

Transport of excitation energy in thylakoid disc in chloroplast at normal temperature

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Abstract: The energy of sunlight absorbed by an antenna chlorophyll inside a thylakoid disc in chloroplast is known to migrate to the reaction center in the form of an exciton. At normal temperature both the mechanisms of resonance transfer and exciton hopping contribute comparably.

The finite-temperature theory of excitons in a molecular aggregate is translated in the language of solid state physics as the treatment of the exciton in a thermal bath of phonons. For the sake of simplicity, the exciton-phonon interaction can be viewed as linear in lattice displacements with higher-order terms neglected. In the interaction picture, the effects of the thermal bath on the dynamics of the exciton can be incorporated into a time-dependent effective potential that involves terms arising from the fluctuation of the medium coordinates from their equilibrium values. The probability of site-to-site exciton transfer is written as a correlation function whose evolution in time can be determined by the cumulant expansion technique.

The exciton clothed by phonons can be defined in a natural way. This procedure leads to coarse-graining, and the correlation function for the coarse-grained exciton is defined in terms of the dressed states and the dressed operators. The zeroth-order term in the cumulant expansion corresponds to the resonance transfer of the dressed exciton while the second- and the higher-order terms lead to an expression for the probability of hopping. The transfer probabilities for a clothed exciton is derived under the Debye approximation for a cubic lattice.

These expressions can be used to determine the nearest-neighbour transfer probabilities in a reasonably realistic model of the thylakoid disc which in turn can be used for a numerical simulation of excitons dynamics. The model aggregate can be spatially and orientationally disordered. So the transfer probabilities at different sites in different directions are all different which is in sharp contrast with the so-called random walk model. In an earlier computer experiment we have shown that if all the excitons are considered to be created simultaneously, physical processes occurring at widely varying time scales (like exciton creation, exciton transfer, exciton decay by fluorescence, exciton trapping, phonon dynamics and electron transfers) are found to be time-wise self-consistent with one another. In this work we view exciton generation as a *continuous process* and derive a few analytical results. An algorithm for a very realistic numerical simulation of exciton generation and its utilization in chloroplast is also presented.

INTRODUCTION

We have recently discussed a general treatment of the migration of excitons to traps in a doped molecular crystal (refs. 1-3). The formalism can be extended rather straight-forwardly to the investigation of exciton diffusion. We follow the philosophy of Simons (ref. 4) that while considering

the dynamical properties of a species in contact with an external medium whose degrees of freedom are at equilibrium, effects of the medium on the species of interest can be incorporated into a time-dependent effective potential. This potential appears as an aggregate of the equilibrium average species-medium interaction and terms arising from fluctuations in medium's coordinates about their equilibrium values. We have also been involved in carrying out numerical simulations of exciton spread in the thylakoid disc (refs. 5-7). In this work we describe a systematic procedure for the investigation of exciton diffusion in a molecular aggregate like the thylakoid disc.

THEORY

The total Hamiltonian of the exciton-phonon system is written as

$$H = H_{\text{ex}}^0 + H_{\text{ph}}^0 + H_{\text{ex-ph}} \quad (1)$$

where H_{ex}^0 is the pure exciton Hamiltonian, H_{ph}^0 represents the pure phonon Hamiltonian and $H_{\text{ex-ph}}$ stands for the interaction between excitons and phonons. Let $a_{\mathbf{k}}^\dagger$ ($a_{\mathbf{k}}$) be the creation (annihilation) operator for an exciton of momentum $\hbar \mathbf{k}$. For a truly dilute system like a molecular aggregate in the presence of ordinary sunlight the exciton Hamiltonian is adequately described in the one-exciton approximation,

$$H_{\text{ex}}^0 = \sum_{\mathbf{k}} \epsilon_{\mathbf{k}} a_{\mathbf{k}}^\dagger a_{\mathbf{k}} \quad (2)$$

The Frenkel exciton operator is merely a Fourier transform of the site exciton operator. That is,

$$a_{\mathbf{k}}^\dagger = N^{-1/2} \sum_j \exp(i\mathbf{k} \cdot \mathbf{R}_j) a_j^\dagger \quad (3)$$

where N is the total number of sites in the crystal and the sum is over all the site exciton states. The exciton Hamiltonian H_{ex}^0 can be written in terms of site exciton operators as

$$H_{\text{ex}}^0 = \sum_{r,s} \hbar \Omega_{r,s} a_r^\dagger a_s \quad (4)$$

A molecular crystal has weak intermolecular forces. So the phonon Hamiltonian can be written in the one-phonon approximation,

$$H_{\text{ph}}^0 = \sum_{\mathbf{q}} (b_{\mathbf{q}}^\dagger b_{\mathbf{q}} + \frac{1}{2}), \quad (5)$$

where $b_{\mathbf{q}}^\dagger$ ($b_{\mathbf{q}}$) is the phonon creation (annihilation) operator for the \mathbf{q} th phonon mode. The exciton-phonon interaction Hamiltonian, $H_{\text{ex-ph}}$, for a molecular crystal is taken to be linear in lattice displacements:

$$H_{\text{ex-ph}} = \sum_{\mathbf{k}, \mathbf{q}} f_{\mathbf{k}+\mathbf{q}, \mathbf{q}} a_{\mathbf{k}+\mathbf{q}}^\dagger a_{\mathbf{k}} (b_{\mathbf{q}} + b_{-\mathbf{q}}^\dagger). \quad (6)$$

This yields the following time-dependent interaction (in the interaction picture)

$$H_{\text{ex-ph}}(t) = \exp[it(H_{\text{ex}}^0 + H_{\text{ph}}^0)/\hbar] H_{\text{ex-ph}} \exp[-it(H_{\text{ex}}^0 + H_{\text{ph}}^0)/\hbar]. \quad (7)$$

If we consider the exciton operators as boson operators we get

$$H_{\text{ex-ph}}(t) = \exp[itH_{\text{ph}}^0/\hbar] \sum_{\mathbf{k}, \mathbf{q}} f_{\mathbf{k}+\mathbf{q}, \mathbf{q}} \exp[-i(\epsilon_{\mathbf{k}} - \epsilon_{\mathbf{k}+\mathbf{q}})t/\hbar] a_{\mathbf{k}+\mathbf{q}} \hat{a}_{\mathbf{k}} (b_{\mathbf{q}} + b_{-\mathbf{q}}) \times \exp[-itH_{\text{ph}}^0/\hbar]. \quad (8)$$

Let us define a time correlation function

$$\Gamma(t) = \langle 1_j | O_1(t) O_2(0) | 1_j \rangle_{\text{R}} \quad (9)$$

where O_1 and O_2 are suitably chosen operators, $|1_j\rangle$ stands for the state vector representing one exciton localized in the j th site and R indicates that the expectation value is to be evaluated for the interacting system with phonons in thermal equilibrium. An especially useful function $\Gamma_{mn}(t)$ can be calculated with $O_1 = a_{j+m} \hat{a}_{j+n}$ and $O_2 = 1$:

$$\Gamma_{mn}(t) = \langle 1_j | \langle a_{j+m} \hat{a}_{j+n}(t) \rangle_{\text{R}} | 1_j \rangle. \quad (10)$$

In particular, $\Gamma_{nn}(t)$ is a direct measure of the probability of exciton propagation over n sites in time t .

The time-dependent operators can be evaluated by using the identity

$$\exp(-iHt/\hbar) = \exp\left[-\frac{i}{\hbar} \int_0^t d\tau V(\tau)\right] \exp[-it(H_{\text{ex}}^0 + H_{\text{ph}}^0)/\hbar]. \quad (11)$$

The trace appearing in the resulting expression for $\Gamma_{mn}(t)$ can be written in terms of Kubo's cumulant expansion (ref. 8):

$$\text{Tr}\left\{\rho(\text{R}) \exp\left[\frac{i}{\hbar} \int_0^t d\tau [V(\tau), \dots] O_1\right\} = \left\{\exp \sum_{m=1}^{\infty} K_m(t)\right\} O_1 \quad (12)$$

where the cumulants K_m 's have well-known expressions (refs. 3, 8), ρ is the density operator (the statistical weight) and R indicates phonon coordinates. As the phonons are in thermal equilibrium only the even-ordered cumulants contribute.

The zeroth-order correlation function has an extraordinarily simple appearance,

$$\Gamma_{mn}(t) = N^{-2} \sum_{\mathbf{k}, \mathbf{k}'} \exp[-i(\mathbf{k}, \mathbf{m} - \mathbf{k}', \mathbf{n})] \exp[i(\epsilon_{\mathbf{k}} - \epsilon_{\mathbf{k}'})t/\hbar]. \quad (13)$$

This represents a purely coherent (Frenkel) propagation. The zeroth-order transfer probability is obtained from the substitution $\mathbf{n} = \mathbf{m}$:

$$P_{\mathbf{m}}(t) = \Gamma_{\mathbf{m}\mathbf{m}}(t) = N^{-2} \sum_{\mathbf{k}, \mathbf{k}'} \exp[-i(\mathbf{k} - \mathbf{k}'), \mathbf{m}] \exp[i(\epsilon_{\mathbf{k}} - \epsilon_{\mathbf{k}'})t/\hbar]. \quad (14)$$

This is precisely the probability derived by Merrifield (ref. 9). Integrals of the types $\langle 1_{\mathbf{k}} | K_2 O | 1_{\mathbf{k}'} \rangle$, $\langle 1_{\mathbf{k}} | K_4 O | 1_{\mathbf{k}'} \rangle$, etc. are involved in the higher-order correlation function. Representative diagrams for these integrals (one each up to fourth order) are given in Fig. 1.

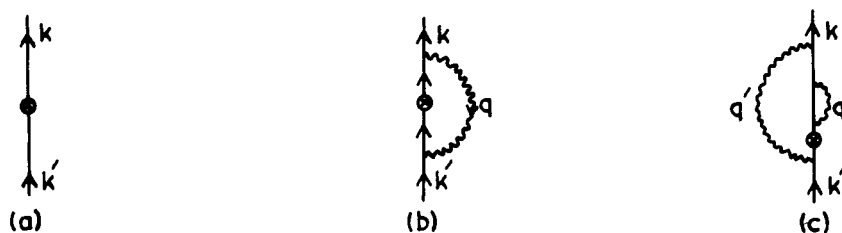


Fig. 1. Diagrammes representing typical (a) zeroth, (b) second and (c) fourth order processes.

EXCITON DIFFUSION

The exciton-phonon interaction directly mixes a particular zeroth-order exciton-phonon state with similar states of the same number of excitons but a different number of phonons. A set of orthonormal final states can be obtained in principle from an infinite order treatment. These perturbed states are *dressed* or *clothed* exciton states. The clothed exciton correlation function can be easily defined (ref. 3). The main physical effect of clothing is that the exciton becomes *localized* or *coarse-grained* (ref. 10). The coarse-grained exciton can jump from one site to the next. The movement becomes incoherent. This can be seen from the expression for the second-order transfer probability. The latter has been found to be proportional to time t in both slow exciton limit and slow phonon limit for $k_B T \gg \hbar \omega_D$ and $t \gg 1/\omega_D$ where ω_D is the Debye frequency (ref. 3).

There is no way to achieve the diffusion of a bare or a clothed exciton from the zeroth-order treatment unless an exciton relaxation process is introduced. There are several possible mechanisms for exciton relaxation. Merrifield (ref. 11) adopted an empirical value of the exciton relaxation time. A similar relaxation time (τ_{rel}) yields a macroscopic diffusion coefficient for the clothed exciton from the zeroth-order transport

$$D^{(0)} = \frac{1}{6} \tau_{rel} a^2 \sum_m m^2 \Omega_m^2. \quad (15)$$

The relaxation time generally decreases as the temperature of the system increases. So $D^{(0)}$ decreases with temperature.

If the temperature is sufficiently high compared to the Debye frequency, the second-order transfer probabilities can be approximately written in the general form

$$P_m^{(2)} = \alpha_m t (1 - e^{-\gamma t}). \quad (16)$$

The constant α_m is found to be proportional to temperature T . This probability contributes the second-order diffusion coefficient

$$D^{(2)} = \frac{1}{6} a^2 \sum_m m^2 \alpha_m \quad (17)$$

that increases linearly with temperature and can be considerably large at a high enough temperature. It is easy to get $D^{(2)} > D^{(0)}$ for a sufficiently small τ_{rel} (wide absorption lines) and in the slow-exciton limit with a reasonably strong exciton-phonon coupling. As T decreases, $D^{(2)} \rightarrow 0$ and the total

diffusion coefficient reduces to the "pure" clothed-exciton diffusion coefficient. Thus the present treatment yields the Merrifield transport (refs. 9, 11) for *clothed excitons* as $T \rightarrow 0$ and a primarily thermal, diffusive transport at a high enough temperature.

NUMERICAL SIMULATIONS

The conditions involved in our investigation of the migration of excitons in a molecular crystal are as follows. The excitons may not be produced with equal probability in all the lattice sites. There can be more than one trap distributed nonuniformly. The probabilities of nearest-neighbor jumps between two hosts, from a host to a trap, and from a trap to a host can all be different. There can be more than one type of host molecule and more than one type of trap. Under these constraints the formulae derived from the random-walk model of Montroll (ref. 12) or the diffusion model of Pearlstein (ref. 13) cannot be utilized. Therefore, we rely on the basic equation of the hopping dynamics of excitons (ref. 10)

$$\frac{dn_s(t)}{dt} = \sum_{\epsilon} [p_{s+\epsilon \rightarrow s}^0 n_{s+\epsilon}(t) - p_{s \rightarrow s+\epsilon}^0 n_s(t)], \quad (18)$$

where $n_s(t)$ is the probability of finding the exciton at site s at time instant t ; the index ϵ varies over the unit vectors in the positive and negative directions of x , y , and z axes (or any such independent axes); and $p_{s' \rightarrow s''}^0$ is the probability of a jump from site s' to site s'' in unit time. *The hopping probability can be determined from the expressions (15) through (17) in the previous section.* For a very small interval Δt (such that $p^0 \Delta t \ll 1$) we write Eq. (18) as

$$n_s(t + \Delta t) = n_s(t) + \sum_{\epsilon} [p_{s+\epsilon \rightarrow s}^0 n_{s+\epsilon}(t) - p_{s \rightarrow s+\epsilon}^0 n_s(t)] \Delta t. \quad (19)$$

This should be modified to accommodate a variety of exciton depleting processes. For example, the molecule at site s may be vibronically coupled with a decay process characterized by a rate constant. The condition $n \geq 1$ also activates *enhanced fluorescence* at selected sites. A direct emission requires a particular site to be overpopulated. For example, if n_q exceeds 2, say, at time instant τ' , an exciton can be assumed lost. A cooperative reaction involves two impurities (i' and i'') of different types each with a population greater than one. We carried out numerical calculation of Eq. (19) for 216 sites in a $6 \times 6 \times 6$ crystal involved in the trivariate process (ref. 6) and found that for a given placement of impurities, the total number of simple chemical reactions depends on the initial distribution of excitons. The number of reactions decreases when other exciton-depleting processes are switched on. The placement of reaction centers is an important factor in determining the number of reactions and how fast these would occur. A random initial distribution equilibrates the excitons over all the sites very quickly and results in fewer reactions. An increase in the number of reaction centers does not necessarily lead to an increase in the total number of reactions: it makes the excitons less available for reactions. A complicated dynamics results when different processes such as the enhanced fluorescence, emission, and cooperative processes occur together. The cooperative reactions appear to be first-order processes with average rate constants of the order of $10^8 - 10^9 \text{ s}^{-1}$.

We carried out another numerical experiment on the time-wise self-consistency of different physical processes involved in the energy transfer in green plant photosynthetic units (ref. 7). It is interesting to note the diversified time scales of the physical processes involved in the energy transport in photosynthesis. Photon absorption takes place in the second scale with normal intensity of sunlight on the surface of the earth. Electron transfers in the Z-scheme take altogether a few milliseconds. Fluorescence occurs within a few nanoseconds. Exciton transport occurs in nano- to pico- second range. Photon dynamics is a picosecond affair. Our main objective was to investigate whether all these widely different time scales are mutually consistent in their operation in the naturally occurring process of photosynthesis in green plants.

The thylakoid was modelled as a $6 \times 6 \times 6$ array of chlorophyll-a with cubic lattice constants $a=b=c=20 \text{ \AA}$ (Fig. 2). Disorder was introduced by substituting chlorophyll-b molecules for some of the chlorophyll-a molecules and by considering that a reaction center occupied a central site in the last xy plane. More disorder was brought in by randomly orienting the transition moments of the chlorophyll molecules. The resulting model systems were used in our investigation on exciton generation, transport, decay by fluorescence and trapping with all the excitons created by a 20 ms exposure to sunlight at high altitudes.

We found that the number of excitons generated is influenced by lattice disorders. Disorder also implies a greater period for the establishment of an equilibrium distribution. Exciton decay by fluorescence was always found to be a monotonic function of time. The energy transfer is adversely affected by a lower degree of orientation in the crystal as evidenced by the increase in the trapping time with disorder (Table 1). The onset of fluorescence of the host molecules and the trap leads to a drastic reduction in the number of trapping. We could also make three specific observations. The first one is that the efficiency of exciton utilization varies from 12% for a completely random arrangement of transition dipoles to 46% for a perfectly ordered arrangement. The experimentally known efficiency is about 20%. The second observation is that the number of excitons trapped varies from 1 to 6. This number tallies with the time scale of electron transfer along the Z-scheme that requires at least two excitons to be trapped in about 20 milliseconds. This clearly indicates that the photon density and the exciton transfer rate are consistent with the rates of electron transfers. As the third observation we noted that the trapping rate indicates the thylakoid disc to be a considerably ordered system.

TABLE 1. Total number of excitons trapped. Time (in μs) taken for the trapping process is indicated in parenthesis.

Case Study	Ordered Crystal		Disordered Crystal	
	chl-a	chl-a+chl-b	chl-a	chl-a+chl-b
Trapping	13 (0.20)	13 (0.28)	9 (0.93)	8 (0.55)
Trapping and trap fluorescence	13 (0.27)	12 (0.17)	8 (0.55)	8 (0.69)
Trapping, host and trap fluorescence	5 (0.05)	6 (0.06)	1 (0.03)	1 (0.04)

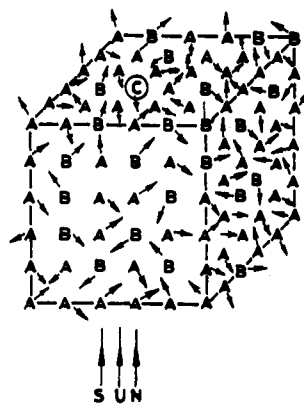


Figure 2. Schematic representation of a green plant thylakoid disc as an aggregate of chlorophyll molecules: (a) disordered orientations of (transition) dipoles shown by arrows and (b) substitutional disorder. A: Chl-a; B: Chl-b; C: reaction center.

MORE REALISM

In nature, exciton generation in green leaves is a continuous process. The continuous creation can be accommodated in the master equation (18) by modifying it into the form

$$\frac{dn_s(t)}{dt} = \sum_e [p_{s+e \rightarrow s}^0 n_{s+e}(t) - p_{s \rightarrow s+e}^0 n_s(t)] + \eta_s \quad (20)$$

The general solution for $n_s(t)$ is

$$n_s(t) = \sum_{i=0}^{\infty} \frac{t^i}{i!} X_{i,s} . \quad (21)$$

The coefficients $X_{i,s}$ can be determined by Laplace transformation technique. We find

$$X_{i,s} = F_{(i-1),s}(\{\eta\}) + F_{i,s}(\{n(0)\}) \quad (22)$$

where

$$F_{0,s}(\{a\}) = a_s, \quad (i = 0), \quad (23)$$

$$F_{i,s}(\{a\}) = \sum_{\epsilon} [p_{s+\epsilon \rightarrow s} F_{i-1,s+\epsilon}(\{a\}) + p_{s-\epsilon \rightarrow s} F_{i-1,s-\epsilon}(\{a\}) - (p_{s \rightarrow s+\epsilon} + p_{s \rightarrow s-\epsilon}) F_{i-1,s}(\{a\})] \quad (i \geq 1). \quad (24)$$

The effect of randomization may be introduced by using the averages $\overline{p^i}$ in $F_{i,s}$. Then an exact analytical expression can be derived for $F_{i,s}$ for a *finite* lattice. The detailed methodology will be discussed elsewhere. This approach has two advantages. First, any specific feature of the disordered lattice transmits itself directly to the time evolution of the hopping dynamics. Second, one needs to compute and store only N^3 numbers in order to calculate the exciton density at any site after *any* arbitrarily large number of time steps.

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