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Theory of excitation energy transfer in the primary processes of photosynthesis. III. Mono-exponential regime

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Abstract

Analytical expressions for the eigenvalues and eigenvectors of the rate constants matrix describing the excitation energy transfer for a cyclic geometry of the photosynthetic unit are obtained. For a general geometry of the photosynthetic unit, the perturbation theory is used. Solutions of the Pauli Master Equation for both cases are found and discussed in detail. It is shown that for sufficiently long times these solutions as well as corresponding fluorescence intensity and other related experimental quantities behave mono-exponentially.

1. Introduction

The elucidation of the principles of the excitation energy transfer in the photosynthetic unit (PSU) is important for the understanding of the mechanism by which cells convert light to chemical energy. The photosynthetic unit consists of a light-harvesting antenna system, with a specific arrangement of pigment molecules, together with a reaction center (RC), where the electron–hole pair is formed.

It is well known that light is absorbed by pigment molecules in PSU thereby resulting in its excitation which migrates within PSU and is eventually trapped in RC. Several kinetic equations have been used to describe the excitation migration within PSU (see e.g. Refs. [1–6]). A kinetic equation describing well the incoherent excitation migration in PSU is the Pauli Master Equation (PME) [7]. Calculations performed till now indicate that the application of the incoherent description of motion is justified for times larger than a few tens of ps following the photon absorption [1,2]. This equation has been applied to the description of the excitation energy transfer in several bacterial light-harvesting systems [1–4].

In general, the solution of PME for the probability of finding the excitation at a given site has a multiexponential form. This has been illustrated in case of a simplified cyclic model of PSU of purple bacteria *Rhodopseudomonas viridis* [2]. Due to the cyclic symmetry of PSU, expressions for the experimental observables like the fluorescence intensity have in this case bi-exponential form. One exponential decays in a few ps while the other decays much slower. This indicates the possibility of substituting the bi-exponential dependence by the mono-exponential one after a certain time t_0 following the photon trapping. In this paper, we want to address some general questions regarding this mono-exponential regime.

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To solve PME diagonalization of the rate constants matrix is needed. The existence of the mono-exponential regime depends on the character of the eigenvalue spectrum of this matrix. The mono-exponential regime appears if the largest eigenvalue is well separated from the others [1]. The existence of the mono-exponential regime is supported also by the experimental results [8–10].

The aim of this paper is to discuss in detail characteristic properties of the eigenvalue spectrum for the cyclic two-dimensional as well as for a general two- and three-dimensional case. Our main interest is in discussing the values of the first two largest eigenvalues and their difference together with their dependence on the PSU geometry. First we investigate the planar cyclic model of PSU (Sections 2 and 3). Due to the symmetry of the problem, the analytic solution of PME is in this case possible and the eigenvalues and eigenvectors of the rate constants matrix can be found. In the second step, we assume general three-dimensional geometry of PSU. Making use of the analytic results for the cyclic geometry as the zero order approximation and using the perturbation theory we derive formulae for the eigenvalues of the rate constants matrix for a general geometry (Section 4). Detailed analysis of the existence of the mono-exponential regime and other questions is performed. The conclusions and results are summarized in Section 5.

2. PSU model with a cyclic symmetry

In this Section, we use the same cyclic PSU model as in Ref. [2]. This model is constructed under the assumption that the antenna system consists of N bacteriochlorophyll (BChl) molecules arranged regularly in a circle of a radius R_c. The reaction center consists of a BChl dimer located at the center of the antenna ring. To estimate the transfer rate constants we use the Förster formula [11,12,1,2]:

$$k(R) = \frac{3}{2}\frac{[\boldsymbol{u}_m\cdot\boldsymbol{u}_n - 3(\boldsymbol{u}_m\cdot\boldsymbol{r})(\boldsymbol{u}_n\cdot\boldsymbol{r})]^2}{\tau_F}(R_0/R)^6 , \tag{2.1}$$

where $\boldsymbol{u}_m$ and $\boldsymbol{u}_n$ are the unit vectors giving the direction of the ($S_0 \rightarrow S_1$) transition dipole moments of the mth and nth molecule. Further, $\boldsymbol{r}$ represents a unit vector collinear with a direction connecting these two molecules, R denotes their distance, $\tau_F = 5$ ns is the fluorescence lifetime and R_0 is the Förster radius. The following parameters appearing in the Förster formula are used: $R_0 = 46$ Å (Förster radius), $R_c = 50$ Å (radius of the antenna ring) and $N = 24$ (number of the antenna BChl molecules) [2,13–15]. It is assumed that one photon is absorbed by PSU at time $t = 0$.

We suppose that each antenna molecule can exist at S_0, S_1 and T_1 energy states. The reaction center can exist at these three states and also at the charge-transfer state (CT). The CT level is important during the electron–hole separation. Excitations to the higher excited states, i.e. S_2, S_3, ... and T_2, T_3, ... , are not considered.

The Pauli Master Equation describing the excitation energy transfer can be written in the form

$$\frac{dP_m(t)}{dt} = \sum_{n=1}^{N+1} F_{mn}P_n(t) , \quad m = 1,\ldots,N+1 , \tag{2.2}$$

where $P_m(t)$ denotes the probability of finding the excitation at RC ($m = 1$) or at the mth BChl molecule ($m = 2,\ldots,N+1$). The constant F_{mn} denotes the intermolecular rate constant between the mth and nth molecule and fulfills the following conditions:

$$\begin{aligned} &F_{nm} = F_{mn} , \quad m,n = 1,\ldots,N+1 ,\\ &F_{11} = -\sum_{n(\neq 1)} F_{1n} - k_{RC} ,\\ &F_{mm} = -\sum_{n(\neq m)} F_{mn} - k_A ,\\ &\quad m = 2,\ldots,N+1 , \end{aligned} \tag{2.3}$$

reflecting the symmetry of the excitation energy transfer and conservation of the total probability. Constants k_A and k_{RC} include radiative and nonradiative losses from the S_1 state of the antenna BChl molecule and the BChl dimer in RC, respectively. These constants are equal to $k_A = k_F^A + k_I^A$ and $k_{RC} = k_{CT} + k_F^{RC} + k_I^{RC}$ [1,2]. Here, the fluorescence and intersystem crossing are described by the rate constants k_F and k_I. The energy transfer into the trap represented by the CT level is described by the rate constant k_{CT}. The values of the rate constants k_F, k_I and k_{CT} are the same as in Ref. [2]: $k_{CT} = 3.3\times10^{11}$ s^{-1} (transition $S_1 \rightarrow$ CT), $k_F^A = 6.7\times10^7$ s^{-1} (transition $S_1 \rightarrow S_0$ in the antenna), $k_F^{RC} = 1.34\times10^8$ s^{-1} (transition $S_1 \rightarrow S_0$ in

RC), $k_1^{RC} = k_1^A = 1.34 \times 10^8\ s^{-1}$ (transition $S_1 \rightarrow T_1$ in RC and in the antenna).

The symmetry of the rate constants matrix $F_{mn} = F_{nm}$ follows from the first principles. The asymmetry of the excitation energy transfer appears as a result of the statistics applied to the observable quantities (like the fluorescence intensity proportional to $\sum_m P_m$) for PSU interacting with the thermal bath. The asymmetry of the matrix F assumed in Ref. [19] is an approximation useful from the numerical point of view, however, it should be used with caution.

Eq. (2.1) can be simplified assuming randomly oriented transition dipole moments in the plane of PSU [16,17,1]:

$$k(R) = (15/8\tau_F)(R_0/R)^6 . \tag{2.4}$$

The expression for the rate constant $k(R)$ depends on R in the form $1/R^6$; it is obvious that the nearest-neighbor interaction considered in what follows is a reasonable approximation. The Pauli Master Equation (2.2) can be written in a matrix form,

$$\frac{d\mathbf{P}}{dt} = \mathbf{FP}. \tag{2.5}$$

Here, $\mathbf{P}$ is a column matrix of probabilities $P_m(t)$ and $\mathbf{F} = \{F_{mn}\}$ is the rate constants matrix. The off-diagonal elements of $\mathbf{F}$ equal (see Ref. [2])

$$F_{1m} = 2k(R_c) = B\,, \quad m = 2,\ldots,N+1\,,$$

$$F_{m\,m+1} = F_{2\,N+1} = k(2R_c|\sin(\pi/N)|) = D\,,$$
$$m = 2,\ldots,N\,. \tag{2.6}$$

For the sake of simplicity we denote also

$$F_{11} = -\sum_{n(\neq 1)} F_{1n} - k_{RC} = A\,,$$

$$F_{mm} = -\sum_{n(\neq m)} F_{mn} - k_A = C\,, \quad m = 2,\ldots,N+1\,.$$

The rate constants matrix described above has the following form:

$$\mathbf{F} = \begin{pmatrix}
A & B & B & \ldots & \ldots & \ldots & \ldots & B \\
B & C & D & 0 & \ldots & \ldots & 0 & D \\
B & D & C & D & 0 & \ldots & \ldots & 0 \\
B & 0 & D & C & D & 0 & \ldots & \ldots \\
B & 0 & 0 & D & C & D & 0 & \cdot \\
\vdots & \vdots & & \ddots & \ddots & \ddots & \ddots & \vdots \\
B & 0 & \ldots & \ldots & 0 & D & C & D \\
B & 0 & \ldots & \ldots & \ldots & 0 & D & C
\end{pmatrix}. \tag{2.7}$$

The solution of PME is a sum of $N+1$ exponentials,

$$P_m(t) = \sum_{i=1}^{N+1} c_i \exp(\lambda_i t) h_m(i)\,,$$
$$m = 1,\ldots,N+1\,, \tag{2.8}$$

where c_i are coefficients given by the initial conditions $P_m(t=0)$. λ_i and $h_m(i)$ are the eigenvalues and components of eigenvectors of the matrix $\mathbf{F}$.

It follows from the conservation of the total probability that eigenvalues λ_i are less than or equal to zero.

3. PME solutions for the cyclic model of PSU

In Ref. [2], the eigenvalues λ_i and eigenvectors $h_m(i)$ of the rate constants matrix $\mathbf{F}$ for the cyclic planar model of the PSU corresponding to the unit irreducible representation of C_{Nv} group were calculated. In this way, two of N eigenvalues λ_i appearing in the expression for the experimental observables were determined. The other eigenvalues, which are important if the symmetry of PSU is removed, were not calculated. The aim of this Section is to determine all eigenvalues and eigenvectors of the matrix $\mathbf{F}$.

The rate constants matrix $\mathbf{F}$ can be partitioned as follows:

$$\mathbf{F} = \begin{pmatrix} A & B \\ B & \mathbf{A} \end{pmatrix},$$

where A is the $(1,1)$ element of the matrix $\mathbf{F}$ corresponding to RC and $\mathbf{A}$ is a $N \times N$ submatrix.

First, we diagonalize the submatrix $\mathbf{A}$ corresponding to the antenna system. The matrix $\mathbf{A}$ can be diagonalized by the unitary transformation $\mathbf{U}^+\mathbf{AU}$, where $\mathbf{U}$ is a unitary matrix formed by the eigenvectors $|\lambda_m\rangle, m = 1,\ldots,N$ of the submatrix $\mathbf{A}$, column by column. The eigenvectors $|\lambda_m\rangle, m = 1,\ldots,N$ are

$$|\lambda_m\rangle = \frac{1}{\sqrt{N}} \begin{pmatrix} \exp[(2\pi/N)(m-1)\cdot \mathrm{i}] \\ \exp[(2\pi/N)(m-1)\cdot 2\mathrm{i}] \\ \vdots \\ \exp[(2\pi/N)(m-1)\cdot N\mathrm{i}] \end{pmatrix}, \quad (3.1)$$

where $\mathrm{i} = \sqrt{-1}$. The corresponding eigenvalues are

$$\lambda_m = C + 2D\cos[(2\pi/N)(m-1)], \quad m = 1,\ldots,N. \quad (3.2)$$

Most of the eigenvalues λ_m are two-fold degenerate. For very long time t, the most important role is played by the eigenvalues $\lambda_1 = C + 2D$ and $\lambda_2 = C + 2D\cos(2\pi/N)$. Substituting the expression for C we get $\lambda_1 = -k_A - B$ and $\lambda_2 = -k_A - B - 2D[1 - \cos(2\pi/N)]$. Their difference is

$$\lambda_1 - \lambda_2 = 2D[1 - \cos(2\pi/N)]. \quad (3.3)$$

Using Eq. (3.2) and the parameters mentioned in the previous Section we get for a cyclic geometry $\lambda_1 = -6.558 \times 10^8\ \mathrm{s}^{-1}$ and $\lambda_2 = -4.962 \times 10^{10}\ \mathrm{s}^{-1}$. We see that the eigenvalue λ_1 is separated from λ_2 and other eigenvalues by a gap of width of about $10^{10}\ \mathrm{s}^{-1}$.

Now we include RC to our calculation. Considering the entire matrix **F** instead of the antenna submatrix **A** and using the unitary transformation $\overline{\mathbf{U}}^{+}\mathbf{F}\overline{\mathbf{U}}$, where

$$\overline{\mathbf{U}} = \begin{pmatrix} 1 & 0 \\ 0 & \mathbf{U} \end{pmatrix},$$

we get

$$\overline{\mathbf{U}}^{+}\mathbf{F}\overline{\mathbf{U}} = \begin{pmatrix} A & \sqrt{N}B & 0 & \ldots & 0 \\ \sqrt{N}B & \lambda_1 & 0 & \ldots & 0 \\ 0 & 0 & \lambda_2 & 0 & \vdots \\ \vdots & & & \ddots & 0 \\ 0 & \ldots & \ldots & 0 & \lambda_N \end{pmatrix}.$$

This matrix has two eigenvalues λ^+ and λ^- related to diagonal elements A and λ_1. The other eigenvalues are the same as eigenvalues $\lambda_2,\ldots,\lambda_N$ (Eq. (3.2)) of the antenna submatrix **A**. The eigenvalues λ^+ and λ^- are

$$\lambda^{\pm} = \tfrac{1}{2}(A + C + 2D) \pm \tfrac{1}{2}\sqrt{(A - C - 2D)^2 + 4NB^2}$$
$$= -\tfrac{1}{2}[(N+1)B + k_{RC} + k_A] \pm \tfrac{1}{2}\sqrt{[k_A - k_{RC} - (N-1)B]^2 + 4NB^2}. \quad (3.4)$$

The element $-\frac{1}{2}[(N+1)B + k_{RC} + k_A]$ is less than or equal to zero. For this reason, λ^+ is the searched eigenvalue with the smallest absolute value and lies close to λ_1. The other eigenvalue λ^- lies close to A. Numerical calculation with the parameters given above yields $\lambda^+ = -6.412 \times 10^8\ \mathrm{s}^{-1}$ and $\lambda^- = -3.412 \times 10^{11}\ \mathrm{s}^{-1}$. We see that the eigenvalue of **F** with the smallest absolute value λ^+ is separated from $\lambda_2 = -4.962 \times 10^{10}\ \mathrm{s}^{-1}$ and other eigenvalues by a gap $\lambda^+ - \lambda_2$. This gap is of the same order as the gap $\lambda_1 - \lambda_2$ for the antenna system without RC.

4. PME solutions for general PSU geometry

In this Section, more general arrangement of the photosynthetic system, in which BChl molecules in the antenna system are displaced from their original (cyclic) positions, is investigated. We use the results of the previous Section as the zero order approximation, apply the perturbation theory to the rate constants matrix and determine the dependence of the eigenvalues on a perturbed PSU geometry.

The matrix elements F'_{mn} for a general geometry can be written as

$$F'_{1\,1} = A + A_1,$$
$$F'_{1\,m} = B + B_{m-1}, \quad m = 2,\ldots,N+1,$$
$$F'_{m\,m} = C + C_{m-1}, \quad m = 2,\ldots,N+1,$$
$$F'_{m\,m\pm1} = D + D_{m-1}, \quad m = 2,\ldots,N+1,$$
$$F'_{2\,N+1} = D + D_N, \quad (4.1)$$

where

$$A_1 = -\sum_{m=1}^{N} B_m \quad \text{and}$$
$$C_m = -B_m - D_m - D_{m-1}, \quad m = 1,\ldots,N.$$

Here, $D_0 = D_N$. Constants A, B, C and D are the matrix elements of the rate constants matrix for the cyclic geometry. Numbers $\{B_m\}_{m=1,\ldots,N}$ and $\{D_m\}_{m=1,\ldots,N}$ reflect displacements of the antenna BChl molecules from the original cyclic positions and equal zero for the cyclic geometry. Values of B_m and D_m depend on the actual geometry of PSU and can be obtained from Eqs. (2.4) and (2.6). We assume that B_m and D_m are

small so that the perturbation theory can be applied to the resulting rate constants matrix. This matrix can be written as $\mathbf{F}' = \mathbf{F} + \mathbf{W}$, where $\mathbf{F}$ is the unperturbed rate constants matrix (2.7) and

$$\mathbf{W} = \begin{pmatrix} A_1 & B_1 & \dots & \dots & \dots & \dots & \dots & B_N \\ B_1 & C_1 & D_1 & 0 & \dots & \dots & 0 & D_N \\ \cdot & D_1 & C_2 & D_2 & 0 & \dots & \dots & 0 \\ \cdot & 0 & D_2 & C_3 & D_3 & 0 & \cdot & 0 \\ \vdots & & & \ddots & \ddots & \ddots & & \vdots \\ \cdot & 0 & \cdot & 0 & D_{N-3} & C_{N-2} & D_{N-2} & 0 \\ \cdot & 0 & \dots & \dots & 0 & D_{N-2} & C_{N-1} & D_{N-1} \\ B_N & D_N & 0 & \dots & \dots & 0 & D_{N-1} & C_N \end{pmatrix}$$

is the perturbation matrix. As in the previous Section, we solve first the eigenvalue problem for the antenna system, $\{F'_{mn}\}, m, n = 2, \dots, N+1$. The corresponding antenna submatrix has the form $\mathbf{A}' = \mathbf{A} + \mathbf{W}_A$ where $\mathbf{A}$ is the unperturbed antenna matrix for the cyclic geometry and matrix $\mathbf{W}_A$ represents the perturbation of the antenna geometry. The eigenvectors of $\mathbf{A}$, Eq. (3.1), can be expressed in the real form

$$|\lambda_m\rangle = \sqrt{\frac{2}{N}} \begin{pmatrix} \cos[(2\pi/N)(m-1)\cdot 1] \\ \cos[(2\pi/N)(m-1)\cdot 2] \\ \vdots \\ \cos[(2\pi/N)(m-1)\cdot N] \end{pmatrix},$$

$m = 1, \dots, N/2$ for N even or $m = 1, \dots, N+1/2$ for N odd,

$$|\lambda_m\rangle = \sqrt{\frac{2}{N}} \begin{pmatrix} \sin[(2\pi/N)(m-1)\cdot 1] \\ \sin[(2\pi/N)(m-1)\cdot 2] \\ \vdots \\ \sin[(2\pi/N)(m-1)\cdot N] \end{pmatrix},$$

$m = N/2+1, \dots, N$ for N even or $m = N+1/2+1, \dots, N$ for N odd.

In the second-order non-degenerate perturbation theory the eigenvalue with the smallest absolute value λ_1^A of $\mathbf{A}'$ can be expressed as

$$\lambda_1^A = \lambda_1 + \Delta_1\lambda_1^A + \Delta_2\lambda_1^A, \tag{4.2}$$

where

$$\Delta_1\lambda_1^A = \langle\lambda_1|\mathbf{W}_A|\lambda_1\rangle = -\frac{1}{N}\sum_{m=1}^{N} B_m, \tag{4.3}$$

$$\Delta_2\lambda_1^A = \sum_{l(\neq 1)} \frac{\langle\lambda_1|\mathbf{W}_A|\lambda_l\rangle\langle\lambda_l|\mathbf{W}_A|\lambda_1\rangle}{\lambda_1 - \lambda_l}. \tag{4.4}$$

The sum (4.4) can be approximated by using only the most significant terms with $l = 2$ and $l = N$. The eigenvalue $\lambda_2 = \lambda_N$ corresponding to this term is two-fold degenerate with eigenvectors $|\lambda_2\rangle$ and $|\lambda_N\rangle$. Therefore, the second-order perturbation (4.4) can be approximately written as

$$\Delta_2\lambda_1^A = \frac{1}{N^2}\frac{2}{D}\frac{1}{1-\cos(2\pi/N)} \times \sum_{m,n=1}^{N} B_m B_n \{\cos[(2\pi/N)(m-n)] + \sin[(2\pi/N)(m+n)]\}. \tag{4.5}$$

Substituting Eqs. (4.3) and (4.5) into (4.2) the antenna eigenvalue λ_1^A with the smallest absolute value can be expressed in the form

$$\lambda_1^A = C + 2D - \frac{1}{N}\sum_{m=1}^{N} B_m + \frac{1}{N^2}\frac{2}{D}\frac{1}{1-\cos(2\pi/N)} \times \sum_{m,n=1}^{N} B_m B_n \{\cos[(2\pi/N)(m-n)] + \sin[(2\pi/N)(m+n)]\}. \tag{4.6}$$

The same approximation that was used to evaluate the contribution $\Delta_2\lambda_1^A$ can be used to find the antenna eigenvector $|\lambda_1^A\rangle$ corresponding to λ_1^A:

$$|\lambda_1^A\rangle = M\left(|\lambda_1\rangle + R|\lambda_2\rangle + S|\lambda_N\rangle\right),$$

where M is the normalization coefficient and R and S equal

$$R = -\frac{1}{N}\frac{1}{D}\frac{1}{1-\cos(2\pi/N)}\sum_{m=1}^{N} B_m \cos[(2\pi/N)m],$$

$$S = \frac{1}{N}\frac{1}{D}\frac{1}{1-\cos(2\pi/N)}\sum_{m=1}^{N} B_m \sin[(2\pi/N)m].$$

Similar expressions can be derived for the non-degenerate eigenvalue $\lambda^A_{(N+2)/2}$ existing for even N.

In order to find the analytical formula for the perturbed antenna eigenvalue with the second smallest absolute value it is necessary to use the degenerate perturbation theory. For the sake of simplicity we limit

ourselves to the first order perturbation theory. The unperturbed eigenvalue λ_2 is two fold degenerate and the perturbation theory leads to the second-order secular equation

$$\det\begin{vmatrix} \lambda_2 - \lambda + W_{22} & W_{2N} \\ W_{2N} & \lambda_2 - \lambda + W_{NN} \end{vmatrix} = 0 .$$

Under the influence of the perturbation the unperturbed eigenvalue $\lambda_2 = \lambda_N$ splits into two eigenvalues

$$\lambda_2^{\pm} = \lambda_2 + \tfrac{1}{2}(W_{22} + W_{NN}) \pm \tfrac{1}{2}\sqrt{(W_{22} - W_{NN})^2 + 4W_{2N}^2} , \qquad (4.7)$$

where $W_{22} = \langle \lambda_2 | \mathbf{W}_A | \lambda_2 \rangle$, $W_{NN} = \langle \lambda_N | \mathbf{W}_A | \lambda_N \rangle$ and $W_{2N} = \langle \lambda_2 | \mathbf{W}_A | \lambda_N \rangle$. The explicit formulae for these matrix elements are not given here. The degenerate perturbation theory can be used to find also the remaining eigenvalues $\lambda_3^{\pm}, \ldots, \lambda_{N/2}^{\pm}$.

It is obvious that introducing the unitary matrix $\tilde{\mathbf{U}}$ formed by the normalized eigenvectors corresponding to $\lambda_1^A, \lambda_2^{\pm}, \ldots, \lambda_{N/2}^{\pm}, \lambda_{(N+2)/2}^A$ (column by column) we can approximately diagonalize the perturbed antenna matrix $\mathbf{A}'$, $\tilde{\mathbf{A}} = \tilde{\mathbf{U}}^+ \mathbf{A}' \tilde{\mathbf{U}}$.

Before we proceed to the diagonalization of $\mathbf{F}'$, it is advantageous to apply first the unitary transformation

$$\hat{\mathbf{U}} = \begin{pmatrix} 1 & 0 \\ 0 & \tilde{\mathbf{U}} \end{pmatrix}$$

to the matrix $\mathbf{F}'$. Here, $\tilde{\mathbf{U}}$ is of the order N and $\hat{\mathbf{U}}$ is of the order $N+1$. This leads to the matrix $\tilde{\mathbf{F}} = \hat{\mathbf{U}}^+ \mathbf{F}' \hat{\mathbf{U}}$,

$$\tilde{\mathbf{F}} = \begin{pmatrix} \tilde{A} & \tilde{B}_1 & \tilde{B}_2^+ & \tilde{B}_2^- & \ldots & \tilde{B}_{N/2}^+ & \tilde{B}_{N/2}^- & \tilde{B}_{(N+2)/2} \\ \tilde{B}_1 & \lambda_1^A & & & & & & \\ \tilde{B}_2^+ & & \lambda_2^+ & & & & & \\ \tilde{B}_2^- & & & \lambda_2^- & & 0 & & \\ \vdots & & & & \ddots & & & \\ \tilde{B}_{N/2}^+ & & & & & \lambda_{N/2}^+ & & \\ \tilde{B}_{N/2}^- & & & 0 & & & \lambda_{N/2}^- & \\ \tilde{B}_{(N+2)/2} & & & & & & & \lambda_{(N+2)/2}^A \end{pmatrix}$$

where

$$\tilde{A} = A + A_1 ,$$

$$\tilde{B}_1 = \langle B^* | \lambda_1^A \rangle ,$$

$$\tilde{B}_m^{\pm} = \langle B^* | \lambda_m^{\pm} \rangle , \quad m = 2, \ldots, N/2 ,$$

$$\tilde{B}_{(N+2)/2} = \langle B^* | \lambda_{(N+2)/2}^A \rangle ,$$

and the row vector $\langle B^* |$ equals

$$\langle B^* | = (B + B_1, \ldots, B + B_N) .$$

We see that the matrix $\tilde{\mathbf{F}}$ has non-zero off-diagonal elements only in the first row and column. This property of the matrix $\tilde{\mathbf{F}}$ is suitable for using the partitioning method. $\tilde{\mathbf{F}}$ is partitioned into two square submatrices along the main diagonal. The first one ($\tilde{F}_{11} = \tilde{A}$) has dimension 1 while the other diagonal matrix $\{\tilde{F}_{mn}\}, m, n = 2, \ldots, N+1$ has dimension N. Following Ref. [18] our eigenvalue problem of the order $N+1$ can be reduced to finding the roots of the following equation,

$$\left[\tilde{A} - \lambda - \frac{\tilde{B}_1^2}{\lambda_1^A - \lambda} - \sum_{l=2}^{N/2}\left(\frac{(\tilde{B}_l^+)^2}{\lambda_l^+ - \lambda} + \frac{(\tilde{B}_l^-)^2}{\lambda_l^- - \lambda}\right) - \frac{\tilde{B}_{(N+2)/2}^2}{\lambda_{(N+2)/2}^A - \lambda}\right] = 0 . \qquad (4.8)$$

Numerical analysis of Eq. (4.8) indicates that the roots of this equation lie very close to the points of intersection of the asymptote of Eq. (4.8) and the λ-coordinate. To find the roots in the analytical form it is convenient to approximate the fractions in Eq. (4.8) by the most significant term having the smallest difference between the searched root λ and the corresponding point of intersection in its denominator.

Making use of this approximation, Eq. (4.8) can be transformed to a set of N independent quadratic equations with the roots

$$\lambda_1^{RC\pm} = \frac{\tilde{A} + \lambda_1^A}{2} \pm \tfrac{1}{2}\sqrt{(\tilde{A} - \lambda_1^A)^2 + 4\tilde{B}_1^2} ,$$

$$\lambda_m^{RC\pm} = \frac{\tilde{A} + \lambda_m}{2} \pm \tfrac{1}{2}\sqrt{(\tilde{A} - \lambda_m)^2 + 4\tilde{B}_m^2} , \quad m = 2, \ldots, N/2 , \qquad (4.9)$$

where λ_m denotes λ_m^+ or λ_m^- and

$$\lambda_{(N+2)/2}^{RC\pm} = \frac{\tilde{A} + \lambda_{(N+2)/2}^A}{2} \pm \tfrac{1}{2}\sqrt{(\tilde{A} - \lambda_{(N+2)/2}^A)^2 + 4\tilde{B}_{(N+2)/2}^2} .$$

Each of N expressions in (4.9) gives two roots. The first root is close to the corresponding point of intersection mentioned above while the second root is close to the point of intersection between the coordinate λ and the straight line $\lambda - \tilde{A}$. The first roots approximate N searched solutions of Eq. (4.8) while the second roots represent different approximations of the last remaining $(N+1)$st solution of Eq. (4.8) close to the diagonal element $\tilde{A}$.

If the absolute value of the element $\tilde{A}$ is larger than the absolute value of the corresponding intersection point, the root (4.9) with a plus sign in front of the square root lies closer to this point than the root with a minus sign. This root has also a smaller absolute value than the root with a minus sign. If the value of the intersection point exceeds the value of $\tilde{A}$ the situation is opposite.

If the value of the element $\tilde{A}$ lies close to the value of any intersection point the situation is more complex. Since the value of the element $\tilde{A}$ is of the order -10^{11} the eigenvalue related to it has much larger absolute value than $|\lambda_2^{RC+}|$ and, therefore, it does not play any significant role in the long time behavior of the solutions of PME.

5. Results and discussion

Till now the eigenvalues of the rate constants matrix have been calculated only numerically. In this paper we present for the first time the analytical formulae for the eigenvalues. It elucidates dependence of the eigenvalues on the geometry of PSU and other parameters as summarized below.

The numerical results of this Section follow from the rate constants mentioned in the Introduction.

First we discuss the eigenvalue gap $\lambda_1 - \lambda_2$ of the cyclic antenna system without RC (Eq. (3.3)). We see that the element $2D[1 - \cos(2\pi/N)]$ present in the expression for the eigenvalue λ_2 is by two orders of magnitude larger than element $k_A + B$. As a result, the eigenvalue λ_1 differs from λ_2 by two orders of magnitude. Therefore, the eigenvalue λ_1 is separated from other eigenvalues by a gap of a width about 10^{10} s^{-1}. This gap has been found assuming the energy transfer between the neighboring BChl antenna molecules only. If the interaction among all the antenna molecules were considered the gap would be probably larger.

Now we discuss PSU with the cyclic antenna system and RC. The eigenvalue spectrum consists in this case of eigenvalue λ^+ with the smallest absolute value (Eq. (3.4)), the eigenvalue λ^- (Eq. (3.4)) and eigenvalues $\lambda_2, \ldots, \lambda_N$ (Eq. (3.2)). The eigenvalues $\lambda_2, \ldots, \lambda_N$ are the same as those for the cyclic PSU without RC. Eigenvalue λ^- exists due to the presence of RC and lies below λ_2 (see Fig. 1). The gap width $\lambda^+ - \lambda_2$ for PSU including RC remains of the same order as the gap width $\lambda_1 - \lambda_2$ for the antenna system without RC.

The same symmetric model of PSU was considered in Ref. [2], where the authors took advantage of the C_{Nv} symmetry of PSU. Application of the group theory to the matrix **F** reduced the problem to the matrix of order 2. Diagonalizing this matrix they found eigenvalues λ^+ and λ^- corresponding to the unit irreducible representation in agreement with (3.4).

Now we suppose general PSU geometry. First we discuss the eigenvalue with the smallest absolute value playing the most important role for the long time behavior of the probabilities $P_m(t)$.

Table 1 shows the dependence of the eigenvalue λ_1^A (for the antenna system without RC) and λ_1^{RC+} (for PSU including RC) having the smallest absolute value on the displacement magnitude μ for the general antenna arrangement. General geometry of the antenna pigment molecules is constructed by displacing the original cyclic positions of each molecule in the interval $R \cdot (-1, 1) \cdot \mu/100$ in any of three dimensions, where R is the distance between the neighboring antenna pigment molecules in the cyclic arrangement and μ represents the magnitude of the molecular displacement. The actual positions of the pigment molecules for the numerical calculations were constructed using the random number generator. Comparing the first and second column in Table 1 we see that the second-order contributions $\Delta_2\lambda_1^A$ are at least by two orders of magnitude smaller than the first-order contributions $\Delta_1\lambda_1^A$. At the same time, the first-order contributions are by two or three orders of magnitude smaller than the unperturbed eigenvalue λ_1. Hence, the eigenvalue λ_1^A differs from eigenvalue λ_1^{RC+} by two or three percents only. Comparing the eigenvalue λ_1^{RC+} to the eigenvalue $\lambda_{1,num}^{RC}$ obtained by the numerical diagonalization we see that they differ negligibly. The analytical formula (4.9) describes the eigenvalue λ_1^{RC+} very well for any

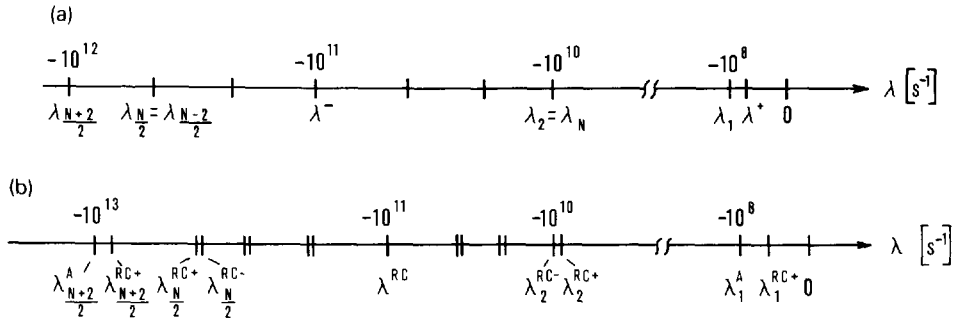

Fig. 1. Eigenvalue spectrum of the rate constants matrix for the cyclic geometry of PSU (a) and for a general geometry (b).

Table 1
Dependence of the eigenvalue λ_1 having the smallest absolute value on the perturbation magnitude μ for a general PSU geometry

μ (%)	$\Delta_1\lambda_1^A$	$\Delta_2\lambda_1^A$	$\lambda_1^A \times 10^8$	$\lambda_1^{RC+} \times 10^8$	$\lambda_{1,num}^{RC} \times 10^8$
0	0	0	−6.557663	−6.412017	−6.412017
5	-2.203×10^5	2.620×10^3	−6.559840	−6.413947	−6.413946
10	-1.217×10^7	4.741×10^2	−6.679408	−6.525741	−6.525836
15	$+1.144 \times 10^7$	4.970×10^3	−6.443238	−6.304731	−6.304556
20	-4.928×10^6	4.486×10^2	−6.606940	−6.458009	−6.457998

μ is the perturbation magnitude, in % of the original intermolecular distance R between the neighboring antenna BChl molecules.
$\Delta_1\lambda_1^A$ is the first-order contribution to eigenvalue λ_1 for the antenna system without RC, Eq. (4.3).
$\Delta_2\lambda_1^A$ is the second-order contribution to eigenvalue λ_1 for the antenna system without RC, Eq. (4.5).
λ_1^A is the eigenvalue with the smallest absolute value for the antenna system without RC, Eq. (4.6).
λ_1^{RC+} is the eigenvalue with the smallest absolute value for the PSU including RC, Eq. (4.9).
$\lambda_{1,num}^{RC}$ is the eigenvalue with the smallest absolute value for PSU including RC obtained by a numerical diagonalization of the matrix $\mathbf{F}'$, Eq. (4.1).

geometry with $0 \leqslant \mu \leqslant 20\%$.

The change of λ_1^A to λ_1^{RC+} caused by the presence of RC is more significant than the change of other eigenvalues (see Tables 1–3). This can be explained by the fact that the element $\tilde{B}_1$ in the numerator of Eq. (4.8) is by one order of magnitude larger than other elements $\tilde{B}_2, \ldots, \tilde{B}_N$. At the same time, the absolute value of the intersection point λ_1^A in the denominator in Eq. (4.8) is by two orders smaller than the values of other intersection points. The change of other eigenvalues caused by the presence of RC is very small (see Table 2 and Table 3).

For determining the gap width $\lambda_1^{RC+} - \lambda_2^{RC+}$ it is necessary to investigate the eigenvalue λ_2 which is the nearest neighbor of λ_1. For determining λ_2^{RC+} in Eq. (4.9), the value $\lambda_m = \lambda_2^+$ should be used.

Table 2 shows the dependence of the eigenvalues λ_2^+ (for the antenna system without RC), λ_2^{RC+} (for PSU including RC) and $\lambda_{2,num}^{RC}$ (obtained by a numerical diagonalization) on μ. We see that the first-order contributions $\Delta_1\lambda_2^+$ have (for $\mu > 10\%$) the same order as the original unperturbed eigenvalue λ_2. This is caused by the presence of the elements D_m in W_{22}, W_{NN} and W_{2N} in Eq.(4.7) contributing to the unperturbed eigenvalues λ_m, $m = 2, \ldots, N$. These elements are more sensitive to perturbation than the elements B_m present in Eq. (4.6) for perturbed eigenvalue λ_1^A as indicated above. This fact is a limiting factor for applicability of the perturbation theory to the eigenvalues of the rate constants matrix. Further we see that the difference between the eigenvalue λ_2^+ (for the antenna system without RC) and λ_2^{RC+} (for PSU system including RC) is negligible.

Table 3 shows all the eigenvalues λ_{num}^A (for the antenna system without RC) and eigenvalues λ_{num}^{RC} (for PSU including RC) for a general antenna arrangement with displacement magnitude $\mu = 40\%$. We see that these two sets of eigenvalues differ in two respects.

Table 2
Dependence of the eigenvalue λ_2 with the second smallest absolute value on the perturbation magnitude μ for a general PSU geometry

$\mu(\%)$	$\Delta_1\lambda_2^+ \times 10^{10}$	$\lambda_2^+ \times 10^{10}$	$\lambda_2^{RC+} \times 10^{10}$	$\lambda_{2,num}^{RC} \times 10^{10}$
0	0	−4.961646	−4.962396	−4.962396
5	−0.2389	−5.200538	−5.200545	−4.677924
10	−0.3751	−5.336706	−5.336707	−4.139646
15	−2.259	−7.220380	−7.220401	−3.438956
20	−4.825	−9.786996	−9.786998	−2.947944

μ is the perturbation magnitude, in % of the original intermolecular distance R between the neighboring antenna BChl molecules.
$\Delta_1\lambda_2^+$ is the first-order contribution to eigenvalue λ_2 for the antenna system without RC.
λ_2^+ is the eigenvalue with the second smallest absolute value for the antenna system without RC, Eq. (4.7).
λ_2^{RC+} is the eigenvalue with the second smallest absolute value for the PSU including RC, Eq. (4.9).
$\lambda_{2,num}^{RC}$ is the eigenvalue with the second smallest absolute value for PSU including RC obtained by a numerical diagonalization of the matrix $\mathbf{F}'$, Eq. (4.1).

Table 3
The eigenvalues λ_{num}^{A} (for the antenna system without RC) and λ_{num}^{RC} (PSU including RC) for a general PSU geometry (μ = 40%) obtained by a numerical diagonalization of the matrix $\mathbf{F}'$, Eq. (4.1). The eigenvalues are arranged in descending order

λ_{num}^{A}	λ_{num}^{RC}	
λ_1	-7.30854×10^8	-7.11168×10^8
λ_2	-1.20511×10^{10}	-1.20511×10^{10}
λ_3	-1.66885×10^{10}	-1.66885×10^{10}
λ_4	-5.40139×10^{10}	-5.40139×10^{10}
λ_5	-8.75185×10^{10}	-8.75185×10^{10}
λ_6	-1.24607×10^{11}	-1.24607×10^{11}
λ_7	-1.90892×10^{11}	-1.90892×10^{11}
λ_8	-2.61696×10^{11}	-2.61696×10^{11}
λ_9	–	-3.43006×10^{11}
λ_{10}	-3.98625×10^{11}	-3.98625×10^{11}
λ_{11}	-4.27721×10^{11}	-4.27721×10^{11}
λ_{12}	-7.26048×10^{11}	-7.26048×10^{11}
λ_{13}	-8.28621×10^{11}	-8.28621×10^{11}
λ_{14}	-8.98495×10^{11}	-8.98495×10^{11}
λ_{15}	-9.40408×10^{11}	-9.40408×10^{11}
λ_{16}	-1.33721×10^{12}	-1.33721×10^{12}
λ_{17}	-2.03346×10^{12}	-2.03346×10^{12}
λ_{18}	-2.73779×10^{12}	-2.73779×10^{12}
λ_{19}	-2.89536×10^{12}	-2.89536×10^{12}
λ_{20}	-4.56576×10^{12}	-4.56576×10^{12}
λ_{21}	-4.77146×10^{12}	-4.77146×10^{12}
λ_{22}	-1.47912×10^{13}	-1.47912×10^{13}
λ_{23}	-3.32930×10^{13}	-3.32930×10^{13}
λ_{24}	-6.47943×10^{13}	-6.47943×10^{13}
λ_{25}	-1.42293×10^{15}	-1.42293×10^{15}

First, only the eigenvalue λ_1 moves significantly due to the presence of RC. In addition to it, there is the eigenvalue λ_9 in the ninth row having an origin in the diagonal element $\tilde{A}$ reflecting the energy trapping and losses in RC. The other eigenvalues are effected by the presence of RC only very little.

It is evident from these results that the value of λ_2^{RC+} has a predominant influence on the gap width $\lambda_1^{RC+} - \lambda_2^{RC+}$ and, therefore, on the existence of the mono-exponential regime. Table 4 shows the dependence of the gap width on μ for the antenna system without RC (G^A), for PSU including RC (G^{RC}) and the gap width obtained by a numerical diagonalization (G_{num}^{RC}). The analytical formulae for the gap width G^{RC} obtained from the perturbation theory are limited to small deviations from the cyclic antenna arrangement only. The gap width decreases when the displacement of the pigment molecules increases. On the other hand, the gap width G^{RC} increases with the increase of μ while G_{num}^{RC} decreases. This can be explained by the fact that the term $(W_{22} + W_{NN})/2$ in Eq. (4.7) is less than zero for displacements generated by a random number generator. For a general geometry, the distances between neighboring BChl molecules are mostly larger than the distances in the cyclic unperturbed geometry. Therefore, the perturbation elements D_m, present in W_{22} and W_{NN}, are mostly less than zero. Only for a special case when the displacements would be headed towards the center of the antenna ring this term would be positive and the gap width would decrease. Using the perturbation theory in higher orders a more accurate expression for the gap width could be obtained. Unfortunately, such expression would have complex structure and could be used for numerical calculations only.

Table 4
Dependence of the gap width $\lambda_1^{RC+} - \lambda_2^{RC+}$ on the perturbation magnitude μ for a general PSU geometry

$\mu(\%)$	G^A	G^{RC}	G^{RC}_{num}
0	4.514241×10^{10}	4.898276×10^{10}	4.898276×10^{10}
5	5.134940×10^{10}	5.136406×10^{10}	4.613785×10^{10}
10	5.269912×10^{10}	5.271450×10^{10}	4.074388×10^{10}
15	7.155948×10^{10}	7.157354×10^{10}	3.375911×10^{10}
20	9.720927×10^{10}	9.722418×10^{10}	2.883364×10^{10}

μ is the perturbation magnitude, in % of the original intermolecular distance R between the neighboring antenna BChl molecules.
G^A is the gap width $(\lambda_1^A - \lambda_2^+)$ for the antenna system without RC, Eqs. (4.6) and (4.7).
G^{RC} is the gap width $(\lambda_1^{RC+} - \lambda_2^{RC+})$ for PSU including RC, Eq. (4.9).
G^{RC}_{num} is the gap width obtained by a numerical diagonalization of the matrix $\mathbf{F}'$, Eq. (4.1).

The statistics applied to the observable quantities mentioned in Section 2 will not probably substantially change the mono-exponential character of the observables. This is supported by the fact that the main properties of the eigenvalue spectrum are not changed even under large perturbation $\mu = 40\%$ of the cyclic arrangement of the antenna geometry.

The contribution of the exponentials $\exp(\lambda_i t)$ to the probabilities $P_m(t)$ depends on the values of the coefficients c_i in Eq. (2.8). Their value is given by the initial conditions $P_m(t = 0)$. The light wave length is large compared to the dimensions of PSU. It implicates a delocalized initial excitation. In the symmetric model [2] the observables contain only the exponentials corresponding to the unit irreducible representation with the eigenvalues given in Eq. (3.4). For the symmetric initial conditions only the coefficients c_i corresponding to these exponentials are different from zero. In case of the perturbed geometry, these eigenvalues become λ_1 and λ_9 in Table 3. More a less regular initial condition should lead to a large contribution of the states with no or small number of changes in sign of components of the eigenvectors h_m. For this reason we expect that the coefficient c_1 plays dominating role also in case of the perturbed geometry.

Summarizing, the results of this paper show that the eigenvalue spectrum of the rate constants matrix for our model of PSU consists of an isolated eigenvalue λ_1^{RC+} which has the smallest absolute value and the remaining eigenvalues separated from λ_1^{RC+} by a gap. For the Förster radius $R_0 = 46$ Å we have estimated $\lambda_1^{RC+} \sim -10^8$ s^{-1}, $\lambda_2^{RC+} \sim -10^{10}$ s^{-1} and the remaining eigenvalues are of the order $(-10^{15}, -10^{10})$ s^{-1} (see Tables 1–3 and Fig. 1). These results hold true for the cyclic plane system as well as for a system with three-dimensional irregular arrangement of the antenna BChl molecules. Eigenvalue λ_1^{RC+} changes only little with the geometry of PSU (see Table 1). Its value oscillates around the unperturbed value $\lambda_1^{RC+} = -6.412 \times 10^8$ for $\mu = 0$ due to the structure of the correction factors $\Delta_1\lambda_1^A$ and $\Delta_2\lambda_1^A$ (see Eqs. (4.3), (4.5) and (4.9)). At the same time, the eigenvalue λ_2^{RC+} is very sensitive to changes of the PSU geometry.

The above mentioned properties of the eigenvalue spectrum hold true for a considerably large class of the PSU geometries. We can conclude that the probabilities $P_m(t)$, Eq.(2.8), can be for times $t \gg |\lambda_2|^{-1}$, $\lambda_2 = \lambda_2^{RC+} \sim -10^{10}$ s^{-1}, approximated by one exponential $P_m(t) \sim \exp(\lambda_1 t)$, $\lambda_1 = \lambda_1^{RC+}$. This mono-exponential regime is valid also for the related experimental observables (fluorescence intensity, the corresponding quantum yield and other quantities [1]). It means that the experimentally gained information on the excitation transfer is for $t \gg |\lambda_2|^{-1}$ rather limited. This information regards mainly λ_1, reflecting the energy losses in the antenna system together with the excitation transfer to RC. The rate constants for the excitation transfer among the antenna BChl molecules do not appear in the expression for λ_1. The other eigenvalues and the corresponding eigenvectors contribute negligibly to the observables for long times. The existence of the mono-exponential regime is in agreement with our suggestion in Refs. [1,2] and with experimental results (see e.g. Refs. [9,10,19]). Changes of the Förster radius R_0 in the range 40–95 Å do not change the main conclusions given above. For R_0 about 64 Å agreement with Ref. [19] is obtained.

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