TPC 16 jan 2018

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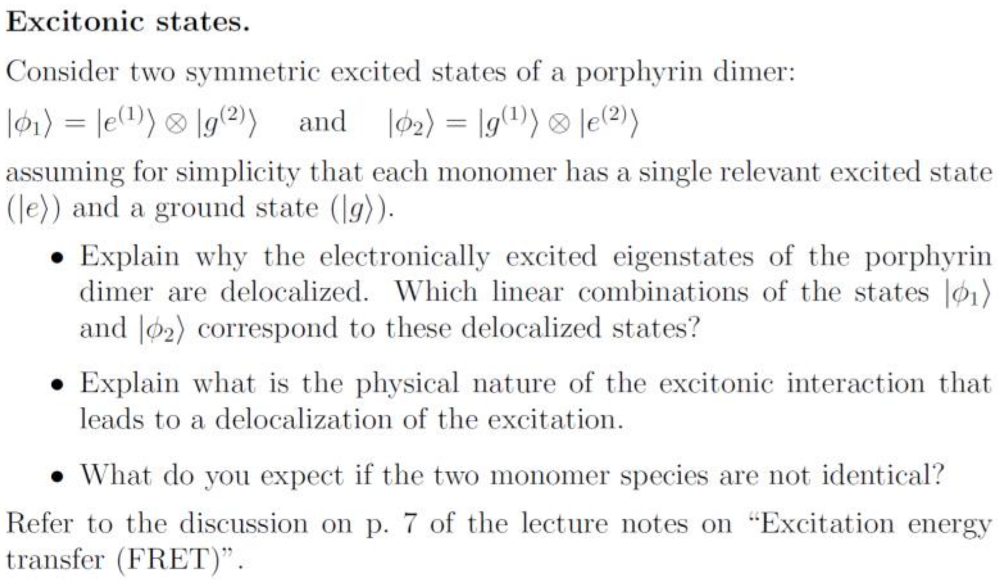

Excitonic states.

Consider two symmetric excited states of a porphyrin dimer:

$|\phi_1\rangle = |e^{(1)}\rangle \otimes |g^{(2)}\rangle$ and $|\phi_2\rangle = |g^{(1)}\rangle \otimes |e^{(2)}\rangle$

assuming for simplicity that each monomer has a single relevant excited state ($|e\rangle$) and a ground state ($|g\rangle$).

- Explain why the electronically excited eigenstates of the porphyrin dimer are delocalized. Which linear combinations of the states $|\phi_1\rangle$ and $|\phi_2\rangle$ correspond to these delocalized states?
- Explain what is the physical nature of the excitonic interaction that leads to a delocalization of the excitation.
- What do you expect if the two monomer species are not identical?

Refer to the discussion on p. 7 of the lecture notes on "Excitation energy transfer (FRET)".

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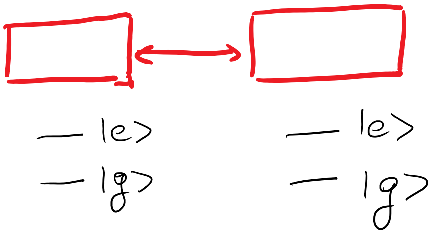
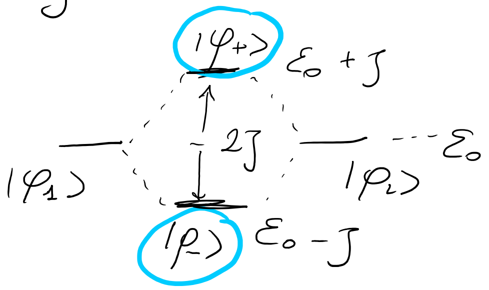


$$\longrightarrow \boxed{\begin{array}{l} |\varphi_1\rangle = |e^{(1)}\rangle \otimes |g^{(2)}\rangle \\ |\varphi_2\rangle = |g^{(1)}\rangle \otimes |e^{(2)}\rangle \end{array}}$$

$$H = \begin{bmatrix} \mathcal{E}_0 & J \\ J & \mathcal{E}_0 \end{bmatrix} \qquad \det \begin{bmatrix} \mathcal{E}_0 - \lambda_\pm & J \\ J & \mathcal{E}_0 - \lambda_\pm \end{bmatrix} = 0$$

$$(\mathcal{E}_0 - \lambda_\pm)^2 - J^2 = 0 \qquad \mathcal{E}_0^2 - 2\mathcal{E}_0\lambda_\pm + \lambda_\pm^2 - J^2 = 0$$

$$\lambda_\pm = +\mathcal{E}_0 \pm \sqrt{\mathcal{E}_0^2 - \mathcal{E}_0^2 + J^2} = \mathcal{E}_0 \pm J$$



$$\begin{bmatrix} \mathcal{E}_0 - \lambda_\pm & J \\ J & \mathcal{E}_0 - \lambda_\pm \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \end{bmatrix} = 0$$

$$\lambda_+ \begin{bmatrix} \cancel{\mathcal{E}_0} - \cancel{\mathcal{E}_0} - J & J \\ J & \cancel{\mathcal{E}_0} - \cancel{\mathcal{E}_0} - J \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \end{bmatrix} = 0 \qquad -Jc_1 + Jc_2 = 0$$

$$\Rightarrow c_1 = c_2$$

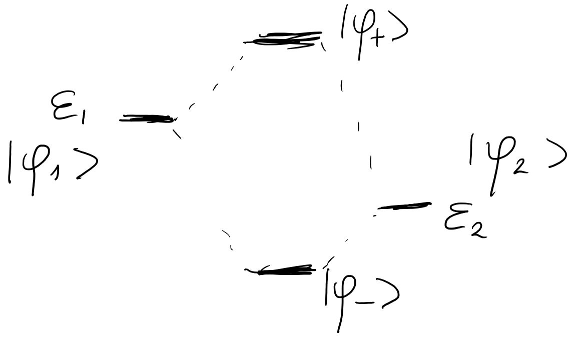
$$\boxed{|\varphi_+\rangle = \frac{1}{\sqrt{2}}\left(|\varphi_1\rangle + |\varphi_2\rangle\right)}$$

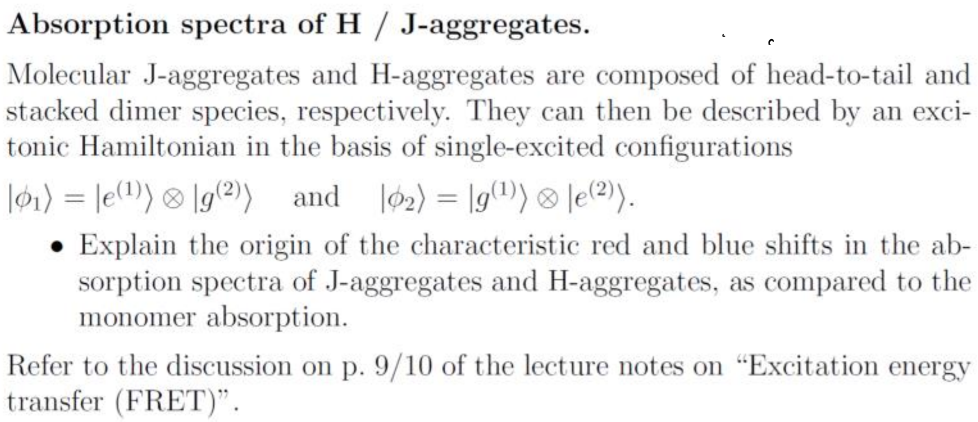
λ_- $\begin{bmatrix} J & J \\ J & J \end{bmatrix}\begin{bmatrix} c_1 \\ c_2 \end{bmatrix} = 0 \Rightarrow Jc_1 + Jc_2 = 0$

$\Rightarrow c_1 = -c_2$

$$\boxed{|\varphi_-\rangle = \frac{1}{\sqrt{2}}\left(|\varphi_1\rangle - |\varphi_2\rangle\right)}$$

J what is the nature of monomer interaction → SEE SLIDE 8 in Lesson 10





Absorption spectra of H / J-aggregates.

Molecular J-aggregates and H-aggregates are composed of head-to-tail and stacked dimer species, respectively. They can then be described by an excitonic Hamiltonian in the basis of single-excited configurations

$|\phi_1\rangle = |e^{(1)}\rangle \otimes |g^{(2)}\rangle$ and $|\phi_2\rangle = |g^{(1)}\rangle \otimes |e^{(2)}\rangle$.

- Explain the origin of the characteristic red and blue shifts in the absorption spectra of J-aggregates and H-aggregates, as compared to the monomer absorption.

Refer to the discussion on p. 9/10 of the lecture notes on "Excitation energy transfer (FRET)".

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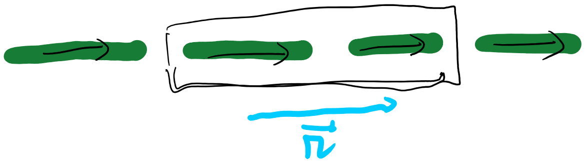
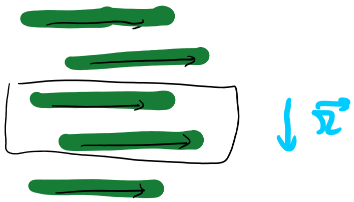
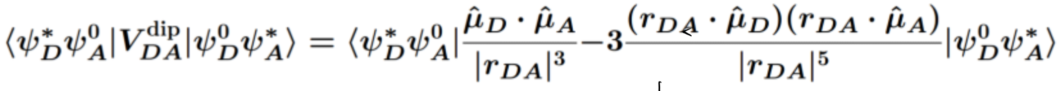
J aggregates
head-to-tail



H aggregates
stacked dimer



$$J = \langle \varphi_1 | V_{dipole} | \varphi_2 \rangle$$



$$\langle \psi^*_D \psi^0_A | V^{dip}_{DA} | \psi^0_D \psi^*_A \rangle = \langle \psi^*_D \psi^0_A | \frac{\hat{\mu}_D \cdot \hat{\mu}_A}{|r_{DA}|^3} - 3 \frac{(r_{DA} \cdot \hat{\mu}_D)(r_{DA} \cdot \hat{\mu}_A)}{|r_{DA}|^5} | \psi^0_D \psi^*_A \rangle$$

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$$\hat{\mu}_1 \parallel \hat{\mu}_2 \parallel \vec{r}$$

$$J = \langle \varphi_1 | \frac{\mu_1 \mu_2}{r^3} - 3 \frac{r\mu_1 r\mu_2}{r^{5\,3}} | \varphi_2 \rangle =$$

$$= \langle \varphi_1 | -2 \frac{\mu_1 \mu_2}{r^3} | \varphi_2 \rangle < 0$$

$$\hat{\mu}_1 \parallel \hat{\mu}_2 \perp \vec{r}$$

$$\vec{r} \cdot \vec{\mu}_1 = 0 \quad \vec{r} \cdot \vec{\mu}_2 = 0$$

$$J = \langle \varphi_1 | \frac{\mu_1 \mu_2}{r^3} | \varphi_2 \rangle > 0$$

$$\boxed{\lambda_\pm = \varepsilon_0 \pm J \rightarrow \begin{cases} |\varphi_+\rangle = \frac{1}{\sqrt{2}}(|\varphi_1\rangle + |\varphi_2\rangle) \\ |\varphi_-\rangle = \frac{1}{\sqrt{2}}(|\varphi_1\rangle - |\varphi_2\rangle) \end{cases}}$$

$\boxed{|\varphi_-\rangle}$ —— $\lambda_- = \varepsilon_0 - J$

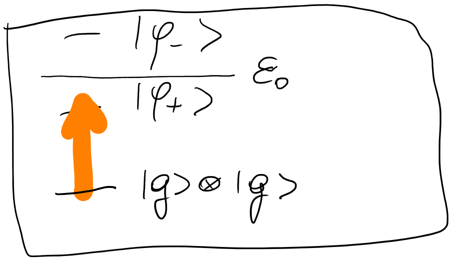
$\boxed{|\varphi_+\rangle}$ —— $\lambda_+ = \varepsilon_0 + J$

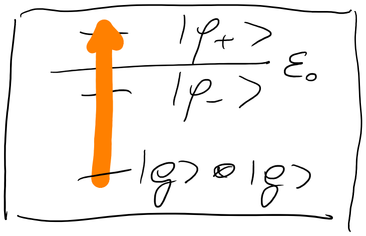
$\boxed{|\varphi_+\rangle}$ —— $\lambda_+ = \varepsilon_0 + J$

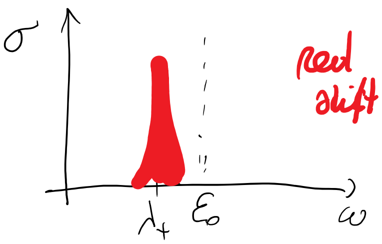
$\boxed{|\varphi_-\rangle}$ —— $\lambda_- = \varepsilon_0 - J$

$$\langle \varphi_- | \hat{M} | \varphi_- \rangle = 0$$

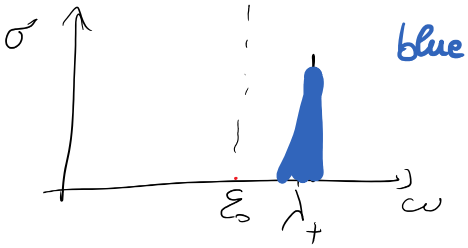
$$\langle \varphi_+ | \hat{M} | \varphi_+ \rangle \neq 0$$





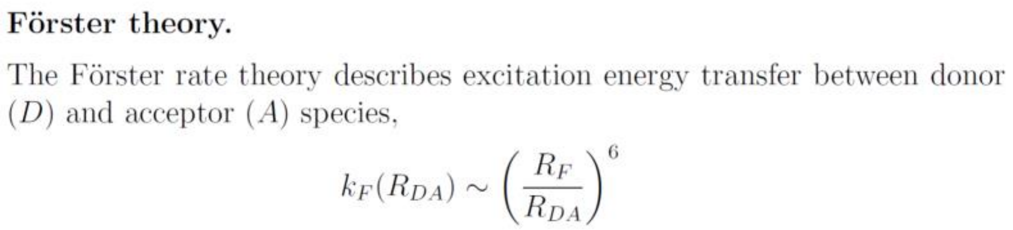


red shift



blue shift

SEE ALSO LECTURE NOTES : LECTURE 10 SLIDES 10-11
(same derivation)



Förster theory.

The Förster rate theory describes excitation energy transfer between donor (D) and acceptor (A) species,

$$k_F(R_{DA}) \sim \left(\frac{R_F}{R_{DA}}\right)^6$$

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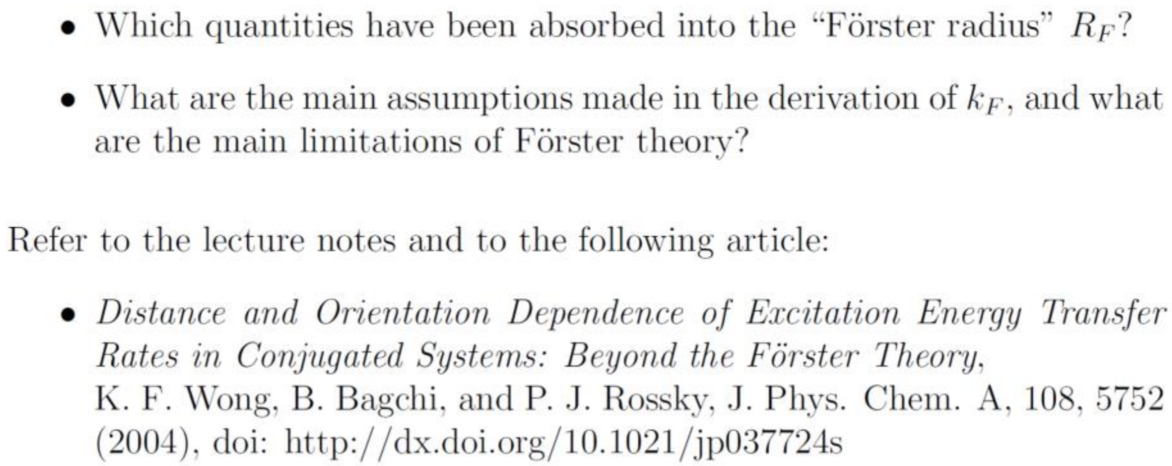

- Which quantities have been absorbed into the "Förster radius" R_F?
- What are the main assumptions made in the derivation of k_F, and what are the main limitations of Förster theory?

Refer to the lecture notes and to the following article:

- *Distance and Orientation Dependence of Excitation Energy Transfer Rates in Conjugated Systems: Beyond the Förster Theory,* K. F. Wong, B. Bagchi, and P. J. Rossky, J. Phys. Chem. A, 108, 5752 (2004), doi: http://dx.doi.org/10.1021/jp037724s

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SEE LECTURE NOTES : LECTURE 10

SLIDE 22 – which quantities are absorbed into R_F

SLIDE 26 – assumptions and limitations of Förster theory