Forster excitation energy transfer

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Part of the lecture note for the Fall 2009 "Introductory Quantum Dynamics" Class

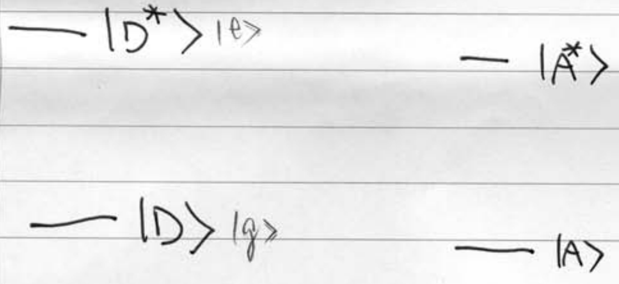
EET

In many cases, the Forster picture is simpler & physically more intuitive.

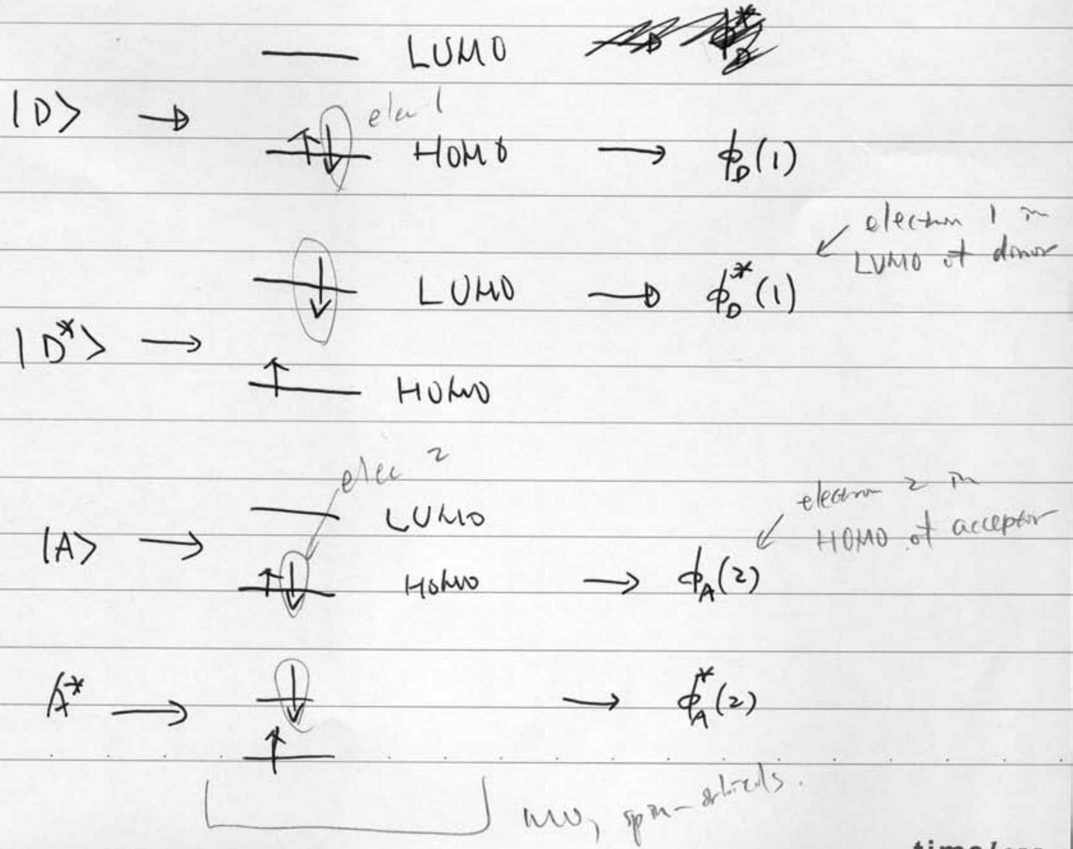
Before we derive the dynamical expression, let's consider the physics of excitation energy transfer.

When two chromophores are close to each other such that they interact with each other, then we need to consider the couplings between them:

Let's consider a donor & an acceptor.



Consider their electronic configurations, using a ~~"single~~ "two electron" model:



⑤

Excitation energy transfer T3

$$D^*A \longrightarrow DA^*$$

anti symmetrized for identical fermions

$$|D^*A\rangle \equiv \frac{1}{\sqrt{2}}\left\{\phi_D^*(1)\phi_A(2) - \phi_D^*(2)\phi_A(1)\right\}$$

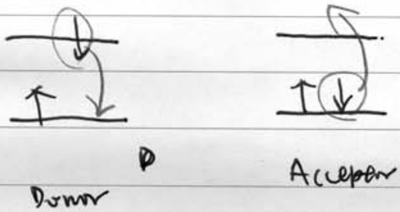
$$|DA^*\rangle \equiv \frac{1}{\sqrt{2}}\left\{\phi_D(1)\phi_A^*(2) - \phi_D(2)\phi_A^*(1)\right\}$$

; their couplings :

$$\begin{aligned}
V_{el} &= \langle D^*A|H|DA^*\rangle \\
&= \frac{1}{2}\Big\{\int \bar\phi_D^*(1)\bar\phi_A(2)\cdot H\cdot\phi_D(1)\phi_A^*(2)\cdot dx_1 dx_2 \\
&\quad - \int \bar\phi_D^*(1)\bar\phi_A(2)\cdot H\cdot\phi_D(2)\phi_A^*(1) \\
&\quad - \int \underbrace{\bar\phi_D^*(\overset{1}{2})\bar\phi_A(\overset{2}{1})\cdot H\cdot\phi_D(\overset{2}{1})\phi_A^*(\overset{1}{2})\cdot dx_1 dx_2}_{\text{exchange } 1,2} \\
&\quad + \int \underbrace{\bar\phi_D^*(\overset{1}{2})\bar\phi_A(\overset{2}{1})\cdot H\cdot\phi_D(\overset{1}{2})\phi_A^*(\overset{2}{1})\cdot dx_1 dx_2}_{\text{exchange } 1,2}\Big\} \\
&= \int \bar\phi_D^*(1)\bar\phi_A(2)\cdot H\cdot\phi_D(1)\cdot\phi_A^*(2)\cdot dx_1 dx_2 \quad \leftarrow \text{Förster} \\
&\quad - \int \bar\phi_D^*(\overset{1}{2})\bar\phi_A(\overset{2}{1})\cdot H\cdot\phi_D(2)\phi_A^*(1)\cdot dx_1 dx_2 . \quad \leftarrow \text{Dexter}
\end{aligned}$$

Forster term resonance

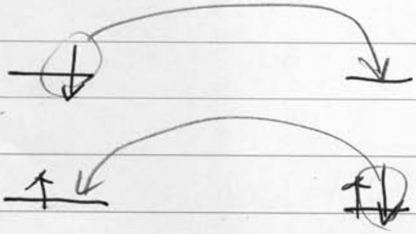
∴ the first term : electron 1 : $\phi_D^* \to \phi_D$
electron 2 : $\phi_A \to \phi_A^*$



∴ direct excitation at the same place, no need to actually exchange electrons, called the resonance term.

Dexter term exchange tunneling

the second term : electron 1 : $\phi_D^* \to \phi_A^*$
2 : $\phi_A \to \phi_D$



∴ exchange electrons between the two molecules
→ called the "exchange" term

$\frac{1}{r^3}$, dipole dipole

⇒ The Forter term is long range, while the Dexter term requires orbital overlap & is only effective at short range ← decay exponentially.

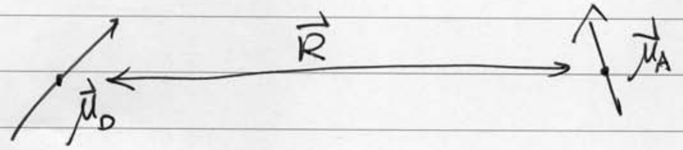
In most cases the Forster term dominated, thus

$$J = \langle D^{*}A | H | DA^{*} \rangle$$

$$\simeq \int \bar{\Phi}_D^{*}(1)\,\bar{\Phi}_A(2) \cdot H \cdot \phi_D(1)\,\phi_A^{*}(2) \cdot dx_1\, dx_2 .$$

In the limit that the two chromophores are well-separated, the ~~Interacting~~ interaction Hamiltonian can be factorized, and the dipole-dipole approximation can be applied:

Why? ↑ on Friday,



$$V = \frac{3 \cdot [(\vec{\mu}_A \cdot \hat{R})(\vec{\mu}_D \cdot \hat{R}) - \vec{\mu}_A \cdot \vec{\mu}_D}{|\vec{R}|^3}$$

$$= \frac{\kappa}{|\vec{R}|^3} \cdot \vec{\mu}_A \cdot \vec{\mu}_D$$

$\vec{\mu}_A = \hat{u}_A \cdot \mu_A$

Where the orientational factor $\kappa = 3 \cdot (\hat{u}_A \cdot \hat{R})(\hat{u}_D \cdot \hat{R}) - \hat{u}_A \hat{u}_D$ contains all the molecular orientational dependence.

→ say

on Friday

~~The~~ We will discuss the details of the validity of the dipole-dipole approximation on Friday and present a generalization of the expression. Here, we assume ~~that~~ it is valid.

also on Friday

say this first!!

Note ~~that~~ $\vec{\mu}_{A,D}$ happens to be the transition dipole of the donor & acceptor, respectively.

independent A & D !!

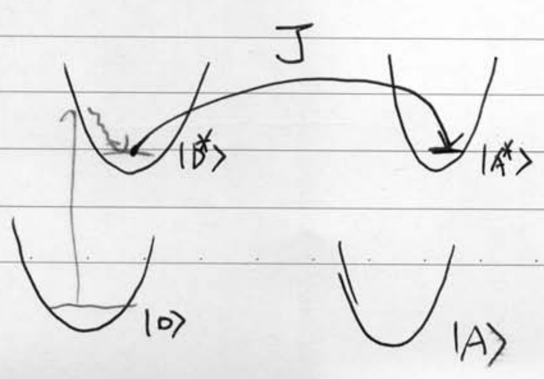
$$\vec{\mu}_{A} = \langle A|H_A|A^*\rangle$$

$$\vec{\mu}_D = \langle D|H_D|D^*\rangle$$

Again, this will be discussed on Friday

define the system

; We consider :



define the problem !!

⑨

The full Hamiltonian involve Four electronic

states : $|DA\rangle$, $|D^*A\rangle$, $|DA^*\rangle$, $|D^*A^*\rangle$

~~And vibrational Hamiltonians : $\hat{h}_D$, $\hat{h}_{D^*}$, $\hat{h}_A$, $\hat{h}_{A^*}$~~

~~Assume the two molecules are independent : $[\hat{h}_A, \hat{h}_D] = 0$.~~

~~The electronic~~ The electronic coupling operator

transition dipole "amplitude" operator

contains ~~the~~ operators for the "orientation" of the molecules

$$V = \overbrace{\hat{\mu}_A \cdot \hat{\mu}_D}\cdot \frac{\kappa}{|R|^3} \cdot \left(|D^*A\rangle\langle DA^*| + |DA^*\rangle\langle D^*A| \right)$$

assume this is real

And vibrational Hamiltonians: $\hat{h}_D(p,q)$, $\hat{h}_{D^*}(p,q)$

$\hat{h}_A(p',q')$, $\hat{h}_{A^*}(p',q')$

Assume the two molecules are well-separated such that their vibrational modes are independent,

$$[q,q'] = [q,p'] = [p,q'] = [p,p'] = 0 .$$

Finally, the initial condition :

$$\rho_{\text{init}} = |D^*A\rangle\langle D^*A| \otimes \sigma^{eq}_{\hat{h}_{D^*}} \otimes \sigma^{eq}_{\hat{h}_A}$$

final state $\rho_{\text{final}} = |DA^*\rangle\langle DA^*| \otimes \boxed{\sigma^{eq}_{\hat{h}_{D^*}} \otimes \sigma^{eq}_{\hat{h}_A}}$

no change because of Franck-Condon principle.

timeless

Recall the time-domain formula for the Fermi's Golden Rule (problem set #2).

for $H = H_0 + V$

$$\underset{\substack{\uparrow \\ \text{final}}}{k}_{n \leftarrow \underset{\substack{\uparrow \\ \text{init}}}{m}} = \frac{2\pi}{\hbar} |V_{nm}|^2 \cdot \delta(\varepsilon_n - \varepsilon_m)$$

$$= \frac{1}{\hbar^2} \int_{-\infty}^{\infty} dt \cdot V_{mn}(t) V_{nm}(0)$$

This is for pure-state only, for the ensemble mode with vibrational modes, we need to use.
(basically average over initial bath condition).

Can be proven

$$k_{A \leftarrow D} = \frac{1}{\hbar^2} \int_{-\infty}^{\infty} dt \cdot \mathrm{Tr}\, V_{mn}(t) V_{nm}(0) \cdot \sigma^{eq}_{\hat{h}_{D^*}} \cdot \sigma^{eq}_{\hat{h}_A}$$

molecular rotational modes, assume decays rapidly

$$= \frac{1}{\hbar^2} \times \frac{1}{|R|^6} \times \int_{-\infty}^{\infty} dt \cdot \underbrace{\langle \kappa(t) \kappa(0) \rangle}_{} \cdot \mathrm{Tr}\, \mu_D(t) \mu_A(t) \mu_D(0) \mu_A(0) \cdot \sigma^{eq}_{\hat{h}_{D^*}} \times \sigma^{eq}_{\hat{h}_A}$$

Separable !!

$$\simeq \frac{\langle \kappa^2 \rangle}{\hbar^2 |R|^6} \times \int_{-\infty}^{\infty} dt \cdot \underline{\mathrm{Tr}\, \mu_D(t) \mu_D(0) \cdot \sigma^{eq}_{\hat{h}_{D^*}}} \times \underline{\mathrm{Tr}\, \mu_A(t) \mu_A(0) \cdot \sigma^{eq}_{\hat{h}_A}}$$

$$= \frac{\langle \kappa^2 \rangle}{\hbar^2 |R|^6} \times \int_{-\infty}^{\infty} dt \cdot \underbrace{\overset{= C_{D^*D^*}(t)}{\langle \mu_D(t) \mu_D(0) \rangle_{\hat{h}_{D^*}}}}_{\text{correlation function for donor emission}} \cdot \underbrace{\overset{= C_{AA}(t)}{\langle \mu_A(t) \mu_A(0) \rangle_{\hat{h}_A}}}_{\text{correlation function for acceptor absorption}}$$

Recall

$$I^{D}_{fluor}(\omega) = \int_{-\infty}^{\infty} dt \cdot e^{i\omega t} \cdot C_{D^*D^*}(t)$$

$$I^{A}_{abs}(\omega) = \int_{-\infty}^{\infty} dt \cdot e^{i\omega t} \cdot C_{AA}(t)$$

$$\Rightarrow C_{D^*D^*}(t) = \frac{1}{2\pi}\int_{-\infty}^{\infty} d\omega \cdot e^{i\omega t} \cdot I^{D}_{fluor}(\omega)$$

$$C_{AA}(t) = \frac{1}{2\pi}\int_{-\infty}^{\infty} d\omega \cdot e^{-i\omega t} \cdot I^{A}_{abs}(\omega).$$

To express the rate k in terms of $I^{D}_{fluor}(\omega)$ & $I^{A}_{abs}(\omega)$, we make use of the Parsival's Theorem:

$$\int_{-\infty}^{\infty} f_1(t) f_2^*(t) \cdot dt = \int_{-\infty}^{\infty} \tilde{f}_1(\omega) \cdot \tilde{f}_2^*(\omega) \cdot d\omega$$

i.e. if a Fourier transform pair is defined for two functions, then the integral over a product of those functions is equal whether evaluated on the time domain or frequency domain.

$$\therefore\ k_{A\leftarrow D} = \frac{1}{\hbar^2}\cdot \overbrace{\frac{\langle|\kappa|\rangle^2}{|R|^6}\times|\mu_{DD^*}|^2|\mu_{AA^*}|^2}^{\text{coupling strength}}$$

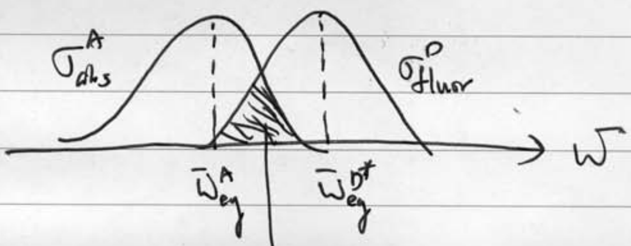
$$\times \underbrace{\int_{-\infty}^{\infty} d\omega\cdot \sigma^{A}_{abs}(\omega)\cdot\sigma^{D}_{fluor}(\omega)}_{\text{overlap, energy conservation}}.$$

σ : normalized lineshape.

⇒ Discussions

① Note that this denotes a "overlap" integral between the "emission" spectrum of a "free" donor & the "absorption" spectrum of a free acceptor, both of which can be measured & tabulated independently!!

This denotes a energy conservation condition required for the resonant energy transfer.



overlap, required for Forster FRET.

② the coupling strength ~ $|J|^2$ essentially, has a $\frac{1}{|R|^6}$ distance dependence and thus very sensitive to distance change. Thus, FRET has become the "standard ruler" on the nano-scale. If we define an effective distance R_0 and ~~the~~ ~~FRET~~ fluorescense lifetime τ_D

then $k_{FRET} = \frac{1}{\tau_D} \cdot \left(\frac{R_0}{|R|}\right)^6$

∴ at the critical distance, $k_{FRET} = \frac{1}{\tau_D}$

In this case, if there is no additional Non-radiative decay channel (big if!) then the FL quantum yield $\simeq \frac{1}{2}$

50%.

③ critical for the success of Froster theory:

→ recognize the driving forces for long-range EET & optical absorption are the same, i.e. transition dipole interactions.

→ give an expression for "system-bath" coupling, or relevant environment DOS that can be measured experimentally.

→ $1/|R|^6$ distance dependence as correctly predicted by the dipole-dipole interactions.

→ is actually classical ~ ha ha

④ problems:

→ far-field expression, i.e. $|R| \gg$ molecular size.

→ no coherence, only valid when J is relatively small!

We will discuss more about this next time

Electric multipole expansion & other issues in the Forster theory

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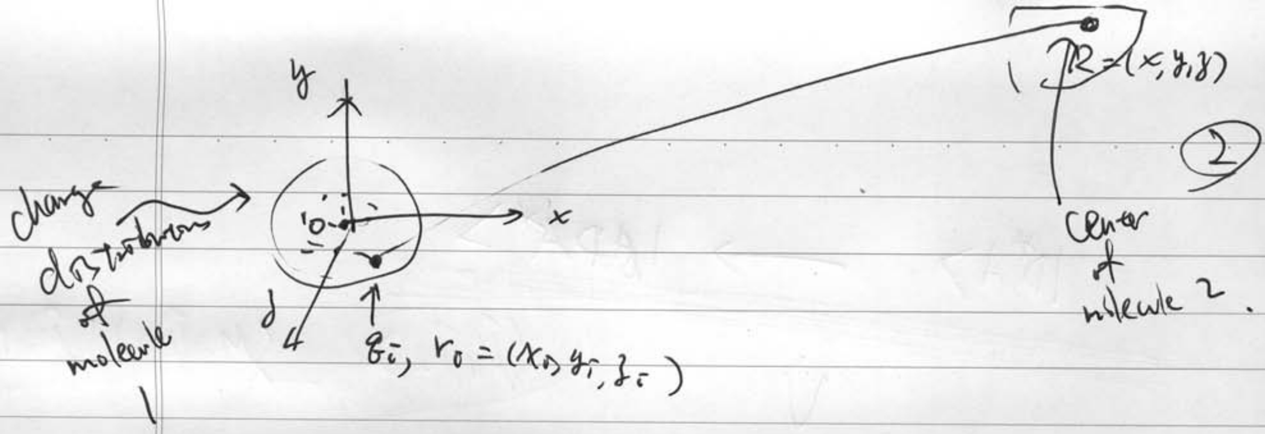
Electric multipole expansion :

Last time we show that excitation energy transfer between molecules depends on Coulomb Interactions ~~eq~~ in the following form :

$$J \approx \int \Phi_D^*(1)\,\Phi_A(2)\,H\,\Phi_D(1)\,\Phi_A^*(2)\,dx_1 dx_2$$

$\uparrow$ the electron-electron coupling $\frac{e_1 e_2}{|r_{12}|}$

To find an approximated form for $\frac{e_1 e_2}{|r_{12}|}$ suitable for molecules, let's consider the electric potential at a point $R=(x,y,z)$ induced by a distribution of charges :



$$\therefore\ V(x,y,z) = \sum_i \frac{q_i}{|\vec r_i|} = \sum_i \frac{q_i}{\sqrt{(x-x_i)^2 + (y-y_i)^2 + (z-z_i)^2}}$$

assume ~~[illegible]~~ $|\vec r_i| << |\vec R|$, we can expand $V(x,y,z)$ around the origin:

$$V = \underbrace{\sum_i q_i \cdot \frac{1}{|\vec R|}}_{\text{monopole}} + \overbrace{\sum_i q_i \left[x_i \cdot \frac{\partial}{\partial x_i}\left(\frac{1}{|\vec r_i|}\right) + y_i \cdot \frac{\partial}{\partial y_i}\left(\frac{1}{|\vec r_i|}\right) + z_i \cdot \frac{\partial}{\partial z_i}\left(\frac{1}{|\vec r_i|}\right) \right]}^{\text{dipole}}$$

$$+ \underbrace{\frac{1}{2} \sum_i q_i \left[x_i x_i \cdot \frac{\partial^2}{\partial x_i^2}\left(\frac{1}{|\vec r_i|}\right) + x_i y_i \cdot \frac{\partial^2}{\partial x_i \partial y_i}\left(\frac{1}{|\vec r_i|}\right) + \cdots \right]}_{\text{quadrupole}}$$

$$+ \cdots$$

⇒ this is the multiple expansion of electric interaction, also works for spins ∴

Assume the molecule is charge neutral → the monopole term is zero, thus the leading nonzero term is the dipole term.

the derivatives of $\frac{1}{|\vec{r}_i|}$ w.r.t. $x_i, y_i, \& z_i$ can be

rewritten by approximation $r_i \approx R$ ← when $|R| \gg |r_i|$

$$\frac{\partial}{\partial x_i}\left(\frac{1}{|\vec{r}_i|}\right) = -\frac{\partial}{\partial x}\left(\frac{1}{|\vec{r}_i|}\right) \approx -\frac{\partial}{\partial x}\left(\frac{1}{|\vec{R}|}\right) = \frac{x}{|\vec{R}|^3}$$

∴, the potential $V(x,y,z) \approx \sum_i q_i \times \frac{1}{|\vec{R}|^3} \times \{x_i \cdot x + y_i \cdot y + z_i \cdot z\}$

$$= \frac{1}{|\vec{R}|^3} \cdot \underbrace{\boxed{\sum_i q_i \cdot \vec{r}_i}}_{\mu_1} \cdot \vec{R}$$

$$= \frac{\vec{\mu}_1 \cdot \vec{R}}{|\vec{R}|^3}$$

↑ exactly where we used in ⟨dipole - molecular electric-dipole interaction⟩

∴, the field @ (x,y,z) is

$$~~E(R)~~ \; E(x,y,z) = -\nabla\left(|\vec{R}|^{-3} \mu_1 \cdot \vec{R}\right)$$

$$= -\hat{\mu}_1 \cdot |\vec{R}|^{-3} - (\hat{\mu}_1 \cdot \vec{R}) \cdot \nabla\{|\vec{R}|^{-3}\}$$

$$= -\hat{\mu}_1 \cdot |\vec{R}|^{-3} - (\hat{\mu}_1 \cdot \vec{R}) \cdot \vec{R} \cdot |\vec{R}|^{-5}$$

finally, the energy of interactions with another dipole $\hat{\mu}_2$.

$$V_{coul} = (\vec{\mu}_1 \cdot \vec{\mu}_2)|\vec{R}|^{-3} - 3(\vec{\mu}_1 \cdot \vec{R})(\vec{\mu}_2 \cdot \vec{R}) \cdot |\vec{R}|^{-5}.$$

↑ dipole-dipole interaction

→ requires distance $|\vec{R}| \gg$ molecular size.

use vector $\vec{\mu}_1, \vec{\mu}_2$ here & then change to $\hat{\mu}_1, \hat{\mu}_2$ via correspondence principle

This approximation is crucial for the success of the $k \sim \frac{1}{|R|^6}$ rule, however, it is very often violated, or, requires extra caution because effective |R| for FRET is $\lesssim 3$ nm,

but many molecular size is ~ 10 Å ⇒ problem. Not to mention objects such as quantum dots, nanowires .... ⇒ take home message, be cautious

To extend this ...

Another problem ~~ke~~ is related to using spectrum to determine both DOS & interaction strength, recall

$$k_{A\leftarrow D} = \frac{1}{\hbar^2}\cdot\frac{\langle\kappa^2\rangle}{|R|^6}\times\int_{-\infty}^{\infty} d\omega\, I^A_{abs}(\omega)\, I^D_{fluor}(\omega)$$

⇒ No transition if $\underbrace{\text{no emission or no abs}}_{\text{dark state}}$.

But this can be misleading. Let's use a excitonically coupled system ~~to demonstrate~~.

⇒ Effect of J.

In addition to induce excitation energy transfer,

J can induce delocalization of exciton ⇒

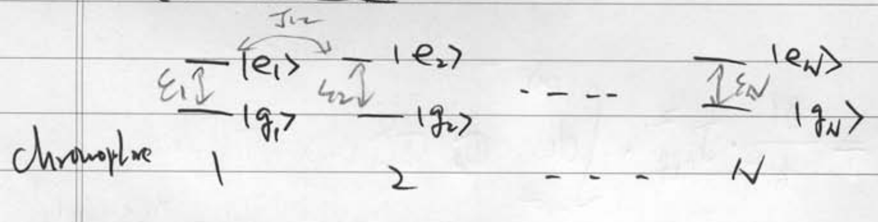
④

Frenkel exciton model

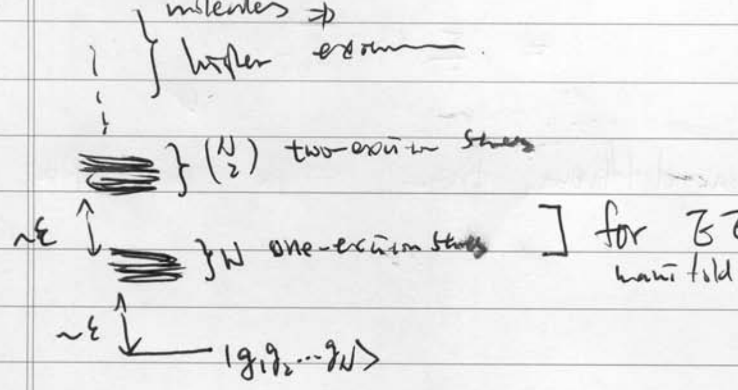
In the basis of localized excitation, i.e. independent free chromophores ; ~~for simplicity~~ ~~[illegible]~~

~~for simplicity, let's~~ In a N- chromophore system;:

~~the "[illegible] exci-~~



group ~~states~~ Group states according to number of excited molecules ⇒



] for EET, focus on this manifold

↳ basis : $|e_1g_2g_3\ldots g_N\rangle$, $|g_1e_2g_3g_4\cdots g_N\rangle$, $|g_1g_2e_3g_4\cdots g_N\rangle$

$$\equiv |e_1\rangle, |e_2\rangle, |e_3\rangle \ \cdots, |e_N\rangle$$

effective Hamiltonian ⇒

$$\begin{pmatrix} \varepsilon_1 & \boxed{J_{12}} & \cdots & \\ J_{21} & \varepsilon_2 & & \\ \vdots & & \ddots & \\ \vdots & & & \boxed{\varepsilon_N} \end{pmatrix}$$

electronic/excitonic couplings.

site-energies

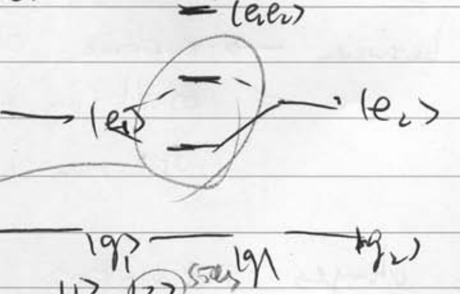
"site basis"

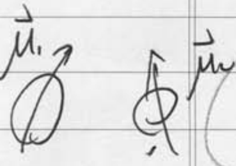
$$\xrightarrow{\text{diag}} \begin{pmatrix} \lambda_1 & & 0 \\ & \lambda_2 & \\ & & \ddots \\ 0 & & & \lambda_N \end{pmatrix} \text{ exciton basis.}$$

⇒ excitons are eigenstates of the Frenkel effective Hamiltonian and thus are superposition states of localized excitations → delocalization.

∴ J induce delocalization, now this has additional consequence, we will illustrate with a dimer model:

dimer





$|1\rangle$ $|2\rangle$ states

$$\Rightarrow H = \begin{pmatrix} \varepsilon_1 & J \\ J & \varepsilon_2 \end{pmatrix} \text{ site basis}$$

if $J \ll \varepsilon_1 - \varepsilon_2$ → localized, Förster ~

for finite J, define $\tan 2\theta = \dfrac{2J}{\varepsilon_1 - \varepsilon_2}$

θ : mixing angle.

(H) exciton states:

$|+\rangle = \cos\theta \cdot |1\rangle + \sin\theta \cdot |2\rangle$

$|-\rangle = -\sin\theta\ |1\rangle + \cos\theta\ |2\rangle$

∴ $\vec{\mu}_+ = \cos\theta \cdot \vec{\mu}_1 + \sin\theta \cdot \vec{\mu}_2 \leftarrow \frac{\varepsilon_1+\varepsilon_2}{2} \textcircled{+} \frac{1}{2}\sqrt{(\varepsilon_1-\varepsilon_2)^2+4J^2}$

功或 sign(J)

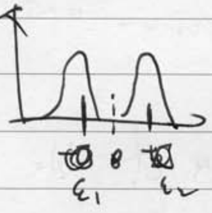
$\vec{\mu}_- = -\sin\theta \cdot \vec{\mu}_1 + \cos\theta \cdot \vec{\mu}_2 \leftarrow$ 〃 − 〃

assume $\vec{\mu}_1 = \vec{\mu}_2$, $\vec{\mu}_1 \parallel \vec{\mu}_2$ → $\vec{\mu}_+ = (\cos\theta + \sin\theta) \cdot \vec{\mu}$

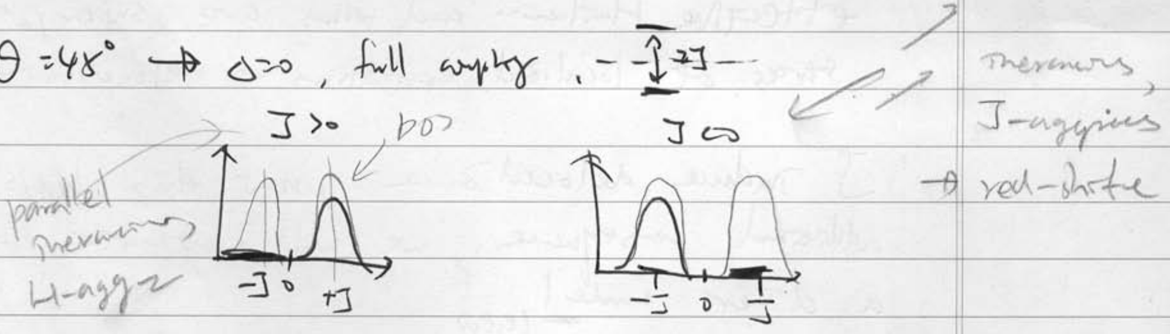
$\vec{\mu}_- = (\cos\theta - \sin\theta)\ \vec{\mu}$

for simplicity, take [illegible].

∴ $\theta = 0 \rightarrow$ no change (no coupling)
~?



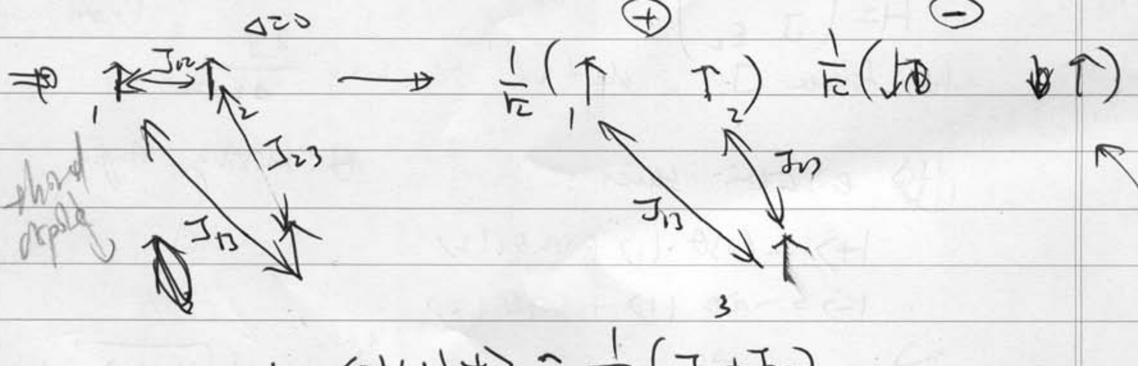
$\theta = 45° \rightarrow \Delta = 0$, full coupling. $2J$



↑ usually in between → excitonic coupling re-distributes oscillating strength & changes spectrum.

blue shift

More over, this changes interactions with other dipoles too!!



$$\therefore \langle 3|H|+\rangle \approx \frac{1}{\sqrt{2}}(J_{13} + J_{23})$$

$$\langle 3|H|-\rangle \approx \frac{1}{\sqrt{2}}(-J_{13} + J_{23}) \neq 0$$

⇒ light field ← far field perspective ← dipole-dipole cancel
$\lambda \sim 800$ nm — no abs.

another molecule $d \sim 3$ nm ← near field " ← no canceling!!!

Near field
expression

In this case; Abs & ~~Fl~~ intensity | no longer yield correct coupling strength

energy transfer from a molecule D to an excitonic eigen state :

$$|\psi\rangle = C_1 \cdot |\phi_1\rangle + C_2 |\phi_2\rangle \ldots$$

localized

$$k = \frac{1}{\hbar^2} \cdot J_{eff}^2 \cdot \int_{-\infty}^{\infty} d\omega \cdot \sigma_{abs}^{A}(\omega)\ \sigma_{fluor}^{D}(\omega)$$

normalized, DOS only.

with $J_{eff} = \langle D|H|\psi\rangle$

$$= \sum_i C_i \cdot J_{Di}$$

✓

often difference from simple point-dipole results.

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