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COHERENT MEMORY FUNCTIONS FOR FINITE SYSTEMS: HEXAGONAL PHOTOSYNTHETIC UNIT *

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ABSTRACT

Coherent memory functions entering the Generalized Master Equation are presented for a hexagonal model of a photosynthetic unit. Influence of an energy heterogeneity on an exciton transfer is an antenna system as well as to a reaction center is investigated

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1. INTRODUCTION

An energy captured in an antenna system (AS) of a photosynthetic unit (PSU) is transferred to a reaction centre (RC) in form of localized Frenkel excitons.

In last years the structure of variety antenna systems has been experimentally established. The most striking property is their prevailing regularity. The photosynthetic membrane of purple bacteries shows well ordered two-dimensional arrays of photosynthetic units in which RC complex is surrounded by a ring like structure. The cyclic assembly forms a hexameric or dodecameric ring.

The simplest model of such photosynthetic units contains antenna globulas (n=1,...,6) placed on the regular hexagon with reaction centre in the centre (n=7).

Pearlstein and Zuber discussed [1] a connection between the regularity of cyclic PSU and the description of exciton transfer. They suggested an incorporation of coherent and intermediate regimes.

In our recent paper we have used [2] a computer modelling of the time dependence of the exciton site occupation probabilities $P_n(t)$ in hexagonal PSU to draw some consequences for different kinds of excitation transfer regimes. We have chosen the Stochastic Liouville Equation method [3,4,5] owing to its capability in describing the coherent regime as well as incoherent one and owing to its proper description of the role of the trap.

The aim of the present paper is to look at the exciton transfer in cyclic hexagonal PSU from the point of view of another method, namely the Generalized Master Equation method [6], which also describes regimes of the exciton transfer between both limits (coherent and incoherent one) and is in this respect comparable to SLE.

On the other hand, the memory functions (MFs), which are crucial quantities for the convolution GME method, are known only for simple examples. Possible necessity of an application of the coherent picture to the exciton transfer in hexagonal PSU calls for calculation of coherent memory functions for such systems.

The aim of the present paper is to generalize our direct method [7] for a linear chain and calculate coherent memory functions for the hexagonal photosynthetic unit taking into account an energy inhomogeneity and a planar superstructure.

The paper is set as follows. In section 2 we generalize our direct technique of calculation of the coherent memory functions to general finite systems. In section 3 a model Hamiltonian for the hexagonal photosynthetic unit is explained. In section 4 we present our calculation of the time dependence of the coherent memory functions for the cyclic hexagonal PSU from which in section 5 some conclusions for further investigation are drawn.

2. The σ - MATRIX TECHNIQUE — MFs

In general, the density operator ρ satisfies the Liouville-von Neumann equation

(1) $$i\partial\rho/\partial t = [H, \rho] = L\rho.$$

Here, H is the Hamiltonian of the system and L is the Liouville superoperator, $\hbar = 1$.

One can use the Nakajima-Zwanzig equation for a projection on a relevant part of the density operator

(2) $$\frac{\partial\rho_D(t)}{\partial t} = -iDL\rho_D(t) - \int_0^t d\tau DLe^{-i\tau QL}QLD\rho_D(t-\tau),$$
$$Q = 1 - D.$$

The kernel of the integral is so called (superoperator) memory function (MF). The initial term is omitted, proper chosen initial conditions are supposed.

Choosing a proper diagonalizing form of D, the term $-iDL\rho_D(t)$ drops, matrix elements of the operator $\rho_D = D\rho$ become site occupation probabilities and the elements of superoperator MF are memory functions in the common sense. The formalism of the projection superoperator D employed in the derivation of (2) from (1) enables us to follow the site occupation probability and thus the exciton migration. It generally involves the influence of phonons or another bath.

As in (2) only the positive time is employed, we complete the definition of the MF in following manner

(3) $$w(t) = -\theta(t)DLe^{-itQL}QLD,$$

where $\theta(t)$ is the (Heaviside) step function. Thus we are able to define the Fourier transformation of (3)

(4) $$w(z) = \int_{-\infty}^{+\infty} w(t)e^{izt}dt, \mathrm{Im}z \geq 0,$$

which may be analytically continued to the lower halfplane

(5) $$w(z) = -iDL(Q(z-L)Q)^{-1}LD.$$

In absence of phonons (or other kind of a bath) we take the following form of D

(6) $$D = \sum_m |m)(m|(|m)(m|, ...),$$

where
$|m)$ is the complete orthonormal set of Wannier-like functions,
$m = 1, 2, ..., N$ is the site index.
Let us concentrate our attention on finite systems with Hamiltonian H

$$H_{ii} = \epsilon_i \text{ for } i = 1, ..., N$$

(7) $$H_{ik} = J_{ik} \text{ for } i \neq k,$$
$$H_{ik} = H^*_{ki}.$$

The matrix $Q(z-L)Q$ which is to be inverted is a four-index quantity (tetradix). Owing to properties of Q, we need only off-diagonal elements of the Hermitian tetradix

(8) $$(QLQ)_{i_1i_2,k_1k_2} = \sigma_{i_1i_2,k_1k_2} \equiv \sigma(i_1i_2, k_1k_2),$$

where $i_1 \neq i_2$ as well as $k_1 \neq k_2$. For every such a pair of combinations of indices $i_1 \neq i_2, i_1, i_2 = 1, .., N$ it is worth introducing a single index $I = 1, 2, ..., N(N-1)$.

Let us denote the lower (upper) half of the set $1, 2, ..., N(N-1)$ by $G_L(G_U)$, i.e.

$$G_L = 1, ..., \frac{N(N-1)}{2}, G_U = \frac{N(N-1)}{2} + 1, ..., N(N-1).$$

To pairs $(i_1i_2)$with $i_1 < i_2$ we ascribe the values of I from G_L in an arbitrary manner. For pairs with $i_1 > i_2$ we assume I from G_U ascribed in such a way that

(9) $$i_1(I) = i_2(I - I_0), i_2(I) = i_1(I - I_0),$$
$$I \in G_U, (I - I_0) \in G_L, I_0 = \frac{N(N-1)}{2}.$$

Taking into account

(10) $$\sigma(I, K) = H_{i_1k_1}\delta_{i_2k_2} - H_{k_2i_2}\delta_{i_1k_1},$$

it takes place

$$\sigma(I,K) = -(\sigma(I-I_0,K-I_0))^* \quad \text{for} \quad I \in G_U, K \in G_U \tag{11}$$

and

$$\sigma(I,K) = -(\sigma(I-I_0,K+I_0))^* \quad \text{for} \quad I \in G_U, K \in G_L. \tag{12}$$

We can draw the conclusion that for our Hamiltonian H the whole σ matrix may be written in the block diagonal form

$$\sigma = \begin{pmatrix} \sigma_P & \tau_P \\ -\tau_P^* & -\sigma_P^* \end{pmatrix}, \tag{13}$$

where $\sigma_P(I,K) = \sigma(I,K)$ for $I,K \in G_L$ and $\tau_P(I,K) = \sigma(I,K)$ for $I \in G_L, K \in G_U$.

In the sets of eigenvalues and eigenvectors of σ we can find to each eigenvalue σ_α with an eigenvector (u_α, v_α) the opposite eigenvalue $-\sigma_\alpha$ with an eigenvector (v_α^*, u_α^*).

Now it is easy to invert matrix σ. The final form of the MFs in the time domain is as follows

$$w_{mn}(t) = -\sum_{\alpha=1}^{2I_0} r_\alpha(m,n) e^{-i\sigma_\alpha t}, \tag{14}$$

where

$$r_\alpha(m,n) = \sum_{I,K=1}^{2I_0} (H_{mi_1}\delta_{mi_2} - H_{i_2m}\delta_{mi_1})\langle I|\alpha\rangle\langle\alpha|K\rangle(H_{k_1n}\delta_{nk_2} - H_{nk_2}\delta_{nk_1})$$

for I,K derived as said above. By the summation only for $\sigma_\alpha \geq 0$ we obtain

$$w_{mn}(t) = -2 \sum_{\alpha(\sigma_\alpha \geq 0)} Re(r_\alpha(m,n)) \cos(\sigma_\alpha t). \tag{15}$$

3. HEXAGONAL PHOTOSYNTHETIC UNIT

We are dealing with a planar structure of photosynthetic units in which antenna globulas form a hexagonal ring around a reaction center. Let us start with one of such units.

We suppose that exciton transfer could be described by Generalized Master Equation and we are looking for memory functions $w_{mn}(t)$ in pure coherent regime. The Hamiltonian H relates to the unperturbed exciton system and includes only the interaction between neighbouring globulas. The symmetry of the problem leads to the following form of the Hamiltonian

$$H = \begin{pmatrix} 0 & J & 0 & 0 & 0 & J & I \\ J & 0 & J & 0 & 0 & 0 & I \\ 0 & J & 0 & J & 0 & 0 & I \\ 0 & 0 & J & 0 & J & 0 & I \\ 0 & 0 & 0 & J & 0 & J & I \\ J & 0 & 0 & 0 & J & 0 & I \\ I & I & I & I & I & I & \epsilon \end{pmatrix} \tag{16}$$

which takes into account different composition of the antenna and reaction centre globulas. The off-diagonal elements of the Hamiltonian H describe the coherent part in the exciton motion. I is the transfer integral between the reaction centre and antenna globulas and J is that for the antenna globulas. ϵ is a globula energy difference between the antenna system and the reaction centre.

4. RESULTS FOR $\epsilon \neq 0, I = J$.

We have calculated the coherent memory functions (15) for hamiltonian (16) taking into account the energy difference ϵ.

The time dependence of the coherent memory functions $w_{12}(t), w_{13}(t)$ and $w_{17}(t)$ is displayed on Fig. 1-3 together with a presentation of amplitudes $r_\alpha(m,n)$. This gives us an insight into a relative importance of various members in series (15).

For the simplicity the energy unit is equal to J and time unit is $1/J$ for $\hbar = 1$. During the calculation we set $J = 1$ and $I = J$.

5. CONCLUSIONS

Our generalized method which we have used for obtaining the memory functions $w_{mn}(t)$ entering as kernel the Nakajima-Zwanzig equations is based on a direct inversion of the superoperator expression (5). This allows us to investigate thoroughly the memory functions in the general finite system in absence of phonons.

The importance of our method, outlined in section 2., is given by the following fact. In our previous paper [7] we documented, that although the solution $P_m(t) = \rho_{mm}(t)$ of the Nakajima-Zwanzig equation is an oscillating function with frequencies

$$\omega_{ij} = E_i - E_j, \tag{17}$$

where E_i, E_j are the eigenenergies of the Hamiltonian H, the frequences σ_α of MFs neither can be generally deduced from ω_{ij} by simple algebraic manipulation, nor they are given by transfer integrals only.

The first principal conclusion concerns behaviour of $w_{mn}(t)$ in real space. As first shown by Kenkre [6] on a simple example, memory functions $w_{mn}(t)$ connect also places m and n which are not directly connected by a corresponding transfer integral J_{mn}. The memory functions $w_{mn}(t)$ have a pronounced long range behaviour.

The second principal conclusion which can be drawn from our calculation states:

As long as the difference between globulas energies ϵ raises appreciably, the memory functions $w_{17}(t)$, connecting directly antenna globulas with the reaction center turn to zero, because $|\sigma_\alpha| \to \infty$, but $r_\alpha(m,n)$ remain finite, it means $w_{17}(t)$ disappear as a distribution. The memory functions connecting globulas in antenna system turn to those for a linear chain with periodic boundary conditions (isolated part), we can observe the dynamical splitting-off of the reaction center.

Up to now we have spoken about the coherent regime of the exciton transfer. Kenkre [6] supposed, that the effect of an exciton-bath (phonon) coupling reduces to an exponentially damped prefactor of the memory functions. We have shown [8,9] that in the homogeneous linear chain, the linear local exciton coupling changes a form of the memory functions more appreciably. The memory functions, in a long time asymptotics, have two mutually connected channels: quasicoherent one, given by the long range coherent memory functions with exponentially damped prefactor and incoherent one, which is phonon assisted.

Our preliminary results stress the importance of derivation of a general form of the memory functions for energetically inhomogeneous systems, which would take into account as phonon-less as phonon-assisted exciton transfer for clarifying exciton transfer regime in cyclic hexagonal photosynthetic units.

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FIGURE CAPTIONS

Fig.1a: Time dependence of $w_{12}(t)$.
Fig.1b: Dependence of amplitudes $r_\alpha(1,2)$ on σ_α.
Fig.2a: Time dependence of $w_{13}(t)$.
Fig.2b: Dependence of amplitudes $r_\alpha(1,3)$ on σ_α.
Fig.3a: Time dependence of $w_{17}(t)$.
Fig.3b: Dependence of amplitudes $r_\alpha(1,7)$ on σ_α.

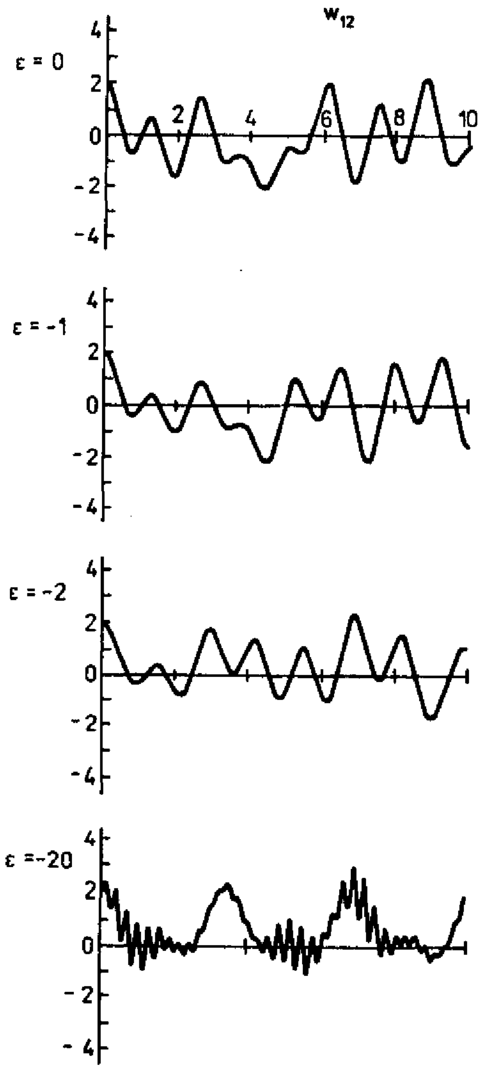

Fig.1a

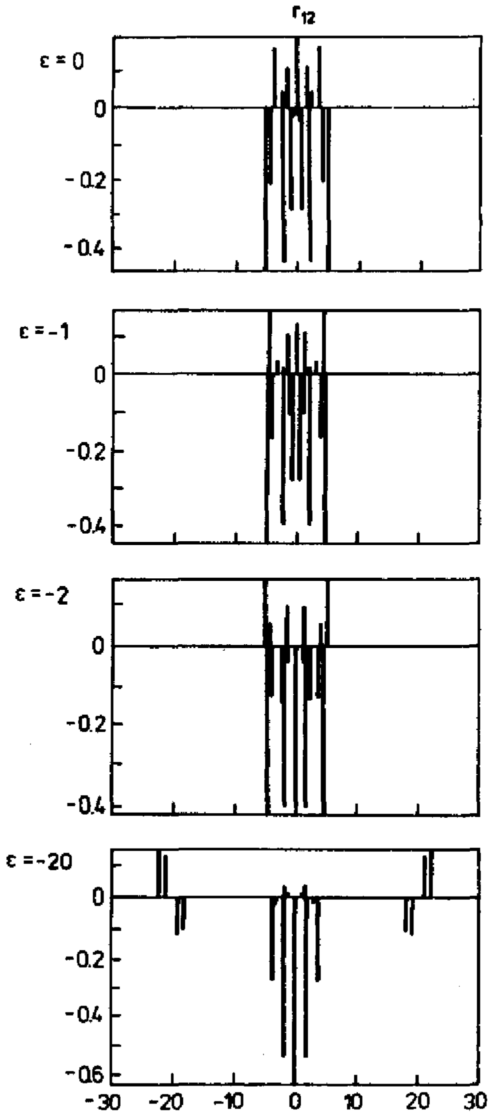

Fig.1b

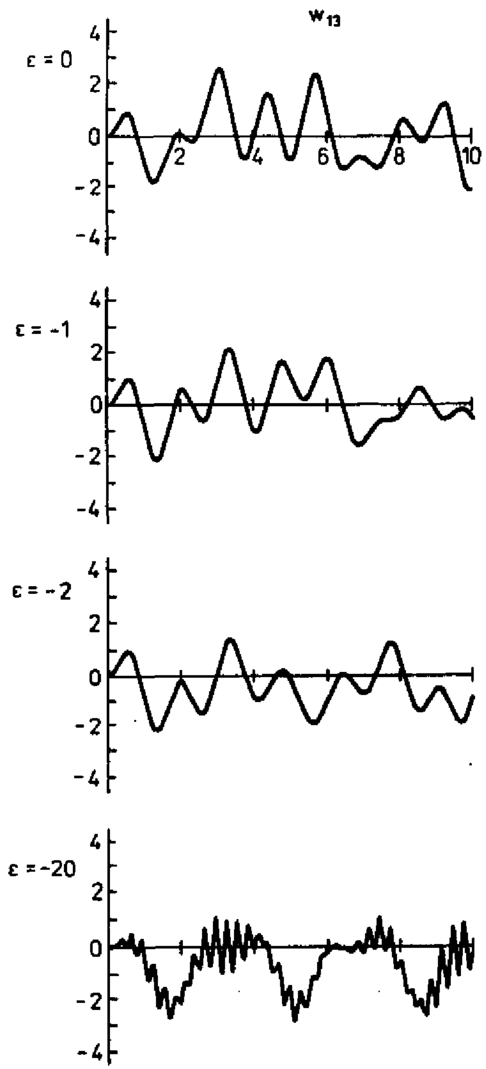

Fig.2a

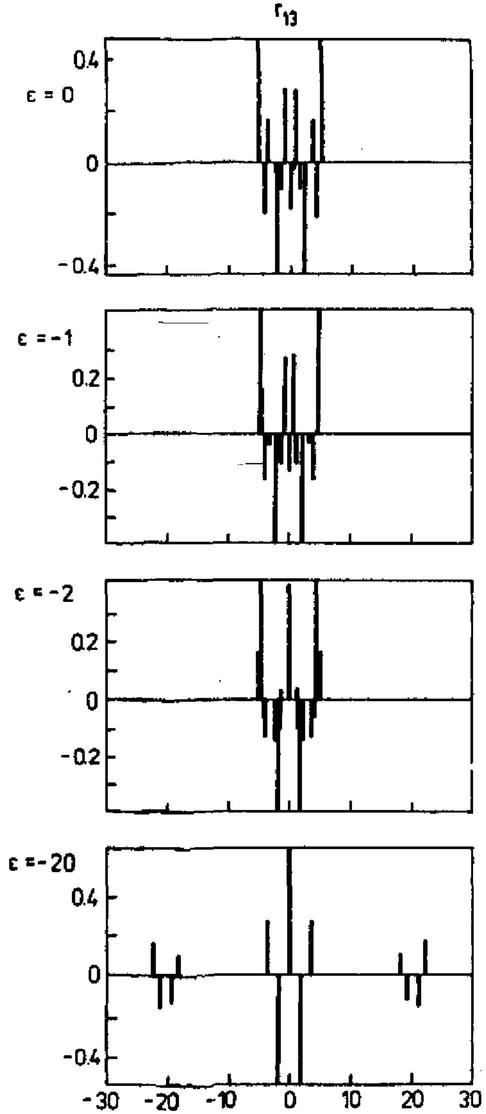

Fig.2b

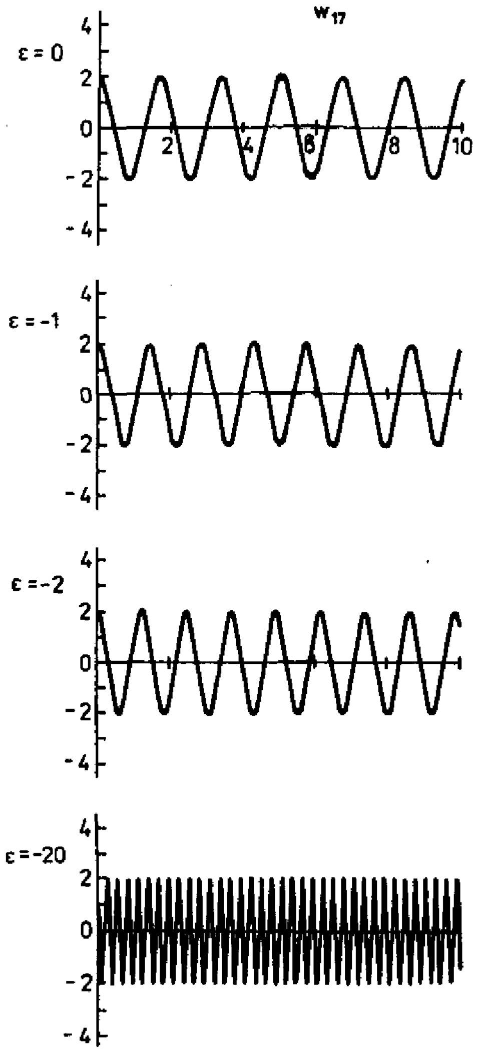

Fig.3a

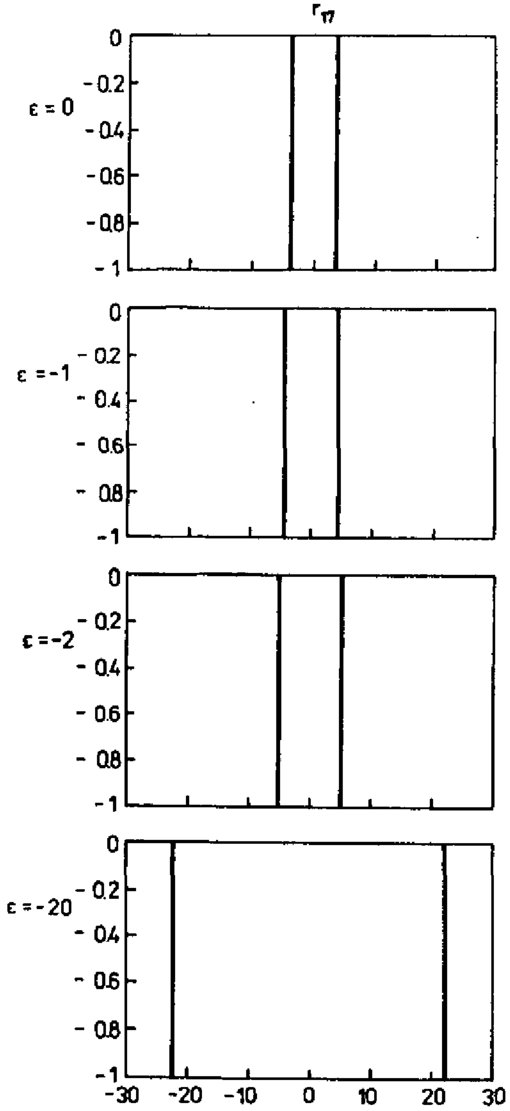

Fig.3b