Light Harvesting Course Note

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Contents

Abstract

This is a note of the course *An Introduction to Light Harvesting in Bacteria and Plants.* The course is more of a research than of a pedagogic taste: ideas and methods are outlined, with reference to the published paper available in the corresponding slides.

This note only aims to provide a guidance to read those slides. The page numbers in this note are the page numbers of each individual PDF, not necessarily the page numbers displayed on the bottom-right corner on those slides.

1 June 29th Wed

In this lecture, the teacher presents background for light-harvesting mechanism in biology systems:

- General background to Biophysics. **(pp.1 to 9)**

- Review of several mechanisms of light harvesting in different species. **(pp.10 to 18)**
- The central topics of this course **(pp.19 to 20)**
  - The natural of exciton in biological ligth harvesting system. Is it of Frenkel (short-ranged) of Wannier (long-ranged) type?
  - The transfer mechanism. (pp.20) It was mentioned that the transfer is much more efficient than predicted by a classical diffusion model.
  - How is active self-regulation archived. (pp.20)

pp.21 displays a observed long-range transport of excitation energy in a biomimetic light-harvesting system. Then, after a review of Quantum Mechanics (**pp.22 to 32**)[1], the teacher illustrated a model to calculate the excitation energy of a dimer.(**pp.33 to 36**) Note that here it is expected that only one of the dimer is excited, because this energetically easier to achieve. Note also that the symbol "†" here denotes neither conjugation nor creation operator, but simply a label for an excited state's wavefunction.

The calculated excited state energys on page 35 are split into two levels. the difference between them, denoted by $\mathcal{E}$, is expressed as a function of the two transition dipole moments and the separation length of two molecules. Details about the interaction potential V_{uv} can be found on the next lecture.

2 July 1th Fri

Begin with a review of two modes of excitons in organic system (**pp.1**), this lecture proceeds to explain in detail the dipole interaction potential (**pp.2 to 3**) V_{uv} mentioned in previous lecture. (**pp.4 to 5**) digresses on the difference between the transition dipole moment and the permanent dipole moment. On page 4, the picture shows the transition dipole moment for a Bacteriacholorophyll (the photosynthetic pigments that occur in various phototrophic bacteria). The right side plot illustrates the absorption spectra for Bacteriacholorophyll. Page 5 originally contains an animated display, which is lost in this PDF file, although the content is not important. (**pp.6 and 7**) also digresses on electronic momenta and oscillator strength.

The following slide comes back to the excitation energy. It states two forms of dimer: the J aggregation (**pp.9 to 10**), and the H aggregation (**pp.11**). The accessible energy level for absorption is determined by conservation of moment. As the result, the J aggregated dimer absorbs less energy than the monomer case, and a red shift will be observed when comparing the absorption spectra. The case of H aggregation is similar. (**pp.12 to 13**) mentions the transition dipole in more complicated cases. [2]

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[1] Interestingly, the teacher mentioned Bohmian Mechanics, an alternative model of Quantum Mechanics that features determinism and nonlocality. A comprehensive discussion of this model could be found here: `http://plato.stanford.edu/entries/qm-bohm/`

[2] Reference could be found in *J. Phys. Chem. B, Vol. 107, No. 35, 2003*.

3 July 6th Wed

This lecture begins with a note on the unbelievable efficiency of biological system. Then it proceeds to review some concepts in quantum statistical mechanics (**page 2 to 21**). Since we are quite familiar with this subject, it will be omitted from this note. The last page mentioned an important equation for the evolution of density matrix in an open system, called the "master equation".[3]

4 July 8th Fri

In the previous lecture, the *master equation* for density matrix [4] could lead to problematic result. When the density matrix propagates as described by the master equation, the eigenvalues for it might evolve into comprising negative values. This is because the added terms are not rigorously derived, but just an approximation. On (**page 2**) the teacher mentioned a specific case.[5] Therefore, one introduces the **Lindblad equations** (**pp.3**). This equation ensures that the density matrix $\rho \geq 0$ (i.e. having all positive eigenvalues). However, this operator sometimes breaks down the symmetries of the system. That is, a system started with translation symmetry at t_0 might not have translation symmetry at $t > t_0$.

The teacher wrote an example for the V_m term on PPT on blackboard:

Considering the case of a harmonic oscillator.

$$H = w_0 a^\dagger a$$

If we add an interaction between the oscillator and other excitons:

$$A^\dagger A(a^\dagger + a) = \text{extra} \otimes \text{bath}$$

Then $A^\dagger A$ is V_m in PPT

Next, the author provided a specific model of energy transfer. [6]

pp.5 shows diagrammatically the exciton transport process. External influence to the system includes trapping, decaying and dissipation Here k_t characterizes the trapping rate. And k_d characterizes the decay rate.

pp.6 explains some notations. Here τ_n characterize the life time of exciton in on state n. [7] We hope that the total life time $\langle t \rangle = \sum \tau_n$ is small, because the shorter an exciton is fixed on a state, the more random the system is and the more likely that the exciton is trapped.

Following are a series of toy cases that has been calculated.

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[3] Suggested reading: PhysRevA.62.033821

[4] Reference not found.

[5] Digression: in the article PRE 65 056120, we can find something about the entanglement between two oscillators.

[6] **Note**: This section's material could be found in *Excitonic energy transfer in light-harvesting complexes in purple bacteria. JChemPhys_ 136_ 245104.pdf*

[7] Here $\rho_n \equiv \rho_{nn}$.

pp.8 to 9 are the $\rho(t)$ for these simple cases.

pp.10 [8] This ring with 16 sites shows that there is always a peek Max population in the opposite site(See upper-right plot). This is because there is always two channels of equal length for excitons to get to the opposite site.

pp.11 is a two ring case, with 8 sites on each ring. The initial configuration is that excitons are evenly excited in the left ring. The right ring comprised of trapping sites.

pp.12 is another two ring case, with a change in the right ring's number of trapping sites. It shows that a asymmetric design would somehow improve the efficiency, since the plot on the right has a maximum region while the left one has none. The next slide shows similar result.

Caution: I am quite confused by the following content, from pp.16 to the end of PPT. Ergo the following notes for this lecture are note well organized. It is advised that one should look at the original literature instead.

pp.15 to 16 shows a more advanced calculation of excited states.

pp.16 Calculating the absorption spectrum, showing that only one level is acceptable.

pp.17 Changing the configuration of laser could result (in generally) more acceptable levels. However, these laser configurations are not practically achievable.

pp.19 Using Frankel-Exciton Model and find very good fit, balabala.

5   July 13th Wed

In this lecture, we start with a review of simple harmonic oscillators in quantum mechanics (**pp.1 to 8**). Then turn to the introduction of Glauber coherent states.

Glauber Coherent States (defined on **pp.9**) is the eigenstate of the annihilation operator:

$$A \ket{\alpha} = a \ket{\alpha} \tag{5.0.1}$$

These states maintain their coherence usually longer those number eigenstates. There are other features of the Glauber coherent state, mentioned in **pp.9 to 10**.

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[8]Could be found on *Efficient energy transfer in light-harvesting systems. Cao and Silbey et al New J Phys (2010)*

The next few deductions will give us a very physical picture of Glauber coherent states. First, express Glauber coherent state as a linear combination of number eigenstates (**pp.11 to 14**). (It is also found that different coherent states are note orthogonal (**pp.15**). Also, the overlap of two coherent state decays exponentially as the difference of the eigenvalues $|\alpha - \beta|$.

Digression: usually, the coherent state representation is much more numerical efficient in computer simulation than the number representation.

Next, we explore several interesting properties of these coherent states:

- **Expectations** (**pp.16 to 17**) It is found that $\langle X \rangle = \sqrt{2}\lambda\mathrm{Re}(\alpha)$, and $\langle P \rangle = \frac{\sqrt{2}\hbar}{\lambda}\mathrm{Im}(\alpha)$. Or: α is related to $\langle \alpha|X|\alpha\rangle$ and $\langle \alpha|P|\alpha\rangle$. Hence a real α means the state $|\alpha\rangle$ is a static state with $\langle P \rangle = 0$. Moreover, this state is the lowest energy eigenstate of a simple harmonic oscillator with the origin shifted from 0 to α.

- **Variance** (**pp.18 to 20**) It is also found that the variance $(\Delta X)^2 = \frac{\lambda^2}{2}$, this is exactly the same as the variance of the ground state of simple harmonic oscillator. And $(\Delta P)^2 = \frac{\hbar^2}{2\lambda^2}$. From the two expression, we see that any coherent states have the same minimal uncertainty: $\Delta X \cdot \Delta P = \frac{\hbar}{2}$.

- **Time Evolution** (**pp.21**) Using the energy eigenstate of simple harmonic oscillator, we can find the time evolution of coherent state as $\alpha(t) = e^{-i\omega t}\alpha_0$. It shows that α is really like a *classical oscillator* and the norm $|\alpha|^2$ is conserved. This is so cool!

The next slide (**pp.22**) summarizes the classical feature of Glauber coherent state.

Then we turn to its application in biophysics.

Polaron dynamics in LH1/LH2   We first introduces polaron (**pp.24 to 25**). The **polaron model**: Polaron is short for polarized electron. In a polarized crystal, an moving electron will deform the lattice. Then polaron is the electron and those deformed part put it together. This seems quite like the copper pair picture in BCS theory. In the light-harvesting system, since only a very small amount of light is captured, the exciton concentration is low. And we can use the polaron picture for electrons.

Next we write out the Hamiltonian for the LH1/2. (**pp.26**) The phonon H_{ph} term contains 16 phonons for 16 pigments in LH1. The exciton term H_{ex} assumes that the interaction is only nearest neighbour interaction. The exciton-phonon interaction $H_{\text{ex-ph}}$ is essentially the usual electron-phonon interaction term in solid state physics.

6   July 15th, Friday

Note: In general, the difficulty in assimilation of ideas is greater in Friday than in Wednesday's speech. I was lost again today.

Teacher first explains the Hamiltonian for off-diagonal coupling (**pp.1 to 2**). (The off-diagonal represents phonon-exciton interaction between different sites.)

Then he took a linear approximation of the phonon band. He mentioned a Hunag-Rhys factor S in $\sum_q g_q^2 \omega_q = S\omega_0$.

pp.4 to 7 reviews the traditional variational approach.

pp.8 introduces the Davydov's Ansatz Note that

$$e^{A+B} = e^A e^B e^{\frac{1}{2}[A,B]}$$

And using this relationship, it could be found that the $|\beta\rangle$ is actually a Glauber coherent state.

Note also that the Davydov Ansatz is not translational invariant.

pp.9 projects the Davydov Ansatz into Bloch states, and get the Toyozawa's Ansatz This Toyozawa Ansatz has a central position. Using this, we get the energy band.

pp.10 shows a Holstein polaron's phase diagram. [9] The region enclosed by the pointed solid line is of particular interests. Outside this thin region, there is always a unique solution (global minimum for the variational parameters). Outside the region, there will be two solutions coexisting. The the solution obtained depends on the initial configuration. The physical picture is that, changing the value of J and g, the size of polaron will change sharply when one transverse the dashed line.

pp.11 shows some results when only diagonal term is considered. [10] The strange wedge in the picture, is the mode of $q = 0$ (in which case it could be found that $\beta_{q=0} = g$). It is called the Goldstone mode. This mode is actually decoupled from the system, as can be found directly in the Hamiltonian. This explains that the constant value inside these plots, when $q = 0$.

pp.13 is the result of off-diagonal coupling. There will be two regions enclosed by solid line.

The remaining slides are not included in this note, because I felt sleepy at that moment. Thankfully the attached papers have all the interesting information.

7   July 20th, Wed

In this lecture, the author first explains that the $q = 0$ mode is de-coupled into a simple Hamiltonian.(**pp.1**) Then he uses the time-dependent variation method developed by Dirac, Frenkel and McLachlan. This method solves the equation:

$$\langle \delta\Psi | i\hbar\dot{\Psi} - H\Psi \rangle = 0 \tag{7.0.2}$$

with the constraint of Ψ being normalized.

It is also established (by McLachlan) that minimize the following value:

$$||i\dot{\Psi} - H\Psi|| \tag{7.0.3}$$

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[9] Could be found in pdf file "nonlocal.pdf".

[10] Could be found on "Toyozawa Ansatzpdf".

is an alternative option.

Next we introduces three different Ansatzes: D_1 (**pp.3**) D_2 and $\widetilde{D}$ (**pp.4**). The D_1 Ansatz is most general and numerically demanding. It accounts for the difference of phonons in different sites of the ring. The second point is ignored in D_2 to reduce the numerical complexity. $\widetilde{D}$ tries to strike a balance between the numerical demand and accuracy by including the factor $\beta(t)e^{-inq}$, which "can be viewed as an Ansatz for the spatial variation of λ_{qn} around this mean value." Details of the following calculation could be found on *Sun J et al PRB 2010* (attached).

The rest of the lecture explores the numerical result. Regretfully, I was distrait by the malfunction in my computer. Details could be found on the aforementioned paper.

8 July 22nd, Friday

I did not attend this lecture because I was preparing for travel. home.

9 License