Theor Chem Acc (2011) 130:1203–1210
DOI 10.1007/s00214-011-1033-6

REGULAR ARTICLE

A schematic model for energy and charge transfer in the chlorophyll complex

H. G. Bohr · F. B. Malik

Received: 28 May 2011 / Accepted: 29 August 2011

Abstract A theory for simultaneous charge and energy transfer in the carotenoid-chlorophyll-a complex is presented here and discussed. The observed charge transfer process in these chloroplast complexes is reasonably explained in terms of this theory. In addition, the process leads to a mechanism to drive an electron in a lower to a higher-energy state, thus providing a mechanism for the ejection of the electron to a nearby molecule (chlorophyll) or into the environment. The observed lifetimes of the electronically excited states are in accord/agreement with the investigations of Sundström et al. and are in the range of pico-seconds and less. The change in electronic charge distribution in internuclear space as the system undergoes an electronic transition to a higher-energy state could, under appropriate physical conditions, lead to oscillating dipoles capable of transmitting energy from the carotenoid-chlorophylls chromophore to the reaction center by sending an electromagnetic wave (a photon) which provides a novel new mechanism for energy production. In the simplest version of the Förster–Dexter theory, the excitation energy of a donor is transferred to an acceptor and then de-excited to the ground state by fluorescence with no electron being transferred. In the process proposed herein, charge and energy both are transferred from donor to acceptor which can further de-excite by fluorescence. The charge transfer time scale involving an actual transfer of electron is in the pico-second range.

Keywords Photosynthesis · Fluorescence resonance energy transfer · Chlorophyll · Bio-Auger process

1 Introduction

There is now considerable evidence of charge and energy transfer between carotenoid and chlorophylls in the carotenoid-chlorophyll protein complexes (CCP) during light-harvesting process in photosynthesis, as noted in many comprehensive review articles on photosynthesis [1] and reported in many recent experiments [2–9]. It is also striking that the energy and charge transfer processes take place in a very short time scale, in pico- to femto- seconds and there may be multiple pathways. Charge transfer is caused by actual transfer of electrons. In the usual description of photosynthesis, the antenna molecule, usually a carotenoid, receives an incoming photon of wavelength around 500 nm leading to a charge and energy exchange between carotenoid and chlorophyll.

Prior to the experimental evidence indicating the electron transfer, the energy transfer component of the process has usually been treated within the standard theory of Förster and Dexter (FD) [10–12]. This, however, led to the realization [12, 13] that the theoretically obtained time scale is far too long compared with those reported in many

---

Dedicated to Professor Akira Imamura on the occasion of his 77th birthday and published as part of the Imamura Festschrift Issue.

H. G. Bohr (✉)
Quantum Protein (QuP) Center, Department of Physics,
Technical University of Denmark, DTU,
2800 Kongens, Lyngby, Denmark
e-mail: hbohr@fysik.dtu.dk

F. B. Malik
Department of Physics, Southern Illinois University,
Carbondale, IL 62901, USA
e-mail: fbmalik@physics.siu.edu

F. B. Malik
Department of Physics, Washington University,
St. Louis, MO 63130, USA

experiments [2, 5] and of course, the theoretical approach is not compatible with the experimentally established fact of charge transfer. The modification of the FD theory by adding a short-range interaction component attributed to orbital overlaps to the screening of the transfer Hamiltonian [14] and by considering the coupling of electronic orbitals to phonons generated by proteins [15] led to a shortening in the energy transfer lifetime of a few pico-seconds. Polivka et al. [16], on the other hand, modified the rate equation of [10, 11] by an overlap integral, the values of which are determined by fitting the absorption spectra of donor and emission spectra of acceptor. These overlap integrals are about 10^{-4}, that is, of the order of the difference between the calculated energy transfer time according to the FD theory and observation. All these theories do not address the mechanism of the charge or actual electron transfer.

The basic premise of the FD theory or its modified versions does not also address the important observed facts associated with the de-excitation process of carotenoids following photo-absorption, aside from the question of charge transfer. Experimentally, the electronic de-excitation or relaxation is determined to be radiationless [2, 6] and fast, of the order of a few pico-seconds. The latter must form an integral part of the theoretical understanding of the energy and charge transfer between carotenoids and chlorophylls.

The recently proposed Bio-Auger (B-A) process by Bohr and Malik [17–20] involves simultaneous electron and energy transfers between two molecules in close proximity, each being a part of the same protein complex. For example, an excited negative ion cofactor, riboflavin, in close proximity of a thymine dimer leads to reduction of this dimer followed by splitting into two thymine monomers by a radiationless process and results in a neutral riboflavin. The riboflavin electron that has been excited to an electronic excited state is either (1) transferred to the dithymine dimer in a photoinduced reduction [18, 19] process which leads to the photoinduced repair (ring opening followed by bond scission which leads to the two thymine monomers) or (2) ejected to the environment (side-chains of the protein) due to energy and charge conservation [18, 20]. Thus, the charge and energy transfer as well as radiationless transitions are an integral part of the B-A phenomenon as they are in Auger process in atoms and ions with inner-shell vacancies, which occurs in a very short, i.e., pico- to femto-second time scale in light elements like C, N, O etc., that are, indeed, the Baustein of molecules in carotenoids and chlorophylls. In this study, we examine the energy, charge and radiationless de-excitation involved in the (CCP) during light-harvesting process in photosynthesis schematically within the context of the B-A theory. Since the FD theory forms the basis of many energy transfer processes, if they are resonant, we, in the next section, provide an outline of the FD process and compare it with the B-A mechanism, an outline of which is given in the subsequent section.

2 Outline of the Förster–Dexter theory

A critical analysis of the FD process has been presented by Artykhov and Maiar [21], much of which was already noted by Förster and Dexter themselves [12, 13]. Strictly speaking, it involves energy transfer between two resonant states, one being excited and the other being the ground state of an acceptor and a donor in close proximity but actually not interpenetrating, i.e., barely penetrating with each other. The transition operator is the Coulomb interaction between electrons of donor and these of acceptor molecules, which after an expansion in multipoles leads to a dipole–dipole interaction in the lowest order between a donor and acceptor as done by Förster–Dexter who evaluated the next order term and included the exchange effect. The energy of a photoactivated donor is thus transferred to an acceptor, which, then decay to the ground state by luminescence. This affects also the spectral line shapes of luminescence. The time scale of the process is strictly speaking of the order of a nano-second. Many energy transfer processes between two molecular components of bichromophore molecules can be described by this process, if it is resonant, e.g., in singlet energy transfer in porphyrin-based donor-bridge-acceptor systems [22]. In many cases particularly involving electron transfer, the FD theory does not deal with electron transfer and the radiation de-excitation of photo absorbed donor. However, the energy transfer data in many cases do not conform with the prediction of the FD theory [13, 22–24].

To rectify the shortcomings of the FD theory to describe the electronic charge and energy transfers, Artkykov and Maiar [21] introduced the concept of super molecule. Whereas in the FD theory, the wave function of the interacting system is taken to the direct product of the donor and the acceptor wave functions in the absence of any interaction between them, the super molecular states include a configuration—mixture (CI) of the direct product states generated by the mutual interaction between the donor and the acceptor. However, the basic premises of the FD model, namely the energy exchange occurs through resonant states only and the actual charge transfer does not take place are kept intact. Taking into account the CI in first-order perturbation theory, they calculated the energy transfer rate constants for the carbazole/naphthalene system and found them to be of the order of one to 10^8 per second for intermolecular radii of 5.5 to 3.5 Å, respectively. The energy transfer observed in experiments [2, 5] are in sharp variance with these calculations. Moreover, [2, 5] clearly report charge transfer between carotenoid and chlorophyll and exhibit that the energy gap between two states of donor and acceptor involved in charge and energy transfer differ significantly from each other and hence, the process is non-resonant and these quantities occur between various other states of acceptor and donor.

Noting that the different assumptions underlying the FD theory are not valid for the energy transfer within chromophore complex Megow et al. [25] applied a slightly different CI to generate supermolecular states and in combination with dynamic simulation established, within the context of a hybrid quantum and classical theory, the energy transfer time among some members of the chromophore complex to be in the pico-second range, which is a few orders of magnitudes shorter than the expected results from the FD theory.

In addition to the work of Artykhov and Maiar [21], a QM supermolecular model in which a fragment technique allows for an analysis of the relevant electronic states has been presented by Pomogaev et al. [26] where it is shown how one can calculate the energy decay and the rate constants for photo-processes. Thus, QM fragment models are able to deal with and give a more modern treatment of the photosynthesis processes than the earlier developed models. Finally, the recently developed statistical quantum mechanical/classical mechanical molecular dynamics method for simulation of both electronic absorption and fluorescence spectra is able to better treat the effects due to changes in the environment on the time it takes to make the measurements [27].

In the Auger process in atoms or atomic ions, the B-A phenomenon deals with the radiationless transition from hole excited electronic states in a biomolecular system. The transition operator is the electronic interaction between two (or many) entangled electrons, which is either bare or screened Coulomb interaction. This operator transfers one of the entangled pair to the hole state, usually in the ground state and the other to any unoccupied state of the adjacent atom or molecule or to continuum allowed by the energy conservation. Thus, both electronic transitions and radiationless transitions in carotenoid reported in [2–6] are compatible with this theory. The time scale is of the order of pico- to femto-second for atomic or molecular constituents of biomolecules, as noted in [17]. Hence, the B-A process has the proper ingredients compatible with the data of [4–9].

An intriguing feature of the B-A process, not enunciated earlier, is its capability to pump electrons from a lower-energy state to higher ones as noted in Sect. 5 of this article. This could ultimately lead to electrons being ejected to the environment, thus providing a natural explanation of electrons emitted by CCP complexes in the presence of light. Charge transfer processes initiated by the B-A mechanism following vacancies in the ground or any inner orbital of a constituent molecule in a bio-molecular or CCP complex have important ramifications, some of them being the followings: (1) It could set up a chain of intra- or intermolecular charge transfer leading to current. Since the underlying process, as discussed in the next section, is akin to electron-hoping, the charge flow pattern is analogous to the one in a semi-conductor. For closed systems, this leads to a situation of current flow in rings. (2) It could lead to oscillating dipoles under certain circumstances of displaced electrons, which under appropriate conditions, could radiate electro-magnetic waves, and (3) “vacancies” caused by the absence of an electron from an inner-shell electronic orbit could lead to a reduction of shielding of repulsive internuclear potential causing a change in vibrational energies. This change in nuclear vibration is the driving force in inducing oscillating electronic dipoles.

Could this oscillating dipole generate electromagnetic wave, as a means of information transfer in reaction centers?

3 Outline of the B-A process

The electron in the ground state configuration $|i\rangle$ is transferred to an excited state $|j\rangle$ of a carotenoid by photo-absorption. In the B-A process, the electronic state $|j\rangle$ interacts with another electronic state $|\alpha\rangle$ transferring both electrons to two unoccupied states. In particular one of these final states $|i\rangle$ could be $|\beta\rangle$ and another in which could be a state in an adjacent atomic component of bio-molecules or continuum. The interaction causing the transition, $H(\text{int})$, is either a pure static Coulomb one as in the case of Auger process in atoms or a shielded Coulomb one, as in plasma or solids. It could also be a process involving tunneling, but experiments with isotopes seem to indicate very little of that, (see Ref. [6] and references within). Thus,

$$H(\text{int}) = \left(e^2/r\right)f(r) \tag{1}$$

where

$$r = \left|\mathbf{r}_j - \mathbf{r}_\kappa\right| \tag{2}$$

and $f(r) = 1$ for Coulomb potential and is the appropriate function for r for shielded potential, usually Gaussian or Yukawa type.

The charge and energy transfer rate is simply proportional to

$$|\langle i\beta|H(\text{int})|\alpha j\rangle|^2 \times [\text{Overlap factor}]^2. \tag{3}$$

A very important aspect of the B-A process is that it treats singlet to singlet, singlet to triplet and vice versa, and triple to triplet transition rates on equal footings. Thus, a singlet to triplet transition or vice versa could occur at fast time scale of sub-pico-second. However, as noted in [17], the transition rate are to be multiplied by an absolute square of an overlap integral, which, if small (e.g., in case of symmetry mismatch, it is zero) will lengthen the lifetime.

The overlap factor is analogous to one in [16] for non-orthonormal basis set but unity for the orthonormal basis. The total linear and angular momenta are also to be conserved. For fixed nuclear distance between two adjacent atoms or molecules, the matrix elements are worked out in [17].

For strongly correlated systems, the B-A process could occur due to the interaction between multiple electronic states. The B-A transition probabilities for such cases must include explicitly the correlation between the interacting electrons, since $H(\text{int})$ is a two-body operator. For such cases, the transition energy could be taken up by the entire system.

It is important to note that the B-A processes operate in an energy range of around 2–6 eV, which is far lower than the usual Auger effect involving core electrons of atoms and being in the KeV energy range. The B-A processes are on the other hand about transitions between excited states involving molecular orbitals, and here, a HOMO–LUMO estimate (given in the next section) will give a hint about the energies involved in the electronic excitations of molecules.

The B-A transition rates quite often compete with the electromagnetic multiple transition rates, T(EM), between the same two-orbitals. The word “compete” is perhaps misleading since both processes are induced by electromagnetic Coulomb operator. The B-A process is radiationless and no photon is emitted, whereas radiative electromagnetic transition emits a photon of definite angular momentum commensurate with a particular multipole operator in the expansion. As noted in [17], in light atoms such as C, N, O, etc, the Auger transition rates occur in pico- to femto-second time scales, whereas the allowed dipole electro-magnetic transition rate has a time scale of about a nano-second or longer. Hence, in biomolecules, which consist of light atoms and ions only, we expect the Auger process to overshadow the allowed dipole rates. This is likely to hold also for metallic constituents such as Mg, Mn, etc, in metalloproteins. Clearly, the B-A process is an efficient means of transferring charge and energy among the orbitals or configurations among constituent atoms of a molecule and among molecules of a bio-system.

The first step in performing the calculation of matrix elements of (3) is to consider the initial state. A preliminary calculation for the initial state has been carried out on a part of a peridinin molecule, 2 bonds to be precise. We start by performing calculation of a single carotenoid analog molecule where the tail of molecule has been removed resulting in 82 atoms. The main function of the tail is anchoring of the head group so for transfer properties it can be neglected. The carotenoid analog was optimized using restricted Hartree–Fock with the 3-21G** basis set implemented in Gamess-US.

The time-dependent DFT calculation (B3LYP hybrid XC functional) with the 6-31G* basis set gave reasonable values concerning the stability of the electronic structure of peridinin and for the Homo–Lumo gap. The program package of General Atomic Molecular Electronic Structure System (GAMESS) was used for the task [28]. The real fermion nature of anticommutating c-numbers has not really been used but certainly the Pauli exclusion principle is considered in one of the standard ways. The calculation analyses the molecules in the gas phase. More realistic calculations for future studies are planned on molecules within the native environment of photosynthesis.

Aside from the above method, we plan to explore the possibility of calculating the excited states in the carotenoid-chlorophyll complex using the recently developed “Elongation Method” [26] including the treatment of the environment and dynamical changes which occur on the time scale of the experimental measurements [27].

4 Charge and energy transfer in the B-A process

Let A, B, C,…, Z be constituent atoms or molecules of a biomolecular system (A, B,…, Z) and (i, j,…) be orbitals in each one of them, with (g.s) denoting the ground and (*) the excited orbital. An incident photon with sufficient energy to cause electronic excitation in A, leads to the following situation

$$h\nu + \left(A_{\text{g.s}}, B, \ldots, Z\right) \rightarrow \left(A_i^*, B, \ldots, Z\right).$$

Depending on the conservation laws, A_i^* may decay to A_j^* isomeric state which cannot decay to $A_{\text{g.s}}$ by radiative transition instantaneously. Interacting with an electron in the vicinity, A_j^* may decay to $A_{\text{g.s}}$ and the transition energy is taken up by the other electron which moves to an orbital i in B^*. Thus, B-A process, noted as BA, leads to

$$\left(A_i^*, B, \ldots, Z\right) \xrightarrow{BA} \left(A^+_{\text{g.s}}, B_R^{*-}, \ldots, Z\right).$$

The process may continue if allowed by energy conservation. In effect, one has the following situation

$$\begin{aligned} h\nu + \left(A_{\text{g.s}}, B, \ldots, Z\right) &\rightarrow \left(A_i^*, B, \ldots, Z\right) \\ &\xrightarrow{BA} \left(A^+_{\text{g.s}}, B_\kappa^{*-}, \ldots, Z\right) \\ &\xrightarrow{BA} \left(A^+_{\text{g.s}}, B_\ell^{*}, C_m^{*-}, \ldots, Z\right) \\ &\xrightarrow{BA} \left(A^+_{\text{g.s}}, B_\ell^{*}, C_n^{*}, \ldots, Z_z^{-}\right) \end{aligned} \tag{4}$$

Energy conservation permitting, one can even get double charge transfer

$$\xrightarrow{BA}\left(A^{+}_{g.s}, B^{*+}_{p}, C^{*-}_{o}, \ldots, Z^{-}_{z}\right).$$

Thus, B-A process initiates fast charge transfer naturally and with that energy transfer among the constituent molecules or atoms. Energy permitting, one or more electrons could be ejected in the environment. These features lead to a natural explanation of charge and energy transfers between carotenoid-Chl-a, and (B800 and B850) as observed in [1–6] and discussed in the subsequent section. In the equations above, the labels symbolizing the orbitals are not following standard Quantum Chemical convention.

5 Charge transfers in chloroplasts

Experimental observations in [4–6] point toward electronic charge and energy transfer between peridinin-chlorophyll-a and (B800, and B850) in CCP. The charge transfer in both cases are well understood in [17] in terms of B-A process. The situations are schematically depicted in Figs. 1 and 2, respectively, and summarized as follows:

The light-harvesting pigments of wavelengths 400–550 nm, corresponding to approximately to 3.0–2.0 eV energies, efficiently excite the ground state of peridinin, S_o, to the higher state S_2, the excitation to the first excited state S_1, being forbidden due to the mismatch of symmetries. Vibrational bands of different oscillator constants are associated with each of these states. Within the framework of the B-A process, the excited electron interacts with another one in its vicinity (i.e., an entangled one) which then transfer one of these to S_1 and another one to Q_x as shown in Fig. 1. In fact, a part of the total strength for transferring to S_1 can be distributed among vibrational states associated with S_2 and S_1. The electron in S_1, its strength being distributed among various vibrational levels, has plenty of time to interact with another electron in its vicinity, thereby causing simultaneous transitions to S_o and Q_y. The electronic state in Q_y can decay by fluorescence to the ground state of Chl-a, as observed. In fact, two electrons from peridinin are transferred to Chl-a. Zigmantas et al. [5] have observed these and has invoked the concept of a special charge transfer state around S_1. But the B-A process provides a natural explanation for this double charge transfer as well as filling up the hole electronic state in Peridinin. The time scale of the observed rates is expected to be the order of pico-seconds in the B-A process which is in line with the observed values. Zigmantas et al. [4] also suspect that the location of another state S_1' close to S_1, but it is not certain. If it does exist, its decay mode is also the B-A transition.

The electron and energy transfer between carotenoid and (B 800 and B850) in CCP can, similarly, be explained by

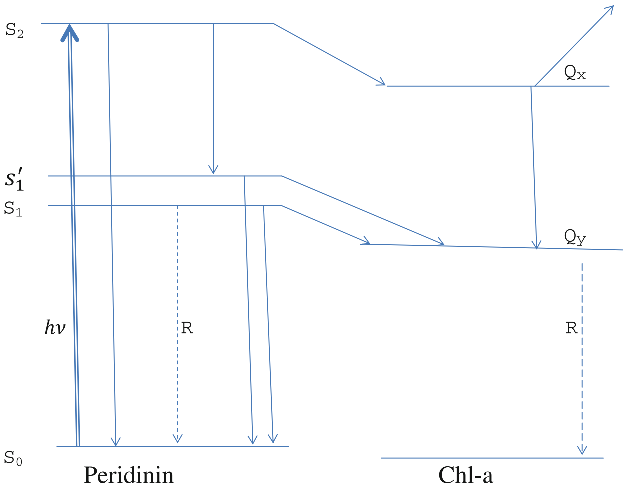

Fig. 1 Schematic representation of Fig. 4 from [5]. S_0, S_1, and S_2 represent, respectively, the ground, first, and second electronic excited states in peridinin and S_1', a possible one close to S_1. Q_x and Q_y represent two excited states of Chlorophyll-a. Associated with each one of these, there are vibrational bands. The radiationless Bio-Auger and radiative electromagnetic transitions are shown also by *solid* and *broken arrows*, respectively. The B-A process transfer between two interacting electrons and simultaneously the trajectories of the partner electron, determined by the energy conservation, are not shown in most of the cases. *R* may not be dipole transition

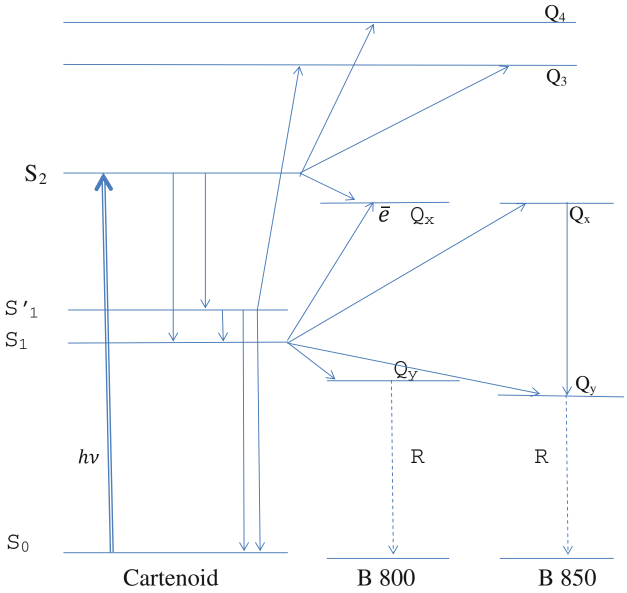

Fig. 2 *Solid* and *broken arrows* represent, respectively, the B-A and radiative transitions which also is denoted by *R*. The very rich electronic pathways allowed in the B-A process are shown partially. Actually, only a few that dominate will be easily detected. Some of the B-A transitions may not be occurring due to selection rules and energy conservation. This is a schematic version of Fig. 5.9 in [6] from each energy level, there could be multiple B-A as well as radiative transitions. As noted in [17], the total width is the sum of all the these partial widths

the B-A process, following its exposure to light-harvesting pigments around the wavelength of 450 nm. The carotenoid being exposed to light is excited to S_2. The observed decay pathways are shown in Fig. 2. The first excited state, S_1 cannot be populated by the absorption of dipole radiation because of symmetry mismatch. Thus, the interaction between entangled electronic state in S_2 can initiate a B-A transition transferring an electron to Q_y state of B800 and B850 and to S_1 state, which can further undergo the B-A process transferring an electron to Q_y state of B800 and B850 and the entangled partner electron to ground state S_o. The observed time scales are again as expected in [17]. The state Q_x then decays to the ground state of B800 and B850 by luminescence, as observed. Actually, a B-A transition from S_2 to S_o is possible if permitted by symmetry and other conservation law but not reported in [6].

6 Boosting the excitation in carotenoid or chlorophyll molecule by the B-A process

A very interesting feature of the B-A process is that it serves as an important conduit to promote electrons from energetically lower states to higher states and even to the continuum. The boosting mechanism is schematically depicted in Fig. 3, where holes and electrons in energy states are, respectively, denoted by open circles and crosses. On the leftmost part of the figure, the hole in the state E(0) can be filled by an electron in e.g., E(1) by the B-A process. Since the B-A process involves interaction between two electrons (for strongly correlated systems, there could be multielectronic transitions), the transition energy of the electron moving from the E(1) to the E(0) state must be taken up by the other interacting electron in the vicinity of E(1) state causing it to move to an energetically higher state E(2) as shown in Fig. 3. Electrons in the vicinity of energy E(2) could make a B-A transition promoting an electron to even a higher-energy state E(3), at the same time filling up a hole in E(1). In principle, if the energy of E(3) state is close to a continuum, the electrons could be pumped out in the environment. The end result is that the energetically lower states are filled leaving no empty holes in upper states and ejecting electrons in continuum.

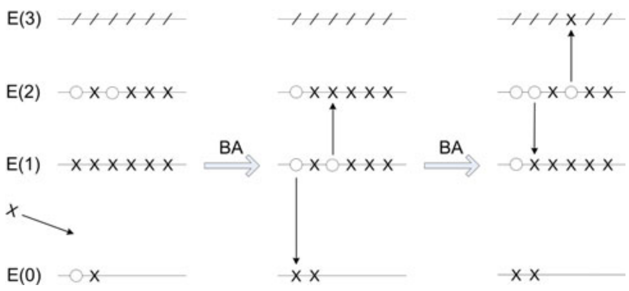

Fig. 3 Schematic diagram exhibiting the upward boosting possibilities of an electron from a lower to a higher-energy level owing to the B-A process. An essential part of the figure is the filling of the hole, shown as *open circles* by an electron, shown as *crosses*, near by

Electrons are emitted in the environment of the CCP compound after it being exposed to light-harvesting pigments. Whereas some of these may be due to the exchange of thermal energy, a fraction could be due to the ejection of electrons following a B-A process.

7 Energy transfer by electro-magnetic radiation (EMR)

The electronic charge distribution in internuclear spaces of atomic nuclei is expected to change significantly for electronically excited states compared with those in the ground state, thus affecting the equilibrium potential for nuclei in such molecules. In fact, in some diatomic molecules, the change in electronic distribution due to electronic excitation leads to even dissociation. In case of peridinin-Chl-a and carotenoid-B complexes, such change in the equilibrium potential of nuclei is likely to manifest itself in two ways: (a) vibrational spectra associated with the ground state and excited states will have different characteristics, (b) for two cases involved in photosynthesis, the charge transfers between peridinin and Chl-a and carotenoid and B800 and B850 which being anchored to respective nuclei, are likely to create dipoles that would be oscillating against each other due to vibronic motion of nuclei to which they are attached. Noting that the time scale of the decay of Q_y state in both cases above is about a nano-second, one may have to investigate this dipole-oscillating mode if the time scale of oscillating is shorter than nano-second. A preliminary investigation of the ramification of such oscillating dipoles done in Ref. [29] raises the possibility of an energy transfer between chloroplast complex and reaction center (RC) by transmission of electro-magnetic waves: the oscillating dipoles act as transmitter and some antenna in RC could act as receiver. Whereas efficiencies and proficiencies of energy transfer by such mechanism is highly dependent on the shape and location of the antennae, a simple case of linear antenna is provided to serve as a simple model. The components of electric fields, E_r and E_θ, emitted by such an oscillating dipole of length 'ℓ' in classical electrodynamics (θ is with respect to z-axis, the axis of dipole) for wavelength $\lambda \gg l$, are [30]

$$E_r = I_0(\ell/4\pi)2\eta\cos\theta\left[1/r^2 - i/\kappa r^3\right]\mathrm{e}^{-i\kappa r} \tag{5}$$

$$E_\theta = I_0(\ell/4\pi)2\eta\cos\theta\left[i\kappa/r + 1/r^2 - i/\kappa r^3\right]\mathrm{e}^{-i\kappa r} \tag{6}$$

where $\eta = \sqrt{\frac{\mu}{\varepsilon}}$, ($\mu$ is permeability in Henry/m and ε is permittivity in Farad/m) is the intrinsic impedence of the medium, κ, the wavenumber $= \frac{2\pi}{\lambda}$, and I_o is the current, in this case, the rate of production of dipole. Assuming the current is uniform, the average Poynting vector $\langle s \rangle$, defined as one half times of the real part of the Poynting vector, is given by

$$\langle s \rangle = (1/8)\eta\left[\sin^2\theta\right](I_0\ell/\lambda r)\hat{e}_r. \tag{7}$$

Thus, the total radiated power P in Watts is

$$P = \left(40\pi^2\right)I_o^2(\ell/\lambda)^2 \tag{8}$$

Setting $\ell = \frac{\lambda}{1{,}000}$ and $I_0 =$ (electric charge of an electron) (oscillating frequency,) one gets, (I_0 in Amp)

$$P = 40\pi^2 I_0^2 10^{-6},\ I_0 \text{ in Amp.} \tag{9}$$

The above amount of power is radiated by a single oscillating dipole but in reality one expects about 10^{20} such dipoles per cm^3. Hence, the emitted power could be substantial. Thus, the amount of energy radiated per cm^3 could be substantial. There is some evidence of the emission of EMR in photosynthesis [31].

It would be interesting experimentally to investigate the feasibility of the above process as an alternative or supplemental method to the usual mechanism of transmitting energy to RC.

8 Conclusions

We have discussed here the possibility of a B-A process as the underlying mechanism for energy and charge transfer between the peridinin and Chl-a; and B800 or B850. The process is also a suitable one for transferring electrons from lower-energy states to higher ones including to continuum state. It is pointed out that electronically excited states could set in vibronic motion of dipoles created by charge transfers that could serve as antenna to send electromagnetic signals.

Acknowledgments We would like to thank Per J. Greisen at the Technical University of Denmark (DTU) for his assistance and help to the project while being at the Quantum Protein (QuP) Center in the Department of Physics at DTU. The authors would also like to thank K. J. Jalkanen for interesting discussions concerning this work and for the comments, critiques, suggestions, and recommendations of anonymous reviewers of various versions of this work, and Ali Abu-Nada for the preparation of the manuscript.

References

1. Barber J (ed) (1992) The photosystems: structure, function and molecular biology. Elsevier, Amsterdam
2. Barber B (ed) (1996) Photosynthesis and the environment. Kluver Academics, Dordrecht
3. Green BR, Anderson JA, Parson WW (2003) Photosynthetic membranes and their light harvesting antennas. In: Green BR, Parson WW (eds) Light-harvesting antennas in photosynthesis. Kluwer Academic Press, Dordrecht, pp 1–28
4. Zigmantas D, Polivka T, Hiller RG, Yartsev A, Sundström V (2001) Spectroscopic and dynamic properties of the peridinin lowest singlet excited states. J Phys Chem A 105:10296–10306
5. Zigmantas D, Hiller RG, Polivka T, Sundström V (2002) Carotenoid to chlorophyll energy transfer in the peridinin-chlorophyll-a protein complex involves an intromolecular charge transfer state. Proc Nat Acad Sci USA 99:16760–16765
6. Sundström V (2009) Exploring excited state processes in photosynthesis features of photosynthetic light harvesting. In: Bohr H (ed) Handbook of molecular biophysics. Wiley, Weinheim, pp 167–192
7. Parson WW, Chu ZT, Warshel A (1998) Reorganization energy of the initial electron-transfer step in photosynthetic bacterial reaction centers. Biophys J 74:182–191
8. Ishizaki A, Fleming GR (2011) On the interpretation of quantum coherent beats observed in two dimensional electronic spectra of photosynthetic light harvesting complexes. J Phys Chem B 115:6227–6233
9. Lin S, Jaschke PR, Wang H, Paddock M, Tufts A, Allen JP, Rosell FI, Mauk AG, Woodbury NW, Beatty JT (2009) Electron transfer in the Rhodobacter sphaeroides reaction center assembled with zinc bacteriochlorophyll. Proc Nat Acad Sci USA 107:8537–8542
10. Förster T (1948) Zwischenmolekulare energie Wanderung und Fluoreszenz. Ann Phys 437:55–75
11. Dexter DL (1963) A theory of sensitized luminescence in solids. J Chem Phys 21:836–850
12. Damjanoric A, Ritz T, Schulten K (1999) Energy transfer between carotenoids and bacteriochlorophylls in light-harvesting complex II of purple bacteria. Phys Rev E 59:3293–3311
13. Müller MG, Slavov C, Luthra R, Rodoling KE, Holzwarth AR (2010) Independent initiation of primary electron transfer in the two branches of the photosystem I reaction center. Proc Nat Acad Sci USA 107:4123–4128
14. Scholes GD, Fleming GR (2000) On the mechanism of light harvesting in photosynthetic parple bacteria: B800 to B850 energy transfer. J Phys Chem B 104:1854–1968
15. Yang M, Damjanovic A, Vaswani HM, Fleming GR (2003) Energy transfer in photosystem I of Cyanobacteria *Synechococcus Elongatus*: model study with structure-based semi-empirical Hamiltonian and experimental spectral density. Biophys J 85:140–158
16. Polivka T, Pascher T, Hiller RG (2008) Energy transfer in the peridinin–chlorophyll protein complex reconstituted with mixed chlorophyllII sites. Biophys J 94:3198–3207
17. Bohr HG, Malik FB (2009) Radiationless Auger-like electronic transfer in biomolecules: B-A forces. In: Bohr H (ed) Handbook of molecuar biophysics. Wiley, Weinheim, pp 67–92
18. Bohr HG, Jalkanen KJ, Malik FB (2005) Electronic pathways in photoactivated repair of UV mutated DNA. Mod Phys Lett B 19:473–487
19. Jalkanen KJ, Jurgensen VW, Claussen A, Rahim A, Jensen GM, Wade RC, Nardi F, Jung C, Degtyarenko IM, Nieminen RM, Herrmann F, Knapp-Mohammady M, Niehaus TA, Frimand K, Suhai S (2006) Use of vibrational spectroscopy to study protein and DNA structure, hydration, and binding of biomolecules: a combined theoretical and experimental approach. Int J Quantum Chem 106:1160–1198
20. Bohr HG, Malik FB (2007) Evidence of Ager-like transitions in repair stage of ultraviolet mutated DNA. Phys Lett A 362:460–462

21. Artyukhov VY, Maiar GV (2001) Quantum- chemical theory of electronic excitation energy transfer in molecular systems. Russ J Phys Chem 75:1034–1040
22. Van Oort B, Alberts M, de Bianchi S, Dall'Osto L, Bassi R, Thrinkunas G, Croce R, Van Amerongen H (2010) Effect of antenna-depletion in photosystem II on excitation energy transfer in *Arabidopsis thaliana*. Biophys J 98:922–931
23. Patterson K, Kyrychenko A, Rönnow E, Ljungdahl T, Mårtensson J, Albinsson B (2006) Singlet energy transfer in porphyrin-based donor- acceptor systems: interaction between bridge length and bridge energy. J Chem Phys 110:310–318
24. Metivier R, Nolde F, Müllen K, Basché T (2007) Electronic ecxitation energy transfer between two single molecular embedded in a polymer host. Phys Rev Lett 98:047802
25. Megow J, Röder B, Kulesza A, Bonačić-Koutlecký V, May V (2011) A mixed quantum-classical description of excitation energy transfer in supermolecular complexes: förster theory and beyond. Chem Phys Chem 12:646–656
26. Pomogaev V, Gu FL, Pomogaeva A, Aoki Y (2009) Elongation method for calculating excited states of aromatic molecules embedded in polymers. Int J Quantum Chem 109:1328–1340
27. Pomogaev V, Pomogaeva A, Avramov P, Jalkanen KJ, Kachin S (2011) Thermo-dynamical contours of electronic-vibrational spectra simulated using the statistical quantum-mechanial methods. Theor Chem Acc. doi:10.1007/s00214-011-0936-6
28. Schmidt MW, Baldridge KK, Boatz JA, Elbert ST, Gordon MS, Jensen JH, Koeski S, Matsunaga V, Nguyen KA, Su SJ, Windus TL, Dupuis M, Montgomery JA (1993) General atomic and molecular electronic structure system. J Comp Chem 14:1347–1363
29. Bohr H, Greisen P Jr, Malik FB (2008) Excited state processes in photosynthesis molecules. Int J Mod Phys B 22:4617–4626
30. Demarest KR (1998) Engineering electromagnetic. Prentice Hall, Englewood Cliffs
31. Day C (2005) Trapping ions in pairs extends the reach of ultraprecise optical spectroscopy. Phys Today 58:24–25