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Suppression of the Transfer Efficiency in the Disordered LH1-RC Photosynthetic Unit

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ABSTRACT

The single-photon transfer efficiency of a disordered LH1-RC complex was investigated. In contrast to uniform couplings, photon-ring coupling disorder significantly suppressed the transfer efficiency within a finite photon-detuning range, while intra-ring coupling disorder had a negligible effect. The lifetimes of the photon, ring excitation, and acceptor-site excitation were also numerically determined. It was found that the minimum in the transfer efficiency for photon-ring disorder decreased exponentially with increasing disorder strength, and was associated with the shortest lifetimes and the absence of a dark-state channel. A phonon dephasing bath decreased the transfer efficiency, except in the near-resonant detuning region where it was enhanced in the presence of photon-ring disorder.

1 Introduction

The process of photosynthetic light harvesting relies on two sets of biochemical complexes: antenna complexes and reaction centres. The antenna complexes harvest photon energy and, via a centralized acceptor core, transfer it to reaction centres where the excitation energy is utilized in the chemical conversion of carbon dioxide and water into carbohydrates¹. Together, these make up the photosynthetic unit. Antenna complexes often consist of many networked molecules that surround an acceptor core. The benefit of this structure, as opposed to having a single molecule perform both duties, is that photosynthesis has both high efficiency and low induction times, even in low irradiance². These benefits are due to the quantum nature of these photosynthetic units and have prompted widespread modelling of these units. The high efficiency of photosynthesis is due to the quantum phenomena of long-lived excited states, the wide wavelength ranges for light absorption, and a great degree of quantum coherence due to high pigment density³. In the case of large photosynthetic units, quantum coherence is integral as it creates collective excitations. Collective excitations refer to the phenomenon of identical particles interfering with each other, and acting as a single quasiparticle via superposition⁴. This also implies that transfer of the excitation among the molecules of the antenna complex does not occur via incoherent hopping but by Rabi oscillations as the excitation sinusoidally oscillates between adjacent molecules⁵.

One photosynthetic unit that has been studied is the light-harvesting core antenna and reaction centre in purple photosynthetic bacteria, the LH1-RC^{6–12}. According to Niwa *et al.*¹³, in *Thermochromatium tepidum*, the antenna, known as the LH1, consists of 16 sub-units arranged to form a ring around the 4 sub-unit reaction centre, known as the RC. Quantum models of the LH1-RC resemble this basic structure, not necessarily in the number of sub-units, but in the basic shape of a ring of donor sites surrounding an acceptor site.

Olaya-Castro *et al.*⁶ modelled an LH1-RC light-harvesting system with variable donor and acceptor ring sizes. They used the quantum jump approach to develop the theory for the transfer efficiency, i.e., the efficiency with which the excitation is passed onto the reaction centre via the acceptor sites. It was found that the transfer efficiency is highly dependent on the quantum superposition properties of the initial state, particularly the degree of symmetry in the superposition of the excitation among sites of the donor ring. Dong *et al.*⁷ considered a model of the LH1-RC consisting of an acceptor atom (coupled to an RC), a donor ring of identical sites with uniform intra-ring coupling strengths, and a single incident photon. By treating the ring as a single quantum system, the model can be analyzed as a three-level Λ -type system, and as a consequence, a dark state channel can be created. The dark state is a superposition of the photon and acceptor states, resulting in high transfer efficiency without the effect of spontaneous decay from the donor ring. Tan and Kuang⁸ modelled the LH1-RC as a system of trimers, each comprised of two neighbouring donor molecules from the LH1 antenna coupled to an acceptor molecule, with each molecule immersed in an Ohmic bath. They found that excitation transfer is maximized at the critical point of quantum phase transition, i.e., when the two lowest energy eigenstates are degenerate. Tan and Kuang⁹ also studied the entanglement dynamics for the same LH1-RC trimer system. The donor-donor and donor-acceptor couplings exhibit marked changes at the same quantum phase transition, with each reacting quite differently to dissipation or dephasing changes. Chuang and Brumer¹⁰

considered the effect of incoherent light and a realistic light harvesting photocycle in the LH1-RC. The photocycle consists of four steps: photon absorption by the LH1, excitation transfer to the RC, charge separation on the RC, and the completion of charge separation resulting in a system in the ground state. This subsequently creates four quantum state combinations, where the LH1 is either excited or not, and the RC is either experiencing a charge separation event or not. As a result, at natural levels of incoherent light, the rate of excitation transfer scales linearly with light intensity, but at higher intensities the act of charge separation becomes a limiting factor, creating an upper limit in the excitation transfer rate. Strümpfer and Schulten¹¹ focus on the reaction centre of the LH1-RC, modelling the six pigment molecules that comprise it. Experimental results for the linear absorption spectrum at 300K were reproduced for the RC. Intra-complex (within the RC) and inter-complex (LH1 to RC) transfer were found to exhibit stark differences depending on the degree to which the RC is coupled to the environment. Weak coupling of the RC to the environment is beneficial since it allows for faster transfer from the RC back to the LH1, helping to moderate the charge separation process.

In this paper, the authors examine a model of the LH1-RC photosynthetic unit consisting of a ring of two-level donor sites, each coupled to a two-level acceptor site, with a single photon coupled to the ring. The transfer efficiency is calculated with disorder in the intra-ring and photon-ring coupling constants, with further investigation into the effect of photon-ring coupling disorder strength. In section 2, we introduce the general theory of the LH1-RC Hamiltonian for cases with and without disorder, and derive the transfer efficiency using the quantum jump approach. In section 3, we give results for the transfer efficiency dependence on photon detuning and spontaneous decay rate of the donor ring. Three cases are considered: no coupling disorder, disorder in the intra-ring coupling constants, and disorder in the photon-ring coupling constants. A probability amplitude analysis is also done for each disorder case. The effect of photon-ring coupling disorder strength on transfer efficiency is then analysed. Finally, a dephasing phonon environment is then included and those results compared to the transfer efficiency dependence without this environment.

2 Theory

2.1 The Hamiltonian of the LH1-RC

The LH1-RC Hamiltonian H is given as

$$H = H_D + H_A + H_p + H_{pD} + H_{DA}. \quad (1)$$

where H_D is the donor ring Hamiltonian, H_A is the acceptor site Hamiltonian, H_p is the photon Hamiltonian, H_{pD} is the photon-ring interaction Hamiltonian, and H_{DA} is the ring-acceptor interaction Hamiltonian.

The donor ring consists of N two-level systems (TLSs) that are coupled together. The energy difference between the ground state $|g\rangle_j$ and the excited state $|e\rangle_j$ of the j th TLS in the ring is given by ϵ_j and the coupling constant between adjacent ring TLSs is $g_{j,j+1}$. Therefore, the donor ring Hamiltonian H_D is given as

$$H_D = \sum_{j=1}^N [\epsilon_j e_j^+ e_j + g_{j,j+1} (e_j^+ e_{j+1} + h.c.)], \quad (2)$$

where $e_j^+ = |e\rangle_{jj}\langle g|$, $e_j = |g\rangle_{jj}\langle e|$, and $h.c.$ stands for Hermitian conjugate. In equation (2), the first term represents the excitation energy of the TLSs and the second term represents the interaction between adjacent TLSs.

The acceptor atom is positioned inside the ring and is coupled to each of the atoms of the donor ring. It is also modelled as a single TLS with ground state $|g\rangle_A$ and excited state $|e\rangle_A$, such that the acceptor site Hamiltonian H_A is given as

$$H_A = \epsilon_A A^+ A, \quad (3)$$

where ϵ_A is the energy separation of the acceptor TLS, $A^+ = |e\rangle_{AA}\langle g|$, and $A = |g\rangle_{AA}\langle e|$.

The incident light is modelled as a single photon of frequency ω with creation (annihilation) operators $b^\dagger$ (b) such that the photon Hamiltonian H_p is given as

$$H_p = \omega b^\dagger b. \quad (4)$$

It is assumed that the light may not necessarily be resonant with the acceptor atom, therefore, there is a detuning parameter defined as $\Delta = \omega - \epsilon_A$.

The photon couples to the j th TLS of the donor ring via the coupling constant J_j , and the resulting photon-ring interaction Hamiltonian H_{pD} is given as

$$H_{pD} = \sum_{j=1}^N J_j (e_j b^\dagger + h.c.). \quad (5)$$

The j th TLS of the donor ring also couples to the acceptor site via the coupling constant ξ_j , and the donor-acceptor interaction Hamiltonian H_{DA} is given as

$$H_{DA} = \sum_{j=1}^N \xi_j (e_j A^\dagger + h.c.). \quad (6)$$

From equation (1), the Hamiltonian H is then given as⁷

$$H = \sum_{j=1}^N [\epsilon_j e_j^\dagger e_j + g_{j,j+1} (e_j^\dagger e_{j+1} + h.c.)] + \epsilon_A A^\dagger A + \omega b^\dagger b + \sum_{j=1}^N J_j (e_j b^\dagger + h.c.) + \sum_{j=1}^N \xi_j (e_j A^\dagger + h.c.). \quad (7)$$

2.2 Lindbladian Equations

From equation (7), we can define a wavefunction $|\Psi(t)\rangle$ as

$$|\Psi(t)\rangle = c_0(t) |0_p 0_{D_1} \dots 0_{D_N} 0_A 0_{RC}\rangle + u(t) |1_p 0_{D_1} \dots 0_{D_N} 0_A 0_{RC}\rangle + \sum_{j=1}^N \left[v_j(t) |0_p 0_{D_1} \dots 1_{D_j} \dots 0_{D_N} 0_A 0_{RC}\rangle \right] + w(t) |0_p 0_{D_1} \dots 0_{D_N} 1_A 0_{RC}\rangle + c_{RC}(t) |0_p 0_{D_1} \dots 0_{D_N} 0_A 1_{RC}\rangle. \quad (8)$$

In equation (8), the state $|0_p 0_{D_1} \dots 0_{D_N} 0_A 0_{RC}\rangle$ with amplitude $c_0(t)$ refers to the vacuum state of the LH1-RC excluding interaction with the protein environment. The state $|1_p 0_{D_1} \dots 0_{D_N} 0_A 0_{RC}\rangle$ with amplitude $u(t)$ refers to the photon state with no excitations on the donor ring or acceptor site. The state $|0_p 0_{D_1} \dots 1_{D_j} \dots 0_{D_N} 0_A 0_{RC}\rangle$ with amplitude $v_j(t)$ refers to an excitation on the j th donor ring site with no excitations on the acceptor site and no free photon. The state $|0_p 0_{D_1} \dots 0_{D_N} 1_A 0_{RC}\rangle$ with amplitude $w(t)$ refers to an excitation on the acceptor site with no excitations on the donor ring and no free photons. The state $|0_p 0_{D_1} \dots 0_{D_N} 0_A 1_{RC}\rangle$ with amplitude $c_{RC}(t)$ refers to no free photons, and the excitation transferred out of the LH1 complex into the reaction centre (RC), which is referred to as the “sink” state.

Three Lindblad superoperators, $\mathcal{L}_D$, $\mathcal{L}_A$ and $\mathcal{L}_P$, are introduced to account for the spontaneous decay from the donor ring due to the protein environment, charge separation events at the acceptor atom and the dephasing due to phonon bath interactions respectively¹⁴. These superoperators can be modelled as Markovian baths, such that decay rates are invariant with site energy but the bath is dependent on absolute temperature T . The superoperators are given as

$$\mathcal{L}_D(\rho) = \sum_{j=1}^N \frac{\kappa \omega_j}{1 - e^{-\frac{\omega_j}{k_B T}}} \left[-\{e_j^\dagger e_j, \rho\} + 2e_j \rho e_j^\dagger \right] \quad (9)$$

$$\mathcal{L}_A(\rho) = \frac{\Gamma \omega_A}{1 - e^{-\frac{\omega_A}{k_B T}}} \left[-\{A^\dagger R R^\dagger A, \rho\} + 2R^\dagger A \rho A^\dagger R \right] \quad (10)$$

$$\mathcal{L}_P(\rho) = \sum_{j=1}^N \frac{\gamma \omega_j}{1 - e^{-\frac{\omega_j}{k_B T}}} \left[-\{e_j^\dagger e_j, \rho\} + 2e_j^\dagger e_j \rho e_j^\dagger e_j \right] \quad (11)$$

where $R^\dagger$ and R are the raising and lowering operators associated with the “sink” state, κ is the rate of spontaneous decay, Γ is the rate of charge separation at the acceptor and γ is the rate of dephasing. Therefore, the final Lindbladian form of the Schrödinger equation is

$$\dot{\rho}(t) = -i[H, \rho(t)] + \mathcal{L}_D(\rho(t)) + \mathcal{L}_A(\rho(t)) + \mathcal{L}_P(\rho(t)) \quad (12)$$

with an initial state of $|\Psi(t=0)\rangle = |1_p 0_{D_1} \dots 0_{D_N} 0_A 0_{RC}\rangle$ to represent a photon incident on the LH1-RC. The transfer efficiency η is subsequently used to determine the effectiveness of the LH1-RC at relaying the photon excitation to a charge separation event at the acceptor, while avoiding spontaneous decay at the donor ring, and is defined as^{6,15}

$$\eta = \int_0^\infty 2\Gamma |w(t)|^2 dt. \quad (13)$$

Figure 1. Transfer efficiency η against the scaled detuning Δ/ξ and the emission rate ratio κ/Γ for (a) no coupling disorder, (b) disorder in J_j , and (c) disorder in $g_{j,j+1}$. Transfer efficiency η against Δ/ξ for the three emission rate ratios $\kappa/\Gamma = 0.5$ (—), $\kappa/\Gamma = 1$ (---), and $\kappa/\Gamma = 2$ (-·-) for (d) no coupling disorder, (e) disorder in J_j , and (f) disorder in $g_{j,j+1}$. Transfer efficiency η against κ/Γ for the three detunings $\Delta = -2.0\xi$ (—), $\Delta = 0$ (---), and $\Delta = 2.0\xi$ (-·-) for (g) no coupling disorder, (h) disorder in J_j , and (i) disorder in $g_{j,j+1}$. It should be noted that the curves for $\Delta = -2.0\xi$ and $\Delta = 2.0\xi$ overlap in (g) and (i).

Figure 2. Contour plot showing the difference in transfer efficiency $\delta\eta$ between the no-disorder case and for disorder in J_j . The legend shows 9 uniformly shaded segments representing regular intervals of 0.1 from 0 to 0.9.

3 Results

3.1 Transfer efficiency with and without disorder

Three cases are investigated: a case with no disorder, one with disorder in the values of J_j , and one with disorder in the values of $g_{j,j+1}$. For all three cases, as in Dong *et al.*⁷, it is assumed that $\xi_j = \xi = 10 \text{ ps}^{-1}$, $\epsilon_A = 12\xi$, $\epsilon = 11.4\xi$, $\Gamma = 0.3\xi$, $\gamma = 0$, and $N = 8$. For the first case with no disorder, the results are based on the solution of the Schrödinger equation with the Hamiltonian H given in equation (7) with $J = 0.1\xi$ and $g = 0.3\xi$. For the second case with disorder in J_j , $g_{j,j+1} = 0.3\xi$ and the values of J_j are randomly selected based on a uniform probability distribution with a lower limit of 0 and an upper limit of $2J$. For the third case with disorder in $g_{j,j+1}$, $J_j = 0.1\xi$ and the values of $g_{j,j+1}$ are randomly selected based on a uniform probability distribution with a lower limit of 0 and an upper limit of $2g$. The results for the two disorder cases were found by averaging over ten realizations of disorder.

Figure 1 shows plots of the variation of the transfer efficiency η with the scaled detuning Δ/ξ and the emission rate ratio κ/Γ for the three cases. Figures 1(a), 1(d), and 1(g) display results for the no disorder case. Figure 1(a) shows the variation of η with κ/Γ and Δ/ξ . Figure 1(d) shows the variation of η with Δ/ξ for $\kappa/\Gamma = 0.5, 1, 2$. It is observed that η achieves a maximum close to 1 at $\Delta = 0$ for all the values of κ/Γ . A narrowing of the resonance curve as κ/Γ increases is also observed with a full width at half maximum (FWHM) of approximately 8 when $\kappa/\Gamma = 0.5$, which decreases to approximately 4 when $\kappa/\Gamma = 2$. Figure 1(g) shows the variation of η with κ/Γ for $\Delta = -2.0\xi, 0, 2.0\xi$. It is observed that the maximum in η which occurs at $\Delta = 0$ shows a linear decline with increasing κ/Γ , whereas, η displays the same exponential variation with κ/Γ for $\Delta = -2.0\xi, 2.0\xi$.

Figures 1(b), 1(e), and 1(h) display results for disorder in J_j . Figure 1(b) shows the variation of η with κ/Γ and Δ/ξ , where η is suppressed for all values of κ/Γ in the region $-2.5\xi < \Delta < 1.5\xi$ and has a minimum value of $\eta = 0.1$ at $\Delta = -0.6\xi$ and $\kappa/\Gamma = 0.3$. Figure 1(e) shows the variation of η with Δ/ξ for $\kappa/\Gamma = 0.5, 1, 2$. It is observed that for $\Delta > 1.5\xi$ and $\Delta < -2.5\xi$, η is unchanged from the no-disorder case shown in Fig. 1(d), but in the range $-2.5\xi < \Delta < 1.5\xi$, η is suppressed, with a minimum occurring at $\Delta \approx -0.5\xi$ for all values of κ/Γ . Figure 1(h) shows the variation of η with κ/Γ for $\Delta = -2.0\xi, 0, 2.0\xi$. Like the no-disorder case in Figure 1(g), η decreases exponentially for increasing κ/Γ for $\Delta = -2.0\xi$ and $\Delta = 2.0\xi$, with the former displaying a slightly greater decrease. When $\Delta = 0$, η decreases from 1 to a minimum of 0.19 at $\kappa/\Gamma \approx 1.4$ with a small steady increase when $\kappa/\Gamma > 1.4$.

Figures 1(c), 1(f), and 1(i) display results for disorder in $g_{j,j+1}$. Figure 1(c) shows the variation of η with κ/Γ and Δ/ξ , which is almost identical to the variation with no disorder as seen in Fig 1(a). Figure 1(f) shows the variation of η with Δ/ξ for $\kappa/\Gamma = 0.5, 1, 2$. It is observed that η achieves a maximum close to 1 when $\Delta = 0$ for all the values of κ/Γ . A narrowing of the resonance curve as κ/Γ increases is also observed with an FWHM of approximately 8 when $\kappa/\Gamma = 0.5$, which decreases to approximately 4 when $\kappa/\Gamma = 2$. Figure 1(i) shows the variation of η with κ/Γ for $\Delta = -2.0\xi, 0, 2.0\xi$. The variation of η is almost identical to the no-disorder case (Fig. 1(g)) for $\Delta = -2.0\xi, 0, 2.0\xi$.

The contour plot of Fig. 2 shows the difference in transfer efficiency $\delta\eta$ between the no-disorder case and the case of disorder in J_j . In Fig. 2, the maximum value of $\delta\eta$ is greater than 0.8 and lies in the region $-1.2\xi < \Delta < 0$ and $0 < \kappa/\Gamma < 2$. $\delta\eta$ decreases for $\Delta > 0$ and $\Delta < -\xi$. It should be noted that $\delta\eta < 0.1$ for $\Delta > 1.6\xi$ or $\Delta < -2\xi$ independent of the value of κ/Γ .

3.2 Probability Analysis with and without Disorder

In Fig. 3, the amplitudes of the wavefunctions in equation (8) were simulated for the three cases: no disorder, disorder in J_j , and disorder in $g_{j,j+1}$ as they were defined in section 3.1. Each graph in Fig. 3 plots the photon probability amplitude $|u(t)|$, the acceptor site probability amplitude $|w(t)|$, and the donor ring probability amplitude $\left(\sum_{j=1}^N |v_j(t)|^2\right)^{1/2}$.

Table 1. Lifetimes of the probability amplitudes for no disorder and $\kappa/\Gamma = 0.5$.

Δ	τ_u (ps)	τ_v (ps)	τ_w (ps)
-2.0ξ	55	47	42
0	235	115	155
2.0ξ	55	47	42

Table 2. Lifetimes of the probability amplitudes for disorder in J_j and $\kappa/\Gamma = 0.5$.

Δ	τ_u (ps)	τ_v (ps)	τ_w (ps)
-2.0ξ	123	60	60
0	165	89	61
2.0ξ	139	62	69

Table 3. Lifetimes of the probability amplitudes for disorder in $g_{j,j+1}$ and $\kappa/\Gamma = 0.5$.

Δ	τ_u (ps)	τ_v (ps)	τ_w (ps)
-2.0ξ	56	40	44
0	235	89	156
2.0ξ	55	40	42

The three probability amplitudes were evaluated using detuning values $\Delta = -2.0\xi, 0, 2.0\xi$ and $\kappa/\Gamma = 0.5$. For all three cases, $|u(t)|$ decreases exponentially to 0.001 with lifetime τ_u , while $\left(\sum_{j=1}^N |v_j(t)|^2\right)^{1/2}$ and $|w(t)|$ undergo initial short-lived oscillations and then decrease exponentially to 0.001 with lifetimes τ_v and τ_w , respectively. Tables 1, 2 and 3 show τ_u , τ_v and τ_w , for no disorder, disorder in J_j , and disorder in $g_{j,j+1}$, respectively.

Figure 4 shows the lifetimes as a function of κ/Γ for disorder in J_j , with $\Delta = 0$. For each plot, the lifetime sharply decreases to a minimum from the initial value and is followed by a steady increase as κ/Γ increases. In Fig. 4(a), the minimum value of τ_u is 142 ps at $\kappa/\Gamma = 1.6$. In Fig. 4(b), the minimum value of τ_v is 56 ps at $\kappa/\Gamma = 3.8$. In Fig. 4(c), the minimum value of τ_w is 52 ps at $\kappa/\Gamma = 1.6$.

3.3 Transfer Efficiency Dependence on the Strength of Disorder in the Photon-Ring Coupling

A parameter σ was introduced in order to control the strength of the disorder. The values of J_j were selected from a uniform probability distribution with an upper limit of $J + \sigma J$ and a lower limit of $J - \sigma J$, where $0 \leq \sigma \leq 1$. As in Dong *et al.*⁷, it is assumed that $\xi_j = \xi = 10 \text{ ps}^{-1}$, $J = 0.1\xi$, $g_{j,j+1} = 0.3\xi$, $\epsilon_A = 12\xi$, $\epsilon = 11.4\xi$, $\Gamma = 0.3\xi$, $\gamma = 0$ and $N = 8$. In Fig. 5, three strengths of disorder were analyzed: $\sigma = 0.1, 0.5, 0.9$. It should be noted that the results for $\sigma = 1$ have already been presented in section 3.1 and 3.2.

Figures 5(a), 5(d), and 5(g) display results for disorder in J_j with $\sigma = 0.1$. In Fig. 5(a), a slight suppression of η occurs for $\kappa/\Gamma < 1.0$ and $-\xi < \Delta < 0$. In Fig. 5(d), suppression of η occurs when $\kappa/\Gamma = 0.5, 1$ but no suppression of η occurs when $\kappa/\Gamma = 2$. In Fig. 5(g), the exponential decreases of η with κ/Γ for $\Delta = -2.0\xi, 2.0\xi$ coincide. At $\Delta = 0$, a steady-state value of $\eta = 0.9$ is achieved for $\kappa/\Gamma \geq 0.5$ after an initial decrease from 1.

Figures 5(b), 5(e), and 5(h) display results for disorder in J_j with $\sigma = 0.5$. In Fig. 5(b), suppression of η occurs for all values of κ/Γ in the region $-2\xi < \Delta < 0$, with a minimum value of $\eta = 0.2$ at $\Delta = -0.25\xi$ and $\kappa/\Gamma = 0.4$. In Fig. 5(e), suppression of η occurs for all values of κ/Γ , with minima at $\Delta \approx -0.5\xi$. In Fig. 5(h), the exponential decreases of η for $\Delta = -2.0\xi, 2.0\xi$ almost coincide. At $\Delta = 0$, after an initial decrease from 1, a minimum of $\eta = 0.32$ at $\kappa/\Gamma = 0.75$ is achieved, followed by a small steady increase when $\kappa/\Gamma > 0.75$.

Figure 3. Plots of the amplitudes $|u(t)|$ (---), $\left(\sum_{j=1}^N |v_j(t)|^2\right)^{1/2}$ (---), and $|w(t)|$ (—) with $\kappa = 0.5\Gamma$ and $\Delta = -2.0\xi$ for (a) no coupling disorder, (b) disorder in J_j , and (c) disorder in $g_{j,j+1}$. Plots of $|u(t)|$ (---), $\left(\sum_{j=1}^N |v_j(t)|^2\right)^{1/2}$ (---), and $|w(t)|$ (—) with $\kappa = 0.5\Gamma$ and $\Delta = 0$ for (d) no coupling disorder, (e) disorder in J_j , and (f) disorder in $g_{j,j+1}$. Plots of $|u(t)|$ (---), $\left(\sum_{j=1}^N |v_j(t)|^2\right)^{1/2}$ (---), and $|w(t)|$ (—) with $\kappa = 0.5\Gamma$ and $\Delta = 2.0\xi$ for (g) no coupling disorder, (h) disorder in J_j , and (i) disorder in $g_{j,j+1}$. It should be noted that the vertical axes on the left are for $|u(t)|$ (---) and the vertical axes on the right are for $\left(\sum_{j=1}^N |v_j(t)|^2\right)^{1/2}$ (---) and $|w(t)|$ (—).

Figure 4. Plots of (a) τ_u , (b) τ_v , and (c) τ_w against κ/Γ for $\Delta = 0$ for the case with disorder in J_j

Figure 5. Plots showing η against Δ/ξ and κ/Γ with disorder in J_j for (a) $\sigma = 0.1$, (b) $\sigma = 0.5$, and (c) $\sigma = 0.9$. Plots showing η against Δ/ξ for $\kappa/\Gamma = 0.5$ (—), $\kappa/\Gamma = 1$ (---), and $\kappa/\Gamma = 2$ (-.-) with disorder in J_j for (d) $\sigma = 0.1$, (e) $\sigma = 0.5$, and (f) $\sigma = 0.9$. Plots showing η against κ/Γ for $\Delta = -2.0\xi$ (—), $\Delta = 0$ (---), and $\Delta = 2.0\xi$ (-.-) with disorder in J_j for (g) $\sigma = 0.1$, (h) $\sigma = 0.5$, and (i) $\sigma = 0.9$. It should be noted that the curves for $\Delta = -2.0\xi$ and $\Delta = 2.0\xi$ overlap in (g)

Figures 5(c), 5(f), and 5(i) display results for disorder in J_j with $\sigma = 0.9$. In Fig. 5(c), suppression of η occurs for all values of κ/Γ in the region $-2\xi < \Delta < 0$, with a minimum value of $\eta = 0.1$ at $\Delta = -0.5\xi$ and $\kappa/\Gamma = 0.8$. In Fig. 5(f), suppression of η for all values of κ/Γ is greater compared to the $\sigma = 0.5$ case in Fig. 5(e), with minima at $\Delta \approx -0.5\xi$. In Fig. 5(i), the exponential decreases of η for $\Delta = -2.0\xi, 2.0\xi$ do not coincide. At $\Delta = 0$, after an initial decrease from 1, a minimum of $\eta = 0.17$ at $\kappa/\Gamma = 1.4$ is achieved, followed by a small steady increase when $\kappa/\Gamma > 1.4$.

Figure 6 shows the numerical values of the minimum value of the transfer efficiency $\eta_{\min}$ versus σ for $\kappa/\Gamma = 0.5$. For $0.05 \leq \sigma \leq 1$, $\eta_{\min}$ occurs at $\Delta \approx -0.5\xi$. In Fig. 1(e) where $\sigma = 1$, $\eta_{\min} = 0.12$ when $\kappa/\Gamma = 0.5$. A best fit of the numerical values of $\eta_{\min}$ against σ gives an exponential curve (with an adjusted R^2 value greater than 0.99) of the form

$$\eta_{\min}(\sigma) = e^{-b\sigma}, \quad (14)$$

where b is a dimensionless constant. In Fig. 6 where $\kappa/\Gamma = 0.5$, $b = 2.36$. When $\kappa/\Gamma = 1$, $b = 2.38$, and when $\kappa/\Gamma = 2$, $b = 2.19$.

Figure 7 shows the lifetimes τ_u , τ_v , and τ_w against $\eta_{\min}$ for $\kappa/\Gamma = 0.5$. Best-fit lines of the numerical values were also

Figure 6. Plot of $\eta_{\min}$ values against σ (○) and the corresponding best-fit curve (—) for $\kappa/\Gamma = 0.5$

Figure 7. Plots of τ_u , τ_v , τ_w against $\eta_{\min}$ (○, ■, △), and the respective best-fit lines (—, ---, -.-) for $\kappa/\Gamma = 0.5$

found with best-fit expressions of

$$\tau_u = 211.1\eta_{\min} + 20.3, \quad (15)$$

$$\tau_v = 103.0\eta_{\min} + 25.1, \quad (16)$$

$$\tau_w = 145.6\eta_{\min} + 7.3, \quad (17)$$

with adjusted R^2 values greater than 0.9.

3.4 Transfer efficiency with a Phonon Dephasing Bath

As in Sec. 3.1, the same three cases are investigated: a case with no disorder, one with disorder in the values of J_j , and one with disorder in the values of $g_{j,j+1}$. As in the previous sections, $\xi_j = \xi = 10 \text{ ps}^{-1}$, $\epsilon_A = 12\xi$, $\epsilon = 11.4\xi$, $\Gamma = 0.3\xi$ and $N = 8$, with $\gamma = 0.5\xi$ in order to include the dephasing effect of a phonon bath. For the first case with no disorder, the results are based on the solution of the Schrödinger equation with the Hamiltonian H given in equation (7) with $J = 0.1\xi$ and $g = 0.3\xi$. For the second case with disorder in J_j , $g_{j,j+1} = 0.3\xi$ and the values of J_j are randomly selected based on a uniform probability distribution with a lower limit of 0 and an upper limit of $2J$. For the third case with disorder in $g_{j,j+1}$, $J_j = 0.1\xi$ and the values of $g_{j,j+1}$ are randomly selected based on a uniform probability distribution with a lower limit of 0 and an upper limit of $2g$. The results for the two disorder cases were found by averaging over ten realizations of disorder.

Figure 8 shows plots of the variation of the transfer efficiency η with the scaled detuning Δ/ξ and the emission rate ratio κ/Γ for the three cases without and with dephasing.

Figure 8(a) shows the variation of η with Δ/ξ for the no-disorder case with $\kappa/\Gamma = 0.5$. It is observed that η achieves a maximum of 1 when $\gamma = 0$ and approximately 0.97 when $\gamma = 0.5\xi$ at $\Delta = 0$. Also, the full width at half maximum (FWHM)

Figure 8. Transfer efficiency η in the absence (—) and presence of a phonon dephasing bath with strength $\gamma = 0.5\xi$ (---) against Δ/ξ for the emission rate ratio $\kappa/\Gamma = 0.5$ for (a) no coupling disorder and (b) disorder in J_j . Transfer efficiency η in the absence (—) and presence of a phonon dephasing bath with strength $\gamma = 0.5\xi$ (---) against κ/Γ for (c) no coupling disorder with detuning $\Delta = -2.0\xi$ and (d) disorder in J_j with detuning $\Delta = 0$.

decreases from approximately 8 when $\gamma = 0$ to approximately 5.5 when $\gamma = 0.5\xi$. The same results are also obtained for the case of disorder in $g_{j,j+1}$. Figure 8(c) shows the variation of η with κ/Γ for the no-disorder case with $\Delta = -2.0\xi$. Approximately exponential decreases of η are observed, with the decrease being much sharper for the finite dephasing bath strength of $\gamma = 0.5\xi$. The same results are also obtained for the case of disorder in $g_{j,j+1}$.

Figure 8(b) shows the variation of η with Δ/ξ for the case of disorder in J_j with $\kappa/\Gamma = 0.5$. It is observed that for both $\Delta > 2.0\xi$ and $\Delta < -2.5\xi$, η displays the same variation as the no-disorder case shown in Fig. 8(a), however in the range $-2.5\xi < \Delta < 2.0\xi$, η is suppressed compared to the no-disorder case. In the absence of a dephasing bath, a minimum of $\eta = 0.1$ is observed and for the finite dephasing bath strength of $\gamma = 0.5\xi$, a minimum of $\eta = 0.25$ is observed, with both minima occurring at $\Delta \approx -0.5\xi$. Figure 8(d) shows the variation of η with κ/Γ for the case of disorder in J_j with $\Delta = 0$. With and without the dephasing bath, a sharp decrease from 1 to a minimum at $\kappa/\Gamma \approx 1.4$, with a small steady increase when $\kappa/\Gamma > 1.4$ is observed. In the absence of a dephasing bath, the minimum value of η is 0.2 and for the finite dephasing bath strength of $\gamma = 0.5\xi$, the minimum value of η is 0.22.

4 Conclusion

In this paper, the authors modelled the interaction of a single incident photon with the LH1-RC photosynthetic unit, consisting of a donor ring coupled to an acceptor site. We extended the analysis given in Dong *et al.*⁷ to include the effects of intra-ring and photon-ring coupling disorder on the transfer efficiency. It was found that photon-ring coupling disorder significantly affected the transfer efficiency, while the intra-ring coupling disorder had negligible effects.

Disorder in the photon-ring coupling significantly suppressed the transfer efficiency in the detuning range $-25 \text{ ps}^{-1} < \Delta < 15 \text{ ps}^{-1}$, with a minimum occurring at $\Delta \approx -5 \text{ ps}^{-1}$ (Fig. 1) for all values of the rate of spontaneous decay κ . The suppression of the transfer efficiency at $\Delta = 0$ is associated with a significant decrease in τ_u , τ_v , and τ_w (tables 1 and 2) associated with disorder in J_j . The negligible values of $\left(\sum_{j=1}^N |v_j(t)|^2\right)^{1/2}$ (Figs. 3(d) and 3(f)) for the no disorder case and for disorder in

$g_{j,j+1}$ is consistent with a dark-state channel for maximum transfer efficiency. This dark-state channel is destroyed by the disorder in J_j (Fig. 3(e)) resulting in a significant decrease in the lifetimes and a suppression of the transfer efficiency.

Outside of the detuning range $-25 \text{ ps}^{-1} < \Delta < 15 \text{ ps}^{-1}$ with and without disorder, the transfer efficiency decreases exponentially with increasing spontaneous decay rate κ . At zero detuning, the transfer efficiency exhibits a marginal linear decrease with increasing κ when there is no disorder or when there is disorder in $g_{j,j+1}$ (Figs. 1(g) and 1(i)). However, with disorder in J_j at $\Delta = 0$, the transfer efficiency decreases significantly to a minimum and then monotonically increases with increasing κ (Fig. 1(h)).

Increasing σ (the strength of the photon-ring disorder) resulted in an exponential decrease of $\eta_{\min}$, which does not vary significantly with κ . In addition, the detuning range in which suppression occurs increases with increasing σ (Figs. 5(d)–5(f)), with a maximum range of $-25 \text{ ps}^{-1} < \Delta < 15 \text{ ps}^{-1}$ at $\sigma = 1$ (Fig. 1(e)). The lifetimes τ_u , τ_v , and τ_w were found to vary linearly with $\eta_{\min}$.

The presence of a phonon dephasing bath was generally found to decrease the transfer efficiency. However, for the case of photon-ring disorder in the detuning region $-1.4\xi < \Delta < 0.1\xi$, the transfer efficiency is enhanced in the presence of a dephasing bath, as is seen in Fig. 8(b). In addition, there is no significant change in the variation of the transfer efficiency with respect to the decay rate ratio, with and without dephasing.

Data Availability

The Wolfram Mathematica Code for this research is available upon request from the authors.

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Author contributions statement

E.W. developed and ran the simulations with the assistance of A.A. and the supervision of R.A. All authors reviewed the manuscript.

Additional Information

The authors declare no competing interests.