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Coherent excitons at different orientation arrangements of local transition dipole moments in circular light-harvesting complexes*

Chu Qian-Jin(储谦谨)†, Yin Hua-Wei(尹华伟), and Weng Yu-Xiang(翁羽翔)

Laboratory of Soft Matter Physics and Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100080, China

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The coherent exciton plays an important role in the photosynthetic primary process, and its functions are deeply dependent on the orientation arrangements of local transition dipole moments (TDMs). We theoretically and systematically study the physical property of the coherent exciton at different orientation arrangements of the local TDMs in circular light-harvesting (LH) complexes. Especially, if the orientation arrangements are different, the delocalized TDMs of the coherent excitons and the energy locations of the optically active coherent excitons (OACEs) can be obviously different, and then there are more manners to capture, store and transfer light energy in and between LH complexes. Similarly, if the orientation arrangements are altered, light absorption and radiative intensities can be converted fully between the OACEs in the upper and lower coherent exciton bands, and then the blue and red shifts of the absorption and radiative bands of the pigment molecules can occur simultaneously at some orientation arrangements. If the systems are in the vicinities of the critical orientation arrangements, the weak static disorder or small thermal excitation can destroy the coherent electronic excitations, and then the coherent exciton cannot exist any more.

Keywords: optically active coherent exciton, transition dipole moment, orientation arrangement
PACC: 7135, 7865T, 8630P

The purple bacterial antenna system is typically made up of two light-harvesting (LH) pigment protein complexes, called LH2 and the reaction centres (RC)-LH1 'core' complexes.[1] These LH complexes capture the light and pass the excitation energy obtained. The progress made in the high-resolution structural and single-molecule spectroscopic studies of different LH complexes[1−8] has strongly stimulated experimental and theoretical investigations to understand the physics of the efficient light energy transfer in photosynthesis. Excitons are widely used to explain the light energy transfer through pigment molecules in and between LH complexes of photosynthetic bacteria, algae and higher plants.[9−21] Yet, in most cases, knowledge about the level structure of the excitons and their dynamics is far from complete.

LH complexes are oligomers of a simple monomeric unit consisting of a pair of $\alpha\beta-$apoprotein. Pigment molecules are enclosed in each $\alpha\beta-$apoprotein pair, and then some of which can form a closed circular ring. The optical properties of such LH complexes are dependent not only on the intrinsic properties of the individual pigment molecules but also on the interactions between them. Owing to the intermolecular interactions, an LH complex sometimes can be treated as a single supermolecule, and the coherent exciton that is delocalized on the whole or part of the supermolecule can be excited by the light with a particular polarization. Now it is universally received that the coherent exciton is important for the efficient light energy transfer in the photosynthetic primary process. Although the LH complexes of different photosynthetic purple bacteria are similar in some aspects, the large differences between them indeed exist due to different growth conditions, habitats, and cellular shapes. The number N of pigment molecules on each ring, for example, can be different in different LH complexes, i.e. the rings of LH complexes can have different sizes. Although the ambient condition for each pigment molecule within one LH complex may be slightly different from each other, it is also different in different species of LH complexes.[10,11] Hence the physical properties of the individual pigment molecules and the interactions between them

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†Corresponding author. E-mail: chuqj@aphy.iphy.ac.cn

will be changed, and then as a single supermolecule, different LH complexes will have different functions in photosynthesis.

The electrostatic interaction is the dominant one between the pigment molecules in LH complexes. When the distance between the pigment molecules is larger than the sizes of the electronic charge distributions of the individual pigment molecules, the dipole-dipole interaction is the dominant one between two uncharged pigment molecules. In the dipole-dipole approximation, the Coulomb interaction between the pigment molecules n and m can be written as[22]

$$t_{n,m} = [\boldsymbol{\mu}_n \cdot \boldsymbol{\mu}_m - 3(\boldsymbol{\mu}_n \cdot \hat{R}_{n,m})(\boldsymbol{\mu}_m \cdot \hat{R}_{n,m})]/R^3_{n,m}, \quad (1)$$

where $\boldsymbol{\mu}_n$ and $\boldsymbol{\mu}_m$ are the local transition dipole moments (TDMs) of the pigment molecules n and m, respectively. $R_{n,m}$ is the distance between the pigment molecules n and m with corresponding unit vector $\hat{R}_{n,m}$ pointing from molecule n to molecule m or in reverse. When pigment molecules have been seated on a circular ring, the orientation arrangement of the TDMs that are localized on every pigment molecules are considerably important not only for the level structure of the coherent exciton, but also for its dynamic property. Owing to different surrounding conditions for pigment molecules in different species of LH complexes, the local TDMs may have different orientation arrangements,[10] and then the physical properties of LH complexes may be changed in different photosynthetic purple bacteria. In addition, in the case where the photosynthetic bacterial complex LH2 was immobilized on mica surface[23] or the surface of TiO_2 nanoparticle in the colloidal solution,[16] the change of the physical property of the coherent exciton on the B850 ring may also be caused by the alteration of the orientations of the local TDMs. In this paper, we theoretically and systematically investigate how the orientation arrangement of the local TDMs in circular LH complexes affects the physical properties of the coherent excitons, and especially the ones that are optical transition allowed, i.e. the optically active coherent excitons (OACEs). We show that the delocalized TDMs of the coherent excitons, the number of the OACEs and their locations in energy space, and also the number of the coherent excitons that are optical transition forbidden, i.e. the optically dark coherent excitons (ODCEs), below an OACE in energy space, are obviously different at the different orientation arrangements. Similarly, if the orientation arrangements are changed, light absorption and radiative intensities can be converted fully between the OACEs in the upper and lower coherent exciton bands, and then the blue and red shifts of the absorption and radiative bands of the pigment molecules can occur simultaneously at some orientation arrangements. In the vicinities of the critical orientation arrangements, the couplings between the nearest-neighbouring (N-N) pigment molecules on the circular rings will be weak, and then a weak static disorder or a small thermal excitation can destroy the coherent electronic excitation, i.e. the coherent exciton cannot exist any more. It is possible that the differences in function among some different LH complexes in natural photosynthesis come from their different orientation arrangements, and some LH complexes in their photosynthetic processes have used the way of changing the orientation arrangements in mediating light energy flow, and also our predicted properties can be useful for the design of synthetic antenna devices.

We consider an LH complex comprised of N two-level pigment molecules located equidistantly on a circular ring with the spatial spacing R and the same energy spacing ε (the electronic excitation energy of the monomers in the LH complex). If we only consider the N-N (dominant) interaction, the electronic excited states of the system can be described by the following Hamiltonian:

$$H = \sum_{n=1}^{N} \varepsilon |n\rangle\langle n| + \sum_{n=1}^{N} t_{n,n+1} \left[|n\rangle\langle n+1| + |n+1\rangle\langle n|\right], \quad (2)$$

where $|n\rangle$ denotes the local electronic excited state, i.e. the localized exciton on the pigment molecule n with $|N+1\rangle = |1\rangle$. The orientations of local TDMs on different monomers are varied in an LH complex, but their magnitudes are assumed to be the same as μ. In the actual situation of interest to us in LH complexes[9−12,15,19] for simplicity we only investigate two common kinds of orientation arrangements of the local TDMs on circular rings, and first we propose that all local TDMs lie in the plane of the circle. In one kind of orientation arrangement, it is assumed that TDMs each are tangential to the circle at the same angle γ, as depicted in Fig.1(a). The angle γ will be positive when $\boldsymbol{\mu}_n$ points to the outside of the circle, and in reverse, it will be taken as a negative value. Then the angle γ is changed within $-\pi < \gamma \leq \pi$. The number N can be even and odd. We call this kind

of orientation arrangement the single-angle model. In another kind of orientation arrangement, which we call the double-angle model, we let the TDMs located on odd sites each be tangential to the circle at the same angle γ_1, and those on even sites each be tangential to the circle at the same angle γ_2 that is different from γ_1, and we also let the angle γ_1 has different zero points from the angle γ and γ_2, then the two local TDMs within a dimer of pigment molecules each be tangential to the circle at different angles, as depicted in Fig.1(b). Being the same as γ, γ_1 and γ_2 will be positive when corresponding $\boldsymbol{\mu}_n$ points to the outside of the circle, and in reverse, they are negative. Angles γ_1 and γ_2 are changed also within $-\pi < \gamma_1, \gamma_2 \leq \pi$, but now the number N can only be even.

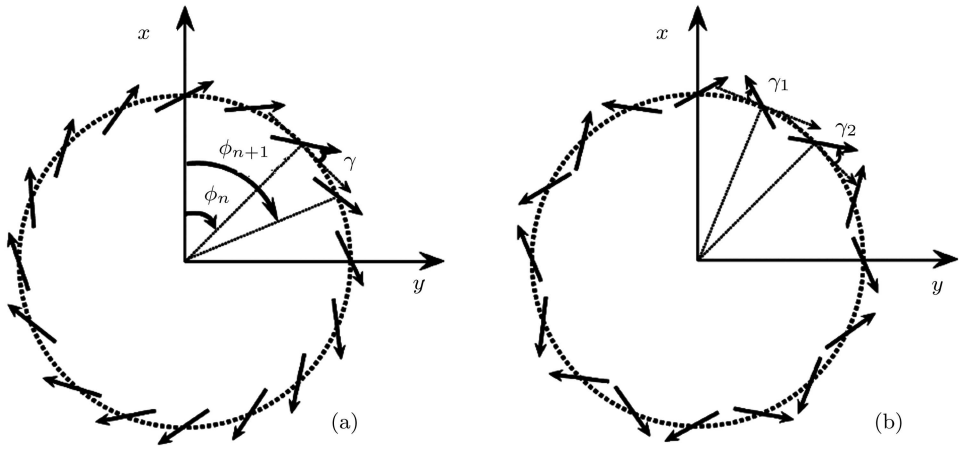


Fig.1. Schematic diagram of the orientation arrangements of the local TDMs in the single-angle model (a) and the double-angle model (b) on the circular rings.

Firstly we study the simplest case, i.e. the single-angle model. From expression (1), the excitation transfer interactions between the N-N pigment molecules on the whole circle are the same as $t = -t_0(3\cos 2\gamma + \cos\phi)$, where $t_0 = \mu^2/2R^3$ and $\phi = \phi_{n+1} - \phi_n = 2\pi/N$ with $\phi_n = n \cdot 2\pi/N = n\phi$. In order to concentrate on the effect of the orientation arrangement on the coherent exciton, we define a coupling coefficient $\eta \equiv t/t_0$, and at present it is $\eta = -3\cos 2\gamma - \cos\phi$. The coherent one-exciton eigenstates of Hamiltonian (2) now are the Bloch state along the circular ring with the wavenumber $k\phi$, the wave function

$$|k\rangle = \sum_{n=1}^{N} \frac{\exp(\mathrm{i}k\phi n)}{\sqrt{N}}|n\rangle \tag{3}$$

and the eigenvalue $E_k = \varepsilon + 2t_0\eta\cos k\phi$. The quantum number k is chosen from 0, 1, 2, $\cdots$, $N-1$, and the coherent excitons $|k=1\rangle$ and $|k=N-1\rangle$, $|k=2\rangle$ and $|k=N-2\rangle$, $\cdots$ are degenerate, respectively. Change the angle γ within $(-\pi, \pi]$, the coupling coefficient η will have different values, and then the locations of the coherent excitons in energy space will be shifted.

The one-photon absorption and radiative intensities of the coherent exciton $|k\rangle$ are proportional to the dipole strength $O_k = \boldsymbol{u}_k^* \cdot \boldsymbol{u}_k$ in the long-wave approximation,[22,24] where $\boldsymbol{u}_k = \sum_{n=1}^{N} a_{kn}\boldsymbol{\mu}_n$ is the delocalized transition dipole moment (TDM) of the coherent eigenstate $|k\rangle = \sum_{n=1}^{N} a_{kn}|n\rangle$, and the delocalized TDM $\boldsymbol{u}_k$ can be obtained once the wave function $|k\rangle$ has been calculated. And at all orientation arrangements of the local TDMs in the single-angle model, it is found to be

$$\boldsymbol{u}_k = -\mathrm{i}\mathrm{e}^{\mathrm{i}\gamma}\mu\sqrt{\frac{N}{2}}\boldsymbol{e}_l\delta_{k,1} + \mathrm{i}\mathrm{e}^{-\mathrm{i}\gamma}\mu\sqrt{\frac{N}{2}}\boldsymbol{e}_r\delta_{k,N-1}, \tag{4}$$

where $\boldsymbol{e}_r = (\boldsymbol{e}_x - \mathrm{i}\boldsymbol{e}_y)/\sqrt{2}$ and $\boldsymbol{e}_l = (\boldsymbol{e}_x + \mathrm{i}\boldsymbol{e}_y)/\sqrt{2}$ are the unit vectors with the polarized properties as the right-handed and left-handed circularly polarized light fields, respectively. $\boldsymbol{e}_x$ and $\boldsymbol{e}_y$ are the unit vectors in x- and y-directions, respectively. Only $|k=1\rangle$ and $|k=N-1\rangle$ have nonzero delocalized TDMs, i.e. only they are the OACEs, and their eigenvalue is redefined as $E_a = \varepsilon + 2t_0\eta\cos\phi$. The polarizations of the delocalized TDMs $\boldsymbol{u}_1 = -\mathrm{i}\mathrm{e}^{\mathrm{i}\gamma}\mu\sqrt{\frac{N}{2}}\boldsymbol{e}_l$ and $\boldsymbol{u}_{N-1} = \mathrm{i}\mathrm{e}^{-\mathrm{i}\gamma}\mu\sqrt{\frac{N}{2}}\boldsymbol{e}_r$ are always orthogonal,[25] and both are different from those of all local TDMs $\boldsymbol{\mu}_n$. The interactions $|\boldsymbol{u}_1^* \cdot \boldsymbol{E}|$ and $|\boldsymbol{u}_{N-1}^* \cdot \boldsymbol{E}|$ of the coherent excitons $|k=1\rangle$ and $|k=N-1\rangle$ with the

external light electric field $\boldsymbol{E}$ both are independent of the orientation arrangements, and both lead to the same constant dipole strength $\mu^2 N/2$.

At different orientation arrangements, the location of E_a in energy space will be different. If the value of angle γ is within $-\pi < \gamma < -\pi/2 - \gamma_c$, or $|\gamma| < \pi/2 - \gamma_c$, or $\pi/2 + \gamma_c < \gamma \leq \pi$, where $\gamma_c \equiv (1/2)\arccos[(1/3)\cos\phi]$, or especially if all local TDMs are oriented near the corresponding tangents to the circle of an LH complex, the coupling coefficient η is negative, and then the OACEs are near the bottom of the coherent exciton band. The situation is corresponding to the red shifts of the absorption and radiative bands of the pigment molecules. There is only one coherent exciton $|k=0\rangle$ that is optical transition forbidden, i.e. the optically dark coherent exciton (ODCE), below the OACEs $|k=1\rangle$ and $|k=N-1\rangle$ in energy space. This ODCE may have the functions of storing and transferring light energy in and between LH complexes. However, if $|\gamma \pm \pi/2| < \gamma_c$, or especially if all local TDMs are oriented near the corresponding normals to the circle of an LH complex, $\eta > 0$, and then the OACEs are near the top of the coherent exciton band. In this case, the blue shifts of the absorption and radiative bands of the pigment molecules may appear. Now there are $N-3$ ODCEs below the OACEs. This situation may be useful for storing light energy in LH complexes, and may give more channels to transfer excitation energy in and between LH complexes, and then leads to more efficient light energy transfer in photosynthetic systems.

Secondly we investigate the double-angle model. Now there are two angles γ_1 and γ_2 which are varied independently. The coupling coefficients between the N-N pigment molecules within and between the dimers on the circular rings generally cannot be equal to each other. But within the dimers there exists the same coupling coefficient $\eta_1 = 3\cos(\gamma_1-\gamma_2)+\cos(\gamma_1+\gamma_2-\phi)$, and between the dimers also there exists the same coefficient $\eta_2 = 3\cos(\gamma_1-\gamma_2)+\cos(\gamma_1+\gamma_2+\phi)$. Being the same as η, coupling coefficients η_1 and η_2 will be varied greatly as γ_1 and γ_2 are changed. If the coupling coefficients are greater than 1 at some orientation arrangements, the interactions between the N-N pigment molecules can be strong as the distances between them are small and the magnitudes of the local TDMs are large, but if the coefficients are close to zero at some other orientation arrangements, the interactions will be weak by all means.

In the double-angle model, it is easy to find that there are only two particular cases of orientation arrangements: $\gamma_1 + \gamma_2 = 0$ and $\gamma_1 = \gamma_2 = \pi$, in which the orientation arrangements are different from those in the single-angle model and the coupling coefficients η_1 and η_2 also can be equal to each other, i.e. $\eta_1 = \eta_2 = 3\cos 2\gamma_2 + \cos\phi$ with the angle γ_2 within $(-\pi, \pi]$. In these two cases, the ambient conditions for two pigment molecules within a dimer must be different from each other. The systems have the same eigenfunction $|k\rangle$ in expression (3) with the eigenvalue $E_k = \varepsilon + 2t_0\eta_2\cos k\phi$, and the quantum number k is also chosen from 0, 1, 2, $\cdots$, $N-1$. But the delocalized TDM of the coherent exciton $|k\rangle$ is different from that in expression (4), and now it is

$$\boldsymbol{u}_k = \mathrm{i}e^{-\mathrm{i}\gamma_2}\mu\sqrt{\frac{N}{2}}\boldsymbol{e}_r\delta_{k,L-1} - \mathrm{i}e^{\mathrm{i}\gamma_2}\mu\sqrt{\frac{N}{2}}\boldsymbol{e}_l\delta_{k,L+1}, \quad (5)$$

where $L = N/2$. There are also only two OACEs: $|k = L-1\rangle$ and $|k = L+1\rangle$ with the same eigenvalue $E_a = \varepsilon - 2t_0\eta_2\cos\phi$. If the value of angle γ_2 is within $-\pi < \gamma_2 < -\pi/2 - \gamma_c$, or $|\gamma_2| < \pi/2 - \gamma_c$, or $\pi/2 + \gamma_c < \gamma_2 \leq \pi$, or especially if two local TDMs within each dimer both are oriented near the corresponding tangents to the circle but the orientation arrangements are different from those in the single-angle model, then $\eta_1 = \eta_2 > 0$, and the OACEs are also near the bottom of the coherent exciton band. In this case, there are the red shifts of the absorption and radiative bands of the pigment molecules. The orientation arrangements of the B850 bands in Fig.5 of Ref.[10] are the examples of this case with $\gamma_1 \approx -11\pi/12$ and $\gamma_2 \approx 11\pi/12$. There is only one ODCE $|k = L\rangle$ with the eigenvalue $E_L = \varepsilon - 2t_0\eta_2$ below the OACEs. If $|\gamma_2 \pm \pi/2| < \gamma_c$, or especially if all local TDMs are oriented near the corresponding normals to the circle but two local TDMs within each dimer point to different sides of the circle, then $\eta_1 = \eta_2 < 0$, and the OACEs are near the top of the coherent exciton band. Thus the blue shifts of the absorption and radiative bands of the pigment molecules may appear. Now there are $N-3$ ODCEs below the OACEs.

In the double-angle model, the coupling coefficients η_1 and η_2 generally cannot be equal to each other, i.e. $\eta_1 \neq \eta_2$, and Hamiltonian (2) also can be solved analytically, but its eigenfunctions are

$$|\pm, k\rangle = \sum_{l=1}^{L} \frac{\exp(2\mathrm{i}k\phi l)}{\sqrt{N}}[\pm\alpha_1(k)\exp(-\mathrm{i}k\phi)|2l-1\rangle + |2l\rangle], \quad (6)$$

where $\alpha_1(k) = [\eta_1\exp(\mathrm{i}k\phi) + \eta_2\exp(-\mathrm{i}k\phi)]/\delta(k)$ with $\delta(k) = \sqrt{\eta_1^2 + \eta_2^2 + 2\eta_1\eta_2\cos 2k\phi}$. Now there are two

bands of the coherent excitons, i.e. the upper and lower coherent exciton bands with the wave functions $|+,k\rangle$ and $|-,k\rangle$, respectively, and the quantum numbers in the two bands both are chosen from $k = 0$, 1, 2, $\cdots$, $L-1$. The states $|+,k\rangle$ and $|-,k\rangle$ have the eigenvalues $E_k^+ = \varepsilon + t_0\delta(k)$ and $E_k^- = \varepsilon - t_0\delta(k)$, respectively. It is easy to prove that $\alpha_1^*(k)\alpha_1(k) \equiv 1$, and this means that the wave functions of all coherent excitons in the two bands have the same amplitude for each monomer. The delocalized TDMs of the coherent excitons $|+,k\rangle$ and $|-,k\rangle$ are

$$\boldsymbol{u}_k^{\pm} = \mathrm{i}\alpha_2(\pm)\mu\sqrt{\frac{N}{8}}\boldsymbol{e}_l\delta_{k,1} - \mathrm{i}\alpha_2^*(\pm)\mu\sqrt{\frac{N}{8}}\boldsymbol{e}_r\delta_{k,L-1}, \tag{7}$$

respectively, where $\alpha_2(\pm) = \pm\alpha_1(1)\mathrm{e}^{-\mathrm{i}\gamma_1} - \mathrm{e}^{\mathrm{i}\gamma_2}$. Now in each of the two bands there exist two degenerate OACEs, hence in total there are four OACEs, which is different from the single-angle model and the two special cases in the double-angle model. In the upper band, the states $|+,1\rangle$ and $|+,L-1\rangle$ are the degenerate OACEs with the eigenvalue $E_a^+ = \varepsilon + t_0\delta(1)$, and it is corresponding to the blue shifts of the absorption and radiative bands of the pigment molecules. In the lower band, the degenerate states $|-,1\rangle$ and $|-,L-1\rangle$ are those of OACEs with the eigenvalue $E_a^- = \varepsilon - t_0\delta(1)$. And this is corresponding to the red shifts of the absorption and radiative bands of the pigment molecules. $|+,1\rangle$ and $|+,L-1\rangle$ have the same dipole strength $O_a^+ \equiv (1-\alpha_0)\mu^2 N/4$, where

$$\alpha_0 = [\eta_1\cos(\gamma_1+\gamma_2-\phi)+\eta_2\cos(\gamma_1+\gamma_2+\phi)]/\delta(1), \tag{8}$$

and $|-,1\rangle$ and $|-,L-1\rangle$ also own the same dipole strength $O_a^- \equiv (1+\alpha_0)\mu^2 N/4$, meanwhile, $(O_a^+ + O_a^-)/N\mu^2 = 0.5$. At the different orientation arrangements, $\boldsymbol{u}_1^+$, $\boldsymbol{u}_1^-$ and $\boldsymbol{u}_{L-1}^+$, $\boldsymbol{u}_{L-1}^-$ are always related to the unit vectors $\boldsymbol{e}_l$ and $\boldsymbol{e}_r$, respectively, but the polarizations of $\boldsymbol{u}_1^+$ and $\boldsymbol{u}_{L-1}^+$, $\boldsymbol{u}_1^-$ and $\boldsymbol{u}_{L-1}^-$ both are always orthogonal to each other, respectively. These properties will determine the interactions of the OACEs with the polarized light.

When the coupling coefficients η_1 and η_2 are not equal to each other but have the same sign, $E_a^+ = \varepsilon + t_0\delta(1)$ is near the top of the upper coherent exciton band and $E_a^- = \varepsilon - t_0\delta(1)$ is near the bottom of the lower coherent exciton band, and then the OACEs all have large shifts from the electronic excitation energy of the monomers in energy space. When L is an even number, the energy gap between the two bands is $2t_0|\eta_1 - \eta_2|$ and the widths of the two bands both are $t_0(|\eta_1+\eta_2| - |\eta_1-\eta_2|)$, but if L is an odd number, these relations are right approximately. There are $N-5$ ODCEs and two OACEs below the OACEs $|+,1\rangle$ and $|+,L-1\rangle$, and there is only one ODCE below the OACEs $|-,1\rangle$ and $|-,L-1\rangle$. If $\gamma_1 = \gamma_2 = \phi/2$, for example, $\eta_1 = 4$ and $\eta_2 = 3+\cos 2\phi$, i.e. η_1 and η_2 both are positive. In this orientation arrangement, all local TDMs on the circle point to the outside of the circle and all are oriented near the corresponding tangents to the circle, as depicted in Fig.1(b). When the size of a circular ring is $N = 18$, then $(E_a^+ - \varepsilon)/4t_0 \approx 1.82$, $(E_a^- - \varepsilon)/4t_0 \approx -1.82$, $O_a^+/N\mu^2 \approx 0.013$, and $O_a^-/N\mu^2 \approx 0.487$. Light absorption and radiative intensities mainly concentrate on the OACEs $|-,1\rangle$ and $|-,L-1\rangle$, and then the red shifts of the absorption and radiative bands of the pigment molecules will be dominant. If $\gamma_1 = \pi/2+\phi/2$ and $\gamma_2 = -\pi/2+\phi/2$, $\eta_1 = -2$ and $\eta_2 = -3+\cos 2\phi$, i.e. this is an example that η_1 and η_2 both are negative. In this example, two local TDMs within each dimer point to different sides of the circle and both are oriented near the corresponding normals to the circle. When we also let $N = 18$, then $(E_a^+ - \varepsilon)/4t_0 \approx 0.99$, $(E_a^- - \varepsilon)/4t_0 \approx -0.99$, $O_a^+/N\mu^2 \approx 0.483$, and $O_a^-/N\mu^2 \approx 0.017$. Now light absorption and radiative intensities mainly concentrate on the OACEs $|+,1\rangle$ and $|+,L-1\rangle$, and then the blue shifts of the absorption and radiative bands of the pigment molecules will be dominant. If $\gamma_1 = \pi/4+\phi/2$ and $\gamma_2 = \phi/2$, $\eta_1 = 2\sqrt{2}$ and $\eta_2 = (3+\cos 2\phi-\sin 2\phi)/\sqrt{2}$, i.e. this is an example that η_1 and η_2 also both are positive. But now when $N = 18$, then $(E_a^+ - \varepsilon)/4t_0 \approx 1.18$, $(E_a^- - \varepsilon)/4t_0 \approx -1.18$, $O_a^+/N\mu^2 \approx 0.134$, and $O_a^-/N\mu^2 \approx 0.366$, i.e. four OACEs $|\pm,1\rangle$ and $|\pm,L-1\rangle$ all are corresponding to the superradiant emission. Hence light absorption and radiative intensities can be converted fully between the OACEs in the upper and lower coherent exciton bands by changing the orientation arrangements, and the blue and red shifts of the absorption and radiative bands of the pigment molecules can occur simultaneously at some orientation arrangements.

When the coupling coefficients η_1 and η_2 are not equal to each other and further have different signs, $E_a^+ = \varepsilon + t_0\delta(1)$ is near the bottom of the upper coherent exciton band and $E_a^- = \varepsilon - t_0\delta(1)$ is near the top of the lower coherent exciton band, and then the OACEs all have small shifts from the electronic excitation energy of the monomers in energy space. Now the energy gap between the upper and lower bands is always $2t_0|\eta_1+\eta_2|$. Between E_a^+ and E_a^-, there are

only two ODCEs. There are two OACEs and $L-1$ ODCEs below the OACEs in the upper band, and $L-3$ ODCEs below the OACEs in the lower band. If $\gamma_1 \approx -\pi$, 0, π and $\gamma_2 \approx \pm\pi/2$, or $\gamma_1 \approx \pm\pi/2$ and $\gamma_2 \approx -\pi$, 0, π, i.e. if one local TDM within a dimer is oriented very near the corresponding tangent to the circle and another one is oriented very near the corresponding normal to the circle, or in reverse, for examples, $\eta_1 \approx \pm\sin\phi$ and $\eta_2 \approx \mp\sin\phi$, i.e. at these orientation arrangements, η_1 and η_2 always have different signs, but the couplings between the N-N pigment molecules will be weak. Now the eigenvalues of the coherent excitons $|\pm, k\rangle$ are $E_k^{\pm} \approx \varepsilon \pm 2t_0 \sin\phi|\sin k\phi|$, respectively, and the energy gap between the upper and lower bands is close to zero at each orientation arrangement. In the upper band, the states $|+, 1\rangle$ and $|+, L-1\rangle$ have the same dipole strength $O_a^+ \approx 0$, i.e. the blue shifts of the absorption and radiative bands of the pigment molecules will disappear. In the lower band, the states $|-, 1\rangle$ and $|-, L-1\rangle$ have the same dipole strength $O_a^- \approx N\mu^2/2$ and the eigenvalue is $E_a^- = \varepsilon - 2t_0\sin^2\phi$, i.e. now the red shifts of the absorption and radiative bands of the pigment molecules are dominant, but the shifts are very small. When the coupling coefficients between the N-N pigment molecules are small, we should further consider the interactions between the pigment molecules that have more large separations, but here we do not discuss them. The level structure of the coherent excitons and their dynamic property are complicated in the double-angle model. However this complication can give more manners to capture, store and transfer light energy, and also give more methods to improve the design of synthetic antenna devices.

Next we consider the system in which the local TDMs do not lie in the plane of the circle, but all have the same angle β with respect to it. If the orientation arrangement of the system within the plane is the same as that of the single-angle model or those for the particular cases of the double-angle model, all coupling coefficients between the N-N pigment molecules on the whole circle are also the same, but now they are $\eta^Z \equiv 2\sin^2\beta + \cos^2\beta \cdot \eta^0$, where $\eta^0 = \eta$ or η_2, respectively. The main change is that the coherent exciton $|k=0\rangle$ now is an OACE with the eigenvalue $E_0 = \varepsilon + 2t_0\eta^Z$ and the delocalized TDM $\boldsymbol{u}_0 = \sin\beta \cdot \mu\sqrt{N} \cdot \boldsymbol{e}_z$, where $\boldsymbol{e}_z$ is the unit vector in z-direction. If the orientation arrangement of the system within the plane is the same as that of the general case of the double-angle model and $\beta \neq \pm\pi/2$, the coupling coefficients η_1^Z within the dimers and η_2^Z between the dimers are not equal to each other, either. There is also only one additive OACE. If $\eta_1^Z + \eta_2^Z > 0$, this additive OACE is $|+, 0\rangle$ in the upper coherent exciton band with $\boldsymbol{u}_0^+ = \sin\beta \cdot \mu\sqrt{N} \cdot \boldsymbol{e}_z$ and $E_0^+ = \varepsilon + t_0(\eta_1^Z + \eta_2^Z)$. If $\eta_1^Z + \eta_2^Z < 0$, it is $|-, 0\rangle$ in the lower coherent exciton band with $\boldsymbol{u}_0^- = \sin\beta \cdot \mu\sqrt{N} \cdot \boldsymbol{e}_z$ and $E_0^- = \varepsilon + t_0(\eta_1^Z + \eta_2^Z)$. When $\beta \neq 0$ and also $\beta \neq \pm\pi/2$, those of OACEs all exist, so do they now in the case of $\beta = 0$, but their delocalized TDMs now all have a multiplier $\cos\beta$ and their energy levels are different from those in the case of $\beta = 0$. Hence the locations of the OACEs in energy space will shift as the angle β is varied.

Finally we discuss the critical orientation arrangement at which the coherent exciton cannot exist on a circular ring any more. For the single-angle model or for the particular cases of the double-angle model, if $\gamma = \gamma^*$ or $\gamma_1 = -\gamma_2 = \gamma^*$, respectively, where the critical angle γ^* satisfies the equation $3\cos 2\gamma^* + \cos(2\pi/N) = 0$, all couplings between the N-N pigment molecules on the whole ring will break off, and thus the system is said to be at the critical orientation arrangement. As the orientation arrangement of one system approaches one of its critical orientation arrangements, the physical property of the coherent exciton will be sensitive to the static disorder, thermal excitation and the size N of the ring. If $N = 8$, the critical angles are $\gamma^* \approx \pm 51.8^\circ$ and $\pm 128.2^\circ$. If $N = 9$, the critical angles are $\gamma^* \approx \pm 52.4^\circ$ and $\pm 127.6^\circ$. The orientation arrangements of the B800 bands in Fig.5 of Ref.[10] are not far from the critical orientation arrangements $\gamma^* \approx 52.4^\circ$ and 127.6° in the single-angle model, respectively, and then the small changes of the orientation arrangements may make the electronic excitations localized on individual pigment molecules at very low temperatures. Even for the B850 rings in LH2 on which pigment molecules are located more compactly, if the orientation arrangement is in the vicinity of one critical orientation arrangement, a very weak static disorder or a small thermal excitation can also destroy the coherent excitation, and then the coherent exciton cannot exist either. But for the B850 bands in Fig.5 of Ref.[10], the coupling coefficients are $\eta_1 \approx \eta_2 \approx 3\cos(\pi/6) + \cos(\pi/9) \approx 3.5$, and then the systems are at the orientation arrangements which are far from the critical orientation arrangements of the double-angle model. If $N = 16$, the critical angles are $\gamma^* \approx \pm 54.0^\circ$ and $\pm 126.0^\circ$, and if $N = 18$, $\gamma^* \approx \pm 54.1^\circ$ and $\pm 125.9^\circ$. When $N = 30$ and also when $N = 32$,

then $\gamma^* \approx \pm 54.5^\circ$ and $\pm 125.5^\circ$.

In summary, we have theoretically and systematically studied the level structures of the coherent excitons and their delocalized TDMs at the different orientation arrangements of the local TDMs in the single-angle model and the double-angle model. We have shown that the delocalized TDMs of the coherent excitons, the number of the OACEs and their energy locations, and also the number of the ODCEs below one OACE in energy space are much different at the different orientation arrangements. Similarly, if the orientation arrangements are varied in the general case of the double-angle model, light absorption and radiative intensities can be converted fully between the OACEs in the upper and lower coherent exciton bands, and then the blue and red shifts of the absorption and radiative bands of the pigment molecules can occur simultaneously at some orientation arrangements. We have also given a few critical orientation arrangements, and if the orientation arrangements of the local TDMs in circular LH complexes approach them, the coherent exciton cannot exist any more. We believe that our results are useful for understanding the physics of the efficient light energy transfer in photosynthesis and also for designing different nanoscale optical devices.

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