Vol 12 No 10, October 2003
1009-1963/2003/12(10)/1096-09

Chinese Physics

© 2003 Chin. Phys. Soc.
and IOP Publishing Ltd

Excitonic level structures of LH1 and LH2 of purple photosynthetic bacteria using an analytical approach*

Yang Guang-Can(杨光参), Wang Li(汪 力)†, and Yang Guo-Zhen(杨国桢)

Laboratory of Optical Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100080, *China*

(Received 4 April 2003; revised manuscript received 25 April 2003)

The excitonic level structure of a ring-like chain of dimers is discussed analytically in order to aid the understanding of the possible spectral properties of LH1 and LH2 of purple photosynthetic bacteria. Under the approximation of dipole–dipole interaction between Bchls, the excitonic levels, bandwidths and energy gap between two Davydov subbands are expressed analytically in terms of interaction energies and configurational parameters of dipoles. Our model includes all the interactions between pigment molecules in the system. The oscillator strengths and circular dichroism (CD) for the excitonic states are also presented analytically. The simulated absorption and CD spectra of LH1 and LH2 complexes reproduce the main features of the measured results.

Keywords: excitonic level, photosynthesis, LH1, LH2
PACC: 3310, 3120, 3690

1. Introduction

Photosynthesis is one of the most important chemical reactions on the earth. It has been shown that the absorption of light by the light-harvesting antenna (LHA) is the initial event in photosynthesis. The absorbed energy is carried by electronic excitations, which is transferred to the reaction centre (RC) rapidly and efficiently. At the RC, charge separation is initiated, so the excitation energy is transformed to chemical energy.[1] In purple photosynthetic bacteria the light-harvesting antenna consists of a core antenna LH1 surrounding the RC and peripheral LH2 antenna. Recently, the crystal structures of LH2 of some purple bacteria, such as *Rhodopseudomonas (Rps.) acidophia* and *Rhodospirillum (Rs.) molischianum*, were determined by high resolution x-ray diffraction.[2−4] And the structure data of LH1 of *Rhodospirillum rubrum* was also resolved, though at a lower 1.1 nm resolution, based on its projection map.[5] Both LH1 and LH2 exhibit highly symmetric structures consisting of Bchla (bacteriochlorophyll a) pairs binding to transmembrane polypeptides, i.e., ($\alpha\beta$-Bchla 2). For example, the B800-850 complex of *Rs. molischianum* consists of a ring with 8-fold symmetry containing 16 Bchls 850, 8 Bchls 800, 8 carotenoids, and 8 α-β peptide subunits. The B850 complex, which absorbs light at 850 nm, consists of an inner ring, in which the distance between neighbouring molecules is 0.89 nm within the same α-β subunit and 0.92 nm from adjacent subunits. The B800 subunit absorbing light at 800 nm corresponds to an outer ring, where the distance between neighbouring molecules is 2.1 nm. The minimum separation between B800 and B850 rings is about 1.9 nm.

According to the structure data of B800-850 complex, it is reasonable to treat the inner B850 ring as a circular chain of dimers, in which two Bchlas belonging to the same α, β- polypeptide pairs form a heterodimer. In contrast, the B800 ring is a circular chain of monomers, each containing a single Bchla. The relatively large distance of 2.1 nm between neighbouring molecules in the B800 ring results in their weak coupling; therefore, the outer ring of the complex is a weak excitonic system and can be considered as consisting of monomers for an analytical model of excitonic level structure because of the small difference between the molecule's site energy and excitonic band of the complex. Of course, this weak excitonic effect may become important in the energy transfer

*Project supported by the Ministry of Science and Technology of China (Grant No G1998010102), and the National Natural Science Foundation of China (Grant No 39890390).

†E-mail: wangli@aphy.iphy.ac.cn

process within B800 and the transfer from B800 to B850. The model of dimer ring has been introduced to analyse the spectral properties, such as absorption and circular dichroism (CD), and excitonic dynamics of LH1 and LH2.[6−12] These theoretical analyses of molecular chains focused on the case of the "nearest neighbour" approximation. In a linear chain, the approximation would be more appropriate since the interaction between Bchls becomes weaker rapidly with increasing separation between them. But for a small circular chain, further interaction should be included as the distance between dimers does not increase linearly with increasing difference of their label indices. For LH1 and LH2 of purple photosynthetic bacteria under investigation, their dimensions are comparable to the distance between adjacent Bchls. Thus, it is necessary to include all the interactions when considering the optical characteristic of LH1 and LH2 of purple photosynthetic bacteria. This paper describes the excitonic level and spectral properties of this kind of ring-like molecular aggregates of dimers by including all the interactions between pigment molecules. It is worth emphasizing that we adopt the analytical approach to explore the excitonic properties of the system, so that all the results can be obtained analytically. A recent publication by Hu *et al*[13] also considered the spectral properties of the ring of dimers including all interactions. They established an effective Hamiltonian and derived the formulae for excitonic band edges where the interactions are summarized in several numerical coefficients.

2. Excitonic level structure

A circular chain with N dimers is considered in this study. Each dimer consists of two identical Bchl or chlorophyll (Chl) molecules, and each molecule is approximated as a two-level system. Neglecting phonons and restricting to states with at most one excitation on the chain, the Hamiltonian of the system can be written as

$$\begin{aligned} H &= \sum_{n\alpha} \Delta_{n\alpha} |n\alpha\rangle\langle n\alpha| + \sum_{n\alpha \neq m\beta} V_{n\alpha,m\beta} |m\beta\rangle\langle n\alpha| \\ &\equiv \sum_{n\alpha} \sum_{m\beta} H_{n\alpha,m\beta} |m\beta\rangle\langle n\alpha|, \end{aligned} \tag{1}$$

where $|n\alpha\rangle$ denotes the state in which molecule α of the nth dimer is excited and all the other molecules are in the ground states. n and m enumerate the position of the dimers in the circular chain and run from one to N, while α and β indicate the polypeptide to which the molecule is bound in a dimer. $\Delta_{n\alpha}$ denotes the $n\alpha$th (molecule α in the nth dimer) molecular excitation energy, and $V_{n\alpha,m\beta}$ is the interaction (transfer integral) between molecules $n\alpha$ and $m\beta$. Because of symmetry, $\Delta_{n\alpha} = \Delta_\alpha$ and $V_{n\alpha,m\beta} = V_{\alpha\beta}(n-m) = V_{\alpha\beta}(n-m+N)$ for the circular chain of dimers.

Defining another set of orthonormal bases

$$|k\alpha\rangle = N^{-1/2} \sum_n |n\alpha\rangle \exp(\mathrm{i}kn),$$

$$k = \frac{2\pi}{N} s, \qquad s = 0, \cdots, N-1, \tag{2}$$

the Hamiltonian becomes

$$\begin{aligned} H &= \sum_{k,\alpha,\beta} L_{\alpha\beta}(k) |k\alpha\rangle\langle k\beta|, \\ L_{\alpha\beta}(k) &= \sum_n H_{1\beta,n\alpha} \exp(\mathrm{i}kn). \end{aligned} \tag{3}$$

Then the problem is simplified into the diagonalization of $L_{\alpha\beta}(k)$. The eigenequation of $L_{\alpha\beta}(k)$ is

$$\sum_\beta L_{\alpha\beta}(k) u_{\beta\nu}(k) = E_\nu(k) u_{\alpha\nu}(k). \tag{4}$$

For the chain of dimers, it can be solved analytically. The eigenvalues are

$$E_\nu = \frac{L_{11} + L_{22}}{2} - (-1)^\nu \sqrt{\left(\frac{L_{11} - L_{22}}{2}\right)^2 + |L_{12}(k)|^2}, \tag{5}$$

and the corresponding eigenfunctions

$$\begin{aligned} u_{1\nu}(k) &= \frac{L_{12}}{\sqrt{|L_{12}|^2 + (E_\nu - L_{11})^2}}, \\ u_{2\nu}(k) &= \frac{E_\nu - L_{11}}{\sqrt{|L_{12}|^2 + (E_\nu - L_{11})^2}}, \end{aligned} \tag{6}$$

under the normalization condition

$$\sum_\alpha |u_{\alpha\nu}(k)|^2 = 1.$$

The exciton vectors are linear combinations of site excitations, and can be written as

$$|k\mu\rangle = N^{-1/2} \sum_{n\alpha} u^*_{\alpha\mu} \exp(\mathrm{i}kn) |n\alpha\rangle. \tag{7}$$

Let the mono-molecular transition dipole moment be $\boldsymbol{d}_{n\alpha}$, the transition dipole for the excitonic level will be

$$\boldsymbol{d}_{k\mu} = N^{-1/2} \sum_{n\alpha} u^*_{\alpha\mu} \exp(\mathrm{i}kn) |n\alpha\rangle \boldsymbol{d}_{n\alpha}. \tag{8}$$

Then the oscillator strength corresponding to the transition to the excitonic state is given by the square of the dipole moment, that is,

$$A_\mu(k) = N^{-1/2} \sum_{\alpha\beta} u^*_{\alpha\mu} u_{\beta\mu} \times \sum_{nm} \boldsymbol{d}_{n\alpha} \cdot \boldsymbol{d}_{m\beta} \exp[\mathrm{i}k(n-m)]. \quad (9)$$

The matrix form of $L(k)$ in Eq.(3) is

$$L(k) = \begin{pmatrix} \sum_{j=1}^{N} H_{11,j1} \exp(\mathrm{i}kj) & \sum_{j=1}^{N} H_{11,j2} \exp(\mathrm{i}kj) \\ \sum_{j=1}^{N} H_{12,j1} \exp(\mathrm{i}kj) & \sum_{j=1}^{N} H_{12,j2} \exp(\mathrm{i}kj) \end{pmatrix}. \quad (10)$$

Considering the symmetry of the system and periodic boundary conditions, it can be expressed in terms of site energy Δ_α and transfer integral $V_{\alpha\beta}(n-m)$. When N is odd, we have

$$L(k) = \begin{pmatrix} \Delta_1 + \sum_{j=1}^{\frac{N-1}{2}} 2V_{11}(j)\cos(jk) & \sum_{j=1}^{N} V_{12}(j)\exp(\mathrm{i}kj) \\ \sum_{j=1}^{N} V_{21}(j)\exp(\mathrm{i}kj) & \Delta_2 + \sum_{j=1}^{\frac{N-1}{2}} 2V_{22}(j)\cos(jk) \end{pmatrix}$$

$$= \begin{pmatrix} \Delta_1 + \sum_{j=1}^{\frac{N-1}{2}} 2V_{11}(j)\cos(jk) & \sum_{j=1}^{N} V_{12}(j)\exp(\mathrm{i}kj) \\ \sum_{j=1}^{N} V_{12}(j)\exp(-\mathrm{i}kj) & \Delta_2 + \sum_{j=1}^{\frac{N-1}{2}} 2V_{22}(j)\cos(jk) \end{pmatrix}, \quad (11)$$

because $V_{11}(j) = V_{11}(N-j)$, $V_{22}(j) = V_{22}(N-j)$, and $V_{21}(j) = V_{21}(N-j)$. The resulting excitonic levels are

$$E_\nu(k) = \Delta_+^{\mathrm{odd}} - (-1)^\nu \sqrt{(\Delta_-^{\mathrm{odd}})^2 + \left| \sum_{j=1}^{N} V_{12}(j)\exp(\mathrm{i}kj) \right|^2},$$

$$\Delta_\pm^{\mathrm{odd}}(k) = \frac{\Delta_1 \pm \Delta_2}{2} + \sum_{j=1}^{\frac{N-1}{2}} [V_{11}(j) \pm V_{22}(j)]\cos(kj). \quad (12)$$

While N is even, the matrix $L(k)$ becomes

$$L(k) = \begin{pmatrix} \Delta_1 - V_{11}\left(\frac{N}{2}\right) + \sum_{j=1}^{\frac{N}{2}-1} 2V_{11}(j)\cos(jk) & \sum_{j=1}^{N} V_{12}(j)\exp(\mathrm{i}kj) \\ \sum_{j=1}^{N} V_{12}(j)\exp(-\mathrm{i}kj) & \Delta_2 - V_{22}\left(\frac{N}{2}\right) + \sum_{j=1}^{\frac{N}{2}-1} 2V_{22}(j)\cos(jk) \end{pmatrix}, \quad (13)$$

and the corresponding exciton spectrum will be

$$E_\nu(k) = \Delta_+^{\mathrm{even}} - (-1)^\nu \sqrt{(\Delta_-^{\mathrm{even}})^2 + \left| \sum_{j=1}^{N} V_{12}(j)\exp(\mathrm{i}kj) \right|^2},$$

$$\Delta_\pm^{\mathrm{even}}(k) = \frac{\Delta_1 \pm \Delta_2}{2} + \frac{V_{11}\left(\frac{N}{2}\right) \pm V_{22}\left(\frac{N}{2}\right)}{2} + \sum_{j=1}^{\frac{N}{2}-1} [V_{11}(j) \pm V_{22}(j)]\cos(kj). \quad (14)$$

Under the approximation of dipole–dipole interaction, the transfer integrals between Bchls can be written as

$$V_{\alpha\beta}(n-m) = \frac{1}{4\pi\varepsilon_0\eta^2} \left[\frac{\boldsymbol{d}_{n\alpha} \cdot \boldsymbol{d}_{m\beta}}{R^3} - \frac{3(\boldsymbol{d}_{n\alpha} \cdot \boldsymbol{R}_{n\alpha,m\beta})(\boldsymbol{d}_{m\beta} \cdot \boldsymbol{R}_{n\alpha,m\beta})}{R^5} \right], \quad (15)$$

where $\boldsymbol{d}_{n\alpha}$ and $\boldsymbol{d}_{m\beta}$ are the transition dipole moments of the corresponding Bchls; $\boldsymbol{R}_{n\alpha,m\beta}$ is the position vector pointing from the $n\alpha$th Bchl to the $m\beta$th one, and R is its module; η denotes the refractive index of the surrounding medium. According to the notation in Fig.1,

$$\begin{aligned}\boldsymbol{d}_{n\alpha}\cdot\boldsymbol{d}_{m\beta} =& d^2\{\sin\theta_\alpha\sin\theta_\beta\cos[\gamma(n-m)\\ &+\gamma'(\alpha-\beta)+\varphi_\alpha-\varphi_\beta]+\cos\theta_\alpha\cos\theta_\beta\}.\end{aligned}$$

Inserting the expression into Eq.(15), we have

$$\begin{aligned}V_{\alpha\beta}(j) =& \frac{d^2}{4\pi\varepsilon_0\eta^2\{2r\sin[\gamma j/2+\gamma'(\beta-\alpha)]\}^3}\\ &\times\{\sin\theta_\alpha\sin\theta_\beta[3\cos(\varphi_\alpha+\varphi_\beta)\\ &-\cos(\varphi_\beta-\varphi_\alpha+\gamma j+\gamma'(\beta-\alpha))]/2\\ &+\cos\theta_\alpha\cos\theta_\beta\},\end{aligned}$$

where α and β denote the position of molecules in a dimer, γ and γ' are the turning angles between the neighbouring molecules from different dimers and within the same dimer respectively, and d is the absolute value of the molecular transition dipole moment.

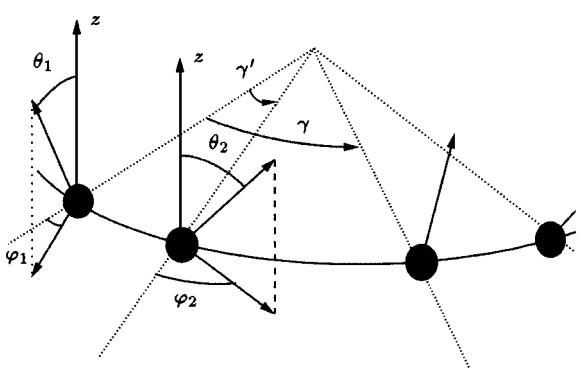


Fig.1. The model of a circular chain of dimers.

Because of periodic boundary condition and symmetry of the system, not all excitonic states are accessible through optical transition. Only transitions into six exciton states are allowable with a finite oscillator strength[8]

$$\begin{aligned}A_\nu(\pm\gamma) =& \frac{1}{2}Nd^2\sum_{\alpha\beta}u_{\alpha\nu}(\pm\gamma)u^*_{\beta\nu}(\pm\gamma)\sin\theta_\alpha\sin\theta_\beta\\ &\times\exp[\pm\mathrm{i}(\gamma'(\alpha-\beta)+\varphi_\alpha-\varphi_\beta)]\end{aligned}\tag{16}$$

for the degenerate states of the chain, and

$$A_\nu(0) = Nd^2\sum_{\alpha\beta}u_{\alpha\nu}(0)u^*_{\beta\nu}(0)\cos\theta_\alpha\cos\theta_\beta\tag{17}$$

for the nondegenerate states. Inserting Eq.(6) into above expressions, we have similar results to Ref.[8],

$$\begin{aligned}A_\nu(\gamma) =& \frac{Nd^2}{2(F_\nu(\gamma)+1)}\Big\{F_\nu(\gamma)^2\sin^2\theta_1+\sin^2\theta_2\\ &+2F_\nu(\gamma)\frac{\mathrm{Re}L_{12}(\gamma)}{|L_{12}(\gamma)|}\cos(\varphi_1-\varphi_2\\ &-\gamma')\sin\theta_1\sin\theta_2\Big\}\end{aligned}\tag{18}$$

and

$$A_\nu(0) = \frac{Nd^2}{F_\nu(0)^2+1}[F_\nu(0)\cos\theta_1+\cos\theta_2]^2,\tag{19}$$

where

$$F_\nu(k) = \frac{|L_{12}(k)|}{E_\nu(k)-L_{11}}.\tag{20}$$

It is noted that the expressions of $F_\nu(k)$ and L_{12} are different from Ref.[8], because all interactions between pigment molecules in the system are included here.

The CD spectrum is more sensitive to the structure of the complex. The general expression of CD is[8,10]

$$\begin{aligned}C_\nu(k) \sim& \frac{1}{N}\sum_{\alpha\beta}u_{\alpha\nu}(k)u^*_{\beta\nu}(k)\\ &\times\sum_{nm}\exp[\mathrm{i}k(m-n)]\\ &\times\boldsymbol{r}_{n\alpha,m\beta}\cdot(\boldsymbol{d}_{n\alpha}\times\boldsymbol{d}_{m\beta}).\end{aligned}\tag{21}$$

Because of the symmetry of circular chain of dimers, we have only six non-zero components of CD. The nondegenerate component is

$$\begin{aligned}C_\nu(0) \sim& -\frac{rNd^2}{F_\nu(0)^2+1}[F_\nu(0)^2\sin2\theta_1\sin\varphi_1\\ &+\sin2\theta_2\sin\varphi_2+2F_\nu(0)H(0)],\end{aligned}\tag{22}$$

where

$$H(0) = \sin\theta_1\cos\theta_2\sin\varphi_1+\cos\theta_1\sin\theta_2\sin\varphi_2.$$

And the component of the degenerate pairs is

$$\begin{aligned}C_\nu(\gamma) \sim& \frac{rNd^2}{2(F_\nu(\gamma)^2+1)}[F_\nu(\gamma)^2\sin2\theta_1\sin\varphi_1\\ &+\sin2\theta_2\sin\varphi_2+2F_\nu(\gamma)H(\gamma)],\end{aligned}\tag{23}$$

where

$$\begin{aligned}H(\gamma) =& \mathrm{Re}\frac{L_{12}(\gamma)}{|L_{12}(\gamma)|}\Big[\sin\theta_1\cos\theta_2\exp\Big(\varphi_1-\gamma'-\frac{\pi}{2}\Big)\\ &+\cos\theta_1\sin\theta_2\exp\Big(\varphi_1-\gamma'-\frac{\pi}{2}\Big)\Big].\end{aligned}\tag{24}$$

The expression of $C_\nu(\gamma)$ is quite similar to Eq.(22) of Ref.[8], but the main difference is the expression of L_{12} with all the interactions between pigments.

It is well known that the excitonic band of an aggregate of N monomers is composed of N excitonic levels, which is called Davydov's splitting. Under the nearest neighbouring interaction approximation, the excitonic band has a width of $4V$, where V is the resonance integral between neighbouring monomers.[14] When the monomers are replaced by dimers, the ring's excitonic spectra will become more complicated. The case of nearest dimer–dimer interaction has been discussed in Ref.[8]. This paper here is to extend it to more general situation when all interactions among chromophore molecules are included.

At first we focus on the case where N is odd. Considering all interactions between Bchls, it can be seen from Eq.(12) that the overall excitonic band width now becomes

$$W = E_+(0) - E_-(0) = 2\sqrt{[\Delta_-^{\rm odd}(0)]^2 + \left|\sum_{j=1}^{N} V_{12}(j)\right|^2}, \tag{25}$$

and the band splits into two Davydov subbands with the same width

$$\begin{aligned} W_\pm^{\rm odd} &= \pm\left[E_\pm(0) - E_\pm\left(\frac{N-1}{N}\pi\right)\right] \\ &= \sum_{j=1}^{\frac{N-1}{2}}[V_{11}(j) \pm V_{22}(j)]\left(1 \mp \cos j\frac{N-1}{N}\pi\right) + \sqrt{[\Delta_-^{\rm odd}(0)]^2 + \left|\sum_{j=1}^{N} V_{12}(j)\right|^2} \\ &\quad - \sqrt{\left[\Delta_-^{\rm odd}\left(\frac{N-1}{N}\pi\right)\right]^2 + \left|\sum_{j=1}^{N} V_{12}(j)\exp\left(\mathrm{i}\frac{N-1}{N}j\pi\right)\right|}, \end{aligned} \tag{26}$$

where subscript "+" denotes the higher subband, "−" the lower subband. The energy gap between the two subbands is

$$G^{\rm odd} = 2\sqrt{\left[\Delta_-^{\rm odd}\left(\frac{N-1}{N}\pi\right)\right]^2 + \left|\sum_{j=1}^{N} V_{12}(j)\exp\left(\mathrm{i}\frac{N-1}{N}j\pi\right)\right|}, \tag{27}$$

when N is even, the structure of excitonic band is similar. The total band width is the same as Eq.(25), but the subband width becomes

$$\begin{aligned} W_\pm^{\rm even} &= \pm\left[E_\pm(0) - E_\pm(\pi)\right] \\ &= \sum_{j=1}^{\frac{N}{2}}[V_{11}(j) \pm V_{22}(j)](1 \mp (-1)^j) \\ &\quad + \sqrt{[\Delta_-^{\rm even}(0)]^2 + \left|\sum_{j=1}^{N} V_{12}(j)\right|^2} \\ &\quad + \sqrt{[\Delta_-^{\rm even}(\pi)]^2 + \left|\sum_{j=1}^{N}(-1)^j V_{12}(j)\right|^2}. \end{aligned} \tag{28}$$

So the gap between the higher and lower subbands is

$$G^{\rm even} = 2\sqrt{[\Delta_-^{\rm even}(\pi)]^2 + \left|\sum_{j=1}^{N}(-1)^j V_{12}(j)\right|^2}. \tag{29}$$

In the absence of heterogeneity of the two molecules in a dimer, i.e., $\Delta_1 = \Delta_2 = \Delta$,

$$\Delta_+^{\rm odd} = \Delta + \sum_{j=1}^{\frac{N-1}{2}}[V_{11}(j) + V_{22}(j)]\cos(jk), \tag{30}$$

$$\Delta_-^{\rm odd} = \sum_{j=1}^{\frac{N-1}{2}}[V_{11}(j) - V_{22}(j)]\cos(jk), \tag{31}$$

and

$$\begin{aligned} \Delta_+^{\rm even} =& \Delta + \frac{1}{2}\left[V_{11}\left(\frac{N}{2}\right) + V_{22}\left(\frac{N}{2}\right)\right] \\ &+ \sum_{j=1}^{\frac{N}{2}-1}[V_{11}(j) + V_{22}(j)]\cos(jk), \end{aligned} \tag{32}$$

$$\begin{aligned} \Delta_-^{\rm even} =& \frac{1}{2}\left[V_{11}\left(\frac{N}{2}\right) - V_{22}\left(\frac{N}{2}\right)\right] \\ &+ \sum_{j=1}^{\frac{N}{2}-1}[V_{11}(j) - V_{22}(j)]\cos(jk). \end{aligned} \tag{33}$$

Inserting them into Eqs.(12), (14), (27) and (29), the modified excitonic levels, band widths and energy gaps can be acquired immediately.

If we confine the treatment to the nearest neighbouring approximation, the problem can be simplified considerably. Let $V_b = V_{12}(0)$ and $V_a = V_{12}(1)$ be the interaction energies between two neighbouring

molecules in the same dimer and from the adjacent dimers respectively, then

$$E_\nu(k) = \frac{\Delta_1 + \Delta_2}{2} - (-1)^\nu \sqrt{\left(\frac{\Delta_1 + \Delta_2}{2}\right)^2 + |L_{12}(k)|^2}, \quad (34)$$

where

$$L_{12}(k) = V_\alpha \exp(-\mathrm{i}kj) + V_b. \quad (35)$$

The results are just the same as Eqs.(8) and (9) in Ref.[8]. So our analytical approach is a reasonable extension of the result of Liuolia *et al.*

The energy difference between the lowest excitonic level and the strongly allowed transition level E_1 (symbol borrowed from Ref.[7]) must be emphasized, since the recent hole burning experiment calculated the lowest level.[7] Koolhaas *et al*[11] identified the excitonic band of *Rhodobacter sphaeroides* directly by a B800-free mutant strain. The band is located at about 780 nm. From Eqs.(12) and (14), we have

$$\Delta E_1^{\mathrm{odd}} = \sqrt{[\Delta_-^{\mathrm{odd}}(0)]^2 + \left|\sum_{j=1}^{N} V_{12}(j)\right|^2} - \sqrt{[\Delta_-^{\mathrm{odd}}(\gamma)]^2 + \left|\sum_{j=1}^{N} V_{12}(j)\cos\left(j\frac{2\pi}{N}\right)\right|^2} - \sum_{j=1}^{\frac{N-1}{2}} [V_{11}(j) + V_{22}(j)]\left[1 - \cos\left(j\frac{2\pi}{N}\right)\right], \quad (36)$$

when N is odd; and

$$\Delta E_1^{\mathrm{even}} = \sqrt{[\Delta_-^{\mathrm{even}}(0)]^2 + \left|\sum_{j=1}^{N} V_{12}(j)\right|^2} - \sqrt{[\Delta_-^{\mathrm{even}}(\gamma)]^2 + \left|\sum_{j=1}^{N} V_{12}(j)\cos\left(j\frac{2\pi}{N}\right)\right|^2} - \sum_{j=1}^{\frac{N}{2}} [V_{11}(j) + V_{22}(j)]\left[1 - \cos\left(j\frac{2\pi}{N}\right)\right], \quad (37)$$

for even N.

3. Applications to LH1 and LH2 complexes

3.1. LH2 complex

In LH2 complex of purple bacteria, the outer BChl800 ring is believed to consist of monomers because of the large separations between the neighbouring BChlas and resulting in small interaction energies. Therefore, the excitonic effect is negligible in the ring.[6] In contrast, in the inner B850 ring the distances between pigment molecules are small and can lead to large interaction energies between them. The resulting strong excitonic effect is important in this case. We focus on the exciton in the B850 ring, which can be approximately modelled as a circular chain of dimers. In previous sections, we have analytically shown that the level structure of the system can be expressed in terms of site energy and interactions between pigment molecules. Now we applied the analytical results to B850 ring of LH2 complex. Up to now, there are two kinds of LH2 complex, *Rs. molischianum* and *Rps. acidophila*, whose high resolution structural data are available. Their structures are similar, but exhibit C_8 and C_9 symmetry respectively. It will result in different excitonic levels. We discuss their spectral properties separately.

Rs. molischianum: Its LH2 complex exhibits 8-fold rotational symmetry. The B850 ring contains 16 Bchl molecules that form 8 dimers. It has 16 excitonic levels including 4 nondegenerate levels and 6 degenerate pairs. Figure 2 shows its simulated excitonic levels. As a common feature of dimer chain, the total excitonic band is split into upper and lower subbands. Among all the 10 levels, only 2 nondegenerate levels and 2 degenerate pairs possess nonzero oscillator strengths because of the symmetric configuration. They forms the upper and lower absorption peaks in the excitonic band. Based on the configuration data in Ref.[13], we can calculate all the interaction energies between pigment molecules under the point dipole approximation by using the dipole–dipole coupling formula. The interactions are listed in Table 1. These data correspond to the dipole strength of 4.673×10^{-58} C^{2}m^2 for Q_y transition of Bchl when the dielectric constant of the surrounding medium is taken to be 1.0. According to these parameters the overall exciton manifold width is 1250 cm^{-1}, with an upper subband width of 468 cm^{-1} and a lower 763 cm^{-1}. By fitting the calculated strongest transition to the maximum absorption peak at 850 nm, the site energy of Bchla is taken to be 12500 cm^{-1}. Assigning each exciton component a Gaussian profile (full width at half maximum (FWHM)=120 cm^{-1}) with the amplitude proportional to the dipole strength, we have a simulation of the absorption spectrum of LH2 as shown in Fig.3. It is noted that we have added the contribution of B800 ring as monomers to the spectrum. The simulated absorbance reproduces the main features of the

experimental results. The calculated amplitude ratio between B850 peak and B800 peak is 0.8, while the experimental value is 0.77.[15] In our calculation, the difference between the strongly allowed level and the lowest one in the excitonic manifold is 103.3 cm^{-1}, which agrees well with the experimental value reported in Ref.[9]. The simulation spectra of nearest neighbouring interactions are also overlaid for comparison with the present model.

Table 1. The interaction energies between pigment molecules for B850 of LH2 of *Rs. molischianum*.

$m-n$	$V(1,1)$	$V(1,2)$	$V(2,1)$	$V(2,2)$
1	–32.68	10.74	319.27	–43.69
2	–3.60	2.16	12.08	–5.35
3	–0.91	0.95	2.59	–1.69
4	–0.49	1.06	1.06	–1.10
5	–0.91	2.59	0.95	–1.69
6	–3.60	12.08	2.16	–5.35
7	–32.67	319.27	10.74	–43.68
8	–	329.90	320.90	–

Note: $m-n$ denotes the dimer index difference and $V(a,b)$ represents the interaction energy (cm^{-1}) between the a-th and the b-th molecules.

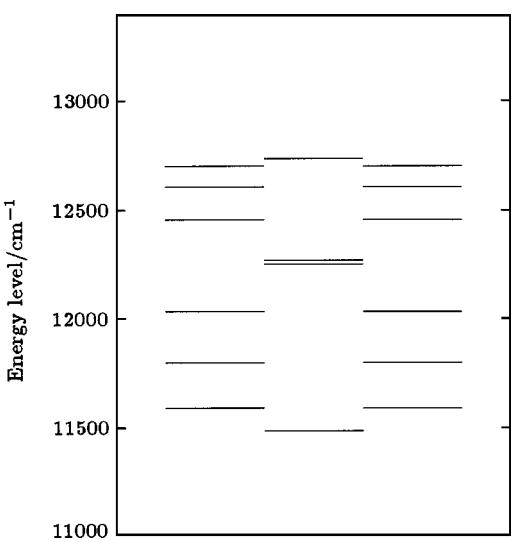


Fig.2. The calculated excitonic level structure for B850 ring of LH2 of *Rs. molischianum*.

CD spectrum: CD spectra are more informative in the configuration study of the assembly of interacting Bchls than are absorption spectra. According to Eqs.(22) and (23), we have calculated the CD signal of the system by assigning each component a Gaussian profile (FWHM=120 cm^{-1}), as shown in Fig.3. It is a conservative CD spectrum, while the recent experimental CD of LH2 of *Rs. Molichianum* is not conservative,[16] where a small positive lobe is present on the blue side and a large negative peak on the red side. It seems that our basic excitonic model is too simple to explain the CD spectral properties of the antenna system.

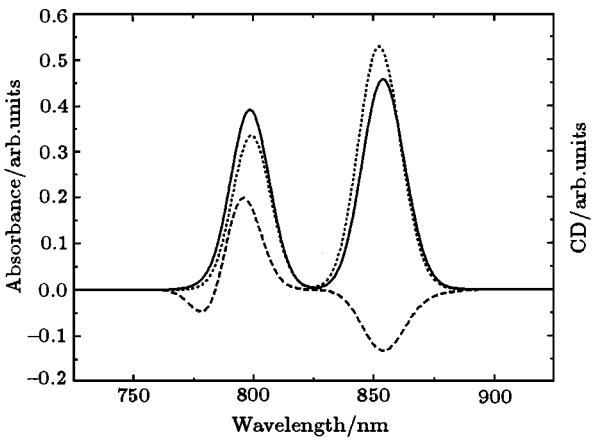


Fig.3. The calculated absorbance (solid line), CD (dashed line) of LH2 of *Rs. molischianum*. The dotted line denotes the simulation absorbance of nearest neighbouring interactions.

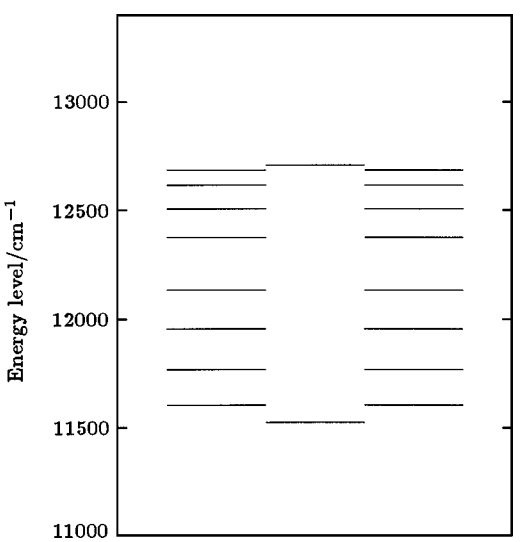


Fig.4. The calculated excitonic level structure for B850 ring of LH2 of *Rps. acidophila*.

Rps. Acidophila: The system exhibits C_9 symmetry and the number of pigment molecules is 18. The 18 excitonic levels are shown in Fig.4. The level structure is quite similar to that of C_8, but with different total level number. The simulated absorbance of the complex, as shown in Fig.5, exhibits a redshifted B850 peak compared with that of *Rs. Molischianum*, because its B850 ring has additional Bchls pairs. The calculated CD is also presented in Fig.5. In this calculation, the same site energy and FWHM of the Gaussian profile are taken as those for *Rs. Molischianum*.

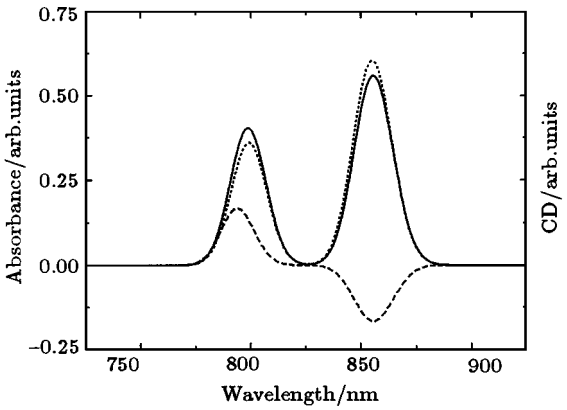


Fig.5. The calculated absorbance (solid line) and CD (dashed line) of LH2 of *Rps. acidophila*. The dotted line denotes the simulation absorbance of nearest neighbouring interactions.

3.2. LH1 complex

Rsp. rubrum: Based on a low-resolution (0.85 nm) projection map of LH1 complex of *Rsp. Rubrum*,[5] a circular aggregate model with a 16-fold rotational symmetry was proposed. The complex has an inner core large enough to house the RC complex. The similarities of protein sequence, spectral and structural features suggest that the structure of LH1 strongly resembles the inner dimer ring of LH2. Therefore, we use a similar structure to discuss its spectral properties. We take the configuration data of LH1 complex presented in Ref.[13]. The resulting excitonic level structure of the complex is plotted in Fig.6. Its absorption and CD spectra, based on the exciton model, are given in Fig.7. The simulated absorbance consists of a large red peak centred at 875 nm and a small blue peak. The two peaks represent the upper and lower excitonic bands due to Davydov splitting. The small blue absorbance has not been emphasized in previous theoretical and experimental works. After carefully examining the recent experimental absorption data for LH1 of *Rs. Molischianum*,[15] we found that a small but distinguishable peak around 780 nm existed indeed. We ascribe it to the upper excitonic band of the complex. Of course, further studies are needed to justify this assignment.

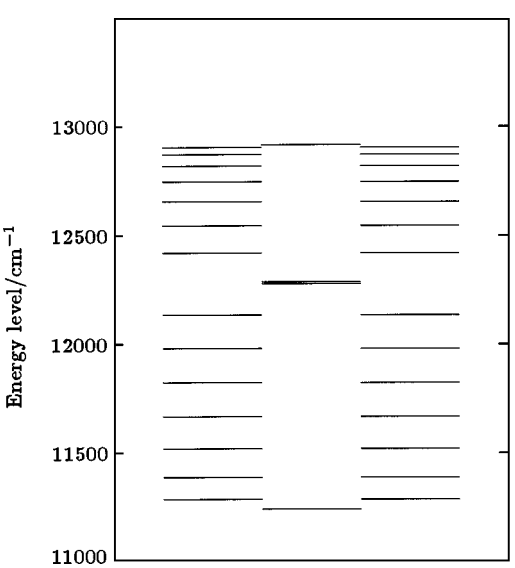


Fig.6. The calculated excitonic level structure of LH1 of *Rsp. rubrum*.

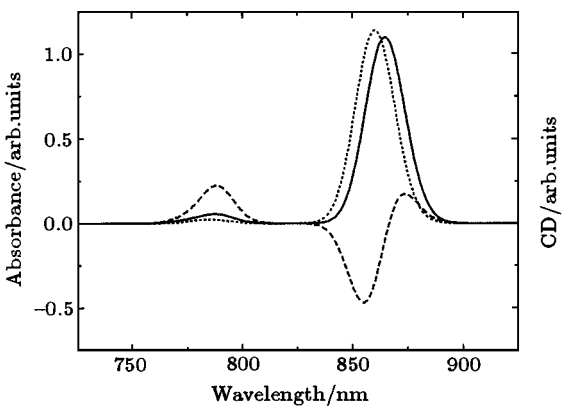


Fig.7. The calculated absorbance (solid line) and CD (dashed line) of LH1 of *Rsp. Rubrum*. The dotted line denotes the simulation absorbance of nearest neighbouring interactions.

4. Discussions

In this paper we adopt an analytical approach to study the excitonic level structure of a tightly coupled ring-like chain of dimers. All the interactions between pigment molecules are included with the point-dipole approximation in the formalism. Although the point-dipole approximation may be satisfactory when the interchromophore distances are large relative to the chromophore dimensions, it could break down in such systems as LH1 and LH2, where the distance between nearest neighbour pigment molecules is smaller than the size of Bchl molecule. An alternative approach could be a point-monopole treatment that distributes the transition moment over the spatial region of the orbitals involved. The point-monopole treatment will produce an 8%–25% increase in the magnitude of the interaction energy, compared with that resulting from the point-dipole approximation.[6] But in this case, the interaction energies can be taken as parameters and we can obtain an equivalent reduced dipole (not actual) value for a Bchl. Then our theoretical treatment is still effective since the equivalent reduced dipole will result in the same excitonic level structure.

In the present formalism, we have not taken into account the interactions of the exciton with the vibrational modes (phonon) of the molecules in the aggregate, nor that of the exciton with the vibrational modes of the surrounding medium. The excitation is treated as delocalizing over the whole molecular ring. At a very low temperature this may be true. But at room temperature, the effect of phonons is not negligible and it will reduce the coherent length of the exciton because a small inhomogeneity causes the exciton to be localized on a limited number of pigments. The exact coherent length of exciton is of much concern by many experimentalists and theorists,[17] and is still an issue for further study. On the other hand, we have neglected the effect of charge transfer (CT) states by introducing shifted site energies as parameters in our simple model. In the strongly coupled molecular ring of dimers, however, the intramolecular Q_y transitions are mixed to various extents with CT transitions.[18−20] Stark spectroscopy of LH1 and LH2 has indicated that the CT states are related to the exchange interactions of Bchl and carotenoid.[21,22] It is necessary to include effects of phonon and CT states in future theoretical simulation. Also, in the present model, all Bchls are approximated as identical two-level systems to obtain an analytical expression of excitonic level structures. But in the LH1 and LH2 complex, the Bchls are bound to α and β peptides respectively by hydrogen bonds. The protein environment may vary the excitation energies of α- and β-bound Bchls. The site energy dependence of CD spectroscopy has been simulated in Ref.[10] numerically, which shows that the rotational strength is quite sensitive to the detailed site energies when degeneracy is lifted. Therefore, the difference in site energies, i.e., effects of protein environment, should be included in a further analytical model.

References

[1] van Grondelle R, Dekker J P, Gillbro T and Sundström V 1994 *Biochem. Biophys. Acta* **1187** 1

[2] McDermott G, Prince S M, Freer A A, Hawthornthwaite-Lawless A M, Papiz M Z, Cogdell R J and Isaacs N W 1995 *Nature* **347** 517

[3] Freer A A, Prince S M, Sauer K, Papiz M, Hawthornthwaite-Lawless A M, McDermott G, Cogdell R J and Isaacs N W 1996 *Structure* **4** 449

[4] Koepke J, Hu X, Muenke C, Schulten K J and Michel H 1996 *Structure* **4** 581

[5] Karrasch S, Bullough P A and Ghosh R 1995 *EMBO J.* **14** 631

[6] Sauer K, Cogdell R J, Prince S M, Freer A A, Isaacs N W and Scheer H 1996 *Photochem. Photobiol.* **64** 564

[7] Wu H M, Reddy N R S and Small G J 1997 *J. Phys. Chem.* B **101** 651

[8] Liuolia V, Valkunas L and van Grondelle R 1997 *J. Phys. Chem.* B **101** 7343

[9] Wu H M, Ratsep M, Lee I J, Cogdell R J and Small G J 1997 *J. Phys. Chem.* B **101** 7654

[10] Koolhaas M H C, van der Zwan G, Frese F N and van Grondelle R 1997 *J. Phys. Chem.* B **101** 7262

[11] Koolhaas M H C, Frese R N, Fowler G J S, Bibby T S, Georgakopoulou S, van der Zwan G, Hunter C N and van Grondelle R 1998 *Biochem.* **37** 4693

[12] Koolhaas M H C, van der Zwan G and van Grondelle R 2000 *J. Phys. Chem.* B **104** 4489

[13] Hu X, Ritz T, Damjanović A and Schulten K J 1997 *J. Phys. Chem.* B **101** 3854

[14] Davydov A S 1971 *Theory of Molecular Excitons* (New York: Plenum)

[15] Visschers R W, Germeroth L, Michel H, Monshouwer R and van Grondelle R 1995 *Biochem. Biophys. Acta* **1230** 147

[16] Ihalainen J A, Linnanto J, Myllyperkiö P, van Stokkum I H M, Ücker B, Scheer H and Korppi-Tommola J E I 2001 *J. Phys. Chem.* B **105** 9849

[17] Monshouwer R, Abrahamsson M, van Mourik F and van Grondelle R 1997 *J. Phys. Chem.* B **101** 7241
Hess S, Akesson E, Cogdell R J, Pullerits T and Sundström V 1995 *Biophys. J.* **69** 2211

[18] Warshel A and Parson W W 1987 *J. Am. Chem. Soc.* **109** 6143
Parson W W and Warshel A 1987 *J. Am. Chem. Soc.* **109** 6152

[19] Thompson M A, Zerner M C and Fajer J 1991 *J. Phys. Chem.* **95** 5693

[20] Alden R G, Johnson E, Nagarajan V, Parson W W, Law C J and Cogdell R J 1997 *J. Phys. Chem.* B **101** 4667

[21] Beekman L M P, Steffen M A, van Stokkum I H M, Olsen J D, Hunter C N, Boxer S G and van Grondelle R 1997 *J. Phys. Chem.* B **101** 7284

[22] Beekman L M P, Frese N F, Fowler G J S, Picorel R, Cogdell R J, van Stokkum I H M, Hunter C N and van Grondelle R 1997 *J. Phys. Chem.* B **101** 7293