseudomonas acidophila* II. Exciton States of and Elliptically Deformed Ring Aggregate. *Biophys. J.* **2001**, *80*, 1604–1614.

TOC Graphic

