Vibronic Excitons in Molecular Systems

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Abstract
Absorption and emission of photons by any molecule is strongly influenced by the molecular environment. When several chromophores are packed together their spectral properties are known to be altered and this is canonically explained by quantum theory as electromagnetic interactions between the dipole moments. If the interaction is strong, the absorption process might be best described as the creation of a so-called exciton. These are not fully understood, especially not in biologically relevant systems. In addition, electronic transitions are in some molecules accompanied by vibrational transitions by such a high probability that these cannot be neglected. Models including these effects have not been used for many systems so far. The peridinin-binding protein complex (PCP) is an interesting system for exciton investigations but the vibrational coupling in carotenoids need to be accounted for. The present work deals with this problem in PCP.

Introduction
Understanding molecular interactions is perhaps the most important application of quantum theory. Both experimentally and theoretically, quantum behavior of molecules is best understood in terms of interactions with light and this is true also for larger systems. In particular, it holds for all light-harvesting protein complexes employed naturally by various photosynthetic organisms. Electronic transitions, both emission and absorption, are altered when chromophores come together; as electrons become delocalized the system can no longer be described by separate units and the excited state is delocalized by coherence and referred to as an exciton (note that this is slightly different from the hole-electron particle definition of excitons in semiconductors). In the chromophore system, one may define a radius within which there is a reasonably large likelihood of having the excess energy. We shall call these couplings between states entering from different chromophore units exciton coherence. A far more understood phenomenon is vibrational coherence which can take place in a single chromophore. A sophisticated theory of exciton interaction should of course also allow for vibrational states of different chromophores to couple with the electronic states, and allow vibrational energy quanta (phonons) to be distributed over molecules.
that are not directly excited electronically (these effects will of course fall into the
category of exciton coherence; an exciton dressed with phonons is called a
polaron). Such a method is described below and originates from [5, Philpott
1979], and has more recently been elaborated by the Spano group, working with
repeated units of conjugated organic molecules exhibiting the vinyl stretching
mode as the most prominent vibration. The aim of this work was to apply
similar methods to less ordered and more complicated systems. Here we can-
not use any periodicity in the aggregate and the wavefunction is not a Bloch
function. The motivation for studying these systems is that they are of fun-
damental importance and could also provide more information about excitons
per se. A short description of one such system will first be given. One of the
polyenes used in photosynthesis is the carotenoid known as peridinin shown
in Figure 1. Peridinin is unusual in the sense that it is highly substituted as
compared to most other carotenoids, with three conjugated rings: an epoxy-
cyclohexane ring, a furanic ring and a cyclohexane ring. Peridinin occurs in
particular in the well-known peridinin-chlorophyll-a-protein, a light-harvesting
complex in dinoflagellate Amphidinium carterae. The universally used abbre-
viation for this protein is PCP and it will be used in the following. What is
striking in the case of PCP is that the carotenoid versus chlorophyll contents
is strongly biased towards carotenoid. In addition, PCP is small-to-medium-
sized (say) and water soluble. Accordingly, the structure has been determined
up to 2 Å. Although PCP has a trimeric structure overall, most photochemical
properties can probably be extracted from investigations of one subunit only.
Each such subunit exhibits a pseudo-two-fold symmetry with two chlorophyll
a molecules and 8 peridinins in total, the chromophores being stuck in the hy-
drophobic core. The peridinin molecules are suspected to be aligned in such a
way that energy transfer can take place efficiently.
Figure 1: Upper: the carotenoid called peridinin. The dipole moment is oriented along the polyene backbone but could possibly be influenced by the conjugated lactone and allene moieties. Lower: the PCP trimer (PDB entry 1PPR). The carotenoids (peridinins) are shown in gray. The chlorophyll a molecules are found in the very center of the complex.
Theory

Hamiltonian

Here a mathematical description of the energy operator (the Hamiltonian $H$) will be given.

According to von Neumann’s postulates of quantum mechanics, the system can be described by a vector $\psi$ (a state vector) in a Hilbert space $\mathcal{H}$ (the state space). We will describe the exciton states of complex molecules in this way. We then need to consider a tensor product $\mathcal{H}_{ex} = \mathcal{H}_e \otimes \mathcal{H}_{ph}$ of Hilbert spaces. Here $\mathcal{H}_e$ is interpreted as the state space of electronic wavefunctions $\varphi$ in the absence of vibrations. Similarly, $\mathcal{H}_{ph}$ contains all the vibrations. Suppose we have a molecular system with $N$ ($N$ a natural number) possible electronic transitions. Then $H_{1e}$ will be the $N$-dimensional state space with an orthonormal basis given by vectors $e_i$ corresponding to excitation at position $i$ for all $i = 1, \ldots, N$. Denote by $|e_i\rangle\langle e_i|$ the projection onto the subspace spanned by $e_i$. Then the unperturbed Hamiltonian takes the form

$$H^0_e := \sum_{i=1}^{N} \varepsilon_i |e_i\rangle\langle e_i|,$$

where the reals $\varepsilon_i > 0$ are the site-energies, i.e. the energy corresponding to excitation at site $i$. The dipole interaction (see below) will be taken into account by

$$H^1_e := \sum_{j=1}^{N} \sum_{i=1}^{N} V_{ij} |e_i\rangle\langle e_j|,$$

where $V_{ij}$ is a $2 \times 2$-matrix to be determined below. As for $\mathcal{H}_{ph}$, let $L$ denote the state space of a single phonon. This phonon is allowed to be of any reasonable energy and supposed to be localized somewhere in the system where molecular vibration energy could reside. This space $L$ can be described as the Hilbert space $L^2(X)$ of all square-integrable functions $f$ on a real vector space $X$. Then the $n$-fold tensor product $L^{\otimes n}$ is the state space of $n$ phonons. Since phonons are bosons, we require that the states $\chi \in L^{\otimes n}$ are represented as symmetric vectors (since by definition the wavefunction of bosons remain unchanged upon particle exchange). If $\oplus$ denotes the direct sum of Hilbert spaces then

$$\mathcal{H}_{ph} = \bigoplus_{n=0}^{\infty} L^{\otimes n},$$

is the desired space indicated above. Explicitly,

$$\mathcal{H}_{ph} = \mathbb{C} \oplus L \oplus L^{\otimes 2} \oplus L^{\otimes 3} \oplus \cdots := \mathbb{C} \oplus L \oplus L \otimes L \oplus \cdots,$$
where we defined $\mathcal{L}^{\otimes 0}$ to be the set of scalars $\mathbb{C}$. Each space $\mathcal{L}^{\otimes n}$ can be identified as the subspace of $H_{\text{ph}}$ formed by the vectors $\chi := (0, \ldots, 0, f_n, 0, \ldots)$ with all components except the $n$'th equal to zero and $f_n \in \mathcal{L}^{\otimes n}$. To get an example, suppose there are three vibrational quanta on molecule $a$ in an aggregate and two vibrational quanta on molecule $b$. The three phonons on $a$ are described by some state vector $f_3(a) \in \mathcal{L}^{\otimes 3}$ and the two phonons on $b$ are described by some vector $g_2(b) \in \mathcal{L}^{\otimes 2}$. This can be written shortly by a $H_{\text{ph}}$-vector as

$$\chi(a,b) := (0, 0, 0, f_3(a)g_2(b), 0, \ldots),$$

since $f_3(a)g_2(b) := f_3(a) \otimes g_2(b) \in \mathcal{L}^{\otimes 5}$. If there instead had been three phonons on molecule $b$, we get $g_3(b) \in \mathcal{L}^{\otimes 3}$ and an element on the 6th position,

$$\chi(a,b) = (0, 0, 0, 0, f_3(a)g_3(b)).$$

To write $f_n(a)$ or $f_n(b)$ to indicate where the boson is located (i.e. on $a$ or on $b$) is a shorthand notation that should be interpreted as $f_n(x_1, \ldots, x_n)$ where $(x_1, \ldots, x_n)$ specifies the coordinates of e.g. molecule $a$ in the coordinate space $X^n$. The reason for using different labels $f, g$ etc. is to allow different vibration modes and different phonons (i.e. different vibrational energy quanta). Thus, even though it is logical to use the same symbol $f$ to describe the same type of phonon on molecule $a$ as on $b$ (but writing $f(a)$ respectively $f(b)$ to mean a phonon localized on $a$ and $b$), we need different phonons for nonidentical molecules or different modes. We will not need several modes on the same molecule in the present work. We shall, however, need different vibration types for different molecules; the chlorophyll a vibration is at about 750 cm$^{-1}$ whereas peridinin has a mode at 1400 cm$^{-1}$.

Another useful construct is provided by introducing a way of creating and annihilating single phonons in $H_{\text{ph}}$. We take an operator approach. This is not the conventional strategy used in physics but it makes use of universal mathematical construct (i.e. the so-called Cuntz algebras, excepts that we have already symmetrized the Hilbert space $\mathcal{L}$; see Evans and Kawahigashi 1998 Section 2.8 for details). For each $f \in \mathcal{L}$ we can define an operator $s^n(f)$ acting on $\mathcal{L}^{\otimes n}$ as

$$s^n(f) := f \otimes g \quad g \in \mathcal{L}^{\otimes n+1} \tag{5}$$

Then $s^n(f) : \mathcal{L}^{\otimes n} \to \mathcal{L}^{\otimes n+1}$ is a shift operator. Then define an operator $s(f)$ on $H_{\text{ph}}$ by

$$s(f) := \bigoplus_{n=0}^{\infty} s^n(f) \tag{6}$$

If we limit ourselves to a certain number $M$ of distinct phonons in $\mathcal{L}$, including all modes and vibration energies needed, then we fix is an orthonormal basis $\{v_i\}_{i=0}^{M}$ for $\mathcal{L}$. If we do so and write $s_i := s(v_i)$ then

$$|v_i\rangle\langle v_i| + \sum_{i=1}^{M} s_i s_i^* = 1, \tag{7}$$
where 1 is the identity operator and $s_i^*$ is the adjoint of $s_i$. Furthermore, for any $f, g \in \mathcal{L}$ we have

$$s(f)^* s(g) = \langle f | g \rangle$$  

(8)

where $\langle f | g \rangle$ denotes the inner product of $f$ and $g$. Thus, if we define a slightly different operator $b(f)$ on $\mathcal{H}_{ph}$ by

$$b(f)^* := \bigoplus_{n=0}^{\infty} (n+1)^{1/2} s^n(f)$$  

(9)

then $b(f)^*$ and its adjoint $b(f)$ are the familiar boson creation and annihilation operators. That is, if $[\cdot, \cdot]$ denotes the commutator then

$$[b(f), b(g)^*] = \langle f | g \rangle 1$$  

(10)

for any $f, g \in \mathcal{L}$. This means that the antilinear map $b : f \rightarrow b(f)$ satisfies the canonical commutation relations. The $C^*$-algebra generated by the operators $\{b(f) : f \in \mathcal{L}\}$ and the identity will then consist of boson operators. In particular, the energy operator in the absence of interactions is given by

$$H_{0}^{0} := \sum_{i=1}^{M} \hbar \omega_{i} c_{i}^{*} c_{i},$$  

(11)

where $\hbar$ is Planck’s constant (divided by $2\pi$) and $\omega_{i}$ is the vibration frequency. Finally, if we attach a matrix $2 \times 2$-matrix $\lambda_{i}$ that is a measure of the nuclear displacement during electronic transition (see below), and if

$$H_{1}^{3} := \sum_{i=1}^{M} \lambda_{i} (b_{i} + b_{i}^{*})$$  

(12)

then the total Hamiltonian becomes

$$H = H_{e}^{0} \otimes H_{ph}^{0} + H_{e}^{1} \otimes H_{ph}^{1}.$$  

(13)

This Hamiltonian $H$ is an hermitian operator on $\mathcal{H}_{ex} = \mathcal{H}_{e} \otimes \mathcal{H}_{ph}$. It operates on wavefunctions $\psi \in \mathcal{H}_{ex}$ representing different exciton states arising from molecular interactions. When we evaluate the electronic coupling $H_{e}^{1}$ we must, since the vibrational coupling strength cannot be neglected when forming the basis of exciton states $\psi$, consider the Franck-Condon factors included in $H_{ph}^{1}$ (see below). By the Franck-Condon approximation we treat the nuclear and electronic motions separately, which is why the Hamiltonians $H_{e}^{1}$ and $H_{ph}^{1}$ can appear as the composition $H_{e}^{1} \otimes H_{ph}^{1}$.

The values of $\varepsilon_{i}, V_{ij}$ and $\lambda_{i}$ for each $i$ and $j$ will determine the spectral properties of the molecular system, as described in more detail below.
Franck-Condon Factors

In order to calculate the transition probabilities we will have to evaluate overlap integrals between the states. There is nothing special about this procedure required for the present work as long as the approach is general enough to allow transitions from any vibronic state to another. The theory behind such an approach will be outlined in the following. For simplicity, \( b = b_i \) throughout this section. We fix a particular type of phonon \( f \in \mathcal{L} \) and do not care whether \( f \) is supported on molecule \( a \) or \( b \) etc. in the system. For a number \( n \) of such phonons we use the notation \( f^n \in \mathcal{L}^\otimes n \). For the corresponding vibrational states \( \chi \in \mathcal{H}_{ph} \) will be written \( \chi := (0, \ldots, 0, f_n, 0, \ldots) \). When the molecule on which \( \chi_n \) resides is electronically excited, the nuclear coordinates will be shifted so that \( f, f_n \) and \( \chi \) change. We therefore make the distinction symbolically clear by writing \( \chi_1^n \) for the phonon in the excited state and \( \chi_0^n \) for the phonon in the ground state. The larger the displacement of the potential minimum upon excitation, the more decreases the value of the inner product \( \langle \chi_1^n | \chi_0^n \rangle \) because of the dissimilarity between \( \chi_1^n \) and \( \chi_0^n \). The interconversion between the displaced and nondisplaced functions will be mediated by a family of displacement operators. A notorious theorem of Stone gives a 1-to-1 correspondence between the one-parameter unitary evolution groups and the self-adjoint operators (see Lax Theorem 35.1). We need operators \( \{D_s\}_{s \in \mathbb{R}} \) that act as

\[
D_s \chi(x) := \chi(x - s), \quad \chi \in \mathcal{H}_{ph},
\]

(14)

where \( x \in \mathbb{R} \) since we consider only one-dimensional displacements. It is well-known that a self-adjoint momentum operator \( P \) is the infinitesimal generator of the unitary group of translations. This can be shown in several ways and an illustrative one is the following. The value of \( \chi(x - s) \) at \( s = 0 \) is \( \chi(x) \) and differentiation with respect to \( x \) gives the same result as with respect to \( s \) (except for a minus sign). Therefore, in a Taylor series expansion around \( s = 0 \)

\[
\begin{align*}
\chi(x-s) &= \chi(x) - s\chi'(x) + \frac{s^2}{2} \chi''(x) + \ldots \\
 &= \left[1 + s \left(- \frac{d}{dx}\right) + \frac{s^2}{2} \left(- \frac{d}{dx}\right)^2 + \frac{s^3}{3!} \left(- \frac{d}{dx}\right)^3 + \ldots \right] \chi(x) \\
 &= \exp\left(- s \frac{d}{dx}\right) \chi(x) = e^{-i s P} \chi(x)
\end{align*}
\]

appears the momentum operator \( P := -i d/dx \). For \( \mathcal{H}_{ph} \) we see that the proper operator is \( P = 2^{-1}(b - i b^*) \). Hence, we conclude that the one-parameter family \( \{D_s\}_{s \in \mathbb{R}} \) of translations consists of the operators given by

\[
D_s := \exp[i s (b^* - b)],
\]

(15)

with \( s \in \mathbb{R} \) being the dimensionless measure of how much the excited potential is shifted by application of the operator \( D_s \). Let now \( s \) and \( t \) be the shifts of the potential minima of electronic states \( \alpha \) and \( \beta \), respectively, compared to
the ground state potential minimum. The overlap integrals to be calculated are then

$$\langle \chi_{\alpha m} | \chi_{\beta n} \rangle,$$  \hfill (16)

where as mentioned above, $m$ and $n$ indicates the number of phonons in the ground and excited states, respectively. The squared quantity $|\langle \chi_{\alpha m} | \chi_{\beta n} \rangle|^2$ is known as a Franck Condon factor. Now write these integrals as

$$\langle D_s \chi_{0m} | D_t \chi_{0n} \rangle = \langle D_s^* D_t \chi_{0m} | \chi_{0n} \rangle.$$  

The operators $\{D_s\}_{s \in \mathbb{R}}$ obviously commute with the commutator $[b, b^*] = 1$ and this ensures the validity of the so-called Baker-Hausdorff formula for two operators $A, B$:

$$e^A e^B = e^{A+B+[A,B]/2}.$$  \hfill (17)

Falling back on this formula (17) is a standard way of manipulating nonabelian operator exponentials. Thus, we go about as in [4] and apply this operator identity to

$$D^*_t D_s = e^{-it(b^*-b)} e^{is(b^*-b)} = e^{(s-t)b^*} e^{-(s-t)b} e^{-(s-t)^2/2}.$$  

Now let $S := (s-t)$ denote the so-called Hyang Rhys factor of the transition. By expanding the action of the exponential operators to the form

$$e^{-Sb} \chi_{0m} = \left( \sum_{k=0}^m \frac{(-1)^k S^k}{k!} b_k \right) \chi_{0m} = \left( \sum_{k=0}^m \frac{(-1)^k S^k}{k!} \sqrt{\frac{k!}{(m-k)!}} \right) \chi_{0(m-k)}$$

it is possible to evaluate the Franck Condon integrals (16) as

$$\langle \chi_{\alpha m} | \chi_{\beta n} \rangle = \sum_{j=0}^n \sum_{i=0}^m (-1)^i S^{i+j} \frac{m!n!}{(m-i)(n-j)i!j!} \delta_{(m-i)(n-j)},$$  \hfill (18)

where $\delta_{ij}$ is Kronecker’s delta. It is interesting to note that the signs turn out to be of fundamental importance.

**Dipole coupling**

In e.g. the PCP, the orientations of the dipole moments can of course not be described in a simple manner. Hence each pair of oscillators must be given some parameters separately in such a way that the magnitude of the dipole-dipole interaction depends properly on the spatial arrangement. Consider two dipoles with transition dipole moments of magnitudes $\mu_1$ and $\mu_2$ separated by a distance $R$. The orientation of the dipoles will contribute to the magnitude of the interaction by a factor (usually denoted $\kappa$) depending on the angles $\alpha$, $\beta_1$ and $\beta_2$ shown in Figure 2. The dipole-dipole interaction $V$ is then given by

$$V = 5.04 \frac{\mu_1 \mu_2}{R^3 n^2} (\cos \alpha - 3 \cos \beta_1 \cos \beta_2) \equiv 5.04 \frac{\mu_1 \mu_2}{R^3 n^2} \kappa,$$  \hfill (19)
where $n$ is the refractive index of the surrounding dielectric (usually taken to equal 2 for protein). The unit of $\mu$ is debye and the distance $R$ is in nanometers. For example, if the dipoles are parallel and aligned along the intermolecular axis we get $\kappa = 2$ and the coupling is negative. This is the situation in a so-called J-aggregate. In a H-aggregate, the molecular dipoles are side-by-side and the coupling is positive since such an arrangement gives $\kappa = 1$. The use of $\kappa$ in the above equation as well as in the famous Frster equation must not give to the impression that we are discussing energy transfer here; the delocalization here is due to coherence between excited states and not simply a population distribution.

Two-particle approximation

It has been shown (as discussed in [7]) that there is no significant loss in information if only those states $\psi \in \mathcal{H}_{ex}$ are included for which all phonons are distributed over at most two dipoles. So the vibrational part of $\psi$ can have the form $\chi(a, b)$ but not $\chi(a, b, c)$ if the arguments $a, b, c$ denotes the distribution of phonons of $\chi$ on molecules $a, b, c$. This two-particle approximation will therefore only require calculations with one dipole excited and at most one other dipole that is not in the $0-0$ level. Of these states $\psi \in \mathcal{H}_{ex}$, only those states $\psi = \varphi \otimes \chi(a)$ with all non-excited dipoles in the $0-0$ level will contribute directly to the absorption spectrum. However, all states $\psi = \varphi \otimes \chi(a)$ will contribute indirectly via the eigenvector coefficients of the diagonalized Hamiltonian.
Methods

Absorption spectra for H- and J-aggregates of up to 20 molecules were simulated as in [7]. The coordinates of the peridinin and chlorophyll a molecules in the PCP were obtained from the Protein Data Bank entry 1PPR. The positions of the chlorophylls were taken as the coordinate of the magnesium ions. The dipole moments of the peridinins were taken to be along the polyene backbone; these dipoles were divided into three for each peridinin to make the model less coarse. Positions for these dipoles were taken as the positions of the C1-C, C14 and O4 atoms on each peridinin. The transition dipoles of chlorophyll a were taken to be aligned with the nitrogen-magnesium bonds of the BChl chlorin ring; the $Q_y$ transition is oriented along the $N_t ext B - N_t ext D$ bond and the $Q_x$ transition is oriented along the $N_t ext A - N_t ext C$ bond. The refractive index of the surrounding medium was taken to be 2.0, which corresponds roughly to a protein environment. Dipole interactions and Franck-Condon integrals were calculated as described in the Methods section. The Hamiltonian (13) was diagonalized and the dipole vectors were expanded with the eigenvector coefficients as

$$\hat{\mu}_\alpha = \sum_{i=1}^{N} C_{i\alpha} \mu_i$$

(20)

to yield the adiabatic transition dipole moments $\hat{\mu}_\alpha$. The absorption spectrum was calculated as

$$A_i(\omega) = \sum_{j=1}^{N} \hat{\mu}_j |\langle \chi_{00} | \psi_j \rangle|^2 e^{-\left(\omega - \omega_j\right)^2/2},$$

(21)

where $\{\psi_j\}_{j=1}^N$ are the excitons with vibrational quanta only at the excited dipole, $\omega_j$ is the eigenvalue of the diagonalized Hamiltonian corresponding to $\psi_j$ and $\sigma$ is a constant giving the homogeneous broadening.

Results and Discussion

Aggregates

The results presented in [7] for absorption and emission of J- and H-aggregates were first repeated to ensure the correctness of the model. We refer to that paper for the basic trends in absorption and emission of these aggregates. The difference in alignment of the molecules in H- compared to J-aggregates completely changes the dipole strength distribution among the states. In H-aggregates, the exciton state corresponding to highest energy is favored, whereas the lowest energy state is favored in J-aggregates. The absorption spectra plotted as a function of the coupling strength $V$ is shown in Figure 3. This kind of plot provides a good visualization of how increased coupling strength forces the eigenvalues to become more different. In order to see also the states without any significant dipole strength, the eigenvalues were also plotted as a function of $V$ (Figure 4).
Figure 3: Absorption spectrum of a H-aggregate (left) and J-aggregate (right) consisting of three identical molecules as a function of the coupling strength (y-axis). A single vibration mode was included with three vibrational levels and Hyang Rhys factor 1.0. The x-axis has units of wavenumber (cm$^{-1}$), increasing to the right.

Figure 4: The eigenvalues (in energy on the y-axis) of a 3-molecule H-aggregate are plotted as functions of the coupling strength $V$. The coupling strength (x-axis) is increasing to the right.

**Peridinin-chlorophyll $a$-binding protein (PCP)**

The simulated and experimental absorption spectra of PCP are shown in Figure 5. The dipole moments of the different molecules were adjusted to fit with
experiment. As can be seen in the recorded spectrum in Figure 5 (left), the PCP absorption (red) exhibits a shoulder at 1800-1900 cm$^{-1}$ compared to the peridinin absorption in solution (green). This feature is captured in the simulation (blue line in the right picture of Figure 5). The characteristic peak at 2500 cm$^{-1}$ seems to have contributions both from the chlorophyll $B_y$ and the peridinin third vibronic state. The model shows that the interaction energy must quite high for this peak to appear; at low interaction energy there is too much red-shifted dipole strength (Figure 5).

Figure 5: Left: The experimental absorption spectrum of the PCP as recorded by Zigmantas et al. 2002. The red line is the PCP and the green line is peridinin in solution. Right: In red is shown the same experimental absorption spectrum as in the left picture. The simulated absorption spectrum is shown in blue. The homogenous broadening $\sigma$ is 0.6. The dipole strengths are peridinin 13 D, $B_x$ 5.0 D, $B_y$ 6.5 D, $Q_x$ 2.5 D, $Q_y$ 6.5 D. Refractive index $n$ is 1.8. In all spectra, the x-axis has unit 1000 times wavenumber (cm$^{-1}$).

Figure 6: The effect of increasing the interaction energy $V$. The experimental absorption spectrum is shown in red and the simulated absorption spectrum is shown in blue. Middle is as in Figure 5, left has refractive index $n = 2.5$ (weaker coupling) and right has $n = 1.5$ (stronger coupling).

The effect of increasing the peridinin dipole moment is shown in Figure 7. The eigenvalues are forced to split when the interaction is strengthened so that
the resulting spectrum becomes enriched in separated peaks. When the dipole moment of peridinin is taken to be more than 14 D (the other dipole strengths being fixed), the model starts to differ as compared to the experimental spectrum [9].

It is tempting to believe that the extra conjugation via ring moieties in peridinin is giving some additional property of the coupling in the in vivo PCP complex. The crystal structure shows that one peridinin molecule leans towards the chlorophyll molecule very tightly. Even without considering the substituted groups, the coupling between the closest peridinins and chlorophylls is very strong (up to 1500 cm\(^{-1}\)), much more so than the peridinin-to-peridinin or chlorophyll-to-chlorophyll coupling. The fluorescence spectrum of the PCP is almost impossible to determine experimentally due to the fact that the \(S_1 \rightarrow S_0\) transition is symmetry-forbidden and due to the short lifetime of the \(S_2\) state. Fluorescence of PCP was therefore not investigated in detail.

**Outlook**

The above results show that the model has the potential of revealing some underlying structure of molecular spectra. With the model in hand, exciton interactions could be proved in practically any system. The emission spectrum of the plant light-harvesting complex II, for example, is one application that will certainly be explored in the future. Another interesting target is the well-studied soluble Fenna-Mathew-Olsen light-harvesting complex.
References


