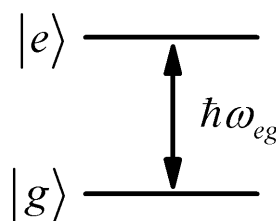


12.3. ABSORPTION SPECTRA OF MOLECULAR AGGREGATES¹

The absorption spectra of periodic arrays of interacting molecular chromophores show unique spectral features that depend on the size of the system and disorder of the environment. We'll investigate some of these features, focusing on the delocalized eigenstates of these coupled chromophores: exciton states. Much of this description has been developed to describe molecular crystals, photosensitizers, and chlorophyll light-harvesting arrays in photosynthesis, although similar topics are appearing in the description of properties of conjugated polymers and in protein vibrational spectroscopy.

The absorption spectrum for isolated molecule is:

$$a_0(\omega) = \sum_f \left| \langle f | \vec{\alpha} \cdot \hat{\epsilon} | g \rangle \right|^2 \delta(E_f - E_g - \hbar\omega)$$



In the case of exponential damping we write the lineshape as:

$$a_0(\omega, \omega_{eg}) = \alpha_{eg}^2 \frac{\Gamma}{(\omega - \omega_{eg})^2 + \Gamma^2}$$

For an ensemble of molecules with a distribution of slightly different frequencies $\delta\omega$ arising from molecules in slightly different environments, the lineshape is

$$\omega_{eg} = \omega_0 + \delta\omega \quad (\text{frequency shift of a molecule relative to the mean})$$

$$\omega_0 = \langle \omega_{eg} \rangle$$

$$P(\delta\omega) = \frac{1}{\sqrt{2\pi}\sigma} \exp\left[-\frac{\delta\omega^2}{2\sigma^2}\right]$$

$$a(\omega) = \int d(\delta\omega) a_0(\omega, \omega_0 + \delta\omega) P(\delta\omega)$$

¹ Follows J. Knoester, "Optical Properties of Molecular Aggregates," in *Proceedings of the International School of Physics "Enrico Fermi" Course CXLIX* (eds. Agranovich, M. & La Rocca, G. C.) 149-186 (IOS Press, Amsterdam, 2002). See also Fayer, M. D. *Elements of Quantum Mechanics* (Oxford University Press, New York, 2001), pp. 125-132.

This is known as the effect of static disorder or inhomogeneous broadening of the lineshape.

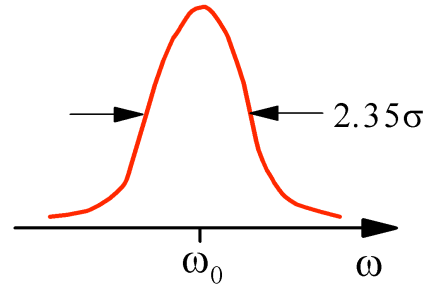
The lineshape is a convolution of “homogeneous lineshape” a_0 and probability distribution P .

This is known as Voigt profile for Lorentzian a_0 and Gaussian P .

In limit $\sigma \gg \Gamma$, $a_0(\omega)$ returns to δ function expression and the lineshape reflects the distribution:

$$a_0 \rightarrow \delta(\omega_0 + \delta\omega - \hbar\omega)$$

$$a(\omega) \propto \exp\left(-\frac{(\omega - \omega_0)^2}{2\sigma^2}\right)$$

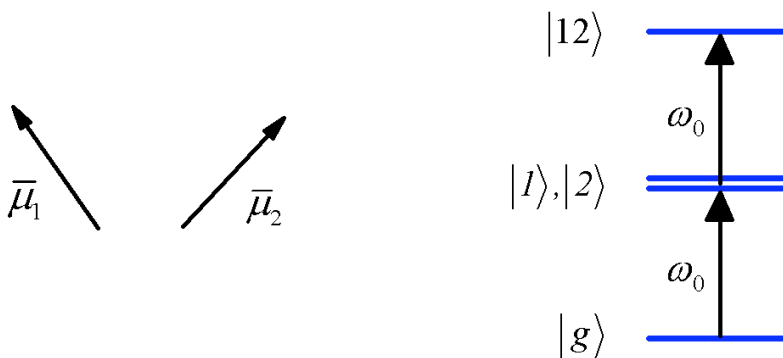


Dimer of two molecules

To describe the spectroscopy of an array of many coupled chromophores, it is first instructive to work through a pair of coupled molecules. This is in essence the two-level problem from earlier.

Two molecules in proximity: Each has transition dipole moment \propto and transition energy $\hbar\omega_0$.

For no coupling between the sites:



Dipoles can have different directions, and the energy can have four states: $|g\rangle$ ground state, $|1\rangle, |2\rangle$ with one of the molecules excited, and $|12\rangle$ where both molecules are excited.

More generally, there will be coupling between the transition dipoles (a resonance interaction) that couples the molecules:

$$V = J (|2\rangle\langle 1| + |1\rangle\langle 2|)$$

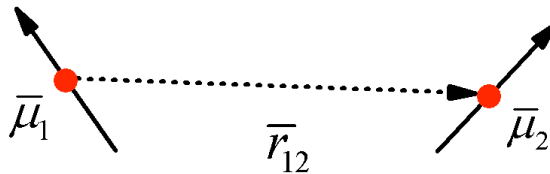
We can take the coupling to be an electrostatic interaction between two point dipoles:

$$J = \frac{(\bar{\alpha}_1 \cdot \bar{\alpha}_2) |\bar{r}_{12}|^2 - 3(\bar{\alpha}_1 \cdot \bar{r}_{12})(\bar{\alpha}_2 \cdot \bar{r}_{12})}{|\bar{r}_{12}|^5}$$

$$= \frac{\alpha_1 \alpha_2}{r_{12}^3} K$$

orientation factor
unit vectors

$$K = (\hat{\alpha}_1 \cdot \hat{\alpha}_2) - 3(\hat{\alpha}_1 \cdot \hat{r}_{12})(\hat{\alpha}_2 \cdot \hat{r}_{12})$$



So we have $H = \begin{pmatrix} \hbar\omega_0 & J \\ J & \hbar\omega_0 \end{pmatrix}$, with two eigenstates that result from mixing:

$$|\pm\rangle = \frac{1}{\sqrt{2}} (|1\rangle \pm |2\rangle)$$

with $E_{\pm} = \omega_0 \pm J$ (Here we neglect interaction between $|g\rangle$ and $|12\rangle$.)

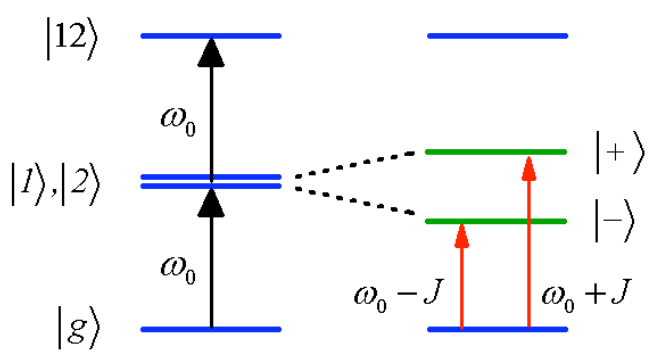
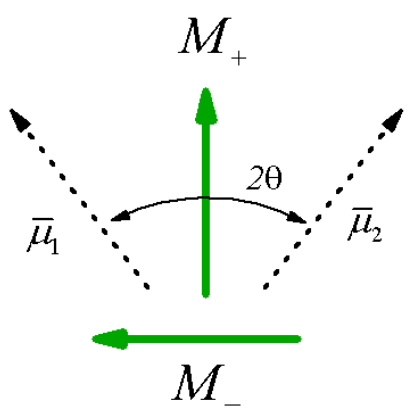
These symmetric and antisymmetric states are delocalized across the two molecules. They are also referred to as one-exciton states.

The dipole operator for the dimer is

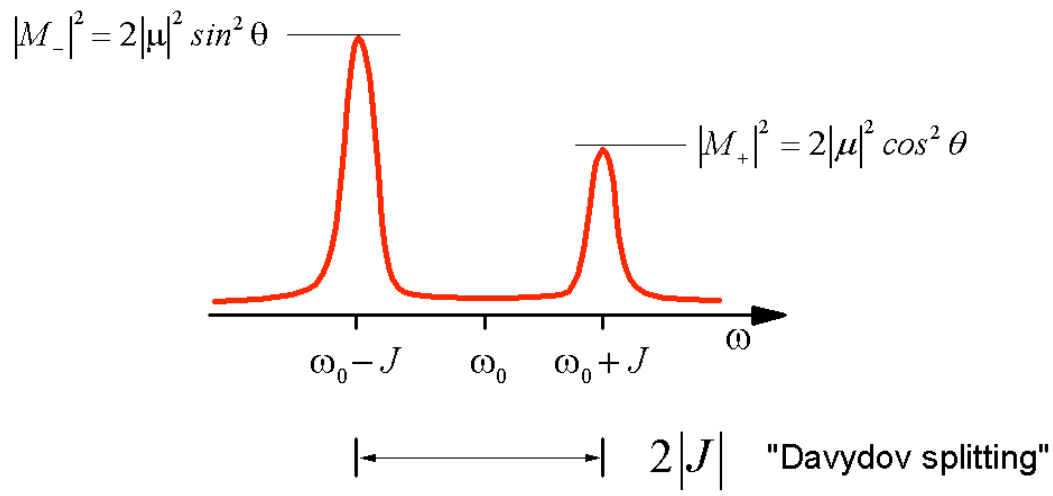
$$\bar{M} = \bar{\alpha}_1 + \bar{\alpha}_2$$

and the transition dipole matrix elements are:

$$M_{\pm} = \langle \pm | \bar{M} | g \rangle = \frac{1}{\sqrt{2}} (\bar{\alpha}_1 \pm \bar{\alpha}_2)$$



So the absorption spectrum is two resonances at $(\omega_0 \pm J)$ which are polarized perpendicular to each other and have amplitudes given by orientation. (assuming unpolarized light)



Note for $\theta = 0^\circ$, all amplitude in one transition with magnitude $2|\alpha_1|^2 \rightarrow$ "super-radiant."

Dimer with disorder

Now, let's consider the case where the energy of the molecular states of the dimer varies:

$$H = \begin{pmatrix} \hbar\omega_1 & J \\ J & \hbar\omega_2 \end{pmatrix}$$

$$E_{\pm} = \frac{1}{2} \left[(\omega_1 + \omega_2) \pm \sqrt{(\omega_1 + \omega_2)^2 + 4J^2} \right]$$

- For large variation in the site (molecular) energies $(\omega_1 - \omega_2)/2 \gg J$ we have the weak coupling limit with two localized transitions.
- For variation in the site energies $(\omega_1 - \omega_2)/2 \ll J$ we have the collective dimer states $|\pm\rangle$ above.

Disorder: Now we can examine what happens when we pick ω_1, ω_2 from a Gaussian random distribution:

$$\omega_i = \omega_i^0 + \delta\omega_i \qquad \omega_i^0 = \langle \omega_i \rangle \qquad i=1,2$$

$$a_0(\omega, \delta\omega_1, \delta\omega_2) = \sum_{f=\pm} |M_{fg}|^2 \delta(E_f - E_g - \hbar\omega)$$

$$E_{\pm} = \frac{\hbar}{2} \left[(\omega_1^0 + \delta\omega_1 + \omega_2^0 + \delta\omega_2) \pm \sqrt{(\omega_1^0 + \delta\omega_1 - \omega_2^0 - \delta\omega_2)^2 + (2J/\hbar)^2} \right]$$

$$a(\omega) = \int d(\delta\omega_1) \int d(\delta\omega_2) a_0(\omega, \delta\omega_1, \delta\omega_2) P(\delta\omega_1, \delta\omega_2)$$

Here $P(\delta\omega_1, \delta\omega_2)$ is the joint probability of having a frequency shift $\delta\omega_1$ and a shift $\delta\omega_2$. For uncorrelated distributions with same width σ :

$$P(\delta\omega_i) = \frac{1}{\sqrt{2\pi}\sigma} \exp\left[-\frac{\delta\omega_i^2}{2\sigma^2}\right]$$

$$P(\delta\omega_1, \delta\omega_2) = P(\delta\omega_1)P(\delta\omega_2) = \left(\frac{1}{\sqrt{2\pi}\sigma}\right)^2 \exp\left[-\frac{\delta\omega_1^2}{2\sigma^2} - \frac{\delta\omega_2^2}{2\sigma^2}\right]$$

More generally a joint probability distribution must account for any correlation in the two frequency distributions:

$$P(\delta\omega_1, \delta\omega_2) = \left(\frac{1}{2\pi\sigma_1\sigma_2} \right) \exp \left[-\frac{\delta\omega_1^2}{2\sigma_1^2} - \frac{\delta\omega_2^2}{2\sigma_2^2} + \rho \frac{\delta\omega_1\delta\omega_2}{\sigma_1\sigma_2} \right]$$

where

$$\rho = \frac{\langle \delta\omega_1\delta\omega_2 \rangle}{\sigma_1\sigma_2}$$

is the correlation coefficient. It varies from a value of +1 for correlated to -1 for anti-correlated distributions. A value of 0 reflects no statistical correlation between distributions.

Case 1: Large disorder $\sigma \gg |J|$, most dimers are in inhomogeneous limit, and spectrum is what you would expect for a distribution of noninteracting molecules.

Set $J \rightarrow 0$

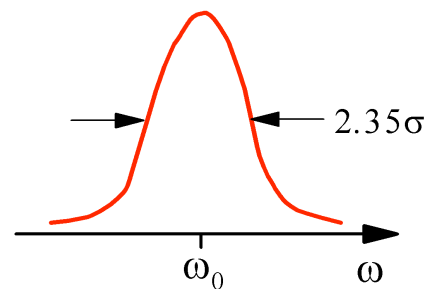
$$\omega_1^0 \approx \omega_2^0 = \omega_0$$

$$E_+ = \hbar\omega_0 + \hbar\delta\omega_1$$

$$E_- = \hbar\omega_0 + \hbar\delta\omega_2$$

$$a(\omega) \propto |\alpha|^2 \sum_{i=1,2} \exp \left(-\frac{(\omega - \omega_i^0)^2}{2\sigma^2} \right)$$

$$\propto 2|\alpha|^2 \exp \left(-\frac{(\omega - \omega_0)^2}{2\sigma^2} \right)$$



Gaussian lineshape with linewidth $\sqrt{8\ln 2} \cdot \sigma$ (FWHM)

Case 2) Weak disorder ($\Gamma \ll \sigma \ll |J|$). If σ is finite but $\sigma \ll |J|$, most dimers in weak inhomogeneity limit, with strong coupling and delocalized one-exciton state.

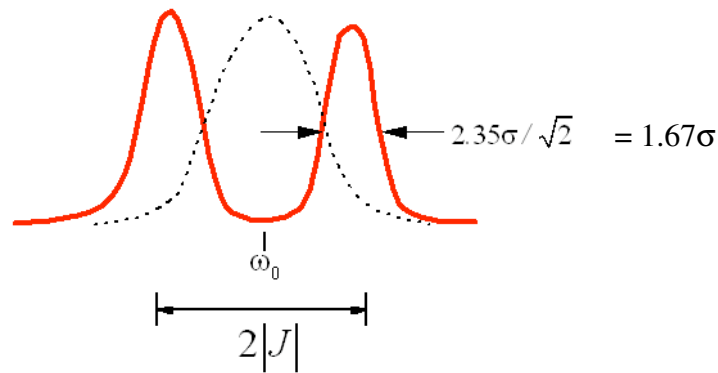
Set $\delta\omega_1, \delta\omega_2 \rightarrow 0$

$$E_{\pm} = \hbar \left(\frac{\omega_1^0 + \omega_2^0}{2} \right) \pm J = \hbar \omega_0 \pm J$$

$$P(\delta\omega_1, \delta\omega_2) \text{ becomes narrower } \rightarrow \left(\frac{1}{\sqrt{2\pi}\sigma} \right)^2 \exp\left(-\frac{\delta\omega^2}{\sigma^2}\right) \quad (\delta\omega_1 \approx \delta\omega_2 = \text{small})$$

Now we have two Gaussian peaks split by J , and the width of the Gaussians is $\sqrt{2}$ narrower than previously:

$$a(\omega) \propto \sum_{i=\pm} |M_i|^2 \exp\left(-\frac{(\omega - \omega_i)^2}{\sigma^2}\right)$$

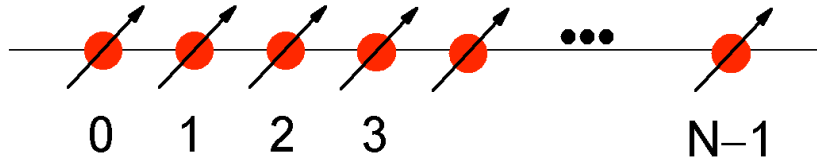


This discussion was for diagonal disorder: variation of the site energies. You can also imagine that the off-diagonal terms (coupling) could vary.

Frenkel excitons

Now let's consider linear aggregate of N equidistant molecules. We will assume that each molecule is a two-level electronic system with a ground state and an excited state. We will assume that electronic excitation moves an electron from the ground state to an unoccupied orbital of the same molecule. That is, there is no charge transfer to another molecule, and the ground state hole and the excited state electron are the same molecule. Coupling between excitations will lead to delocalized electronic states known as **Frenkel excitons**. This behavior is usually applicable to describe molecular crystals and molecular aggregates such as light harvesting complexes and photosensitizers. Wannier excitons refer to the case when charge transfer is considered.

The linear aggregate will be taken to have N molecules. We will label the molecules with numbers n between 0 and $N-1$:



The coupling between molecule n and molecule m is J_{nm} . We will assume that a molecule interacts only with its neighbors, so that

$$J_{nm} = J \delta_{n,m\pm 1}$$

Also, we use start with periodic boundary conditions, which for the coupling will mean that every molecule interacts with two neighbors and $J_{1,N} = J_{N,1} = J$. This leads to a Hamiltonian with high symmetry.

If the molecules are separated along the chain by a lattice spacing α , then the size of the chain is $L = \alpha N$. The molecules each have a transition dipole moment α , which makes an angle β with the direction of the chain. The case where $\beta < 54.7$ degrees leads to $J < 0$, and is known as a J-aggregate.

We can imagine specifying the state of the system as product states in the eigenstates of the N molecules. When all molecules are in the ground state, we have

$$\begin{aligned} |G\rangle &= |0\rangle|1\rangle|2\rangle \dots |N-1\rangle \\ &= |g, g, g, \dots, g\rangle \end{aligned}$$

If we excite one of the molecules within the aggregate, we have a singly excited state in which the n^{th} molecule is excited.

$$|E\rangle = |g, g, g, \dots, e, \dots, g\rangle \equiv |n\rangle$$

It has an energy ω_0 . In the absence of coupling, you can see that this is an N -fold degenerate state.

The optical properties of the aggregate depend on the eigenstates of the Hamiltonian, which we can write

$$H_0 = H_n + H_{nm}$$

$$H_0 = \sum_{n=1}^N \omega_0 |n\rangle\langle n| + \sum_{n,m=1}^N J_{nm} |n\rangle\langle m|$$

Rather than diagonalizing this Hamiltonian (for which the aggregate has a complete basis of 2^N states), we can take advantage of symmetry to solve for the eigenstates.

The symmetry of our Hamiltonian (with periodic boundary conditions) is such that it is unchanged by any number of lattice translations (an integral number of lattice spacings). This also dictates that the eigenstates must also be unchanged by lattice translation. Making use of our spatial displacement operator (problem set 1), this suggests that the N eigenstates will have the property:

$$|\psi_k(x + \alpha)\rangle = e^{i\kappa_k \alpha} |\psi_k(x)\rangle$$

where the wave vector

$$\kappa_k = \frac{2\pi}{L} k \quad k = 0, 1, 2, \dots, N-1 \quad (\text{k indexes the eigenstate})$$

Since any lattice translation $n\alpha$ is possible, the eigenstates can be written

$$|k\rangle = \frac{1}{\sqrt{N}} \sum_{n=0}^{N-1} e^{in\kappa_k \alpha} |n\rangle$$

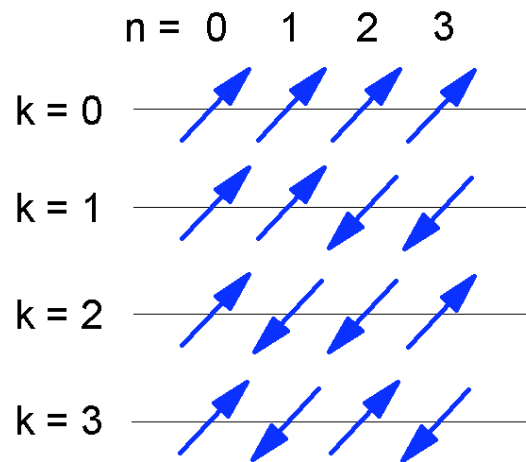
Note that this is just expressing one of the eigenstates $|k\rangle$ as a superposition of states $|n\rangle$ where the coefficients are just a phase factor $c_n = \exp(in\kappa_k \alpha)$. Each $|n\rangle$ has equal amplitude for each $|k\rangle$, but with a different, position-dependent phase factor. The eigenstates have the same number of nodes as k . For $k=0$, all dipoles oscillate in phase. For $k=N-1$ there is a node between each dipole.

For example, if $N = 2$, we recover the dimer:

$$|k=0\rangle = \frac{1}{\sqrt{2}} \sum_{n=0}^1 |n\rangle = \frac{1}{\sqrt{2}} (|n=0\rangle + |n=1\rangle) \quad (\kappa=0)$$

$$|k=1\rangle = \frac{1}{\sqrt{2}} \sum_{n=0}^1 e^{in\pi} |n\rangle = \frac{1}{\sqrt{2}} (|n=0\rangle - |n=1\rangle) \quad (\kappa = \pi / \alpha)$$

Schematically for $N = 4$ we see:



Now we can solve for the energy eigenvalues:

$$H|k\rangle = \Omega_k |k\rangle \quad H = H_n + H_{mn}$$

$$H|k\rangle = \left[\sum_{n=1}^N \omega_n |n\rangle \langle n| + \sum_{m,n=1}^N J |m\rangle \langle n| \right] \left[\frac{1}{\sqrt{N}} \sum_{n=1}^N e^{i(n-1)\kappa_k \alpha} |n\rangle \right]$$

$$H_n |k\rangle = \omega_0 |k\rangle$$

With $J_{m,n} = J \delta_{n,m\pm 1}$ we write:

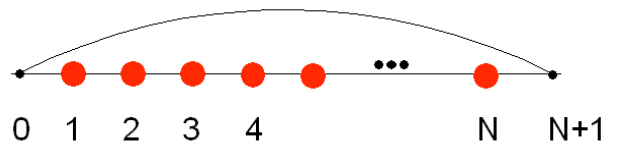
$$\begin{aligned}
 H_{mm} |k\rangle &= \frac{1}{\sqrt{N}} \sum_{n=0}^{N-1} J \left[e^{in\kappa_k \alpha} |n+1\rangle + e^{in\kappa_k \alpha} |n-1\rangle \right] \\
 &= \frac{1}{\sqrt{N}} J \sum_{n=0}^{N-1} \left[\underbrace{e^{-i\kappa_k \alpha} e^{i(n+1)\kappa_k \alpha}}_{\substack{\uparrow \\ \text{With P.B.C., sums over these terms are just } |k\rangle}} |n+1\rangle + e^{+i\kappa_k \alpha} \underbrace{e^{i(n-1)\kappa_k \alpha}}_{\substack{\downarrow \\ \text{With P.B.C., sums over these terms are just } |k\rangle}} |n-1\rangle \right] \\
 &= J \left[e^{-i\kappa_k \alpha} + e^{+i\kappa_k \alpha} \right] |k\rangle \\
 &= 2J \cos \kappa_k \alpha
 \end{aligned}$$

$$\Omega_k = \omega_0 + 2J \cos \kappa_k \alpha$$

You predict that the band of states varies in energy from $\omega_0 - 2J$ to $\omega_0 + 2J$. This is the exciton band. κ is taken from $-\pi/\alpha$ to $+\pi/\alpha$. If we take J as negative, $k=0$ is at the bottom of the band.

A more careful approach that doesn't use periodic boundary conditions has solutions that are reminiscent of particle in a box states. Here you use the condition that $\psi = 0$ at sites 0 and $N+1$. Here the eigenstates are bound at the end of the chain. The change in boundary condition gives *sine* solutions:

$$|k\rangle = \sqrt{\frac{2}{N+1}} \sum_{n=1}^N \sin\left(\frac{\pi kn}{N+1}\right) |n\rangle$$



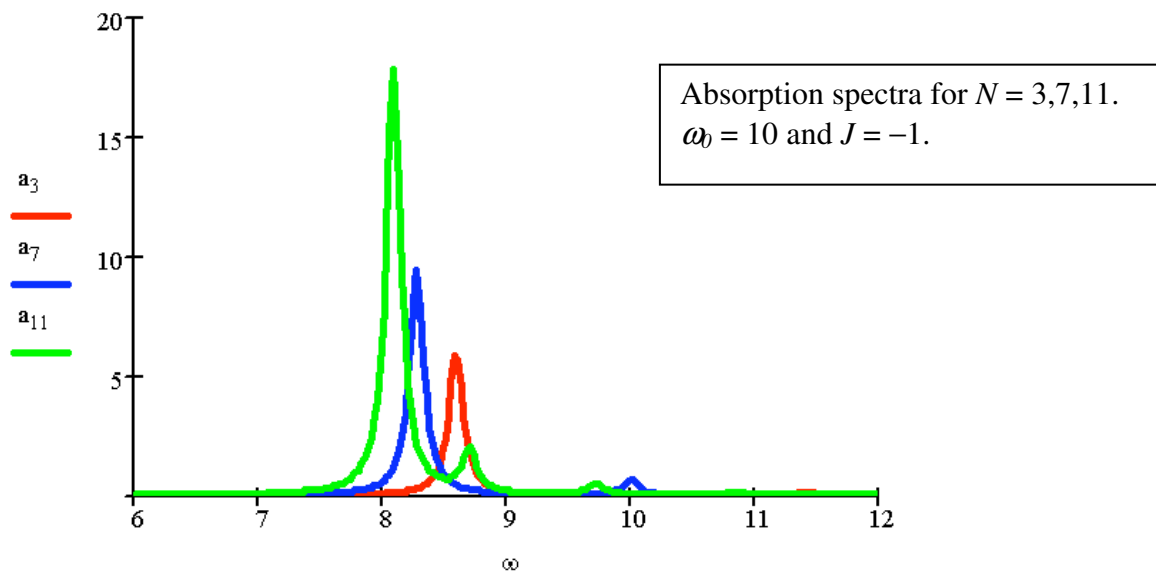
Here $k = 1, 2, \dots, N$, and the labels on the molecules also runs from $n = 1, 2, \dots, N$. The energy eigenvalues are

$$\Omega_k = \omega_0 + 2J \cos\left(\frac{\pi k}{N+1}\right)$$

You can confirm that these also give the dimer solution. If you calculate the oscillator strength:

$$\alpha_{k_1g}^2 = \left| \langle k | M | g \rangle \right|^2 = \left(\frac{1 - (-1)^k}{2} \right)^2 \frac{2\alpha^2}{N+1} \cot^2 \left(\frac{\pi k}{2(N+1)} \right)$$

This result shows that most of the oscillator strength lies in the (now) $k=1$ state for which all oscillators are in phase. For large N , $\alpha_{k=1}^2 = 0.81\alpha^2$. Much of the rest is in the $k=3$ state with 2 nodes $\alpha_{k=3}^2 = 0.09\alpha^2$.



The shift in the peak of the absorption relative to the monomer gives the coupling J . Including long-range interactions has the effect of shifting the exciton band asymmetrically about ω_0 .

$$\Omega_1 = \omega_0 + 2.4J \quad (\text{k=1, bottom of the band with } J \text{ negative})$$

$$\Omega_N = \omega_0 - 1.8J \quad (\text{Top of band})$$

Exchange Narrowing

If the chain is not homogeneous, i.e., all molecules have same energy ω_0 , then we can model this as Gaussian random disorder:

$$\omega_n = \omega_0 + \delta\omega_n$$

$$H = H_n + H_{dis} + H_{nm}$$

$$H_{dis} = \sum_n \delta\omega_n |n\rangle\langle n|$$

The effect is to shift and mix the homogeneous exciton states.

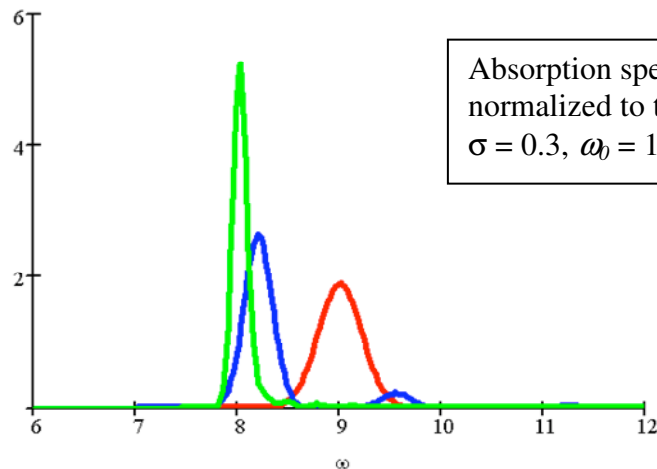
$$\delta\Omega_k = \langle k | H_{dis} | k \rangle = \frac{2}{N+1} \sum_n \sin^2\left(\frac{\pi kn}{N+1}\right) \delta\omega_n$$

We also find that these shifts are also Gaussian random variables, with a standard deviation:

$$\sigma_{kk} = \sigma \sqrt{\frac{3}{2(N+1)}}$$

where σ is the standard deviation for site energies. So, the delocalization of the eigenstate averages the disorder over N sites, which reduces the distribution of energies by a factor scaling as \sqrt{N} . So, delocalization has the effect of narrowing the absorption lineshape \rightarrow exchange narrowing. This depends on the distribution of site energies being relatively small. Specifically:

$\sigma \ll \frac{3\pi|J|}{N^{3/2}}$ which is strongly size-dependent.



Readings

ⁱ P. F. Barbara, T. J. Meyer, and M. A. Ratner, "Contemporary issues in electron transfer research." *J. Phys. Chem.* **100**, 13148-13168 (1996), and references within.

J. Jortner, "The temperature dependent activation energy for electron transfer between biological molecules." *J. Chem. Phys.* **64**, 4860-4867 (1976).