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ENERGY TRANSFER
IN THE WEAK AND STRONG COUPLING REGIME

[1] Vekshin, N. L. Energy transfer in macromolecules; Society of Photo-optical Instrumentation Engineers: Bellingham, Washington state, 1997.

[2] May, V.; Kuhn, O. Charge and Energy Transfer Dynamics in Molecular Systems; Wiley- VCH: Berlin, 1 ed., 2000.

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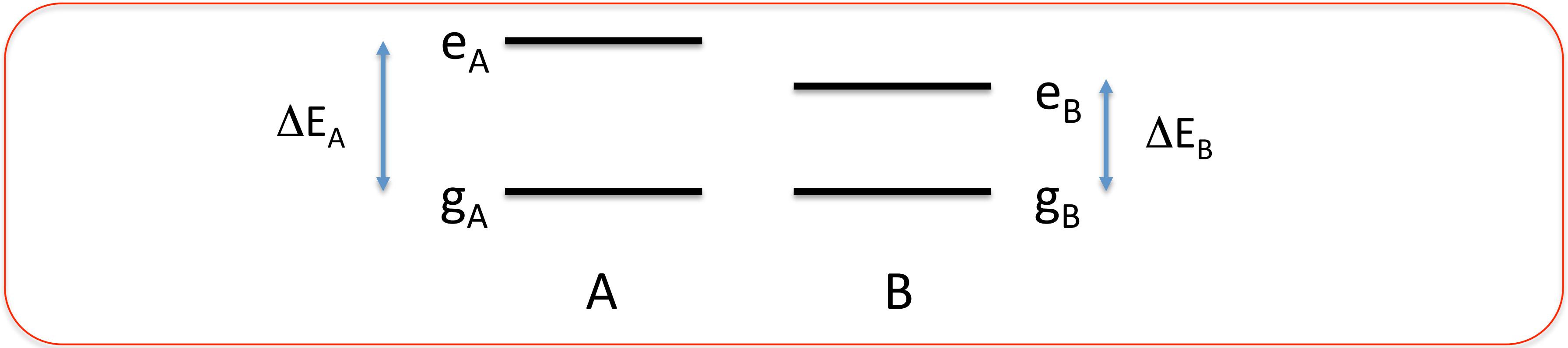
isolated system of two two-levels chromophores (molecular dimer):



System Hamiltonian:

$$H = H_A + H_B + \boxed{V}$$

Interaction!!!

1) When the chromophores do not interact (V=0), the dimer is described by:

a ground state: $\left|g_A g_B\right\rangle$

two singly excited states: $\left|g_A e_B\right\rangle ; \left|e_A g_B\right\rangle$

a double excited state: $\left|e_A e_B\right\rangle$

2) When V≠0

- Neglecting (i) exchange correlations; (ii) electrostatic interactions between electron clouds and (iii) strongly off-resonant coupling terms (Heitler-London approx.)
- Considering the chromophores far apart enough -> point dipole approximation

The interaction V may be written as:

$$V = \frac{\vec{\mu}_A \vec{\mu}_B^*}{\left|\vec{R}\right|^3} - 3\frac{\left(\vec{R}\cdot\vec{\mu}_A\right)\left(\vec{R}\cdot\vec{\mu}_B^*\right)}{\left|\vec{R}\right|^5}$$

$\vec{R}$ = vector connecting the point dipoles

STRONG COUPLING (1)

system initially in the state $|e_A g_B\rangle$ for arbitrarily strong coupling V. The energies of the stationary states of such a system may be solved by expanding them in the states with one of the sites excited: $|\psi_i\rangle = C_A|e_A g_B\rangle + C_B|g_A e_B\rangle$, and then solving the matrix eigenvalue equation :

$$\begin{bmatrix} \Delta E_A & V \\ V^* & \Delta E_B \end{bmatrix} \begin{bmatrix} C_A \\ C_B \end{bmatrix} = E \begin{bmatrix} C_A \\ C_B \end{bmatrix}$$

The eigenvalues of this equation are the new energies E_+ and E_- of the coupled states, which from the secular equations are found to be:

$$\Delta E_{\pm} = K + \sqrt{\Delta^2 + |V|^2} \quad where \quad K = \tfrac{1}{2}(\Delta E_A + \Delta E_B) \quad \Delta = \tfrac{1}{2}(\Delta E_B - \Delta E_A)$$

Note that the coupling splits up the energies of the states;
writing V as $|V|e^{-i\phi}$ and using the normalization condition $|C_A|^2 + |C_B|^2 = 1$, the eigenvectors are:

$$|\psi_{\pm}\rangle = \sqrt{1/2}\left(|g_A e_B\rangle \pm |e_A g_B\rangle\right)$$

If V real and V>>Δ (strong coupling)

STRONG COUPLING (2)

$P_B(t)$: probability that the excitation resides on B at the time *t*, if at *t*=0 was initially on A:

$$P_B(t) = \frac{|V|^2}{\Delta^2 + |V|^2} \sin^2 \frac{\sqrt{\Delta^2 + |V|^2}}{\hbar}$$

with $P_A(t) = 1 - |C_B(t)|^2$. This shows that the new states are coherent superpositions of the 'A-excited' and 'B-excited' states and that the excitation will coherently oscillate back and forth between chromophores A and B at the frequency:

$$\Omega = \left(\Delta E_+ - \Delta E_-\right) / \hbar = 2\sqrt{\Delta^2 + |V|^2} \, / \, \hbar$$

WEAK COUPLING

In the weak coupling regime, the electronic levels of the single chromophores are little perturbed by *V* and the spectrum of the dimer is identical to the sum of the spectra of the two chromophores. In this case the energy transfer probability can be calculated using perturbation theory:

$$P_B(t) = \left|C_B(t)\right|^2 = \frac{|V|^2}{\hbar^2}\left(\frac{\sin^2\left(\frac{1}{2}\Omega_0 t\right)}{\left(\frac{1}{2}\Omega_0 t\right)^2}\right) \quad where \quad \Omega_0 \equiv \Omega(V \approx 0) = \left(\Delta E_B - \Delta E_A\right)/\hbar = 2\Delta/\hbar$$

which is the limit for small *V* of the expression obtained previously in the strong coupling regime.

Note that for long *t*, significant ET occurs only when $\Omega_0 \approx 0$ and then we can write:

$$P_B(t) = \frac{|V|^2 t^2}{\hbar}\int d\Omega_0\left(\frac{\sin^2\left(\frac{1}{2}\Omega_0 t\right)}{\left(\frac{1}{2}\Omega_0 t\right)^2}\right) = \frac{2\pi}{\hbar}|V|^2 t$$

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Strong coupling regime: Frenkel excitons model

[1] S. Davydov, *Theory of molecular excitons*, Plenum Press, New York, 1971.
[2] H. Van Amerongen, L. Valkunas and R. Van Grondelle, *Photosynthetic Excitons*, World Scientific, Singapore, 2000.

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Frenkel excitons

In the Frenkel exciton model, a system of N chromophores is represented by the Hamiltonian:

$$H_e = \sum_{n=1}^{N} \varepsilon_n |n\rangle\langle n| + \sum_{n<m} J_{nm} \left(|n\rangle\langle m| + |m\rangle\langle n|\right)$$

$|n\rangle$ is molecular excited state at site *n* with energy ε_n, and J_{nm} is the excitonic coupling between the n-th and m-th chromophore.

Diagonalization of H_e gives rise to eigenstates $|\alpha\rangle$, called exciton states, such that:

$$H_e|\alpha\rangle = E_\alpha|\alpha\rangle$$

$$|\alpha\rangle = \sum_{n=1}^{N} c_n^\alpha |n\rangle$$

Exciton states form a new basis for the description of optical properties and energy transfer dynamics.
site basis ≠ exciton basis (eigenbasis)

DETAILS:

If one neglects additional (e.g., nuclear) degrees of freedom, the calculation of eigenstates and eigenfrequencies can be performed analytically.

- ☐ If each of the *N* molecules can be in two states, the Hamiltonian has 2^N eigenstates, linear combinations of single-molecule's states, each with a fixed number of single-molecule excitations present. They separate into groups (manifolds) according to the number of excitations they contain (ν).
- ☐ The nondegenerate ground state is the direct product of the *N* molecular ground state wave functions
- ☐ there are *N* excited-state manifolds, each labelled by ν; the ν^{th} manifold contains $N!/(N-\nu)!\,\nu!$ independent ν-exciton states in which ν molecules are excited and *N*–ν molecules are unexcited.
- ☐ the one-exciton band (ν = 1) is formed by *N* eigenstates, know as Frenkel excitons, characterized by a single quantum number *k.* The exact expression of eigenstates and eigenenergies of the Hamiltonian describing this system can be calculated by diagonalization under suitable boundary conditions.

E.Collini, PCCP, 14 (2012) 3725 *and references therein*

Example: diagonalization for a linear assembly of N molecules:

one-exciton band	$|k\rangle^L = \sqrt{\frac{2}{N+1}}\sum_{n=1}^{N}\sin\left(\frac{\pi k n}{N+1}\right)|n\rangle \qquad k = 1,2,\ldots,N$ (a)
one-exciton eigenfrequencies	$\Omega_k^L = \omega + 2J\cos\left(\frac{\pi k}{N+1}\right)$
dipole moments from the ground state to the one-exciton band	$\mu_{k,0}^L = \mu_{mon}\sqrt{\frac{2}{N+1}}\,\frac{1-(-1)^k}{2}\cot\left[\frac{\pi k}{2(N+1)}\right]$ (b)
two-exciton band	$|k_1,k_2\rangle^L = \frac{2}{N+1}\sum_{n_2>n_1=1}^{N}\left[\sin\left(\frac{\pi k_1 n_1}{N+1}\right)\sin\left(\frac{\pi k_2 n_2}{N+1}\right) - \sin\left(\frac{\pi k_1 n_2}{N+1}\right)\sin\left(\frac{\pi k_2 n_1}{N+1}\right)\right]|n_1,n_2\rangle$ (c)
two-exciton eigenfrequencies	$\Omega_{k_1k_2}^L = \Omega_{k_1}^L + \Omega_{k_2}^L$

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Including also the environment, the hamiltonian reads: $H_{TOT}=H_e+_{HB}+H_{SB}$

Linear system-bath coupling:

$$H_{SB} = \sum_n |n\rangle\langle n| \cdot q_n$$

where q_n= collective bath coordinate

It is usually assumed that the bath modes modulating different chromophores are independent, so H_{SB} represents independent phonon-induced fluctuations of the site energies. The dynamics is related to spectral density $\rho_n(\omega)$ which represents the coupling strength and density of states of the phonon bath.

The strenght of the system-bath coupling is measured by the reorganization energy λ_n:

$$\lambda_n = \int_0^\infty d\omega\, \rho_n(\omega)/\omega$$