Vibronic energy localization in weakly coupled small molecular aggregates

Motivation

- Excitation of an aggregate leads to excitation formation
- Time-dependent perturbation takes place
- Localization of excitation energy

Models

**Dimer Model**

- Ground state: uncoupled monomers
- Excited state: two excited state configurations
  - Weakly coupled
  - Degenerate
- Localized one-exciton picture
- \( M_1 \) or \( M_2 \) is excited

Excited states dimer Hamiltonian:

\[
\hat{H}_D = \left\{ \hat{V}_g + \hat{T} \right\},
\]

where \( \hat{V}_g \) is the potential energy operator and \( \hat{T} \) the operator for the kinetic energy.

**Unperturbed Two Level System**

\[ E_1 = E_2 = \frac{\omega}{2} \]

**Perturbed Two Level System**

\[ E_{1/2} = E_{1/2}^{pert} = \frac{\omega}{2} \]

\[ \Delta E = \sqrt{\left(E_1 - E_2\right)^2 + 4 J^2} \]

Figure 1: One-exciton model: Degenerate excited state configurations \( \{1\}, \{2\} \), and coupling \( J \).

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

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

Perturbation: \( W(t) = \Phi(t) \Delta \)

- Shape function \( \Phi(t) \)
- Energy shift \( \Delta \) due to interaction with surrounding
- \( \langle \Phi(t) \rangle = \langle \Phi_0 \rangle + W(t) \)

Vibronic Model

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

\[
\begin{align*}
\hat{\epsilon}_1 &= \hbar \omega_1, \\
\hat{\epsilon}_2 &= \hbar \omega_1 \left( r_1 - \epsilon_{eq1} \right)^2 + \frac{1}{2} \hbar \omega_1 \left( r_2 - \epsilon_{eq2} \right)^2 + E_x \\
\hat{\epsilon}_3 &= \hbar \omega_1 \left( r_3 - \epsilon_{eq3} \right)^2 + E_x \\
\hat{\epsilon}_4 &= \hbar \omega_1 \left( r_4 - \epsilon_{eq4} \right)^2 + E_x
\end{align*}
\]

where \( \omega = 0.175 \) eV

and \( E_x = 2.33 \) eV

Figure 4: Excited state potentials: Shifted harmonic oscillators.

Larger Aggregates

- Linear chain of harmonic oscillators
- \( N \) vibrational degrees of freedom
- \( N \) coupled excited states
- Wave packet propagation with MCTDH method

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

Results

- 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)

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

Nonlinearity at different perturbation strengths:

- 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):

- \( \Delta = 0.0175 \) eV
- Perturbation of monomer \( n=3 \) leads to similar results as in the dimer case:
  - Excitation energy localizes
  - Localization on the perturbed monomer
  - After perturbation population oscillates.

Resonantly Perturbed Nonamer (bottom panel):

- \( \Delta = 0.175 \) 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 vibronic eigenstates in the electronically excited states via an electric field allows analysis of the influence of the nodal structure on the localization effect:

\[ \omega_{field} = 2.55 \text{ eV} \]

\[ \omega_{field} = 2.525 \text{ eV} \]

\[ \omega_{field} = 2.70 \text{ eV} \]

- Weakly localized excitation with increasing number of nodes in the initial wavefunction.

First order perturbation theory

\[
P_i(t) = P_i(0) - \frac{2J}{\hbar} \left( \cos \Delta i - 1 \right) \lambda_{j,k} A(t)
\]

\[
\lambda_{j,k} = \frac{\left( \frac{\hbar}{J} \right)^2 (r_j - \epsilon_{eqj})^2}{2} \int_0^\infty dt \ e^{-t^2} \left( \epsilon_{eqj} - \epsilon \right)^2 L_j^2(e^{-t^2})(\epsilon_{eqj} - \epsilon)^2
\]

\[ j, k: \text{ quantum numbers for } \epsilon_{eqj} \]

\[ l_m: \text{ quantum numbers for } \epsilon_{eqk} \]

Huang-Rhys factor \( \xi = \frac{\lambda_{j,k} A(t)}{2} \)

\[ L_j^2(e^{-t^2}): \text{ Laguerre Polynomials} \]

References & Contact


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