RELATIONSHIP BETWEEN STRUCTURE AND FUNCTIONALITY OF LIGHT HARVESTING SYSTEMS

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This thesis can be considered as the continuation of the work previously done in collaboration with A. Valzelli (Bachelor Thesis, "Relationship between structure and functionality of light harvesting systems", A.A. 2015/2016) aimed at the study of the relationship between structure and functionality of light harvesting systems.

In the present work we concentrated mainly on tubular structures of Chlorobium Tepidum bchQRU mutant, belonging to the family of Green Sulfur bacteria. These photosynthetic organisms are able to survive in deep water where only few hundreds of photons per second can penetrate. The efficiency of such complexes stems from the particular geometrical symmetry of the molecules, which interact coherently with the external electromagnetic field, originating, among the others, superradiance effects to whom we are particularly interested.

The functionality of these structures depends on the synergy between superradiance and robustness to environmental disorder, that are both consequences of the cooperativity. In this thesis, the starting point is a non Hermitian Hamiltonian model that describes the interaction with the electromagnetic field and the environment. This Hamiltonian represents a fruitful approach to the study of the absorption of the incident radiation, which is maximal for superradiant states. An essential condition that makes possible the superradiance is the delocalization, which we studied analyzing the eigenstates participation ratio. We have numerically found that the ground state is superradiant and has the highest participation ratio, so that a large number of molecules in the ground state is able to cooperate during the absorption of the light. Moreover, our results highlight that this kind of cooperativity allows to achieve robustness to the disorder generated by environmental fluctuations. In more details, if the disorder strength is
greater than a critical value (the so-called ”localization disorder”) the Anderson localization regime is induced so that the superradiance is quenched. Differently from the single ring structures, in which the localization disorder is strongly dependent on the system size, in the tubular model this dependence is very weak. This result concludes the present work and is a promising starting point for future deeper investigations.
Quantum effects in photosynthetic systems

2.1 Quantum Biology

Recently various contributions by quantum mechanics to biology have allowed to investigate deeply the role of quantum effects, as some natural aggregates are characterized by length and timescales which let a fruitful application of quantum dynamics, despite the presence of environmental fluctuations.

Quantum biology is focused on the study of light-initiated reactions in photosynthetic organisms, which display a quantum-coherent behavior at ambient conditions: in particular, excitation transfer can be accompanied by superposition of quantum states with well-defined phase relationships for times long enough to affect transport at the molecular scale. This would clearly indicate that Nature makes use of quantum effects to perform some fundamental biological processes. Moreover a deep analysis of the interplay between Biology and Quantum Physics has let to elaborate solutions for new applications at the bio-nano scale [21].
In the last century the transmission of energy absorbed from the sun inside a photosynthetic system was described by the Forster equation \[22\]:
the mechanism is a semi-classical diffusive transfer process, in which excitation is transferred between two molecules with a large number of incoherent "jumps". These "jumps" occur every 2-3 ps and the transmission length is proportional to the square root of the number of steps, leading to a transfer process much slower than the coherent one. In the last decades the growth of new experimental techniques (such as 2D spectroscopy) led to new evidences often in contrast with the models predicted using the Forster equation. The experimental observation of coherent oscillations during the energy transfer dynamics has started debates focused on the function of such quantum-coherent behaviour and also in the way it could be exploited for efficient photovoltaic nanotechnologies. The quantum-coherent dynamics is essential for biological function as it lets us infer important properties related to the control and regulation of energy transport in molecular systems, which must adapt their functions to several environmental conditions.

![Figure 2.1: Biological systems are organized in hierarchical structures. The continuous refinement of experimental tools permits the investigation of ever finer detail giving rise to the discovery of novel phenomena. At a certain level we expect quantum physical properties to become relevant. Whether nature has evolved to take benefit (quantum enhanced efficiency) or to avoid their effects (quantum noise) represents one of interesting open question at the heart of Quantum biology \[21\].](image)

### 2.2 Photosynthesis

During the photosynthesis, the Sun’s energy is captured and stored by a series of events that convert the pure energy of light into the biochemical
energy necessary to power life.

Photosynthesis is carried out by a wide variety of organisms and usually occurs in localized sub-cellular structures known as chloroplasts. The chloroplast contains all the chlorophyll pigments and in most organisms carries out all the main phases of the process of photosynthesis. Chloroplasts are about the size of bacteria so a few micrometers in diameter and are provided by an extensive membrane system internally. All the chlorophylls and other pigments are associated with these membranes, which are known as thylakoids (or lamellae). Inside thylakoids are present subunits called Reaction Centers (RC), supported by an ensemble of molecular aggregates, the Antenna systems, which make possible photosynthetic processes.

![Figure 2.2](image)

**Figure 2.2:** A section of a leaf expanded showing the membrane and chloroplasts (first enlargement), a chloroplast (second enlargement), the thylakoid packing inside a chloroplast (third enlargement) and the molecular aggregates (RC and Antenna systems) inside a thylakoid (last enlargement).

Photosynthesis can be explained as a process occurring in four phases:

- light absorption and energy delivery by antenna systems,
- primary electron transfer in reaction centers,


- energy stabilization by secondary processes,
- synthesis and export of stable products.

We will explain the first process in the next section. During the second phase the transformation from the pure energy of excited states to chemical changes in molecules takes place in the reaction center, a multishubunit protein complex embedded in the photosynthetic membrane. The reaction center consists of a pigment-protein complex, incorporating both chlorophylls and other electron transfer cofactors, along with extremely hydrophobic peptides that thread back and forth across the membrane multiple times. A chlorophyll-like pigment is promoted to an excited electronic state, either by direct photon absorption or, more commonly, by energy transfer from the antenna system: in this step of photosynthesis, the energy has been transformed from electronic excitation to chemical redox energy.

The initial, or primary, electron transfer event is followed by separation of the positive and negative charges by a very rapid series of secondary chemical reactions.

The final phase of photosynthetic energy storage involves the production of stable high energy molecules (like sugars) and their utilization to power a variety of cellular processes.
2.3 Antenna Systems

Why isn’t every chlorophyll molecule capable of carrying out complete photosynthesis?

The intensity of full sunlight in the photosynthetically active region (450-750 nm) is distributed over the solar spectrum. The photon flux can be displayed as a rain of photons on the surface of the leaf. Even with full sunlight, absorption of photons by any given molecule lasts approximately a tenth of a second and this process can easily be several orders of magnitude longer under most conditions. This time is an eternity on the molecular scale. If every chlorophyll molecule was associated with the entire electron transfer chain, then these expensive components would sit idle most of the time, only occasionally springing into action when a photon is absorbed. This would obviously be wasteful and ultimately such an arrangement would be unworkable. In addition, in all cases, photochemistry produces unstable initial products that will be lost if a second photochemical event does not take place in a relatively short time. If all pigments were functionally independent, most of these unstable products would be lost. All these factors demand that photons are collected and their energy transmitted to and used in the RC: this is the main function of an antenna system.

Almost all antenna complexes are pigment-proteins, in which the chlorophyll or other pigment is specifically associated with proteins in a unique structure. The only known exception to this rule is the Chlorosome antenna complex found in the Green Sulfur bacteria, in which pigment-pigment interactions are of primary importance. These systems are organized in a manner that eases the energy transmission through the complex to the RC.

Indeed, according to the Planck relation, excited states populated by short-wavelength photons are relatively high in energy. Subsequent energy transfer processes are from these high-energy pigments physically distant from the reaction center to lower-energy pigments that are physically closer to the reaction center. With each transfer, a small amount of energy is lost as heat and the excitation is moved closer to the reaction center. The energy lost in each step provides a degree of irreversibility to the process, so the net result is that the excitation is "funnelled" to the reaction center, where some of the energy in it is stored by photochemistry.
3.1 Introduction

Object of our study is the family of Green Sulfur bacteria, with a particular interest towards the family of Chlorobaculum. It represents a class of photosynthetic bacteria able to survive at hard natural conditions at 100 m of depth in water, where only few photons per second can penetrate [6]. Owing to their simple structure these organisms are phototrophs, namely they respond with cellular growth to sunlight that is converted into chemical energy by the reaction center, which makes possible other metabolic functions: recent studies [20] made on Chlorobium Tepidum bacterium have proposed a quantitative metabolic flux analysis for this species, enlightening the primary role of sunlight for producing ATP energy (essential to cellular respiration and photosynthesis). To endure at great depths, these bacteria exploit LHC containing efficient self-assembled antennae complexes called Chlorosomes, which are the largest known antenna systems and can contain thousands of BChl bacteriochlorophyll $c,d,e$ molecules that do not require protein for efficient light harvesting processes [12]. Then the flux of excitation energy is possible due to two protein structures: the baseplate and Fenna-Matthews-Olson (FMO) complexes. An atomistic apparatus of Chlorobium Tepidum has been proposed in some recent studies [9], in which the functional unit consists of 3988 pigments excluding the reaction center itself: the chlorosome is a double-walled roll, the baseplate lattice (whose structure has not yet been experimentally verified) contains CsmA proteins, the FMO protein complex is located under the baseplate. FMO complex is an aggregate of 3 identical subunits, each containing 7 BChl $a$ so that we notice 21 total pigments. The nearest-neighbour distances between Mg atoms vary from 11 Å to 14 Å.
Experimental methods for studying Green Sulfur bacteria involve mainly time resolved fluorescence, X-ray crystallography and absorption spectroscopy, which have contributed to more specific studies of light harvesting systems also typical of the species of Acaryochloris Marina [2], a particular cyanobacterium discovered in 1996 by Miyashita et al. Other experimental techniques are cryo-electron microscopy [18], which has shown a very complex structure of Chlorobium Tepidum that alternates tubular and lamellar shape by embedding those bacteria into amorphous ice.
Owing to its capability to exploit efficient light harvesting processes, the typical tubular structure of *Green Sulfur* bacteria has found many applications to technology and dye nanotubes (like J aggregates), artificial structures in which it is crucial to exploit energy transport across distances of many hundreds of nanometers \[8\]. Some experiments have recently discovered the usefulness of tobacco mosaic virus protein to build similar structures of hundreds of nanometers: exploiting this technique, it would be possible to ease energy transport across long distances \[17\]. Various models of organic nanotubes have been recently investigated \[4\] and have enlightened why a tubular shape is preferred, for example, over a one-dimensional chain structure: in particular, transport properties are strongly dependent on the dimensionality of system and, in particular, the diffusion coefficient must be proportional to the radius of structure \[7\] and independent of temperature, disorder, noise parameters.

Because of the complexity and heterogeneity of natural structures (made of hundreds of cromophores composed of tubular and lamellar shapes), recent simplified models of cylindrical aggregates \[13\] have been proposed to study the most important properties of *Green Sulfur* bacteria. We will examine the models of *Chlorobium Tepidum* bchQRU triple mutant and wild type (WT) \[1\], \[13\], comparing their structures and paying attention to the relationship between superradiance and energy. In this third chapter our aim consists on looking over the link between the molecules organization and the ground state energy in order to show that natural structures realize an optimal energy harvesting compared to some artificial models. Then we will discuss the cooperative effects of the system in function of some parameters such as the cylindrical length in order to represent how the energy of the ground state varies. Finally we will compute the dipole strength in order to find which are the most probable light absorption transitions.

### 3.1.1 Hamiltonian of the system

In our simulations we use the Hamiltonian introduced by Frenkel in \[14\] for the large tubular aggregates of bacteriochlorophylls with geometries analogous to those proposed for *Chlorobium Tepidum* chlorosomes. When the pigments are physically very close, which usually means a distance less than 10 Å for chlorophylls, the interaction between them is manifested in a manner known as exciton coupling. The exciton-coupled ensemble is most productively viewed as a supermolecule with delocalized electronic transitions rather than a collection of individual molecules with localized transitions. In order to calculate the excitonic states of an aggregate with \(N\) monomers we can describe the molecule as a two-level system consisting of a ground state and a single electronically excited state, thus the Hamiltonian is:

\[
\hat{H} = \sum_i^N \epsilon_0^i \langle i | i \rangle + \sum_{i \neq j}^N \Delta_{ij} \langle j | i \rangle - i \sum_{i,j}^N Q_{ij} \langle j | i \rangle
\]
where $e_0$ is the energy of the quantum jump to the first excited state in the $i^{th}$ molecule whose excited state is described by the wave function $|i\rangle$. The molecular wave function (related to the state $|i\rangle$) is a product of the ground state of the (N-1) non-excited molecules and the excited state wave function for the $i^{th}$ excited molecule. The $|i\rangle$ basis is called "site basis" and indices $i, j \in [1, N]$. The interaction with the external electromagnetic field (EMF) is represented by a real term, $\Delta_{ij}$, and by a purely imaginary term, $Q_{ij}$. This imaginary contribution represents the non-Hermitian part of the Hamiltonian, explicitly it is given by:

\[
\Delta_{ij} = \frac{3\gamma}{4} \left( -\frac{\cos(k_0 r_{ij})}{k_0 r_{ij}} + \frac{\sin(k_0 r_{ij})}{(k_0 r_{ij})^2} + \frac{\cos(k_0 r_{ij})}{(k_0 r_{ij})^3} \right) \cos \varphi_{ij} - \frac{3\gamma}{4} \left( -\frac{\cos(k_0 r_{ij})}{k_0 r_{ij}} + 3\frac{\sin(k_0 r_{ij})}{(k_0 r_{ij})^2} + 3\frac{\cos(k_0 r_{ij})}{(k_0 r_{ij})^3} \right) \cos \vartheta_i \cos \vartheta_j,
\]

\[
Q_{ij} = \frac{3\gamma}{4} \left( \frac{\sin(k_0 r_{ij})}{k_0 r_{ij}} + \frac{\cos(k_0 r_{ij})}{(k_0 r_{ij})^2} - \frac{\sin(k_0 r_{ij})}{(k_0 r_{ij})^3} \right) \cos \varphi_{ij} - \frac{3\gamma}{4} \left( \frac{\sin(k_0 r_{ij})}{k_0 r_{ij}} + 3\frac{\cos(k_0 r_{ij})}{(k_0 r_{ij})^2} - 3\frac{\sin(k_0 r_{ij})}{(k_0 r_{ij})^3} \right) \cos \vartheta_i \cos \vartheta_j,
\]

where $r_{ij}$ is the distance between the $i^{th}$ dipole and the $j^{th}$ dipole, $\varphi_{ij}$ is the angle between them, $\vartheta_i$ represents the angle between the $i^{th}$ dipole and $r_{ij}$, $\vartheta_j$ is the angle between the $j^{th}$ dipole and $r_{ij}$. Here $k_0$ indicates the wave vector linked to molecular electronic transition and $\gamma$ represents the radiative decay of the single molecule: both these quantities are connected to the site energy $e_0$ of each site.

This Hamiltonian, which has been considered in literature [15], [16], can be written as:

\[
H_{\text{eff}} = e_0 |i\rangle \langle i| + \Delta_{ij} - iQ_{ij} = H_0 + H_{\text{em}}.
\tag{3.1}
\]

The initial degeneracy of the localized excited stated is lifted by the interaction $H_{\text{em}}$ and results in a set of energy levels called the exciton band. Assuming the limit $k_0 r_{ij} \ll 1$, which corresponds to a realistic situation in our natural harvesting complexes, we have:

\[
Q_{ij} = \frac{\gamma}{2} \cos \varphi_{ij},
\]

\[
\Delta_{ij} = \frac{3\gamma}{4(k_0 r_{ij})^3} \left( \cos \varphi_{ij} - 3 \cos \vartheta_i \cos \vartheta_j \right).
\]

If the medium is the air as in our calculations, we have [3], [14]:

- $e_0 = 15390 \, \text{cm}^{-1}$ as the energy of the two level system [14],
- $k_0 = 2\pi e_0 \cdot 10^{-8} = 9.670 \cdot 10^{-4} \, \text{Å}^{-1}$ as wave vector linked to the molecular electronic transition frequency $\omega_0 = k_0 c$, which corresponds to $\lambda_0 = 6498 \, \text{Å},$
3. Tubular structure model

- \( \mu = \sqrt{30} \text{ D} \) as the transition dipole matrix element between the ground state and the first excited state [3], so that \( \mu^2 = 151024 \text{ Å}^3 \cdot \text{cm}^{-1} \) [19],

- \( \gamma = \frac{4}{3} |\mu|^2 k_0^3 = 1.821 \cdot 10^{-4} \text{ cm}^{-1} \), so that \( \gamma / \hbar \) is the radiative decay rate of a single molecule.

If we consider our system in a bulk solution with a refractive index \( n = 1.33 \) for water [31] and dielectric constant \( \varepsilon_r = 2.1 \) (typically used for proteins [30]), we can modify the last parameters:

<table>
<thead>
<tr>
<th>Air</th>
<th>Bulk solution ((n = 1.33; \varepsilon_r = 2.1))</th>
</tr>
</thead>
<tbody>
<tr>
<td>( e_0 = 15390 \text{ cm}^{-1} )</td>
<td>( e_0 = 15390 \text{ cm}^{-1} )</td>
</tr>
<tr>
<td>( k_0 = 2\pi e_0 \cdot 10^{-8} = 9.670 \cdot 10^{-4} \text{ Å}^{-1} )</td>
<td>( k = n(2\pi e_0 \cdot 10^{-8}) = 1.286 \cdot 10^{-3} \text{ Å}^{-1} )</td>
</tr>
<tr>
<td>( \mu = \sqrt{30} = 5.48 \text{ D} )</td>
<td>( \mu' = \sqrt{\frac{\mu}{\varepsilon_r}} = 3.78 \text{ D} )</td>
</tr>
<tr>
<td>( \lambda_0 = 6498 \text{ Å} )</td>
<td>( \lambda = 4885.84 \text{ Å} )</td>
</tr>
<tr>
<td>( \gamma = \frac{4}{3}</td>
<td>\mu</td>
</tr>
</tbody>
</table>

Table 3.1: In the first column we report parameters for aggregates in air while the second refers to a medium with index of refraction \( n \) and dielectric constant \( \varepsilon_r \).

The refractive index \( n \) is of the bulk solution, whereas the relative dielectric constant \( \varepsilon_r \) is of the direct surroundings of the chromophore. For the antenna complexes the relative dielectric constant of the protein is essentially not known [31]. It is important to clarify that we do our numerical simulations considering the tubular structures in air and not in solution, so we use the parameters shown in the first column of the table. The second column has been shown for completeness since many authors study these aggregates in their natural environment.

Cromophores are modeled with dipoles and the validity of this approximation depends on the ratio \( L_D/|r_{ij}| \) between the dipole length \( L_D \) and the intermolecular distance \( r_{ij} \), since this ratio is a series expansion parameter for the Coulomb interaction. Here \( L_D = |\mu|/e \) where \( e \) is the electron charge and \( \mu \) is the transition dipole moment of the single molecule.

In our simulations the shortest distance between sites is \( r_{ij} = 6.4 \text{ Å} \), the squared dipole moment is \( \mu^2 = 30 \text{ D}^2 \) and the dipole length measures \( L_D = 1.1 \text{ Å} \), so that \( (L_D/|r_{ij}|)_{\text{max}} = 0.18 \ll 1 \) and the dipole-dipole approximation can be applied. Note that some authors often erroneously assume that the ratio between the molecule size and the intermolecular distance is the series expansion parameter, which indeed can be close to 1 in many cases [14]. In our Hamiltonian the dipole-dipole term is a perturbation, but if the dipole moment lengths are comparable to the distance between chromophores this approximation is not valid. In this case the point dipole
is substituted by opposite point charges $+\delta$ and $-\delta$ at a finite distance $l$:

$$J_{nm} = \frac{D^2}{4\pi\varepsilon_0 l^2} \left( \frac{1}{r_{++}} + \frac{1}{r_{--}} - \frac{1}{r_{+-}} - \frac{1}{r_{-+}} \right).$$  \tag{3.2}

where $r_{\pm\pm}$ represents the distance between the positive (negative) charge of the point dipole of the first molecule to the positive (negative) charge of the point dipole of the second molecule \cite{28}. In Fig. 3.3 the panel (A) illustrates the situation corresponding to the formula (3.2) while the panel (B) shows the regime in which the dipole approximation is valid. For further explanation we have examined this question on appendix A.

The transition dipole moment $\mu$ is particularly important because it provides information about the polarization properties of transitions and orientations of molecules. The transition dipole moment is strongly related to the absorption process of the light in a molecule, in which the interaction between matter and light has a primary role. The effect of the light is to couple itself to the electrons in the molecule and cause them to change their spatial distribution: this is due to the coupling between electric field and dipole moment of the molecule, which changes orientation depending on this interaction. This is described using the formalism of Quantum Mechanics and an important result that we can use in a qualitative way is that the transition has a directionality within the molecule, which is evident both in a theoretical and an experimental background. If plane-polarized light is used to cause the transition, molecules oriented with their transition dipole moments parallel to the electric field of the light will absorb a photon with highest probability, while this process will be denied for those molecules with dipole moments perpendicular to the electric vector of the light. The intensity of the absorption is proportional to the squared transition dipole moment and is measured in units of Debye \cite{19}.
A: $L_D \approx r_{ij}$

Figure 3.3: (A) Point charges $+\delta, -\delta$ in the regime $L_D \approx r_{ij}$: mind that here $L_D = l$ and the interaction term is given by (3.2). In this case the dipole approximation is not allowed since all distances between the point charges are comparable ($r_{++}, r_{+-} \approx r_{+--}, r_{-+-}$). (B) Two couples of opposite charges in the regime $L_D \ll r_{ij}$: in this case, the vertical distance between opposite charges is much smaller than the diagonal one. This allows to neglect the repulsion between point charges of the same sign.
3. Tubular structure model

3.2 The model

We consider cylindrical structures of interacting dipoles, modelling any two-level system able to be excited by light. The single site (called cromophore) is represented by a dipole and they are arranged into $N_2$ coaxial rings that form a cylindrical structure of radius $R$. Each ring has $N_1$ sites and its vertical distance from consecutive rings is $h$. We will study the radiative decay $\Gamma/\gamma$ as a function of parameters like the ground state energy, the number of dipoles and the height of cylinder. In particular we have simulated five structures:

- parallel dipoles (with respect to the cylindrical axis),
- tangent dipoles (with respect to the cylindrical surface),
- random orientation dipoles,
- *Chlorobium Tepidum* wild type (WT),
- *Chlorobium Tepidum* bchQRU triple mutant, which we will call more simply "mutant".

We will illustrate some particular absorption properties of these tubular models, putting particular emphasis to the light absorption between natural aggregates of the family of *Chlorobium* and artificial structures in which molecules are modeled as parallel, tangent and random dipoles.

3.2.1 Chemical composition: bchQRU mutant and WT

There are different models of *Green Sulfur* bacteria, but here we will consider only two types of *Chlorobium Tepidum*: the wild type and the bchQRU mutant. WT chlorosomes are much more heterogeneous than chlorosomes of the bchQRU mutant and contain BCHl c molecules with a greater proportion of S-chirality at carbon $C - 3^1$ and variable degrees of methylation at carbons $C - 8^2$ [13]. BCHls c, d and e are found only in chlorosome-producing bacteria and are unique among chlorophylls because of methylations that occur at the $C - 8^2$ and $C - 12^1$ carbons. Two genes required for these methylation reaction were identified and designated *bchQ* and *bchR* and they catalyze the methil group transfers [29]. Recent advances in understanding the biosynthesis of BCHl c have led to a well-characterized *bchQ*bchR*bchU* *C. tepidum* triple mutant. This mutant synthesizes well-defined, extended chlorosomes that contain > 95% 17-farnesyl-R-[8-ethyl, 12-methyl] BCHl d [13].
Chlorosomes are assembled from BChl c,d,e and natural structures combine heterogeneous molecular mixtures of BChls \([13]\). In the wild type: \(R_1 = \text{Me}; R_2 = \text{Et}, n - \text{Pr}, i - \text{Bu}; R_3 = \text{Me}, \text{Et}\). In the bchQRU mutant \(R_1 = H; R_2 = \text{Et}; R_3 = \text{Me}\).

Creating in laboratory *Chlorobium Tepidum* wild type will be very complex, in fact natural aggregates are characterised by great heterogeneity which is reflected also, for example, in their energy spectra [1]: sample preparation in laboratory could provide more regular pattern, distinguished by more uniform absorption. Recently various mutant species of *Chlorobium Tepidum* have been created artificially by exploiting the typical *syn-anti* organization of pigments [13]: every unit cell is composed by two pythol tails oriented in opposite directions (the helical shape of the cylinder is due to the fact that these tails are linked by hydrogen bonds pigments from different rings).
3. Tubular structure model

The following figures illustrate how different chemical structures are reflected on lattice organization between bchQRU, bchR mutants and the WT.

![Figure 3.5: Left. (c) Basic structural element used for the BChl arrangement within a molecular aggregate. The grid features a unit cell with lattice parameters $a$ and $b$ that are inclined by an angle $\gamma$ with respect to each other. Each unit cell contains two molecules whose transition dipoles make an angle $\eta$ with the $a$ axis and are tilted by small alternating angles $\pm \alpha$. (d-f) Structures for BChl aggregates obtained by wrapping the grid under an angle of $\delta$ with respect to the $a$ axis onto a cylinder. Right. Bravais lattice with lattice vectors of length $a = 1.25$ nm and $b = 0.98$ nm enclosing an angle of $\gamma = 122^\circ$ for the arrangement of the BChl molecules. The vector $C$ refers to the rolling vector for the model structures proposed for the wild type ($C_{WT}$ perpendicular to the $a$ axis), the bchQRU mutant ($C_{QRU}$ parallel to the $a$ axis) and the bchR mutant ($C_R$ enclosing an angle $\delta = 69^\circ$ with the $a$ axis).]

3.2.2 Lattice organization of bchQRU mutant

In *Chlorobium Tepidum* bchQRU mutant all dipoles are arranged on stacked equidistant rings of radius $R$, forming a tubular aggregate of $n = 6000$ sites. We introduce some parameters widely used in literature [1], [5], [14], that let us infer the position of dipoles placed on the Bravais lattice. The Bravais lattice figure is analogous for each model, but the various cases are different because of the angle $\delta$ between the $a$ axis and the rolling vector. We consider these parameters:

- $N_1 = 100$ as the total number of rings;
- $N_2 = 60$ as the total number of the dipoles on a ring;
- $n_1, n_2$ are labels respectively referred to the ring and to the dipoles on a ring;
- $\xi = \gamma - 90 = 32^\circ$ as the shift between two rings;
3. Tubular structure model

- $\phi = \frac{360^\circ}{N_2}$ as the azimuthal angle between adjacent dipoles within a ring;

- $R = 60$ Å is chosen as the radius of cylinder;

- $h = 8.3$ Å as the distance between two rings. Note that $h$ is perpendicular to the plane of the ring.

It is important to clarify that the correct number of sites located on each ring has not been experimentally determined yet, so we propose aggregates in which total number of dipoles is $n = 6000$ (analogously to 4), estimated as arranged on $N_1 = 100$ rings so that averagely each ring contains $N_2 = 60$ sites. In our simulations, the ratio between the number of dipoles per ring and the radius of the cylinder is constantly equal to 1.

![Figure 3.6: Structure of bchQRU mutant provided by a detailed representation of Bravais lattice. $\gamma$ is the angle between $a$ and $b$ axes so that $\gamma - \xi = 90^\circ$ and $h$ is the distance between two consecutive rings, taken as orthogonal to the plane of the ring.](image)

If we fix the reference frame as shown in Fig. 3.7, we can estimate the angle $\theta$ between the position vector of the dipole and the $x$ axis:

$$\theta = n_1 \xi + n_2 \phi$$

and we can find the position $\vec{r}$ of each monomer on the cylinder:

$$\vec{r} = \begin{cases} r_x = R \cos \theta \\ r_y = R \sin \theta \\ r_z = hn_1 \end{cases}$$

(3.3)
Figure 3.7: We have fixed the reference frame in the center of all the coaxial rings of the cylinder and we have measured $\theta = n_1 \xi + n_2 \phi$ as the angle between the position vector $\vec{r}$ and the $x$ axis.

3.2.3 Lattice organization of wild type

*Chlorobium Tepidum* wild type has $\delta = 90^\circ$, so we must consider different parameters: Fig. 3.8 illustrates the arrangement of dipoles on vertical chains with $\xi = 0^\circ$. Furthermore dipoles on adjacent chains are not at the same height but they are shifted by a certain quantity $\kappa_{n_1}$ to originate the helical structure of Fig. 3.8. We must consider:

- $N_1 = 60$ as the total number of chains;
- $N_2 = 100$ as the total number of dipoles on a chain;
- $n_1, n_2$ are labels respectively referred to the chain and to the dipoles on a chain;
- $\phi = \frac{360^\circ}{N_1}$ as the azimuthal angle between adjacent chains;
- $R = 60$ Å is chosen as the radius of cylinder;
- $h = \frac{a}{2} = 6.25$ Å as the distance between two dipoles in the same chain.

The shift between the dipoles on adjacent chains is $\kappa_{n_1} = n_1 b \sin \varepsilon$, where $b = 9.8$ Å is the axis of the Bravais lattice, while $\varepsilon = \gamma - 90^\circ = 32^\circ$ (Fig. 3.8).
3. Tubular structure model

As $\xi = 0^\circ$ it follows that $\theta = n_2 \phi$ is the angle between the position vector $\vec{r}$ and the $x$ axis, so we can find the position of each monomer on the cylindrical structure:

$$\vec{r} = \begin{cases} 
  r_x = R \cos \theta \\
  r_y = R \sin \theta \\
  r_z = h n_2 + n_1 b \sin \varepsilon - f h 
\end{cases} \tag{3.4}$$

Here the correction $fh$ involves the parameter $f = \text{int} \left[ \frac{n_1 b \sin \varepsilon}{h} \right]$, which denotes the number of dipoles necessary to complete the chain preserving the cylindrical symmetry, so $f$ must be integer.

### 3.2.4 Distribution of dipoles in bchQRU and wild type species

Given the dipole moment $\vec{\mu}$, its components $\vec{\mu}_x, \vec{\mu}_y, \vec{\mu}_z$ are normalized so it is possible to define some parameters for each dipole:

- $\alpha$ as the angle that the projection of the dipole on the $xy$ plane creates with the tangent to the circumference of the ring as in Fig. 3.9;
- $\beta$ as the angle that each dipole generates with the cylindrical axis;
- $\theta$ as the previously indicated angle, different from the bchQRU to the wild type.
Figure 3.9: Projection on $xy$ plane of $\vec{\mu}$ is denoted with $\vec{\mu}_{xy}$: $\alpha$ stands for the angle between local tangent to the ring and $\vec{\mu}_{xy}$ and it could point outward or inward, so that if a dipole is directed inward ($\alpha = +4^\circ$) the next one points outward ($\alpha = -4^\circ$). This behavior characterizes the whole ring of bchQRU mutant, while in the wild type dipoles on the same chain point outward and inward.

Transition dipoles components are expressed by:

$$\vec{\mu} = \begin{cases} 
\mu_x = \sin \beta \sin(\theta \pm \alpha) \\
\mu_y = \sin \beta \cos(\theta \pm \alpha) \\
\mu_z = \cos \beta 
\end{cases}$$

The following figure Fig. 3.10 represents the projection on $xy$ plane of the dipoles for bchQRU mutant: it is remarkable the alternation $\alpha = \pm 4^\circ$ which makes consecutive dipoles pointing inward and outward.

Figure 3.10: View from above of 1 ring of bchQRU mutant: to illustrate better the alternation of angles we have chosen $\alpha = \pm 20^\circ$. 
3.3 Decay width and superradiance

In this section we examine the superradiance in the models of *Chlorobium Tepidum* bchQRU mutant and wild type. We will observe which energy state concentrates most of the superradiance selecting the maximum radiative peak, which is linked to the capability of transferring and absorbing excitation. Changing the displacement of the dipoles on Bravais lattice, we study the superradiance for tangent and parallel dipoles. Finally we make a comparison between the natural systems (wild type and bchQRU mutant) and our numerical simulations for tangent, parallel and random dipoles.

Superradiance occurs when a group of emitters emits coherently with a very high intensity. It has been studied for supramolecular complexes and in the light harvesting apparatus of bacterial photosynthesis [28].

We consider the Non-Hermitian Hamiltonian previously discussed (3.1), we diagonalize it and we find the eigenvalues $\varepsilon$, which have a real and an imaginary part: $\varepsilon = \text{Re}(\varepsilon) + i \text{Im}(\varepsilon)$. To study the decay properties of the eigenstates, we consider the imaginary part of the eigenvalues and in particular in our graphs we plot the ratio $\Gamma/\gamma$ as a function of the real part of the eigenvalues, where $\Gamma = 2|\text{Im}(\varepsilon)|$ and $\gamma$ is the decay rate of a single molecule.
3. Tubular structure model

3.3.1 Parallel dipoles

We consider 6000 parallel dipoles forming a cylinder of \( N_2 = 100 \) rings (so that every ring contains averagely \( N_1 = 60 \) sites) and we plot \( \Gamma/\gamma \) as a function of the energy \( E - e_0 \). We take \( h = 8.3 \) Å, \( R = 60 \) Å, \( \alpha = 0^\circ \), \( \beta = 0^\circ \) and \( \xi = 0^\circ \). Those parameters will be used in the previous relations to determine positions and components of the dipoles (3.3) and (3.5), then we obtain the cylindrical structure with parallel dipoles.

![Image of cylinder](attachment:image.png)

**Figure 3.11:** Section of cylinder made of 10 rings of parallel dipoles, each containing 60 sites.

![Image of decay width](attachment:image.png)

**Figure 3.12:** Decay width \( \Gamma/\gamma \) as a function of the energy \( E - e_0 \) (cm\(^{-1}\)) of the system. It is remarkable that the ground state does not coincide with the superradiant state, which is the 1805\(^{th}\) excited state.
Now we vary the number of rings in order to display how superradiance of the states varies.

**Figure 3.13**: The figure shows the comparison between different numbers of dipoles, illustrating $\Gamma/\gamma$ in logarithmic scale as a function of the energy. Note that the peak of superradiance never reaches the ground state, but it moves towards the least excited states if the number of rings increases.

Fig. 3.13 makes us hypothesize that, increasing the number of rings, more and more states close to the ground state acquire width: this effect is cooperative since the decay width increases with the number of dipoles.
3. Tubular structure model

3.3.2 Tangent dipoles

We consider a tubular structure of 6000 dipoles forming a cylinder of \( N_2 = 100 \) rings with \( N_1 = 60 \) sites per ring and we plot \( \Gamma/\gamma \) as a function of the energy \( E - \varepsilon_0 \). We take \( h = 8.3 \, \text{Å}, \) \( R = 60 \, \text{Å}, \) \( \alpha = 0^\circ, \) \( \beta = 90^\circ \) and \( \xi = 0^\circ \) and we can use (3.3) and (3.5) in order to obtain the cylindrical structure with tangent dipoles.

\[ \text{Figure 3.14: Section of cylinder made of 10 rings of tangent dipoles, each containing 60 sites.} \]
Figure 3.15: Decay width $\Gamma/\gamma$ as function of the energy $E-e_0$ (cm$^{-1}$) of the system. We observe that the peak does not reach the ground state, which is not a superradiant state. In this case the superradiant states are the 671$^{th}$ and the 672$^{th}$ excited states: compared to the parallel dipoles model (Fig. 3.12), in this case we notice two superradiant states (671,672) less excited than the only superradiant state of the parallel dipoles structure (1805).
3. Tubular structure model

3.3.3 Random orientation dipoles

We take into account a tubular structure in which the dipoles are characterized by random orientation, then we study the radiative decay as a function of the eigenstate. Here we consider a radius $r = 60 \, \text{Å}$ and a vertical distance between rings $h = 8.3 \, \text{Å}$. In the following figure we represent a section of an aggregate containing 600 dipoles, organized into 10 rings, each composed by 60 units.

![Figure 3.16: Section of cylinder made of 10 rings of random dipoles, each containing 60 sites.](image)

We aim at observing what happens to the superradiance when the geometrical symmetry of the structure we consider is lost. We made 10 realizations in order to obtain an average of $\Gamma / \gamma$ for each eigenstate of the Hamiltonian. However each realization has a random energy spectrum, so that the eigenvalues could be very different in the different cases. This is the reason for whom we choose the eigenstate and not the eigenvalue as a variable. In Fig. 3.17 we have made the study of $\Gamma_{\text{average}} / \gamma$ as a function of the eigenstate for three cases of the total number of random dipoles: 600 (panel (A)), 3000 (panel (B)), 6000 (panel (C)). It could be very interesting to notice, in each case of Fig. 3.17 that the lack of geometrical symmetry is reflected in the absence of a well-defined peak of superradiance. Indeed, the geometrical symmetry plays a key role for the quantum coherence in the absorption of the light: when provided by regular distribution, the molecules cooperate and superpose their single contributions to interact with the light. If one chooses a random distribution of the molecules, the quantum coherence disappears so that the sites have to be considered like independent systems: superradiance does not arise.

Let us display the situation of the panels (A), (B), (C): as one can observe, the maximum peak of $\Gamma_{\text{average}} / \gamma$ does not exceed 10 and does not increase with the number of sites. This is another distinctive characteristic of such random structures, which does not appear in the other cases (like, for example, that of parallel dipoles 3.13).
Figure 3.17: Average of decay width $\Gamma_{\text{average}}/\gamma$ as a function of the eigenstates of the system of random dipoles. These graphs have the lowest values of the decay width $\Gamma_{\text{max}}/\gamma$, which depends on the random displacement of the dipoles. The lack of geometrical symmetry of the random structure prevents the superradiance since the molecules tend to behave like independent systems in this regime as opposed to the natural structures. The absence of a peak implies that there are no states able to supertransfer energy excitation.
3.3.4 Chlorobium Tepidum wild type

We study the supramolecular path of *Chlorobium Tepidum* wild type, computing the decay width $\Gamma/\gamma$ as a function of the energy $E - e_0$. We can reproduce its structure using (3.4) and (3.5) and the parameters shown before for the WT structure with $\alpha = \pm 4^\circ$ and $\beta = 35^\circ$.

![Figure 3.18: Section of Chlorobium Tepidum wild type. Its structure is helical shaped.](image1)

![Figure 3.19: Decay width $\Gamma/\gamma$ as function of the energy $E - e_0$ (cm$^{-1}$) of the system. The ground state is not superradiant in fact the peak corresponds to the 5th excited state that, however, is much closer to the ground state with respect to the other cylindrical models made of parallel (Fig. 3.12) and tangent dipoles (Fig. 3.15). Note that the first four states have a degeneracy on the same energies two by two.](image2)
3.3.5 *Chlorobium Tepidum bchQRU* triple mutant

Now we consider the case of bchQRU triple mutant, computing the trend of the decay width $\Gamma/\gamma$ as a function of the energy $E-e_0$ and considering the model proposed in [13]. We take $h = 8.3$ Å, $R = 60$ Å, $\alpha = 4^\circ$, $\beta = 55^\circ$ and $\xi = 32^\circ$ and we use the (3.3) and (3.5) to reproduce its structure.

![Figure 3.20: Section of *Chlorobium Tepidum* bchQRU mutant made of 10 rings, each containing 60 sites.](image)

**Figure 3.20:** Section of *Chlorobium Tepidum* bchQRU mutant made of 10 rings, each containing 60 sites.

![Figure 3.21: Decay width $\Gamma/\gamma$ as function of the energy $E-e_0$ (cm$^{-1}$) of the system. The panel on the right indicates that the superradiative state coincides with the ground state ($\Gamma_{\text{max}}/\gamma \approx 1751$): this matter of fact typically distinguishes the bchQRU mutant from the previous structures (Fig. 3.12 3.15 3.19).](image)

**Figure 3.21:** Decay width $\Gamma/\gamma$ as function of the energy $E-e_0$ (cm$^{-1}$) of the system. The panel on the right indicates that the superradiative state coincides with the ground state ($\Gamma_{\text{max}}/\gamma \approx 1751$): this matter of fact typically distinguishes the bchQRU mutant from the previous structures (Fig. 3.12 3.15 3.19).
Fig. 3.19 and Fig. 3.21 suggest that the bchQRU and the Wild Type have the maximal decay width concentrated into the ground state (MT) or the first excited states (WT): by comparing this trend with that of tangent (Fig. 3.15), parallel (Fig. 3.12) and random dipoles (Fig. 3.17) we conclude that only the natural systems can have the property to supertransfer excitation at low energy. The majority of superradiative states is focused on lower energies so that Nature is able to engineer structures characterized by particular geometrical symmetries, capable to supertransfer at low energy and to superabsorb at high energy. However we could suppose that, for example, structures of parallel dipoles will ideally have the peak if number of dipoles $N$ is very large, namely in the limit $N \to +\infty$ (Fig. 3.13).
3. Tubular structure model

3.4 Structural dependence of cooperativity

Now we consider the model of *Chlorobium Tepidum* bchQRU triple mutant to analyze how cooperative regime is influenced by the length of the rod. The radius \( r \) of cylinder is fixed at \( r = 60 \) Å, each ring has \( N_1 = 60 \) sites and the vertical distance between two consecutive rings is \( h = 8.3 \) Å. Increasing the number of rings, namely the tube’s length, we can plot the value of \( \Gamma_{\text{max}}/\gamma \) as a function of \( L/\lambda_0 \), where \( L \) is the length of the tube and \( \lambda_0 = 6498 \) Å stands for the wavelength associated to \( \epsilon_0 \).

\[
\Gamma_{\text{max}}/\gamma = 13600x + 32.877
\]

**Figure 3.22:** From the graph, we could conclude that \( \Gamma_{\text{max}}/\gamma \) is linearly proportional to \( L/\lambda_0 \), which does not exceed 0.127 in this case.

Fig. 3.22 shows that the radiative decay of the superradiant state \( \Gamma_{\text{max}}/\gamma \) is linearly proportional to the rod’s length \( L \). This occurs in the regime \( L<\lambda_0 \). We could infer that this condition makes the coupling between the sites stronger than the coupling between the sites and the external E.M.F., so it promotes cooperativity between cromophores. In this situation, the external EMF is approximated as uniform for all the cromophores so that an *all-to-all* coupling prevails.

When \( L \geq \lambda_0 \) the cooperative regime is broken as the dimensions of the aggregate do not grant an *all-to-all* coupling between sites: the external EMF does not appear as uniform and interacts differently with the cromophores. Supposing that the linear fit is conserved until \( L = \lambda_0 \), we can calculate \( \Gamma_{\text{max}}/\gamma \) when \( L/\lambda_0 = 1 \): we obtain that \( \Gamma_{\text{max}}/\gamma = 13632.877 \) corresponding to \( \Gamma_{\text{max}} = 2.483 \).
3.5 Dipole strength

A key function of the BChl aggregate in the light harvesting complexes is the optical absorption, which can be characterized by estimating the radiative decay $\Gamma/\gamma$ and the dipole strength: in other words, states with a high radiative decay (then, high dipole strength) are capable to supertransfer excitation energy.

Not all light absorption transitions have equal probabilities: in some cases the absorption is very intense, while in others it is so weak to be undetectable. Symmetry properties of the molecules and the type of transition involved will determine the intensity of transitions, which depends on quantum-mechanical selection rules. Transitions that are very intense are called ”allowed” while those that are very weak are called ”forbidden”, albeit there is possibility of intermediate cases in complex molecules. Singlet to triplet transitions are forbidden and are therefore very weak. There are several quantitative measurements of the intensity of an absorption transition. One is related to the dipole strength $|\vec{D}|^2$ (also called oscillator strength in analogy to a classical oscillator): it is unitless and ranges from 0 for a forbidden transition to 1 for a fully allowed one.

If $N$ is the number of molecules in an aggregate, it will contain $N$ eigenstates that can be expressed through the single excitations of individual molecules as follows:

$$|\phi_j\rangle = \sum_{i=1}^{N} C_{j,i} |i\rangle \quad n = 1, ..., N$$

(3.6)

where $C_{j,i}$ are complex coefficients that can be evaluated doing the projection of an exciton state $|\phi_j\rangle$ over the site basis $|i\rangle$. The transition dipole moment $\vec{D}_j$ connected with the single photon excitations of the exciton state $|i\rangle$ is:

$$\vec{D}_j = \sum_{i=1}^{N} C_{j,i} \vec{\mu}_i$$

(3.7)

where $\vec{\mu}_i$ is the transition dipole moment for the $i^{th}$ molecule. The oscillator strength associated to the transition towards the state $|\phi_j\rangle$ is given by $|\vec{D}_j|^2$. The exciton states can be assumed to be orthonormal, i.e.:

$$\langle \phi_j | \phi_k \rangle = \delta_{jk}.$$  

From this property using (3.7) and the orthonormality of the site basis, it follows:

$$\sum_{j=1}^{N} |\vec{D}_j|^2 = \sum_{i=1}^{N} |\vec{\mu}_i|^2 = N$$
since all the molecules carry identical oscillator strengths (equal to 1 if the dipole moments is normalized).

In the case of an uncoupled system all the molecules have the same oscillator strength; however, in the case of coupled monomers the resulting exciton states do not share the oscillator strength equally. As an example, if all the dipoles are tangent to the circumference they create a perfect circular symmetry so the two states with degenerate energies \( E_2 \) and \( E_3 \) carry all the oscillator strength.

Now let us consider only the real part of the Hamiltonian [3.1] and calculate the dipole strength estimating \( |\overrightarrow{D}_{ij}| \): in this section we will study the squared dipole strength as a function of the eigenvalues of the system.

In order to evaluate eigenvalues and eigenstates of the system we take into account the following Hamiltonian:

\[
H_{eff} = H_0 + \Delta_{ij}
\]

where \( H_0 \) is the matrix whose diagonal has \( \epsilon_0 \) as site energy, and is 0 out of diagonal, while \( \Delta_{ij} \) represents the interaction with the electromagnetic field.

\[
\Delta_{ij} = \frac{3\gamma}{4} \left( -\frac{\cos(\theta_{ij})}{k_0 r_{ij}} + \frac{\sin(\theta_{ij})}{(k_0 r_{ij})^2} + \frac{\cos(\theta_{ij})}{(k_0 r_{ij})^3} \right) \cos \varphi_{ij} - \frac{3\gamma}{4} \left( \frac{\cos(\theta_{ij})}{k_0 r_{ij}} + \frac{3\sin(\theta_{ij})}{(k_0 r_{ij})^2} + \frac{3\cos(\theta_{ij})}{(k_0 r_{ij})^3} \right) \cos \vartheta_i \cos \vartheta_j.
\]

Here \( r_{ij} \) is the distance between the \( i \)-th dipole and the \( j \)-th dipole, \( \varphi_{ij} \) is the angle between them, \( \vartheta_{i,j} \) is the angle between the \( i \)-th (respectively, \( j \)-th) dipole and \( r_{ij} \).
3. Tubular structure model

3.5.1 Single ring of Chlorobium Tepidum bchQRU mutant

Now we take into account a ring of Chlorobium Tepidum bchQRU mutant made of 60 dipoles, we calculate the dipole strength and the decay width, finally we compare them all.

\[ |D|^2 \text{ as a function of the energy } E_e \text{ (cm}^{-1}\text{)}. \]

The dipole strength is concentrated in the first three states (ground state, 1\(^{st}\) excited state, 2\(^{nd}\) excited state), the superradiant ones. The other states have a negligible dipole strength since they are subradiant.

\[ \text{Vectors are mutually orthogonal. As one can see, the ground state has dipole strength parallel to the } z \text{ axis which coincides with the cylindrical axis. The dipole strength of the first and the second excited states lie on the } xy \text{ plane.} \]
Now we can compare the decay $\Gamma/\gamma$ with the dipole strength $|D|^2$ for one ring of *Chlorobium Tepidum* bchQRU mutant.

![Graph showing dipole strength and decay width as a function of energy](image)

**Figure 3.25:** Dipole strength $|D|^2$ and decay width $\Gamma/\gamma$ as a function of the energy $E-e_0$ (cm$^{-1}$). The two graphs are analogous so, in other words, states with large decay width are also characterized by great dipole strength.

Fig. 3.25 shows that the superradiance corresponds to the maximal dipole strength. This suggests that the superradiative states are capable to superabsorb light during the interaction with the external EMF. The high dipole strength is a consequence of the kind of interaction between the system and the external EMF, which is reflected on the Hamiltonian (3.1): when the molecules are coupled with the light, the circular symmetry of the ring makes possible to gather the superradiance in the first three states. If the system does not interact with the external EMF, it is decoupled and so the oscillator strength is equally distributed on all over the sites of the system: in other words, superradiance does not appear.
3. Tubular structure model

3.5.2 Chlorobium Tepidum bchQU mutant

We analyze the tubular model of *Chlorobium Tepidum* bchQU mutant previously proposed, composed by 6000 sites organized into 100 equal and coaxial rings in order to evaluate dipole strength.

![Graph showing $|D|^2$ as a function of the energy $E-E_0$ (cm$^{-1}$). Most of the dipole strength is concentrated in the ground state, there are also other peaks referred to the dipole strength of other excited states: the $82^{th}$ and the $83^{th}$ excited states. Note that this graph is perfectly analogous to Fig. 3.21.](image1)

**Figure 3.26:** $|D|^2$ as a function of the energy $E-E_0$ (cm$^{-1}$). Most of the dipole strength is concentrated in the ground state, there are also other peaks referred to the dipole strength of other excited states: the $82^{th}$ and the $83^{th}$ excited states. Note that this graph is perfectly analogous to Fig. 3.21.

![Diagram illustrating vectors corresponding to the three states with the highest dipole strength $|\vec{D}|^2$: we can see that the ground state has the highest dipole strength (parallel to the z axis, the cylinder’s axis), while $82^{th}$ and the $83^{th}$ excited states have dipole strengths parallel to xy plane. Vectors are mutually orthogonal.](image2)

**Figure 3.27:** Vectors corresponding to the three states with the highest dipole strength $|\vec{D}|^2$: we can see that the ground state has the highest dipole strength (parallel to the z axis, the cylinder’s axis), while $82^{th}$ and the $83^{th}$ excited states have dipole strengths parallel to xy plane. Vectors are mutually orthogonal.
3. Tubular structure model

3.5.3 Chlorobium Tepidum wild type

We take into account the model of Chlorobium Tepidum wild type, showing $|\vec{D}|^2$ as a function of the energy of the system.

Figure 3.28: $|\vec{D}|^2$ as a function of the energy $E-e_0$ (cm$^{-1}$). The highest peak of the graph does not correspond to the ground state, but to the 4th excited state. Note that this graph is completely analogous to Fig. 3.19.

Figure 3.29: Vectors corresponding to the three states with the highest dipole strength $|\vec{D}|^2$: the 5th, the 26th, the 28th excited states. We can see that the fifth excited state has the highest value of $|\vec{D}|^2$, that is directed along the cylinder’s axis ($z$ axis). The 26th and the 28th excited states have dipole strengths in the $xy$ plane. Vectors are mutually orthogonal.
We can see that, even if formed by a large number $N$ of transition dipole moments, our system behaves as a great dipole moment whose main component is directed along the $z$ axis, which is the cylinder’s axis: this argument will be useful to characterize the optical absorption of the whole aggregate and to introduce some approximations, that will be discussed in the next chapter.

3.6 Conclusion

In this chapter we have studied the displacement of dipoles on the Bravais lattice in the case of *Chlorobium Tepidum* bchQRU mutant and wild type, then we have found the superradiant state and we have seen that it coincides with the ground state in *Chlorobium Tepidum* bchQRU mutant, while in the wild type it corresponds to the fifth excited state. This may be due to a different geometry from the wild type to the bchQRU mutant.

We have also made a comparison between the real models and structures with tangent and parallel dipoles. Our results show that only the real structures have superradiant low energy states: this means that the natural aggregates are capable to emit coherently when they are in the ground state or in lower energy states. However, we underline that this kind of behavior is preserved only if the dimension of the aggregate is smaller than the wavelength of the incident electromagnetic radiation. Furthermore, our results show that the superradiance is broken by including a degree of geometrical disorder as in the case of the random dipoles.

In the second part of the chapter we have investigated the dipole strength in different models: since dipole strength and radiative decay are analogous, we may observe that bchQRU mutant and wild type tend to concentrate most of the dipole strength in the lowest states. We have studied what happens for the single ring of *Chlorobium Tepidum* bchQRU mutant, in which the ground state is characterized by the highest dipole strength: this means that the whole ring might be approximated with the dipole corresponding to the state with the highest dipole strength. In the next chapter we aim to discuss deeper this question.
In the previous chapter we have remarked some important properties of *Chlorobium Tepidum* bchQRU mutant and wild type, underlining that the Nature tends to select structures capable to supertransfer at low energies, which can grant them to survive at hard environmental conditions. In particular we have observed that:

- in the bchQRU mutant the ground state is the superradiant state, while in the wild type the superradiance is mostly concentrated into the fifth excited state,

- high dipole strength means high probability of optical absorption of the light and the dipole strength is analogous to the radiative decay,

- cooperativity of the states is possible due to the dimensions of the system, that allow to approximate the external electromagnetic field as uniform and make possible a coherent behavior of the molecules.

The present chapter will be focused on the bchQRU mutant. We will start by reducing the model of *Chlorobium Tepidum* bchQRU mutant previously proposed, made of 100 rings, to a couple of rings in order to evaluate the intensity of coupling between molecules as a function of the distance \( h \) between rings: we will verify that our results do not depend on the number of rings. This kind of analysis will suggest that whenever the distance \( h \) is greater than the radius \( r \) of the cylinder, the only non-zero couplings are among the superradiant states (with high dipole strength). Then if \( h \) is smaller than the radius \( r \) (as in the realistic model) we will see that the coupling between sites does not depend on the intensity of the dipole strength: in other words all molecules of both rings are coupled. This matter of fact will be examined deeper taking into account:
4. Structural characterization of energy spectrum

- the transition probability between states, which is higher for strongly coupled states,
- the approximation of the Hamiltonian of the system with a particular Hamiltonian of dipole interaction, which depends on the dimensions of the system.

Next, we will return to the mutant model made of 6000 dipoles to observe that the couplings between the molecules could turn to our advantage to check some approximations of the energy spectrum. Then we will focus on the ground state in order to evaluate the probability of the single molecules to be in the ground state. However the probability to be in the ground state does not provide information about its delocalization on the single molecules of the whole aggregate, so we calculate the participation ratio associated to it and to the excited states. In order to study these quantum effects in a more realistic environment, we introduce a static disorder in the Hamiltonian \( H \) to see how this perturbation affects the participation ratio and the decay rate of the superradiant states. These calculations will be a promising starting point for a future deeper analysis of robustness and cooperative resistance, which play a crucial role for the quantum transport in tubular shaped aggregates similar to the bchQRU mutant.

4.1 Coupling between rings

We consider only a couple of rings of *Chlorobium Tepidum* bchQRU mutant, with a radius \( r = 60 \) Å and a vertical distance between rings \( h = 8.3 \) Å. Let us write the Hamiltonian \( H \) of the system: it will be a \( 120 \times 120 \) matrix in which the \( 60 \times 60 \) upper left block corresponds to the first ring, the \( 60 \times 60 \) lower right block stands for the second ring and the out-of-diagonal blocks represent the reciprocal interactions between rings. We make a partial diagonalization of this Hamiltonian, first we diagonalize the upper left block and then the lower right block. We aim to write the whole matrix on the basis composed by the eigenkets obtained from these blocks: the upper left and the lower right blocks will be diagonal while the out-of-diagonal blocks will quantify the coupling between the states of both rings. By this way we are able to see how the eigenstates of these two systems are coupled, so we will talk about a "coupling between states". Here we denote the \( \alpha \) eigenstate of the first ring with \( |\phi_{(1)}^{(\alpha)}\rangle \) and the \( \beta \) eigenstate of the second ring with \( |\phi_{(2)}^{(\beta)}\rangle \), with \( \alpha, \beta = 1, ..., 60 \).

4.1.1 Coupling and distance between rings

We would like to investigate the relationship between the vertical distance \( h \) of the rings and the coupling between the states. Let us indicate the
4. Structural characterization of energy spectrum

partially diagonalized 120 × 120 Hamiltonian from (3.1) with $H$ and let us suppose to write the out-of-diagonal blocks on the basis composed by the eigenkets of both rings. If we evaluate the coupling between the $\alpha$ eigenstate of the first ring $|\phi^{(1)}\rangle$ and the $\beta$ eigenstate of the second ring $|\phi^{(2)}\rangle$, we can indicate it as $[H(\phi^{(1)}_{\alpha}, \phi^{(2)}_{\beta})]$:

$$[H(\phi^{(1)}_{\alpha}, \phi^{(2)}_{\beta})] = \left| \langle \phi^{(1)}_{\alpha} | H | \phi^{(2)}_{\beta} \rangle \right|. \quad (4.1)$$

We assume a radius $r = 60$ Å and different distances between rings: $h = 8.3, 83, 830$ Å. Calculating (4.1) for these cases we are able to evaluate how the coupling between the states varies.

We may conclude from Fig. 4.1 (A) that in the bchQRU mutant the coupling between the states does not depend on the superradiance (so, on the intensity of the dipole strength): all the states, superradiant or subradiant, are coupled. The panel (B) shows a transition regime, in which the distance between rings $h = 83$ Å makes possible a coupling between the lowest excited states. The panel (C) shows that, if the dimensions of the rings are smaller than their vertical distance, a non-zero coupling is possible only between superradiant states.
Figure 4.1: Coupling between states as a function of the vertical distance $h$. The $x$ axis contains the eigenstate index for the first ring, the $y$ axis reports the eigenstate index for the second ring. The intensity of the coupling between states (cm$^{-1}$) is referred to the colorbox on the right and increases when colors become lighter in each case. It is noteworthy that the coupling between states does not vanish only for the states with higher dipole strength if $h = 830$ Å, while it does not depend on the dipole strength if $h = 8.3$ Å.
4. Structural characterization of energy spectrum

4.1.2 Transition probability between states

Let us focus on the couple of rings of bchQRU mutant as in the previous subsection, in which the Hamiltonian is a $120 \times 120$ matrix. Let us indicate the temporal evolution operator from $t_1 = 0$ to $t_2 = t > 0$ for this system with $U_2(t_1, t_2) = U_2(t)$. We suppose that for $t_1 = 0$ the wavefunction of the system coincides with the $\alpha$ eigenstate of the first ring $|\phi^{(1)}_{\alpha}\rangle$. We aim to evaluate the temporal probability of transition at the time $t_2 = t$ towards the $\beta$ eigenstate of the second ring $|\phi^{(2)}_{\beta}\rangle$. Let us indicate the probability of transition between these states with $P_{\alpha,\beta}(t)$, so that we can estimate it as:

$$P_{\alpha,\beta}(t) = \left| \left\langle \phi^{(2)}_{\beta} | U_2(t) | \phi^{(1)}_{\alpha} \right\rangle \right|^2.$$ (4.2)

The transition probability is deeply related to the lifetime of the eigenstates. In our simulations (Fig. 4.2) we have fixed $r = 60 \, \text{Å}$ and $h = 8.3, 83 \, \text{Å}$ for $\alpha = \beta = 1$ (ground state) and $\alpha = \beta = 30$ ($29^{th}$ excited state) to observe how probability of transition changes.

Let us pay attention to the relationship between the radiative lifetime of the system and the period of oscillation in these transitions. We can define the radiative lifetime of the single molecule $\tilde{\tau}$:

$$\tilde{\tau} = \frac{\hbar}{\gamma}.$$ 

We consider $\hbar = 5.29 \, \text{cm}^{-1} \cdot \text{ps}$ and $\gamma = 1.821 \cdot 10^{-4} \, \text{cm}^{-1}$, so that we obtain:

$$\tilde{\tau} = 2.9 \cdot 10^4 \, \text{ps}.$$ 

Now let us compare the radiative lifetime $\tilde{\tau}$ of the single molecule with the period of oscillations: we may notice that the period $T$ is shorter than the radiative lifetime $\tilde{\tau}$ for strongly coupled states (Fig. 4.2 panels (A), (B), (C)), just the opposite of non-coupled states (Fig. 4.2 panel (D)). Moreover the superradiant states are characterized by large decay width $\Gamma/\gamma \gg 1$, so that the lifetime $h/\Gamma$ is shorter than the radiative lifetime of the single molecule, while the subradiant states have a small decay width $\Gamma/\gamma \ll 1$, so that lifetime $h/\Gamma$ is longer than the radiative lifetime of the single molecule. Transition period and lifetime shorter than the radiative lifetime of the single molecule are distinctive features of the superradiant states and they are due to the cooperativity and to the quantum coherence.
4. Structural characterization of energy spectrum

Figure 4.2: (A) Transition between the ground states of both rings, $h = 8.3$ Å: the coupling between the ground states is near to $237$ cm$^{-1}$ with a period $T \approx 0.07$ ps. The maximum of probability reaches $1$.

(B) Transition between the 29$^{th}$ excited states of both rings, $h = 8.3$ Å: the coupling between the 29$^{th}$ excited states is near to $170$ cm$^{-1}$ with a period $T \approx 0.045$ ps. The maximum of probability reaches $0.8$.

(C) Transition between the ground states of both rings, $h = 83$ Å: the coupling between the ground states is near to $2.66$ cm$^{-1}$ with a period $T \approx 6$ ps. The maximum of probability reaches $1$.

(D) Transition between the 29$^{th}$ excited states of both rings, $h = 83$ Å: the coupling between the 29$^{th}$ excited states is near to $10^{-6}$ cm$^{-1}$ with a period $T \approx 2 \cdot 10^6$ ps. The maximum of probability reaches $0.1$.

Now one can make a question: does this probability depend on the number of rings we consider? Let us take into account a system composed for example by 3 rings with radius $r = 60$ Å and vertical distance $h = 8.3$ Å. We could focus only on the ground state, so we make a partial diagonalization of the Hamiltonian (3.1), which is a $180 \times 180$ square matrix. We obtain that the ground states of the three rings are $|\phi_1^{(1)}\rangle$, $|\phi_1^{(2)}\rangle$, $|\phi_1^{(3)}\rangle$. Let us indicate with $\hat{U}(t_1, t_2) = \hat{U}(t)$ the temporal evolution operator (referred to the $180 \times 180$ Hamiltonian) from $t_1 = 0$ to $t_2 = t > 0$ and let us suppose that the state of the system coincides with the ground state of the first ring $|\phi_1^{(1)}\rangle$ at $t_1 = 0$. 
In the Fig. 4.3 we compute the following transition probabilities:

- probability to remain into the ground state of the first ring:
  \[ P_{1,1}^{(1)}(t) = |\langle \phi_1^{(1)} | \hat{U}_3(t) | \phi_1^{(1)} \rangle |^2, \]

- transition probability to the ground state of the second ring:
  \[ P_{1,1}^{(2)}(t) = |\langle \phi_1^{(2)} | \hat{U}_3(t) | \phi_1^{(1)} \rangle |^2, \]

- transition probability to the ground state of the third ring:
  \[ P_{1,1}^{(3)}(t) = |\langle \phi_1^{(3)} | \hat{U}_3(t) | \phi_1^{(1)} \rangle |^2. \]

**MT, 3 rings, h=8.3 Å**

Initial state: ground state of the first ring

**Figure 4.3:** Transition probabilities vs time (ps) for 3 rings of bchQRU mutant, radius \( r = 60 \text{ Å} \), vertical distance \( h = 8.3 \text{ Å} \). Black line represents the probability to remain into the ground state of the first ring \( P_{1,1}^{(1)}(t) \), red dash line is the transition probability to the ground state of the second ring \( P_{1,1}^{(2)}(t) \), green dash-dot line stands for the transition probability to the ground state of the third ring \( P_{1,1}^{(3)}(t) \). The sum of these probabilities is always 1 (blue dash-dot-dot line) which implies a possibility of transition only between the ground states.
4. Structural characterization of energy spectrum

In the Fig. 4.3 we have noticed that the total sum of transition probabilities is always equal to 1. This allows us to conclude that a transition only between the ground states of the three rings is possible, coherently with the results obtained in the Fig. 4.1. This implies a non-vanishing coupling only for homologous states of different rings. From a comparison between Figures 4.2, 4.3 we may notice that for a two rings system the two ground states are a two-level system characterized by oscillations with fixed frequency, while the ground states of three rings behave like a three-level system. However in each case the eigenspaces referred to different eigenstates are decoupled that is to say: if the initial state is the ground state of a certain ring, the only non-zero transition probabilities are directed towards the ground state of another ring (or of the same ring). This analysis can be easily extended to all the other eigenstates with a generic number of rings, which allows to reply an analysis of the coupling between sites and states for the whole aggregate.

4.1.3 Structural characterization of the coupling

Since a study focused on a couple of rings is not restrictive, now we take into consideration only two rings of bchQRU mutant (radius $r = 60 \, \text{Å}$, vertical distance $h = 8.3 \, \text{Å}$) in order to qualify the nature of the interaction between sites belonging with different rings. Let us consider the $i^{th}$ molecule of the first ring in the state $|j^{(1)}_i\rangle$ and the $j^{th}$ molecule of the second ring whose state is expressed by $|j^{(2)}_j\rangle$. They are chosen to be nearest neighbours between rings, so that $|j^{(2)}_j\rangle = |(i \pm 1)^{(2)}_j\rangle$.

The coupling of nearest neighbours between rings can be expressed using (3.1) written on the site basis and it will coincide with $|H(i^{(1)}_i; (i \pm 1)^{(2)}_j)\rangle$

Using analogous conventions we can indicate the coupling of nearest neighbours on the first ring with $|H(i^{(1)}_i; (i \pm 1)^{(1)}_j)\rangle$. From the panel (A) of Fig. 4.1 it is reasonable to hypothesize that the coupling between homologous states of different rings would have the same order of magnitude of the coupling of nearest neighbours between rings, so we aim to compare this quantities. We can partially diagonalize the Hamiltonian from (3.1) in order to estimate the intensity of coupling between the ground state of both rings $|H(\phi^{(1)}_1, \phi^{(2)}_1)\rangle$, according to the method discussed in the first subsection.
4. Structural characterization of energy spectrum

Table 4.1: The first row reports the coupling of nearest neighbours on the same ring (1st ring in this case), while the second and the third rows illustrate respectively the coupling of nearest neighbours between rings and between the ground state of both the rings. The last row shows their ratio which is very close to 1, which implies that they have the same order of magnitude.

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4.1.4 Dipole approximation

We aim to study the coupling between two rings of *Chlorobium Tepidum* bchQRU mutant with radius $r = 60$ Å when their vertical distance $h$ is increased over 8.3 Å.

Let us observe the panel (C) of Fig. 4.1: when $h > r$, the coupling between rings strongly depends on the dipole strength, that is to say that are coupled only the superradiant states. In Fig. 3.24, we verified that for the single ring of bchQRU mutant these states coincide respectively with the ground state, the 1st excited state and the 2nd excited state, coherently with the results shown in Fig. 4.1, panel (C).

Under the condition $h > r$ we may approximate the interaction between the single sites of the rings with the following Hamiltonian representing the dipole interaction $H_{\text{dip}}$:

$$H_{\text{dip}} = \mu^2 \frac{\hat{p}^{(1)}_i \cdot \hat{p}^{(2)}_j - 3(\hat{p}^{(1)}_i \cdot \hat{r}_{ij})(\hat{p}^{(2)}_j \cdot \hat{r}_{ij})}{r_{ij}^3}.$$  (4.3)

Here $\mu^2 = 151024$ Å$^3 \cdot$cm$^{-1}$ is the transition dipole moment, $\hat{p}^{(1)}_i$ is the dipole moment of the $i$th molecule of the 1st ring, $\hat{p}^{(2)}_j$ is the dipole moment of the $j$th molecule of the 2nd ring, $r_{ij}$ represents the reciprocal distance between the molecules and $\hat{r}_{ij}$ is its versor.

Let us expand the ground state of the first ring $|\phi^{(1)}_1|$ on the site basis of the first ring, whose states are $|i^{(1)}|$:

$$|\phi^{(1)}_1⟩ = \sum_{i=1}^{60} c^{(1)}_i |i^{(1)}⟩.$$  

Now we consider (4.3) in order to evaluate its expectation value on the ground state of both rings:

$$⟨\phi^{(1)}_1 | H_{\text{dip}} | \phi^{(2)}_1⟩ = \sum_{i,j=1}^{60} c^{(1)}_i c^{(2)}_j ⟨i^{(1)} | H_{\text{dip}} | j^{(2)}⟩ =$$
4. Structural characterization of energy spectrum

\[
\begin{split}
\sum_{i,j=1}^{60} \mu^2 c_i^{(1)} c_j^{(2)} \left( p_i^{(1)} \cdot p_j^{(2)} - 3(r_i^{(1)} \cdot \tilde{r}_{ij})(r_j^{(2)} \cdot \tilde{r}_{ij}) \right) = 0, \\
\end{split}
\]

(4.4)

Here \( c_i^{(1)} \) is the complex conjugate of \( c_i^{(1)} \).

In the regime \( h > r \) we make the following approximation:

\[ r_{ij} \approx h \hat{z}. \]

As noticed in Figure 3.24 of the previous chapter, the ground state concentrates the majority of dipole strength, indicated as \( D_1^{(1)} \) for the first ring and as \( D_1^{(2)} \) for the second one. This lets us to write:

\[
\begin{align*}
\sum_{i=1}^{60} \tilde{c}_i^{(1)} p_i^{(1)} &= D_1^{(1)}, \\
\sum_{j=1}^{60} c_j^{(2)} p_j^{(2)} &= D_1^{(2)}. \\
\end{align*}
\]

We have that \( D_1^{(1)} = D_1^{(2)} = \sqrt{\frac{1}{\gamma}} \approx 19.65 \).

Now let us observe the Fig. 3.24 of the previous chapter: we can conclude that both \( D_1^{(1)} \) and \( D_1^{(2)} \) are parallel to the \( z \) axis, so that (4.1.4) is simplified as follows:

\[
\langle H_{	ext{dip}} \rangle = \langle \phi_1^{(1)} | H_{\text{dip}} | \phi_1^{(2)} \rangle \approx \frac{\mu^2}{h^3} \left[ D_1^{(1)} \cdot D_1^{(2)} - 3D_1^{(1)} D_1^{(2)} \right] = -2\frac{\mu^2 \Gamma_1}{h^3 \gamma}. 
\]

(4.5)

This calculation could provide an estimation of the energy of the system when the vertical distance \( h \) between rings is increased over 8.3 Å. We aim to compare \( |\langle \phi_1^{(1)} | H_{\text{dip}} | \phi_1^{(2)} \rangle | = |H_{\text{dip}}(\phi_1^{(1)}, \phi_1^{(2)})| \) with the coupling of the ground state of both rings \( |\langle \phi_1^{(1)} | H | \phi_1^{(2)} \rangle| = |H(\phi_1^{(1)}, \phi_1^{(2)})| \) computed with (3.1).
4. Structural characterization of energy spectrum

Figure 4.4: Coupling between the ground state of two rings as a function of the vertical distance $h$: blue for the Hamiltonian proposed by Mukamel (3.1), green for the Hamiltonian of dipole interaction (4.3). The second value ($h = 8.3$ Å) corresponds to the model of *Chlorobium Tepidum* bchQRU mutant and we see that the dipole approximation is not applicable to this structure as the dimensions of the rings are comparable with their vertical distance $h$: reciprocal interactions between cromophores are not negligible. Increasing distance $h$ until $10^3$ Å, the difference between the two calculations tends to zero.

We could conclude that in the realistic model of *Chlorobium Tepidum* bchQRU mutant the interaction between the ground states of both the rings is comparable with the coupling of nearest neighbours between rings. In the regime $h \gg 8.3$ Å the coupling between rings is a kind of dipole interaction, expressed by (4.3). In particular, the only non-zero coupling is among super-radiant states, that is to say that the whole ring can be represented by their dipole strength and the coupling between rings by the dipole interaction between these dipole strengths.
4.2 Approximation of energy spectrum

From the table 4.1 we infer that in the model of the bchQRU mutant, we could approximate the coupling of nearest neighbours between rings with the coupling of the ground states of both rings. This result may turn to our advantage to elaborate some approximations of the energy spectrum for the whole aggregate of *Chlorobium Tepidum* bchQRU mutant (100 rings, 60 sites per ring, $r = 60$ Å, $h = 8.3$ Å).

Using the Hamiltonian proposed by Mukamel [3.1], we obtain the exact spectrum of the system. Considering Fig. 4.1 we have underlined that only the homologous states of different rings are coupled. This allows to divide the whole aggregate into $\alpha = 1,\ldots,60$ independent chains, each composed by $k = 1,\ldots,100$ units: the $\alpha$ index is referred to the $\alpha^{th}$ eigenstate of the system, the $k^{th}$ index indicates the $k^{th}$ ring. Note that these chains are necessarily independent, this is to say that they are not interacting because they represent decoupled eigenstates. We would study these chains with the model proposed by Anderson if noise was included [33], [34], but in our simulations we just consider the tight-binding Hamiltonian for 1D systems without disorder [35].

Let us consider the $k^{th}$ unit of the $\alpha^{th}$ chain in order to estimate its energy $E_k^\alpha$:

$$E_k^\alpha = e^\alpha - 2\Omega^\alpha \cos \left( \frac{2\pi k}{n+1} \right).$$

(4.6)

Here, $e^\alpha$ is the energy of the $\alpha^{th}$ excited state of the single ring, $\Omega^\alpha$ is the coupling of the $\alpha^{th}$ excited state of different rings, $k = 1,\ldots,n$ is referred to the $k^{th}$ unit, $n = 100$ is the total number of units per chain.

In Fig. 4.5 we compare the energy spectrum of the whole aggregate obtained from the Hamiltonian [3.1] with the approximation (4.6), which could be referred to as a "nearest neighbour chain" approximation. We observe that the two energy spectra are identical, except for the ground state and the least excited states: the percent difference between the two calculations for the ground state is about 13.75 %. Despite that gap, one can build the energy spectrum of the whole aggregate composed by 100 rings only focusing on the single ring and on its coupling with the nearest neighbours.
Focusing on the gap between the ground states in the two calculations, one can ask: does this discrepancy depend on the specific number of rings we consider? For both the calculations, we can compute $\Delta E = E_{\text{max}} - E_{\text{min}}$, i.e. the difference between the energy of the most excited state $E_{\text{max}}$ and the energy of the ground state $E_{\text{min}}$, varying the number of the rings. In Fig. 4.6 we notice that the difference between the two calculations tends to increase for small values of the number of the rings and then reaches a plateau. Note that $\Delta E$ of both calculations does not increase indefinitely with the number of rings. Consequently, the average density of the states $\bar{\rho}(E) = N/\Delta E$ (here $N$ is the total number of states), it is not constant but grows linearly with $N$. 

Figure 4.5: Energy spectra computed with (3.1) (violet line) and with (4.6) (cyan line). It is remarkable a percent difference of about 13.75 % for the ground state in the two calculations, which begin to be very close at about the 1200th unit.
4. Structural characterization of energy spectrum

Figure 4.6: Comparison between energy spectra for different numbers of rings: blue square indicates $\Delta E$ calculated with the Hamiltonian proposed by Mukamel \[3.1\], violet star represents $\Delta E$ computed with \[4.6\]. The difference between the two cases is more evident for highest values of the total number of rings. Despite this matter of fact, the gap remains constant and does not increase with the number of rings.

4.3 Delocalization of the energy states

Let us consider the model of *Chlorobium Tepidum* bchQRU mutant, characterized by $n = 6000$ dipoles, organized into $N_2 = 100$ coaxial rings, each provided by $N_1 = 60$ sites. From Fig. 3.21 we notice that the ground state is superradiant, which plays a crucial role for the quantum transport in the tubular structure. In particular we aim to calculate the probability of each molecule to be in the ground state and the participation ratio (PR) of the ground state. The probability of each site to be in the ground state indicates how much it is involved in the superradiance, that is to say how much the single site can absorb the light. However, this information does not suffice to know how much the ground state is delocalized all over the molecules of the aggregate: for this reason, we study the participation ratio of this state. A large value of PR stands for high delocalization of the ground state, which corresponds to an efficient and more homogeneous absorption of light by the structure, since an increasing number of molecules is involved in the superradiance.
4. Structural characterization of energy spectrum

4.3.1 Probability of the ground state

We denote the state of the $i^{th}$ site with $|i\rangle$: here we have $i = 1, ..., 6000$. Taking into account the Hamiltonian (3.1), we could expand $|i\rangle$ on the basis composed by the eigenvectors $|\phi_j\rangle$ as follows:

$$|i\rangle = \sum_{j=1}^{6000} c_{i,j} |\phi_j\rangle = c_{i,1} |\phi_1\rangle + \sum_{j=2}^{6000} c_{i,j} |\phi_j\rangle.$$ 

Note that in our study we use $i$ as the cromophore index and $j$ as the eigenvector index: they are referred to different basis although $i, j = 1, ..., 6000$. Let take into account the previous expression of $|i\rangle$ in order to calculate probability of the $i^{th}$ molecule to be in the ground state:

$$P_{i,1} = |c_{i,1}|^2$$ \hspace{1cm} (4.7)

with the condition that $\sum_{i=1}^{6000} P_{i,1} = 1$. In the following graph we show such probability for each cromophore in bchQRU mutant:

Figure 4.7: (A) Probability to be in the ground state for the $i^{th}$ molecule: we may notice that it is maximum for $i \sim 3000$, namely at half heigth of the rod. (B) 60 molecules of the 28$^{th}$ ring: the probability is higher for the first thirty sites and smaller for the second ones. This is due to the optical angle $\alpha = \pm 4^\circ$ that characterizes the mutant structure and that makes consecutive dipoles point inward and outward.
Now we can analyze the probability to be in the ground state as a function of the number of rings. The ring’s index is $r$ so that $r = 1, \ldots, 100$. Since each ring contains 60 sites, we obtain the probability to be in the ground state for the single ring by summing the probabilities of all the 60 sites. In other words, we can consider the $r^{th}$ ring ($r = 1, \ldots, 100$) and obtain its probability to be in the ground state $P^{(r)}$ from (4.7):

$$P^{(r)} = \sum_{i=1}^{60} |c_{i,1}^{(r)}|^2,$$

with the condition that:

$$\sum_{r=1}^{100} P^{(r)} = 1.$$

Let us show the probability to be in the ground state for the single ring $P^{(r)}$ as a function of the ring’s index $r$:

![Figure 4.8: Probability $P^{(r)}$ as a function of the ring’s index $r$. This graph is analogous to Fig. 4.7. The probability of the single ring to be in the ground state is given by the sum of the probabilities for the 60 sites composing it.](image)

From Figs. 4.7, 4.8 we see that the sites located at half height in the cylinder have the highest probability of being in the ground state. This result shows clearly that the ground state is delocalized all over the sites in the cylinder. Let us see if also the other states are delocalized analyzing their participation ratio.
4. Structural characterization of energy spectrum

4.3.2 Participation ratio of the states

Let us consider the previous expansion of $|i\rangle$ on the energy basis:

$$|i\rangle = \sum_{j=1}^{6000} c_{i,j}|\phi_j\rangle.$$ 

We just consider the $j^{th}$ eigenstate ($j = 1, ..., 6000$) and calculate $\langle \phi_j|i\rangle$:

$$\langle \phi_j|i\rangle = c_{i,j}.$$ 

This coefficient defines the participation ratio $PR_j$ of the $j^{th}$ eigenstate:

$$PR_j = \frac{1}{\sum_{i=1}^{6000} |c_{i,j}|^2}.$$ (4.8)

Here $i$ is the molecule index. From (4.8) it follows that when $PR_j = 1$ the $j^{th}$ eigenstate is fully localized in a single molecule, while when $PR_j = 6000$ the $j^{th}$ eigenstate is totally delocalized over all the sites of the aggregate.

For the ground state we have obtained the following value of $PR_1$:

$$PR_1 \approx 4603.$$ 

This suggests that the ground state is quite delocalized, which is crucial for amplifying the superradiance effects all over the rod. More generally we can investigate the participation ratio for all the eigenstates of the Hamiltonian (3.1), whose behavior is illustrated in Fig. 4.9. We see that all the states, both subradiant and superradiant, are delocalized. In particular, the ground state has the greatest degree of delocalization (about 77%) so that the superradiance is located into the majority of the molecules of the aggregate: this is a meaningful interpretation of the cooperativity.

The analysis we have just proposed does reaffirm openly the importance of the quantum coherence for the superradiance, so for the efficiency of the rod-like structures during their interaction with an external EMF. However another decisive property of these models regards the robustness to the environmental fluctuations, which does play a crucial role for the delocalization of the superradiance. Let us study in detail this topic in the next section.
4. Structural characterization of energy spectrum

The ground state has the highest PR!

Participation ratio PR
Energy $E-e_0$ (cm$^{-1}$)

Figure 4.9: Participation ratio $P_{R_k}$ as a function of energy $E-e_0$ (cm$^{-1}$). We may notice that all the energy states have a PR between $n=3$ and about $5n/6$, which means that they are delocalized.

4.4 Robustness to the static disorder

The species of bacteria we consider live in a natural habitat in which environmental fluctuations of the temperature may play a significant role for their efficiency. In the previous results we neglected the effects of this factor, considering always a temperature $T=0$ K. If the temperature is increased, it generates a thermal energy whose contribution represents an Hamiltonian term. In particular, a certain temperature $T$ creates a static disorder $W$ whose strength is given by:

$$W \approx k_B \cdot T.$$  

Here, $T$ is the temperature and $k_B \approx 0.695$ cm$^{-1}$/K is the Boltzmann’s constant.

Let us consider the Hamiltonian proposed by Mukamel (3.1) written on the sites basis: the static disorder is reflected on the diagonal elements $H_{\text{eff}}(i, i)$ (here $i = 1, ..., 6000$). Each diagonal element could be arranged as follows:

$$H_{\text{eff}}(i, i) = (e_0 + \Delta e)|i\rangle \langle i| + \Delta_{ii} - iQ_{ii}. \quad (4.9)$$

Here, $\Delta e$ is a shift of the single site energy randomly distributed in the range $[-W/2, W/2]$, $W$ represents the static disorder, $e_0 = 15390$ cm$^{-1}$ is the site
energy.

Mind that we work in the regime of uniform distribution: this is to say that $\Delta e$ is selected with equal probability for all the possible values in the range $[-W/2, W/2]$. In Fig. 4.10 we can see how the static disorder could affect the superradiance in the model of Chlorobium Tepidum wild type, assuming a temperature $T_{\text{amb}}=300$ K. At the temperature $T=0$ the decay width $\Gamma/\gamma$ has the same behavior we observed in Fig. 3.19. Then increasing the degree of static disorder we observe that the maximum decay width tends to decrease (Fig. 4.10 (A)). Let us observe the panel (B): the superradiant state is the 4th excited state for disorder $W\in[0, k_B T]$ and its $\Gamma_{\text{max}}/\gamma$ ranges between 3413 for $W=k_B T$ and 3657 for $W=0$. This result implies a certain robustness of the superradiance to the environmental fluctuations up to the room temperature. However, let us analyze the panel (C): the superradiance is destroyed when $W=10k_B T$. For such temperatures ($T\approx 3000$ K), we cannot recognize a specific superradiant state but only the 6th excited state has $\Gamma_{\text{max}}/\gamma\approx 330$, comparable with the other values of $\Gamma/\gamma$.

![Chlorobium Tepidum WT](image)

FIGURE 4.10: $\Gamma/\gamma$ as a function of the energy $E-e_0$ (cm$^{-1}$) for the wild type model previously proposed. (A) For a disorder $W\in[0, k_B T]$, the superradiance is robust to the environmental fluctuations, while for $W=10k_B T$ the superradiance is nearly broken. (B) $\Gamma_{\text{max}}/\gamma$ for $W\in[0, k_B T]$. We notice that $\Gamma_{\text{max}}/\gamma$ ranges between 3413 ($W=k_B T$) and 3657 ($W=0$), which confirms the cooperative robustness to the disorder. (C) For $W=10k_B T$, the superradiance is broken. The 6th excited state gathers the highest value of $\Gamma/\gamma\approx 330$, which is about the 9.3% of $\Gamma_{\text{max}}/\gamma$ for $W=0$. 
For completeness we underline that the static disorder differs from the dynamical one, that stems from a different kind of interaction with the environment. There could be several sources of dynamical noise: for example in the case of *Chlorobium Tepidum* some authors (Ishizaki, Fleming, [36]) have studied the interaction between electron and phonons as a source of it. Other authors have characterized the dynamics of the *Chlorobium Tepidum* bchQRU mutant [37] proposing an electromagnetic study of the chlorosome antenna complex of this bacterium. One of the most important characteristics of the dynamical disorder is that the fluctuations related to it oscillate on a much shorter timescale compared to the dynamics of the system [37]. From now on, we are interested to the static disorder in the structure of *Chlorobium Tepidum* bchQRU mutant. The whole analysis we present can be reduced to a fundamental question: how much the rod-like structure of the mutant is robust to the static disorder?

### 4.4.1 Single ring of bchQRU mutant

In the model of bchQRU mutant we presented in the previous chapter, we consider a density $\rho_s$ of sites per ring equal to $1 \text{ Å}^{-1}$:

$$\rho_s = \frac{N_1}{r} = \frac{60 \text{ sites}}{60 \text{ Å}}.$$  

Here, $r$ is the radius of the ring and $N_1$ corresponds to the number of sites per ring. We aim to evaluate the effects of the diagonal static disorder as in (4.9) in a single ring with fixed density $\rho_s = 1 \text{ Å}^{-1}$. Here, the geometrical path of the molecules composing the ring follows that of the bchQRU mutant. Fig. 4.11 shows how the participation ratio of the ground state varies increasing the static disorder strength. As one can observe in Fig. 3.24, in the single ring the most superradiant state is the first excited state, even if also the ground state and the second excited state have a high dipole strength. In each case we notice that the participation ratio of the ground state begins to drop at a certain value of the static disorder, that could be named "critical disorder". In particular, as one can see in Fig. 4.11 the participation ratio decays more rapidly increasing the number of sites, that is to say the critical disorder decreases on increasing the number of sites. This result agrees with the calculations made for similar structures (38, 39). Studying the participation ratio of the ground state could illustrate important effects of the static disorder on the superradiance: for very large intensities of the static disorder, the ground state is completely localized according to the Anderson localization. Moreover, this means that the superradiance is quenched and all the states decay independently with the common width $\gamma$.

Now we reply the same analysis of Fig. 4.11 for the mutant type, made of various coaxial rings separated by a vertical distance $h = 8.3 \text{ Å}$. 

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4. Structural characterization of energy spectrum
4. Structural characterization of energy spectrum

4.4.2 Coaxial rings of bchQRU mutant

The rod-like structure of *Chlorobium Tepidum* bchQRU mutant presented in the previous chapter has a series of equal coaxial rings, each containing 60 sites and having a fixed radius $r = 60 \text{ Å}$ and a vertical distance between rings $h = 8.3 \text{ Å}$. We analyze how the static disorder affects the superradiance in this particular structure only varying the number of rings. We highlight that the ground state is not always superradiant because this matter of fact is tied to the number of rings $N_2$. The table 4.2 has two columns in which the first indicates the numbers of rings of the aggregate and the second shows the corresponding superradiant state. This result is very important in an analysis focused on the relationship between superradiance and static disorder. In the panel (A) of the Fig. 4.12 we show how the static disorder influences the participation ratio of the superradiant state when the number of rings ranges from 1 to 60. The panel (B) illustrates how much the maximum decay width (corresponding to the superradiant state) is affected by the static disorder. The two situations are very similar.
Table 4.2: The first column displays the number of equal coaxial rings composing the tubular aggregate, the second one indicates the corresponding superradiant state. In spite of changing, the ground state continues to be very close to the ground state.

and in both cases there is a weak dependence of the critical disorder on the number of rings.

Now let us compare this result with the previous one, investigated for the single ring whose dimensions vary so that the density $\rho_s = 1 \text{ Å}^{-1}$ is fixed. In that regard we know that the critical disorder strength in the single ring-like structures, which induces the Anderson localization, is given by $[38]$:

$$W_{loc} \propto \frac{1}{\sqrt{N^3}}.$$ 

Here, $N$ stands for the system size. If we consider the structure of the single ring this result might be applicable since $W_{loc}$ decreases with the system size $N$. In the tubular aggregate made of many coaxial and equal rings this result does not give a realistic description. We do not consider this subject here since it should deserve a deeper future investigation. One for example might hypothesise that there would be a link between the independence of $W_{loc}$ and the variation of the superradiant state which does not coincide with the ground state in each case. This characteristic distinguishes the tubular structure from the single ring structure, in which the superradiant state is always the ground state.
Figure 4.12: (A) Participation ratio $PR_{SR}$ of the superradiant state as a function of the static disorder $W$ (cm$^{-1}$). It seems that the localization disorder does not depend on the number of the rings and it is located near $W \approx 100$ cm$^{-1}$. Increasing the static disorder over $10^6$ cm$^{-1}$ one can see that the participation ratio is 1, which means that the system is in the Anderson localization regime: the superradiant state is completely localized into one site.

(B) Decay width of the superradiant state $\Gamma_{\text{max}}/\gamma$ as a function of the static disorder $W$ (cm$^{-1}$). This graph is analogous to the situation in the panel (A), then the critical disorder is near to 100 cm$^{-1}$.

These results were calculated on 10 disorder realizations in every case.
4.5 Conclusions

The study made in this chapter has allowed us to reach a deeper knowledge about how the structural organization of the tubular aggregates influences properties deeply linked to the superradiance. Firstly, we have reduced the structure made of many coaxial rings to a single couple of rings. Then one can easily extend the properties of a simpler system to a more complex one: in other words, speaking about a two rings structure or about the whole aggregate is similar. The particular structure of the bchQRU mutant makes possible a non-zero coupling between the homologous states of different rings independently of their dipole strength. We stress that the decoupling of different states of different rings lets us elaborate a good approximation of the energy spectrum of the aggregate.

In the second part of the chapter, we focus on the superradiant state: for 100 equal and coaxial rings it coincides with the ground state, which is the most delocalized in the whole aggregate. Albeit the superradiant state varies with the number of rings, its robustness to the static disorder seems to be independent of the number of sites. This is absolutely a nontrivial matter, which opens new perspectives about the Anderson localization regime for these structures.
Conclusions

This work has put in evidence a complex and interesting role of the structural organization in the functionality of light harvesting systems. Why does Nature tend to select structures such as that of *Chlorobium Tepidum* wild type or very similar to the bchQRU mutant? The reason consists on the geometrical distribution of the molecules, which makes possible to concentrate the superradiance into the ground state or very close to it. In the mutant type made of 100 equal and coaxial rings the superradiant state coincides with the ground state, the most delocalized one. It follows that the highest number of molecules is capable to supertransfer excitation: in this process the quantum coherence plays a role of primary importance. On the other hand, differently from the single-ring structures the multi-ring ones show a different behaviour in presence of static disorder, which might induce a localization independent of the number of rings.

This work is the starting point to investigate more deeply the tubular structure model, principally we will aim to study:

- how can we display the behaviour of the tubular structures in presence of static disorder, according to the model of Anderson localization?

- what happens if we consider a cylindrical aggregate made of many concentric surfaces?

The present work has to be intended as the framework in which we try to formulate an answer to these questions.
In this appendix we explain some questions investigated in our work, such as the Hamiltonian of the system and some of the structural approximations.

### 6.1 Tubular structure

Most of the papers we have read present the tubular structure model as a characteristic feature of both natural models of *Green Sulfur* bacteria and of artificial complexes such as J aggregates. In particular, the analysis we made in the present thesis is based upon the aggregate of *Chlorobium Tepidum* studied by Ganapathy *et al.* [13], who propose a detailed structural analysis of the *syn-anti* organization typical of its molecular path.

[3] The authors study exciton dynamics of *Chlorobium tepidum*, in particular BChl c aggregates, and *Chloroflexus aurantiacus*. In these aggregates, the single molecule is approximated with a dipole, whose squared dipole moment is $\mu^2 = 30 \text{ D}^2$, the same we use in our simulations [1].

[4] The paper investigates the linear dichroism and the exciton-exciton scattering in J aggregates and explains why, in particular in the field of technological applications, a tubular shape is better than the one-dimensional chain model. The authors consider 5 models of cylinders, each containing N=6000 dipoles divided into coaxial and equal rings. The single dipole makes an angle $\alpha = 0^\circ$ with the tangent to the tubular surface in every case. Then, the paper focuses on the rod aggregate labelled as I. It is characterized by the following parameters: $\beta = 47.4^\circ$ (angle between the dipole and the cylindri-
cal axis), $\gamma = 6.74^\circ$ (helical angle of shifting between two consecutive rings), radius $R = 54.55$ Å, $N_1 = 2$ molecules per ring, dipole moment of the single molecule $\mu = 11.4$ D.

The authors analyze the aggregate of *Chloroflexus Aurantiacus* and other synthetic structures obtained by self-assembly. The rod-model of *Chloroflexus Aurantiacus* is organized into equal and coaxial rings and is distinguished by the following quantities: $N_1 = 6$ equidistant sites per ring, $\alpha = 189.6^\circ$ is the angle with the local tangent to the ring, $\beta = 36.7^\circ$ represents the angle between the single dipole and the cylindrical axis, $\gamma = 20^\circ$ is the helical angle between two rings. The radius of the structure measures $R = 22.97$ Å and the vertical distance between two rings is $h = 2.16$ Å. The single-molecule transition dipole is $\mu = \sqrt{20}$ D and the absorption peak is located at $\lambda = 6750$ Å. This paper aims to study dichroism spectrum for different values of number of rings $N_2$.

This paper investigates the structure of *Chlorobium tepidum* bchQRU mutant and, in particular, its particular Bravais lattice starting from the sample preparation. A distinction is made between the bchQRU and the bchR species, characterized by two different supramolecular arrangement: one of the most relevant differences is that the bchQRU type does not have oblique rings, opposed to the bchR type. The authors propose a tubular model of the bchQRU species in which parameters are: vertical distance between consecutive rings $h = 8.3$ Å, angle between the single dipole and the cylindrical surface $\alpha = 176^\circ, 184^\circ$, angle between the single dipole and the cylindrical axis $\beta \approx 55^\circ$, angular shifting between two consecutive rings $\gamma = 122^\circ$.

A complete study of the structure of *Chlorobium tepidum* double-walled rod and *Chloroflexus aurantiacus* is presented: for both species, the authors consider a site energy $e_0 = 15390$ cm$^{-1}$. Once focused on a particular cylindrical surface, they examine most of the structural parameters such as angles and number of sites. Moreover, for example the energy spectrum as a function of the number of sites per ring is studied.

### 6.2 Dipole approximation and Hamiltonian of the system

An important starting point for the analysis we made in the present work is to consider the single site in the dipole approximation. This assumption strongly depends on the dimensions of the system, that is to say one can not neglect the reciprocal interactions between the sites if they are too close and the dipole approximation loses its validity for these cases.
The authors study two particular structures of the *Chlorobaculum tepidum* (bchQRU triple mutant, Wild Type), assuming the Hamiltonian proposed by Frenkel in the regime of dipole approximation: here we report a brief piece of the article.

**Model Simulations.** The model for the microscopic structure of a cylinder is obtained by wrapping in a helical way the 2D lattice structure obtained previously from NMR and molecular modeling onto a cylindrical geometry. The electronically excited states (excitons) are found using a Frenkel exciton model that accounts for the molecular excitation energy and resonance transfer interactions between the molecules within the point dipole approximation. For multilayered cylinders, the dipole interactions between molecules situated on different walls are neglected. Numerical diagonalization of the Frenkel Hamiltonian yields the exciton eigenstates and exciton energies, which in turn may be used to calculate the fluorescence excitation spectrum using standard techniques. More details are provided in the Supporting Information. Values for the molecular and structural model parameters are taken from previous publications and in some cases (indicated in the main text) were fine-tuned to improve the fit to experiment; the remaining unknown parameters (rolling angle and several optical line widths) were determined from fitting the experimental excitation spectra.

In Supporting information the authors get $|\mu|^2 = 30 \text{ D}^2$ that coincides with the value we assumed in our simulations.

b) Model Hamiltonian

We have used the standard Frenkel exciton Hamiltonian in the Hellman-London approximation:

$$H = \sum_{n} E_n |n\rangle \langle n| + \frac{1}{2} \sum_{n,m} V_{nm} |n\rangle \langle m|$$

where $|n\rangle$ indicates the state with molecule $n$ excited and all others in the ground state, $E_n$ corresponds to the transition energy of a monomer, and $V_{nm}$ is the excitation transfer interaction between molecules $n$ and $m$. The latter was calculated in the point-dipole approximation

$$V_{nm} = \frac{\vec{\mu}_n \cdot \vec{\rho}_{nm} - \frac{1}{3} (\vec{\rho}_n \cdot \vec{\rho}_m) \vec{\rho}_{nm}}{|\vec{\rho}_{nm}|^3} \cdot \vec{\rho}_{nm}$$

where $\vec{\mu}_n$ and $\vec{\rho}_{nm}$ correspond to the transition-dipole moments of molecules $n$ and $m$, and $\vec{\rho}_{nm}$ refers to their relative position vector.
This paper focuses on the *Chlorobium Tepidum* chlorosomes in the dipole approximation and explains under which conditions this regime is valid.

As in our previous work (Prokhorenko et al., 2000a), we will use the simplest approximation (Frenkel Hamiltonian) for calculating the excitonic states of an aggregate with \( N \) monomers, thus neglecting the interaction of the electronic transition with the phonons,

\[
\hat{H} = \sum_i \nu_i |i\rangle \langle i| + \sum_{i,k \neq i} J_{ik} |k\rangle \langle i|,
\]

where \( \nu \) is the energy of the \( S_0 \rightarrow S_1 \) electronic transition of the \( i^{th} \) molecule whose excited state is described by the wave function \( |i\rangle \), indices \( i, k \in [1, N] \), and \( J_{ik} \) is the Coulomb interaction energy between the \( i^{th} \) and the \( k^{th} \) molecule for which we will use the point dipole-dipole approximation (Agranovich and Galanin, 1982):

\[
J_{ik} = \frac{\hat{\bm{\mu}}_i \cdot \hat{\bm{\mu}}_k}{|\hat{\bm{R}}_{ik}|^3} - 3 \frac{(\hat{\bm{\mu}}_i \cdot \hat{\bm{R}}_{ik})(\hat{\bm{\mu}}_k \cdot \hat{\bm{R}}_{ik})}{|\hat{\bm{R}}_{ik}|^5}.
\]

Here the transition dipole moment of the \( i^{th} \) molecule is denoted by \( \hat{\bm{\mu}}_i \), and the distance vector (defined with respect to the central magnesium atoms for BCHls) is \( \hat{\bm{R}}_{ik} \). The validity of the dipole-dipole approximation for describing the interaction energy depends on the ratio between the dipole length \( L_D = |\mu|/e \), where \( e \) is the electron charge) and the intermolecular distance \( L_D/|\hat{\bm{R}}_{ik}| \), since this ratio is a series expansion parameter for the Coulomb interaction. The shortest distance between monomers in our structural model is 6.4 Å (within a stack, see below), and the dipole length for BCHl \( c \) is 1.1 Å (calculated using a dipole strength of 30 D \(^2\) as defined in Prokhorenko et al., 2000a) so that \( (L_D/|\hat{\bm{R}}_{ik}|)_{max} = 0.18 \), and thus the dipole-dipole approximation can be applied. (Note that authors often erroneously assume that the ratio between the molecule size and the intermolecular distance is the series expansion parameter, which indeed can be close to 1 in many cases. This question has been clarified, however, by Davydov, 1971.)
The authors propose an analytical approach to evaluate the effectiveness of the dipole approximation. The ratio between \( \mu \) and the electric charge \( e \) is the dipole length \( L_D \), so that if the distance between the \( j \)th and the \( i \)th dipole is \( r_{ij} \), the validity of the dipole approximation is expressed by the condition \( L_D / r_{ij} \ll 1 \). When \( L_D / r_{ij} \approx 1 \), the point dipole is substituted by opposite charges at a finite distance.

In this paper, the authors analyze the structure of *Chloroflexus aurantiacus*, in which they do not apply the dipole approximation as \( L_D \) is comparable with \( r_{ij} \).

Approximation is not valid in the present regime where the dipole moment lengths are comparable to the distance between different chromophores. A better approximation is given by the extended dipole-dipole interaction [32]. A point dipole is substituted by opposite charges +\( \delta \) and −\( \delta \) at a finite distance \( l \):

\[
J_{nm} = \frac{D^2}{4\pi \varepsilon_0 l^2} \left( \frac{1}{r_{++}} + \frac{1}{r_{--}} - \frac{1}{r_{+-}} - \frac{1}{r_{-+}} \right)
\]

(2)

where \( r_{\pm\pm} \) represent the distance between the positive (negative) charge of the point dipole associated with the first molecule and the positive (negative) charge of the point dipole associated with the second molecule. In the case of BCHl C pigments the dipole length \( l \) is taken to be 8\( \AA \) and the squared dipole strength \( D \) as 25 Debye\(^2\). The values for the disorder are taken from Ref. [8] and are quoted on Table I.


[19] In SI units we have $1 \text{D} \approx 3.33564 \cdot 10^{-30} \text{C} \cdot \text{m}$ while in ESU-CGS and Gaussian systems we can estimate $1 \text{D}^2 = 10^{-12} \text{cm}^2 \cdot \text{g} \cdot \text{s}^{-2} \cdot \text{Å}^3$ and $\hbar c = 1.98644582 \cdot 10^{-16} \text{cm}^3 \cdot \text{g} \cdot \text{s}^{-2}$, so we obtain $\mu^2 = \mu^2 \cdot \text{cm}^{-1} \cdot \text{Å}^3$ dividing $\mu^2$ by $\hbar c$, both expressed in ESU-CGS system.


[27] G. D. Scholes; Chemical Physics, 275, 373 - 386 (2002).


