Low-lying excited states of light-harvesting system II in purple bacteria

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(Received 10 January 2003; revised manuscript received 25 September 2003; published 31 March 2004)

The low-lying excited states of a B850 ring of Rhodospirillum (Rs.) molischianum are determined accurately by a semiempirical INDO/S method. Results obtained are found to fit extremely well with a Frenkel exciton model with long-range dipolar interactions, and the spatial size of the electron-hole pair is confirmed to fall predominantly within one bacteriochlorophyll with a small leakage to its nearest neighbors. More importantly, the nearest neighbor exciton coupling constants are found to be close to those evaluated directly from dimers, and thus, an existing discrepancy between calculated results of dimers and B850 rings has been resolved.

DOI: 10.1103/PhysRevE.69.032902

PACS number(s): 87.15.-v, 87.16.Ac, 87.17.Aa

The basic energy source for virtually all organisms is photosynthesis, via which the energy of sunlight is used to convert carbon dioxide and water into the simple sugar glucose. Photosynthetic systems have developed various antenna systems in order to better capture sunlight. The structures of the light-harvesting apparatus in purple bacteria, such as Rhodospirillum (Rs.) molischianum, have been resolved by x-ray crystallography [1,2]. The photosynthetic unit (PSU) in these purple bacteria is composed of light-harvesting aggregates of bacteriochlorophyll (LHII) and carotenoids, and a reaction center (RC). The LHII (B875) aggregate encircles the reaction center while the LHII aggregate (B800 and B850) forms a peripheral network of pigment-protein complexes located next to the LHII aggregate.

The LHII complex of Rs. molischianum is an eight-unit circular aggregate built from αβ-heterodimers forming with $C_8$ symmetry. Each unit contains a pair of α and β apoproteins, three bacteriochlorophylls-a (BChls-a) molecules and one carotenoid. The BChl-a molecules form two rings named the B800 ring in Fig. 1(a). For the B850 ring, the BChls-a bind to the α-apoprotein and β-apoprotein are labeled as α-BChl-a and β-BChl-a, respectively. The Mg to Mg distance is about 9.36 Å for the 1α-1β dimer, and about 8.78 Å for the 1β-2α dimer (center to center values in Ref. [3]). By eliminating the phytyl tail and some alkyl groups, each BChl-a is truncated to 46 atoms [cf. Fig. 1(b)]. The total number of atoms for the B850 ring in Fig. 1(a) is thus 736. Exciton-mediated energy transfer occurs via the low-energy absorption $Q_y$ band of BChl-a which includes the $Q_x$ and $Q_y$ transitions with transition dipole moments lying along two perpendicular directions $[4,5]$ in the porphin ring as shown in Fig. 1.

Two possible mechanisms have been proposed for energy transfer dynamics from LHII to RC via LHII, namely, the Forster incoherent hopping and the coherent exciton migration. Which mechanism dominates the transfer process inside LHII is determined by dynamic and static energetic disorder in LHII as well as the dimeric coupling constants for 1α-1β and 1β-2α dimers which are denoted as $J_1$ and $J_2$, respectively. Thus, central to the study of energy transfer dynamics is the evaluation of $J_1$ and $J_2$. By applying the CEO method to BChl-a dimers Tretiak et al. [7] gave estimates of $J_1$ and $J_2$ to be 408 and 366 cm$^{-1}$, respectively. Using a point-dipole approximation (PDA) Sundstrom et al. [3] found the $J_1$ and $J_2$ to be 339 and 336 cm$^{-1}$, respectively. Cory et al. [8] performed an INDO/S-CIS calculation on the entire B850 ring in order to construct the low-lying excitonic states a Frenkel exciton model with long-range dipolar interactions. Their CI expansion includes 4096 configurations for each of two symmetry representations, and their reported values for $J_1$ and $J_2$ are 790 and 369 cm$^{-1}$, respectively. From ab initio molecular orbital calculations Scholes et al. [6] estimated the couplings $J_1$ and $J_2$ in the B850 ring of Rps. acidiphila to be 320 and 255 cm$^{-1}$, respectively. With the exception of work done by Schulten, Zerner and co-workers on entire B850 rings [8], all other calculations were on absorption spectra of monomers or dimers. Calculated values for $J_1$ and $J_2$ vary from 300 cm$^{-1}$ to 800 cm$^{-1}$ while calculated results from dimers differ significantly from those of the entire rings. One possible cause for the discrepancy is that long range Coulombic interactions are absent in the calculation of dimers. The long range interactions may affect the exciton wavefunctions significantly. A drawback of the INDO/S-CIS calculations is the cutoff of molecular orbitals near the highest occupied and lowest unoccupied molecular orbitals, which may lead to an overestimation of $J_1$ and $J_2$. Here we employ an accurate linear-scaling localized-density-matrix (LDM) at the INDO/S level to calculate the low-lying excited state energies of the B850 ring. Developed for computing the excited state properties of large molecular systems, the LDM method has been previously employed to calculate the absorption spectra of polyacetylene oligomers [9] and carbon nanotubes [10].

The INDO/S Hamiltonian in the presence of an external field $E$ reads [11]

$$
H = \sum_{ab} \sum_{i=a,j=b} t_{ij} c_{ai}^\dagger c_{bj} + \frac{1}{2} \sum_a \sum_{ijmn} V_{ijmn} c_{ai}^\dagger c_{aj} c_{am}^\dagger c_{bn} + \frac{1}{2} \sum_a \sum_{i=b,j=a} V_{ijab} c_{aj}^\dagger c_{ai} c_{bm}^\dagger c_{bn} - E \sum_m \sum_{ab} P_{ab} c_{am} c_{bn},
$$

(1)

where $c_{ab}^\dagger (c_{bj})$ is the creation (annihilation) operator for an electron at a localized atomic spin orbital $i (j)$ on atom $a (b)$. $t_{ij}$ is the one-electron hopping term, $V_{ijab}$ is one-center repulsion term and $\gamma_{ab}^\dagger$ is the two-center repulsion term.
The geometry is based on the recently resolved crystal structure. Hydrogen atoms are added using the Protein Data Bank of the Research Collaboratory for Structural Bioinformatics. The absorption energies for \( \alpha \)-BChl-a and \( \beta \)-BChl-a are 1.17 eV (2.16 eV) and 1.15 eV (1.98 eV), respectively. The \( Q_y \) transition carries the strongest oscillator strength. In contrast to a symmetric porphin molecule, the asymmetric BChl-a molecule has a significant dipole strength for the \( Q_y \) transition. Our calculations confirm that the \( Q_y \) transition is red-shifted little with an added protein environment and carotenoids (<0.01 eV). Therefore, the proteins and carotenoids are removed in subsequent calculations.

The absorption energies for \( Q_{y1} \) and \( Q_{y2} \) for the \( 1 \alpha-\beta \), \( (1 \beta-\alpha) \) dimer are 1.08 eV and 1.21 eV (1.09 eV and 1.21 eV), respectively. It follows that the electronic splitting for the \( 1 \alpha-\beta \), \( (1 \beta-\alpha) \) dimer are 0.132 eV (0.114 eV). These values are somewhat larger than those from Ref. [7] (0.102 eV and 0.091 eV for the \( 1 \alpha-\beta \) dimer and the \( 1 \beta-\alpha \) dimer, respectively). One reason for the discrepancy is that slightly different geometries are used in the two calculations. Adopting a procedure employed in Ref. [7], we arrive at an estimation of inter-monomer coupling constants for two types of dimers, \( J_1 = 528 \text{ cm}^{-1} \) for the \( 1 \alpha-\beta \) dimer and \( J_2 = 455 \text{ cm}^{-1} \) for the \( 1 \beta-\alpha \) dimer, which are compared with coupling constants obtained via other methods in Table 1.

To determine an appropriate density-matrix cutoff length for the B850 ring, we carried out calculations on trimers and pentamers with and without the density-matrix truncations. The off-diagonal elements of reduced single-electron density matrix between nearest BChl-a neighbors are fully included if the density matrix is truncated by a cutoff length of 15 Å. Absorption spectra obtained from calculations with and without the 15-Å cutoff are found to be nearly identical. For instance, the pentamer lowest absorption peaks are found at 0.99 eV for spectra calculated both with and without the 15-Å cutoff. The fact that the absorption spectra of trimers and pentamers differ little upon the introduction of the cutoff length 15 Å confirms that the spatial extent (or the electron-hole distance) of low-lying excitons is confined to two BChls-a. Further analysis of the resulting density matrices of

<table>
<thead>
<tr>
<th>Method</th>
<th>LDM</th>
<th>LDM</th>
<th>CEO</th>
<th>ZINDO</th>
<th>PDA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Configuration</td>
<td>dimer</td>
<td>ring</td>
<td>dimer</td>
<td>ring</td>
<td>dimer</td>
</tr>
<tr>
<td>( J_1 ) ( (1 \alpha-\beta, \text{ cm}^{-1}) )</td>
<td>528</td>
<td>593</td>
<td>408</td>
<td>790</td>
<td>339</td>
</tr>
<tr>
<td>( J_2 ) ( (1 \beta-\alpha, \text{ cm}^{-1}) )</td>
<td>455</td>
<td>491</td>
<td>366</td>
<td>369</td>
<td>336</td>
</tr>
</tbody>
</table>
The major absorption peak at low energies is attributed to the absorption spectrum of a B850 ring with a cutoff length of 15 Å. The excitons find that the size of the electron-hole pair is mostly limited to one BChl-a.

Dimerization splits the one-exciton band of the B850 ring into a lower band and an upper band. The only significant dipole-allowed excitation occur between the ground state and the excited states with momenta \( k = \pm \pi/4 \) of the lower one-exciton band along the ring [14]. Figure 2(a) shows the absorption spectrum of a B850 ring with a cutoff length of 15 Å. The major absorption peak at low energies is attributed to the \( k = \pm \pi/4 \) state in the lower exciton band. The other 14 low-lying excited states have little or no oscillator strengths, and therefore, can not be resolved from Fig. 2(a).

Instead of resorting to nonlinear spectroscopy, we introduce fictitious external fields with an individual phase on each BChl-a in the B850 ring. One may flip the orientation of (i.e., adding a 180° phase to) the external field on the eight monomers in the upper half of the ring so that dipole-allowed transitions are now from the ground state to one-exciton excited states of momenta \( k = 0, \pm \pi/2, \pi \) of the lower band, and \( k = \pm \pi/2, \pi \) of the upper band. The previous allowed \( k = \pm \pi/4 \) states of the lower band, however, are no longer optically bright. Similar techniques can be applied to find out other symmetry forbidden transitions.

We find that a simple excitonic model for a dimerized LHII ring incorporating only nearest-neighbor interactions can not fit our calculated results. Schulten and co-workers have introduced a more realistic description of the hexadecamer that takes the form of the Hamiltonian

\[
\hat{H} = \begin{pmatrix}
\varepsilon_1 & J_1 & W_{1,3} & \cdots & \cdots & J_2 \\
J_1 & \varepsilon_2 & J_2 & \cdots & \cdots & W_{2,2N} \\
W_{3,1} & J_2 & \varepsilon_1 & \cdots & \cdots & \cdots \\
\cdots & \cdots & \cdots & \varepsilon_2 & J_2 & W_{2N-2,2N} \\
\cdots & \cdots & \cdots & J_2 & \varepsilon_1 & J_1 \\
J_2 & \cdots & W_{2N,2N-2} & J_1 & \varepsilon_2 & \cdots \\
\end{pmatrix}
\]

(2)

where \( \varepsilon_1 \) and \( \varepsilon_2 \) are the excitation energies of the \( Q_y \) state of an individual BChl-a, \( J_1 \) and \( J_2 \) are the coupling constants between the nearest neighbors, and \( N \) equals 8 as the system is of \( C_{58} \) symmetry. In addition to the nearest-neighbor interactions \( J_1 \) and \( J_2 \), the matrix \( W_{i,j} \) in Eq. (2) adds dipolar couplings due to non-nearest neighbors:

\[
W_{i,j} = C \left[ \frac{d_i \cdot d_j}{|r_i|^3} - \frac{(d_i \cdot r_{ij})(d_j \cdot r_{ij})}{|r_i|^5} \right],
\]

(3)

where the factor \( C \) is the proportionality constant to be determined, and \( r_{ij} \) is the vector connecting the \( i \)th and \( j \)th monomers. The direction of the transition dipole of the \( i \)th BChl-a is represented by a unit vector \( d_i \).

A least-square fit to the low-lying excited state energies is utilized to determine \( J_1, J_2, \varepsilon_1, \varepsilon_2 \) and \( C \) in Eq. (2). To ensure that the sum of the low-lying excited state energies is invariant, a constraint is imposed during the fitting procedure:

\[
\sum \varepsilon_i = \text{constant}
\]

as is the proportionality constant.


\[ 8 \varepsilon_1 + 8 \varepsilon_2 = \sum_k E_k, \]

where \( E_k \) is the energy of the eigenstate \( k \). The agreement between the LDM results and the Frenkel exciton model is excellent. In Fig. 2(b), the INDO/S-LDM result is represented by crosses, and the fitting result by pluses. The total rms error is 118 cm\(^{-1}\). The corresponding parameters are \( J_1 = 594 \text{ cm}^{-1} \), \( J_2 = 491 \text{ cm}^{-1} \), \( \varepsilon_1 = \varepsilon_2 = 9117 \text{ cm}^{-1} \), and \( C = 640725 \text{ Å}^3 \text{ cm}^{-1} \).

Compared with the results in Ref. [8] our results are much more in line with those calculated directly from the dimer results. To further justify the parametrized Frenkel exciton Hamiltonian, we calculate the transition dipole moment \( \mu \) of the monomer \( Q_y \) state and obtain \( \mu = 2.326 \text{e} \cdot \text{Å} \). Assuming each BChl-a in the B850 ring has the same transition dipole as that of a monomer, and the coupling among the transition dipoles is described by Eq. (3), \( C \) is found to be 639800 \text{ Å}^3 \text{ cm}^{-1} \), which is consistent with the fitting result for the entire B850 ring (640725 \text{ Å}^3 \text{ cm}^{-1} \).

Transition dipoles of the chromophores approximately form a head-to-tail pattern with neighboring dipoles oriented in opposite directions. The ensuing polarization effect on the BChls-a is partially responsible for the vanishing \( \varepsilon_1 - \varepsilon_2 \) for a B850 ring. Compared with a center BChl-a in a trimer, a BChl-a in a ring experiences an additional long-range dipolar field from 13 other BChls-a. Energies due to the ground-state dipolar fields acting on a specific \( \alpha \)-BChl-a or a \( \beta \)-BChl-a due to its non-nearest neighbors are found to be \( -194 \) and \( -153 \text{ cm}^{-1} \), respectively. Due to differing long-range dipolar fields on adjacent BChls-a, the difference between \( \varepsilon_1 \) and \( \varepsilon_2 \) is found to be significantly reduced.

So far our molecules are treated in the gas phase. To take into account solvent effects, the ground state Fock operator is modified by adding the Onsager dipolar term [15,16]. Solvent effects are found to increase the ground state dipole moment from 7.7 to 22.0 D, in agreement with other studies [7,8]. For the excited state, the Hamiltonian term due to interactions with the external fields is modified to [16]

\[ \hat{H}_\text{ext} = -E \cdot (\hat{\mu}_g^T \cdot \hat{\delta \mu}) - \frac{D' - 1}{2D' + 1} + \frac{2(\eta^2 - 1)}{2\eta^2 + 1} \hat{\mu}_g^T \cdot \hat{\delta \mu}, \]

where \( \hat{\mu}_g \) and \( \hat{\delta \mu} \) are the ground-state and field-induced dipole moments, respectively, \( \eta \) is the index of refraction due to instantaneous response of the solvent electrons ( \( \eta \approx 1.6 \) [17]), and \( D' \) is the contribution to the bulk dielectric due toorientations of the solvent molecules (\( D' = 1.75 \)). The \( Q_y \) peak of \( \alpha \)-BChl-a is shifted from 1.17 to 1.42 eV, while the \( Q_x \) peak remains at about 2.15 eV (experimentally, the peaks are found at 1.60 and 2.16 eV for the \( Q_y \) and \( Q_x \) excitations, respectively [18]). Applying Eq. (5) to dimers, we find that both \( J_1 \) and \( J_2 \) are reduced by 25%. Therefore, we estimate that the solvent-adjusted coupling constants \( J_1 \) and \( J_2 \) of a B850 ring are 445 and 368 cm\(^{-1} \), respectively, which are consistent with experimental findings [19].

We have successfully carried out a sophisticated electronic structure calculation for a B800 ring with 16 BChls-a in *Rs. molischianum*. All valence electrons are included explicitly for 736 atoms and 2176 orbitals in the B850 ring. Our calculations were done with relatively inexpensive computational resources (700-MHz CPU and 500-MB memory). Therefore, this work has demonstrated that the INDO/S-LDM approach is well-suited for very-large-scale electronic structure calculations. Our calculation shows clearly that the electron-hole pair is predominantly localized on one BChl-a with a tiny charge-transfer component between two neighboring BChls-a, and thus the excitons are of the Frenkel type. The calculated low-lying excited state energies are fitted extremely well with the Frenkel exciton Hamiltonian with long-range dipolar interactions. In addition, the so-obtained parameters of the dipolar Frenkel exciton Hamiltonian can be well accounted for by the calculated results of the monomers and dimers, and the \( J_1 \) and \( J_2 \) values of the B850 ring are consistent with those of the dimers. All these show that the Frenkel exciton model provides an accurate description of the low-lying excited states in the B850 ring.

Support from the Hong Kong Research Grant Council (RGC) and the Committee for Research and Conference Grants (CRCG) of the University of Hong Kong is gratefully acknowledged. The authors thank S. Yokojima and W. Z. Liang for making the LDM codes available for the calculations.