Vibronic energy localization in weakly coupled small molecular aggregates

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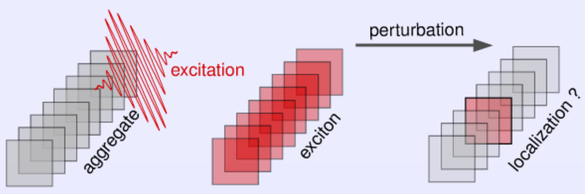
Motivation



- Excitation of an aggregate leads to exciton formation
- Time-dependent perturbation takes place
- Localization of excitation energy?[1]

Models

Dimer Model

- Ground state: uncoupled monomers
- Excited state: two excited state configurations
  - Weakly coupled
  - Degenerate
  - localized one-exciton picture
    → M_{r_1} or M_{r_2} is excited

Excited states dimer hamiltonian:

$$\hat{H}_D^* = \begin{pmatrix} \hat{V}_{e_1} + \hat{T} & J \\ J & \hat{V}_{e_2} + \hat{T} \end{pmatrix}$$

where $\hat{V}_{e_n}$ is the potential energy operator and $\hat{T}$ the operator for the kinetic energy.

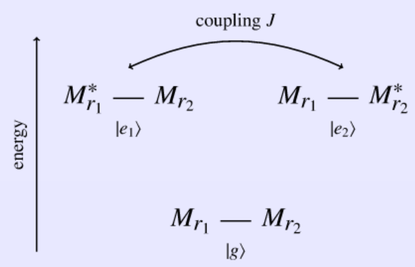


Figure 1: One-exciton model: Degenerate excited state configurations $|e_1\rangle$, $|e_2\rangle$, and coupling J.

Unperturbed Two Level System

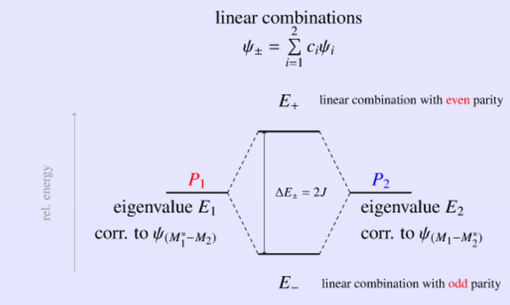
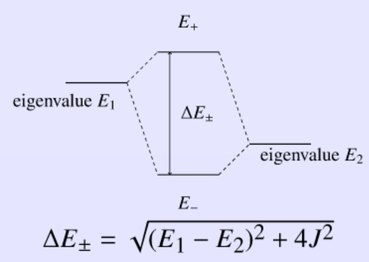


Figure 2: Unperturbed electronic two level system: Linear combination of degenerate states with energies E_1 and E_2 leads to splitting $\Delta E_\pm = 2J$.

Perturbed Two Level System

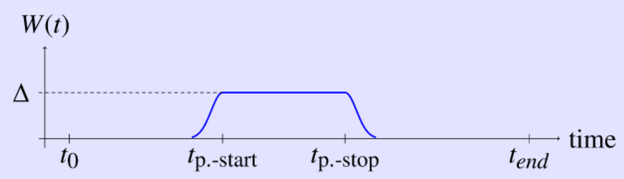


$$\Delta E_\pm = \sqrt{(E_1 - E_2)^2 + 4J^2}$$

Figure 3: Perturbed electronic two level system: Due to perturbation E_1 is shifted. The splitting $\Delta E_\pm$ between energies E_1 and E_2 increases.

Perturbation: $W(t) = g(t)\Delta$

- Shape-function $g(t)$
- Energy shift Δ due to interaction with surrounding
- $\hat{V}_{e_1}^{\text{pert.}} = \hat{V}_{e_1} + W(t)$



Vibronic Model

- One vibrational degree of freedom per monomer
- Harmonic oscillator potentials

$$\hat{V}_{e_1} = \frac{1}{2}\omega^2 (r_1 - r_{eq})^2 + \frac{1}{2}\omega^2 r_2^2 + E_e$$
$$\hat{V}_{e_2} = \frac{1}{2}\omega^2 r_1^2 + \frac{1}{2}\omega^2 (r_2 - r_{eq})^2 + E_e$$

where $\omega = 0.175\,\text{eV}$
and $E_e = 2.35\,\text{eV}$

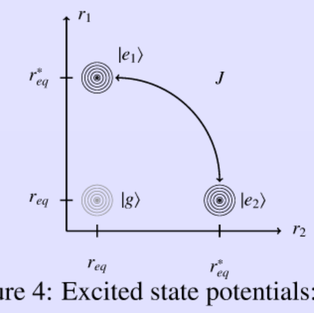


Figure 4: Excited state potentials: Shifted harmonic oscillators.

Larger Aggregates

- Linear chain of harmonic oscillators
- N coupled excited states
- N vibrational degrees of freedom
- Wave packet propagation with MCTDH method[2]

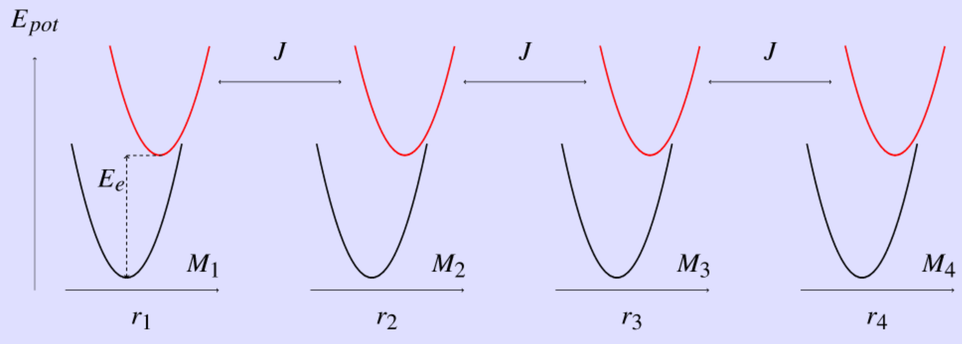


Figure 5: Model for oligomers obtained by expansion of vibronic model.

Results

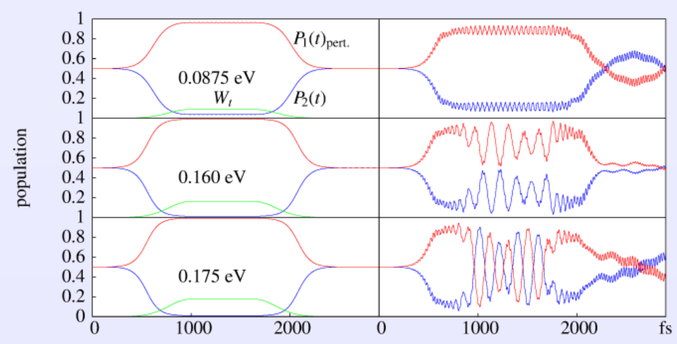
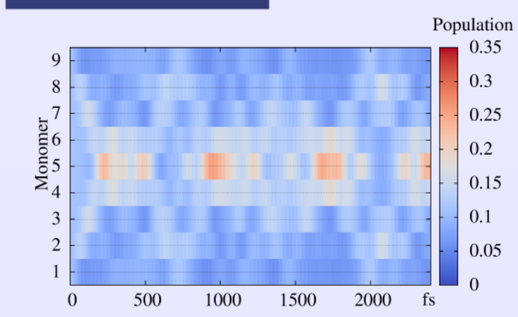


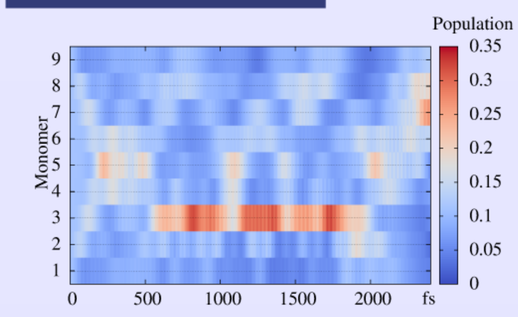
Figure 6: Time dependency of population for different strengths of perturbation: Left: Two level system. Right: Vibronic-model.

- Localization effect in all cases
- Two level system very similar for all perturbation strengths
- Additional oscillations due to complex vibronic interactions in vibronic model
- Effective population transfer in vibronic model; increasing with perturbation strength
- Resonant exchange of energy at perturbation strength 0.175 eV (equals vibrational quantum)

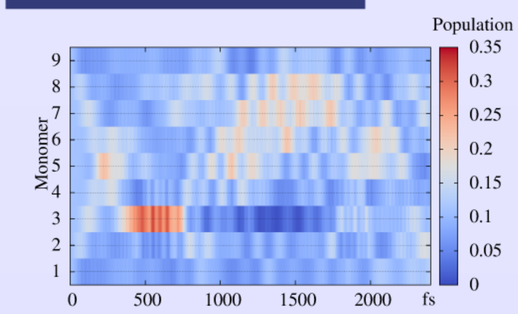
Unperturbed Nonamer



Weakly Perturbed Nonamer



Resonantly Perturbed Nonamer



Nonamer at different perturbation strengths

Unperturbed Nonamer *(top panel)*:

- Uniformly distributed excitation
- Due to boundary effects population moves along the chain
- On average, monomer unit five is most strongly populated

Weakly Perturbed Nonamer *(middle panel)*:

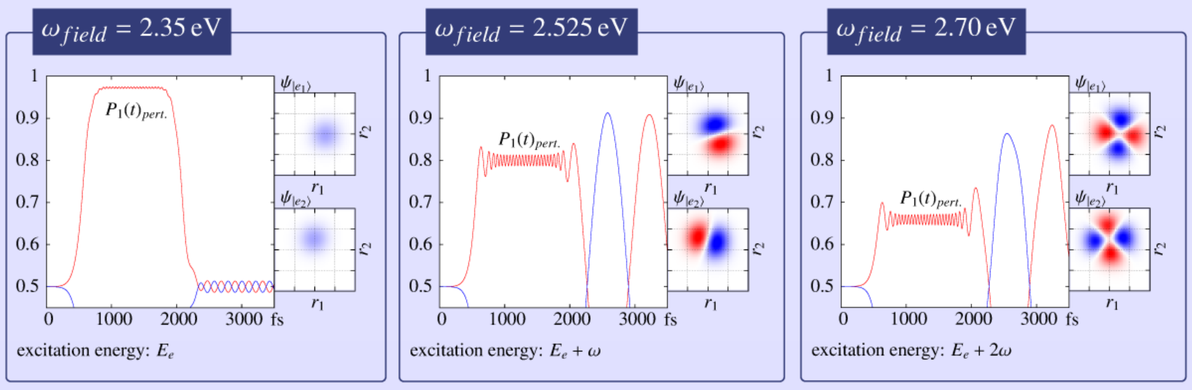
- $\Delta = 0.0175\,\text{eV}$
- Perturbation of monomer n=3 leads to similar results as in the dimer case:
  - Exciton energy localizes
  - Localization on the perturbed monomer
  - After perturbation population oscillates.

Resonantly Perturbed Nonamer *(bottom panel)*:

- $\Delta = 0.175\,\text{eV}$
- At first - like in the unperturbed case - monomer five is populated most strongly
- Energy localizes during the perturbation on perturbed monomer
- Vibrational resonance leads to fast depopulation of perturbed monomer

Influence of nodal structure

Preparing vibrational eigenstates in the electronicly excited states via an electric field allows analysis of the influence of the nodal structure on the localization effect:



→ Weaker localization effect with increasing number of nodes in the initial wavefunction.

First order perturbation theory

$$P_1(t) = P_1(t_0) - \frac{2J}{\Delta}\Big(\cos(\Delta\, t) - 1\Big)\ \mathrm{a}_{j,k,l,m}$$

$$\mathrm{a}_{j,k,l,m} = \left(\frac{l!}{j!}\,\xi^{j-l}\,\mathrm{e}^{-\xi}\right)^{\frac{1}{2}} \mathbf{L}_l^{j-l}(\xi)\ \left(\frac{k!}{m!}\,\xi^{m-k}\,\mathrm{e}^{-\xi}\right)^{\frac{1}{2}} \mathbf{L}_k^{m-k}(\xi)$$

j, k: quantum numbers for $|e_1\rangle$
l, m: quantum numbers for $|e_2\rangle$
Huang-Rhys factor $\xi = \dfrac{(\Delta r_{eq})^2 \omega}{2}$
$\mathbf{L}_l^{j-l}(\xi)$: Laguerre Polynomials

References & Contact

[1] J. Wehner, A. Schubert, V. Engel, *Chem. Phys. Lett.*, **541**, 49 (2012)
[2] M.H. Beck, A. Jäckle, G.A. Worth, H.-D. Meyer, *Physics Reports*, **324**, 1 (2000)

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