Partially-Coherent Transport:
Computational Analysis and Overcoming Anderson Localization

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Motivation

- **In solar cells and other applications, hopping transport of electrons is slow**
- **Coherent motion is faster: coherent = wavelike**
- **Coherence lifetimes are usually very short: electrons localized by environment interactions**
- **How to design systems to control transport?**

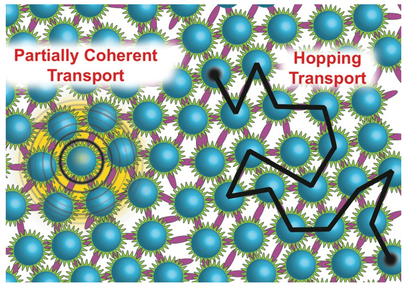


Image from Mark Lusk

Background and Model

Hamiltonian: Sum of Electronic, Phonon, Electron-Phonon Coupling, Reorganization Energy

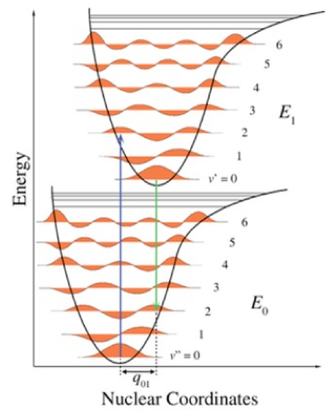
$$\mathcal{H} = \mathcal{H}_{ex} + \mathcal{H}_{phon} + \mathcal{H}_{ex-ph} + \mathcal{H}_{reorg}$$

- **The Heirarchical Equations of Motion (HEOM) model time evolution of the reduced density operator, ρ(t).**
- **ρ(t) includes information on exciton population and coherence.**

$$\frac{\mathrm{d}}{\mathrm{d}t}\rho(t) = -\frac{\mathrm{i}}{\hbar}\mathcal{L}_{\mathrm{ex}}\rho(t) + \sum_m \frac{\mathrm{i}}{\hbar}V_m^{\times}\sigma^{(0,\ldots,n_m=1,\ldots,0)}(t)$$

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t}\sigma^{(n_1,\ldots,n_N)}(t) &= \big(-\frac{\mathrm{i}}{\hbar}\mathcal{L}_{\mathrm{ex}} - \sum_m n_m\nu\big)\sigma^{(n_1,\ldots,n_N)}(t) \\ &+ \sum_m \frac{\mathrm{i}}{\hbar}V_m^{\times}\sigma^{(n_1,\ldots,n_m+1,\ldots,n_N)}(t) \\ &+ \sum_m n_m\theta_m\sigma^{(n_1,\ldots,n_m-1,\ldots,n_N)}(t).\end{aligned}$$

Parameter Analysis



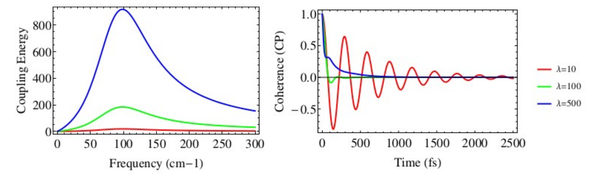
- **Reorganization energy (λ) is dissipated as the first excited state relaxes**
- **Spectral density quantifies electron-phonon coupling**

<u>Maximize coherence with:</u>

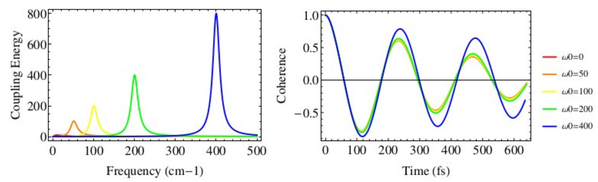
- **Low reorganization energy**
- **A spectral density that is coupled narrowly to phonon modes, skewed to high frequencies**

Vary parameters in Drude Lorentz peak, which approximates spectral density:

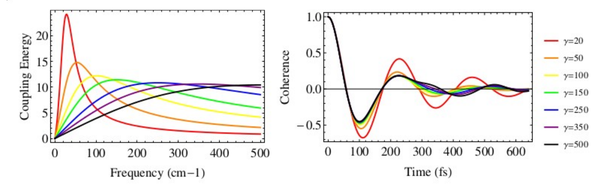
$$\mathcal{J}(\omega) = \frac{2\lambda\gamma\omega}{(\omega-\omega_0)^2+\gamma^2}$$



(a) Spectral Densities (b) Coherence Behaviors



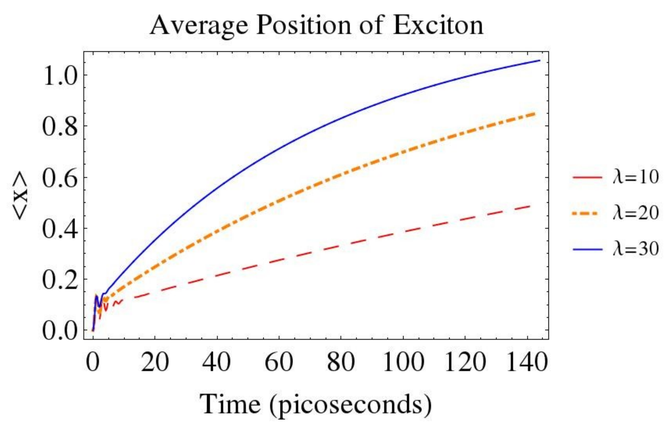
(e) Spectral Densities (f) Coherence Behaviors



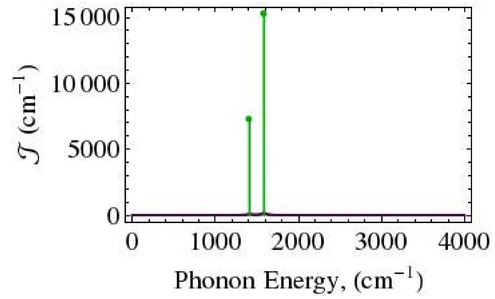
(c) Spectral Densities (d) Coherence Behaviors

Anderson Localization

- **In systems with disorder, exciton will localize at disorder**
- **Simulated a long chain of sites, with random site excitation energies**
- **If reorganization energy was zero, the exciton would localize immediately**
- **Plot of average exciton position (with exciton starting at site 0) shows that increasing λ increases transport speed.**
- **Found that electron-phonon coupling is necessary to delay localization**
- **Energy is transferred between phonons and excitons**



Modelling Naphthalene



- **Density functional theory provides spectrally resolved reorganization energies**
- **Fit Drude-Lorentz peak to discrete spectral density**
- **Use resulting parameters in HEOM to model naphthalene chain**

Future Work

- **Use electronic coupling from DFT to model bridges between sites**
- **Investigate better site geometries for creating desired transport characteristics**

Acknowledgements

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References

[1] Ishizaki, Fleming. J. Chem. Phys. 130, 234111 (2009)

[2] C. Kreisbeck, "Quantum transport through complex networks – from light-harvesting proteins to semiconductor devices," Dissertation. (Universität Regensburg, 2012).